



Exposure Assessment of Pesticides in Surface Waters of Ontario, Canada Reveals Low Probability of Exceeding Acute Regulatory Thresholds

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Abstract

The objectives of this study were to: (1) characterize the exposure of aquatic ecosystems in Southern Ontario, Canada to pesticides between 2002 and 2016 by constructing environmental exposure distributions (EEDs), including censored data; and (2) predict the probability of exceeding acute regulatory guidelines. Surface water samples were collected over a 15-year period by Environment and Climate Change Canada. The dataset contained 167 compounds, sampled across 114 sites, with a total of 2,213 samples. There were 67,920 total observations of which 55,058 were non-detects (81%), and 12,862 detects (19%). The most commonly detected compound was atrazine, with a maximum concentration of 18,600 ngL⁻¹ and ~4% chance of exceeding an acute guideline (1,000 ngL⁻¹) in rivers and streams. Using Southern Ontario as a case study, this study provides insight into the risk that pesticides pose to aquatic ecosystems and the utility of EEDs that include censored data for the purpose of risk assessment.

Keywords Environmental monitoring · Pesticides · Water quality

Introduction

Pesticides can be transported into aquatic ecosystems through spray drift, leaching, agricultural tile drainage, or runoff during precipitation or thaw events (Lewan et al. 2009). A number of jurisdictions have developed programs to monitor the exposure of surface water to agriculture pesticides (Boye et al. 2019). In Canada, various provinces have established programs to monitor agricultural pesticides in surface waters (Raby et al. 2022). Ultimately, the data collected from these monitoring programs play an important role in being able to assess the risk that pesticides may pose to aquatic ecosystems in a particular region (Solomon et al. 1996; Rico et al. 2021). The largest effort in Canada for

monitoring pesticides by Environment and Climate Change Canada (ECCC) has occurred in southern Ontario (ECCC 2011), which contains approximately a quarter of Canada's farms (Statistics Canada 2017). Approximately 40% of the land used for crop production in the province is located in southern Ontario, and 50% of the province's production of soybeans, winter wheat, and corn occurs in this region (OMAFRA 2017). These data collected by ECCC as part of the Great Lakes Water Quality Monitoring and Surveillance Program on pesticides is publicly available through the Government of Canada's open data online portal (Government of Canada 2018). However, few have attempted to conduct an exposure assessment of Ontario's surface waters to pesticides using the ECCC data, and those that have, have focused on a limited number of active ingredients (e.g., glyphosate) or a specific class of pesticide (e.g., neonicotinoid insecticides) (Struger et al. 2008, 2017). Also, these studies did not construct environmental exposure distributions (EEDs) for any of the pesticides using the ECCC data to assess the risk in a probabilistic manner. The construction of EEDs is critical to being able to conduct a probabilistic risk assessment to quantify the risk of pesticides to aquatic ecosystems (Solomon et al. 2000). At this time, a

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significant challenge in characterising pesticide exposure data is what to do with non-detects. A growing number of studies are beginning to incorporate the censored data [i.e., the concentration of the pesticide in the water sample that was below the method detection limit (MDL) or limit of detection (LOD)] in their exposure assessment of pesticides in surface waters as opposed to using the conventional methods of eliminating this data, or using arbitrarily chosen values such as the LOD, half the value of the LOD, or zero (Wang et al. 2016; Rodríguez-Gil et al. 2018). These conventionally used methods limit the ability to accurately assess the presence or absence of pollutants in the environment and may lead to inaccurate conclusions (Shoari and Dubé 2018). Thus, it is important that left-censored data be included in order to effectively assess pesticide exposure in surface waters (Cantoni et al. 2020). The primary objective of this study was to use the above-mentioned ECCC data to assess the exposure of aquatic ecosystems in southern Ontario, Canada to pesticide compounds through the construction of EEDs that include the censored data for each compound. We will use the EEDs to predict the probability of exposure for each compound by site, by site type, and by year, where data permit. The constructed EEDs will also be used to determine the probability of exceeding regulatory guidelines for each compound by site, by site type, and by year. This study will provide important insight into the risk that pesticide compounds can pose to aquatic ecosystems in southern Ontario, and the approach taken here could be applied in other jurisdictions.

Materials and Methods

Source of Data

Surface water samples were collected from the Great Lakes (Ontario, Canada) and their tributaries over a 15-year period and analyzed by ECCC's Water Quality Monitoring and Surveillance Division. We accessed and downloaded these pesticide concentration data and associated metadata on February 22, 2020 from the Great Lakes Water Quality Monitoring and Aquatic Ecosystem Health Data, specifically the Great Lakes Water Quality Monitoring and Surveillance Data (ECCC 2018). Summaries of the data can be found in the University of Guelph Research Data Repository at <https://doi.org/10.5683/SP3/3TRFVJ>.

Data Clean-Up and Formatting

Data clean-up, formatting, processing, and analyses were performed using RStudio version 1.3.1056 and R version 4.0.2. Clean-up of the dataset included editing and

recoding compounds that were doubled due to spelling differences or different naming conventions. For example, both "Dichlorprop" and "2-(2-4-Dichlorophenoxy)-Propionic Acid" appeared throughout the dataset, and were recoded to "(Dichlorprop (2,4-DP)". CAS Registry Numbers were compiled based on the provided compound name then added to the main pesticide dataset. The final cleaned-up CSV files of the pesticide datasets can be found in the University of Guelph Research Data Repository at <https://doi.org/10.5683/SP3/XY5WI5>. All concentrations and their associated method detection limits (MDL) were converted to ngL^{-1} for consistency. Later steps in the data analyses required concentration data to be reported as a range between two concentration values. For this purpose two new columns were created in the dataset (labelled "upper" and "lower") (Rodríguez-Gil et al. 2018). In the case of quantified samples above the limit of detection (listed in the original ECCC dataset with an "NA" value in the "flag" variable, i.e. no special flags), the upper and lower values were set as identical and equal to the measured concentration. For samples below the MDL (i.e. the analytical limit of detection (LOD), flag = "<") the lower value was set to zero and the upper concentration value was set to the value of the MDL. Samples with trace amounts (originally listed as flag = "T") were treated in the same manner. Due to samples being collected for a variety of purposes and analyzed by different agencies, many of the MDLs of compounds changed over the duration of this dataset so care was taken to ensure each sample was clearly linked to the right MDL for its specific analysis.

Dataset Summary

Sampling of 167 distinct compounds was performed from 2002 to 2016 across 114 unique sites in the Great Lakes watershed, Ontario, Canada (Table S1, Fig. 1). Of these 114 sampled sites, there were five site types: (a) rivers or streams – 94 sites, (b) ponds – 9 sites, (c) wetlands – 7 sites, (d) lakes – 3 sites, and (e) groundwater – 1 site. The total number of sites sampled each year fluctuated, with the most sampled in 2007 at 40 sites and only eight sites in 2011 (Table S1). The total number of years individual sites were sampled varied from 1 to 14 years, half of which were only 1 year, and none were sampled for the entire 15-year duration of this dataset (Table S2). Since there were no sample IDs associated with the data in this dataset, we defined a sample as a unique combination of site and date. With this definition, the dataset contained 2,213 unique samples. The most consistent sampling occurred from 2004 to 2008, with 2007 having the greatest number of samples taken in a year (256 samples) and 2011 the least (67 samples) (Table S1). The top 10 most sampled sites ranged from 55 to 193

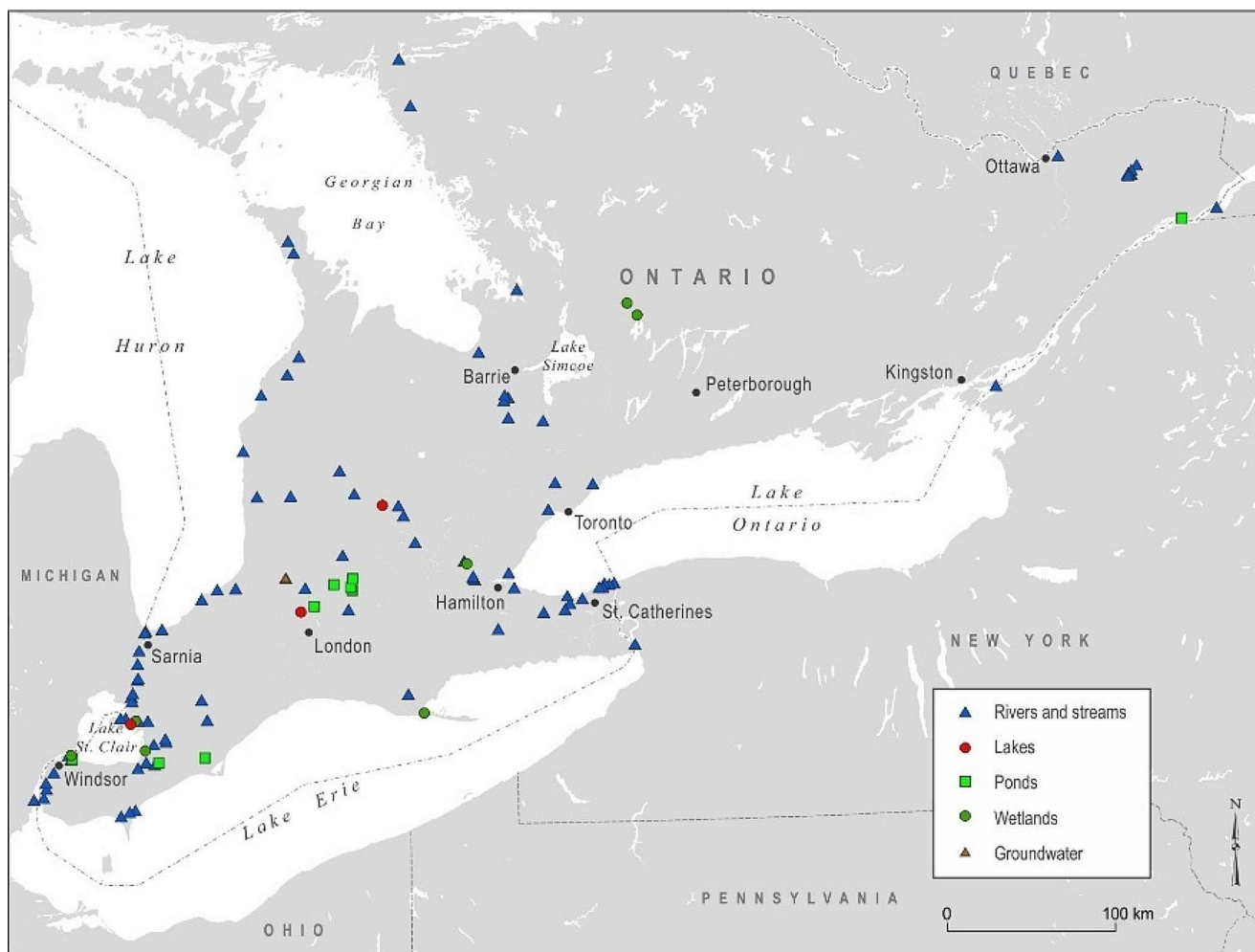


Fig. 1 The 114 individual sites of this dataset sampled by ECCC in the Great Lakes watershed, Ontario, Canada. Each of the five site types is represented by a different symbol (see legend).

collected samples (Table S2). Lastly, over the 15-year dataset, the top 25 most sampled compounds ranged from 971 to 1,095 samples, based on the number of measurements of a compound in the total 2,213 samples (Table S3 to S5).

Assessment of Detection Trends Over Time

The percent of samples containing non-detects played a vital role in the following steps of our EED distribution fits, since data subsets containing < 10% detection would yield unreliable model fits. Additionally, we wanted to investigate the role that changing MDLs over the studied period played in the observed detection frequencies. For this purpose we compiled temporal information on raw number of samples collected/detected as well as the proportion of samples with quantified/non-detects throughout the period of study for each compound (Figures S1 and S3). These figures also contain a representation of the MDL and its changes over time for each compound.

Environmental Exposure Distributions (EEDs)

Exposure distribution analysis was conducted on four sets of data: (1) each combination of site type (e.g. rivers and streams, ponds, etc.) and compound; (2) each combination of individual site and compound, and; (3) each combination of site, compound, and year, and; (4) all samples collected for a compound. For each of these sets of data, the following steps were taken. First, detection frequencies were calculated by dividing the number of samples with concentration values above the LOD (i.e. where the compound was detected) by the total number of samples taken (within each of the above-listed data subsets). Then, prior to modeling, the data were subset to those with greater than 10% detection frequency to provide the model with an appropriate minimum number of quantified samples required for an accurate fit. Environmental exposure distributions (EEDs) were generated by fitting the models to six different distributions (Lognormal, Gamma, Exponential, Pareto,

Weibull, and Log-logistic), using the *fitdistcens* function in the R package *fitdistrplus* (Development Core Team 2008; Delignette-Muller and Dutang 2015). This function allows for both quantified data and censored data to be plotted and fitted to the various distributions. Thus, including the “non-detect” samples in the analysis. For each EED, the best fit of the six plotted distributions was chosen based on the lowest Akaike information criterion (AIC), then fitted via non-parametric bootstrapping using the *bootdistcens* function of package *fitdistrplus* (1000 iterations) (Development Core Team 2008). Lastly, the same function was used to calculate 95% confidence intervals, only for the “all samples” dataset.

Acute Water Quality Benchmark Selection and Assessment

Water quality benchmark concentrations for acute and chronic scenarios were compiled from three sources: the Canadian Council of Ministers of the Environment (CCME) Canadian Environmental Quality Guidelines, the United States Environmental Protection Agency’s (USEPA) Office of Pesticide Programs (OPP) Aquatic Life Benchmarks, and the European Union’s Environmental Quality Standards (European Union, 2008; USEPA 2019; CCME 2020). Of the 167 compounds, acute benchmark concentrations were found for 104. Compounds for which no acute benchmark concentration was found were removed from the dataset for the risk assessment portions. The lowest USEPA aquatic life benchmarks for acute scenarios categorized by fish, invertebrates, nonvascular plants, and vascular plants, or CCME water quality guideline was chosen as a conservative approach. Additionally, some of the USEPA concentrations are preceded by a “greater-than” symbol, or a “less-than” symbol, representing that the benchmark was derived from values that may overestimate or underestimate toxicity (USEPA 2019). There was one compound for which the smallest USEPA value had a “less-than” symbol (atrazine) and five compounds that had a “greater-than” symbol (i.e., acifluorfen, dacthal, dinotefuran, flonicamid, and nicosulfuron). Ultimately these symbols were removed and values kept as is for the analysis. For the majority of compounds, 99 of 104 total, the USEPA acute benchmark concentrations was selected. For 4 compounds, the CCME Environmental Quality Guideline was chosen. Lastly, for the remaining compound, hexachlorobenzene, the EU maximum allowable concentration environmental quality standard for inland surface waters was selected. The full list of compounds, their chosen acute benchmark source, and acute benchmark concentrations can be found in the SI (Table S6). For each compound we calculated the percentage of samples that exceeded their associated acute benchmark concentration when the samples with non-detects were included and

when they were removed (i.e., total number of samples with concentration which exceeded the acute benchmark concentration, divided by the total number of samples taken for that compound, or divided by the total number of samples in which the compound was detected). The EEDs generated for (a) each compound at each site; and (b) each compound at each site type, were used to calculate the percentage of the generated distributions which exceeded the associated acute benchmark concentration for each compound.

Mixture Toxicity Assessment

A cursory assessment of the risk posed by mixtures of pesticides in individual samples was completed for each individual class of pesticides under the assumption that a concentration addition (CA) framework would be applicable within a particular pesticide class due to a shared, or similar, mode of action (Backhaus and Faust 2012). First, for each entry in the database, a hazard quotient (HQ) was calculated by dividing the measured concentration by the applicable acute water quality benchmark (see previous section) for that chemical. This was only possible for those compounds for which a benchmark value was available. For instances where the analytical results were below the MDL, a surrogate value of $\frac{1}{2}$ MDL was used for the HQ calculation. Then, we categorized each pesticide in the database within a standardized class (a.k.a. subactivity) as defined in the British Crop Production Council’s Compendium of Pesticide Common Names (formerly Alan Wood’s Compendium of Pesticide Common Names) (BCPC 2024). Finally, HQ values for each individual sample (as described earlier) were grouped by pesticide class/subactivity and summed up to create a Hazard Index (HI) for the mixture of compounds belonging to that class in that particular sample (EC 2012). Generally a HI value higher than 1 would indicate potential concern (EC 2012).

Results and Discussion

Detection Frequencies

In the overall dataset, of the 67,920 total observations, pesticides were detected in 12,862 samples (19%), and pesticides were not detected in 55,058 (81%). A total of 61 of the 167 compounds had detection frequencies of $> 10\%$ for all samples collected, ranging from 10.3 to 91.4% (Table S7), for full list of detection frequencies see Tables S7 & S8. The top 10 overall most detected compounds include: atrazine (91.4%), the three most widely used neonicotinoid insecticides in Canada – clothianidin (75.7%), thiamethoxam (72.3%), and imidacloprid (67.3%), and other prominent

herbicides used in Canada, and Ontario (2,4-D – 78.6%, dicamba – 69.5%) (Table S7) (PMRA 2020). It is interesting to note that the fungicides in the top ten; metalaxyl (77.3%), propiconazole (74.1%), boscalid (72.3%), and azoxystrobin (68.6%), are not used in very large quantities across Ontario (OMAFRA 2008; Farm & Food Care Ontario, 2015). The interpretation of these data, however, needs to consider the detection limit of the analytical method employed. Throughout the 15-year dataset, several method detection limits were used, either increasing or decreasing the limit of detection and consequently impacting the observed detection frequencies. For example, simazine, which was among the top 25 most sampled compounds and had an overall detection frequency of 25.8%, with an increase in detection frequency from 8.3% in 2006 to 63.1% in 2008, and steadily decreasing again for the following years (Table S7, Figure S1). However, this is coupled with detection limits dropping by approximately an order of magnitude over the 2007–2009 period which had obvious impacts in the frequency of detection (Tables S8, S9, & Figure S1). The same is seen with the samples and detection frequencies of metolachlor (overall 59.9% detection). When the method detection limit drastically improved between 2008 and 2009, the percent sample detection increased along with it (Figure S1). Discussions about temporal patterns in contaminant environmental exposures are frequent in the literature (e.g. Gilliom et al. 2006; Stenrød 2015), however these comparisons are often made without taking into consideration any changes in MDL during the period of study, which can lead to erroneous interpretation of patterns in detection frequency data.

Environmental Exposure Distributions (EEDs)

Once filtered to greater than 10% detection, the combinations of “samples” in each set of data were reduced drastically to: (a) each combination of site and compound – from 6,067 to 1,352 combinations; (b) all samples taken of a compound by site type – from 365 to 95 combinations; (c) each combination of site, compound, and year – from 10,966 to 2,732 combinations, and; (d) all sites where a compound was sampled – from 891 to 308 combinations. Table S10 summarises the most relevant centiles of the EEDs calculated from the “all samples” dataset (at least 10% detection frequency), ordered by the estimated 50th centile concentrations, giving insight into the compounds that appeared more commonly at higher concentrations. Arranged this way, glyphosate-Pond ($2,004 \text{ ngL}^{-1}$), glyphosate-River or stream (383 ngL^{-1}), and aminomethyl phosphonic acid (AMPA)-River or stream (159 ngL^{-1}) were the three compound-site type combinations showing the greatest “average” concentrations in the dataset. The upper centiles can provide further information on the observed, or expected,

peak concentrations for each compound-site type combination (e.g., in 5% or 1% of the observed cases, for the 95th and 99th centiles, respectively). When the list of relevant centiles is reordered by the 99th centile values glyphosate-River or stream ($55,190 \text{ ngL}^{-1}$), aminomethyl phosphonic acid-River or Stream ($27,288 \text{ ngL}^{-1}$), and glyphosate-Pond ($16,051 \text{ ngL}^{-1}$) show the greatest 99th centile concentrations. The 99th centile concentrations generated from the EEDs can be compared with measured values to see how likely are the observed maximum concentrations. There were 45 cases where the maximum measured concentration was less than or equal to the estimated 99th centile concentration (e.g. glyphosate-River or stream, atrazine-Lake, metolachlor-Pond, chlorimuron-Groundwater, and dichlorprop (2,4-DP)-Pond). This can indicate that the fitted distributions likely capture uncommon peak exposure events for these compound.

On the other hand, the rest of compounds in the list had maximum measured concentrations that were greater than the estimated 99th centile concentration, indicating that the occurrence of high concentrations such as those observed are rare events (less than 1% of the measured samples). This included 10 of the 14 compounds which had measured maximum concentrations that exceeded their respective water quality benchmarks (the remaining four had less than 10% detection and do not have associated EEDs – azinphos-methyl, chlorpyrifos, naled, and malathion). Where the maximum measured concentration was greater than the estimated 99th centile, these events can point to the potential existence of higher peak concentrations missed in sampling or indicate outliers in the sampling. This distinction is particularly difficult to interpret for the Groundwater, Lake, Pond, and Wetland cases (34 of 45) due to the limited number of samples taken at these site types (Tables S1 & S11). In either case, these examples point to a common limitation in the basic design of monitoring programs based on grab samples, the difficulty of capturing pulses or transitory high-concentration events (Chow et al. 2020).

Regardless of high detection frequencies in these compound-site combinations – over half of these cases had greater than 40% detection – there is an elevated uncertainty around the estimated centiles attributed to the low number of samples taken since none were sampled more than 19 times, and several less than 5 times (Tables S1 & S11). For the river or stream cases, detection frequencies were between 11.5% and 40.7% with number of samples ranging from 26 to 401 (Table S11). Due to the larger number of samples, there is greater confidence that these are accurately modelled. Despite this, none of these cases with measured maximum concentrations greater than the 99th centile had 99th centile values which exceeded the acute water quality benchmarks.

Where conventional methods of characterizing environmental exposure distributions would have either removed or substituted the censored data, the above constructed EEDs explicitly included them, providing a more accurate representation of the probability of exposure to specific pesticides in the monitored surface waters (Wang et al. 2016; Rodríguez-Gil et al. 2018). The elimination method inherently ignores left-censored data, which is not missing data. The substitution method includes those data, hence improving the estimates, however it is still based on an arbitrary choice. Both cases place greater emphasis on the higher detected values, skewing the EED to the right, which can overestimate the exposure. Monitoring databases typically include a large amounts of censored data due to low environmental concentrations or the use of methods with not enough sensitivity, as was the case with the ECCC dataset – 12,862 detects (19%) and 55,058 no-detects (81%). Additionally, they may include samples analyzed at several laboratories with different analytical methods and MDLs, or lower MDLs over the years as instrumentation improves. Over the 16 years of data collection there were 66 compounds which fit this criteria (e.g. both 2,4-D and MCPA have five different MDLs, three different analytical methods each; metolachlor: six MDLs and two analytical methods). Of 167 compounds analyzed, 101 had a single MDL used for the entire duration of the dataset, but only 38 of the 62 for which we had generated EEDs for all sample by site type (Tables S9 & S11). Incorporating the censored data in the analysis can easily accommodate these changes and yield a more accurate assessment of the distribution of exposures for compounds analyzed and, therefore, can help improve our assessment of the risk they may pose.

Nonetheless, no method is perfect. Due to the uncertainty associated with the estimated centiles generated in these

types of EEDs, the application of this method to datasets with greater than 80% censoring and low sampling effort should be done with caution, even though this type of modelling analysis is generally robust (European Food Safety Authority 2010; Antweiler 2015).

Exceedances of Water Quality Guidelines

Of the 104 compounds for which benchmark data was available, 14 had maximum measured concentrations that exceeded their associated acute water quality guideline values (fungicides: pyraclostrobin; herbicides: atrazine, dicamba, diuron, imidacloprid, methylechlorophen oxypropionic acid (MCP), and metolachlor; insecticides: azinphosmethyl, chlorpyrifos, diazinon, naled, endosulfan sulphate total, malathion, and permethrin total) (Tables S12 – S17). The selected acute benchmark concentrations were compared to the generated EEDs of all samples collected for a compound by site type. Twelve compound-site type combinations resulted in greater than 0.01% exceedance of the acute water quality benchmark (seven herbicides-site type combinations, four insecticides-site type combinations, and one fungicides-site type combination). These EEDs are shown in Figure S2. Table 1 lists the associated percent of samples in the distributions that exceeded the selected water quality guidelines (> 0.1%), alongside the percent exceedance of the detected and censored samples themselves. Note that for a number of these compounds (e.g. imidacloprid) we observed “exceedance” of the water quality guidelines by non-detect samples. This can occur when the MDL is higher than the water quality benchmark and hence a precautionary exceedance is flagged.

The protection of 95% of the species 95% of the time is a commonly used protection goal in environmental risk

Table 1 Each compound-site type combination with associated acute water quality benchmarks where the percent of samples in the distributions that exceeded the benchmark was greater than 0.1%, alongside the percent exceedance of the detected and censored samples themselves (the full list of exceedances can be found in Table S12).

Compound	Site type	Benchmark		Exceedance of the model (%)	Detected samples			Non-detect samples		
		Source	Conc. (ngL ⁻¹)		No. of samples	No. of exceedances	Exceed (%)	No. of samples	No. of exceedances	Exceed (%)
Endosulfan sulfate total	River or stream	CCME Acute	60	7.24% (2.56–11.63)	22	2	9.09	32	0	0
Imidacloprid	River or stream	EPA Acute Invertebrates	385	6.03% (4.84–7.21)	629	56	8.9	283	129	45.58
Atrazine	River or stream	EPA Acute Non-vascular Plants	1,000	4.27% (3.33–5.24)	921	46	4.99	83	0	0
Diazinon	River or stream	EPA Acute Invertebrates	105	2.85% (2.01–3.74)	108	25	23.15	785	0	0
Flumetsulam	River or stream	EPA Acute Vascular Plants	3,100	0.28% (0.12–0.5)	178	0	0	401	0	0
Metolachlor	River or stream	EPA Acute Non-vascular Plants	8,000	0.26% (0.15–0.41)	612	3	0.49	392	0	0
Permethrin total	River or stream	EPA Acute Invertebrates	19.5	0.18% (0–1.64)	12	1	8.33	72	0	0

assessment (Solomon and Takacs 2001). As such, benchmark concentration values will aim to protect 95% of the species, for example by deriving this value from the concentration hazardous to 5% of the species as determined from a species sensitivity distribution (Newman et al. 2000; Posthuma et al. 2001). With benchmark concentrations aiming to protect 95% of the species, situations where exceedances from these levels are maintained below 5% would satisfy the overall protection goal. For the overall studied dataset, we can then see that for the time frame covered by the data, the risk posed by most of the individual chemicals satisfied that goal, with only endosulfan and imidacloprid exceeding it by a small margin at 7.24% and 6.03% of the cases respectively.

To examine these acute exceedances more closely, we looked at each combination of unique sampling site and compound to see if there were any specific sites of concern. There were 31 compound-site combinations in the generated EEDs that exceeded the acute water quality guidelines in greater than 5% of the samples (Table S18). Of these, 12 of the 31 occurrences of exceedances were for atrazine, and sites of concern that are found more than once across this list were: Sturgeon creek ($n=4$), Prudhomme creek (old vineland creek) ($n=3$), Richardson's creek ($n=3$), and Two mile creek ($n=3$), all located in southern Ontario. These sites are associated with intense agricultural practices and more focused monitoring is likely needed in these areas.

The availability of tools to incorporate censored data has improved substantially in recent years, yielding the need for "proxy" methods (e.g. substitution) that can introduce bias in exposure assessments obsolete. Moving forward, the adoption of methods able to incorporate non-detects in any

probabilistic exposure assessment is encouraged. To facilitate this, the support of the environmental chemistry community will be needed. In the reporting of monitoring data, clear description of method detection limits (e.g. MDLs, LODs, LOQs), for each compound, sample, etc. must be provided. Of course, no data analysis technique will ever be able to address issues arising from limitations in the design of the sampling program itself, particularly for compounds such as pesticides characterised by pulsed applications and often quick water column dissipation rates – especially in lotic systems. Drawing a clear picture of the exposure to these compounds might require high-frequency sampling approaches when trying to characterise acute exposures or time-integrated sampling approaches (e.g. passive samplers) for a chronic exposure assessment.

Mixture Toxicity Assessment

A total of 12 pesticide classes (or subactivities as listed in the BCPC database) were represented within the dataset. Pyrethroids represented the most diverse group with 12 chemicals, followed by aliphatic organothiophosphates ($n=5$), and triazoles ($n=5$). Table 2 lists the distribution of HI values for the subsets of combinations of site type (e.g. lake, wetland, etc.) and subactivity for which the number of samples with a HI > 1 was greater than zero. SI Figures XX show the distribution of HI values for each subactivity and site type. A total of 13 subactivities (7 insecticides classes, 5 herbicides classes, and 1 fungicides class) are represented in this list with nitroguanidine insecticides (represented by neonicotinoid insecticides such as imidacloprid, or clothianidin) being the only class where HI values > 1 were found

Table 2 Distribution of Hazard Index (HI) values for each combination of chemical class (i.e. subactivity) and site type where a Hazard Index greater than 1 were observed. The number of samples considered within each combination is presented in the column "n". (The complete distributions of HIs for each class/site type are presented in SI Figure 4).

Site type	Activity	Subactivity	n	HI between 0 and 0.1	HI between 0.1 and 1	HI between 1 and 10	HI > 10	Total Hi > 1
Pond	insecticides	nitroguanidine	6	0.00	0.00	100.00	0.00	100.00
Wetland	insecticides	nitroguanidine	3	0.00	0.00	100.00	0.00	100.00
River or stream	insecticides	nitroguanidine	912	64.25	14.14	21.05	0.55	21.60
Lake	insecticides	nitroguanidine	10	90.00	0.00	10.00	0.00	10.00
River or stream	insecticides	aryl organothiophosphate	893	6.38	87.23	5.60	0.78	6.38
River or stream	herbicides	chlorotriazine	1004	66.53	28.69	4.48	0.30	4.78
River or stream	insecticides	chlorinated cyclodiene	54	70.37	25.93	3.70	0.00	3.70
River or stream	insecticides	arylalkyl organothiophosphate	893	20.60	76.48	2.02	0.90	2.92
River or stream	insecticides	pyrethroid	84	5.95	92.86	1.19	0.00	1.19
River or stream	insecticides	aliphatic organothiophosphate	893	6.05	92.95	0.90	0.11	1.01
River or stream	herbicides	chloroacetamide	1004	95.52	4.18	0.30	0.00	0.30
River or stream	fungicides	methoxycarbamate	440	97.50	2.27	0.23	0.00	0.23
River or stream	herbicides	phenylurea	597	95.81	4.02	0.17	0.00	0.17
River or stream	insecticides	organophosphate	839	0.00	99.88	0.12	0.00	0.12
River or stream	herbicides	benzoic acid	1066	99.62	0.28	0.09	0.00	0.09
River or stream	herbicides	phenoxypropionic	1054	99.24	0.66	0.09	0.00	0.09

in sites other than rivers and streams. This group (neonicotinoids) was also the one with the highest percent of samples with $HI > 1$, with 100% of samples showing $HI > 1$ for wetlands as well as ponds, 21.6% for rivers/streams, and 10% for lakes. However, these estimates likely represent an overestimation of the risk mixture since all $HI > 1$ cases for wetlands, ponds, and lakes, resulted from samples $< MDL$, where a $\frac{1}{2}$ MDL value was used for the estimation of the HI. Even for rivers and streams, for which more data were available, approximately $\frac{2}{3}$ of the samples which resulted in $HI > 1$ did so based on concentration data $< MDL$ (SI Figure 4). This issue was noted earlier when discussing the exceedances for imidacloprid itself and highlights the need for analytical methods able to quantify concentrations below water quality benchmark values. After the nitroguanidine insecticides, aryl organothiophosphate insecticides (e.g. chlorpyrifos and diazinon) were the group with the highest percentage of samples with $HI > 1$ (6.4%). Finally, the last group where the number of samples with $HI > 1$ exceeded 5% were the chlorotriazine herbicides (atrazine and simazine). For all other pesticide classes the number of samples resulting in $HI > 1$ was below 5%. The results from this mixture toxicity assessment generally agree with what was observed for the individual compounds where imidacloprid, atrazine, and diazinon showed some of the highest exceedances of water quality guideline values. Although elevated HI values for some classes appear to be dominated by a few select chemicals within each class, we tend to see the greatest increase in risk (i.e., HI) in classes encompassing more compounds. An example is the nitroguanidine insecticides, which appear as the class showing the highest percent of samples with $HI > 1$, ahead of the chlorinated cyclodienes, despite endosulfan, the only representative of the chlorinated cyclodiene class, being the individual compound with the highest percent of exceedances of the water quality values (7.2% as estimated from the EED, Table 1).

With the exception of the nitroguanidine insecticides for which, as discussed, the risk could be overestimated due to overly high MDLs, the rest of the chemical classes showed HI values > 1 in less than 6.5% of the samples, generally remaining below, or fairly close to the overall goal of protecting 95% of the species 95% of the time (Solomon and Takacs 2001). Of course, this exercise is only considering mixture effects within each of these chemical classes, and it is not considering effects resulting from the combined effects (additive or otherwise) of various chemical classes occurring at once. A more complex mixture toxicity assessment approach would be needed to capture these potential interactions.

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Declarations

Ethics approval and consent to participate The authors have no competing interests to declare that are relevant to the content of this article.

References

- Antweiler RC (2015) Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets. II. Group comparisons. *Environ Sci Technol* 49:13439–13446
- Backhaus T, Faust M (2012) Predictive Environmental Risk Assessment of Chemical mixtures: a conceptual Framework. *Environ Sci Technol* 46:2564–2573
- BCPC (2024) Compendium of pesticide common names. British Crop Production Council
- Boye K, Lindström B, Kreuger J (2019) Long-term data from the Swedish national environmental monitoring program of pesticides in surface waters. *J Environ Qual* 48:1109–1119
- Cantoni B, Delli Compagni R, Turolla A, Epifani I, Antonelli M (2020) A statistical assessment of micropollutants occurrence, time trend, fate and human health risk using left-censored water quality data. *Chemosphere* 257:127095
- CCME (2020) Canadian Environment Quality guidelines. Canadian Council for Ministers of the Environment, Winnipeg, MB, Canada
- Chow R, Scheidegger R, Doppler T, Dietzel A, Fenicia F, Stamm C (2020) A review of long-term pesticide monitoring studies to assess surface water quality trends. *Water Res X* 9:100064
- Delignette-Muller ML, Dutang C (2015) Fittedplus: an R package for fitting distributions. *J Stat Softw* 64:1–34
- R Development Core Team (2008): a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria
- EC (2012) In: Consumers D-G (ed) Toxicity and assessment of chemical mixtures. (Ed.). European Commission, Brussels. [f.H.a](https://doi.org/10.1007/978-92-897-0000-0)
- ECCC (2011) Presence and levels of priority pesticides in selected Canadian aquatic ecosystems. Environment and Climate Change Canada, Ottawa, ON, Canada
- ECCC (2018) Great Lakes Water Quality Monitoring and Aquatic Ecosystem Health Data. Environment and Climate Change Canada, Ottawa, ON, Canada
- EU (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. European Parliament, Council of the European Union, Brussels, Belgium
- European Food Safety Authority (2010) Management of left-censored data in dietary exposure assessment of chemical substances. *EFSA J* 8:1557
- Farm & Food Care Ontario (2015) Survey of Pesticide Use in Ontario, 2013/2014. Estimates of Pesticides Used on Field Crops and Fruit and Vegetable Crops. Farm & Food Care Ontario, Guelph, ON, Canada.
- Gilliom RJ, Barbash JE, Crawford CG, Hamilton PA, Martin JD, Nakagaki N, Nowell LH, Scott JC, Stackelberg PE, Thelin GP, Wolock DM (2006) Pesticides in the Nation's streams and Ground Water, 1992–2001. Circular, Reston, VA

- Government of Canada (2018) Great Lakes Water Quality Monitoring and Surveillance Data. Government of Canada, Ottawa, ON, Canada
- Lewan E, Kreuger J, Jarvis N (2009) Implications of precipitation patterns and antecedent soil water content for leaching of pesticides from arable land. *Agric Water Manage* 96:1633–1640
- Newman MC, Ownby DR, Mezin LCA, Powell DC, Christensen TRL, Lerberg SB, Anderson BA (2000) Applying species-sensitivity distributions in ecological risk assessment: assumptions of distribution type and sufficient numbers of species. *Environ Toxicol Chem* 19:508–515
- OMAFRA (2017) Southern Ontario Region at a glance. Ontario Ministry of Agriculture, Food, and Rural Affairs, Guelph, ON, Canada
- OMAFRA (2008) Survey of pesticide use in Ontario, 2008. Ontario Ministry of Agriculture, Food, and Rural Affairs, Guelph, ON, Canada
- PMRA (2020) Update on the Neonicotinoid Pesticides (January 2020). Health Canada, Pest Management Regulatory Agency, Ottawa, ON, Canada
- Posthuma L, Suter GW, Traas II, T.P (2001) Species sensitivity distributions in ecotoxicology. CRC, Boca Raton, Florida, USA
- Raby M, Lissemore L, Kaltenecker G, Beaton D, Prosser RS (2022) Characterizing the exposure of streams in southern Ontario to agricultural pesticides. *Chemosphere* 294:133769
- Rico A, Dafouz R, Vighi M, Rodríguez-Gil JL, Daam MA (2021) Use of Postregistration Monitoring Data to evaluate the Ecotoxicological risks of pesticides to Surface Waters: a Case Study with chlorpyrifos in the Iberian Peninsula. *Environ Toxicol Chem* 40:500–512
- Rodríguez-Gil JL, Cáceres N, Dafouz R, Valcárcel Y (2018) Caffeine and paraxanthine in aquatic systems: global exposure distributions and probabilistic risk assessment. *Sci Total Environ* 612:1058–1071
- Shoari N, Dubé J-S (2018) Toward improved analysis of concentration data: embracing nondetects. *Environ Toxicol Chem* 37:643–656
- Solomon KR, Takacs P (2001) Probabilistic risk assessment using species sensitivity distributions. In: Posthuma L, Suter GW, II, Traas TP (eds), *Species sensitivity distributions in ecotoxicology*. CRC Press, Boca Raton, Florida, USA, 309–338
- Solomon KR, Baker DB, Richards RP, Dixon KR, Klaine SJ, La Point TW, Kendall RJ, Weisskopf CP, Giddings JM, Giesy JP, Hall LW, Williams WM (1996) Ecological risk assessment of atrazine in north American surface waters. *Environ Toxicol Chem* 15:31–76
- Solomon K, Giesy J, Jones P (2000) Probabilistic risk assessment of agrochemicals in the environment. *Crop Prot* 19:649–655
- Statistics Canada (2017) Cropland in Ontario grows despite fewer farms. Government of Canada, Ottawa, ON, Canada
- Stenrød M (2015) Long-term trends of pesticides in Norwegian agricultural streams and potential future challenges in northern climate. *Acta Agriculturae Scand Sect B — Soil Plant Sci* 65:199–216
- Struger J, Thompson D, Staznik B, Martin P, McDaniel T, Marvin C (2008) Occurrence of glyphosate in surface waters of southern Ontario. *Bull Environ Contam Toxicol* 80:378–384
- Struger J, Grabuski J, Cagampan S, Sverko E, McGoldrick D, Marvin CH (2017) Factors influencing the occurrence and distribution of neonicotinoid insecticides in surface waters of southern Ontario. *Can Chemosphere* 169:516–523
- USEPA (2019) Aquatic life benchmarks and ecological risk assessments for registered pesticides. United States Environmental Protection Agency, Washington, DC, USA
- Wang D, Singhasemanon N, Goh KS (2016) A statistical assessment of pesticide pollution in surface waters using environmental monitoring data: Chlorpyrifos in Central Valley. *California* 571:332–341

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