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Pesticides at the Mouths of Lake Saint-Pierre Tributaries (2003–2008)

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COMMENTS TO READERS

Please send all comments about the content of this report to the Quebec Water Quality Monitoring and Surveillance Section, Water Science and Technology Directorate, Environment Canada, 105 McGill Street, 7th Floor, Montréal, QC H2Y 2E7.

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St. Lawrence Plan
For a Sustainable Development

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Management Perspective

Agriculture in Quebec has evolved in recent decades and is now a highly specialized and mechanized industrial activity. The reduction in the surface area of pasture lands in favour of a significant increase in grain crops has resulted in the greater use of chemical fertilizers and pesticides. These phenomena have contributed to the degradation of the water quality in rivers in agricultural areas.

This was the situation when, in 1987, the Inland Waters Directorate established a monitoring network to track pesticides entering the agricultural tributaries of the St. Lawrence River. The results obtained during the first two years (1987 and 1988) of this network were published in a report by Forrest and Caux (1989). Another report (Rondeau 1996) was produced using the results of surface-water sampling conducted between 1989 and 1991 to characterize pesticide contamination in the Yamaska, Nicolet, Richelieu, L'Assomption, Saint-François, and de la Tortue rivers. This report identified the most problematic pesticides for these aquatic environments and indicated which rivers were the most contaminated by these substances.

In the wake of these two reports, a pesticide surveillance network was established in 2003 on the three largest tributaries on the south shore of Lake Saint-Pierre as part of the Pesticide Science Funds activities of Environment Canada. Since 2006, pesticide monitoring in these tributaries is also done through the National Water Quality Monitoring and Surveillance Program of Environment Canada and the Canada–Québec *St. Lawrence Plan for Sustainable Development*. The present report provides a more complete snapshot of the pesticides released to the surface waters of the St. Lawrence River between 2003 and 2008 at Lake Saint-Pierre, a site of great ecological importance.

These results will enable Environment Canada to provide Canadians with information on pesticide concentrations near the mouths of the main south shore tributaries of Lake Saint-Pierre. The database created to hold the monitoring data could also be useful for other researchers and contribute to the decision-making processes of various governmental organizations such as Environment Canada, the Pest Management Regulatory Agency, the Quebec Ministère du Développement durable, de l'Environnement et des Parcs, Agriculture and Agri-Food Canada, and municipal authorities.

Perspective de gestion

L'agriculture québécoise a évolué au cours des dernières décennies et constitue aujourd'hui une activité industrielle très spécialisée et mécanisée. La diminution des superficies consacrées au pâturage au profit d'une augmentation importante des cultures de céréales a conduit à une plus grande utilisation d'engrais chimiques et de pesticides. Ces phénomènes ont contribué à la dégradation de la qualité de l'eau des rivières en milieu agricole.

Dans ce contexte, la Direction générale des eaux intérieures a établi, en 1987, un réseau de surveillance des pesticides dans les tributaires agricoles du Saint-Laurent. Les résultats obtenus lors des deux premières années de ce réseau (1987 et 1988) ont déjà fait l'objet d'un rapport (Forrest et Caux, 1989). Un autre rapport a été produit avec les résultats de l'échantillonnage des eaux de surface réalisé entre 1989 et 1991, afin de caractériser la contamination des rivières Yamaska, Nicolet, Richelieu, L'Assomption, Saint-François et de la Tortue par les pesticides (Rondeau, 1996). Ce rapport a permis de déterminer les pesticides les plus problématiques pour le milieu aquatique ainsi que les rivières les plus contaminées par ces substances.

À la suite de ces deux rapports, un réseau de surveillance des pesticides a été établi en 2003 dans trois tributaires importants de la rive sud du lac Saint-Pierre dans le cadre des activités du Fonds pour la science des pesticides d'Environnement Canada. Depuis 2006, le suivi des pesticides dans ces tributaires s'effectue aussi par l'entremise du Programme national de monitoring et surveillance de la qualité de l'eau d'Environnement Canada et de l'entente Canada-Québec « Plan Saint-Laurent pour un développement durable ». Le présent rapport permet d'avoir une image plus complète des pesticides qui ont été rejetés dans les eaux de surface du fleuve Saint-Laurent entre 2003 et 2008 à la hauteur du lac Saint-Pierre, un site de grande importance écologique.

Ces résultats permettront à Environnement Canada d'informer les citoyens au sujet des concentrations de pesticides près de l'embouchure des principaux tributaires du sud du lac Saint-Pierre. La base de données qui a été créée pour le suivi pourra également être utilisée par d'autres chercheurs et contribuer aux décisions de différents organismes gouvernementaux tels que Environnement Canada, l'Agence de réglementation de la lutte antiparasitaire, le ministère du Développement durable, de l'Environnement et des Parcs, Agriculture Canada et les municipalités.

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Abstract

The vast areas of farmland in the St. Lawrence Valley require the use of large quantities of pesticides. Consequently, they have the potential to contaminate nearby sources of fresh water. The pesticide applied will vary according to the type of crop. In Quebec, the proportion of farm fields devoted to corn and soybeans has increased considerably over the past few years, leading to an increase in the use of pesticides such as atrazine, metolachlor and, more recently, glyphosate on genetically modified crops. Since the late 1980s, the surface waters of the St. Lawrence River and some of its tributaries have been sampled in Quebec to determine which pesticides are found in watercourses and at what concentrations.

Lake Saint-Pierre is a fluvial lake upstream from Trois-Rivières. It has great ecological importance because of its rich biodiversity and its wetlands, which represent almost half of the wetlands along the St. Lawrence River. The lake was designated a Ramsar site in 1998 under the *Convention on Wetlands of International Importance* and declared a UNESCO Biosphere Reserve in 2000. Because Lake Saint-Pierre drains watersheds that are characterized by intensive farming activity, it is vitally important to understand the types and concentrations of contaminants released to it and their effects on living organisms. This report presents the results of pesticide monitoring of the surface waters near the mouths of the three major tributaries on the south shore of Lake Saint-Pierre—the Nicolet, Saint-François and Yamaska rivers—from 2003 to 2008.

The results show that the waters entering the wetlands on the south side of Lake Saint-Pierre carry a considerable cocktail of pesticides in summer. Every year, the main pesticides detected are herbicides such as atrazine, metolachlor, glyphosate, bentazone and dicamba. Between 2003 and 2008, for example, these pesticides were detected in the Yamaska River at frequencies of 98%, 100%, 65%, 65% and 62%, respectively. In Quebec these herbicides are mainly applied on corn and, with the exception of atrazine, other crops such as soybean, wheat, barley and oat. In addition, glyphosate is used in orchards. Insecticides and fungicides are detected much less frequently and at maximum concentrations that are often lower than those for herbicides, yet a few are sometimes detected at levels exceeding their water quality criteria.

Despite the relatively high water discharge at the mouths of these large rivers, a few of the pesticides analysed exceeded the Canadian criterion for the protection of aquatic life and were found at a maximum frequency of 7.7% per river (chlorpyrifos at 7.7%, diazinon at 1.3%, chlorothalonil at 1.3% and atrazine at 1.1%). Dicamba and MCPA often exceeded their criteria for the use of irrigation water (as often as 62% and 24%, respectively).

Overall, it is the Yamaska River that carries the widest variety of pesticides and the greatest pesticide loads into Lake Saint-Pierre during the growing season (e.g. up to 417 kg of atrazine and deethylated atrazine, 326 kg of bentazone, 302 kg of glyphosate and AMPA, 284 kg of metolachlor, and 196 kg of dicamba). Locally, the pesticide load released into Lake Saint-Pierre from these three rivers is considerable and an in-depth investigation into its impacts on the vulnerable wetlands of this lake is warranted.

The monitoring of pesticides in the tributaries of Lake Saint-Pierre is essential to obtaining an overall snapshot of the state of health of this fluvial lake, and the results of this report represent important complementary knowledge. Nonetheless, more sensitive detection limits and a more complete suite of water quality criteria would provide information on a wider range of pesticides and support better interpretation of the data. From an environmental and sustainable development policy perspective, we must also consider the potential effects of climate change, such as lower water levels in Lake Saint-Pierre, on the concentrations of these pesticides in surface waters and their impact on the biodiversity of the Lake Saint-Pierre wetlands.

Résumé

Les vastes superficies de terres en culture dans la vallée du Saint-Laurent entraînent l'utilisation de quantités importantes de pesticides et, par conséquent, un risque de contamination des eaux douces avoisinantes. Les pesticides utilisés varient selon le type de culture. Au Québec, la proportion des terres allouées à la culture du maïs et du soya a augmenté considérablement ces dernières années. Ces cultures sont de grandes utilisatrices de pesticides comme l'atrazine, le métolachlore et maintenant le glyphosate pour les variétés génétiquement modifiées. Depuis la fin des années 1980, les eaux du fleuve Saint-Laurent et de plusieurs de ses tributaires ont été échantillonnées au Québec afin de déterminer quels pesticides et à quelles concentrations ils se retrouvent dans les cours d'eau.

Le lac Saint-Pierre, un lac fluvial en amont de Trois-Rivières, est un site écologique de grande importance à cause de sa riche biodiversité et ses milieux humides qui représentent près de la moitié des milieux humides du Saint-Laurent. Ce lac a d'ailleurs été désigné site Ramsar en 1998, en vertu de la Convention relative aux zones humides d'importance internationale et a été déclaré Réserve de la biosphère en 2000 par l'UNESCO. Comme le lac Saint-Pierre draine des bassins versants à forte activité agricole, il est critique de connaître la nature des contaminants qui y sont rejetés, leurs concentrations et leurs effets sur les organismes vivants. Le présent rapport dévoile les résultats du suivi des pesticides dans les eaux de surface près de l'embouchure des principaux tributaires du côté sud du lac Saint-Pierre, soit les rivières Nicolet, Saint-François et Yamaska, de 2003 à 2008.

Les résultats montrent que les eaux qui se jettent dans les milieux humides du côté sud du lac Saint-Pierre transportent avec elles un cocktail important de pesticides durant l'été. À chaque année, les principaux pesticides détectés sont des herbicides tels que l'atrazine, le métolachlore, le glyphosate, le bentazone et le dicamba. Ces pesticides ont été détectés, par exemple, de 2003 à 2008 dans la rivière Yamaska à une fréquence de 98 %, 100 %, 65 %, 65 % et 62 %, respectivement. Ils sont épandus au Québec surtout sur les cultures de maïs, et à l'exception de l'atrazine, ils sont également utilisés sur d'autres cultures comme celles du soya, du

blé, de l'orge et de l'avoine. Le glyphosate est aussi employé dans les vergers. Les insecticides et les fongicides sont beaucoup moins fréquemment détectés, et à des concentrations maximales souvent plus faibles que celles des herbicides, mais quelques-uns sont parfois détectés à des concentrations supérieures aux critères de qualité de l'eau qui s'y appliquent.

Malgré les débits relativement importants aux embouchures des grandes rivières, quelques-uns des pesticides analysés dépassaient le critère canadien pour la protection de la vie aquatique et à une fréquence maximale par rivière de 7,7 % (7,7 % pour le chlorpyrifos; 1,3 % pour le diazinon; 1,3 % pour le chlorothalonil; 1,1 % pour l'atrazine). Le dicamba et le MCPA dépassaient souvent leur critère pour l'utilisation de l'eau à des fins d'irrigation agricole (jusqu'à 62 % et 24 %, respectivement).

Au total, c'est la rivière Yamaska qui transporte la plus grande variété de pesticides au lac Saint-Pierre ainsi que les charges les plus importantes de pesticides durant la saison de croissance (p. ex. jusqu'à 417 kg d'atrazine et d'atrazine dééthylée, 326 kg de bentazone, 302 kg de glyphosate et d'AMPA, 284 kg de métolachlore et 196 kg de dicamba). À l'échelle locale, la charge de pesticides déversés par ces trois rivières dans le lac Saint-Pierre est considérable, et les impacts sur les milieux humides fragiles du lac méritent une étude approfondie.

Un suivi des pesticides dans les tributaires du lac Saint-Pierre est indispensable afin de dresser un portrait global de l'état de santé de ce lac fluvial, et les résultats du présent rapport constituent un complément important. Néanmoins, des limites de détection plus sensibles et un ensemble plus complet de critères de qualité de l'eau permettraient d'obtenir de l'information pour un plus grand éventail de pesticides et une meilleure interprétation des données. Dans une perspective de politique environnementale et de développement durable, il faut également considérer les effets potentiels des changements climatiques comme la baisse du niveau de l'eau dans le lac Saint-Pierre, sur la concentration des pesticides dans les eaux de surface et leurs répercussions sur la biodiversité des milieux humides du lac Saint-Pierre.

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1 Introduction

1.1 ISSUE

For nearly a century, industrial, agricultural, urban and recreational activities have produced considerable loads of toxic substances in aquatic ecosystems, whose deteriorating health is becoming a growing concern. Agricultural activities, in particular, can have a major impact on aquatic ecosystems, causing soil erosion, eutrophication, and contamination of the water (surface and subsurface) and sediments as a result of farmland leaching, runoff and percolation. The intensity of agricultural activities in the St. Lawrence Lowlands therefore contributes to the deteriorating quality of the surface water in the river and its tributaries. At present in Quebec, corn—cultivated in rotation or in combination with soybeans—utilizes the second largest land area after forage crops (ISQ 2008) and requires large quantities of pesticides to combat weeds and pests. Appendix 1 contains a list of pesticides recommended in Quebec for corn and soybean crops. Some can be used for both crops. One-third of pesticides, particularly herbicides, sold in Quebec are used on corn and soybean crops. Atrazine continues to be among the most widely used for corn, but glyphosate use is on the rise with the increasing proportion of genetically modified varieties. Since 1996, grain corn and feed corn cultivation have expanded significantly in Quebec, occupying as much as 497 000 hectares (450 000 ha of grain corn and 47 000 ha of feed-corn) in 2007 (ISQ 2008). This major increase in corn crops may be linked to the growth in pork production, which uses corn as feed and the resulting slurry to fertilize cropland (Giroux 2004; 2002, MENV 2002).

Nearly half the St. Lawrence River's wetlands are found in Lake Saint-Pierre. These ecosystems play important ecological roles, such as filtering the water and providing a wide variety of ecological niches where hundreds of animal and plant species can live. In 1998, Lake Saint-Pierre was designated a Ramsar site under the *Convention on Wetlands of International Importance* and, in 2000, was also declared a UNESCO Biosphere Reserve. Nevertheless, few measures are currently in place to protect these wetlands.

The seaway's current is concentrated in the centre of Lake Saint-Pierre, and water flow is slowed in the shallow flanks of its vast wetlands. Montreal's greater metropolitan area, which is upstream from Lake Saint-Pierre, and the tributaries that drain farmland upstream and directly into the lake significantly degrade the lake's water quality and frequently lead to exceedances in the water quality criteria (Hudon and Carignan 2008). The St. Lawrence River, and especially Lake Saint-Pierre, is therefore very vulnerable to pesticide contamination of its water because of the numerous tributaries that cut across heavily farmed lands. Although Lake Ontario is considered a primary source of pesticides in the river, the observation in Lake Saint-Pierre of distinct water masses originating from these tributaries (Désilets and Langlois 1989) suggest that some of the lake's wetlands could be contaminated in the same proportions as the agricultural tributaries that feed into them.

1.2 SITUATION

In Canada, pesticide management is shared between the federal government, provincial and territorial governments and, to a lesser extent, municipal governments. The mandate of the federal government's Pesticide Management Regulatory Agency (PMRA) is to manage the *Pest Control Products Act*, which governs the registration of pesticides before they are put on the Canadian market. With a view to protect human health, this Act requires that consideration be given to total exposure to pesticides, cumulative effects of pesticides with a common mechanism of toxicity, different sensitivities of infants and children, and endocrinal effects (Giroux 2004, MDDEP 2002a).

Quebec has passed its own pesticide legislation governing the activities of people who sell and use these pesticides. The sale and use of pesticides are therefore regulated by the *Pesticides Act*, which is complemented by the *Environment Quality Act*. The objectives of the *Pesticides Act* include preventing and reducing harmful effects on the environment and human health as well as rationalizing and reducing pesticide use. In 2003, the Quebec Government also passed a *Pesticides Management Code* for stricter governance over pesticide sale and use in Quebec (Giroux 2004, MDDEP 2002a).

The Pesticide Reduction Strategy put forward by the Ministère de l'Agriculture, des Pêcheries et de l'Alimentation du Québec (MAPAQ) and its partners—the Union des Producteurs Agricoles (UPA) and the Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP)—is based on the integrated management approach, also called "integrated pest management." It aims to reduce pesticide sales and expand the areas that use the integrated management approach, mainly for target crops such as corn, soybeans, grain crops, apples and potatoes (Giroux 2004, MDDEP 2002a). Municipalities have the power to establish more restrictive regulations on urban pesticide use, for example, taking into account their individual local situations (MDDEP 2002a).

Since 1992, the MDDEP has been tracking pesticides in the surface waters of Quebec rivers, particularly rivers found in agricultural watersheds where intensive cultivation of corn and soybeans is practised—that is, the Chibouet River (Yamaska River watershed), des Hurons River (Richelieu River watershed), Saint-Zéphirin River (Nicolet River watershed) and Saint-Régis River (a small tributary of the St. Lawrence). Findings have shown that pesticides are regularly present in surface waters during the summer. These pesticides are mainly herbicides used on corn and soybean crops such as atrazine, metolachlor, bentazon, dicamba, 2,4-D and dimethenamid. Certain insecticides, new-generation herbicides (e.g. sulfonylureas), and the herbicide called clopyralid were also detected. The frequent detection of a new-generation herbicide is very surprising considering the minimal application rate per hectare. Furthermore, the lack of water quality criteria for these herbicides means that their potential effects on aquatic species cannot be assessed. At this time, therefore, it would appear that the new-generation herbicides are not a sustainable solution to the problem of pesticide contamination of rivers (Giroux 2002, Giroux et al. 2006, MENV 2002).

MDDEP findings also revealed some exceedances of Canadian water quality criteria. In the case of the criteria for the protection of aquatic life (see Appendix 2), exceedances were observed for atrazine, metolachlor, diazinon, carbaryl and chlorpyrifos. In the case of the crop irrigation criteria, exceedances were observed for numerous herbicides, including dicamba and MCPA, which means that certain crops could be damaged if irrigated by these waters. Furthermore, atrazine continues to be one of the most dominant herbicides in agricultural tributaries. Since 1996, however, the MDDEP has seen a downward trend in atrazine concentrations in rivers, partially as a result of decreased use of this pesticide, according to reported pesticide sales. However, the presence of atrazine in all river samples taken is very worrying for the protection of aquatic life due to its harmful effects on the biota, even at low doses. The large number of pesticides detected in rivers in June and July (as many as

20 pesticides in the Saint-Régis River) is also of great concern because of the sublethal effects on aquatic species at low doses or the combined or synergistic effects of pesticide mixtures in water (Giroux et al. 2006, Giroux 2002, MDDEP 2002a). The use of new-generation herbicides and the introduction of transgenic varieties that are tolerant to glyphosate, among other substances, have contributed to decreased water concentrations of atrazine and bentazon. Yet pesticide contamination of water bodies remains a reality; atrazine continues to be frequently detected, and the presence of new-generation herbicides in aquatic ecosystems is not a desirable alternative (Giroux et al. 2006, MENV 2002).

This pesticide monitoring work of the MDDEP also revealed a seasonal cycle of pesticides in surface waters. Concentrations are low or below detection limits in early spring, gradually increasing in May and reaching significant values by late May to mid-June. Occasional peaks are also observed, concomitant with periods of heavy rainfall throughout the summer. Concentrations then gradually drop, reaching low levels by summer's end (Giroux 2010, Giroux et al. 2006).

Environment Canada has been monitoring the water quality of the St. Lawrence River near Quebec City since 1995. Findings show that pesticide concentrations fluctuate on a seasonal basis, but no trends, either upward or downward, have been recorded over the years. However, the highest concentrations measured in summer appear to be linked to pesticide application on farmlands in the St. Lawrence Lowlands (Rondeau 2005). A study by Rondeau (1996) measured atrazine concentrations in watersheds of agricultural tributaries at levels up to 36 300 ng/L (Chibouet River in the Yamaska basin) in early and/or mid-summer between 1989 and 1991. With the criterion for the protection of aquatic life (chronic effect) set at 1800 ng/L in Canada, such concentrations could have a major impact on aquatic ecosystems, such as a drop in phytoplankton production and of macrophyte photosynthesis (Pham et al. 2000, Huber 1993, De Noyelles et al. 1982). Atrazine also apparently has feminizing endocrinal effects on amphibians (Hayes et al. 2002).

Based on pesticide monitoring work in the St. Lawrence Lowlands (Giroux et al. 2010, Giroux 2006, Pham et al. 2000, Rondeau 1996), the extent of contamination of the waters of the St. Lawrence appears to depend on the various physicochemical properties of these pesticides, the quantity of each product applied in the tributary basins, the hydrology of the watersheds, and weather conditions following pesticide application. It has been noted that maximum herbicide concentrations in the river and its tributaries are generally found during the month following application and that minimum concentrations are recorded during spring freshet because of the meltwater's diluting effect.

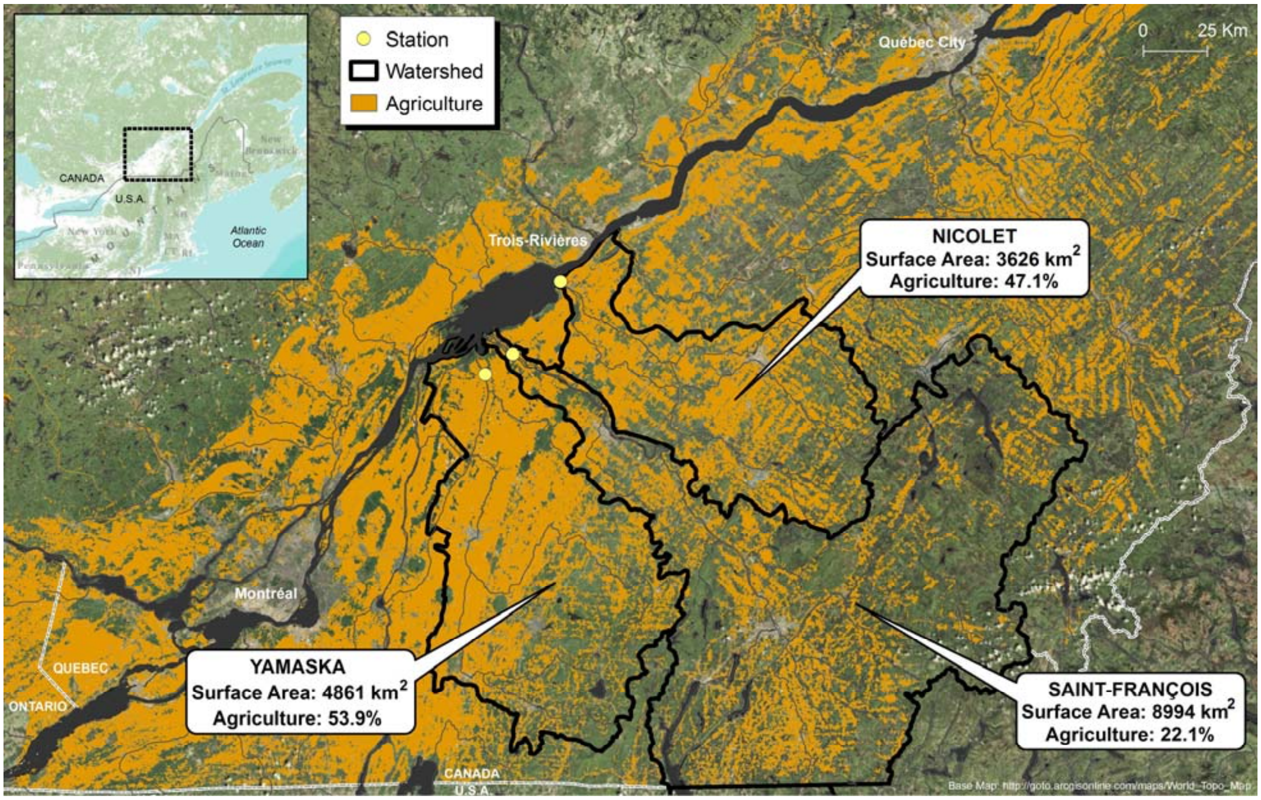
1.3 OBJECTIVES

There are few studies on the pesticide contamination in the St. Lawrence River. This monitoring work is intended to supplement our knowledge of the scope and the fate of water contamination in the St. Lawrence, primarily at the mouths of the agricultural tributaries of Lake Saint-Pierre, a site of great ecological importance.

The findings presented in this document are those of the Environment Canada’s Quebec Water Quality Monitoring and Surveillance Section (WQMS-QC), which has been monitoring the presence and seasonal variations of several pesticides and degradation products in surface waters near the mouth of Lake Saint-Pierre's main tributaries (the Nicolet, Saint-François and Yamaska rivers) during the pesticide-application period since 2003.

2 Study Environment

2.1 STUDY ENVIRONMENT DESCRIPTION



Sources: Natural Resources Canada and Environment Canada.

Figure 1 Sampling stations

2.1.1 Nicolet River

The Nicolet River watershed covers 3626 km^2 on the south shore of Lake Saint-Pierre (Figure 1). The watershed is divided into two main sub-basins: that of the Nicolet River and that of the Southwest Nicolet River. These rivers originate in the mountainous lakes of the Appalachians and cut across the St. Lawrence Lowlands down to the river's mouth near the town of Nicolet (Giroux and Simoneau 2008). Their hydrological characteristics include annual and summer mean flows at the river mouth (estimated from 1995–2007 data) that are one to two orders of magnitude lower (Table 1) than those of large rivers such as the Richelieu (374 m^3/s), the Saint-Maurice (700 m^3/s) and the Ottawa (1937 m^3/s) rivers (Berryman 2008).

Nearly half of the Nicolet River watershed is dedicated to agricultural activity. The remaining area is mainly forest with a small percentage of urbanized regions, open-water areas and wetlands (Table 1).

Table 1
Characteristics of watersheds under study

Watershed	Total area in km^2	Area in km^2 by land-use type (% of total area)				Mean flow, 1995 to 2007 (m^3/s)	
		Agriculture (animals and crops)	Forest	Wetland and open water	Urban and other**	Annual	Summer
Nicolet River	3626	1707 (47.1%)	1644 (45.4%)	128 (3.5%)	147 (4.1%)	44.5	31.4
Saint-François River*	8994	1988 (22.1%)	5803 (64.5%)	459 (5.1%)	744 (8.3%)	190.5	149.8
Yamaska River	4861	2619 (53.9%)	1854 (38.1%)	138 (2.8%)	250 (5.1%)	81.9	51.5

Note: Areal data generated by Environment Canada based on Landsat 5-TM and Landsat 7-ETM images, 2000.

* Quebec watershed area (85% of total area)
** The 'Other' category includes roads, cutting areas, golf courses, and so on.

2.1.2 Saint-François River

The Saint-François River watershed is among the vastest watersheds of the St. Lawrence River's south shore and the largest of the three watersheds under study (Figure 1). From its source in the U.S. Appalachians to its mouth at Lake Saint-Pierre, the watershed covers some 10 228 km^2, including 8994 km^2 within Quebec. The shape of this watershed is very unique: it forms a T, with each of its extremities harbouring the largest lakes of the St. Lawrence River's south shore: Lake Memphremagog to the southwest and Lake Saint-François to the northeast (Painchaud 2007). It has the highest mean annual and summer flows (also estimated between 1995 and 2007, Table 1) for the south shore of Lake Saint-Pierre (excluding the Richelieu River, which drains into the river just upstream of Lake Saint-Pierre). The Saint-François River is an average-sized tributary when compared to major rivers such as the Richelieu, the Saint-Maurice and the Ottawa.

Its watershed consists mainly of forest land, but agricultural land also makes up a significant portion of it—nearly one-quarter of its area—particularly in the St. Lawrence

Lowlands (Table 1). The remainder (urban areas, wetlands, etc.) represents just over 10% of the watershed's total area.

2.1.3 Yamaska River

The Yamaska River watershed covers 4861 km^2 (Figure 1). From its source in Lake Brome, located in the Appalachians, to its mouth at Lake Saint-Pierre, the Yamaska River is subdivided into three similar-sized branches: the Yamaska, Southeast Yamaska and North Yamaska rivers (Berryman 2008). Its hydrological characteristics as measured between 1995 and 2007 indicate that mean annual and summer flows at the river mouth are nearly twice those of the Nicolet River (Table 1) but still much lower than those of the Saint-François River and the other large rivers above mentioned.

The Yamaska River basin is at the heart of Quebec’s agricultural land. Farmland takes up just over half of the area, while forested areas take up just over one-third. This leaves less than 10% for other land cover like urban areas and open water. The basin's cultivated area has remained relatively stable in the past 20 years, but agricultural activities have greatly changed: wide-row crops, such as corn and soybeans, more than tripled between 1976 and 2006 (from 22% to 69% of total cropland) (Poissant et al. 2008).

2.2 SOCIOECONOMIC DESCRIPTION OF WATERSHEDS

2.2.1 Nicolet River

In 2007, the total population in the Nicolet River watershed was estimated at 97 000. The area's main cities are Victoriaville (pop. 39 799), Nicolet (pop. 7963) and Asbestos (pop. 6627) (Giroux and Simoneau 2008). Among the 57 municipalities located entirely or partially within the watershed's area, the larger ones use surface water as a source of drinking water, while the rest draw their water from one or more municipal wells (Giroux and Simoneau 2008).

Approximately 60 industries operating in the agri-food, pulp and paper, and surface-finishing sectors are located within the Nicolet River basin. The watershed's rivers and lakes also support a flourishing recreational tourism industry. Numerous linear or theme parks, campgrounds and golf courses also utilize the water bodies of this watershed (Giroux and Simoneau 2008).

Agricultural activities take up a major portion of the watershed, mainly in its downstream section. In 2006, the watershed had 1689 farms (MDDEP 2007). The cultivated section is mainly concentrated in the watershed's northwestern half. The farmland is divided by crop type; their respective proportions are shown in Table 2. Half of the cropland is dedicated to forage crops (alfalfa, pasture, hay, etc.). Wide-row crops are dominated by grain corn and soybean crops, which require large quantities of fertilizers and pesticides because of the large areas they occupy. As for close-row crops, they consist predominantly of barley and oats, for which pesticides are much less used (Giroux and Simoneau 2008). In 2006, livestock numbers reached 130 800 head of cattle, nearly two-thirds of which were cattle (MDDEP 2007). Although its livestock numbers are the smallest of the three watersheds, the Nicolet River watershed is one of the seven agricultural watersheds with a surplus of manure compared to the capacity that the land can support. Studies by Gélinas et al. (2004) and Rousseau et al. (2004) found that excess phosphorus in the Nicolet River watershed was on the order of 13.3 kg/ha, yet this is the lowest figure among the seven agricultural watersheds with a manure surplus.

2.2.2 Saint-François River

At one time, the Saint-François River watershed was the centre of industrial development in Quebec. Beginning in the 19th century and continuing through the early 20th century, various industries from the mining, textile, pulp and paper, and hydroelectric sectors developed there. Agriculture had been established in the St. Lawrence Lowlands as early as the 17th century and gradually expanded during the 19th and 20th centuries to include parts of the piedmont and the Appalachians (Painchaud 2007).

Table 2
Surface area of various crop types in the watersheds under study in 2006

Watershed	Total cultivated area in km^2	Area of different crop types in km^2 (% of total area)				
		Wide-row crops		Close-row crops[2]	Forage crops[3]	Other crop types[4]
		Corn	Other[1]			
Nicolet River	1225	328 (27%)	128 (10%)	153 (12.5%)	607 (49.5%)	9 (1%)
Saint-François River[5]	1311	231 (17%)	87 (6%)	139 (10%)	904 (66%)	16 (1%)
Yamaska River	2278	1099 (48%)	400 (18%)	160 (7%)	587 (26%)	32 (1%)

Note: All data compiled in 2007 by the Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP 2007) based on the Statistics Canada 2006 Census of Agriculture.

[1] Includes the wide-row crops of soybeans, potatoes, peas, beans, vegetables, sunflowers, etc.
[2] Includes cereals (wheat, barley, oats, rye, buckwheat, canola, etc.).
[3] Includes alfalfa, sorghum, clover, birdsfoot trefoil, bromegrass hay, reed canarygrass, pastures, hay, etc.
[4] Includes fruit trees, small fruits, nurseries, greenhouses, sod, etc.
[5] Quebec area only

The 76 municipalities located entirely or partially within the watershed have a total estimated population of approximately 345 068. The main urban centres are Sherbrooke (pop. 150 751), Drummondville (pop. 68 841), and Magog (pop. 24 322) (Painchaud 2007).

Although the Saint-François River watershed is now known as a vacation and recreational tourism destination, industrial activity in the region is still present and highly diversified. Sherbrooke and Drummondville are the watershed's main industrial centres. The region has a large pulp and paper sector (seven paper mills) as well as significant textile, agri-food and metallurgical sectors. The region also has old copper mines whose tailings areas are still in existence and could have a major impact on the quality of aquatic environments (Painchaud 2007).

The Saint-François River watershed has 44 dams, 13 of which are large reservoir dams used to generate hydroelectric power, regulate water levels and flow or water supply. How these dams are managed can have a major impact on water quality (e.g. pollutants less diluted during summer and winter low-flow periods) and aquatic communities, especially fish (e.g. Lake Saint-François tidal range) (Painchaud 2007).

The agricultural sector is thriving in the Saint-François River watershed. Statistics Canada's last Census of Agriculture revealed that, in 2006, this watershed contained 2592 farms and large areas were being cultivated, particularly in the St. Lawrence Lowlands

(MDDEP 2007). The predominant agricultural activities are cattle farming and forage-crop cultivation (Table 2), while wide-row crops, especially corn, dominate in the downstream section of the watershed, near the river mouth.

2.2.3 Yamaska River

The Yamaska River watershed cuts across two natural regions of very distinct soils and topographies: the St. Lawrence Lowlands and the Appalachians. Since the early days of colonization, the fertile plains of the lowlands have been ideal for agricultural development. Agriculture therefore expanded to become the predominant form of land use in the region. Large-scale crops like corn occupy vast areas of land here (Berryman 2008).

The total population in the Yamaska River watershed has been estimated at over 250 000. The two main cities are Granby (pop. 59 606) and Saint-Hyacinthe (pop. 51 984). Among the 90 municipalities located entirely or partially within the watershed, the eight largest ones use surface water as a source of drinking water. Drinking water demand in the city of Granby is significant enough to affect the North Yamaska River, which must maintain a minimum flow to support aquatic life (Berryman 2008).

The region has a diversified and growing industrial sector. Urban and industrial businesses thrive in the Appalachians, which are less conducive to agriculture. In 1996, the region boasted 808 businesses in the agri-food, metal processing, textile and chemical sectors, primarily concentrated in the major industrial centres of Granby (main industrial city), Cowansville, Bromont, and Valcourt. Intensive agriculture along the river has also helped develop the agri-food sector (mills, slaughterhouses, agricultural cooperatives, processing plants, etc.). The town of Saint-Hyacinthe has become the agri-food capital of the region with a concentration of processing plants and centres of expertise in agronomy (Berryman 2008). Vacationing and recreational tourism activities have been developed extensively around the forests, mountains and lakes of the Appalachian side of the watershed. Recreational activities are mainly concentrated on lakes Brome and Waterloo, in Roxton Pond, Bromont and the Choinière reservoir in Yamaska National Park (Berryman 2008).

Intensive agriculture in the Yamaska River watershed has significantly transformed the land. For example, the lowlands have practically no more forest cover, and the exposed rivershores and denuded soils are prone to erosion. These alterations have degraded aquatic ecosystems in agricultural environments. In 2006, the watershed sustained the activities of 3311 farms (MDDEP 2007) covering nearly half the watershed. Hog farming, primarily, followed by cattle farming, is bigger here than in any of the three watersheds (a total of nearly 320 000 head of cattle in 2006) (MDDEP 2007). Two-thirds of the cropland was devoted to wide-row crops (mainly corn), while forage crops represented only one-quarter of the area (Table 2) (MDDEP 2007). Because wide-row crops dominate in the downstream portion of this watershed, large quantities of pesticides and fertilizers are used. In addition, the large numbers of hogs and cattle produce considerable quantities of manure and slurry, which is mainly useful when applied to wide-row crops such as grain corn (Berryman 2008). A study by Gangbazo and Le Page (2005) found that the total phosphorus load transported by the Yamaska River reached 329 tonnes per year, 76% of which comes mainly from agricultural sources. This annual load also places the Yamaska River on the list of agricultural watersheds with a manure surplus relative to the capacity that the land can support.

3 Methodology

3.1 STATION LOCATIONS

Since 2003, samples have been taken from the three main agricultural tributaries on the south shore of Lake Saint-Pierre to assess pesticide contamination in surface waters and to determine their potential contribution to the contamination of the St. Lawrence waters and Lake Saint-Pierre wetlands. Sampling stations are located near the mouths of the Nicolet, Saint-François and Yamaska rivers (Figure 1 and Table 3). The waters of these three tributaries first mix with the water masses on the south side of Lake Saint-Pierre before moving toward the lake's outflow (Figure 2).

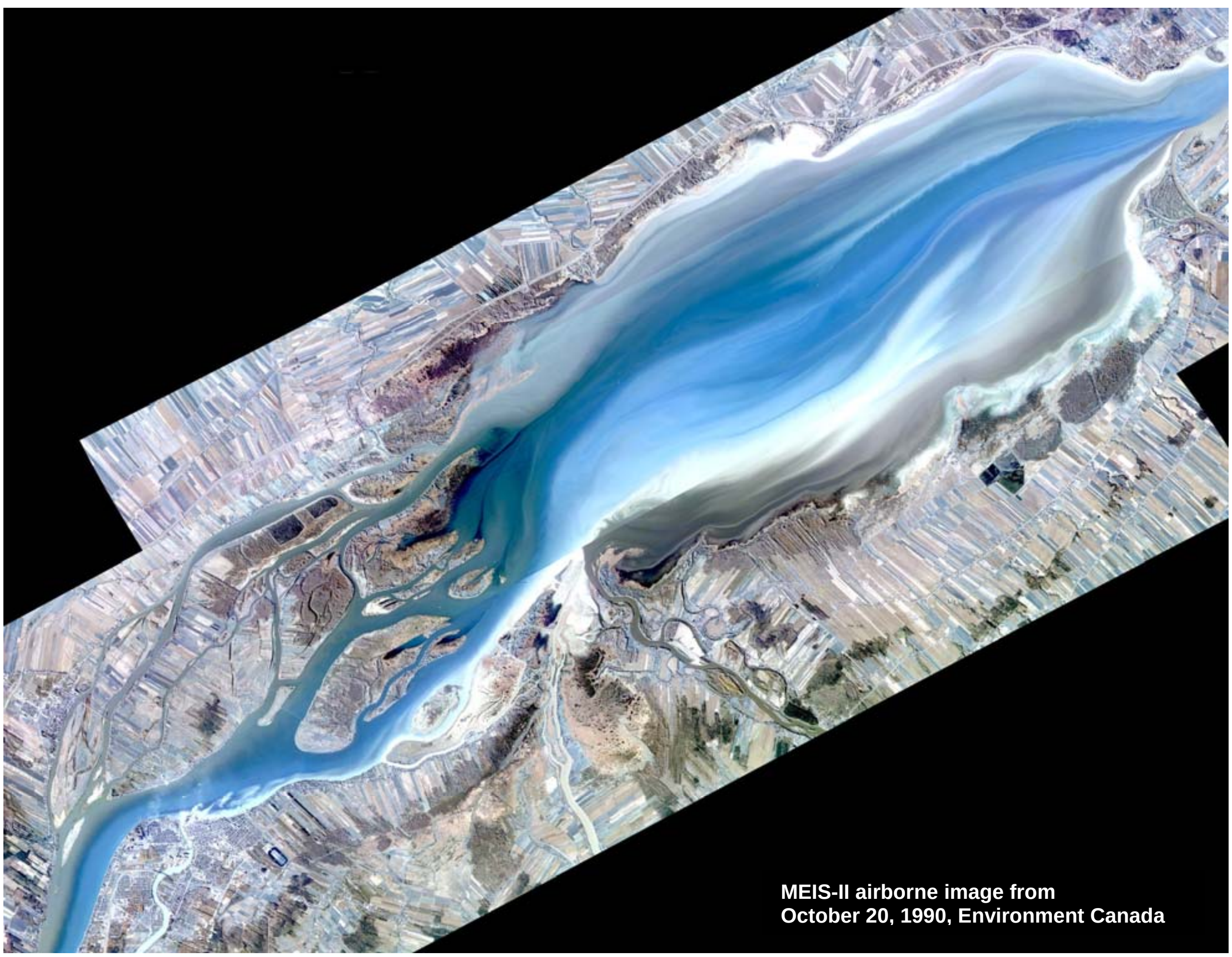


Figure 2 Lake Saint-Pierre water masses

Table 3
Location and description of pesticide monitoring program sampling stations

Longitude	Latitude	Site description
-72.6512	46.2454	Nicolet River, in Nicolet (0.3 km from mouth)
-72.8122	46.0664	Saint-François River, in Pierreville under Highway 132 bridge (11 km from mouth)
-72.9101	46.0051	Yamaska River, in Yamaska under Highway 132 bridge (14 km from mouth)

3.2 PESTICIDES MONITORED

To get an accurate reading on contamination levels by pesticides applied in these watersheds, 60 pesticides and degradation products were selected and measured (Table 4). The analyzed pesticides belong mainly to the broader chemical families of organophosphorus (OP) pesticides, carbamates, triazines, substituted urea herbicides, and phenoxy acids.

Table 4
Pesticides and degradation products analyzed and Canadian Water Quality Guidelines for these contaminants

Pesticides and degradation products	Canadian Water Quality Guidelines (ng/L)			Method detection limit (ng/L)
	Protection of aquatic life (chronic effect)[1, 2]	Water used for irrigation[2]	Prevention of contamination (water and aquatic organisms)[1]	
Herbicides				
2,4,5-T			9 000	10
2,4-D	4 000–220 000		100 000	20
2,4-DB	25 000		90 000	20
Atrazine	1 800	10 000	5 000	20
Deethylatrazine			5 000	30–40
Deisopropylatrazine			5 000	30–50
Bentazon	510 000		300 000	30–40
Bromoxynil	5 000	330	5 000	20
Butylate	56 000		400 000	20–30
Chloroxuron				80–130
Clopyralid			4 100 000	30
Cyanazine	2 000	500	10 000	30–50

Table 4 (cont.)

Pesticides and degradation products	Canadian Water Quality Guidelines (ng/L)			Method detection limit (ng/L)
	Protection of aquatic life (chronic effect)[1, 2]	Water used for irrigation[2]	Prevention of contamination (water and aquatic organisms)[1]	
Dicamba	10 000	6*	120 000	30
Dichlorprop			100 000	20–30
Diclofop-methyl	6 100	180	9 000	20
Dimethenamid	5 600			20–30
Dinoseb	50	16 000	10 000	40
Diuron	1 600		150 000	240–250
EPTC	39 000			20–30
Fenoprop (Silvex)	30 000		9 000	10
Flumetsulam				20
Glyphosate	65 000		280 000	40
AMPA				200
Imazethapyr				10
Linuron	7 000	71		40–70
MCPA	2 600	25	2 000	10
MCPB	7 300			10
Mecoprop	13 000		10 000	10
Metolachlor	7 800	28 000	50 000	10
Metribuzin	1 000	500	80 000	20
Nicosulfuron				10
Picloram	29 000		190 000	20
Rimsulfuron				10
Simazine	10 000	500	10 000	10–20
Tebuthiuron	1 600	270	500 000	240–290
Triclopyr				20
Trifluralin	200		45 000	20–50
Insecticides				
Azinphos-methyl	5–10 *		20 000	200–220
Bendiocarb			40 000	10–50
Carbaryl	200		90 000	30–70
1-naphthol				20–60
Carbofuran	1 800		90 000	60–90
Chlorfenvinphos				50–60
Chlorpyrifos	2*		90 000	20–30
Diazinon	4*		20 000	20–30
Dichlorvos				20–30
Dimethoate	6 200		20 000	40

Table 4 (cont.)

Pesticides and degradation products	Canadian Water Quality Guidelines (ng/L)			Method detection limit (ng/L)
	Protection of aquatic life (chronic effect)[1, 2]	Water used for irrigation[2]	Prevention of contamination (water and aquatic organisms)[1]	
Disulfoton			700	30
Fenitrothion			8 000	30–40
Fonofos			10 000	10–20
Malathion	100		190 000	20
Methidathion				20
Mevinphos				30–60
Parathion	13*		50 000	20–160
Parathion-methyl			9 000	30–60
Phorate			2 000	30–70
Phosalone				30–40
Terbufos			1 000	40–50
Fungicides				
Chlorothalonil	180	5 800	1 500	50–60
Myclobutanil	11 000			20–50

Note: Degradation products are in italics under their parent product.

[1] MDDEP 2002b.
[2] CCME 1999.
* The established criterion is lower than the MDL.

3.3 SAMPLING METHOD AND FREQUENCY

The sampling frequency was established based on the hydrological characteristics of the agricultural tributaries' watersheds and the period of pesticide application. The tributaries have been sampled generally once a week from late May to late August since 2003, except in 2006, when sampling ended in late July. This report presents the data gathered from 2003 to 2008 inclusively.

Water samples were taken from fixed structures such as bridges using a steel device covered in epoxy paint. The samples were collected in bottles of different sizes and compositions, depending on the pesticide. For glyphosate: 250-mL polyethylene bottles; 1-L glass bottles for phenoxy acids, and 500-mL glass bottles for the other pesticides. The bottles were supplied, washed and prepared, by the Centre d'Expertise en Analyse Environnementale du Québec

(CEAEQ). For the Ops and sulfonylureas, the insides of the caps had to be covered with aluminum foil to prevent adsorption by the plastic, and for the phenoxy acids, the cap insides had to be covered with Teflon and the water sample itself had to be acidified to a pH of < 2 by adding 5 mL/L of H_2SO_4 10N. Water samples were transported in a cooler (maximum of 4^oC) to the CEAEQ laboratory in Quebec City within 24 hours to be analyzed there.

3.4 LABORATORY ANALYSES

Samples were analyzed at the Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ). Phenoxy acid pesticides were extracted using an octadecyl column (C-18) then esterified using a diazomethane solution, purified using a silica gel column and then measured by gas chromatography and detected using mass spectrometry (MA. 403-P. CHLP 2.0 method). The sulfonylurea, triazolopyrimidine and imidazolinone families of herbicides were extracted using a 500-mg ENVI-Carb column. After elution, the extracts were measured using liquid chromatography combined with tandem mass spectrometry (MA. 403-FRIN 1.0 method). Glyphosate and AMPA were measured using liquid chromatography followed by post-column derivatization and fluorescent detection (MA. 403-GlyAmp 1.0 method). Organophosphorus, triazine, carbamate and substituted urea pesticides in the water were analyzed by extracting the pesticides using an octadecyl column (C-18), measured using gas chromatography and detected by mass spectrometry (MA. 403-Pest 3.1 method). Detailed protocols for CEAEQ analysis methods are available on the CEAEQ website at www.ceaeq.gouv.qc.ca/methodes/chimie_org.htm (in French only).

The analytical pesticide detection limits associated with the analysis methods (method detection limit or MDL) are presented in Table 4. Laboratory MDLs are dependent upon available equipment and the quantity of water used. For this monitoring, the MDLs were generally low enough to produce a good profile of the concentrations of various pesticides during the application period. However, certain MDLs were higher than the water quality criteria. Farmers are also increasing their use of new-generation pesticides, which may require only minimal quantities during application (in grams or even in milligrams per hectare). These pesticides are therefore found in surface waters at concentrations on the order of parts per trillion, which require much more precise and much more costly analysis methods.

3.5 DATA PROCESSING AND ANALYSIS

Environment Canada collated, verified and validated the data for the period from 2003 to 2008. Descriptive statistics—such as detection frequency and frequency of water quality criteria exceedances—were also calculated by station for the entire 2003–2008 period.

Pesticides are generally detected in surface waters between mid- or late May and late August. Therefore, more comprehensive descriptive statistics are presented for cases where a pesticide was detected in 45% or more of samples per year between May 30 and August 30. For these calculations, a value equal to half the MDL was used on dates when the pesticide was not detected. This method is currently employed when a pesticide has a detection frequency of 50% or more. For the present monitoring activity, the number of samples per station per year is relatively low and often irregular (from 9 to 13 samples between May 30 and August 30), which is why all pesticides detected in 45% or more of the samples were taken into account. These additional descriptive statistics by year consist of detection frequency, average concentration and standard deviation, the median and the minimum and maximum concentrations observed. The detection percentage and number of pesticides detected by year were compared among rivers by an analysis of variance.

Seasonal and annual variations in the most frequently detected pesticides (≥ 45% of samples) are illustrated and compared among the various tributaries. Regression analyses were also conducted to determine whether pesticide concentrations are linked to precipitation and river flow.

Lastly, summer pesticide loads (a *load* being the quantity of a pesticide exported by a river to a given location for a given period) were estimated for each tributary and compared among them. Because no relationship was observed between pesticide concentration and flow, the weighted-average-concentration method was used to calculate loads (Pham et al. 2000, Cossa et al. 1998, Meybeck et al. 1992). Total pesticide concentrations (i.e. dissolved and particulate phases) were considered, but since the particulate phase is negligible in surface water (Squillace and Thurman 1992), the load equation for the dissolved phase was used (Cossa et al. 1998).

Loads were calculated for a 92-day period (from May 30 to August 30) using the following equation:

$$F = 92\overline{Q}\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i}$$

where F is the summer load, $\overline{Q}$ is the average daily flow for the 92-day period between May 30 and August 30, C_i is the instantaneous concentration, Q_i is the instantaneous flow, and n is the number of observations.

Errors associated with loads for the same period were calculated using the following variance equation (the root mean square error is equal to the square root of the variance):

$$\sigma_F^2 = 92\left(\frac{m-n}{m}\right)\frac{\overline{Q^2 \sum_i Q_i^2}}{\left(\sum_i Q_i\right)^2}\sigma_c^2$$

where σ_F^2 is the load variance, m is the number of days in the period between May 30 and August 30, inclusively, and σ_C^2 is the variance in measured concentrations (Cossa et al. 1998).

The specific load of atrazine (e.g. kilograms of pesticide in the water per square kilometre of cropland) was then estimated based on the summer load and the watershed area to establish a link between the quantity of atrazine applied and the quantity of atrazine found in surface water.

4 Results and Discussion

4.1 PESTICIDES DETECTED

In the Nicolet River, a total of 20 pesticides (16 herbicides, 3 insecticides and 1 fungicide) out of the 54 analyzed were detected at least once in this river from 2003 to 2008 (Table 5). Among these, three herbicides and one degradation product of atrazine had a detection frequency of 45% or more between May 30 and August 30 in at least five of the six years sampled (Appendix 3). In order, atrazine, metolachlor and dicamba are the most frequently detected pesticides. MCPA was detected only in 2006 at a frequency of ≥ 45%. Atrazine detection frequencies observed near the mouth of the Nicolet River between 2003 and 2008 are comparable to the 1991 frequency (Rondeau 1996).

The Saint-François River had the lowest number of detected pesticides, with a total of 15 (10 herbicides, 3 insecticides and 2 fungicides) out of the 54 analyzed (Table 5). Similarly, atrazine was the most frequently detected herbicide, even though it was less frequent than in the Nicolet River (Appendix 3). Metolachlor came in second with a detection frequency greater than 45% only since 2006. As for 2,4-D, it was only detected in just under half of the samples taken in 2008.

The largest number of detected pesticides was in the Yamaska River, with a total of 26 pesticides (21 herbicides, 3 insecticides and 2 fungicides) out of the 60 analyzed in all (Table 5). The most frequently detected pesticides were atrazine and metolachlor, followed by bentazon and dicamba. Dimethenamid was detected more than 45% of the time from 2003 to 2005 only, and MCPA was detected at over 45% only in 2006, as in the Nicolet River (Appendix 3). Glyphosate and its degradation product, AMPA, have been analyzed since 2007 and are both frequently observed in surface-water samples. Atrazine and metolachlor detection frequencies observed near the mouth of the Yamaska River between 2003 and 2008 continued to be just as high, compared to 1989–1991 data (Rondeau 1996).

Median concentrations, almost always lower than the averages (Appendix 3), show that pesticides are present in relatively low concentrations in summer and that the highest concentrations are seen only sporadically during this period. The highest concentrations are almost always seen between early June and mid-July. The data distribution is rarely normal;

therefore, the median, in this case, gives a better measure of the main trend. In general, median pesticide concentrations were greater in the Yamaska River than in the Nicolet and Saint-François rivers (e.g. atrazine, deethylatrazine, dicamba and metolachlor), even when maximum concentrations were similar within the same year (e.g. atrazine in the Nicolet and Yamaska rivers in 2006).

4.1.1 Inter-annual comparison

The average number of herbicides detections per year varies significantly from one river to another (one-way analysis of variance; $p \leq 0.001$). The largest number of detections was in the Yamaska River, from 55 to 94 herbicide detections annually (not counting detections of glyphosate and AMPA, only sampled in this river since 2007) (Appendix 4). In the Nicolet River, there were 1.4 to 2.3 times fewer (38 to 56) detections per year and, in the Saint-François River, 1.9 to 8.5 times fewer (11 to 33) detections per year. The number of detections remained relatively stable in the Nicolet River between 2003 and 2008; in the Saint-François River, however, it is on the rise (three times greater in 2008 than in 2003) even though the number is still relatively low. In the Yamaska River, the number of detections seemed to be on a downward trend in 2006 and 2007 but rose again in 2008 to a level comparable to that of 2003 to 2005. Sampling has been done for only a few years but, to date, only the linear regression of the Saint-François River showed a significant upward trend in the number of detections ($p = 0.007$). In the case of insecticides and fungicides, the total number of detections was still very low, between zero and three detections per year per river.

As with the annual average number of detections, the average number of pesticides detected per year was much greater in the Yamaska River than in the Nicolet and Saint-François rivers (one-way analysis of variance; $p \leq 0.001$) (Appendix 4). From 2003 to 2008, the pesticide cocktails to which aquatic organisms were exposed in the Yamaska River contained 10 to 15 different pesticides (up to 17 when glyphosate and AMPA are included). Aquatic organisms in the Nicolet and Saint-François rivers were exposed to mixtures of 7 to 12 and 6 to 10 pesticides per year, respectively. Once again, the number of years sampled is relatively small but, to date, no significant trend—upward or downward—in the number of pesticides detected annually has been observed in any of the rivers since 2003. Note that, if all of the pesticides used in the watersheds had been analyzed, the pesticide mixture would likely be even bigger.

Minimum and maximum concentrations and average standard deviations (Appendix 3) show that pesticide concentrations in surface waters tend to vary widely in the tributaries over the course of the summer, unlike the variations seen in the St. Lawrence River (Pham et al. 2000). Conversely, variations and maximum concentrations observed near the mouths of the rivers under study are lower than those observed in the tributaries farther upstream in the watersheds (Giroux 2010, Giroux et al. 2006, Rondeau 1996). Probably the best explanation for this observation is that the pesticides that reach surface waters in the vast St. Lawrence watershed are increasingly diluted heading downstream.

Also of note is that the most frequently detected pesticides and degradation products are all herbicides. Furthermore, all of these herbicides are on the list of pesticides used on corn and soybean crops (Appendix 1), the type of crops known for occupying a large proportion of cropland and, therefore, for using large quantities of pesticides in the St. Lawrence Lowlands. These results are no surprise and are consistent with those obtained by the MDDEP in tributaries farther upstream in the same watersheds (Giroux 2010, Giroux et al. 2006).

All of this data on pesticides near the mouths of the Nicolet, Saint-François and Yamaska rivers strongly suggest that the fragile ecosystems on the southern side of Lake Saint-Pierre are exposed to numerous pesticides over the course of the summer.

4.1.2 Uses of the most frequently detected pesticides

The main pesticides detected accurately reflect the crops for which they are used in Quebec (Table 6). Forage crops occupy a large proportion of cropland but these are not the crops that require large quantities of pesticides. Corn crops, however, require extensive pesticide use, and the area occupied by this crop, especially in the Yamaska River watershed, explains, in large part, the presence of the main pesticides detected (atrazine, metolachlor and glyphosate) in the surface waters of the three rivers under study. Metolachlor and glyphosate are also used on soybean crops. The other frequently detected pesticides include dicamba, bentazon, 2,4-D, MCPA, dimethenamid and mecoprop, all of which are also used on corn, soybeans, wheat, barley and oat crops, to name just a few. Glyphosate is also used in orchards. Insecticides and fungicides—though rarely detected—are used mainly on several fruit and vegetable crops as well as wheat, forage and corn crops.

Table 5
Complete list of pesticides and degradation products analyzed in Lake Saint-Pierre tributaries as well as their detection frequencies and frequency of exceedances of Canadian Water Quality Guidelines from 2003 to 2008

Pesticides	River								
	Nicolet			Saint-François			Yamaska		
	n	Detection frequency (%)	Exceedance frequency (%)	*n*	Detection frequency (%)	Exceedance frequency (%)	*n*	Detection frequency (%)	Exceedance frequency (%)
Herbicides									
2,4,5-T	78	0	n/a	77	0	n/a	79	0	0
2,4-D	78	10	0	77	26	0	79	25	0
2,4-DB	78	5.1	0	77	0	0	79	0	0
Atrazine	81	90	0	78	69	0	88	98	1.1[a]
Deethylatrazine	81	43	n/a	78	6.4	n/a	88	74	n/a
Deisopropylatrazine	81	4.9	n/a	78	5.1	n/a	88	20	n/a
Bentazon	78	23	0	77	0	0	79	65	0
Bromoxynil	78	0	0	77	1.3	0	79	5.1	0
Butylate	81	0	0	78	0	0	87	0	0
Chloroxuron	81	1.2	n/a	78	0	n/a	88	0	n/a
Clopyralid	87	1.3	n/a	77	0	n/a	79	8.9	n/a
Cyanazine	81	0	0	78	0	0	88	0	0
Dicamba	78	42	42[b]	77	20	20[b]	79	62	62[b]
Dichlorprop	78	0	n/a	77	0	n/a	79	0	n/a
Diclofop-methyl	78	0	0	77	0	0	79	0	0
Dimethenamid	81	1.2	0	78	0	0	88	42	0
Dinoseb	78	0	0	77	0	0	79	0	0
Diuron	80	1.2	0	78	0	0	88	0	0
EPTC	81	0	0	78	0	0	88	2.3	0
Fenoprop (Silvex)	78	0	0	77	0	0	79	0	0
Flumetsulam[d]							10	30	n/a
Glyphosate[c]							31	65	0
AMPA[c]							31	94	n/a
Imazethapyr[d]							10	10	n/a
Linuron	81	1.2	0	78	0	0	88	0	0
MCPA	78	29	24[b]	77	3.9	1.3[b]	79	28	23[b]
MCPB	78	0	0	77	0	0	79	1.3	0
Mecoprop	78	3.8	0	77	10	0	79	27	0
Metolachlor	81	69	0	78	38	0	88	100	0
Metribuzin	81	0	0	78	0	0	88	1.1	0
Nicosulfuron[d]							10	10	n/a
Picloram	78	0	0	77	0	0	79	0	0
Rimsulfuron[d]							10	0	n/a
Simazine	81	6.2	0	78	5.1	0	88	11	0
Tebuthiuron	81	0	0	78	0	0	88	0	0
Triclopyr	77	0	n/a	77	0	n/a	79	0	n/a

Table 5 (cont.)

Pesticides	River								
	Nicolet			Saint-François			Nicolet		
	n	**Detection frequency (%)**	**Exceedance frequency (%)**	***n***	**Detection frequency (%)**	**Exceedance frequency (%)**	***n***	**Detection frequency (%)**	**Exceedance frequency (%)**
Trifluralin	81	0	0	78	0	0	88	0	0
Insecticides									
Azinphos-methyl	81	0	0*	78	0	0*	88	0	0*
Bendiocarb	81	0	n/a	78	0	n/a	88	0	n/a
Carbaryl	81	1.2	0	78	1.3	0	88	1.1	0
1-naphthol	78	0	n/a	74	0	n/a	85	0	n/a
Carbofuran	81	0	0	78	0	0	88	0	0
Chlorfenvinphos	81	0	n/a	78	0	n/a	88	0	n/a
Chlorpyrifos	81	4.9	4.9[a] *	78	7.7	7.7[a] *	88	1.1	1.1[a] *
Diazinon	81	0	0*	78	1.3	1.3[a] *	88	0	0*
Dichlorvos	80	0	n/a	78	0	n/a	87	0	n/a
Dimethoate	81	3.7	0	77	0	0	88	2.3	0
Disulfoton	58	0	n/a	58	0	n/a	65	0	n/a
Fenitrothion	81	0	n/a	78	0	n/a	88	0	n/a
Fonofos	81	0	n/a	78	0	n/a	88	0	n/a
Malathion	81	0	0	78	0	0	88	0	0
Methidathion	81	0	n/a	78	0	n/a	88	0	n/a
Mevinphos	81	0	n/a	78	0	n/a	88	0	n/a
Parathion	81	0	0*	78	0	0*	88	0	0*
Parathion-methyl	81	0	n/a	78	0	n/a	88	0	n/a
Phorate	77	0	n/a	73	0	n/a	83	0	n/a
Phosalone	80	0	n/a	78	0	n/a	88	0	n/a
Terbufos	77	0	n/a	73	0	n/a	83	0	n/a
Fungicides									
Chlorothalonil	81	0	0	78	1.3	1.3[a]	88	1.1	0
Myclobutanil	81	1.2	0	78	1.3	0	88	2.3	0

n = total number of samples for entire period between 2003 and 2008. This number may be greater than the sum of *n*s per pesticide per river in Appendix 3, which, for statistical analysis purposes, considers only those samples taken between May 30 and August 30.

% in bold: Means the pesticide was detected at 45% or more in at least one year between 2003 and 2008.

Exceedance frequencies are calculated in relation to the total *n* value.

* The MDL used is higher than the established criterion for the protection of aquatic life; the exceedance frequency may, therefore, be underestimated.

n/a: Exceedance frequency impossible to determine because the water quality criteria for protection of aquatic life are unknown.

[a] Frequency at which the criterion for protection of aquatic life (chronic effect) was exceeded.
[b] Frequency at which the water used for irrigation criterion was exceeded.
[c] Only sampled in 2007–2008 in the Yamaska River.
[d] Only sampled in 2004 in the Yamaska River.

Table 6
Examples of Quebec crops associated with the pesticides detected (from most to least frequently detected)

Pesticide	Pesticide type	Pesticide mode of action	Examples of associated crops
Herbicides			
Atrazine	Triazine	Inhibits photosynthesis[1]	Corn
Metolachlor	Chloroacetamide	Inhibits synthesis of lipids (very long chain fatty acids)	Corn, soybeans
Glyphosate	Glycine	Inhibits the EPSPS enzyme needed to synthesize aromatic amino acids	Corn, soybeans, apples
Dicamba	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, spring and fall wheat, barley, oats
Bentazon	Benzothiadiazole	Inhibits photosynthesis[1]	Corn, soybeans, peas, flax, snap beans, highbush blueberries, new plantings of apples, pears
2,4-D	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, spring and fall wheat, barley, oats
MCPA	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, peas, vineyards, pastures, seedlings of white, ladino, alsike or red clover sowed alone or under wheat, oats, barley, rye
Dimethenamid	Chloroacetamide	Inhibits synthesis of lipids (very-long-chain fatty acids)	Corn, dry beans, soybeans, storage onions and non-productive vines
Mecoprop	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, spring and fall wheat, barley, oats
Simazine	Triazine	Inhibits photosynthesis[1]	Corn, berries, vines, established asparagus, yellow sweet-clover, raspberries, loganberries, blackberries, highbush blueberries, alfalfa, apples, pears
Clopyralid	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn
2,4-DB	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, alfalfa, spring and fall wheat, barley, oats
Bromoxynil		Inhibits photosynthesis[1]	Corn, spring wheat, barley, oats, fall rye, millet, triticale, forage sorghum, garlic and numerous true grasses
Flumetsulam	Triazolopyrimidine	Inhibits the ALS enzyme needed to synthesize branched-chain amino acids	Corn, soybeans
EPTC	Thiocarbamate	Inhibits lipid synthesis	Potatoes, alfalfa, yellow sweet-clover, snap or dry beans, flax, sunflower
Chloroxuron	Substituted urea	Inhibits photosynthesis[1]	Soybeans, onions, strawberries, celery
Diuron	Substituted urea	Inhibits photosynthesis[1]	Vines, asparagus, gladioli

Table 6 (cont.)

Pesticide	Pesticide type	Pesticide mode of action	Examples of associated crops
Herbicides			
Imazethapyr	Imidazolinone	Inhibits the ALS enzyme needed to synthesize branched-chain amino acids	Corn, soybeans
Linuron	Substituted urea	Inhibits photosynthesis[1]	Corn, soybeans, carrots, celery, dill, parsnips, potatoes, asparagus, wheat, oats, barley, gladioli, fruit trees
MCPB	Phenoxy acid	Imitates auxin, a growth phytohormone[2]	Corn, peas, vineyards, pastures, seedlings of white, ladino, alsike or red clover sowed alone or under wheat, oats, barley, rye
Metribuzin	Triazine	Inhibits photosynthesis[1]	Potatoes
Nicosulfuron	Sulfonylurea	Inhibits the ALS enzyme needed to synthesize branched-chain amino acids	Corn, soybeans
Insecticides			
Chlorpyrifos	Organophosphorus	Neurotoxin[3]	Wheat, vegetables (broccoli, various cruciferous vegetables, etc.)
Dimethoate	Organophosphorus	Neurotoxin[3]	Apples, beans, various cruciferous vegetables, peas, peppers, potatoes, tomatoes, alfalfa, forage crops, pears, strawberries
Carbaryl	Carbamate	Neurotoxin[3]	Apples, other fruits and vegetables
Diazinon	Organophosphorus	Neurotoxin[3]	Corn, peas, various cruciferous vegetables, potatoes and several other vegetables, apples and other tree fruits, small fruits, berries, vines, tobacco
Fungicides			
Myclobutanil	Triazole	Inhibits the enzyme needed to synthesize ergosterol (constituent of a cell membrane)	Apples, vines, strawberries and other fruits, potatoes
Chlorothalonil	Chloronitrile	Inhibits spore germination and is toxic to the cell membrane	Potatoes, several vegetables (e.g. the gourd family, tomatoes), small fruits, corn, soybeans

[1] Inhibits photosynthesis at photosystem II
[2] Pesticides that imitate the growth phytohormone auxin remain in the plant longer than normal and cause physiological disorders (e.g. stunted growth, thickened leaves, deformed stalks) as well as plant death.
[3] Neurotoxic compound that inhibits the acetylcholinesterase enzyme, which regulates the acetylcholine neurotransmitter.

4.2 SEASONAL AND ANNUAL VARIATIONS IN THE PESTICIDES MOST OFTEN DETECTED

4.2.1 Seasonal and annual variations in pesticide concentrations

4.2.1.1 Atrazine

Overall, maximum concentrations of this pesticide in tributary surface waters are generally observed in mid- to late June (Figure 3), but sometimes there is a second, often smaller, peak in July after heavy rainfall. Atrazine concentration normally drops to a relatively low level (< 100 ng/L) at the end of August. In 2008, atrazine was measured in the Yamaska River until the end of September, and still at very low concentrations (20–30 ng/L).

From year to year, maximum atrazine concentrations and the dates on which concentration peaks are observed vary among tributaries. Concentration increases and decreases in tributaries sometimes coincide (e.g. in 2008), but usually, they are out of sync by a few days. In addition, the Nicolet and Saint-François rivers drain approximately the same agricultural areas, but seasonal and annual variations in atrazine concentrations are less pronounced in the Saint-François River. The Saint-François River's higher flow could dilute and therefore reduce pesticide concentrations in surface water. Maximum atrazine concentrations in the Nicolet and Yamaska rivers are sometimes similar (e.g. in 2004 and 2006), but usually, the highest concentrations are observed in the Yamaska River, which is consistent with de percentage of agriculture in these basins.

4.2.1.2 Metolachlor

In the three rivers, seasonal and annual variations in metolachlor more or less coincide with those of atrazine (Figure 3). This was predictable because farmers often use a combination of atrazine and metolachlor on corn crops. As with atrazine, maximum concentrations of this pesticide in tributary surface waters are generally observed in mid- to late June. Sometimes, second and third peaks are observed in July before the concentration drops to a relatively low level (< 100 ng/L) at the end of August.

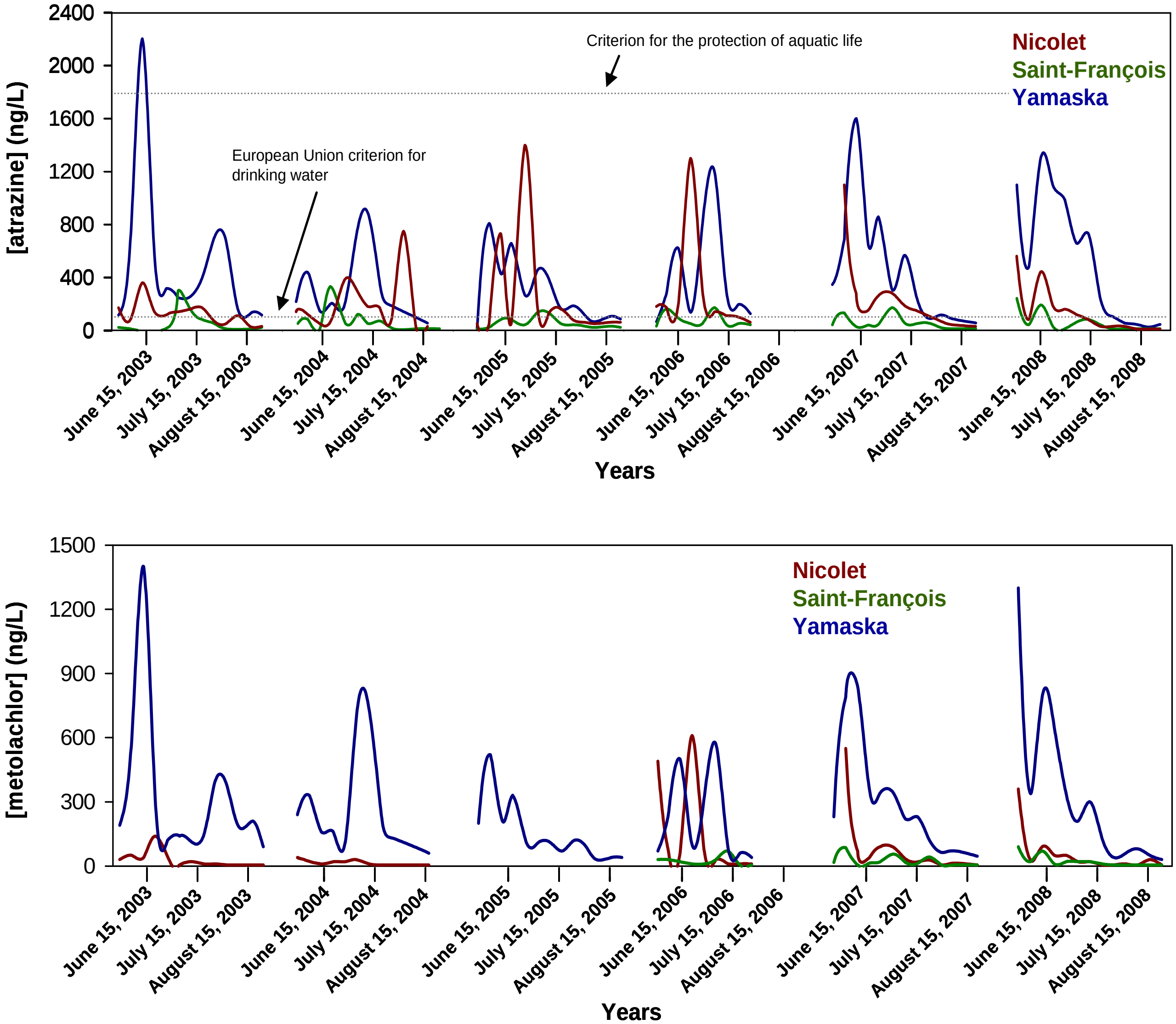


Figure 3 Comparison of seasonal and annual variations in atrazine and metolachlor in the main tributaries of Lake Saint-Pierre

In short, the seasonal variations observed for a given pesticide seem to be independent from one watershed to the next. For example, it is impossible to accurately predict when maximum atrazine concentrations will be detected in the Nicolet River surface waters based on the atrazine concentrations observed in the Yamaska River. Despite the proximity of the watersheds being studied, they can be different enough for the relative pesticide input in rivers, and therefore the concentration peaks, not always to coincide. This may be due to differences in the dates and quantities of precipitation, combined with pesticide runoff and leaching time, which can be affected by slight differences in slope, soil composition, etc. Differences in application dates can also be a contributing factor.

As shown in Figure 3, in summer, pesticide concentration peaks near the mouths of the three watersheds being studied are not always observed on the same dates. However, within a single watershed, the concentration peaks of various pesticides often appear on the same sampling dates (Figure 4).

4.2.2 Annual variations in median pesticide concentrations

Median atrazine concentrations in the three tributaries have been fairly stable since 2003 near the mouth of the Nicolet River and the Saint-François River, but have been increasing in the Yamaska River, although none of the regressions are significant (Figure 5). However, median and maximum atrazine concentrations in the Yamaska River have decreased significantly compared to those observed from 1989 to 1991 (Rondeau 1996). For example, from 1989 to 1991, median concentrations varied from 610 to 1700 ng/L, and maximum concentrations, from 4030 to 9480 ng/L, whereas from 2003 to 2008, they varied from 190 to 480 ng/L and from 810 to 2200 ng/L, respectively. Giroux (2010) observed a similar trend in the Chibouet River, further upstream in the same watershed (trend based on 16 consecutive years of data since 1992). In the Nicolet River, median and maximum atrazine concentrations in 1991 (Rondeau 1996) were 160 ng/L and 440 ng/L, respectively, which is comparable to 2003–2008 data. Giroux (2010) observed more of a downward trend in the Saint-Zéphirin River, located further upstream in the same watershed.

As with atrazine, median and maximum metolachlor concentrations in the Yamaska River are lower than those observed in 1990 (600 ng/L and 2900 ng/L, respectively) (Rondeau 1996). The highest median and maximum concentrations between 2003 and 2008 were 200 ng/L and 1400 ng/L, respectively. Giroux (2010) observed a similar trend in the Chibouet River from 1992 to 2008.

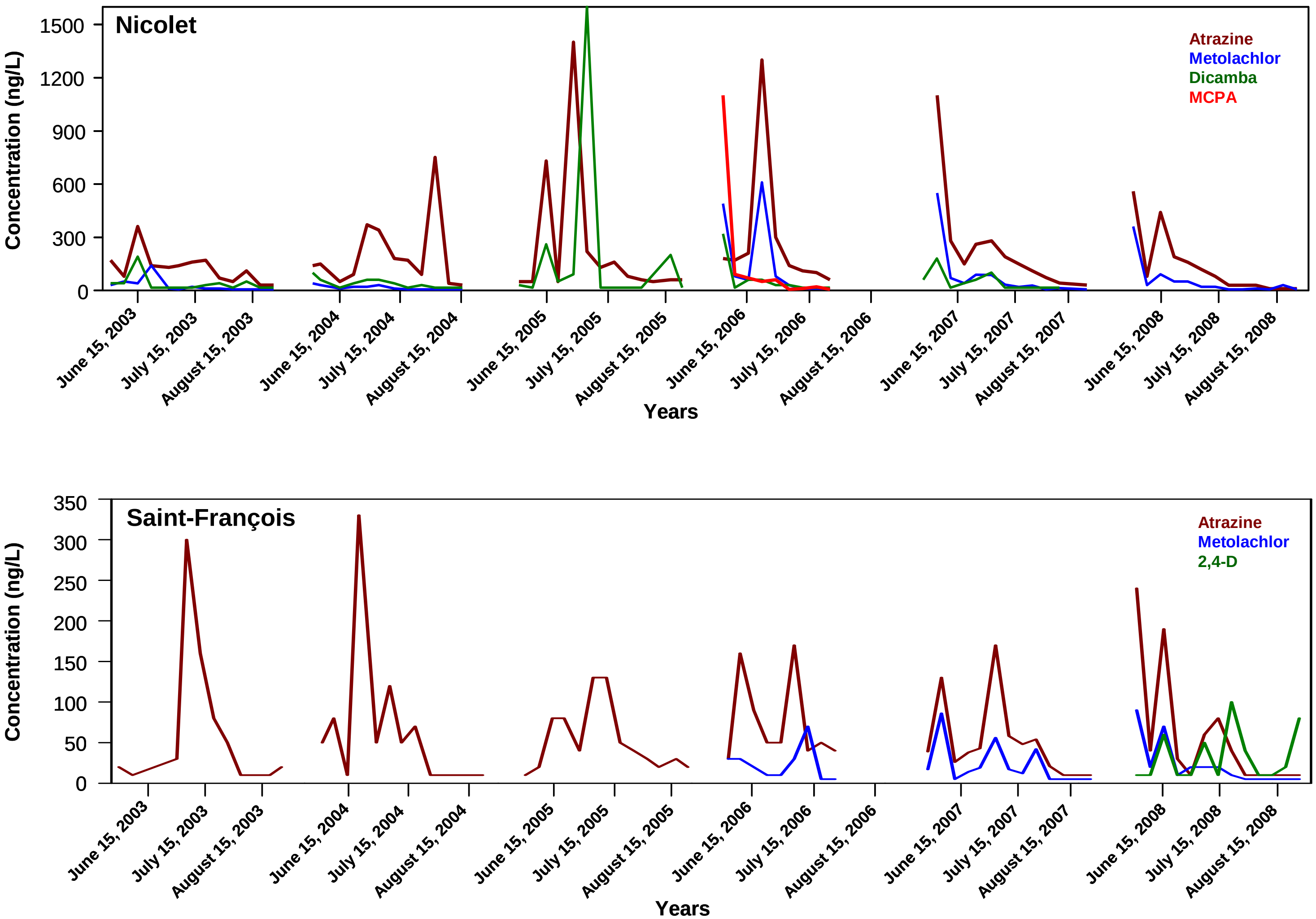


Figure 4 Comparison of concentration peaks for the pesticides most often detected, by river

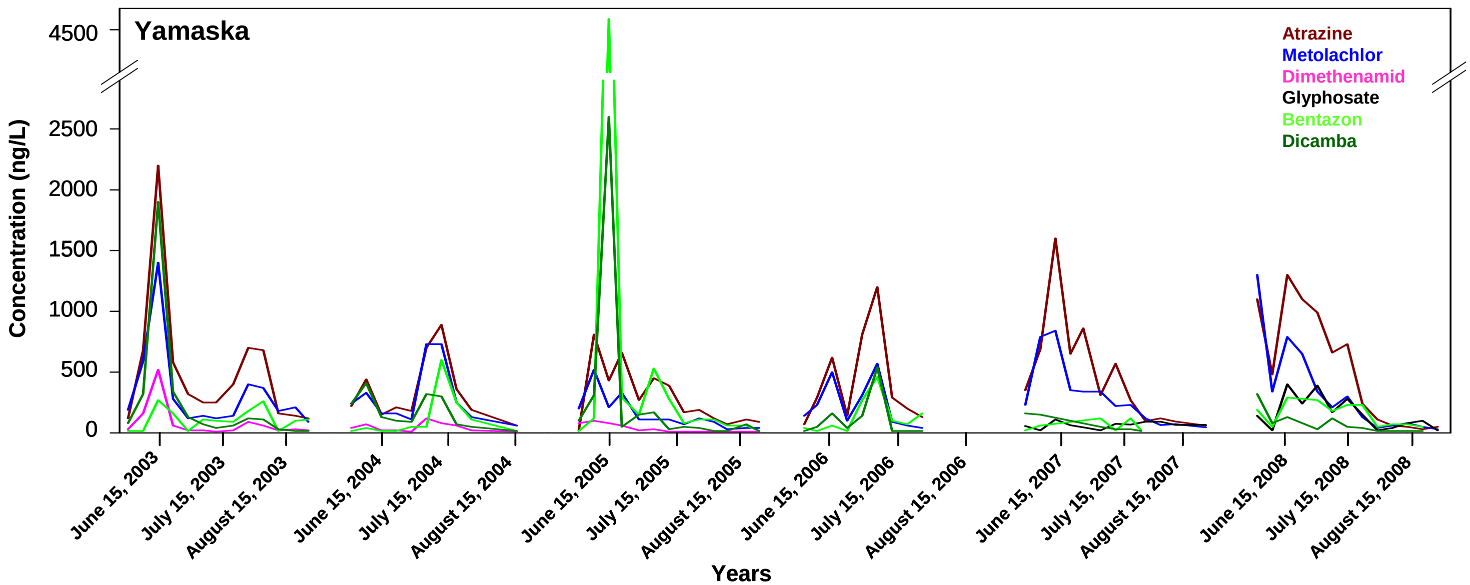


Figure 4 (cont.)

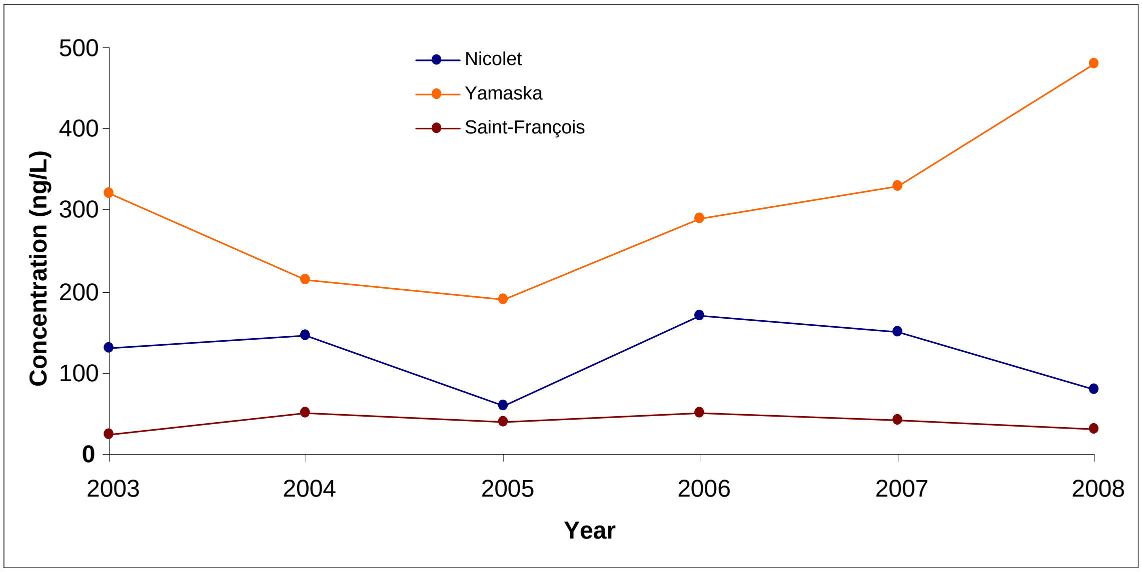


Figure 5 Comparison of median atrazine concentrations in summer in the main tributaries of Lake Saint-Pierre

In the Yamaska River, none of the other pesticides often detected showed a significant upward or downward trend from 2003 to 2008 (Figure 6). The same goes for dicamba; there does not seem to be any downward trend like that observed by Giroux (2010), but our observations are based on a shorter period. However, dimethenamid seems to be used less and less, since its median concentrations decreased until 2005, after which it was no longer detected often enough to establish medians. Also, we do not have enough data on glyphosate, but an upward trend would probably be observed in surface waters if this pesticide had been analyzed for a few years, as stated by Giroux (2010) and indicated by Quebec's reported sales.

It should be pointed out that median atrazine and metolachlor concentrations in the Nicolet and Yamaska rivers are approximately 1.5 to 2 times lower than those detected in tributaries further upstream in the same watersheds (in the Saint-Zéphirin River and the Chibouet River, respectively), as reported by Giroux (2010).

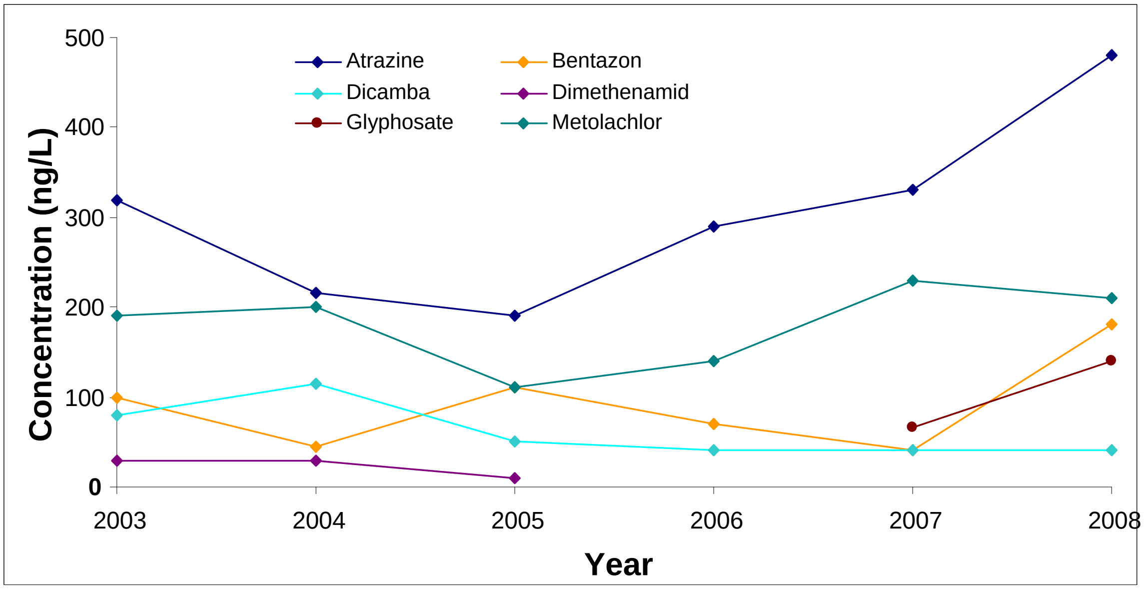


Figure 6 **Comparison of median summer concentrations of the pesticides most often detected in the Yamaska River**

4.2.3 Pesticide ratio and degradation product

Of the degradation products analyzed, deethylatrazine (DEA) is among the most frequently detected. DEA concentrations are always relatively low (up to 280 ng/L), whereas atrazine concentrations can be much higher, especially in June (up to 2200 ng/L). It may take atrazine anywhere from a few days to several years to break down (Lazorko-Connon and Achari 2009, Schottler and Eisenreich 1997, Forrest and Caux 1989). Its degradation, or at least partial degradation, by photolysis and hydrolysis in surface water following application helps explain the behaviour of atrazine and DEA over the summer. The ratio of atrazine and DEA is generally higher in late May to early June and decreases over the summer to reach nearly 1:1 in mid-August (day 80; Figure 7). These variations can be explained by the following: in late May to early June, the ratio is generally high because the atrazine applied to soil has already started to pollute the surface waters of nearby waterways, and the level of degradation is still low, so there is little DEA. As the season progresses, the ratio decreases and nears 1:1 as the quantity of atrazine applied decreases and breaks down and the quantity of DEA increases. Sometimes, the ratio is low at the end of May ([atrazine] ≈ [DEA]), like in 2005 and 2006. This ratio may indicate that sampling was done before atrazine was applied and that the concentrations measured are due to leaching of the atrazine and DEA remaining in the soil from the previous year. Therefore, atrazine concentrations generally decrease over time after the application period as the product breaks down in the environment. Conversely, DEA concentrations are lower at the beginning of the season and tend to increase and/or remain stable toward the end of the summer to reach levels similar to those of atrazine.

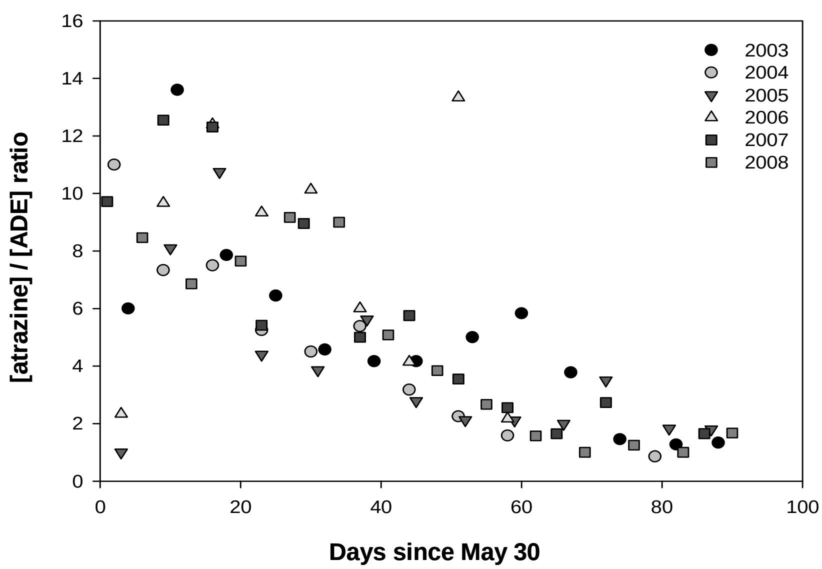


Figure 7 Ratios of the concentrations of atrazine and its degradation product in the Yamaska River

Glyphosate and AMPA ratios in summer 2007 and 2008 follow a pattern similar to that of atrazine and DEA: lower ratios early in the season, followed by higher ratios after the pesticide application period, and a decrease in the ratios over the course of the summer to reach levels similar to pre-application levels (Figure 8). The major difference is in the magnitude of the ratios. Contrary to the case of atrazine and DEA, AMPA concentrations are often higher than concentrations of its parent product. In soil, glyphosate has a half-life of 20 to 100 days and AMPA breaks down slowly, whereas in surface waters, glyphosate undergoes rapid microbial degradation and sometimes even has a half-life of less than 24 hours (Health Canada 1987). Therefore, it is normal to detect higher concentrations of AMPA than of glyphosate further from the source (further downstream in the watershed) and from the application period. Unlike atrazine, which is applied to young corn shoots, glyphosate can be used at various crop growth stages, which could explain why ratios slightly increase again in July and August.

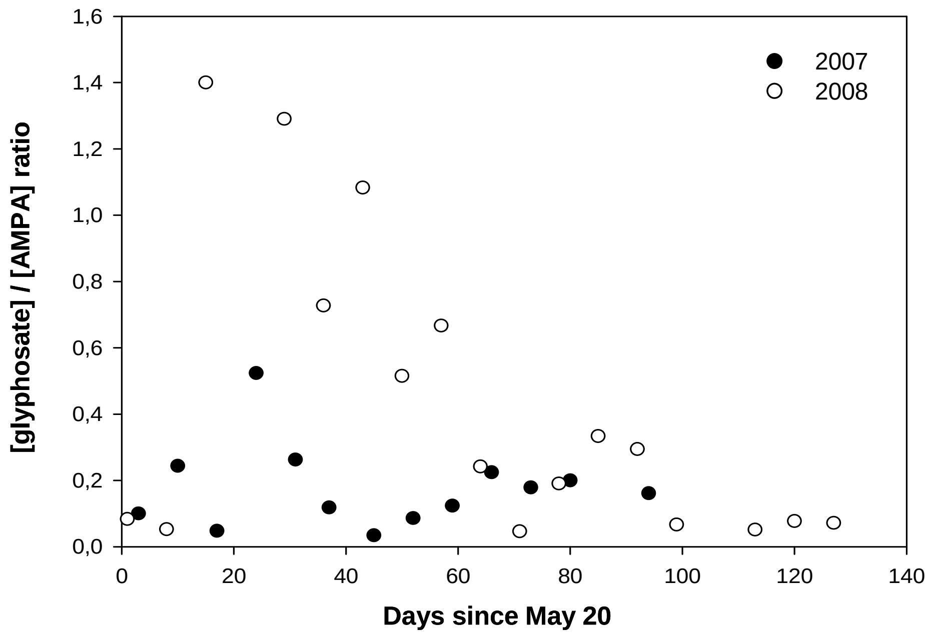


Figure 8 Ratios of the concentrations of glyphosate and its degradation product in the Yamaska River

4.3 FREQUENCY OF WATER QUALITY CRITERIA EXCEEDANCE

Pesticide concentrations in the rivers being studied were compared to three water quality criteria: criteria for the protection of aquatic life (chronic effect); irrigation water use; and the prevention of contamination of water and of aquatic organisms. The criterion for the protection of aquatic life (chronic effect) establishes the highest concentration of a substance that will not have any harmful effects on aquatic organisms or their offspring after daily exposure to it for their entire lives (MDDEP 2002b). The criterion for the protection of irrigation water is established based on the sensitivity of non-targeted crops and the maximum crop irrigation rate to calculate species maximum acceptable toxicant concentrations (CCME 1999). The criterion for the prevention of water contamination is established to protect water and aquatic organisms from any type of contamination that could negatively affect current and future human consumption. This criterion is often the same as the Canadian standard established for drinking water, which applies to water that is ready for consumption, but it is not designed to apply directly to raw water supplies such as the surface waters sampled for this report (MDDEP 2002b, CCME 1999). Certain water treatment technologies may partly eliminate pesticides from drinking water to different degrees (Lazorko-Connon and Achari 2009).

According to our observations, at least six of the pesticides analyzed exceeded at least one of the water quality criteria (Table 5). Giroux (2010) also observed exceedances in the same pesticides in the rivers further upstream within the Yamaska River and Nicolet River watersheds. However, the frequency of the exceedances observed by Giroux (2010) is still greater than the frequency of those observed near the mouth of the Yamaska River and the Nicolet River. As the distance from the source of pesticide application increases, river flow increases and pesticides are more diluted and more likely to be broken down.

4.3.1 Criteria for the protection of aquatic life (chronic effect)

The herbicide atrazine exceeded the criterion established for the protection of aquatic life (1800 ng/L) in the Yamaska River at a frequency of 1.1%: it exceeded the criterion once in 2003 with a concentration of 2200 ng/L. This frequency of exceedance is lower than that observed by Giroux (2010) in smaller rivers like the Chibouet River in the Yamaska River watershed (14.7% from 2005 to 2007) and the Saint-Zéphirin River in the Nicolet River watershed (3.2% from 2005 to 2007).

Three other pesticides (two insecticides and one fungicide) exceeded the criterion for the protection of aquatic life. It should be noted that the frequency of exceedance for the two insecticides chlorpyrifos and diazinon is potentially underestimated since the method detection limits (MDLs) for these pesticides are above the criteria (Table 4). Therefore, every time these pesticides are detected, they exceed the quality criteria, and thus, the frequency of exceedance could be even higher than estimated if the MDLs were lower.

Chlorpyrifos is the pesticide that exceeded its criterion for the protection of aquatic life most often, 11 times in total, with concentrations varying from 20 to 240 ng/L: twice in 2005 and twice in 2006 in the Nicolet River; twice in 2003, three times in 2005 and twice in 2006 in the

Saint-François River; and once in 2008 in the Yamaska River. The insecticide diazinon exceeded its criterion (4 ng/L) only once in the Saint-François River in June 2006, with a concentration of 540 ng/L. The fungicide chlorothalonil was found to be above its criterion (180 ng/L) only once in 2003 in the Saint-François River, with a non-negligible concentration of 4200 ng/L.

The insecticides azinphos-methyl and parathion were not detected from 2003 to 2008, but no conclusions can be drawn on their frequency of exceedance since the MDL for these pesticides was also above the criterion. Furthermore, the frequency of exceedance can be estimated for only 25 of the 60 pesticides analyzed because the criteria for the protection of aquatic life have not been established.

Canadian water quality guidelines are normally established based on basic risk analysis principles and laboratory test results and are subject to change upon reception of new data (MDDEP 2002b). These criteria are not standards; rather, they are guidelines and they have limitations. For one thing, the criteria do not take into account possible interactions within a mixture of substances, and in an agricultural environment, living organisms could be exposed to a cocktail of contaminants. For example, in 2008, a total of 16 pesticides and degradation products (13 pesticides and 3 degradation products) were observed in Yamaska River surface water from mid-May to late September (Appendix 4), and these figures do not include substances that were not analyzed, such as new-generation pesticides. In the same year, a total of 10 pesticides and 3 degradation products were observed in a single day (June 18). A comparable number of substances, 11 pesticides and 2 degradation products, were also observed on June 16, 2003. In a mixture of pesticides, some may act in synergy, while others may have a similar mode of action, and their effects could be cumulative (Table 6). A recent study conducted by Relyea (2009) showed that wetland communities could be dramatically affected when exposed to a combination of pesticides, even if the concentration of each pesticide is low. The same researcher also demonstrated that some pesticides could have negative effects on the biodiversity of aquatic invertebrates and amphibians (Relyea 2005). To gain a more comprehensive view of the situation and adopt a more ecosystemic approach, it is essential to obtain information on the interactions and potential synergy of various contaminants and their combined effects on living organisms at all trophic levels. Understanding the additive effects of a cocktail of pesticides is certainly no easy task, but it would help make water quality criteria, which are our best means of comparison to date, more realistic.

4.3.2 Criteria for irrigation water use

The frequency of exceedance could only be estimated for 13 of the 60 pesticides that have an established irrigation water use criterion. Only 2 of the 13 pesticides detected exceeded this criterion.

The herbicide MCPA exceeded its criterion (25 ng/L) in nearly one-quarter of the samples taken from the Yamaska River and the Nicolet River, but only once in the Saint-François River.

In the case of dicamba, as with chlorpyrifos and diazinon, its frequency of exceedance was equal to its detection frequency in the three tributaries, since the MDL (30 ng/L) was above the established criterion (6 ng/L). Therefore, the frequency of exceedance could also be underestimated.

4.3.3 Criteria for the prevention of contamination (water and aquatic organisms)

None of the pesticides detected exceeded their Canadian criteria for the prevention of contamination of water and aquatic organisms. For atrazine, among others, the criterion is the same as the standard for drinking water. Based on a recent literature review conducted by Lazorko-Connon and Achari (2009), the criterion for atrazine in drinking water varies from 0.1 to 5 µg/L around the world. They reported that the Canadian interim criterion is 5 µg/L, including atrazine metabolites, and that this criterion is less stringent than that of the United States, Australia, and the European Union. Australia and the European Union have the most stringent criteria at 0.1 µg/L (also including atrazine metabolites). According to Lazorko-Connon and Achari (2009), although the municipalities that use the river surface water treat it before using it as drinking water, not all drinking water treatment technologies effectively eliminate atrazine from water. Atrazine concentrations in the tributaries on the south shore of Lake Saint-Pierre often exceed the European and Australian criteria during the summer, especially in the Yamaska and Nicolet rivers (Figure 3).

4.4 RELATIONSHIPS BETWEEN PESTICIDE CONCENTRATIONS, FLOW AND PRECIPITATION

Generally, there is a time lag of a few days (~ 1–5 days) between an episode of heavy rainfall (≥ 10 mm) and elevated pesticide concentrations in agricultural tributaries, because of the time it takes for water to travel through each of the watersheds. However, no significant relationship was found between precipitation and pesticide concentrations, or between flow and pesticide concentrations. Cossa et al. (1998) also found no relationship between flow and pesticide concentrations. Flow and pesticide concentrations tend to increase after heavy rainfall (Figure 9), but the complexity of these systems because of factors such as floods and low-flow periods is probably the reason that no clear relationship has been detected between precipitation, flow and pesticide concentrations in the studied rivers. Furthermore, weekly sampling does not always allow to detect pesticide concentration peaks after an episode of heavy rainfall. For example, sampling conducted just before a heavy rainfall or a significant increase in flow (e.g. early August sampling in Figure 9) may not detect an increase in pesticide concentrations.

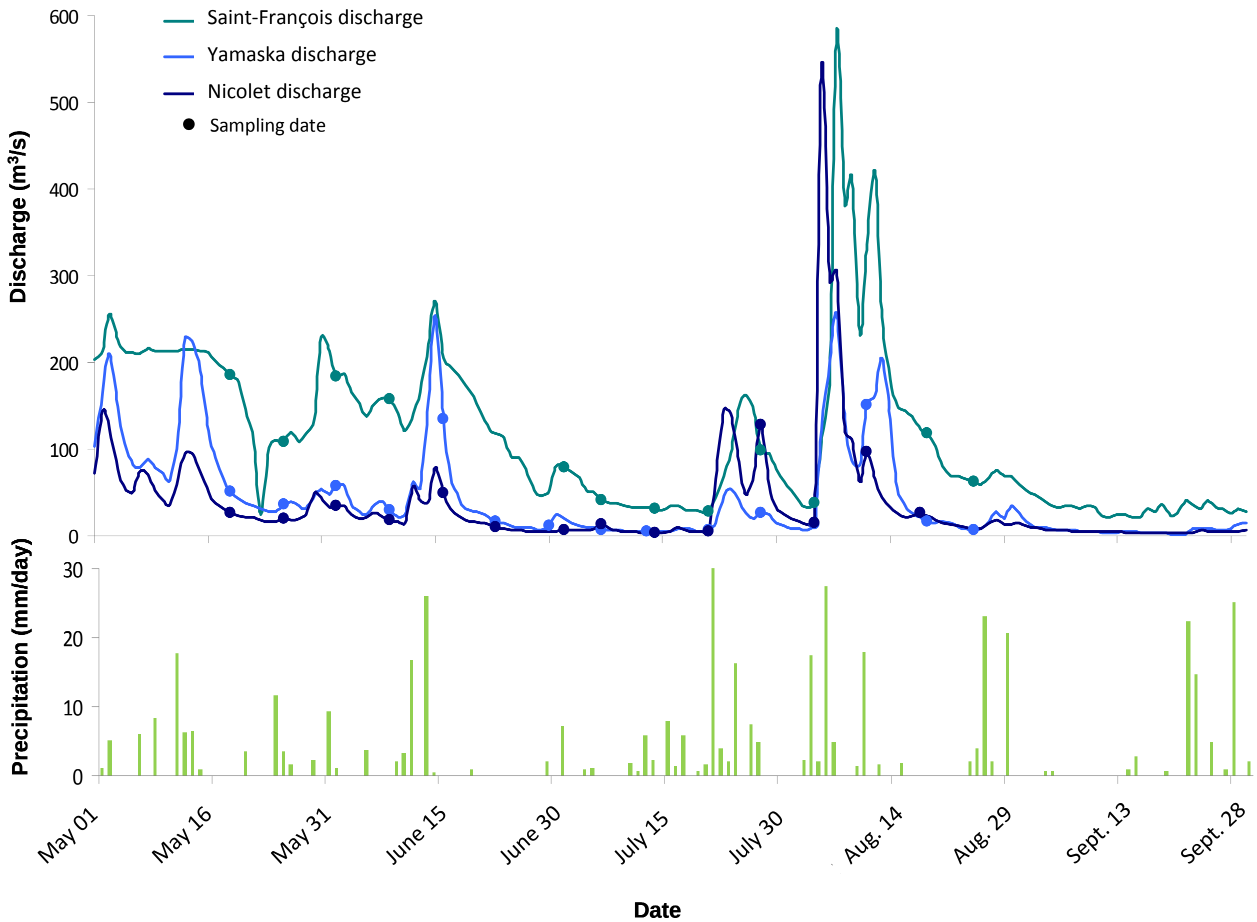


Figure 9 Example of temporal variations in precipitation and flow in the Nicolet, Saint-François and Yamaska rivers in 2003

4.5 SUMMER LOAD ESTIMATES FOR THE PESTICIDES MOST OFTEN DETECTED

Surface water pesticide concentrations provide a good indication of the exposure of living organisms in the environment sampled. However, to get a better idea of total pesticide input in the wetlands on the southern side of Lake Saint-Pierre, pesticide loads near the mouths of tributaries must also be considered. The pesticide load is the quantity of pesticides carried away by a river to a given location for a given period, taking into account each river's pesticide concentrations and discharge. The Yamaska River transports the largest quantity of pesticides, followed by the Nicolet River and the Saint-François River, even though the Yamaska River's average discharge is generally two to three times lower than that of the Saint-François River (Table 7). The Nicolet River, which had considerably higher pesticide concentrations than the Saint-François River, ultimately transports loads comparable to those transported by the Saint-François River because its average flow is much lower than that of the Saint-François River. A comparison of the Nicolet River and the Yamaska River shows that pesticide loads are much larger in the Yamaska River, despite the fact that its flow is only 1.5 to 2 times higher.

Based on the geographic location of the mouth of these three rivers and their watersheds, it can be seen that the largest quantity of pesticides originates from the Yamaska River and drains into the wetlands in the upstream portion of Lake Saint-Pierre (Figure 1). The Saint-François River, although less contaminated, adds its pesticide input just downstream of the Yamaska River. According to Figure 2, surface waters from the Yamaska and Saint-François rivers could run alongside and contaminate the wetlands along the length of the south side of the lake before reaching the outlet. Pesticide loads in the Nicolet River contaminate wetland water only in the downstream portion of the lake just before the outflow. Note that a significant portion of the farmland along the southern side of the lake is not included in the watersheds being studied and that it is possible that pesticides applied in this region are transported more directly toward the wetlands along the lake by small streams.

According to Pereira and Hostettler (1993) and Schottler and Eisenreich (1997), the atrazine load in the rivers of a watershed should be 0.25 to 1.5% of the total quantity applied to corn fields during the farming season. Poissant et al. (2008) reported that the average annual application rate for atrazine in the Yamaska River watershed was 49.6 kg/km^2 (2006–2007 data). Based on our 2003–2008 estimates, the average atrazine load (including deethylatrazine) from May 30 to August 30 near the mouth of the Yamaska corresponds to approximately 262 kg of active ingredients. When this quantity is divided by the surface area of corn crops in this watershed, the average specific load is 0.24 kg/km^2. This represents 0.48% of the average application rate of atrazine in corn fields ($100 \times 0.24\ kg/km^2/49.6\ kg/km^2$), which is in line with what Pereira and Hostettler (1993) and Schottler and Eisenreich (1997) suggest.

Table 7
Summer load estimates (May 30 to August 30) for the pesticides and degradation products most often detected

River	Year	Average discharge (m^3/s)	Load ± standard error (kg)								
			Atrazine	*DEA**	Metolachlor	Bentazon	Dicamba	Dimethenamid	2.4-D	Glyphosate	*AMPA**
Nicolet	2003	40	40 ± 11	18 ± 2.9	6 ± 4.6	–	18 ± 5.8	–	–		
	2004	28	65 ± 15	–	3 ± 0.9	–	8 ± 2.0	–	–		
	2005	21	64 ± 26	9 ± 2.0	–	–	47 ± 30	–	–		
	2006	26	68 ± 32	9 ± 1.7	43 ± 19	–	19 ± 8.0	–	–		
	2007	17	100 ± 23.7	8 ± 2.0	48 ± 13	–	17 ± 4.4	–	–		
	2008	50	55 ± 20	13 ± 2.1	18 ± 11	–	49 ± 29	–	–		
Saint-François	2003	122	40 ± 31	–	–	–	–	–	–		
	2004	130	58 ± 30	–	–	–	–	–	–		
	2005	102	49 ± 9.9	–	–	–	–	–	–		
	2006	190	125 ± 27.8	–	38 ± 11	–	–	–	–		
	2007	116	54 ± 14	–	27 ± 7.2	–	–	–	–		
	2008	226	110 ± 37.3	–	44 ± 14	–	–	–	49 ± 16		
Yamaska	2003	41	270 ± 74.2	46 ± 8.9	185 ± 47.2	38 ± 12	196 ± 67.7	58 ± 18	–		
	2004	54	119 ± 40.8	41 ± 13	98 ± 38	46 ± 28	60 ± 21	17 ± 5.6	7 ± 3.3		
	2005	39	113 ± 24.3	26 ± 4.0	57 ± 14	326 ± 124	174 ± 70.2	14 ± 3.3	–		
	2006	97	356 ± 93.0	49 ± 13	225 ± 46.9	–	–	–	–		
	2007	27	121 ± 43.8	14 ± 3.3	108 ± 25.9	104 ± 32.8	–	–	–	10	96
	2008	97	352 ± 116	65 ± 13	284 ± 92.1	98 ± 25	64 ± 24	–	–	100	202

Note: Glyphosate and AMPA have been analyzed since 2007 in only the Yamaska River.

* Degradation products are in italics to the right of their parent product.

–: Not enough data to estimate a load for this period, either because the detection frequency is below 45% or because the sampling period ended in late July instead of late August.

As expected, the average specific load of atrazine for the farming season in the two other watersheds is comparable to that in the Yamaska River (0.20 and 0.32 kg/km^2 in the Nicolet and Saint-François rivers, respectively). This calculation was performed only for atrazine, since there was not enough data on the use of other pesticides.

4.5.1 Comparison of pesticide concentrations and loads in the tributaries to those in the river

A station at the mouth of the St. Lawrence near Quebec City (City of Lévis water intake) is also included in Environment Canada's monitoring activities (Environment Canada 2004) to assess trends in concentrations of contaminants, including pesticides, in the St. Lawrence. This station provides information on the concentrations and annual variations of about 15 pesticides in the river, and on the integration of upstream sources of contamination (e.g. the tributaries being studied).

The maximum pesticide concentrations detected in the waters of the St. Lawrence River near Quebec City are one to two orders of magnitude lower than those measured near the mouths of the agricultural tributaries of Lake Saint-Pierre. From 2003 to 2008, the maximum atrazine concentration observed was 115 ng/L (unpublished Environment Canada data), compared to 2200 ng/L in the Yamaska River. Such a significant difference between the tributaries and the St. Lawrence River is largely due to the much higher flow of the St. Lawrence (average annual discharge of 12 000 m^3/s) compared to its tributaries (between ~40 and 200 m^3/s) and to the mixing of the green waters of the St. Lawrence with the brown waters of the tributaries on the north shore, which contain very little atrazine (Pham et al. 2000).

Cossa et al. (1998) found that atrazine and metolachlor loads in Cornwall and Quebec City were similar, suggesting that the Great Lakes basin is the main source of pesticide contamination in the St. Lawrence River. Calculations of mass balances revealed that Lake Ontario constitutes the main source of the triazines (approximately 90%) measured in the waters of the St. Lawrence River, which shows that the Great Lakes contribute very significantly to pesticide loads in the waters of the St. Lawrence that pass through the river near Quebec City (Pham et al. 2000). Estimated atrazine loads in Quebec City for the summers of 1995 and 1996 (May 15 to September 30) were 6600 and 8200 kg, respectively. Since concentrations of this pesticide in Quebec City are still on the same order of magnitude as they were in 1995–1996, atrazine loads from 2003 to 2008 should be similar to those for that period. For the Nicolet, Saint-François and Yamaska rivers, estimated atrazine loads for 2003 to 2008 vary between 225 and 550 kg for the period from May 30 to August 30. These loads represent 3 to 8% of summer loads and 1 to 3% of annual loads observed at Quebec City. Pham et al. (2000) suggested that atrazine loads from St. Lawrence tributaries in Quebec accounted for 5 to 10% of the annual atrazine load in the river near Quebec City. The annual load estimates in this document are lower than those suggested by Pham et al. (2000), but they do not take into account all pesticide sources in the river between Cornwall and Quebec City.

Atrazine inputs to the St. Lawrence from the tributaries are relatively low. In Lake Saint-Pierre, on the other hand, after the pesticide application period, high concentrations and loads of this herbicide are observed in the tributaries and wetlands on the south shore of the lake and are a major source of contamination for the organisms living in these habitats.

5 Conclusion

Data on the pesticides near the mouths of the Nicolet, Saint-François and Yamaska rivers strongly suggest that the fragile ecosystems on the south shore of Lake Saint-Pierre are exposed to multiple pesticides over the summer period. Furthermore, based on the flow of water masses along the edges of the lake, frequencies of exceedance similar to those in the rivers are likely to be observed in the shallow waters along the south shore of Lake Saint-Pierre.

The main pesticides detected in the Nicolet, Saint-François and Yamaska rivers are the herbicides atrazine and metolachlor. Although glyphosate has been sampled only since 2007 in the Yamaska River, it is also frequently detected. These three herbicides are used mainly on corn and soybean crops. Other herbicides of concern in these watersheds include dicamba, bentazon, 2,4-D, MCPA, dimethenamid and mecoprop. These herbicides are also all used on corn and other crops such as soybean, wheat, barley and oat crops, as well as in orchards, to name just a few examples. Very few insecticides have been detected in these rivers, and the detection frequency is low. Those detected include chlorpyrifos, dimethoate, carbaryl and diazinon. The two fungicides analyzed, chlorothalonil and myclobutanil, are rarely detected. These insecticides and fungicides are used mainly on potato crops and several kinds of fruits and vegetables, as well as in wheat, forage and corn crops.

Overall, the Yamaska River transports the largest number of pesticides and the largest pesticide loads to Lake Saint-Pierre, even though its flow is lower than that of the Saint-François River.

Despite the relatively high discharges of these rivers compared to others further upstream, the water quality criteria are still exceeded for certain pesticides near the mouth of the Nicolet, Saint-François and Yamaska rivers. The herbicide atrazine, the insecticide diazinon and the fungicide chlorothalonil each exceeded their criterion for the protection of aquatic life (chronic effect) once in six years. The insecticide chlorpyrifos, however, exceeded this criterion 11 times in 6 years. Dicamba and MCPA were also found to exceed their criteria for irrigation water use several times. Moreover, the frequency of exceedance for chlorpyrifos, diazinon and dicamba is probably underestimated, since the method detection limits are higher than the criteria. No pesticides exceeded their criteria for the prevention of contamination of water and aquatic organisms or drinking water, despite the fact that this criterion for atrazine is much less stringent in Canada (5 μg/L) than in Europe (1 μg/L), where use of atrazine is even prohibited.

Pesticide monitoring in the tributaries of Lake Saint-Pierre is essential to obtaining an overall picture of the health of this fluvial lake. The results presented in this report are a key addition but the pesticide picture is still incomplete in several areas. More sensitive detection limits would help in estimating the loads and average concentrations of a wider range of pesticides and in detecting new-generation pesticides, which are applied in much lower quantities. Also, it is crucial to develop a more comprehensive set of water quality criteria and to study the potential cumulative and synergistic effects of various mixtures of pesticides, to better reflect the conditions to which living organisms are exposed in their natural environments. This would undoubtedly require more laboratory and field research.

Monitoring and research efforts should focus on the pesticides currently being used. From an environmental policy and sustainable development perspective, it would be interesting to consider the effects of pesticides in relation to climate change and biodiversity. Climate change experts anticipate a significant decrease in the river's mean water levels in the medium term, which could transform Lake Saint-Pierre's ecosystems. The effects of a reduction in water levels, especially in summer, could have the effect of considerably increasing the concentration of pesticides and other contaminants in the river, particularly in the shallow, rich aquatic environments along the south shore of Lake Saint-Pierre.

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Appendices

1 Examples of pesticides used on corn and soybean crops

Pesticide type	Active ingredient	Trade name	Corn	Soy
Herbicides	Atrazine	480 SU, AATREX	√	
	Atrazine/dicamba	MARKSMAN	√	
	Bentazon	BASAGRAN	√	√
	Bromoxynil	PARDNER	√	
	Clopyralid/flumetsulam	FIELDSTAR	√	
	2,4-D	2,4-D AMINE	√	
	2,4-DB	CALIBER, COBUTOX	√	
	Dicamba	BANVEL	√	
	Diclofop-methyl	HOE-GRASS		√
	Dimethenamid	FRONTIER	√	√
	EPTC	ERADICANE, EPTAM	√	
	Ethalfluralin	EDGE DC		√
	Flumetsulam	FLUMETSULAM	√	
	Flumetsulam/s-metolachlor	BROADSTRIKE/DUAL MAGNUM		√
	Flumetsulam/trifluralin	BROADSTRIKE/TREFLAN		√
	Glyphosate	ROUNDUP, GLYFOS	√	√
	Imazethapyr	PURSUIT	√	√
	Imazethapyr/atrazine	PATRIOT	√	
	Imazethapyr/pendimethalin	VALOR		√
	Linuron	LOROX, LINURON	√	√
	MCPA	MCPA amine, sodium or potassium	√	
	MCPB/MCPA	CLOVITOX	√	
	S-metolachlor	DUAL MAGNUM		√
	S-metolachlor/benoxacor	DUAL II MAGNUM	√	
	S-metolachlor/benoxacor/atrazine	PRIMEXTRA II MAGNUM	√	
	Metribuzin	SENCOR, LEXONE, METRIBUZIN	√	√
	Nicosulfuron	ACCENT	√	
	Rimsulfuron	ELIM	√	
	Rimsulfuron/nicosulfuron	ULTIM	√	
	Simazine	SIMAZINE, PRINCEP NINE T	√	
	Trifluralin	TREFLAN, RIVAL		√
Insecticides	Acephate	ORTHENE	√	
	Bacillus thuringiensis (Bt)	DIPEL	√	
	Carbaryl	SEVIN	√	
	Carbofuran	FURADAN	√	
	Chlorpyrifos	LORSBAN, PYRIFOS	√	
	Dimethoate	CYGON, LAGON		√
	Endosulfan	THIODAN, THIONEX	√	
	Methomyl	LANNATE	√	
	Tefluthrin	FORCE	√	
	Trichlorfon	DYLOX	√	
Fungicides	Chlorothalonil	BRAVO	√	
	Propiconazole	TILT	√	√

2 Information on the criteria associated with pesticide detection

The information presented in this appendix is taken from Giroux (2002 and 2004) and Giroux et al. (2006) and can also be found on the Ministère du Développement durable, de l'Environnement et des Parcs Internet site at www.mddep.gouv.qc.ca/eau/criteres_eau/index.htm (in French only), as well as on the Canadian Council of Ministers of the Environment Internet site at www.ccme.ca/publications/ceqg_rcqe.html.

Water quality criteria are established based on the toxicity of a single substance and certain environmental conditions, such as pH, temperature, hardness of water, etc. They do not take into account the toxicity of the degradation products of pesticides, which can be even more toxic than their parent products, or any potential endocrine disrupting effect. In addition, since aquatic organisms are often exposed to a number of contaminants, either simultaneously or sequentially, ecotoxicological risks could therefore be underestimated.

Criterion for the protection of aquatic life (chronic aquatic toxicity)

This criterion is used to assess risks to aquatic species and corresponds to the maximum concentration of a product (one or more pesticides, in this case) to which aquatic organisms can be exposed for their entire lives without any harmful effects. It is established based on studies of various aquatic species. The species most sensitive to each of the products determines the value of the criterion.

Small deviations above the criterion from time to time will not necessarily have harmful effects on aquatic species. However, since some aquatic organisms have very short life cycles, there could be harmful effects if the concentration of these products remains above the criterion for more than four days or when concentrations are well above the chronic toxicity criterion. The chosen criterion for the protection of aquatic life is generally more stringent (lower value) than the chosen criteria for drinking water quality, since it includes the exposure of aquatic species that can be very sensitive (algae, insects, fish, etc.).

Water quality criteria have not been established for all pesticides. An interim criterion has been determined for certain pesticides using the method of calculating water quality criteria for toxic substances (MENVIQ, 1990) described on the following site (in French only): www.mddep.gouv.qc.ca/eau/criteres_eau/preambule.htm. In addition, for certain pesticides such as azinphos-methyl, chlorpyrifos and diazinon, the water quality criterion for the protection of aquatic life is below the detection limit of the analytical method. When these pesticides are detected in water, they automatically exceed the quality criterion. However, when they are not detected in water, this does not necessarily mean that they are not present in concentrations that are harmful to aquatic life.

3 Descriptive statistics by agricultural tributary for pesticides with a detection frequency of 45% or higher per year from May 30 to August 30

Nicolet River

Pesticide	Year	*n*	Detection frequency (%)	Average ± standard deviation (ng/L)	Median (ng/L)	Minimum-maximum concentrations (ng/L)
Atrazine	2003	13	100	126 ± 87	130	30–360
	2004	12	100	200 ± 204	145	30–750
	2005	13	100	238 ± 395	60	50–1400
	2006	9	100	286 ± 387	170	60–1300
	2007	11	100	242 ± 298	150	30–1100
	2008	13	77	135 ± 174	80	20–560
Deethylatrazine	2003	13	46	36 ± 24	20	40–100
	2005	13	46	41 ± 30	20	40–120
	2006	9	67	37 ± 21	40	40–80
	2007	11	55	36 ± 25	31	31–82
	2008	13	46	30 ± 19	15	30–70
Dicamba	2003	13	46	38 ± 47	15	30–190
	2004	12	58	39 ± 27	35	30–100
	2005	12	50	193 ± 450	23	20–1600
	2006	9	56	62 ± 98	30	30–320
	2007	9	56	56 ± 55	40	40–180
MCPA	2006	9	78	157 ± 355	50	10–1100
Metolachlor	2003	13	62	26 ± 37	10	10–140
	2004	12	58	15 ± 12	10	10–40
	2006	9	100	153 ± 229	60	10–610
	2007	11	82	85 ± 157	33	13–550
	2008	13	69	52 ± 96	20	10–360

Saint-François River

Pesticide	Year	*n*	Detection frequency (%)	Average ± standard deviation (ng/L)	Median (ng/L)	Minimum-maximum concentrations (ng/L)
2,4-D	2008	13	46	32 ±31	10	20–100
Atrazine	2003	10	70	69 ± 94	25	20–300
	2004	11	64	72 ± 93	50	50–330
	2005	13	92	52 ± 41	40	20–130
	2006	9	100	76 ± 53	50	30–170
	2007	12	83	54 ± 48	41	21–170
	2008	13	54	57 ±74	30	30–240
Metolachlor	2006	9	78	23 ± 20	20	10–70
	2007	12	67	24 ± 25	16	12–86
	2008	13	62	22 ± 27	10	10–90

Yamaska River

Pesticide	Year	*n*	Detection frequency (%)	Average ± standard deviation (ng/L)	Median (ng/L)	Minimum-maximum concentrations (ng/L)
2,4-D	2004	10	50	23 ± 22	15	20–80
Atrazine	2003	13	100	508 ± 555	320	120–2200
	2004	10	100	340 ± 266	215	60–890
	2005	13	100	291 ± 243	190	20–810
	2006	9	100	417 ± 382	290	70–1200
	2007	11	100	473 ± 444	330	61–1600
	2008	13	100	531 ± 475	480	30–1300
Deethylatrazine	2003	13	92	102 ± 66	90	50–280
	2004	10	80	94 ± 81	65	40–280
	2005	13	85	74 ± 40	70	40–150
	2006	9	78	61 ± 57	50	30–200
	2007	12	100	71 ± 34	68	34–130
	2008	13	100	95 ± 52	90	30–190
Bentazon	2003	13	69	111 ± 88	100	90–270
	2004	10	60	116 ± 185	45	40–600
	2005	13	85	494 ± 1242	110	60–4600
	2006	9	78	132 ± 147	70	40–460
	2007	6	50	60 ± 49	40	60–120
	2008	11	100	153 ± 96	180	50–290
Dicamba	2003	13	85	248 ± 507	80	30–1900
	2004	10	90	173 ± 135	115	50–410
	2005	13	77	278 ± 703	50	30–2600
	2006	9	56	110 ± 171	40	40–540
	2007	6	83	73 ± 65	40	30–160
	2008	11	64	75 ± 91	40	30–320
Dimethenamid	2003	13	92	82 ± 138	30	20–520
	2004	10	80	45 ± 37	30	20–120
	2005	13	46	34 ± 34	10	20–100
Glyphosate	2007	12	83	64 ± 27	66	46–110
	2008	13	77	158 ± 134	140	40–400
AMPA	2007	12	100	429 ± 183	410	210–860
	2008	13	85	315 ± 138	330	210–620
MCPA	2006	9	56	31 ± 30	30	30–90
Metolachlor	2003	13	100	325 ± 353	190	90–1400
	2004	9	100	290 ± 244	200	60–730
	2005	14	100	152 ± 138	110	30–520
	2006	9	100	227 ± 195	140	40–570
	2007	11	100	303 ± 263	230	46–840
	2008	13	100	332 ± 376	210	30–1300

Note: Minimum concentrations correspond to the minimum values observed in the field and not half of the MDL.

When the detection frequency is approximately 50%, the median is less than or equal to the minimum concentration observed, since a value equal to half of the MDL corresponds to the dates on which the pesticide was not detected.

A pesticide's detection frequency for a given year may be greater than or equal to 45% even if it is less than 45% for the entire 2003–2008 period in Table 4.

Glyphosate and AMPA were analyzed starting in 2007 in the Yamaska River alone.

4 Summary of the number of detections per year of the pesticides analyzed

Pesticides	**Nicolet River**						**Saint-François River**						**Yamaska River**					
	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008
Herbicides																		
2,4,5-T																		
2,4-D	1	5	1	1				4	5	1	3	7	4	7	5	2		2
2,4-DB		2		2											1			
Atrazine	13	13	15	9	12	12	7	7	13	9	11	7	14	12	15	13	13	19
Deethylatrazine	6	5	6	6	6	6				1	1	3	12	8	11	8	12	13
Deisopropylatrazine		1		1	1	1				2		2	2	2	1	4	3	6
Bentazon	3	5	3	4	1	2							9	6	12	10	3	11
Bromoxynil								1					1	1	1	1		
Butylate																		
Chloroxuron			1															
Clopyralid				1									3	3	1			
Cyanazine																		
Dicamba	6	8	6	5	5	3		2	3	2	4	4	11	10	10	5	5	8
Dichlorprop																		
Diclofop-methyl																		
Dimethenamid													12	10	7	2	4	2
Dinoseb																		
Diuron			1															
EPTC															1			1
Fenoprop (Silvex)																		
Flumetsulam[2]														3				
Glyphosate[1]																	10	10
AMPA[1]																	13	18
Imazethapyr[2]														1				
Linuron			1															
MCPA	2	3	4	7	3	4	1		1	1			3	2	5	5	2	5

Pesticides	**Nicolet River**						**Saint-François River**						**Yamaska River**					
	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008
Herbicides (cont'd)																		
MCPB																1		
Mecoprop	1	1		1			2	5				1	5	6	5	2		3
Metolachlor	9	9	6	9	10	11	1	2	2	7	9	9	15	12	16	13	13	19
Metribuzin													1					
Nicosulfuron[2]														1				
Picloram																		
Rimsulfuron[2]																		
Simazine	1	4						1	1	1	1		2	3	3	2		
Tebuthiuron																		
Triclopyr																		
Trifluralin																		
Insecticides																		
Azinphos-methyl																		
Bendiocarb																		
Carbaryl						1						1						1
1-naphthol																		
Carbofuran																		
Chlorfenvinphos																		
Chlorpyrifos			2	2			2		3	1								1
Diazinon										1								
Dichlorvos																		
Dimethoate	1	2												2				
Disulfoton																		
Fenitrothion																		
Fonofos																		
Malathion																		
Methidathion																		

Pesticides	**Nicolet River**						**Saint-François River**						**Yamaska River**					
	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008	2003	2004	2005	2006	2007	2008
Insecticides (cont'd)																		
Mevinphos																		
Parathion																		
Parathion-methyl																		
Phorate																		
Phosalone																		
Terbufos																		
Fungicides																		
Chlorothalonil							1						1					
Myclobutanil			1				1											2
Total number of detections	43	58	47	48	38	40	15	22	28	26	29	34	95	89	94	68	78	121
Herbicide detections	42	56	44	46	38	39	11	22	25	24	29	33	94	87	94	68	78	117
Insecticide detections	1	2	2	2	0	1	2	0	3	2	0	1	0	2	0	0	0	2
Fungicide detections	0	0	1	0	0	0	2	0	0	0	0	0	1	0	0	0	0	2
Number of pesticides detected	10	12	12	12	7	8	6	7	7	10	6	8	15	17	15	13	10	16
Number of herbicides detected	9	11	10	11	7	7	4	7	6	8	6	7	14	16	15	13	10	13
Number of insecticides detected	1	1	1	1	0	1	1	0	1	2	0	1	0	1	0	0	0	2
Number of fungicides detected	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1

www.**ec**.**gc**.**ca**

Additional information can be obtained at:

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Fax: 819-994-1412
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