Temporal and spatial analysis of surface water pesticide occurrences in the Maritime Region of Canada.

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Abstract

This study measured both nutrient and pesticide concentrations at up to 13 different freshwater sites in New Brunswick, Nova Scotia and Prince Edward Island between 2013-2018. Up to sixty-two different pesticides were analysed in 248 discreet samples. A large majority of pesticides were below the detection limit of the laboratory while seven pesticides had at least 20% or more detections throughout the years of this study. The four pesticides which had the highest frequency of detection were the insecticides chlorantraniliprole, clothianidin, imidacloprid, and thiamethoxam of which the last three are categorised as neonicotinoid insecticides.

Keywords; Pesticides, Maritimes, Neonicotinoid, Imidacloprid, Thiamethoxam, Clothianidin, Chlorantraniliprole, Herbicides

Introduction

The Maritime region of Canada possesses some areas where agricultural activities dominate the landscape. In particular some watersheds in Prince Edward Island and in the Annapolis Valley of Nova Scotia are surrounded by fields growing a variety of forage crops, vegetables and tuberous crops (corn, potato, root vegetables), orchard fruits (apples, grapes) and berries (cranberry, blueberry, grapes, hops, strawberry, raspberry). While PEI is dominated by potato crops, the Annapolis Valley is more diversified into both vegetable and fruit production (Xing et al 2012). These various crops are treated with numerous different pesticides such as insecticides, herbicides and fungicides which are applied at different time frames (spring, summer, fall) and frequencies (Xing et al 2012). For example, it has been reported that orchard fruit pest management may result in up to 15 applications of pesticides, while a corn crop requires 2 to3 applications per year (Ernst 2009). All of the areas where agriculture occurs are well drained by stream and rivers of various sizes. Those waterbodies vary from small headwater streams no more than one metre across to large rivers such as the Cornwallis and Annapolis rivers.

There are two major pathways for pesticides to enter surface water in the Maritimes; spray drift and runoff after rainfall or snowmelt. The magnitude of pesticide concentrations in surface waters in the Maritimes has been known to be influenced by rate of application, rainfall, land use and land

management (Xiang et al 2012). Runoff in turn is usually heavily influenced by the intensity of the storm, the topographical conditions of the fields and the relative size and effectiveness of buffer zones (Denning et al 2004). Therefore, a particular focus on rain events was part of this study.

The Freshwater Quality Monitoring and Surveillance division of Environment and Climate Change Canada (ECCC) has conducted a Risk-based Adaptive Management Framework (RBAMF) to determine waterbodies in Canada at high risk for water quality impairment. That work demonstrated that agriculture in many areas in Canada, including the Great Lakes, Saint Lawrence River and parts of the Maritime Provinces contributes to an elevated risk to water quality health, due primarily to pesticide uses in those areas. Statistics Canada has developed similar maps using data on specific groups of pesticides (insecticides, herbicides and fungicides) which support the overall agricultural stressor findings of the RBMAF. The purpose of this study was to generate information on pesticide concentrations in surface waters in the Atlantic Coastal sub-watershed in order to determine if in fact, water quality was being impacted due to pesticide inputs. Therefore waterbodies were determined to be at high risk of impairment due to agricultural activities were the focus of sampling efforts.

Methods

Sampling Strategy

The number and locations of sampling sites for pesticide surveillance has changed throughout the six years of this study (2013-2018). Nova Scotia (NS) had the highest number of sites with nine, while Prince Edward Island (PEI) and New Brunswick (NB) had three and one each respectively. Sites were located on the Big Presqu'Ile River in NB, and the Wilmot and Dunk Rivers in PEI. Sampling sites in Nova Scotia were located on tributaries of the Cornwallis and the Annapolis Rivers as well as one site on the main stem of the Cornwallis River. Some sites were only sampled one year (Table 1), others for a few years and two sites were sampled all six years (Wilmot River, PEI and Cornwallis River, NS) (Table 1). Stream orders which indicates the level of branching in a river system were obtained for each sampling site (Table 1).

Grab sampling at all sites occurred during the months of May to September, approximately six times per growing season. Sampling included ambient (dry weather) sampling as well as even-based (heavy rainfalls) to target potential worst-case acute impacts to aquatic systems. Three of the six yearly sampling events were conducted during dry spells while three yearly sampling events were conducted during, or shortly after, rain events.

Pesticide samples were collected in 1L laboratory certified clean amber bottles and total phosphorus, total nitrogen and TOC samples were collected in plastic bottles. In all cases, bottles were kept in the dark, refrigerated until overnight delivery to the analytical laboratory. Field measurements of pH, dissolved oxygen, specific conductance, temperature and turbidity were also taken at the time of sampling using a pre-calibrated YSI™ or Hydrolab™ sonde. Samples were not filtered and therefore the results reflect concentrations of pesticides dissolved in the water column as well as bound to suspended sediments.

Wherever possible, efforts were made to align target pesticides with Pest Management Regulatory Agency (PMRA) priorities in addition to our primary focus, which is risk to aquatic ecosystems. The selection of analytes was limited somewhat by the analytical groupings of analyses at the ECCC laboratories. THE ECCC grouping comprised the neonicotinoid suite (8 pesticides) which includes imidacloprid, thiamethoxam and clothianidin. It also contained the organophosphate pesticides suite (13 pesticides) which includes malathion, naled and dimethoate and the neutral herbicide suite (15 pesticides) which includes metribuzin.

Table 1. Sampling site locations.

Sampling site	Location	Range of median flows (m^3/s)	Area (km^2)	Dominant types of agricultural area	Years	Stream order
New Brunswick						
Big Presqu'Ile	46.426°N, 67.709°W	1-50	484	Row crops, forage,	2013-15	4
Prince Edward Island						
Dunk River	46.345°N, 63.632°W	1-5	213.5	Row crops, forage,	2017-18	4
Wilmot River	46.393°N, 63.658°W	1-2	82.9	Row crops, forage,	2013-18	3
Wilmot River	46.408°N, 63.597°W	<1-2	5.7	Row crops, forage,	2017-18	2
Nova Scotia						
Cornwallis River	45.065°N, 64.635°W	2-15	90.8	Row crops, forage, orchards	2013-18	4
Coleman Brook	45.085°N, 64.599°W	n/a	48.2	Row crops, forage, orchards	2016	3
Rand Brook	45.057°N, 64.758°W	n/a	6.6	Row crops, forage, orchards	2016	2
Skinner Brook	45.029°N, 64.812°W	n/a	19.3	Row crop, cranberry	2016	2
Watton Brook	45.955°N, 65.027°W	n/a	5.1	Row crop, forage	2016	2
Lawrence Brook	45.089°N, 64.605°W	n/a	18.6	Row crops, forage, orchards	2017-18	2
Patterson	45.028°N, 64.822°W	n/a	7.2	Row crops, cranberries	2017-18	2
Palmer	45.004°N, 64.852°W	n/a	4.6	Row crop, forage	2017-18	1
Walker	45.009°N, 64.931°W	n/a	7.7	Row crop/ forage	2017-18	2

n/a; not available.

Laboratory analysis

Over the duration of the project, the pesticide analyte list has included such general groupings as organo-phosphate pesticides, base neutral pesticides, neonicotinoids, herbicides, pyrethroids and

organo-chlorine pesticides. Samples were sent to two Environment and Climate Change Canada (ECCC) laboratories; Atlantic Laboratory of Environmental Testing (ALET, Moncton, NB) and the National Laboratory of Environmental Testing (NLET, Burlington, ON). Pesticides were analysed at ALET from 2013-2015 and NLET from 2016-2018 while neonicotinoids were analysed at NLET from 2015-2018. Total phosphorus, total nitrogen and total organic carbon were always analysed at ALET. Laboratory methodology details for both pesticides and nutrients are presented in Appendix 1.

Statistical Analysis

Since many of the pesticide concentrations were below the detection limit of the laboratories, summary statistics for some pesticides were calculated using the NADA package in R (Helsel 2012). Differences in pesticide concentrations due to changes in categorical values such as rain/dry events, locations (provinces) or years were assessed using the cendiff command of the NADA package for R (Helsel 2012). The cendiff command uses censored data in its estimates of the differences in groups using a non-parametric Wilcoxon test. Associations of individual pesticides with water quality parameters (TP, TN, TOC, pH, specific conductivity, turbidity) were analysed using Kendal rank correlation (Kendal's tau) which is a non-parametric method. The benefit of using the non-parametric method is that it does not assume residuals to be normally distributed. The correlations were calculated using the NADA for R package (Helsel 2012).

Results and Discussion

With the large number of pesticides monitored during this study, it was important to summarize the data according to the frequency of detections, which varied greatly from no detections whatsoever to detections in over 90% of samples. The dataset was summarized in three categories; pesticides with no detections, pesticides with a low frequency of detections (less than 10%) and pesticides with a higher frequency of detections.

Pesticides with no detections

The following pesticides had no detections over the course of this project; azamethiphos, azoxystrobin, benzoylprop-ethyl, carbaryl, carbofuran, chloropicrin, cyazine, cyfluthrin, cyhalothrin, cypermethrin, deltatamethrin, diallate I, diallate II, diclofep , dinotefuran, esfenvale, ethafluarilin, ethion, fenoxapro, flonicamid, flupyradifuron, fonofos, heptachlor, hexazinone, metalaxyl, metobromuron, parathiomn, permethrin, phorate, piperonyl, resmethrin, spirodiclofen, spiromesife, spirotetramat, sulfoxalor, terbacyl, terbufos, triallate.

Pesticides with less then 10% frequency of detections

The following pesticides had less than 10% frequency of detections over the course of this project (Table 2). Disulfoton had 5 detections all occurring in 2016 and ranging in concentration from 27 to 36 ng/L. Phosmet was detected 7 times from 2013-2018, ranging from 1.25 to15.1. Neither of these pesticides have Canadian Council of the Ministers of the Environment (CCME) guidelines for the protection of aquatic life. The three detections for trifluarin ranged from 3.52 to 13.1 ng/L while the Canadian guideline is set at 200 ng/L. Linuron had 5 detections occurring in 2015 with a range of 50 to 270 ng/ L compared to the CCME guideline of 7000 ng/L. Simazine had nine total detections from 2013 to 2018. Simazine values ranged from 11 to 149 ng/L while the CCME guideline is 10000 ng/L. Malathion had 7 detections which ranged from 7.95 to 1750 ng/L while the CCME guideline is set at 100 ng/L. Of the seven malathion detections, two were above guidelines and both of those were obtained during a dry event sample in Nova Scotia. Since malathion biodegrades rapidly in surface water, the high detections we found during "dry" weather events likely resulted from applications of this insecticide on row crops located close to the sampling site. Thiacloprid is an insecticide which, in this study, had a low detection frequency of 6% and a concentration range from 0.57 to16.4 ng/L . Similarly, Hladik et al (2018) did not detect thiacloprid in any of their monthly samples on ten river in the United States. Thiacloprid does not volatilize, does not hydrolyze and is stable to aqueous-photolysis (EPA 2003).

Table 2. Pesticides with a low detection frequency.

Pesticides	# detections	# of samples	Frequency (%)	# of samples above guidelines
azynphos methyl	1	238	0.4	na
Beta-Endosulfan	3	38	8	na
butylate	1	238	0.4	na
diazinon	1	238	0.4	na
dibrom	1	127	0.8	na
Alpha-Endosulfan	3	38	8	na
Disulfoton	5	127	4	na
Phosmet	7	248	3	0
Trifluarin	3	248	1	0
Linuron	5	121	4	0
Simazine	9	248	4	0
Malathion	7	122	6	2
Thiacloprid	11	172	6	na

*na; no available Canadian freshwater quality guideline

Pesticides with higher frequencies of detections

The following pesticides had 10% or more detections during the course of this study (Table 3). The pesticides with the greatest number of individual detections were three neonicotinoid insecticides (clothianidin, imidacloprid and thiamethoxam). Atrazine and metalochlor, which are both herbicides,

rounded the top five pesticides detected during this study (Table 3). The median in Table 3 is calculated using all the samples with detections. A subsequent median was calculated and presented in Table 4 which included the censored values as well. Five pesticides were detected above CCME guidelines (Table 3).

Table 3. Pesticide results (uncensored values) from this study (2013-2018)

Pesticide	Total # of samples	Frequency of detections (%)	years	Min (ng/L)	Max (ng/L)	Median** (ng/L)	Guideline (ng/L)
Acetaprimid	162	22	2015-18	0.21	27.3	0.39	---
Atrazine	247	34	2013-18	5.16	**18800**	29.1	1800
Chlorantraniliprole	47	87	2018	1.84	155	15	4500
Chlopyrifos	122	27	2014-18	0.7	**601**	3.67	20*
Clothianidin	162	90	2015-18	1.94	**204**	19.4	1.5-1500*
Desethyl atrazine	126	10	2016-17	23	331	23.3	--
Dimethoate	239	13	2013-18	3	46	14.1	6200
Imidacloprid	162	82	2018-18	1.33	193	5.81	230
Metalochlor	248	22	2014-18	4.64	270	19.7	7800
Metribuzin	210	13	2014-18	11	**1160**	32.25	1000
Thiamethoxam	162	77	2015-18	1.44	**838**	3.55	26-9000*

*short term exposure; ** median (detections only)

Herbicides

Atrazine had 82 detections, four of which were above the CCME guideline and all of thoseoccurred during wet events in Nova Scotia. The guideline is based on a chronic toxicity endpoint for a model ecosystem with a safety factor of 10 (CCME 1999). Atrazine does not photodegrade easily with a half-life in water ranging from days to 7 months (CCME 1999). Accordingly, atrazine had a 33% frequency of detections in the streams sampled in this study (Table 3). Desethyl atrazine is the degradation product of atrazine and it was detected in 10% of the samples collected during 2016-2017 (Table 3).

Metolachlor had a detection frequency of 22% and ranged in concentrations from 4.64 to 270 ng/L. None of the samples in this study exceeded the CCME guideline of 7800 ng/L (Table 3). Metolachlor is mildly persistent in soil and highly persistent in water with a low photodegradation rate (EXTOXNET 2019). Interestingly only one of the 55 detections occurred outside of Nova Scotia where detections occurred during both dry and wet events.

Metribuzin had 26 detections, one of which was above the CCME guideline of (Table 3), from a Nova Scotia stream during a rain event in 2017. Runoff events occurring two weeks after soil application are the most important pathway with respect to delivery to watercourses (CCME 1999).

Insecticides

Acetaprimid, a neonicotinoid, was detected on 36 occasions ranging in concentration from 0.21 to 27.3 ng/L. The frequency of detection of acetaprimid was 22%. In comparison, monthly samples on ten rivers draining to Lake Erie in the United States only yielded a 2% detection rate for this pesticide (Hladik et al. 2014). According to EPA (2002), acetaprimid degrades rapidly in soil and therefore is not considered to be persistent.

Chlorantraniliprole was detected with the highest frequency of all pesticides measured in this study at 87%. This pesticide was analysed only in 2018 which explains the low total number of samples. It was measured at all the sampling sites during both dry and wet events. EPA (2008) mentions that chlorantraniliprole doesn't degrade substantially (soil $t^{1/2}$ is 631 days) in primary and rotational crops and this may explain its high detection frequency in samples of this study.

Chlopyrifos had 7 detections above the CCME short term guideline (Table 3). Five out of seven samples were obtained from a single location in Nova Scotia (NS01DC0045). Exceedances occurred both during dry and wet events in 2016 and 2018. Furthermore, chlopyrifos had a frequency of detections of 27% (Table 3). The frequency of detections may be explained by its low water solubility and its low partition from soil to water (EPA 1999). Chlopyrifos found in water is likely a result of soil-bound concentrations from eroding soil rather than dissolved (EPA 1999).

Dimethoate concentrations ranged from 3 to 46 ng/L while the guideline is 6200 ng/L. It had a detection frequency of 13%. According to HC (2015), dimethoate breaks down rapidly and therefore is rarely found in groundwater. Dimethoate has also a low Koc and high water solubility (CCME 1999) and therefore is very likely to move into surface waters.

The three main neonicotinoids in use in the Maritimes (clothianidin, imidacloprid and thiamethoxam) had similar and very high rates of detections from 77 to 90% (Table 3). All three insecticides were detected at all sites as well as during both dry and wet events. There is no Canadian water quality guideline at the moment for two of these neonicotinoids pesticides although one is in place for Imidacloprid (230 ng/L). The maximum concentration of imidacloprid (193 ng/L) approached the guideline value, but there were no exceedances.

Clothianidin may persist in soil from one growing season to the next and stabilizes after 3-5 years (HC 2018a). It may enter water through runoff or spray drift and is moderately persistent to persistent in water systems containing sediment (HC 2018a). HC (2018a) calculated a species sensitivity distribution (SSD) for clothianidin based on 37 toxicity studies using various freshwater aquatic invertebrates. The

5^{th} percentile of the SSD, HC_5, is used to identify the concentration which is expected to protect 95% of the species in the community. HC (2018a) calculated both an chronic and acute toxicity HC_5 of 0.0015 ug a.i./L and 1.5 ug a.i./L respectively (HC 2018a). None of the clothianidin values measured during this study were above the acute toxicity endpoint, however all of the detected values were above the chronic toxicity endpoint of 1.5 ng/L. Since clothianidin was detected in almost 90% of the samples submitted for analysis, it appears that clothianidin exceeds the chronic values at all sites in the Maritimes on almost every occasion it was sampled. Furthermore, the detection limit of the laboratory is 1.76 ng/L compared to the chronic toxicity endpoint of 1.5 ng/L.

Thiamethoxam will move to soil and may persist from one growing season to another (HC 2018b). Thiamethoxam may enter water through spray drift or runoff but it is not expected to be persistent as it breaks down easily. However, thiamethoxam may breakdown to clothianidin, which is more persistent (HC 2018b). HC (2018b) calculated a species sensitivity distribution (SSD) to thiamethoxam based on 52 toxicity studies using various freshwater aquatic invertebrates. HC (2018b) calculated both an acute and chronic toxicity HC_5 for thiamethoxam of 9 ug a.i./L and 0.026 ug a.i./L, respectively (HC 2018b). Thiamethoxam was detected in 77% of the samples, however none were above the acute toxicity endpoint. Nine out of the 125 samples had concentrations above the chronic value and all of those samples were obtained in Nova Scotia and all but one during rain events. The frequency of detection of thiamethoxam in our study is more than 3 times that of Hladik *et al* (2018) since the detection limit of pour laboratory was substantially lower than that of the Hladik et al (2018) study.

Imidacloprid, which is considered persistent in soil, is transported to waterways through spray drift, soil erosion and runoff (CCME 2007). Based on its Koc of 225, it has a medium to high sorption tendency (CCME 2007). The interim water quality guideline for Imidacloprid for the protection of aquatic life is 0.23 ug a.i./L. None of the samples of this study exceeded the guideline, although one sample was close to the guideline at 0.193 ug/L. The detection frequency of imidacloprid is also quite high at 82% with a range from <1.28 to 197 ng/L (Table 3). Imidacloprid was also detected more frequently than all other neonicotinoid pesticides analysed in the Hladik et al (2018) study but still at a lower frequency than our study. It was detected with a high frequency in PEI buffer zones in 2001 and 2002, even increasing in concentration with increasing distance away from the field in 2002 (Denning et al 2004). Its water solubility and/or field dynamics may have contributed to the Denning et al (2004) result.

Censored Data Analysis

The dataset of this study included various frequencies of censored data due to the nature of the chemical analysis (organics) and the detection limit of the laboratories. For the seven pesticides with the highest frequency of detections, summary statistics were calculated using the most appropriate method that utilized the censored and uncensored data (Helsel 2012 (Table 4). Pesticides which had over 80% of their data censored were not included as this level of censoring is too high to compute summary statistics (Helsel 2012). Summary statistics using the censored data for only the seven pesticides with higher rates of detection were used throughout the next sections. Pesticides such as

clothianidin, chlorantraniliprole, imidacloprid and thiamethoxam had a low frequency of censored values compared acetaprimid, atrazine or metalochlor (Table 4).

Table 4. Summary statistics of pesticides in this study with censoring below 80%.

Pesticides	n	% censored	Median (ng/L)	Standard deviation (ng/L)	Method*
Acetaprimid	162	77	0.01	2.6	ROS
Atrazine	247	66	7.19	1417	KM
Chlorantraniliprole	47	13	9.7	43.0	ROS
Clothianidin	162	11	14.3	82.9	MLE
Imidacloprid	162	18	4.4	25.2	MLE
Metolachlor	248	77	2.54	114.4	KM
Thiamethoxam	162	23	2.89	70.7	MLE

*ROS; regression on order statistics, KM; Kaplan Meier, MLE; maximum likelihood estimation

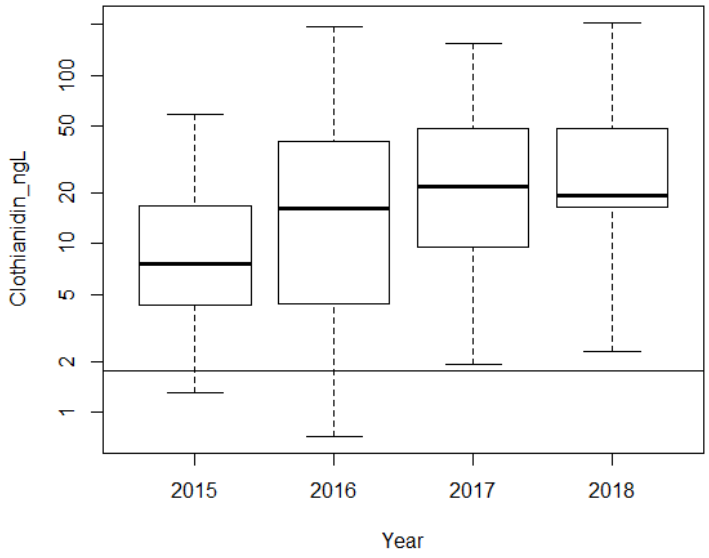
Temporal and rainfall event based variations

The datasets of the seven pesticides with the highest frequency of detections were analysed to determine differences in concentrations as a function of the year and rainfall events, using the cendiff command in the NADA package of R (Table 5). Five of those seven pesticides had significant differences in concentration between years (Table 5) and of those clothianidin showed the largest difference between groups ($p<0.001$). Clothianidin concentrations have shown a statistically significant increase (Figure 1) over the four years of study. This could be due to increasing usage of the pesticide or it may simply be due to changes in sampling locations between the years of this study.

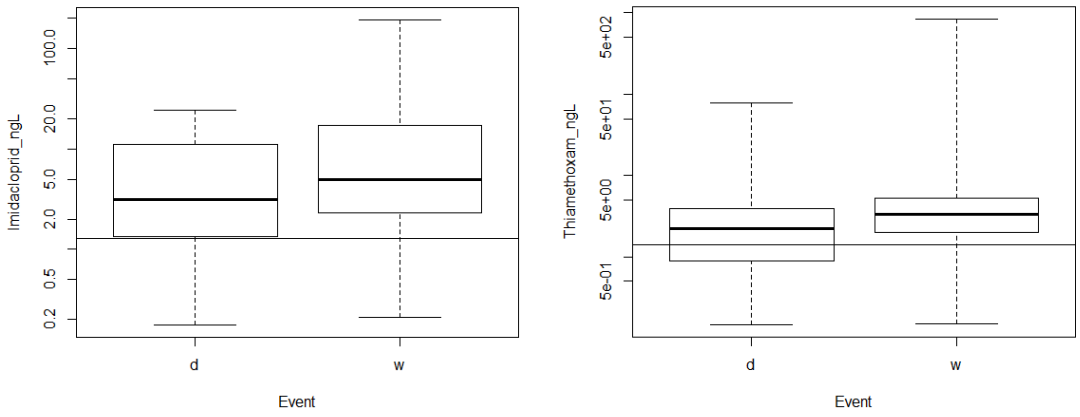
Table 5. Cendiff results (p values) of pesticide concentrations as a function of years and rainfall events.

Pesticides	**Years**	**Rainfall**
Acetaprimid	0.02	0.4
Atrazine	0.007	1
Chlorantraniliprole	0.007	0.9
Clothianidin	<0.001	0.3
Imidacloprid	0.6	0.02
Metolachlor	0.2	0.3
Thiamethoxam	0.02	0.002

Figure 1. Censored boxplots of clothianidin concentrations as a function of years



Figures 2 and 3. Imidacloprid and Thiamthoxam concentrations as a function of sampling based events (dry or wet).



The datasets of the seven pesticides with the highest frequency of detections were also used to calculate differences of concentrations as a function of the (dry or wet) events when the samples were obtained using the cendiff command in the NADA package of R (Table 5). Of the seven pesticides, only two had significant differences between groups (events) (Table 5), with thiamethoxam having the largest difference. Subsequent box plots (Figures 2 and 3) revealed that for both pesticides the

concentrations in samples obtained during wet events was significantly higher than the concentrations in samples obtained during dry events.

Interestingly, the concentrations of those other five pesticides (acetaprimid, atrazine, chlorantraniliprole, clothianidin and metolachlor) did not significantly differ between rainfall or dry events. This leads us to hypothesize that a significant source of pesticide in the watercourses we sampled could be derived from a groundwater source and not only from a surface driven (runoff) mechanism. Pesticide contamination of groundwater occurs regularly in heavily farmed areas especially by pesticides which do not have a high affinity to soil particles (Trautmann and Porter, 2012). All five pesticides have K_{oc} values which catagorises them as moderate to highly mobile. Both atrazine and metolachlor concentrations were higher in groundwater compared to surface water in a study by Hilderbrandt *et al* (2008). Many of the streams we sampled as part of this study have a small watershed (less than 10 km^2) and therefore during dry events, a greater proportion of their flow is made up by groundwater. We suggest that the groundwater is contributing to the pesticide concentrations we measured during dry events. The groundwater along the Annapolis Valley floor (where all of our Nova Scotia sites were located) is described as the most vulnerable to contamination due to the high permeability of the sediments, the flat topography and elevated value of recharge (Webster et al. 2012).

in our study the differences in frequencies of detections of these seven pesticides were always higher during rain events compared to dry events, with differences ranging from 2 to 19%. The largest differences in frequencies were obtained for Clothianidin, Imidacloprid and Thiamethoxam. This is corroborated by the study of Hadik et al (2014) where rainfall events were associated with neonicotinoids pulses in streams in midwestern USA. These detections could represent a combination of pesticides in surface runoff and groundwater infiltrate together.

Correlations between water quality parameters and pesticide concentrations.

Again, the seven pesticides with the highest frequency of detections were used to explore possible relationships with water quality variables. During each sampling event, water quality samples were analysed for total phosphorus (TP), total nitrogen (TN) and total organic carbon (TOC) while a sonde was used to measure specific conductivity and turbidity. Since the dataset contained a large proportion of censored values and the observations do not follow a normal distribution, the cenken command of the NADA package in R was used to described possible relationships between water quality and pesticide concentrations. Results from the cenken are listed in Table 6. Slope of the relationship, tau and p values are also listed in Table 6.

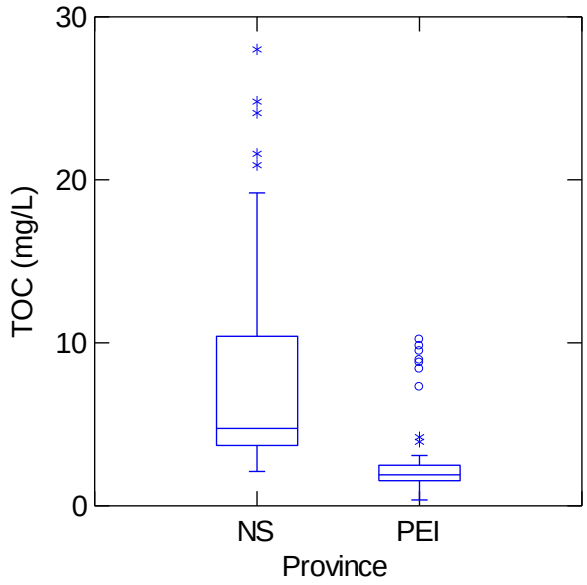
Table 6. Cenken correlations between pesticide concentrations and water quality parameters

Pesticides		Total phosphorus	Total nitrogen	Total organic carbon	Turbidity	Specific conductivity
Acetamiprid	slope	7.79		0.13	0.039	0.0053
	tau	0.145		0.102	0.073	0.059
	p	**0.0027**		**0.035**	0.149	0.24
Atrazine	slope	8	2.92	0.36	0.0155	-0.0155
	tau	0.166	0.03	0.24	0.0495	0.145
	p	**0.0002**	0.68	**<0.0001**	0.25	**0.00099**
Chlorantraniliprole	slope	-4.51		-0.146	0.00986	0.0113
	tau	-0.017		-0.293	0.182	0.341
	p	0.089		**0.00369**	0.0761	**0.000842**
Clothianidin	slope	0.0972		-0.0247	0.0134	0.00252
	tau	0.00385		-0.0531	0.141	0.0648
	p	0.944		0.323	**0.012**	0.248
Imidacloprid	slope	0.038		-0.0718	0.0189	0.00219
	tau	0.00226		-0.133	0.17	0.0585
	p	0.968		**0.0129**	**0.00239**	0.295
Metolachlor	slope	9.17	22.1	0.241	0.0176	-0.0125
	tau	0.144	0.0116	0.136	0.0526	-0.0765
	p	**0.00138**	0.872	**0.00244**	0.222	0.0783
Thiamethoxam	slope	2.9		0.0874	0.000583	-0.00217
	tau	0.181		0.176	0.00852	-0.0615
	p	**0.000792**		**<0.001**	0.88	0.27

Total phosphorus was significantly correlated with acetaprimid, atrazine, metolachlor and thiamethoxam while total nitrogen had no significant correlations. Correlations statistics could not be produced for all pesticides due to high frequency of censored data. Total phosphorus correlations all had positive slopes indicating an increase in TP coincided with an increase in concentrations of certain pesticides (Table 6). This is corroborated somewhat by a study by Palma et al. (2010) which stated that an intensification of agricultural activities led to an increase in total phosphorus and total nitrogen and ultimately to an increase in herbicide concentrations in surface water. Another possible explanation of the positive relationship between pesticides and total phosphorus is described in a study by Hébert *et al*. (2019). In that study, the authors present evidence which suggests that the application of glysophate, which contains 18.3% phosphorus by mass, leads to greater anthropogenic inputs and

greater phosphorus exports from soils to water bodies. Although glysophate is in use in the Maritimes (sales of 57 000 kg in PEI in 2014), its relative risk ranking was very low compared to other pesticides in use in this region (Dunn 2004) and therefore was not part of the monitoring strategy of this study.

Total organic carbon had the highest number of statistically significant correlations with pesticide concentrations, with significant correlations for all but one pesticide (Table 6). However, some of the slope coefficients' were positive (acetaprimid, atrazine, metolachlor and thiamethoxam) while others were negative (Table 6). Hung et al (2007) had shown highly significant positive correlations between TOC and total pesticide concentrations in marine sediment and suggested that pesticides in sediment are controlled by the distribution of organic matter. Our dataset also shows some negative correlations of which the strongest is for chlorantraniliprole. A scatterplot indicates a strong negative correlation between TOC and chlorantraniliprole. The log K_{ow} of 2.26 and log K_{oc} of 2.51 suggests that this substance is somewhat hydrophobic and will be bound to soil particles (less mobile), therefore a positive relationship to TOC would be expected. Results from our study do not reflect these characteristics. However, chlorantraniliprole is also highly persistent and will reach a plateau of concentrations in soil after 6 years of application due its persistence in soil ranging from 25-52% of applied (EFSA 2013). We hypothesize that the inverse relationship with TOC is due to the locations of the samples obtained. The average concentrations of chlorantraniliprole in PEI was 102.1 ng/L while only 7.7 ng/L in NS (with n =18 and 23 respectively). However TOC concentrations were inversed with a higher mean for NS sites (12.76 mg/L) than for PEI sites (4.29 mg/L). Changes in organic matter across Prince Edward Island have been monitored since 1998 and have shown an island wide decline (Nyiraneza et al 2017) which would explain the low TOC measurements in this study.



Metolachlor is readily absorbed onto organic matter in soil and little leaching occurs in soil with high organic content (Health Canada 1986) which may explain its significant and positive relationship with TOC in our study. Nova Scotia had the overwhelming proportion of detections in this study, with 54/55 detections of metolachlor occurring in that province. A search in PEI's open data of the results from the province's pesticide monitoring program revealed 9 samples obtained in 9 different rivers of the province with concentrations below the detection limit of the laboratory (<0.025 ng/mL). The 2013 and 2014 retail sales of metolachlor in PEI revealed amount sold (not necessarily applied) of only 2994 and 2249 kg, respectively, which also offers a line of evidence in the lack of detection of this pesticide in this province.

Both clothianidin and imidacloprid showed statistically significant (and positive) correlations with turbidity (Table 6). Imidacloprid is persistent in soil (half-life of 2 years) and also may sorb to sediment (EC 2006). These characteristics may explain the positive and significant correlation to turbidity since turbidity may be driven by the runoff from fields during rain events. Clothianidin is also subject to be transported via runoff to surface water bodies (EPA 2003b) which may explain the positive and significant correlation measured in this study.

Atrazine had a significant negative correlation with specific conductivity (Table 6). A lower specific conductivity at most of our sites is usually associated with rain events where ion salt and organic matter were diluted by the rainfall. Also the highest concentrations of atrazine were measured during this study were during rain events which may explain the negative correlation between the two (Table 6).

Chlorantraniliprole had a significant and positive correlation with specific conductivity. This relationship may be explained similarly to the influence of TOC on pesticide concentrations, described in the previous paragraphs. High specific conductivity is usually associated with dry conditions where the ions are not diluted by rain. However, dry conditions would usually limit the runoff occurring from fields resulting in a negative relationship with pesticide concentration, which was not the case for chlorantraniliprole. Instead, for this pesticide, dry conditions (high conductivity) is associated with the highest pesticide concentrations. However a careful examination of the relationship between TOC and conductivity reveals a significant and negative relationship (R^2=0.31, $p<0.001$). Therefore, this relationship is likely a reflection of the high concentrations of chlorantraniliprole in PEI with the combination of low TOC at the sites in PEI. In turn, the low TOC concentrations in PEI are highly correlated to high specific conductivity.

Comparison to other Maritime-based studies/ databases.

The results of our study were compared to previously published concentrations of pesticides in freshwater systems of the Maritimes. An Environment Canada study (EC 2011) is one of the largest effort to synthesize pesticide data for a period from 2003-2005 and it included sites in NS, NB and PEI. The Prince Edward Island government published stream pesticide concentrations on line (Available at

https://data.princeedwardisland.ca/Environment-and-Food/OD0001-Pesticide-Analysis-for-Stream-Water/jj4n-qqq2) while the study by Xing et al (2012) was the largest and latest published study we could find on pesticide concentrations in streams for this region. The PEI pesticide database includes data for the following pesticides; atrazine, chlorantraniliprole, imidacloprid and clothianidin in both rivers where we sampled (Dunk and Wilmot). One of the most interesting aspect is the change in pesticides most frequently detected. Xing et al (2012) studied streams in NS, NB and PEI from 2003 to 2007 and found that chlorothalonil, linuron and metalaxyl were the three most detected pesticides (frequency of 17-22%).

Of all the pesticides most frequently detected in our study (Table 3), only atrazine was also detected somewhat frequently in the Xing et al. (2012) study. That study provided an annual mean of atrazine from <DL to 730 ng/L and a mean frequency of detection (across sites and years) of 5.6%. In comparison, out study had a high frequency of detections for atrazine of 34% (Table 3). The PEI database (PEI 2018) included 46 samples from the Dunk and Wilmot Rivers, and all were below the detection limit of the laboratory (DL<10 ng/L). The EC (2011) study had atrazine detection frequencies of 0% in both PEI and NB but 25% in Nova Scotia, although no concentrations are included in the report. Our study also showed that almost all of the detections (82/83) were for sites located in Nova Scotia. Atrazine is often used in pre-emergence scenarios on corn fields and this may explain the lack of detections at our PEI sites, which were located in an intensive potato growing region.

Thiamethoxam was measured in our study and in the Xing *et al* (2012) study, however results from Zing et al (2012) showed thiamethoxam to be under the detection limit of the laboratory (10 ug/L) at both Dunk and Wilmot (42 samples). In comparison, our study had a lower detection limit of 1.39 ng/L. Nevertheless, in comparing our results with the higher detection limit of the Zing et al (2012) study, there would still have been 22 samples above 10 ng/L. Interestingly, all the samples above the 10 ng/L were from Nova Scotia and not PEI which means our dataset is very similar to the PEI database.

Chlorantraniliprole was measured with high detection frequency and also reported above detection limits in the PEI database. Both the Dunk and Wilmot rivers had concentrations ranging from >20 ng/L to 80 and 130 ng/L respectively. Our study's detection limit was substantially lower at 1.18 ng/L. However, concentrations of chlorantraniliprole in PEI streams from our study were all above the detection limit of the province database and ranged from 58.3 to 155 ng/L, which is similar to the results from the province of PEI.

Clothianidin was also measured with high detection frequency and measured above detection limits in the PEI database. The Dunk and Wilmot rivers had concentrations ranging from >10 to 30 and 120 ng/L,

respectively. Our study's detection limit was substantially lower at 1.76 ng/L. However, concentrations of clothianidin in PEI streams from our study were again all above the detection limit of the provincial database and ranged from 16.2 to 192 ng/L, which is a little higher than those provincial results.

Idimacloprid was measured both in the PEI database and in the EC (2011) study in NS, PEI and NB. None of the 48 and 82 samples obtained from 2003 to 2005 in NB and PEI respectively had detections, although the detection limit in that study was high (100 ng/L). Nova Scotia had two detections above 100 ng/L during 2003-2005. In comparison, the PEI database had detections in both the Dunk and Wilmot rivers, with ranges from < 20 to 50 and 60 ng/L respectively. Interestingly, imidacloprid was not detected in PEI samples (PEI 2018) in 2017-2018. Results from our study show similar concentrations ,ranging from 7 to 71.2 ng/L in PEI rivers.

Other considerations

On April 11, 2019, Health Canada through the PMRA published a re-evaluation of thiamethoxam, clothianidin and imidacloprid and its associated products (PMRA 2019a, b and c). Health Canada has determined that with required amendments certain uses of these products are acceptable but other uses are cancelled due to the potential risks of concern to pollinators (PMRA 2019a, b,c). Health Canada has also changed the timing of application uses of thiamethoxam and imidacloprid to minimize bee exposure especially around blooms (PMRA 2019a and c) and limited the maximum number of foliar applications of clothianidin to cucurbit vegetables to one per season (PMRA 2019b). These additional risk mitigation measures are scheduled to be implemented over the next 24 months, and may be noticeable in similar data collected over the next number of years.

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Appendix 1. ECCC analytical laboratories methodology for nutrients and pesticides.

Analyte	Methodology
Total organic carbon	This automated Carbon Analyzer method is applicable to the analysis of total organic carbon (non-purgeable) (NPOC) and dissolved organic carbon (non-purgeable) (DOC) in surface water, ground water and seawater. The purgeable (volatile) organic carbon fraction is lost during sparging, performed for inorganic carbon removable; however in these types of waters the purgeable organic carbon contribution is negligible and in practice the value obtained is reported as Total Organic Carbon (TOC). Total Organic Carbon is performed on unfiltered samples, whereas Dissolved Organic Carbon samples are first filtered through a 0.45 micron pore size filter. The applicable range for TOC and DOC is 0.25 mg/L to 30.0 mg/L. The reporting limit and the method detection limit is 0.25 mg/L for TOC and DOC. TOC and DOC is analyzed on samples preserved to a pH < 2 using HCl, this converts the inorganic carbon fraction to CO_2. The CO_2 is then removed when the sample is sparged with oxygen gas for 5 minutes (300 seconds). A 200 uL sample aliquot is injected into the 850ºC furnace where catalytically aided combustion (platinum catalyst) is used to oxidize, in the carrier gas flow, the remaining organic carbon species to carbon dioxide. The test gas (combusted sample) is dried and corrosive gases removed by the scrubber before being fed to the non-dispersion infrared detector (NDIR).
Total Phosphorous	Unfiltered, Acidic Persulphate Oxidation, CFA, Ascorbic Acid, Molybdenum Blue, Colorimetric Method: A whole water sample is collected in a 125 mL flint glass bottle and preserved with sulphuric acid to a pH of < 2. The sample is shaken, a 10 mL aliquot is poured in a glass digestion tube and a mixture of sulphuric acid/persulfate is added. The sample is then digested in an autoclave for 30 minutes at 121°C. The oxidative-acid digestion releases organically bound phosphorous as orthophosphate, PO4. Orthophosphate is also formed in the digestion

Analyte	Methodology
	from the hydrolysis of inorganic condensed phosphorous (pyro-, meta-, and other polyphosphates). The digest is analyzed in a continuous segmented flow analyzer (CFA) where the orthophosphate is reacted in an acid medium with ammonium molybdate and potassium antimony tartrate to form antimony-phosphomolybdate acid. This is then reduced with ascorbic acid to form the molybdenum blue complex. The absorption of radiation by the complex is proportional to the total phosphorous concentration in the sample and is determined by the CFA colorimeter at 880 nm wavelength. Quantification is achieved by calibration of the colorimeter with known solutions of phosphorous standards spread across the analytical range. For a filtered sample, a whole water sample is filtered through a 0.45 um cellulose acetate membrane filter. For particulate phosphorus, a known volume of a whole water sample is filtered through a 0.45 um cellulose acetate membrane filter. The filter is placed in a sample container (100 mL flint glass bottle), and 100 mL phosphorus free water is added. It is preserved by adding 1.0 mL of 30% sulphuric acid solution. NLET Method 01-1191. Reference Method: Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 4500-P B(Section 5) + 4500-P F. **Analytical Range:** total phosphorus concentrations up to 0.5 mg/L P.
Total nitrogen	Alkaline Persulfate Oxidation, Automated Flow Injection Analyzer (FIA), Hydrazine Reduction, Azo Dye Photometric Method: Organic and inorganic nitrogen compounds in a shaken whole water sample are oxidized to nitrate during digestion in an autoclave (121°C) with alkaline potassium persulfate. The digest is then analyzed in an automated flow injection analyzer (FIA), where the reduction of nitrate to nitrite is accomplished by means of an alkaline hydrazine sulphate solution containing a copper catalyst. The nitrites are reacted under acidic conditions with sulphanilamide ($NH_2C_6H_4SO_2NH_2$) to form a diazo compound, which is then coupled with N-1-naphthyl-ethylenediamine dihydochloride ($C_{12}H_{16}C_{12}N_2$) to form a reddish- purple azo dye. The absorption of radiation by the dye is proportional to the total nitrogen concentration in the whole water sample and is determined by the FIA photometer at 520 nm wavelength. Quantification is achieved by calibration with known solutions of nitrogen (NO_3_N) standards spread across the analytical range. Results are reported in mg/L N. For dissolved total nitrogen a water sample is filtered through a 0.45 cellulose acetate filter paper and the filtrate analyzed as above. **Analytical Range:** TN concentrations up to 1.50 mg/L N
Neonicotinoid	Five neonicotinoid insecticides in water were simultaneously extracted by an automated Autotrace SPE Workstation. A sample volume of 900 mL is loaded onto a Waters OASIS-HLB SPE cartridge at a flow rate of 5mL/min, dried with nitrogen for 1 minute and eluted with 10mL of methanol. The extract is then concentrated to 1.45 mL using nitrogen and 50uL of the internal standard is added to each extract prior to ESI-LC-MS/MS analysis.
Fungicides	Eleven fungicides in water were simultaneously extracted by an automated Autotrace SPE Workstation. A sample volume of 800 mL is loaded onto a Waters OASIS-HLB SPE cartridge at a flow rate of 5mL/min, dried with nitrogen for 1 minute and eluted with 10mL of methanol. The extract is then concentrated to 0.95 mL using nitrogen and 50uL of the internal standard is added to each extract prior to ESI-LC-MS/MS analysis.
Carbamate	Seven Carbamate Fungicides in water were simultaneously extracted by an automated Autotrace SPE Workstation. A sample volume of 500 mL is loaded onto a Supelco Envi-carb cartridge at a flow rate of 4mL/min, dried with nitrogen for 1 minute and eluted with 4 mL of methanol and 8 mL of 80/20 DCM/methanol. The extract is then concentrated to 0.9 mL using nitrogen and 100uL of the internal standard is added to each extract prior to ESI-LC-MS/MS analysis.

Analyte	Methodology
Acid herbicides	Acid herbicides; A 1 litre water sample is acidified to pH <2 with 50% sulphuric acid and extracted with dichloromethane (CH_2Cl_2). The extract is concentrated and the residue reacted with 5% (v/v) PFBBr (pentafluorobenzyl bromide) to form its corresponding PFB esters. Silica gel column cleanup is used to remove extraneous substrates and unreacted PFBBr. The PFBBr esters are eluted and collected in two fractions. Acid herbicide esters are measured using gas chromatography - negative ion chemical ionization mass spectrometry (GC/NICIMS).
Neutral herbicides	Neutral herbicides; A 1 litre water sample is extracted with dichloromethane (CH_2Cl_2). The extract is concentrated, cleaned up using a florisil column, eluted and collected into two separate fractions. Analysis is provided using a gas chromatograph equipped with a mass selective detector (GC/MSD).