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By:
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Management perspective

Title: Fate and impacts of pesticides applied to potato cultures: the Nicolet River Basin.

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EC Priority/Issue:

This document addresses the EC priorities/issues related to Toxics. Pesticides, which are by design toxics, have been detected in groundwater and surface waters in the Nicolet River Basin, Quebec. This documents assesses the mechanisms which lead to the transport of these pesticides to the groundwater environment and the reasons for their persistence, with the goal of prevent future releases of these toxics into the aquatic environment.

Current status:

The study is now complete, and the results have been published. Results of this work will influence the decision making process of Environment Canada with respect to pesticide approval and usage.

Next steps:

No future work is being considered at this time.

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Fate and Impact of Pesticides Applied to Potato Cultures: The Nicolet River Basin

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The fate of cash-crop (potato) pesticides was monitored from the fields on which they were applied to the nearby streams. The investigation took place in the Nicolet River basin in the province of Quebec, Canada. The main pesticides under study were aldicarb, fenvalerate, metribuzin, and phorate. Aldicarb was never detected in any of the samples. The other pesticides were all detected in soils at low concentrations. Only fenvalerate and metribuzin were detected in tile drain. Metribuzin concentrations of up to 0.25 μg/g were detected in the soil giving rise to a concentration of 1.3 μg/liter in tile drain and 47.1 μg/liter in surface runoff. Low concentrations of metribuzin up to 0.41 μg/liter were detected in the nearby streams. The CREAMS model simulating pesticide movement in the fields overestimated metribuzin losses in the runoff at a concentration of 107 μg/liter. The subsurface EXPRES model using a PRZM time series adequately estimated a metribuzin field subsurface runoff concentration of 0.5 μg/liter. According to the Canadian Water Quality Guideline for the protection of aquatic life, the concentrations of pesticides found in surface waters of this potato-growing region of Quebec do not have a potential to impact on the aquatic life in these systems.

INTRODUCTION

Studies on cash-crop (e.g., potato and tobacco) pesticides are scarce in the province of Quebec. An extensive sampling program conducted in 1987–1988 (Forrest and Caux, 1990) and later in 1989–1990 (Caux and Forrest, 1991) reported pesticide monitoring results in six intensively cultivated river basins. Maximum concentrations for seven pesticides exceeded the permissible threshold levels for the protection of aquatic life in the rivers under study. The pesticides of concern were atrazine, diazinon, 2,4-DP, lindane, endosulfan, DDT, and DDE. In regions where potatoes were grown (Manarbachie, 1993) pesticides exceeded freshwater guideline concentrations; maximum concentrations of 47 μg/liter of carbofuran and 11.9 μg/liter of metribuzin were detected in well water. Another pesticide used on potato, the insecticide aldicarb, has been the subject of a surveillance program in well water conducted for 30 municipalities within the province from 1984 until 1989. Of the wells sampled (502), 24% of the wells (120) exceeded the freshwater guideline concentration (Giroux, 1990).

The above studies were initiated because of a concern that these pesticides had an effect on humans and/or the environment and to obtain an insight on site-specific conditions on which the chemical fate and toxicological behavior of pesticides depends. Several other factors are also considered prior to initiating a water-quality surveillance program in a region. A pesticide surveillance program requires data on sales estimates for the river basin, groundwater vulnerability maps, pesticide chemistry and fate characteristics, climatological data, and finally geological and hydrogeological data for the particular region.

For the cash-crop region under study, sales data were provided in a provincewide compendium of sales for 1988 (Sage, 1988). It was found that farmers in the Nicolet River basin had an increasingly greater dependence on cash crops such as the potato. No known data exist reporting pesticide uses and impacts on this river basin. Furthermore, no data are available on pesticide transport from potato fields in Quebec. Potato crop utilizes a large quantity of pesticides, especially insecticides. Potato herbicides are used less because their development is fairly recent (Roberts, 1982).

Many insecticides are used against the Colorado potato beetle (Agriculture Canada, 1995). Persistence of the insecticides is needed as infestation may continue over a period of days or weeks and a compromise in effective control is required to avoid environmental contamination (Matthew, 1984). In use is aldicarb, a known hazard. Also in use are disulfulfan, endosulfan, and phorate, all of which are soil incorporated. In Quebec, as elsewhere, aldicarb is under strict regulations. Reports of the occurrence of aldicarb in Canadian surface and groundwaters are plentiful (Caux *et al.*, 1994). The herbicide metribuzin is the choice compound for the control of weeds in potato crops. Reports on its occurrence in the Canadian environment are confined to the province of Ontario (Frank *et al.*, 1987).

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The current investigations report studies conducted on two potato fields in Saint-Léonard d'Aston, Quebec, to measure concentrations of pesticides in the soil, in surface runoff in tile drain, and in the adjacent streams. The objectives of the study were to monitor pesticide losses from this crop practice to the aquatic ecosystem, to relate this exposure to the environmental threshold limits, and finally to run simulations on data obtained from the region to obtain an insight on general and site-specific factors affecting the movement of these pesticides.

Canadian Water Quality Guidelines

Regulations are a resource drain and governments are opting for less onerous methods to protect the environment. Canadian Water Quality Guidelines provide nonregulatory, recommended targets for environmental decision making. As models of federal–provincial harmonization, Canadian Water Quality Guidelines help to ensure that nationally consistent levels of environmental quality are prescribed and maintained across the country. Canadian Water Quality Guidelines are also used as environmental quality targets and criteria for regulatory evaluations (Caux and Kent, 1994). In these investigations the fate of in-use pesticides applied to cash crops have been followed from the soil compartment to the aquatic ones with both field and modeled data. The levels of pesticides in these individual compartments were compared to Canadian Water Quality Guidelines for an immediate indication of their potential environmental impact.

MATERIALS AND METHODS

Survey of Pesticide Usage in the Study Area

A survey on pesticide usage was done in the Saint-Léonard region near the Nicolet River in 1989. Ten agricultural producers were interviewed about the type of crops, surface area seeded, agricultural practices, and pesticides used.

Fields and Agronomic Practices

Two subsurface drained fields in St. Léonard d'Aston were selected for the study (fields 1 and 2) and were cropped with potato. The study site is located in Nicolet county, about 120 km northeast of Montreal, Quebec. These fields drain to the Nicolet River, which is a tributary of the St. Lawrence River. Field 1 was bedded. The drainage areas of the beds ranged from 0.46 to 0.66 ha. The slope along the bed furrows was 0.7%. There were subsurface drains on the field, spaced 18 m apart, at a depth of 1 m. The subsurface drained area was 4.87 ha. Field 2 was flat (no beds). There were subsurface drains, spaced 30 m apart, at a depth of 1 m. The subsurface drained area in this field was 5.45 ha. A grassed waterway separated the fields.

Streams

Three streams (subbasins) were sampled during the period in which the pesticides were applied, from April to September 1990 (triplicate samples were collected eight times at three sites during the 6-month period, for a total of 72 samples). The streams were in proximity to the two fields described above and drained numerous agricultural fields in the St. Léonard d'Aston region. The pesticides analyzed in the samples were atrazine, metribuzin, endosulfan, azinphos–methyl, aldicarb, carbofuran, diazinon, butylate, methamidophos, metolachlor, dicamba, 2,4-DP, 2,4-D, silvex, 2,4,5-T, 2,4-DB, picloram, MCPA, and phorate.

Sampling and Analysis

Instrumentation. Each subsurface drain outlet was instrumented with a V-notch weir and stage recorder for flow rate determination. HS-flumes and recorders were also installed for measuring surface runoff from the two fields. Rainfall data were obtained with a tipping bucket rain gauge. Surface runoff and subsurface drain flow water samples were collected manually before the pesticide application, after the pesticide application, and also after rainfall events.

In 1989, soil and water samples were analyzed for aldicarb, fenvalerate, and metribuzin concentrations, and in 1990 the samples were analyzed for metribuzin and phorate concentrations. During the 1989 period, 69 water samples and 60 soil samples were collected. As for 1990, 111 water samples and 38 soil samples were collected. The pesticide used on the two sites are listed in Table 1.

Soil samples. Soil samples were taken three times (April, July, September) during the growing season to determine pesticide concentrations. Samples were taken at five locations along a diagonal on each field. The depths sampled were the surface layer (0–5 cm) and at 25 cm below the surface. Samples were frozen until extraction. Analyses of pesticide residues were performed by gas chromatography at the same commercial laboratory.

The soil samples were dried with sodium sulfate and extracted three times with dichloromethane. The extracts were combined, dried, and concentrated to 1 ml. The concentrate was injected into a Hewlett–Packard 5890A gas chromatograph equipped with an N-P thermionic selective detector. The extracts analyzed for fenvalerate were injected in a gas chromatograph with a 3% OV-17 column.

Water samples on the field and in the streams. One-liter water samples were collected using prewashed amber bottles. The samples were kept in an on-site refrigerator at 4°C until dispatched to the analytical lab. The samples were analyzed by a gas chromatograph at a commercial analytical lab in Montreal, Quebec. Samples were taken in triplicate for quality control purposes.

The water samples were extracted twice with dichloromethane (pH <2) and twice again extracted with dichloromethane after the addition of the salt NaCl. The extracts were analyzed as described above for the soil samples.

TABLE 1
Pesticides Used on Sites

Pesticide	Type	Solubility	Field	Date	Application rate
Aldicarb (Temik)	Insecticide	6 g/liter	1	06/22/89	2 kg/ha
Fenvalerate (Belmark)	Insecticide	1 mg/liter	2	06/13/89	1000 mg/ha
Metribuzin (Sencor)	Herbicide	1.2 g/liter	1 and 2	06/3 and 4/89	1 kg/ha
			1	06/12/90	1 kg/ha
			2	06/06/90	1 kg/ha
Phorate (Thymet)	Insecticide	50 mg/liter	2	05/12/90	10 kg/ha
			1	05/20/90	10 kg/ha

Creams Simulations

Model. The CREAMS (chemicals, runoff, and erosion from agricultural management systems) model was used to simulate pesticide concentrations in surface runoff. Predicted values were compared with the measured ones. Simulations were run using data for the 1989 and 1990 growing seasons. A hydrology submodel was first run to obtain surface runoff volumes. An erosion submodel and a pesticide submodel were then run. The Breakpoint option was chosen in the hydrology component because Enright and Madramootoo (1990) found that the daily option in the hydrology component underestimated the surface runoff for the Nicolet area.

The input parameters required for the hydrology, erosion, and pesticide components were from the field measured values and CREAMS recommendations from the manual and pertinent literature.

Rainfall and hydrology parameters. Two-parameter input data are required to run the hydrology submodel: rainfall and hydrology data for the site. The rainfall data were recorded from the site using a tipping bucket rain gauge and a data logger. These data were used for the 1989 and the 1990 simulations. Long-term average temperature and solar radiation were obtained from the Environment Quebec weather station in Saint-Wenceslas, about 12 km northeast of the site. The CREAMS model requires data on several soil properties such as saturated hydraulic conductivity, bulk density, particle size distribution, moisture retention, and soil organic matter content. These soil properties and other components related to the hydrology of the area were measured at the sites.

The saturated hydraulic conductivity was found using the falling head permeater method (Mehuys, 1986). Soil samples were collected twice in 1989 and three times in 1990 in order to measure the spatial and temporal variation of the saturated hydraulic conductivity and bulk density. Soil cores were taken at different locations along two diagonals of the two fields. Undisturbed soil cores were taken at two depths: surface (0–10 cm) and 30 cm. The soil cores were sealed in plastic bags to minimize soil loss during transport to the laboratory. Soil moisture content was estimated at the time of sampling. Bulk density measurements were carried out using these soil cores. Following hydraulic conductivity measurements, soil cores were dried in the oven for 24 to 48 hr at 105°C. Particle size distribution was determined by a combination of mechanical sleeves and the hydrometer method (Mehuys, 1986). A soil moisture characteristic curve was measured using Haine's suction funnel and the pressure plate apparatus (Mehuys, 1986). The soil moisture characteristic curve determined the field capacity, porosity, and permanent wilting point of the soils. The sites were sampled for organic matter determination in May 1990. Samples were taken at the soil surface (0–10 cm) and at 30 cm depth. The samples were analyzed by a chemical method for organic matter content (Page *et al.*, 1982).

EXPRES Simulations

EXPRES stands for expert system for pesticide regulatory evaluation simulations. The knowledge-based system simulates the transport and transformation of pesticides in the subsurface by providing all the necessary hydrogeological and modeling data. The model incorporated two pesticide transport models (LEACHM and PRZM) into the knowledge-based system. The model further incorporates a data base of the chemical characteristics of numerous pesticides employed in Canada, a second data base of values which characterize the physical, pedological, hydrological, and meteorological settings, as well as the agricultural practices in 10 regions of Canada (Mutch *et al.*, 1993). The purpose of using the EXPRES system was to identify the key factors affecting the leaching potential of the above-mentioned pesticides in the study area.

RESULTS

Survey of Pesticide Usage in the Study Area

The surface area used for agriculture totaled 1214 ha. The types of crops were distributed as follows: 41% in cereals, 26% in hay, 19% in corn, and 14% in potatoes. Only one farmer of 10 did not use any chemicals for pest control. The most popular pesticides among the farmers are atrazine (5 of 10), metribuzin (3 of 10), metolachlor (3 of 10), dithane (3 of 10), and aldicarb (2 of 10).

TABLE 2
Soil Physical Properties

Field	Property					
	% OM	% Sand	% Silt	% Clay	$K_{saturated}$ (cm/h)	Bulk density (g/cm^3)
1	2.93	90.3	8.0	1.7	10.19	1.17
2	2.77	71.0	23.3	5.7	10.89	1.29

Soil Characteristics .

The soil type on both fields is a St. Jude sandy loam (humoferric podzol) (Bastien, 1991). This soil type is a dominant soil group in Quebec. The parent material of this soil type is a sandy, glaciofluvial deposits. The soil tends to be acidic and requires chemical fertilizing to improve its limited fertility. Table 2 lists some of the measured soil physical properties. The organic matter content of the soil surface layer is also listed.

Pesticide Concentration in Soil Samples, 1989–1990

In 1989, analysis of the soil samples revealed that the residues of metribuzin were slightly greater in field 1 than in field 2. This herbicide had higher concentrations in the surface layer (0–5 cm) than in the 25- to 30-cm depth at both sites and at both sampling dates where it was detected (Table 3). Concentrations at the 25- to 30-cm depth, however, did increase during the growing season at the sites. Aldicarb which was applied in site 1 was not detected. Fenvalerate, applied to field 2, was found on the last sampling date (September 21, 1989) at a concentration of 0.013 μg/g for the surface layer (Table 3).

In 1990, metribuzin was mostly detected in the surface layer (0–5 cm) with concentrations up to 0.23 μg/g (Table 3). Phorate concentrations up to 0.020 μg/g were detected in fields 1 and 2. Phorate was applied on May 12, 1990 on field 1 and on May 20, 1990 on field 2. Phorate was detected on the first sample date (May 25, 1990) in field 2, and in both field on the last sampling date (September 30, 1990) (Table 3).

Pesticide Concentrations in Water Samples

1989 water samples. The 1989 summer growing season was very dry in comparison to other years. Metribuzin was never detected in the subsurface drain flow from field 1. The quantity of drain flow for the 1989 growing season (May to September) ranged from 0.3 to 5.9 mm per month which is relatively small. Thus, metribuzin was not transported into the tile drains at concentrations above the detection limit of 0.1 μg/liter.

June 27 was the only day where field 1 had surface runoff. Samples from this field were collected 24 days after the application of metribuzin. The average metribuzin concentration detected was 47.1 μg/liter. The expected concentration following a CREAMS model simulation was 106.8 μg/liter.

In field 2 subsurface drain flow samples, metribuzin was detected on two occasions; September 1 and November 15

TABLE 3
1989–1990 Soil Detections (μg/g)

Date	Field 1						Field 2					
	0–5 cm			25–30 cm			0–5 cm			25–30 cm		
	1	2	3	1	2	3	1	2	3	1	2	3
04/25/89	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
07/11/89	0.1	ND	ND	0.004	ND	ND	0.25	ND	ND	ND	ND	ND
09/21/89	0.061	ND	ND	0.013	ND	ND	0.053	0.013	ND	0.009	0.001	ND
	1	4		1	4		1	4		1	4	
05/24/90	0.002	ND		ND	ND		ND	0.001		ND	ND	
07/24/90	0.23	ND		0.03	ND		0.15	ND		0.02	ND	
09/30/90	0.04	0.008		0.02	0.002		0.02	0.02		0.02	0.005	

Note. 1, metribuzin; 2, fenvalerate; 3, aldicarb; 4, phorate. ND, nondectable.

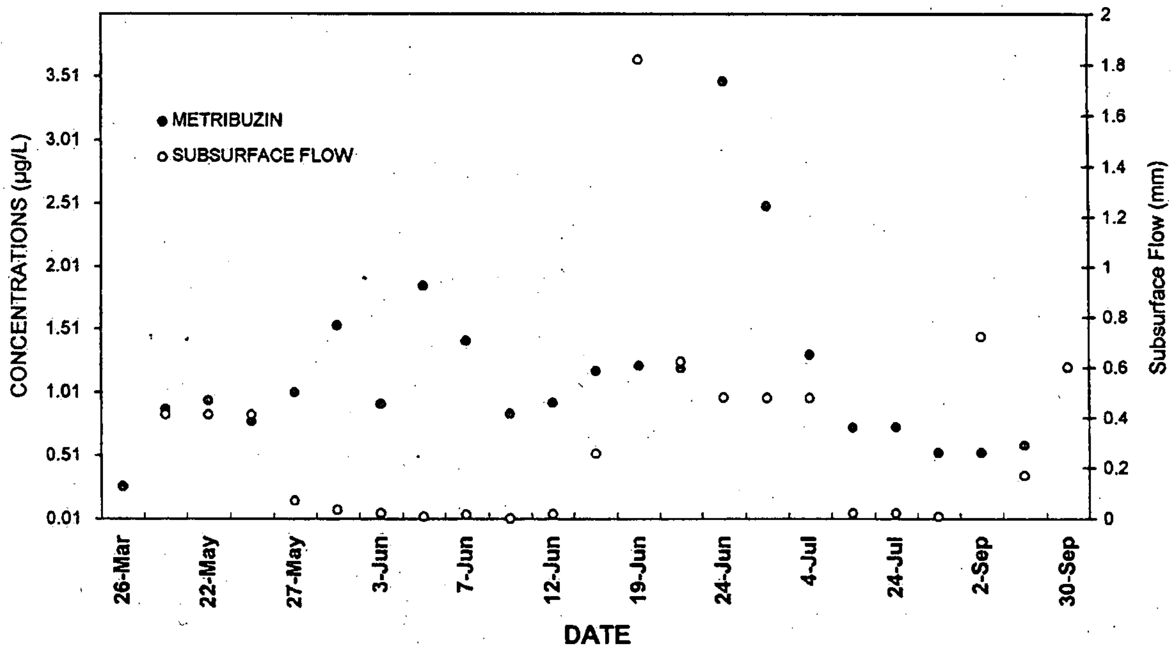


FIG. 1. Metribuzin concentrations in subsurface drain flow for field 1, 1990 season.

with levels of 1.325 and 0.58 µg/liter, respectively. Tile water samples were not available every rainfall event during the 1989 growing season since there was a lack of flow during dry periods.

Surface runoff samples were taken twice during the 1989 period from field 2. On June 27, the average metribuzin concentration detected was 47.086 µg/liter. An average concentration of 3.175 µg/liter was detected on September 1. Fenvalerate was detected on June 27 with an average concentration of 0.05 µg/liter in the surface runoff sample. This was the only fenvalerate detection in the investigation. Aldicarb was never detected in any of the water samples during the 1989 period.

1990 water samples. The 1990 growing season was an average year in terms of the precipitation. At a detection limit (DL) of 0.05 µg/liter, metribuzin levels ranging from 0.464 to 3.47 µg/liter were detected in all subsurface drain flow samples from field 1 (Fig. 1). Prior to its application on June 12, 1990, metribuzin concentration ranged from 0.264 to 1.536 µg/liter.

In field 2, metribuzin was found at concentrations of up to 0.162 µg/liter in subsurface drain flow samples prior to the June 6 application data. Concentrations in the range of 0.667 to 2.453 µg/liter were found after the application date (Fig. 2).

Phorate was not detected in any of the subsurface drain flow samples. No surface runoff events were taken during the 1990 period.

The results of samples taken in streams are presented in Fig. 3. Of the 19 pesticides monitored, metribuzin and atrazine were the only ones recovered during the sampling campaign. Metribuzin detections were observed on June 12 and 28 at concentrations nearing that of the detection limit (DL) of 0.1 µg/liter. Atrazine was also detected at low concentrations (DL 0.02 µg/liter) in July and September.

CREAMS simulation model. The CREAMS model was used to simulate pesticide concentrations in surface runoff. Predicted and measured values were compared. Simulations were run using field 1 for the 1989 and 1990 growing seasons. Simulations were not done for field 2 because the subsurface drainage in the field did not work properly.

The hydrology, erosion, and pesticide components are summarized in Table 4.

The CREAMS pesticide model predicted values were converted from g/ha to µg/liter for comparison with the observed values. Most surface runoff events were not sampled because the depth of runoff was negligible. The CREAMS pesticide component predicted aldicarb losses in June and July 1989 of 65 and 17 µg/liter respectively. In the surface runoff samples taken in June 1989, no aldicarb residues were detected. Metribuzin was only detected on June 27, 1989, when surface runoff at field 1 contained an average concentration of 48 µg/liter. The CREAMS model predicted a concentration of 107 µg/liter. The model overestimated the pesticide losses to surface runoff. Predicted pesticide concentrations in surface runoff are presented in Table 5.

EXPRES Simulation Model

A PRZM time series simulation plot was run for a period of 4 years (Figs. 4–8). Metribuzin was recorded at a depth

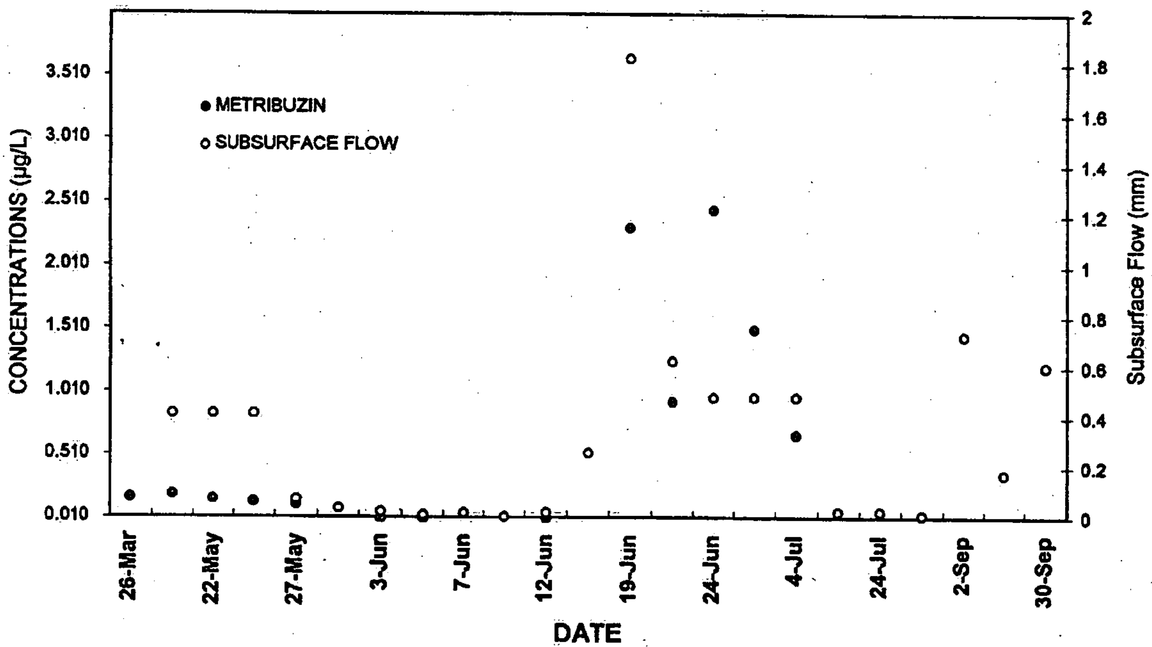


FIG. 2. Metribuzin concentrations in subsurface drain flow for field 2, 1990 season.

of 1 m after having been applied (1 kg/ha) early in June of the second year and again early in June of the third year. Simulations were run in years of average precipitation (1970–1974). In the first year of the simulation, no pesticide was applied in order to let the water input equilibrate in the system. Maximums of 0.5 and 0.25 μg/liter of metribuzin were predicted in subsurface flow for early October of the second year and for mid-March of the fourth year, respectively. Several key factors were identified that influenced the leaching potential of metribuzin at a 1-m depth in the field. Demonstrating an effect were f_{oc} (soil organic content), K_{oc} (adsorption coefficient/f_{oc}), half-life in the field, precipitation and the application rate. From the plots, effects were observed both temporally and in the amounts of herbicide being leached. The K_{oc}, half-life, and f_{oc} influenced the amounts leached more than did the application rate and precipitation. An increase in the half-life of the herbicide not only increased the leached amounts but delayed this leaching by several months.

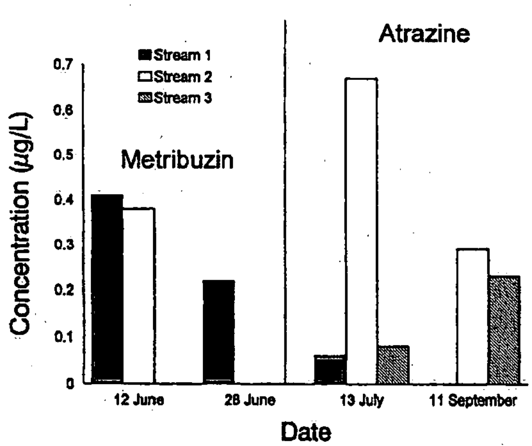


FIG. 3. Metribuzin and atrazine concentrations in three streams adjacent to the investigation site at St. Léonard d'Aston, Nicolet region.

DISCUSSION

Like many agricultural regions in the province of Quebec, the study area of St-Léonard d'Aston is increasing its activities in the production of potato, as demonstrated from the survey to local farmers. Notwithstanding the fact that this practice is very limited, data on the environmental impacts are scarce. In the current study, pesticides were detected in the soil, tile drain water, surface water, and nearby streams. This situation begs the question as to whether there are potential environmental effects.

The fields under study have been characterized as having a sandy, glaciofluvial deposit, a soil type common to the St-Lawrence lowlands. Soil analysis revealed that only residues of metribuzin and fenvalerate were found. Aldicarb, a known rapid leacher (McRae, 1989), was not detected because this event was undoubtedly missed. Aldicarb has a log octanol–water partition coefficient (log K_{ow}) of 1.36 (WHO, 1991) and is highly soluble in water (6 g/liter) (Kidd and James, 1991). Thus, the compound does not readily adsorb to soils

TABLE 4
CREAMS Input Components—Hydrology, Erosion, and Pesticide Parameters

Hydrology parameters	
Description	**Value**
Drainage Area (acres)	1.5
Effective hydraulic conductivity (in./hr)	0.5
Fraction of pore space filled at field capacity	24
Fraction of available water that is filled at start	1.0
Soil evaporation parameter	4.5
Soil porosity (in./in.)	0.54
Wilting point (in./in.)	0.11
Depth of surface soil layer (in.)	0.4
Depth of root zone (in.)	22.0
Effective capillary tension (in.)	3.0
Manning's n for overland flow	0.01
Effective hydrologic slope	0.007
Effective slope length (ft)	79.0

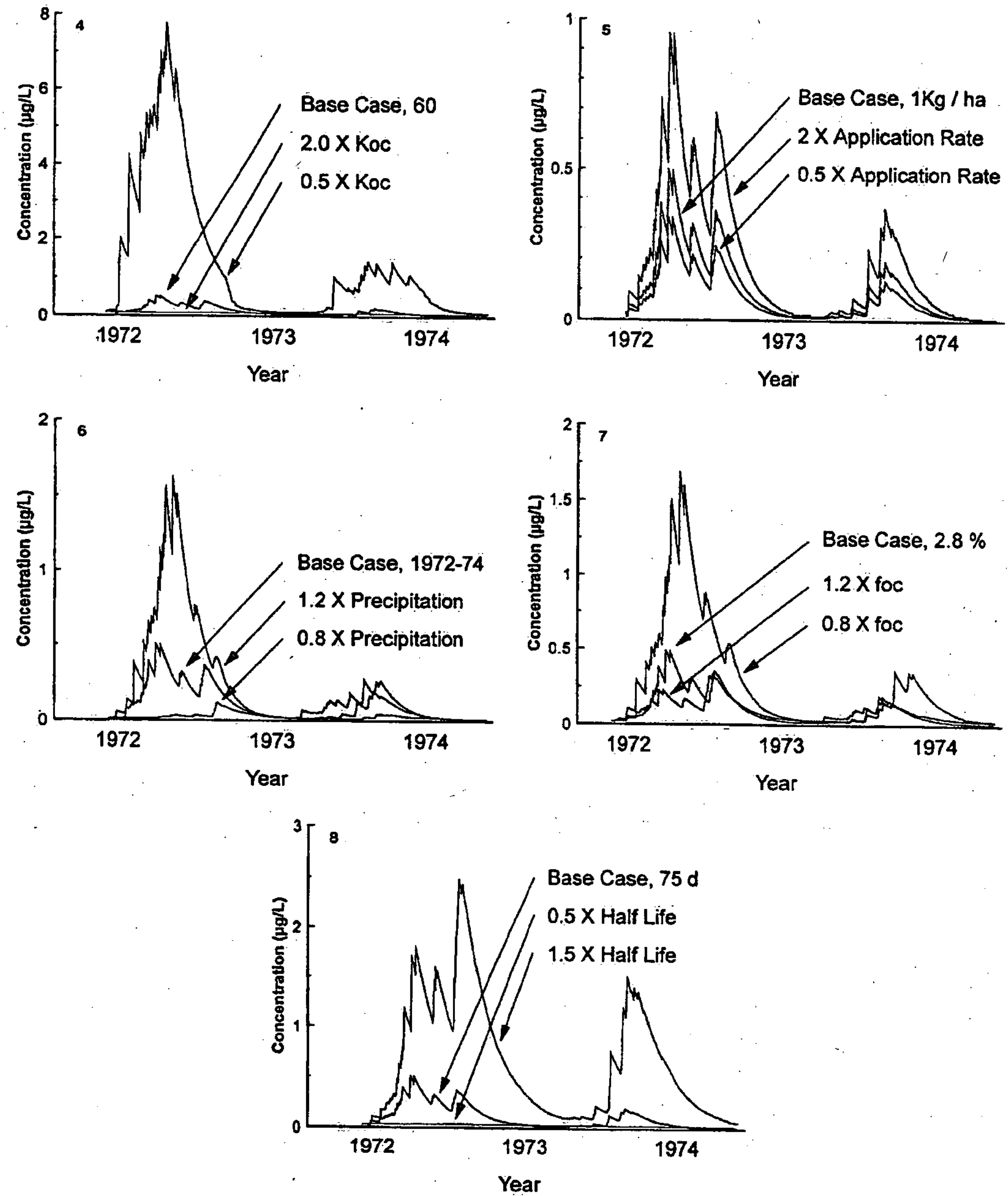
Pesticide parameters	
Description	**Value**
Soil porosity (in./in.)	0.54
Field capacity (in./in.)	0.24
Organic matter (% of soil mass)	0.02
Number of pesticides	2

Erosion parameters	
Description	**Value**
Kinematic viscosity (ft^2/sec)	1.41e-05
Manning's n for overland flow	0.02
Weight density of soil (lbs/ft^3)	77.0
Soil erodibility	0.135
Manning's for channel flow	0.03
Yalin constant for sediment transport	0.64
Fraction of clay in the surface layer	0.02
Fraction of silt in the surface layer	0.08
Fraction of sand in the surface layer	0.90
Fraction of organic matter in the surface layer	0.029
Specific surface area of clay particles (m^2/g)	20.0
Specific surface area of silt particles (m^2/g)	4.0
Specific surface area of sand particles (m^2/g)	0.05
Specific surface area of organic matter particles (m^2/g)	1000.
Drainage area represented by overland flow profile (acres)	1.46
Slope length of representative overland flow profile (ft)	982.4
Average slope of representative overland flow profile (ft/ft)	0.007
Slope at the upper end of profile (ft/ft)	0.0071
Slope of midsection (ft/ft)	0.0010
Slope at the lower end of profile (ft/ft)	0.0122
Distance from top of slope (start miduniform) (ft)	403.6
Elevation above lowest point (start of miduniform) (ft)	4.6
Distance from top of slope (end miduniform section) (ft)	505.6
Elevation above lowest point (end miduniform section) (ft)	4.46
Slope segments—changes in soil erodibility factor	1
Horizontal distance (ft) top of slope to bottom of segment	1
Soil erodibility factor for soil segment	1

and prefers the dissolved phase, making it ideal for root absorption and systemic translocation, and prone to leaching to groundwaters. Fenvalerate, on the other hand, was detected once in the surface layer and at a very low concentration (0.001 μg/g) in the 25-cm layer. This insecticide was most likely subjected to soil microbial degradation (Fan, 1995, personal communication). Fenvalerate with a log K_{ow} of 6.2 (WHO, 1990) is not expected to be mobile in soils.

TABLE 5
Predicted CREAMS Values (Pesticide Concentrations in Surface Runoff in μg/liter)

1989			1990		
Date	Aldicarb	Metribuzin	Date	Phorate	Metribuzin
June 10	131	224	June 18	1.9	172
June 27	65	107	June 19	1906	136
June 28	55	95	July 17	759	40
July 10	17	38	July 19	727	39
September 2	1.6	3.3	July 23	554	13
September 4	0.02	0.25	July 31	422	7.2
October 2	0.0013	0.018	August 27	131	0.28
October 16	0	0.007	August 28	113	0.15
November 9	0	0.00044	August 29	109	0.14
			September 23	48	0.05
			September 30	31	0.01
			October 11	17	0.001
			October 18	12	0.0004



FIGS. 4–8. EXPRES simulations for the concentration of metribuzin in the subsurface (1 m). Parameters modification to K_{oc}, application rate, precipitation, f_{oc}, and half-life.

Phorate was found in both the surface (0–5 cm) and deeper (25–30 cm) layers at low concentrations. It has low to moderate water solubility (50 mg/liter) (Worthing and Walker, 1987) and has been deemed to be a nonleacher according to McRae (1989).

Metribuzin was demonstrated to migrate from the surface layer to the root zone in both fields which signifies that, like most triazines, this herbicide will be partly dispersed via the dissolved phase of soils. Losses of soil-applied triazine-type herbicides such as metribuzin occur through movement in the water phase of soil runoff as opposed to translocation with eroded soil sediment (Glotfelty *et al.*, 1984). Metribuzin's estimated log K_{ow} is 1.87 (Banerjee *et al.*, 1980) and it is fairly soluble in water (1.2 μg/liter) (Worthing and Walker, 1987). A concentration of 0.25 μg/g metribuzin in soils can represent a concentration of approximately 26 μg/liter in water. Although this concentration is above the Canadian Water Quality Guidelines for the protection of aquatic life of 1 μg/liter, it is considered bound and thus not bioavailable. Smith and Walker (1989) found that metribuzin did not leach below 10 cm in a Regina clay soil. Small concentrations of metribuzin, up to 0.013 μg/g, were detected in the 25-cm depth samples in fields 1 and 2. The presence of organic matter at this depth suggests that metribuzin was adsorbed into soil particles.

In the tile drain the only pesticide found was metribuzin. When applied at recommended rates, it can leach from the crop root zone under soil and climate conditions common to potato production in Quebec. The concentrations of metribuzin measured in this study are similar to those reported in tile drainage studies in other areas of Canada and the United States. Runoff events occurring within 2 weeks after a soil application of metribuzin are the most important with respect to delivery to surface waters. Tile drainage does not appear to be a major route for transport of metribuzin to surface waters due to its relatively nonpersistent nature in soils (Pauli *et al.*, 1990). Metribuzin was applied to corn at rate of 0.56 kg/ha on tiled drained, sandy loam soil in Quebec (Muir and Baker, 1976). Concentrations up to 1.65 μg/liter were detected in tile drain water during the summer of 1974. The results of that study suggest that the amount of rainfall may govern the quantity of herbicide residues in the tile drain water (Muir and Baker, 1976). In the current investigation, however, there was no positive correlation between the subsurface flow and the amount of metribuzin detected. The transport of nonadsorbed chemical in runoff is very much affected by the initial soil moisture which affects both the timing and the redistribution of the chemical within the soil during a rainfall event (Heathman *et al.*, 1985). The more humid conditions of 1990 resulted in increased metribuzin movement in the subsurface drain flow. The dry season of 1989 enabled metribuzin to dissipate by other means, such as microbial degradation. The degradation of metribuzin occurs at a greater rate in the surface soil than in the subsoil (Bastien, 1991). Furthermore, during the 1990 season, metribuzin levels were found in water and soil samples taken before the pesticide application. Smith and Walker (1989) noted that metribuzin may be carried over in soils from one year to the next.

The only appreciable event observed in surface runoff water samples was detections of metribuzin with a maximum of 70 μg/liter after a storm in June 1989. Fenvalerate was also detected near its detection limit of 0.02 μg/liter. In terms of the potential environmental impact, this concentration of metribuzin is nearly two orders of magnitude above the Canadian Water Quality Guideline for the protection of aquatic life (1 μg/liter). Metribuzin like other triazines has a relatively low log K_{oc} of 1.78 (Wauchope *et al.*, 1992) and a $t_{1/2}$ of 37–115 days (Verschueren, 1983; Wauchope *et al.*, 1992), respectively. This signifies that metribuzin is mobile because the adsorption and desorption between water and soil/sediment particles occurs readily. Of concern, therefore, are pluvial events strong enough to cause surface runoff that will carry excessive amounts of metribuzin.

The nearby streams contained very low concentrations of metribuzin. These concentrations were not necessarily observed following a strong precipitation. The low levels, however, seem to indicate that these streams are able to dilute a loading of metribuzin from surface runoff and tile drain in an agricultural area where 14% of the cultures are potato cultures. Unlike the detrimental effects to the aquatic life observed in corn-producing areas of Canada attributed to atrazine (Caux and Kent, 1995), these areas of low potato production are not expected to perturb the aquatic life in their agricultural basin.

CREAMS Simulations (Surface Runoff)

CREAMS is a computer model that predicts runoff, erosion, sedimentation, and chemical losses from agricultural fields (Knisel, 1980). The model was developed to evaluate agricultural management practices by incorporating an improved understanding of the hydrology. In the current investigation, the CREAMS model did not give accurate predictions for pesticide losses. The model tended to overestimate the losses of pesticide to surface runoff and did not consider the pesticide losses through percolation or other routes of pesticide dissipation. Modifications to the pesticide submodel are needed to obtain more accurate simulations of pesticide transport. Suggested changes in this area are CREAM linkages to the pesticide subsurface model LEACHM.

EXPRES Simulations (Subsurface Runoff)

The EXPRES simulation predicted a very low dissolved pesticide concentration at a 1-m depth (Figs. 4–8, base case). A maximum concentration of 0.5 μg/liter occurred early in October. *In situ* monitoring revealed that metribuzin soil concentrations (25 cm) at the end of September 1990 were 0.02 μg/g (20 μg/kg) and its concentration in tile drain (located 1 m below ground level) was 1.2 μg/liter. With an average bulk density of agricultural soils at 1300 kg/m^3 or 1.3 g/cm^3 (Koorevaar *et al.*, 1983), a metribuzin water concentration could be estimated at 26 μg/liter at a 25-cm depth. Since this herbicide is bound to soil particles at a 25-cm depth, it could well be envisioned that a fraction of the compound is slowly being released into the dissolved phase. Thus, the model predicted very well this herbicide's concentration in the dissolved phase; however, the model did not predict the time of release. From the field data (Figs. 1 and 2) maximum release into tile drain (3.5 μg/liter) is mid-June compared to October for the simulation. The application rate and timing were the same for both the simulation and the *in situ* field investigations. The model predicted that the metribuzin concentration in the dissolved phase increased through the summer and fall months to maximum levels in October after which there was a steady decline in concentrations. The precipitation events for the simulation were those actually recorded for the average time period of 1970–1974, thus the movement of metribuzin was not attributable to a constantly even water input. From the *in situ* field investigations, there was no apparent positive correlation between subsurface flow and metribuzin concentrations (Figs. 1 and 2).

Subsurface transport is not the major route by which metribuzin is dissipated. By investigating this route with EXPRES, however, the most influential key factors in defining the leaching potential of metribuzin in the subsurface for this study site were identified (Figs. 4–8). By halving the K_{oc}, the contribution to subsurface flow has increased by more than an order of magnitude. Because K_{oc} depends on the organic content of the soil (f_{oc}), the amount of metribuzin in the subsurface flow will greatly vary among different agricultural fields in the province of Quebec. An order of magnitude increase in the subsurface, however, is still an order of magnitude below that potentially carried in the surface waters.

CONCLUSION

The environmental impact attributable to agricultural pesticides can only be assessed once the pesticide leaves the field to which it was applied. These off-site impacts are characterized as effects to nontarget biota. Of the numerous dissipation routes available to pesticides, water transports pesticides off site. Once detected in aquatic systems (e.g., groundwater, streams, lakes), their concentrations can be compared to Canadian Water Quality Guidelines to assess the potential environmental risk involved. The current investigations looked at pesticides used to curtail pests in the Nicolet potato-growing region of Quebec. These pesticides were detected in the soil, in the surface water, in the tile drain, and in the nearby streams. Only fenvalerate and metribuzin were carried off-site from the two fields. The concentrations of these pesticides in the nearby streams were too low for them to elicit an effect on the in-stream aquatic life.

Following a storm, metribuzin was found at high concentrations in field surface runoff (46 μg/liter). From the known literature (Caux and Kent, 1995; Smith, 1985) and through modeled data such as the ones provided by the CREAMS model, triazine-like pesticides are expected to be quickly desorbed after a rain event and get carried off-site at high concentrations by water runoff. In areas where the land use for a particular crop is small-scaled, as was the case for the current investigations, the watershed was able to buffer the toxicant loadings. In areas where large-scale uses of triazines are made (Caux and Kent, 1995), the river basin was perturbed. Much of the aquatic impact associated with the use of triazine pesticides is simply a question of the amounts used in a river basin. The more use, the greater the risk of high concentrations ultimately reaching the streams and rivers via field runoff. As mentioned previously, more attention should be focused on this delicate balance between triazine adsorption and desorption from soil/sediment matter to water in order to obtain pesticide formulations with controlled, active-ingredient releases.

REFERENCES

Agriculture Canada (1995). *Regulatory Information on Pesticide Products.* RIPP Database (CCINFODISK). Produced by Agriculture Canada and distributed by the Canadian Centre for Occupational Health and Safety (CD-ROM).

Banerjee, S., Yalkowski, S., and Valvani, S. (1980). Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation. *Environ. Sci. Technol.* **14,** 1227–1229.

Bastien, C. (1991). *Pesticide Levels in Agricultural Drainage Systems in Quebec.* M.Sc. Thesis, McGill University Agricultural College, Montreal, Quebec.

Caux, P.-Y., and Forrest, S. (1991). Pesticides in tributaries of the St. Lawrence River (1989–1990). In *Pesticides Research and Monitoring: Annual Report 1989–1990 and 1990–1991* (P.-Y. Caux, Ed.), pp. 47–48. Environment Canada, Commercial Chemicals branch, Ottawa, Ontario, Canada K1A 0H3.

Caux, P.-Y., and Kent, R. A. (1994). *Canadian Water Quality Guidelines for Pesticides and Industrial Substances.* Canadian Association on Water Quality Monograph Series No. 4.

Caux, P.-Y., and Kent, R. A. (1995). Towards the development of a site-specific water quality objective for atrazine in the Yamaska River Quebec, for the protection of aquatic life. *Water Qual. Res. J. Can.* **30,** 157–178.

Enright, P., and Madramootoo, C. A. (1990). *Application of the Creams Hydrology Component for Runoff Prediction in Quebec.* ASAE International Winter Meeting, December 18, 1990, Chicago, IL.

Forrest, S., and Caux, P.-Y. (1990). *Pesticides in Tributaries of the St. Lawrence River.* 1987–1988 Program Report. Government report available as a Saint-Lawrence Centre publication.

Frank, R., Clegg, B. S., Ripley, B. D., and Braun, H. E. (1987). Investigations of pesticide contaminations in rural wells, 1979–1984, Ontario, Canada. *Arch. Environ. Contam. Toxicol.* **19,** 319–324.

Giroux, I. (1990). Rapport sur l'échantillonnage de l'aldicarbe au Québec de 1984 à 1988. Direction de la gestion et du contrôle des pesticides. Ministère de l'environnement du Québec.

Glotfelty, D. E., Taylor, A. W., Isensee, A. R., Jersey, J., and Glenn, S. (1984). Atrazine and simazine movement to Wye River estuary. *J. Environ. Qual.* **13,** 115–121.

Heathman, G. C., Ahuija, L. R., and Lehman, O. R. (1985). The transfer of soil surface-applied chemicals to runoff. *Trans. ASAE* **28**(4), 1909–1915, 1920.

Kidd, H., and Janes, D. R. (Eds.) (1991). *The Agrochemicals Handbook,* 3rd ed. Royal Society of Chemistry, Cambridge, England.

Knisel, W. G. (Ed.) (1980). *CREAMS: A Field-Scale Model for Chemical, Runoff and Erosion from Agricultural Management Systems.* Conservation Research Report no 26, U.S. Dept. of Agriculture Washington, DC.

Koorevaar, P., Menelik, G., and Dirksen, C. (1983). *Developments in Soil Science: Elements of Soil Physics,* Vol. 13. Elsevier, Amsterdam, The Netherlands.

Manarbachie (1983). *Analyse de pesticides dans les eaux de Saint-Catherine et de Saint-Raymond.* Assainissement Agricole. Ministère de l'environnement du Québec, Québec.

Matthew, G. A. (1984). *Pest Management.* Longman Group Ltd., New York.

McRae, B. (1989). *The Characterization and Identification of Potentially Leachable Pesticides and Areas Vulnerable to Groundwater Contamination by Pesticides in Canada.* Pesticides Directorate. Agriculture Canada, Ottawa, Ontario. Backgrounder 89–01.

Mehuys, G. R. (1986). *Soil Physics Laboratory Manual.* Dept. Renewable Resources, Macdonald College of McGill University, Sainte-Anne-de-Bellevue, January 1986.

Muir, D. C., and Baker, B. E. (1976). Detection of triazine herbicides and their degradation products in tile-drain water from fields under intensive corn (maize) production. *J. Agric. Food Chem.* **24**(1), 122–125.

Mutch, J. P., Crowe, A. S., and Resler, O. (1993). *EXPRES: An Expert System for Assessing the Fate of Pesticides in the Subsurface.* Environment Canada Scientific Series No. 201.

Page, A. L., Miller, R. H., and Keeney, D. R. (Eds.) (1982). *Methods of Soil Analysis. II. Chemical and Microbiological Properties,* 2nd ed. American Society of Agronomy. Madison, WI.

Pauli, B. D., Kent, R. A., and Wong, M. P. (1990). *Canadian Water Quality Guidelines for Metribuzin.* Environment Canada Scientific No. 179.

Roberts, H. A. (1982). *Weed Control Handbook: Principles.* Blackwell Scientific, London, England.

Sage (1988). *Receuill des principaux pesticides en usage au Québec* (D. Cossette, I. Giroux, and R. Poulin, Eds.), Sage Ltée., Québec, Québec.

Smith, A. E. (1985). Persistence of triazine herbicides in Canadian soils. *Can. J. Plant Sci.* **65,** 811–812.

Smith, A. E., and Walker, A. (1989). Prediction of the persistence of the triazine herbicides atrazine, cyanazine and metribuzin in Regina heavy clay. *Can. J. Soil Sci.* **69,** 587–595.

Verschueren, K. (1983). *Handbook of Environmental Data on Organic Chemicals,* 2nd ed. Van Norstrand–Reinheld Co.

Wauchope, R. D., Buttler, T. M., Hornsby, A. G., AgustijnBeckers, P. W. N., and Burt, J. P. (1992). The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.* **123,** 1–155.

WHO (1990). *Environmental Health Criteria 95: Fenvalerate.* World Health Organization, Geneva.

WHO (1991). *Environmental Health Criteria 121: Aldicarb.* World Health Organization, Geneva.

Worthing, C. R., and Walker, S. B. (Eds.) (1987). *The Pesticide Manual, A World Compendium,* 8th ed. British Crop Protection Council, 20 Bridgeport Rd., Thornton Heath, UK.

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