Changes in Urban Stream Water Pesticide Concentrations One Year after a Cosmetic Pesticides Ban

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Aaron K. Todd

Environmental Monitoring and Reporting Branch
Ontario Ministry of the Environment

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For more information:
call 416-325-4000 or toll free 1-800-565-4923
picemail.moe@ontario.ca
www.Ontario.ca/Environment

Executive Summary

On April 22, 2009, the sale and use of pesticides for cosmetic purposes were banned in Ontario. The Ontario Ministry of the Environment worked in cooperation with five Conservation Authorities to monitor pesticide concentrations in ten urban Ontario streams before (July-October 2008) and after (June-October 2009) the ban took effect. A total of 168 stream water samples were collected and analyzed in a laboratory for up to 105 pesticides and pesticide degradates (breakdown products of pesticides). Selected results are presented in this report to describe changes in urban stream water pesticide concentrations in the first year after the ban and to provide a reference point for further hypothesis testing, discussion and monitoring. The three main objectives of the study and a brief summary of related results are as follows.

Objective #1: Determine which pesticides were detectable in urban stream water at low levels of laboratory detection.

Thirty-three pesticides and three degradates were detected at a concentration greater than 1 ng L^{-1} (part per trillion) – a low level of laboratory detection. Combinations of two or more pesticides were detected in all samples. Herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, glyphosate and methylchlorophenoxypropionic acid (MCPP) and the insecticide carbaryl were the dominant pesticides in samples collected in 2008. Cosmetic uses of these pesticides were banned and, with the exception of glyphosate, sales of domestic products containing these pesticides were prohibited when the ban took effect.

Objective #2: Determine whether concentrations changed after the implementation of the cosmetic pesticides ban.

Concentrations of 2,4-D, dicamba, MCPP, total phenoxy herbicides and total insecticides were significantly lower in 2009 and a decrease in carbaryl concentrations approached statistical significance. Depending on the stream, median and maximum concentrations of 2,4-D, dicamba and MCPP were up to 94% (mean 67%) and 97% (mean 65%) lower in 2009, respectively. Rainfall was similar between the two study periods leading to the cautious conclusion that reductions in pesticide use after the cosmetic pesticides ban, and not changes in runoff, were responsible for the observed changes in stream water pesticide concentrations. Some of the study watersheds were potentially affected by golf courses and pre-existing municipal bylaws restricting cosmetic pesticide use. Differences in concentrations of 2,4-D, dicamba and MCPP remained statistically significant when samples from these watersheds were excluded from the analysis. Concentrations of glyphosate and its degradate aminomethylphosphonic acid (AMPA) were not significantly different between 2008 and 2009 which may reflect that there are exceptions to the ban for certain uses of glyphosate.

Objective #3: Compare concentrations of detected pesticides to water quality criteria for the protection of aquatic life to assess potential effects on stream ecosystems.

Water quality criteria for the protection of aquatic life have been developed for over half (21/33) of the pesticides that were detected at a concentration > 1 ng L^{-1}. Pesticide concentrations in urban stream water samples rarely exceeded these criteria. In 2008, carbaryl exceeded a criterion in 12.5% (3/24) of samples, permethrin 4.2% (1/24) and total phenoxy herbicides 3.4% (3/88). The only pesticide to exceed a criterion in 2009 was the insecticide permethrin, with one exceedance in 24 samples. Permethrin is registered for use in Canada in a variety of domestic insecticide products and certain exceptions for permethrin use are allowed under Ontario's cosmetic pesticides ban.

Table of Contents

List of Figures

List of Tables

1. Introduction

Non-agricultural uses of pesticides can be an important source of pesticide loading to streams draining urban watersheds (Skark et al. 2004). Monitoring studies show that pesticides commonly used for non-agricultural purposes are routinely detected in urban streams, often at higher concentrations than in agricultural streams (Hoffman et al. 2000; Phillips and Bode 2004; Gilliom et al. 2006), and the number of pesticides detected in urban streams is generally larger as the proportion of urban land cover in the watershed increases (Phillips and Bode 2004; Sprague and Nowell 2008). Elevated concentrations of pesticides in urban streams have the potential to impact aquatic ecosystems. Eighty-three percent of 30 urban streams monitored as part of National Water Quality Assessment Program in the United States had pesticide concentrations that exceeded one or more water quality guidelines for the protection of aquatic life (Gilliom et al. 2006).

Concerns regarding the potential impacts of pesticides on the environment and human health have prompted some political jurisdictions to implement restrictions on the sale and use of pesticides for cosmetic purposes such as broadleaf weed control in urban lawns. On April 22, 2009, Ontario's cosmetic pesticides ban took effect. The requirements of the ban are detailed in Ontario Regulation 63/09 made under the Pesticides Act, which has been amended by the Cosmetic Pesticides Ban Act, 2008. More than 180 domestic pesticide products are banned for sale and the cosmetic uses of over 90 pesticide ingredients are prohibited (Ontario Ministry of the Environment 2010). Pesticides cannot be used for cosmetic purposes on lawns, vegetable and ornamental gardens, patios, driveways, cemeteries, and in parks and school yards. There are no exceptions for pest infestations in these areas and the use of biopesticides and pesticide alternatives are recommended. Exceptions to the ban are allowed for industries such as agriculture, forestry and golf courses, and consumers are still able to purchase domestic pesticide products for health or safety reasons such as controlling plants poisonous to the touch and stinging insects.

Struger and Fletcher (2007) reported pesticide concentrations in two urban Ontario streams between 1998 and 2002. They found that 72% of stream water samples contained at least one pesticide attributable to applications for lawn care. The most frequently detected pesticides were methylchlorophenoxypropionic acid (MCPP), diazinon and 2,4-dichlorophenoxyacetic acid (2,4-D) at detection limits ranging from 20 ng L^{-1} for diazinon to 100 ng L^{-1} for MCPP and 2,4-D. Concentrations of four pesticides exceeded water quality criteria for the protection of aquatic life including diazinon (28% of samples) and atrazine, carbofuran and chlorpyrifos (<1% of samples).

In the United States, a federally mandated phase out of diazinon and chlorpyrifos in 2001 resulted in declines in the concentrations of these insecticides in urban streams (Banks et al. 2005*a*; Banks et al. 2005*b*; Phillips et al. 2007). Phillips et al. (2007) observed decreases of over 50% in summer diazinon concentrations with a corresponding decrease in the frequency of diazinon concentrations exceeding a water quality criterion for aquatic life, from 10% to less than 1% of summer samples before and after the phase out, respectively.

The Ontario cosmetic pesticides ban is unique in North America, and perhaps the world, in terms of the large number of pesticide ingredients that have been banned and the immediate (as opposed to phased-in) prohibition of use *and* sales of a large number of domestic pesticide products. This provided a unique opportunity to investigate changes in environmental concentrations of pesticides following a major shift in pesticides management policy. This study measured pesticide concentrations in ten urban Ontario streams before and after the implementation of the cosmetic pesticides ban. The objectives of the study were to:

(a) determine which pesticides were detectable in urban stream water at low levels of laboratory detection;

(b) determine whether concentrations changed after the implementation of the cosmetic pesticides ban; and,

(c) compare concentrations of detected pesticides to water quality criteria for the protection of aquatic life to assess potential effects on stream ecosystems.

In a recent editorial, Cohen (2010) encouraged scientists to take a more active role in informing pesticides regulation and management. This report presents the results of a two-year (2008-2009) monitoring study of urban stream water pesticide concentrations before and after Ontario's cosmetic pesticides ban. The results are useful to researchers and government agencies interested in understanding the influence of such regulations on environmental concentrations of pesticides and provide a reference point for further hypothesis testing and monitoring.

2. Materials and Methods

2.1 Sampling Site Selection

Ten streams draining watersheds with urban-residential land uses were selected to isolate the influence of cosmetic uses of pesticides on surface water quality from other pesticide uses excepted from the cosmetic pesticides ban including agriculture and golf courses. Selected watersheds met the following criteria: high proportion of urban land cover; no point sources (e.g. sewage treatment plants); limited agriculture; and, no golf courses (with a few exceptions). Stream monitoring sites and the locations of the nearest Environment Canada weather monitoring stations are illustrated in Figure 1. The watersheds are described in Table 1. Weather data were collected to United Nation's World Meteorological Organization standards. The mean distance between the weather monitoring stations and the study watersheds was 11 km (range 0 – 28 km).

Watersheds ranged from 1.4 km^2 (Masonville Creek) to 75 km^2 (Highland Creek) in drainage area (mean 29 km^2). The proportion of urban land cover ranged from 35% to 97% (mean 72%). Four of the watersheds selected for this study (Chippewa, Highland, Mimico and Schneider's Creeks) were covered by existing municipal (local government) bylaws restricting cosmetic pesticide use prior to 2008. These bylaws did not restrict sales of domestic pesticide products. The bylaw covering Schneider's Creek restricted cosmetic pesticide use in the months of July and August only. Three of the watersheds (Chippewa, Indian and Mimico Creeks) contain golf courses comprising < 2% of the watershed area. Agricultural land uses comprised < 4% of the watershed area in Indian and Schneider's Creeks and 38% of the Fletcher's Creek watershed.

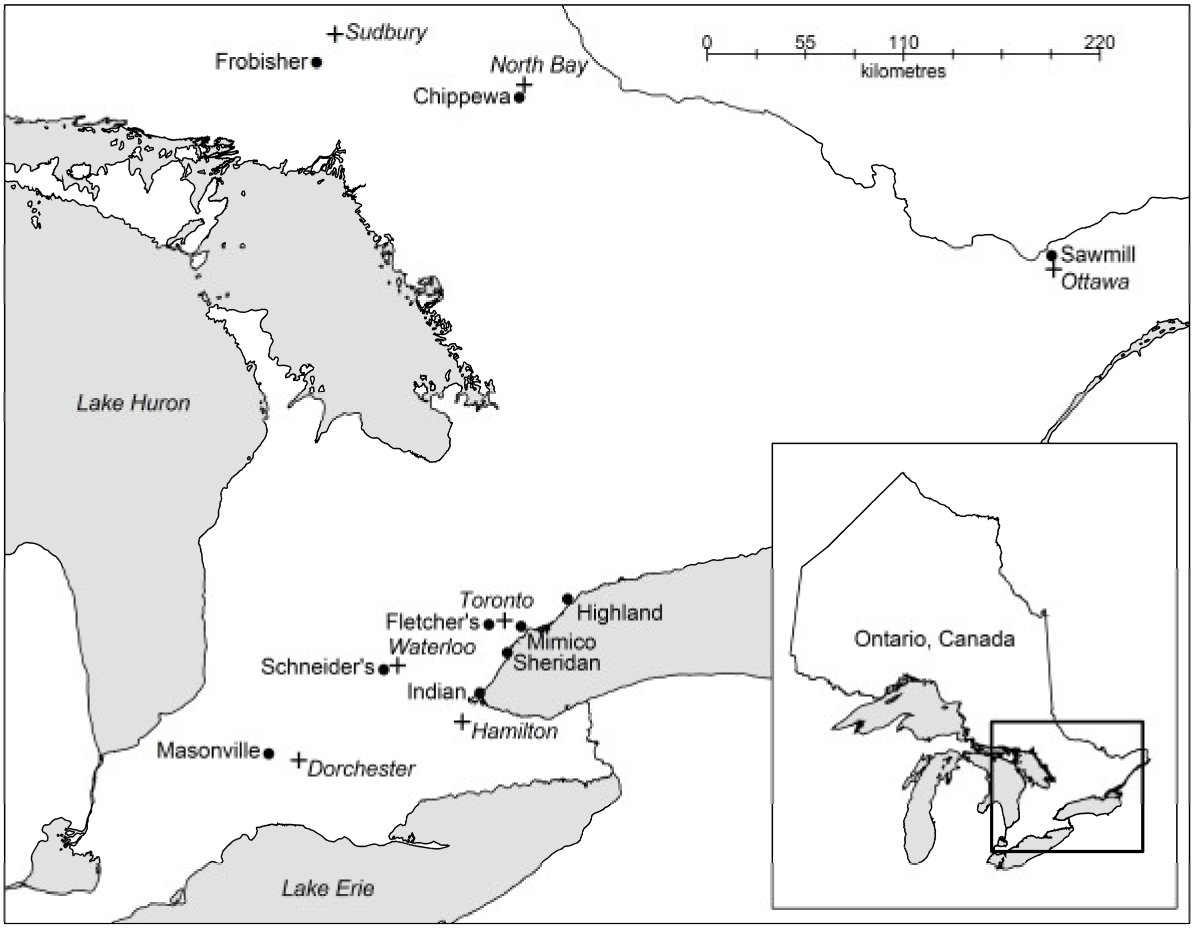

Figure 1. Locations of the ten urban stream water sampling sites (dots) and the nearest weather monitoring stations with rainfall data for the study period (crosses).

Table 1. Description of the urban stream watersheds and the number of stream water samples analyzed per study year.

Creek	Watershed Area (km^2)	Stream Length (km)	Urban Land Use (%)	Agricultural Land Use (%)	Golf Course Land Use (%)	Municipal Bylaw Restricting Cosmetic Pesticide Use (date)	Samples 2008 (#)	Samples 2009 (#)
Chippewa	40.2	49.1	38	0	1.2	February 2005	7	8
Fletcher's	31.2	77.1	58	38	0		9	8
Frobisher	4.4	2.5	35	0	0		8	8
Highland	74.8	60.3	89	0	0	April 2004	9	8
Indian	22.3	70.8	73	4	1.7		9	8
Masonville	1.4	3.6	69	0	0		10	8
Mimico	60.0	52.5	96	0	1.6	April 2004	9	8
Sawmill	21.6	29.8	71	0	0		9	8
Schneider's	30.1	27.1	91	4	0	January 2007	9	8
Sheridan	8.3	4.8	97	0	0		9	8

2.2 Sample Collection and Storage

Stream water samples were collected on an approximately biweekly basis between July and October in 2008 and June and October in 2009 from a site located near the outlet of each stream. Samples collected in 2008 and 2009, respectively, represent stream water quality before and after the implementation of the cosmetic pesticides ban on April 22, 2009. All samples from all streams were analyzed for acid-extractable herbicides. Samples from Highland, Sawmill and Schneider's Creeks were analyzed for a broader suite of pesticides (105 analytes) including 53 insecticides, 28 herbicides, six fungicides and 18 degradates. Analytes included banned, phased out and currently used pesticides.

Samples were collected in certified clean 1 L amber glass bottles except for the glyphosate samples which were collected in 1 L polypropylene bottles. Most samples were collected using grab sampling techniques across a range of stream flow conditions from low flow (dry periods) to high flow (after rain storms). All samples were collected 0.1 m to 1 m below the water surface and stored in coolers with ice packs for shipping to the laboratory. The samples were stored at 4 °C prior to extraction and analysis. A portion of the samples from Highland and Mimico Creeks were collected using an auto-sampler whereby samples were pumped from the streams using a peristaltic pump and Teflon tubing into a stainless steel canister rinsed previously with hexane. Samples were then transferred to 1 L sample bottles for shipment to the laboratory.

2.3 Laboratory Analysis of Samples

Stream water samples were analyzed by AXYS Analytical Services (Sidney, British Columbia, Canada) using isotope dilution and internal standard quantification methods capable of measuring pesticide concentrations at the sub-nanogram per litre level for most analytes. Materials, extraction and analysis methods for acid-extractable herbicides, multi-residue pesticides and glyphosate are described in detail in Woudneh et al. (2006), United States Environment Protection Agency (US EPA) (2007) and Woudneh et al. (2009) and Byer et al. (2008), respectively. Carbamates were analyzed using an AXYS in-house method based on the principals of US EPA 1600 series guidance (US EPA 2007). Samples for carbamates analysis were spiked with isotopically labeled surrogate standards and liquid-liquid extracted in dichloromethane. Extracts were dried over sodium sulfate, reduced in volume and cleaned-up on a solid-phase extraction cartridge. The eluent was spiked with recovery standard and analyzed using liquid chromatography coupled with a tandem mass spectrometer (LC-MS/MS). Target analyte concentrations were quantified using the internal standard method, comparing the area of the quantification ion to that of the surrogate standard and correcting for response factors. Analyte concentrations were automatically corrected for losses during extraction and cleanup.

2.4 Quality Control

Samples were analyzed in batches with additional laboratory quality control samples consisting of 5% procedural blanks and 5% spiked reference samples. Fifty-seven of 105 analytes were detected at least once in laboratory blanks; however, 93% (154/165) and 98% (162/165) of these detections were < 1 ng L^{-1} and < 5 ng L^{-1}, respectively. Median analytical recoveries in spiked samples for the four analytical methods (105 analytes) ranged from 12% to 166%, and 82% of recoveries were between 60 and 140%. Recovery values of ^{13}C- and deuterium-labeled quantification standards were measured to assess analytical method performance on a sample-to-sample basis. Median recoveries of 36 labeled standards for the four analytical methods ranged from 58% to 139%.

For the high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analyses (acid-extractable herbicides and multi-residue pesticides), sample specific method detection limits were calculated for each sample based on the actual analytical results taking into account the labeled standard recovery, matrix effects and instrument performance. For the LC-MS/MS analyses (glyphosate and carbamates), analyte concentrations were reported to the lowest calibration level. Detection limits for 73% (77/105) and 95% (100/105) of analytes were < 1 ng L^{-1} and < 5 ng L^{-1}, respectively. Analytes with higher levels of detection were aminomethylphosphonic acid (AMPA), glufosinate, glyphosate and tebuconazole (18-20 ng L^{-1}) and methoprene (47 ng L^{-1}).

2.5 Data Analysis

Prior to plotting and statistical analysis, analyte concentrations were blank corrected and analytes reported as not detected were assigned a value of the mean of the sample detection limits. Total concentrations of varying pesticide types (e.g. total phenoxy herbicides) were calculated as the sum of their respective components. Plots of frequency versus concentration showed skewness (a measure of asymmetry of a distribution around its mean) for most analytes as a result of outliers (infrequent peaks in pesticide concentrations). The Mann-Whitney nonparametric rank-sum test (Helsel and Hirsch 2002) was used to determine if significant statistical differences existed between pesticide concentrations before (2008) and after (2009) the implementation of the cosmetic pesticides ban (*see* Supplementary Tables 1-3 for the test results). The Mann-Whitney test is based on ranks and therefore is more robust (less likely to indicate spurious significance in the presence of outliers) compared to a parametric Students *t*-test. However, the Mann Whitney test is comparatively less powerful when normality holds, especially at small sample sizes. Tests were considered significant if the observed *p* value was less than a critical *p* value of 0.05. Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment (CCME) 1999) and National Recommended Water Quality Criteria (US EPA 2009) were used to assess potential toxicity. The criterion for total phenoxy herbicides recognizes that individual phenoxy herbicides have similar modes of toxic action and therefore their concentrations should be summed to assess potential toxicity (CCME 1999).

3. Results and Discussion

3.1 Pesticide detection in urban Ontario streams

Of the 105 pesticides and degradates monitored in 2008 and 2009, 33 pesticides and three degradates were detected at a concentration > 1 ng L^{-1} (Table 2). Of these, four pesticides (2,4-D, dicamba, diazinon and MCPP) and one degradate (desethylatrazine) were detected in 100% of samples in 2008 and 2009. The occurrence of these compounds is consistent with pesticide applications for urban lawn care and atmospheric deposition of agricultural pesticides. A 1993 survey showed that 2,4-D, MCPP, dicamba and diazinon accounted for 61% of the total amount of pesticides used by professional lawn care applicators in Ontario (Hunter and McGee 1994). Sales of more than 80 domestic pesticide products containing one or more of 2,4-D, MCPP and dicamba were prohibited when the Ontario cosmetic pesticides ban took effect in April 2009, comprising nearly half of the total number of products that were banned. Cosmetic uses of diazinon were previously phased out by 2006 (Struger and Fletcher 2007). The maximum diazinon concentration (30 ng L^{-1}) measured in the present study was almost two orders of magnitude lower than the maximum concentration measured by Struger and Fletcher (2007) suggesting that concentrations have declined since cosmetic uses were phased out. Atrazine, one of the most used pesticides for agriculture in Ontario (McGee et al. 2004), and its degradate desethylatrazine, are frequently detected in rainfall in Canada and the United States (Hall et al. 1993; Goolsby et al. 1997). Previous studies have concluded that atmospheric deposition is largely responsible for the presence of atrazine and desethylatrazine in urban streams (Hoffman et al. 2000; Phillips and Bode 2004). Agricultural uses of pesticides in small areas of the predominately urban study watersheds also may have contributed.

High frequencies of pesticide detection relative to previous stream monitoring studies in Ontario (Frank and Logan 1988; Frank et al. 1991; Struger and Fletcher 2007) were due largely to low levels of laboratory detection. Almost 90% (5,326/5,999) of pesticide detections were < 10 ng L^{-1} and only two pesticides (2,4-D and MCPP) were detected at a concentration > 1,000 ng L^{-1}. Effects on aquatic life at these concentrations are discussed later in this report. Selected pesticides accounted for the bulk of the total pesticide concentration in most samples. When concentrations were censored at 50 ng L^{-1} (a level above the laboratory detection limit for all of the 105 analytes), the mean number of pesticides detected per sample was 2.6 in 2008 and 2.0 in 2009. The dominant pesticides remained relatively consistent between 2008 and 2009 (Table 3). The most frequently detected mixtures (combinations of two or more pesticides in a sample) were comprised of varying combinations of 2,4-D, MCPP, glyphosate, carbaryl, AMPA and dicamba in 2008 and 2,4-D, AMPA, glyphosate and MCPP in 2009.

Table 2. Summary of urban stream water pesticide monitoring results (2008-2009) with regulatory status, analytical method detection limit, water quality criterion (WQC) and WQC exceedance frequency.

Pesticide[a]	Regulatory Status[b]	Detection Limit (ng L^{-1})	n	Detection Frequency (%)	Maximum Concentration (ng L^{-1})	Water Quality Criterion (WQC)[c]	n_{2008} > WQC	n_{2009} > WQC
Fungicides								
Quintozene	B	0.1	48	67	1.6	n/a		
Tebuconazole	R	17.8	48	33	962	n/a		
Herbicides								
Alachlor	N	0.6	48	23	2.1	n/a		
Atrazine	B	1.0	48	96	194	1,800[C]	0	0
Dacthal	B	0.1	48	90	1.6	n/a		
Dicamba	B	0.1	168	100	601	10,000[C]	0	0
Dimethenamid	R	0.1	48	40	38	n/a		
Glufosinate	S	18.7	47	11	56	n/a		
Glyphosate	S	19.8	47	74	562	65,000[C]	0	0
Metolachlor	R	0.3	48	90	54	7,800[C]	0	0
Pendimethalin	R	3.2	48	2	9.6	n/a		
Simazine	B	1.0	48	67	4.1	10,000[C]	0	0
Triclopyr	B	0.1	168	99	284	n/a		
Insecticides								
Bendiocarb	R	1.3	48	2	15	n/a		
beta-Endosulfan	B	0.2	48	65	1.5	3[C]	0	0
Carbaryl	B	0.7	48	94	418	200[C]	12.5% (3/24)	0% (0/24)
Chlorpyriphos	S	0.2	48	69	1.6	3.5[C]	0	0
Diazinon	B[d]	0.1	48	100	30	170[U]	0	0

Table 2. Continued from previous page.

Pesticide[a]	Regulatory Status[b]	Detection Limit (ng L^{-1})	n	Detection Frequency (%)	Maximum Concentration (ng L^{-1})	Water Quality Criterion (WQC)[c]	n_{2008} > WQC	n_{2009} > WQC
Dioxacarb	N	0.6	48	10	1.9	n/a		
Dimethoate	B	4.8	48	4	3.3	6,200[C]	0	0
Imidacloprid	B	1.3	48	85	25	230[C]	0	0
Lindane	N	0.1	48	88	1.3	10[C]	0	0
Linuron	R	1.7	48	6	6	7,000[C]	0	0
Methoprene	R	47.1	48	8	308	530[C]	0	0
Parathion-Ethyl	N	0.7	48	2	3.3	65[U]	0	0
Permethrin	S	0.9	48	17	16	4[C]	4.2% (1/24)	4.2% (1/24)
Piperonyl butoxide	S	0.1	48	100	11	n/a		
Propoxur	B	0.6	48	67	29	n/a		
Phenoxy Herbicides								
2,4,5-T	N	0.1	168	57	6.9	[e]		
2,4-D	B	1.2	168	100	8,230	[e]		
Dichlorprop	B	0.4	168	88	137	[e]		
MCPA	B	0.4	168	96	16	[e]		
MCPP	B	0.6	168	100	3,250	[e]		
Total Phenoxy Herbicides			168		11,623	4,000[C]	3.4% (3/88)	0% (0/80)
Degradates								
AMPA		19.1	47	85	223	n/a		
Desethylatrazine		0.2	48	100	118	n/a		
Diazinon-Oxon		0.8	48	2	2.1	n/a		

Table 2. Continued from previous page.

[a] Pesticides and degradates detected at a concentration > 1 ng L^{-1} are shown.

[b] N = Not registered for use in Canada; R = Registered for use in Canada; B = Registered for use in Canada but sale and use for cosmetic purposes prohibited in Ontario; S = Registered for use in Canada, sale and use for cosmetic purposes prohibited in Ontario but sales of selected domestic products allowed for specific non-cosmetic purposes (Ontario Ministry of the Environment 2010; Pest Management Regulatory Agency of Canada 2010).

[c] C = Canadian Water Quality Guideline for the Protection of Aquatic Life (CCME 1999); U = National Recommended Water Quality Criteria (US EPA 2009); n/a = no criterion.

[d] Domestic uses of diazinon in Canada were phased out by 2006.

[e] Individual phenoxy herbicide concentrations were summed and compared to the water quality criterion for total phenoxy herbicides.

Table 3. Most frequently detected pesticide mixtures in urban Ontario streams before (2008) and after (2009) the cosmetic pesticides ban.

2008 (n = 24)		2009 (n = 24)	
Pesticides in mixture	Percentage of samples with mixture	Pesticides in mixture	Percentage of samples with mixture
2,4-D; MCPP	50	2,4-D; AMPA	29
2,4-D; glyphosate; MCPP	42	2,4-D; glyphosate	29
2,4-D; carbaryl	29	2,4-D; MCPP	29
2,4-D; carbaryl; glyphosate; MCPP	25	AMPA; glyphosate	29
2,4-D; AMPA; MCPP	21	glyphosate; MCPP	25
2,4-D; dicamba; glyphosate, MCPP	21	2,4-D; glyphosate; MCPP	25

Mixtures include pesticides detected at > 50 ng L^{-1} (a level above the laboratory detection limit for all of the 105 analytes).

3.2 Influence of Ontario's cosmetic pesticides ban

Urban stream water pesticide concentrations before (2008) and after (2009) the implementation of Ontario's cosmetic pesticides ban are shown for the individual pesticides from Table 3 (Figure 2) and by pesticide type (Figure 3). Box plots of 2,4-D, dicamba, MCPP and total phenoxy herbicide concentrations are based on combined results from ten Ontario streams ($n_{2008} = 88$; $n_{2009} = 80$). Box plots for other pesticides and degradates are based on combined results from Highland, Sawmill and Schneider's Creeks ($n_{2008} = 23$; $n_{2009} = 24$).

Concentrations of 2,4-D, dicamba, MCPP and total phenoxy herbicides were significantly different between 2008 and 2009 ($p < 0.0001$). Median concentrations decreased from 119 ng L^{-1} to 23 ng L^{-1} (2,4-D), 14 ng L^{-1} to 2.4 ng L^{-1} (dicamba), 70 ng L^{-1} to 20 ng L^{-1} (MCPP) and 183 ng L^{-1} to 48 ng L^{-1} (total phenoxy herbicides) in 2008 and 2009, respectively. The contribution of these pesticides to the total pesticides concentration also decreased. Collectively, 2,4-D, dicamba and MCPP comprised up to 87% (mean 37%) of the total pesticides concentration in 2008 samples and up to 63% (mean 19%) in 2009 samples.

Concentrations of 2,4-D, dicamba and MCPP were significantly different ($p < 0.05$) between 2008 and 2009 in at least half of the ten streams that were monitored (Table 4). Depending on the stream, median and maximum concentrations of 2,4-D, dicamba and MCPP were up to 94% (mean 67%) and 97% (mean 65%) lower in 2009, respectively. The absolute maximum concentrations across all of the streams decreased from 8,230 ng L^{-1} to 637 ng L^{-1} (2,4-D), 601 ng L^{-1} to 75 ng L^{-1} (dicamba), 3,250 ng L^{-1} to 348 ng L^{-1} (MCPP) and 11,623 ng L^{-1} in to 989 ng L^{-1} (total phenoxy herbicides) in 2008 and 2009, respectively.

Stream water concentrations of 2,4-D, dicamba and MCPP are expected to respond rapidly to changes in application and runoff. In water, these herbicides are moderately to highly mobile and have half-lives of much less than a year (Mackay et al. 1997). 2,4-D and dicamba are relatively volatile and have been detected in air and rain (Majewski and Capel 1996); however, atmospheric deposition rates have been shown to be very low relative to application rates (Waite et al. 1995). The primary pathway for these herbicides to enter surface waters is runoff; especially in urban landscapes where impervious surfaces promote runoff and storm water systems increase drainage efficiency. The highest and lowest concentrations of pesticides in urban streams generally occur during stormflow and baseflow, respectively (Phillips and Bode 2004).

Stream discharge and runoff data were of limited availability for the study streams. More readily available rainfall data were used as a surrogate for runoff. It is possible that some local variability in rainfall was not measured given that the weather stations were generally located outside of the study watersheds; however, the data were assumed to provide a reasonable measure of total rainfall over each sampling period for each study region. Mean rainfall was roughly equivalent in the sampling periods (June-October) of

2008 and 2009 at 494 mm and 485 mm, respectively (Table 5). The mean number of days with > 10 mm of rainfall, a measure of rainfall intensity, was also roughly equivalent at 17.3 and 18.1, respectively. Therefore, it is reasonable to assume that there were no appreciable differences in runoff from rainfall between the two sampling periods and that year-over-year decreases in the concentrations of 2,4-D, dicamba, MCPP and total phenoxy herbicides were a result of decreased application amounts following the Ontario ban on the sale and use of cosmetic pesticides. These findings are consistent with Banks et al. (2005*a*) who measured a significant decrease in surface water concentrations of chlorpyrifos within a year of the cessation of retail sales in Texas.

Significant differences ($p < 0.05$) in the concentrations of one or more of 2,4-D, dicamba and MCPP were observed in three of the four streams (Chippewa, Mimico and Schneider's Creeks) where municipal bylaws restricting cosmetic pesticide use were in effect at least one year prior to the Ontario ban (Table 4). Differences in stream water concentrations of 2,4-D, dicamba and MCPP between 2008 and 2009 remained statistically significant when data from watersheds with pre-existing municipal bylaws and/or golf courses were excluded from the Mann-Whitney test (*see* Supplementary Table 3). Municipal bylaws imposed varying restrictions on cosmetic uses of pesticides but did not restrict the sale of domestic pesticide products. The ongoing commercial availability of domestic pesticide products may have limited the effectiveness of the municipal bylaws in eliminating cosmetic uses. Exceptions to the cosmetic pesticides ban are allowed for golf courses and therefore it was assumed that pesticides application practices on golf courses were similar before and after the ban. Rice et al. (2010) cite studies showing that golf course turf often requires multiple applications of pesticides at rates that exceed those typically found in agricultural or residential environments. There is no evidence to suggest that stream water concentrations of pesticides were disproportionately higher in the three watersheds with a golf course. This was expected given that golf courses comprised < 2% of the total watershed area in the each of the three study watersheds where they occurred (Table 1).

Median concentrations of 2,4-D, dicamba and MCPP in Fletcher's Creek were consistently amongst the highest measured in the ten study streams (Table 4). It is possible that agricultural uses of pesticides in the Fletcher's Creek watershed may have influenced the observed stream water pesticide concentrations. Enhanced spatial resolution in monitoring of this watershed should be considered in future studies to assess the relative influence of agricultural pesticide use on stream water pesticide concentrations.

Glyphosate and its degradate AMPA collectively comprised up to 33% (mean 18%) and 46% (mean 24%) of the total pesticides concentration in 2008 and 2009, respectively; however, the maximum measured concentration of 562 ng L^{-1} of glyphosate (Table 2) was over two orders of magnitude lower than the water quality criterion (65,000 ng L^{-1}). Concentrations of glyphosate and AMPA were not significantly different ($p > 0.05$) between 2008 and 2009 (Figure 2). Cosmetic uses of glyphosate were prohibited by the

Ontario cosmetic pesticides ban; however, certain uses of glyphosate for health and safety purposes were permitted and domestic pesticide products containing glyphosate were still commercially available after the Ontario ban took effect. The ongoing availability and use of glyphosate was likely the reason that concentrations did not differ before and after the ban.

Cosmetic uses of the insecticide carbaryl were prohibited and over twenty domestic pesticide products containing carbaryl were banned for sale when the Ontario ban took effect. Differences in carbaryl concentrations between 2008 and 2009 approached statistical significance (p = 0.053). The median concentration of carbaryl in urban stream water decreased from 14.4 ng L^{-1} in 2008 to 6.9 ng L^{-1} in 2009 (Figure 2). This contributed to a significant difference (p = 0.01) in total insecticides concentration between 2008 and 2009 (Figure 3). The median concentration of total insecticides decreased from 111 ng L^{-1} in 2008 to 96 ng L^{-1} in 2009.

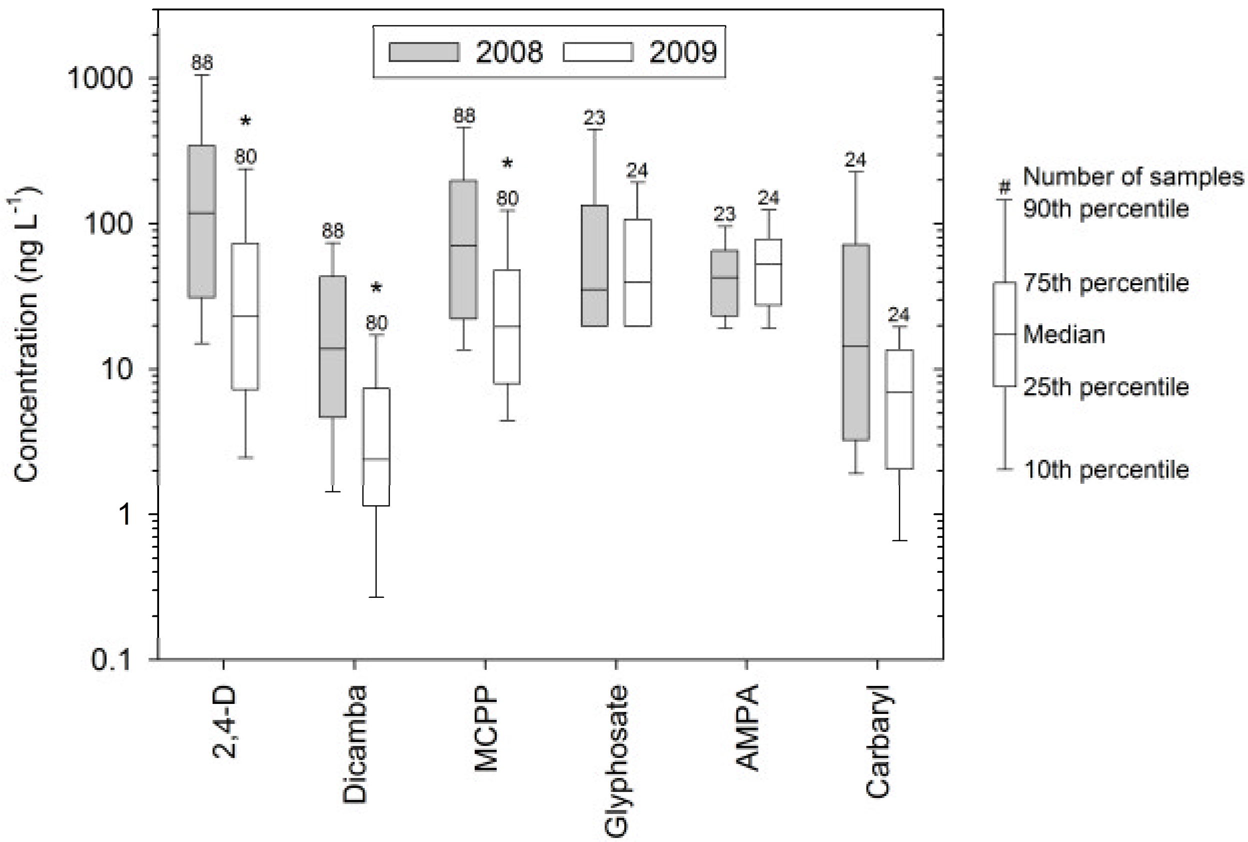

Figure 2. Pesticide concentrations in urban stream water samples before (2008) and after (2009) Ontario's cosmetic pesticides ban. An asterisk (*) indicates a significant ($p < 0.05$) difference between 2008 and 2009 concentrations based on a Mann-Whitney test.

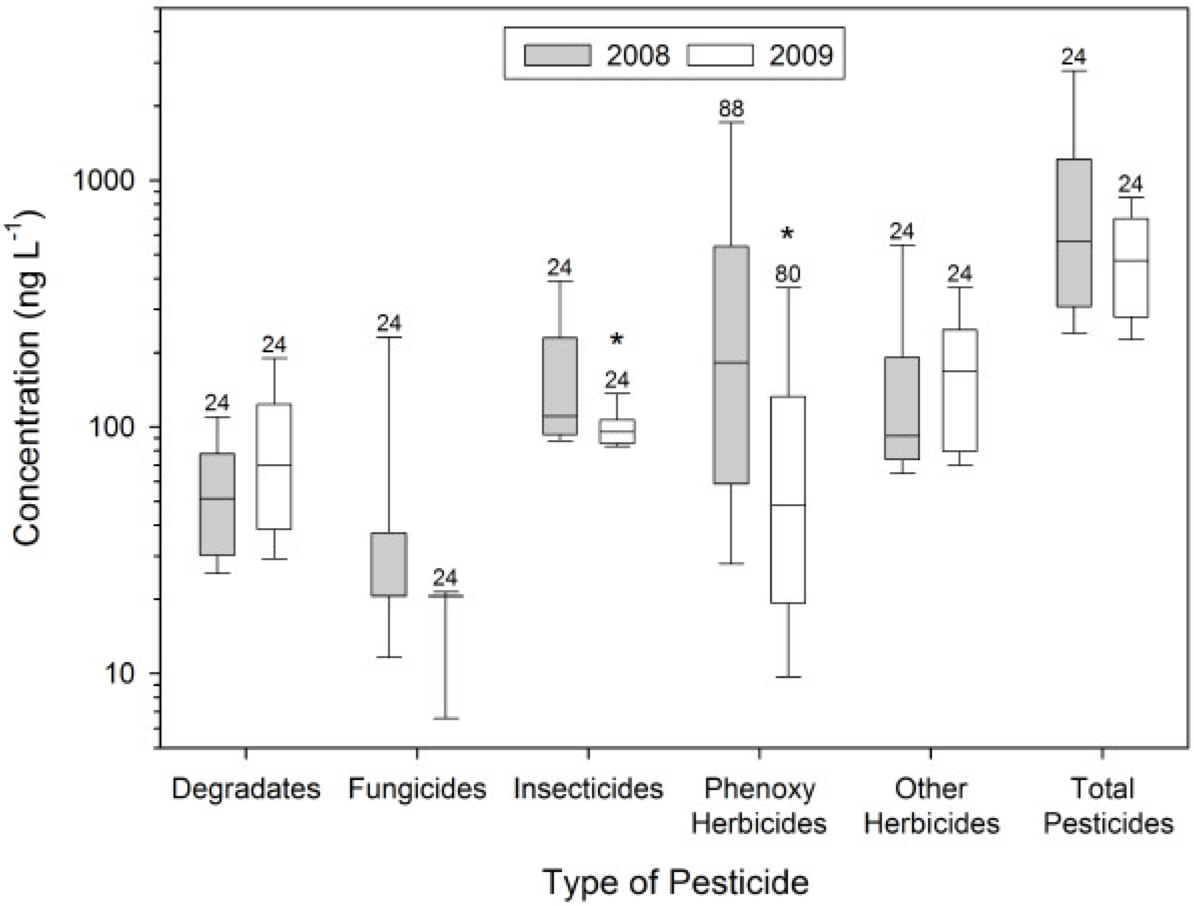

Figure 3. Urban stream water pesticide concentrations by type before (2008) and after (2009) Ontario's cosmetic pesticides ban. An asterisk (*) indicates a significant ($p < 0.05$) difference between 2008 and 2009 concentrations based on a Mann-Whitney test. See Figure 2 for an explanation of the box plots.

Table 4. Summary statistics for 2,4-D, dicamba and MCPP concentrations in ten Ontario urban streams before (2008) and after (2009) the cosmetic pesticides ban.

		2,4-D		Dicamba		MCPP	
Stream	Statistic	2008	2009	2008	2009	2008	2009
Chippewa	median	20	2.3*	2.0	0.4*	19	4.3*
	range	6.5-567	1.3-13	0.6-43	0.2-1.5	9.5-202	4.0-8.6
Fletcher’s	median	585	80	62	6.1*	274	72
	range	34-5,130	6.1-343	16-74	0.7-66	35-789	7.0-240
Frobisher	median	75	14	4.4	0.3	43	18
	range	1.3-292	2.2-166	0.09-15	0.07-1.5	14-114	6.0-55
Highland	median	57	118	7.0	9.1	50	57
	range	8.8-1,160	4.8-477	1.4-74	0.5-14	11-917	8.7-262
Indian	median	113	23*	10	2.3*	79	17*
	range	19-1,040	3.9-247	2.9-81	0.6-18	22-423	5.4-73
Masonville	median	458	34*	44	2.8*	236	13*
	range	47-8,230	13-247	8.8-601	1.2-48	24-3,350	7.4-102
Mimico	median	166	68	40	8.4*	131	51*
	range	38-1,230	6.9-637	22-128	2.3-75	54-581	13-348
Sawmill	median	94	17*	6.7	1.4	38	13*
	range	15-177	0.9-36	1.5-24	0.2-46	12-86	3.5-20
Schneider’s	median	481	58	27	4.1*	333	41
	range	30-2,530	2.0-208	3.2-190	0.3-10	34-1,140	4.3-72
Sheridan	median	102	15*	12	3.2*	40	14
	range	18-360	5.5-213	3.7-53	1.4-22	10-188	4.3-214

An asterisk (*) denotes a significant difference ($p < 0.05$) between the 2008 and 2009 concentrations using a Mann-Whitney test. n = 8 to 10 samples/stream/year.

Table 5. Rainfall for the sampling period (June to October) for 2008 and 2009 and long-term normal rainfall (June to October) at weather stations near the stream monitoring sites.

		June to October total rainfall (mm) with number of days with rainfall > 10 mm in parentheses		
Stream	Weather Station	2008	2009	1971-2000
Chippewa	North Bay	591 (18)	498 (18)	501 (17.2)
Fletcher's, Highland, Mimico, Sheridan	Toronto	519 (18)	410 (17)	369 (12.0)
Frobisher	Sudbury	447 (15)	479 (19)	423 (13.9)
Indian	Hamilton	523 (21)	543 (24)	405 (13.8)
Masonville	Dorchester	450 (15)	483 (19)	479 (16.8)
Sawmill	Ottawa	405 (15)	572 (17)	423 (13.9)
Schneider's	Waterloo	520 (19)	411 (13)	410 (14.2)
	Mean (all stations)	*494 (17.3)*	*485 (18.1)*	*430 (14.5)*

Rainfall data are from the National Climate Archive (Environment Canada 2010). The nearest weather station to each stream monitoring site with a complete rainfall dataset was selected. The mean distance between the weather stations and study watersheds was 11 km (range 0 – 27 km).

3.3 Assessing the effects of pesticides on stream ecosystems

Comparisons of measured stream water pesticide concentrations with water quality criteria for protecting aquatic life (CCME 1999; US EPA 2009) provide a screening-level assessment of potential effects. Criteria have been developed for over half (21/33) of the pesticides detected at a concentration > 1 ng L^{-1} (Table 2). In 2008, carbaryl exceeded a criterion in 12.5% (3/24) of samples, permethrin 4.2% (1/24) and total phenoxy herbicides 3.4% (3/88). The only pesticide to exceed a criterion in 2009 was the insecticide permethrin, with one exceedance in 24 samples. Permethrin is highly toxic to aquatic invertebrates and fish (CCME 1999). This is reflected in the relatively low criterion of 4 ng L^{-1}. Permethrin is registered for use in Canada in a variety of domestic insecticide products (e.g. flea and tick control for household pets) and certain exceptions for permethrin use are allowed under Ontario's cosmetic pesticides ban.

Phillips and Bode (2004) found that most exceedances of water quality criteria in urban streams occurred during storm flow conditions. Samples in this study were collected across a range of stream flow conditions, including many low flow samples, and therefore maximum concentrations and the number of pesticides exceeding a guideline may be underrepresented. Conversely, peak pesticide concentrations are generally inversely related to stream size (Richards and Baker 1993; Crawford 2001). In the small urban streams monitored in this study, the close proximity of the sampling sites to the source of pesticide application likely limited the assimilation of pesticides (including dilution and degradation) prior to sample collection.

Some chemical mixtures can have additive, synergistic or antagonistic toxic effects (Battaglin and Fairchild 2002; Laetz et al. 2009). Most of the individual pesticides measured in this study were below their respective criteria; however, pesticide mixtures in Ontario's urban streams were commonly observed and the effects of multiple pesticides on aquatic life are the subject of ongoing research. In addition, the water quality of the urban streams monitored in this study is influenced by other compounds such as sodium chloride from de-icing salt (Perera et al. 2009). Fagiano et al. (2010) suggest that it would be interesting to investigate the link between predicted risk posed by pesticide mixtures and observed effect with biological samples; however, this would be especially challenging in urban streams where impacts from land uses include but are not limited to pesticide loading.

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6. Supplementary Information

Supplementary Table 1. Results of Mann-Whitney test for differences in pesticide concentrations between 2008 and 2009 by individual pesticide and pesticide type across streams.[ab]

Pesticide	n_{2008}	n_{2009}	$median_{2008}$ (ng L^{-1})	$median_{2009}$ (ng L^{-1})	*Z*	*p* value (two tailed)
2,4,5-T	88	80	0.1	0.1	-1.08	0.28
2,4-D	88	80	119	23	-5.39	< 0.0001
AMPA	23	24	43	53	-0.94	0.35
Atrazine	24	24	4.2	14	-3.29	< 0.01
Atrazine (June and early-July 2009 results omitted)[c]	24	15	4.2	6.9	-1.49	0.14
beta-Endosulfan	24	24	0.2	0.2	-1.48	0.14
Carbaryl	24	24	14	6.9	-1.94	0.053
Chlorpyriphos	24	24	0.3	0.2	-0.93	0.35
Dacthal	24	24	0.2	0.2	-1.23	0.22
Desethylatrazine	24	24	3.9	8.6	-2.26	0.02
Desethylatrazine (June and early-July 2009 results omitted)[c]	24	15	3.9	5.3	-0.30	0.76
Diazinon	24	24	1.3	1.0	-1.03	0.30
Dicamba	88	80	14	2.4	-6.00	< 0.0001
Dichlorprop	88	80	0.9	1.1	-1.07	0.28
Glyphosate	23	24	35	40	-0.42	0.68
Imidacloprid	24	24	3.9	1.6	-3.14	< 0.01
Lindane	24	24	< 0.1	< 0.1	-1.38	0.17
MCPA	88	80	1.1	1.3	-0.48	0.63
MCPP	88	80	70	20	-5.64	< 0.0001
Metolachlor	24	24	1.3	4	-3.00	0.003
Metolachlor (June and early-July 2009 results omitted)[c]	24	15	1.3	1.8	-1.11	0.27
Piperonyl butoxide	24	24	1.6	1.2	-0.98	0.33
Propoxur	24	24	1.7	0.9	-0.63	0.53
Simazine	24	24	1.3	1.1	-0.14	0.89
Triclopyr	88	80	1.1	1.4	-0.89	0.37

Supplementary Table 1. Continued from previous page.

Pesticide	n_{2008}	n_{2009}	$median_{2008}$ (ng L^{-1})	$median_{2009}$ (ng L^{-1})	*Z*	*p* value (two tailed)
Total Concentration by Pesticide Type						
Degradates	24	24	51	70	-1.90	0.06
Fungicides	24	24	21	21	-1.65	0.10
Insecticides	24	24	111	96	-2.52	0.01
Phenoxy Herbicides	88	80	183	48	-5.42	< 0.0001
Other Herbicides (excluding Phenoxy Herbicides)	24	24	92	169	-1.07	0.28
Total Pesticides	24	24	568	473	-1.27	0.20

[a] Confidence interval = 95%

[b] Differences for individual pesticides were tested only for those pesticides detected in at least 50% of samples annually in 2008 and 2009.

[c] Sample collection for agricultural pesticides commenced in early-June in 2009 compared to mid-July in 2008. When the June and early-July 2009 sample results were omitted, the differences between 2008 and 2009 were not significant ($p > 0.05$).

Supplementary Table 2. Results of Mann-Whitney tests for differences in 2,4-D, dicamba and MCPP concentrations between 2008 and 2009 by stream.

	2,4-D		Dicamba		MCPP	
Stream	*U*	*p* value (two tailed)	*U*	*p* value (two tailed)	*U*	*p* value (two tailed)
Chippewa	2	< 0.01	5	< 0.01	0	< 0.01
Fletcher's	19	0.11	7	< 0.01	17	0.08
Frobisher	24	0.43	16	0.10	16	0.10
Highland	35	0.92	33	0.81	35	0.96
Indian	14	0.04	10	0.01	7	< 0.01
Masonville	8	< 0.01	6	< 0.01	3	< 0.01
Mimico	22	0.19	10	0.01	13	0.03
Sawmill	11	0.02	16	0.06	10	0.01
Schneider's	18	0.08	9	0.01	17	0.08
Sheridan	13	0.03	14	0.04	20	0.14

Confidence interval = 95%. Summary statistics by stream and year are shown in Table 4.

Supplementary Table 3. Results of Mann-Whitney test for differences in 2,4-D, dicamba and MCPP concentrations between 2008 and 2009 for varying groups of streams.[a]

Pesticide	$median_{2008}$ (ng L^{-1})	$median_{2009}$ (ng L^{-1})	*Z*	*p* value (two tailed)
2,4-D				
All Streams	119	23	-5.39	< 0.0001
Golf courses excluded[b]	135	29	-4.41	< 0.0001
Municipal bylaws excluded[c]	136	22	-4.84	< 0.0001
Golf courses and bylaws excluded[d]	137	22	-4.36	< 0.0001
Dicamba				
All Streams	14	2.4	-6.00	< 0.0001
Golf courses excluded[b]	13	2.8	-5.12	< 0.0001
Municipal bylaws excluded[c]	14	2.0	-5.27	< 0.0001
Golf courses and bylaws excluded[d]	16	1.7	-4.76	< 0.0001
MCPP				
All Streams	70	20	-5.64	< 0.0001
Golf courses excluded[b]	57	20	-4.42	< 0.0001
Municipal bylaws excluded[c]	75	17	-5.10	< 0.0001
Golf courses and bylaws excluded[d]	66	17	-4.39	< 0.0001

[a] Confidence interval = 95%

[b] Includes data only for the seven streams without a golf course in the upstream watershed (n_{2008}=63; n_{2009}=56).

[c] Includes data only for the six streams that did not have municipal bylaws restricting cosmetic pesticide use (n_{2008}=54; n_{2009}=48).

[d] Includes data only for the five streams without a golf course and that did not have municipal bylaws restricting cosmetic pesticide use (n_{2008}=45; n_{2009}=40).