

## **Nonylphenol, Octylphenol and Nonylphenol Ethoxylates Dissemination in the Canadian Freshwater Environment**

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### **Abstract**

Nonylphenol, octylphenol and nonylphenol ethoxylates are man made compounds which are only discharged in the environment due to anthropogenic activities. The objectives of this study were to determine the current concentrations of these substances in the Canadian freshwater environment and to determine if past regulatory actions were beneficial to the environment. Freshwater samples (n=241)

were collected and analysed for 4-nonylphenols (NP), nonylphenol monoethoxylate (NP<sub>1</sub>EO), nonylphenol diethoxylate (NP<sub>2</sub>EO) and octylphenols (OP) at 35 sites in Canada from 2014 to 2019 with individual compound concentrations ranging from 1.29 to 477.22 ng/L. In addition, 18-65 % of the samples were reported to be under the laboratory detection limit, depending on the compound. Sampling sites were categorised into five groups based on the dominant activities present upstream in their watersheds; mixed use sites, municipal waste water treatment plant (MWWTP)-associated sites, textile mill-associated sites, urban and reference sites. All four compounds in the study were detected more frequently in urban and MWWTP-associated sites than at other locations. Additionally, there is a statistically significant ( $p < 0.05$ ) downward temporal trend in NP concentrations in Canadian surface waters from 2014-2019. There were no exceedances of the Canadian Water Quality Guideline of 1000 ng/L.

## Introduction

Nonylphenol (NP) is a broad category of isomeric compounds each consisting of a nine-carbon alkyl chain attached to a phenol ring, with the chemical formula  $C_{15}H_{25}O$  (CCME 2002). The various isomers can differ in the position of the phenol ring to which the alkyl chain is attached as well as in the degree of branching of the alkyl chain. In the past, most of the NP produced commercially were in the form of 4-nonylphenol with varied alkyl chain branching (CCME 2002). Major derivatives of NP are nonylphenol ethoxylates (NPEs) (CCME 2002). Nonylphenol ethoxylates (NPEs) are organic compounds composed of a phenol bearing a 9 carbon-tail and have the general formula:  $C_{15}H_{24}O + (OCH_2CH_2)_nOH$  where  $n$  may range from 1 to 100, but with most NPEs containing between 6 and 12 ethoxilate groups (EC and HC 2001, CCME 2002). NPEs have been in use since the 1960s as detergents, degreasers, wetting agents, dispersing agents, paints, and emulsifiers in various industrial sectors such as steel manufacturing, pest control products, power generation, pulp and paper processing, institutional cleaning products and textile processing (EC and HC 2001). The main areas of use of octylphenol (OP) are as an intermediate in the production of phenol/formaldehyde resins (98% of use) and in the manufacture of octylphenol ethoxylates (2% use) (OSPAR 2006). Octylphenol may also occur as an impurity from 1-10% when manufacturing NP (OSPAR 2006).

NP, NPEs and OP are not produced naturally and their presence in the environment is, therefore, exclusively a consequence of anthropogenic emissions or transformation from parent compounds in the environment (EC and HC 2001). Wastewater treatment, landfill and sewage sludge recycling were the three top contributors of NP and NPEs according to Soares *et al.* (2008). Releases of NP, NPEs and OP to the environment can occur at various points in the product life cycle – such as, during primary production of NPEs or OPEs, manufacture of NPE-containing products, product use and disposal of the product to landfill, septic systems or wastewater treatment plants (EC and HC 2001). A 1998-1999 Canadian survey revealed that the bulk of NP-NPEs releases were from the use of soaps and detergents while textile discharges came in second place (EC 2004). Sabik *et al.* (2003) also added the potential use of NPEs as surfactants in solvents in pesticide formulations and therefore could be present in tributaries draining major farming areas, however this has never been evaluated in the Canadian environment.

Once NPEs are released to wastewater treatment systems, several conversions may occur. In general, there is an initial loss of some ethoxylate (EO) groups from the original moiety. Under aerobic and anaerobic treatment conditions, biodegradation to more toxic metabolites occurs. These products are NP, nonylphenol ethoxylate (NP<sub>1</sub>EO) and nonylphenol diethoxylate (NP<sub>2</sub>EO) (EC and HC 2001). In aquatic environments, primary biodegradation of NPEs is rapid, but the resultant products, such as NP<sub>1</sub>EO, NP<sub>2</sub>EO, and NP, are moderately persistent, especially under anaerobic conditions.

Nonylphenol is an endocrine disruptor and xenoestrogen (Mergel 2014). NPs and NPEs with only one or two EO groups are highly toxic to aquatic organisms (EPA 2014). In general, toxicity to aquatic organisms increases with decreasing degrees of ethoxylation for NP compounds (EPA 2014). NPEs with greater degrees of ethoxylation, while less toxic, degrade to the more toxic and persistent, less ethoxylated forms of these chemical substances in the environment (EPA 2014). Available data indicate that NP/NPEs are highly toxic to fish and invertebrates, causing lethality on an acute basis and various non-lethal effects such as on growth, development, metabolism, reproduction, and fecundity with low-level chronic exposures (EPA 2014). At typical environmental concentrations and for conventional toxicity endpoints, the mode of toxicity for NP and for short chain NPEs is narcosis (CCME 1999). If these substances are all acting through narcosis, then additivity of their effects (as opposed to synergism or antagonism) is most likely (Servos *et al.* 2000). OPs are very similar in structure and behaviour to NPs

and likely act through a similar mode of action (Servos et al. 2000, CCME 2002). Because if this additivity in effects, the Canadian Council of Ministers of the Environment (CCME) has established a Canadian Water Quality Guideline of 1000 ng/L for nonylphenols and their ethoxylates based on a Toxic Equivalency (TEQ) Approach (CCME 2002).

Under past use patterns, NP and NPEs in Canada have resulted in environmental concentrations that exceeded the levels of concern in textile mill, pulp and paper mill and MWWTP effluents. In the late 1990s in Canada, NP/NPEs concentrations ranged from <10 to over 9000 ng/L downstream of textile mill, pulp and paper mill and MWWTP (Bennie et al. 1997, 1998, 2003). Risk management instruments were put in place for a reduction in the use and release of these compounds in the processing of textiles and pulp and paper, and in the manufacturing or importation of soap and cleaning products, with the intent to reduce environmental exposure (Environment Canada 2016). Environment and Climate Change Canada has estimated the total amount of NP and NPEs used in manufacturing products to be reduced to 86 tonnes and imports to 27 tonnes in 2014 compared with 2100 tonnes used in manufacturing and 850 tonnes imported in 1998 base year (Environment Canada 2016). Furthermore textile mill using a wet process were shown to have decreased the use of NP and NPEs by 99.7% from 1998 to 2006 (Environment Canada 2007).

Past international studies have also measured a wide range in concentration of alkylphenol compounds from < 10 ng/L up to 3940 ng/L (Komori et al. (1997), Klecka et al. (2010), Wang et al (2011), Gorga et al (2015), Tabe et al. (2016), Liu et al 2017). Generally, decreasing trends were noted in countries where various regulatory mechanisms were put in place during the last two decades. Internationally, alkylphenols have been regulated as a dangerous substance under the OSPAR convention (Convention for the Protection of the Marine Environment of the North-East Atlantic), Alkylphenols are also managed in Annex XVII of REACH (Registration, Evaluation and Registration of Chemicals), the Toxic Substance Control Act (United States Environmental Protection Agency- TSCA), K-REACH (Korea) and the Rotterdam Convention for severely restricted compounds. Nonylphenol are also regulated in the Japanese environmental quality standard for water pollution (Hong et al 2020).

This monitoring study was initiated to determine current levels of these substances in aquatic environments in Canada for comparison with established environmental quality guidelines and toxicity thresholds, while also serving to demonstrate whether regulatory actions taken in Canada have had a beneficial impact on the environment. To date, this is the largest Canadian study conducted to establish the impact of the regulatory actions on NP and NPEs concentrations in freshwater throughout the country.

## **Material and Methods**

### **Monitoring approach**

This study focusses on four alkylphenolic compounds: 4-nonylphenols (4-NP, CAS 84852-15-3), 4-nonylphenol monoethoxylates (NP<sub>1</sub>EO), 4-nonylphenol diethoxylates (NP<sub>2</sub>EO) and 4-n-octylphenol (4-n-OP, CAS 1806-26-4). Previous studies in Canada have demonstrated that NP, OP and NPE releases to surface water environments were largely from municipal wastewater treatment systems and textile industry discharges (Klecka et al. 2010, EC and HC 2001), therefore this study focussed largely on sites downstream of urban MWWTP as well as MWWTP that received textile discharges (Figure 1, Table 1). Nevertheless in order to obtain a clear picture of NP, OP and NPEs concentrations across Canada, additional sites of urban streams, mixed developed sites and a reference site were also sampled (Table 1). Therefore, sites in this study were categorized in five groupings; reference, mixed development, urban, MWWTP-associated and textile-associated sites. The reference site (upstream Mill Creek) was chosen where upstream disturbance is minimal. Eight sites were located in high-density urban sites (e.g., Still Creek, Thames River, Highland Creek) to assess environmental concentrations not related to wastewater sources. Another eight sites were located in mixed development areas which could be somewhat influenced by MWWTPs, but are at such a distance and associated with such a high volume of river discharge that direct association with those plants was unlikely. Since MWWTPs have been found previously to be the most likely sources of NP/NPEs (Klecka et al. 2010, EC and HC 2001), eighteen sites were selected immediately downstream of MWWTPs. Of those eighteen sites, four were chosen due to the presence of a textile mill within the MWWTP collection system. In addition, four sites were sampled both upstream (up) and downstream (down) of MWWTPs to assess the magnitude of the potential input of NP/NPEs to the environment from a municipal wastewater source. Those sites were located on the Saint John River, Grand River, Thames River and Red River (Table 1).

The frequency of sampling ranged from a monthly to an annual basis, with collection frequencies and sites being adjusted each year, depending on capacity and on previous years' results. Some sites were sampled for only one year while others were sampled up to 6 years (Table 1). Over the course of this study, a total of 241 samples were collected and analysed for NP, NP<sub>1</sub>EO, NP<sub>2</sub>EO and OP. Characteristics of the sampling sites are listed in Table 1, including population (either in the whole watershed or only the largest urban centre upstream of each site), distance to the closest MWWTP, and river discharge (range or annual average, if available).

**Table 1. List of monitored sites, years of sampling and geographical characteristics. Abbreviations are as follows; DD: decimal degrees, up: upstream, dn: downstream, NB: New Brunswick, Qc: Québec, ON: Ontario, MB: Manitoba, NFLD: Newfoundland and Labrador, NS: Nova Scotia, BC; British Columbia, SK: Saskatchewan.**

Site Name (province)	Years	Latitude (DD)	Longitude (DD)	Watershed population	MWWTP (km)	River Discharge (m <sup>3</sup> /s)
<b>Mixed Development Sites</b>						
Saint John River (up), NB	2019	45.948	-66.869	< 5 000	36	350- 6 100
St. Lawrence River (Quebec), QC	2016-19	46.806	-71.187	538 238	13	> 12 000
St. Lawrence River (Lavaltrie), QC	2016-19	45.875	-73.281	3 824 221	29	> 10 000
St. Lawrence River (Wolfe I.), ON	2017-19	44.211	-76.237	11 000 000+	90	>8000
Niagara River, ON	2017, 19	43.255	-79.055	12 000 000+	15	>5800
Thames River (up), ON	2014-19	43.038	-81.223	< 40 000	33	5 - 70
Grand River (up), ON	2014-19	43.482	-80.481	15 000	30	n/a
Red River – Selkirk (up), MB	2016-19	50.141	-96.869	633 450	28	>3200

Site Name (province)	Years	Latitude (DD)	Longitude (DD)	Watershed population	MWWTP (km)	River Discharge (m <sup>3</sup> /s)
Red River – Emerson, MB	2016-19	49.001	-97.223	665	4.5	>1 200
<b>Urban Sites</b>						
Waterford River, NFLD	2016-19	47.529	-52.741	24 284	none	1.1-3.3
Little Sackville River, NS	2016-19	44.763	-63.6888	21 379	none	0.017-8.52
Dicks Creek, ON	2017-19	43.154	-79.243	17 931	none	n/a
Beaver Dams Creek, ON	2017-18	43.103	-79.217	131 900	none	n/a
Taylor Creek, ON	2017-18	43.701	-79.312	n/a	none	n/a
Highland Creek, ON	2017-18	43.778	-79.191	360 000	none	1 - 40
Mill Creek (dn), BC	2016	49.883	-119.499	117 312	none	19.4
Still Creek, BC	2016-18	49.259	-122.969	100 000	none	0.04-0.4
<b>Textile - Associated Sites</b>						
Berthierville, QC	2016-19	46.087	-73.167	4091	0.25	n/a
Rivière Blanche, Qc	2016-19	46.205	-71.902	5693	0.25	n/a
Chaudière River, QC	2017-19	46.336	-70.921	4722	0.25	12-1100
Saint Victor, QC	2016-19	46.157	-70.919	2509	0.25	<5-60
<b>MWWTP - Associated Sites</b>						
Saint John River (dn) (NB	2019	45.953	-66.624	56 224	0.25	500 - 7120
St. Lawrence River (Trenton), ON	2014	44.059	-77.334	11 000 000+	<1	n/a
St. Lawrence River (Prescott), ON	2014	44.436	-75.285	11 000 000+	<1	n/a
Credit River, ON	2018	43.909	-80.078	30729	0.75	0.75-10.25
Thames River (dn), ON	2014-19	42.965	-81.389	366 151	6	10 - >500
Grand River (dn), ON	2014-19	43.385	-80.385	507 096	5	25-300

Site Name (province)	Years	Latitude (DD)	Longitude (DD)	Watershed population	MWWTP (km)	River Discharge (m <sup>3</sup> /s)
Grand River (Galt WWTP), ON	2016-19	43.320	-80.314	>700 000	2	25-1100
Hamilton Harbour 914, ON	2014-19	43.268	-79.781	>500 000	1.5	n/a
Hamilton Harbour 926, ON	2014-17	43.183	-79.483	>175 000	0.25	n/a
Hamilton Harbour 1001, ON	2014-17	43.297	-79.802	>700 000	1.5	n/a
Red River -Selkirk (dn), MB	2016-17	50.191	-96.844	9 934	2.75	>3200
Red River – Winnipeg, MB	2016-17	49.950	-97.098	633 450	0.1	n/a
Wascana Creek (dn), SK	2016-18	50.499	-104.800	193 100	8.5	<5 - 60
<b>Reference site</b>						
Mill Creek (reference), BC	2012-17	49.9835	-119.352	<50	none	n/a

### Sample collection

Most samples were collected with a sampling pole or from mid-span of bridges. Samples from Hamilton Harbour and Berthierville were collected from a boat. Samplers used clean polyethylene gloves during the sampling procedure. All samples were collected in 1L laboratory certified clean amber glass bottles (OSWER Directive 9240.0-05A), and were kept on ice and delivered to the analytical laboratory within 24 – 48 hours. Field measurements of temperature, conductivity, dissolved oxygen, and pH were made by a recently calibrated (less than 5 days) water quality sonde. Quality assurance and control samples for the field components included field blanks, which were included in ten different field collections. Each field blank consisted of a 1L glass bottle filled with ultra-pure water, which was exposed for 15 seconds on site. Field duplicates or triplicates accounted for 5% of the total number of samples obtained.

### Laboratory Analysis

Laboratory analyses were overseen by AXYS Analytical Services Ltd. Using AXYS method MLA-004 v4 (AXYS 2017). Samples were spiked with  $^{13}\text{C}$ -labelled surrogate standards ( $^{13}\text{C}_6$ -4-nonylphenol and  $^{13}\text{C}_6$ -4-nonylphenol diethoxylate) prior to extraction. Samples were extracted with hexane and then subjected to aqueous acetylation steps and then were cleaned up by column chromatography on a 28% deactivated basic silica column (AXYS 2017). After cleanup and before instrumental analysis recovery, a standard was added. The typical final extract volume was 500  $\mu\text{L}$ . The target compounds in the extract were analyzed by gas chromatography with mass spectrometry (GC-MS). The compounds were separated chromatographically on a Restek Rtx-5 capillary column and analyzed using an electron impact ionization source coupled to a mass selective detector operated at unit mass resolution. Target analytes were detected using multiple ion detection with acquisition of at least two characteristic ions for each target analyte and stable isotope internal standard (AXYS 2017). Initial calibration was performed using a six point calibration series of solutions that encompass the working concentration range. Typical concentration of calibration standards varied from 150 to 75 000 ng/mL (AXYS 2017).

Sample-specific detection limits were determined individually for every sample by converting the area equivalent of 3.0 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. Sample-specific detection limits varied between sample batches and compound but ranged from 0.4 to 32.9 ng/L and averaged from 0.76 to 3.2 ng/L. Samples were analysed in batches consisting of a maximum of twenty samples, one procedural blank and one spiked matrix sample. For sample data to be reportable, the batch QC data must meet the established acceptance criteria including sample specific detection limits, procedural blank level and acceptable matrix spike recovery which are all analyte-dependant (AXYS 2017). Blank contamination is a well-known problem in ultra-trace analysis of alkylphenols (Salgueiro-Gonzales et al. 2012) and is further discussed in the results and discussion section.

### **Statistical analysis**

Statistical tests were performed using Systat™11 and R (2013). A large proportion of the dataset is below the detection limit of the laboratory (censored value). The inclusion of the censored data is important to

correctly depict the dataset; but a mere substitution of the censored value has been associated to errors summary statistics estimates (Helsel 2006). To prevent this, non-parametric methods, included in the Non-detects And Data Analysis (NADA) user-written package for R, were used to describe the dataset. The details of these methods are described by Helsel (2005, 2012). The NADA package uses survival analysis methods to produce descriptive statistics. Helsel (2012) further suggests using the robust regression of order statistics (ROS) when the dataset contains multiple detection limits and the sample size is less than 50. ROS is a semi-parametric tool used to estimate summary statistics using both censored and uncensored data. Censored box plots were also produced using the NADA package in R (Helsel 2005; Helsel and Lee 2006). Censored data were also included in the assessments of differences in groups (non-parametric Wilcoxon) using the `cendiff` command in the NADA package (Helsel 2012; Helsel and Lee 2006).

## **Results and Discussion**

### **Quality assurance and control**

As part of the quality assurance and quality control of this study, there were 10 field blanks submitted and analysed as part of this study. Overall, 70% of the blanks had detectible levels of NP, 30% had detections of NP<sub>1</sub>EO and 10% had detections of both NPE<sub>2</sub>O and OP (Table 2). Such a high number of detection in blanks may be surprising to some but a literature review quickly reveals similar rates of detection in past studies.

As described by Loos et al. (2008), Stottmeister et al. (2009), Salguiero-Gonzalez et al. (2012) and Vanderford et al. (2014), alkylphenols analyses are often fraught with blank contamination issues. A decade ago, Loos et al. (2008) even suggested that reporting of nonylphenol less than 100 ng/L was not advised due to blank problems. Salguiero-Gonzalez et al. 2012 suggested not performing filtration of the sample since it could lead to contamination and adsorption problems and that refrigeration should be limited to 5 days due to a 30% decline of both NP and OP after eight days of refrigeration. Since

alkylphenols are used in the fabrication of cleaning products, it is imperative that none of the equipment or laboratory ware be cleaned with detergents (Stottmeister et al. 2009, Salguiero-Gonzalez et al. 2012). Stottmeister also suggested that false positive results such as in blanks can result from compounds interfering with the peak pattern of the target analysis that is used for quantification. False positives in a study by Vanderford et al. 2014 ranged from 23 to 69 % of OP and NP samples. Those findings are very similar to ours for NP where 70% of our blanks had some level of contamination (Table 2). However, in our study OPs were only detected in 10% of the blank samples (Table 2). Gong et al. (2016) measured average NP concentrations of 12 ng/L in blank water samples which is similar to the median value of NP (8.5 ng/L) in this study (Table 2). Unfortunately, there does not appear to be consensus on the use of any method over another to reduce these blank issues for NP/NPEs. A review of the available literature for this issue did not yield one common methodology to deal with reporting values for NP where blank contamination has occurred. However, it seems the majority of published papers had followed a method where blanks contamination were subtracted from the final concentrations obtained for a sample (Loos et al. 2008; Gong et al 2016). Although Salguiero-Gonzalez et al. (2012) cautioned that blank subtraction could cause quantification errors if the blanks do not remain constant but did not offer any other methodology to deal with this issue. Based on the advice of those other researchers and the nature of our data, we decided the best way to deal with the blank contamination issue in this study was to blank subtract. The blank subtract methodology used in this study is helpful to ensure that the batch containing a blank contamination of 644 ng/L is not included in the summary statistics or trend analysis of this study.

**Table 2.** Range and median concentrations (ng/L) for the target analytes in the field blanks.

	<b>NP</b>	<b>NP<sub>1</sub>EO</b>	<b>NP<sub>2</sub>EO</b>	<b>OP</b>
% of blank samples with detections	70	30	10	10
Range (or single values) detected in blanks (ng/L)	0.8 - 644	1.68 - 6.89	4.35	0.336
Median of values detected in blanks (ng/L)	8.57	1.86	4.35	0.336

### Frequency of detections

Frequency of detections varied greatly both by site and by compound (Table S1 in Supplemental information). Table S1 presents the proportion of values that are uncensored (above the DL of the laboratory) separated by sampling sites and compounds (NP, NP<sub>1</sub>EO, NP<sub>2</sub>EO and OP). Nonylphenol had the highest detection frequency (77%) while NP<sub>2</sub>EO had the lowest (20%) (Table S1). Since a large proportion of the results of this study were under the detection limit of the laboratory, it was prudent to use both uncensored and censored (under the detection limit of the laboratory) data in the subsequent analysis to correctly depict the situation in the Canadian environment.

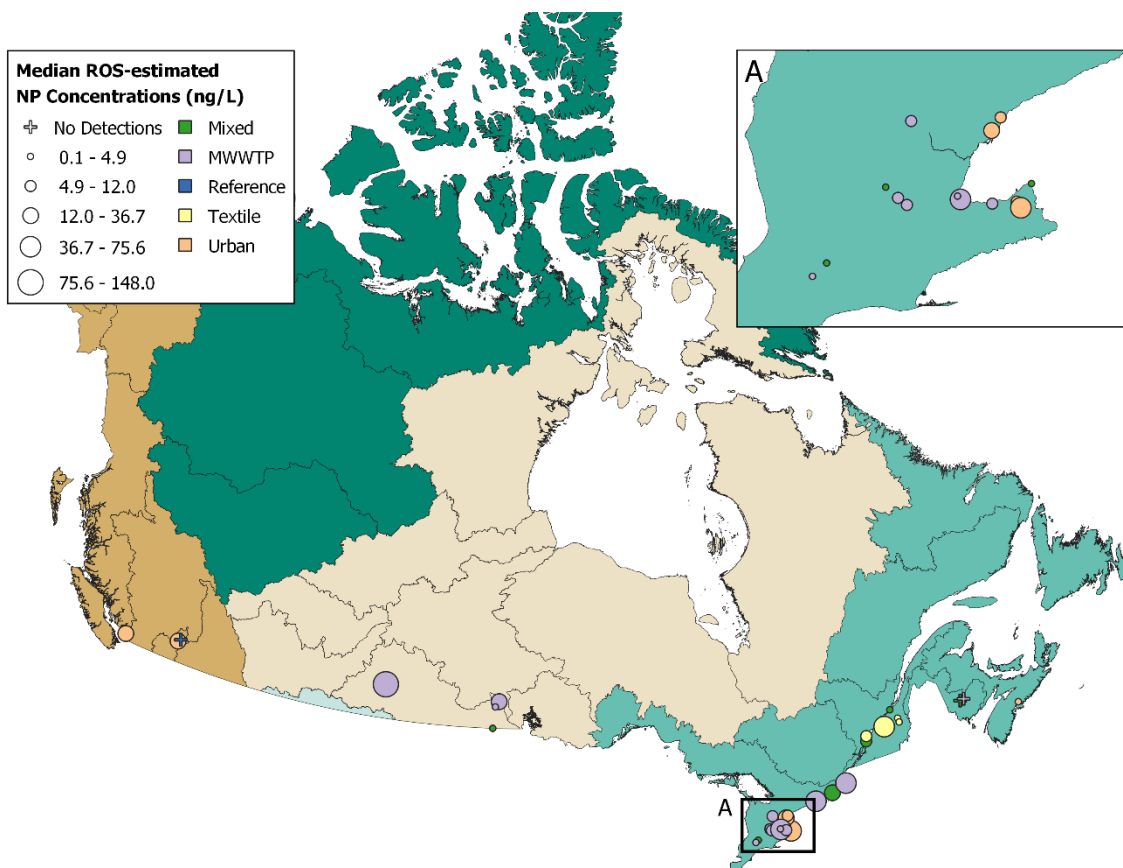
The frequency of detection is similar to Shah and Smyth (2013) who reported a detection frequency of 89% for NP downstream of 12 municipal WWTPs in Canada. Interestingly, our detection frequency for OP was substantially higher at 31% compared to 1.2% in the Shah and Smyth (2013) study. That difference may have been due to lower OP use within their study area, or higher OP use in more recent years, as the Shah and Smyth (2013) study was conducted in 2010-2011. In contrast, in a large study of alkylphenols in the Great Lakes of North America by Klecka et al (2010), NPs and OPS were detected in 36% and 25% of samples, respectively.

The concentrations of alkylphenols measured in this study ranged from 1.29 to 477.22 ng/L, with NP having the largest range of concentrations. Generally, the highest concentrations of all alkylphenols were measured at a handful of sites such as Wascana Creek, Still Creek, Hamilton Harbour and Blanche River (Table 3). Historically, concentrations of NPs found in Canadian fresh waters have ranged from <10 to 4250 ng/L (Bennie et al 1997, EC 2001, CCME 2002) (Table 5). In comparison, NP values in this study ranged from 1.29 to 477.22 ng/L, which is a full order of magnitude lower. This is supported by results from the study by Gauthier et al. (2013), which demonstrated NPE concentrations downstream of textile influenced-MWWTP decreased by 89% between 2003 and 2010.

**Table 3. Alkylphenol concentration range, median and standard deviation (sd) for each site and each compound using the ROS\* method. Blank cells in the table represent all values at these sites were under the detection of the laboratory. up: upstream, dn: downstream. Number of samples collected at each site are listed in brackets in the site name column.**

Site Name (# of samples)	Median and (sd) NP (ng/L)	Median and (sd) NP <sub>1</sub> EO (ng/L)	Median and (sd) NP <sub>2</sub> EO (ng/L)	Median and (sd) OP (ng/L)
<b>Mixed sites</b>				
Wolf Island (3)	17.6 (13.7)			
Lavaltrie (24)	8.8 (91.8)	1.17 (2.4)	2.02 (0.3)	0.63 (0.26)
Red River-Selkirk (9)	8.2 (11.4)	0.85 (3.2)	12	7.8
St Lawrence R (Quebec) (5)	4.52 (2.80)	2.28		0.3
Grand River (up) (11)	3.1 (33.7)	31.4		0.94 (0.7)
Niagara-on-the-Lake (2)	1.75	13.2		
Red River-Emerson (9)	1.5 (7.9)	2.33 (0.96)	4.9	
Thames River (up) (10)	1.1 (21.7)	7.05		
Saint John River (up) (8)				
<b>Urban sites</b>				
Beaver Dams Creek (2)	45.9 (8.7)			
Still Creek (19)	36.7 (49.2)	22.2 (25.8)	8.1 (83.5)	0.5 (0.2)
Taylor Creek (3)	26.9 (79.90)	11.1 (23.7)	11.6 (13.2)	
Mill Creek (lower) (3)	16.2 (10.8)	9.02		
Dick's Creek (3)	12 (24.2)	45.8		
Highland Creek (3)	9.4 (33.5)	2.01 (13.6)		
Waterford River (9)	1.2 (1.2)	0.4 (6.8)		
Little Sackville River (8)	0.002 (83.3)			
<b>Textile-associated sites</b>				
Rivière Blanche (8)	58.4 (53.1)	10.5 (15.1)	0.4 (4.8)	1.1 (1.0)
Berthierville (9)	6.5 (8.4)	4.94		0.5 (0.2)
Saint-Victor (9)	0.441 (0.8)			0.9 (0.6)
Chaudière (7)	0.001 (13.4)			1 (0.9)
<b>MWWTP- associated sites</b>				
Wascana (18)	148 (128.2)	60.7 (59.6)	41.9 (60.7)	1.7 (4.3)
Hamilton Hbr-914 (6)	75.6 (55.6)	36.9 (50.9)	18.4 (80.8)	
Trenton (1)	44			
Prescott (1)	44			

Site Name (# of samples)	Median and (sd) NP (ng/L)	Median and (sd) NP <sub>1</sub> EO (ng/L)	Median and (sd) NP <sub>2</sub> EO (ng/L)	Median and (sd) OP (ng/L)
Red R.-Selkirk (dn) (2)	23.7 (11.7)	7.9		
Grand R. (Galt WWTP) (10)	11.9 (31.9)	2.7 (2.6)	1.6 (4.8)	1.2 (0.3)
Grand R. (dn) (10)	11.3 (12.7)			0.7 (0.9)
Credit River (3)	11 (21.8)	8.19 (12.8)	31.4	0.7 (3.2)
Thames River (dn) (11)	4.66 (31.7)	1.9 (5.9)	0.36 (8.2)	0.2 (1.4)
Hamilton Hbr-926 (4)	6.63 (10.3)	3.5 (7.4)		
Hamilton Hbr-1001 (2)	4.9 (5.1)			
Red River-Winnipeg (4)	2.1 (15.7)	3.6		
St John River (down)(8)				
<b>Reference site</b>				
Mill Creek (3)		1.1		



**Figure 1. Median NP concentrations in Canadian major drainage areas and site type. ROS is the implementation of a regression on order statistics to utilise less than detection limit values without a substitution method. Similar figures for NP<sub>1</sub>EO, NP<sub>2</sub>EO and OP are included in the supplemental information.**

Of all the sampling sites in this study, Wascana Creek and Hamilton Harbour 914 had the highest median concentrations of NP, NP<sub>1</sub>EO and NP<sub>2</sub>EO (Table 3). Both of these sites are located in an area that receives MWWTP effluents, which are known sources of alkylphenols (EC 2001, Klecka et al. 2010). Red River at Selkirk and Wascana Creek had the two highest median concentrations of OP (Table 3). Once again, those high concentrations may be explained by the presence of a MWWTP upstream of the sampling point. The result for Red River at Selkirk is to be used with caution as there was only one OP detection out of 9 samples analysed (Table S1).

### Summary of alkylphenols as a function of water quality parameters

Simple correlations and linear regressions between field measurements and nonylphenols, octylphenol and NPEs revealed significant relationships with conductance but no statistically significance for pH or dissolved oxygen. However, caution must be used when interpreting those results as the number of field readings ranged from 32 to 82 observations. Results are tabulated in Table 4. Field measurements results are presented in Table S2 in supplemental information.

Table 4. Regression results of nonylphenol, NPEs and octylphenol as a function of conductance.

Compounds	n	Equation	P value	R <sup>2</sup>
NP	82	$NP=19.85+0.066[\text{Conductance}]$	<0.001	0.199
NP <sub>1</sub> EO	46	$NP_1EO =9.225+0.035[\text{Conductance}]$	<0.001	0.295
NP <sub>2</sub> EO	32	$\text{Log}_{10}(\text{NP}_2\text{EO}) =-0.873+0.782[\text{Conductance}]$	0.004	0.251
OP	42	$\text{Log}_{10}(\text{OP}) =-0.965+0.458[\text{Conductance}]$	<0.001	0.364

All the relationships described in Table 4 above were of nonylphenol compounds concentrations increasing significantly as conductance increased. This is likely due to the presence of wastewater treatment effluent at some of our sites, which increased the conductance of the surface water and is likely the largest source of the nonylphenols and derivatives (Soares et al. 2008).

### Spatial analysis of nonylphenol concentrations

With the majority of values above the detection limit of the laboratories (censored), it was prudent to use both the uncensored and censored values of NP, NPEs and OP using the NADA package in R. Alkylphenol concentrations were evaluated to determine if the type of watershed usage influenced the range of values obtained during this study. Sampling sites were categorised as mixed-use, MWWTP-associated, textile-associated and urban (Table 1). Figure 2 depicts the differences in NP concentrations as a function of watershed usage. The median values for mixed-use and textile-associated are both below the highest detection limit of the laboratory (5 ng/L). However, the median concentrations for MWWTP-associated or urban categories are of similar values at around 20 ng/L (Figure 2). There was not enough data to represent the reference category in the boxplots.

The non-parametric Wilcoxon for NP, OP and NPEs all revealed significant difference ( $p < 0.001$ ) between the types of waterbodies sampled. For NP and NP<sub>1</sub>EO both MWWTP and urban sites had a statistically higher range of concentrations than that of the other types. For NP<sub>2</sub>EO the mixed-use sites have a lower concentration than that of all other types. OP concentrations are highest at both the textile-associated and MWWTP-associated sites compared to the other types.

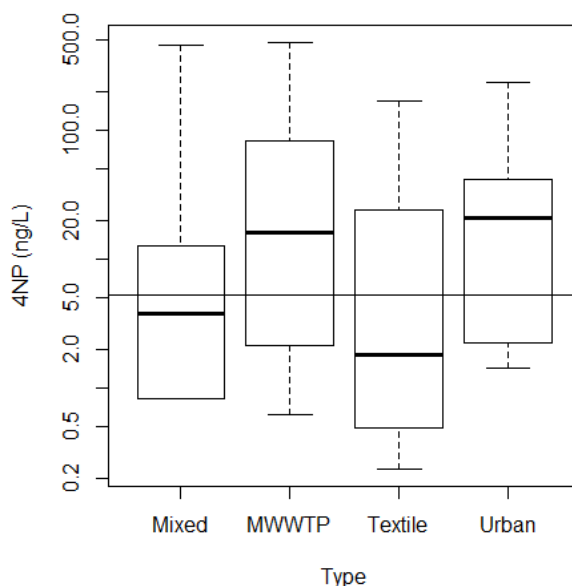
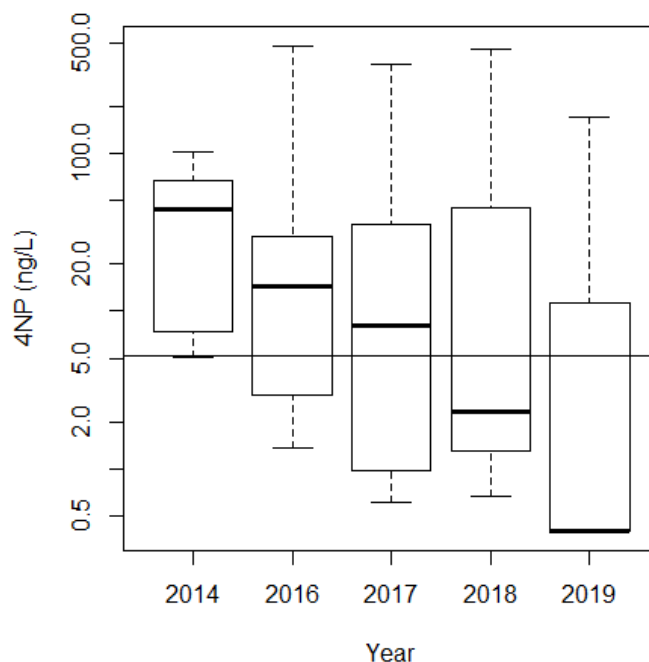


Figure 2. NP concentration in surface waters as a function of watershed usage. The median is shown as the line in the middle of the boxes, while the first and third quartile are the end of both sides of the boxes. The minimum and maximum values are represented at the tip of each lines.

### Temporal analysis of nonylphenol concentrations

The non-parametric Wilcoxon was used to test for a statistically significant difference in alkylphenol concentrations by year, using both censored and uncensored data. The test revealed a significant difference ( $p=0.002$ ) between years for both NP and NP<sub>1</sub>EO. The boxplots clearly show that the difference is due to a general decrease of 4-NP and NP<sub>1</sub>EO concentrations over the period of this study (Figure 3). The concentrations of NP<sub>2</sub>EO did not significantly change ( $p=0.3$ ) over the years of the study while the OP concentrations had a significant difference between years with the highest concentrations in 2019. However, the 2019 data only contained three detections with the rest of the samples (35) under the detection limit of the laboratory and therefore caution must be used in the interpretation of this result for OP. A typical Mann Kendall trend analysis could not be conducted at the present as this study did not have enough years of data.



**Figure 3.** Concentrations of NP in surface waters as a function of years. The median is shown as the line in the middle of the boxes, while the first and third quartile are the end of both sides of the boxes. The minimum and maximum values are represented at the tip of each lines. The straight line is the highest detection limit of the dataset (5 ng/L).

Since NP and NPEs typically occur together in the aquatic environment, it is useful to assess the combined effects of these compounds through the use of a toxic equivalency approach (TEQ). The Canadian Council of the Ministers of the Environment (CCME 2002) developed such a water quality guideline with a value of 1000 ng/L for the protection of freshwater aquatic life. This Canadian value is more protective than the EPA (2006) chronic four day average of 6600 ng/L or the acute criteria of 28 000 ng/L. The TEQ approach uses different toxic equivalent factors for various alkylphenols to characterize the toxicity of a mixture of related compounds (CCME 2002). Within our study, there were no exceedances of the 1000 ng/L TEQ guideline. The highest 20 TEQ values for individual sites and sampling dates range from 111 to 477 ng/L. Five of the six highest TEQs were found at one site, downstream of the Regina MWWTP at Wascana Creek. Surprisingly, a sample obtained at Lavaltrie in the St Lawrence River had the second highest TEQ of this study while two urban sampling sites rounded

the top ten TEQ concentrations. Interestingly, moderate rain events occurred the days prior or the day of the sampling at both of the urban sampling sites. Another way to evaluate the results of this study to the Canadian TEQ and the many censored values in the dataset is to use a Kaplan-Meier (KM) estimation. An estimation of median TEQs for each sampling site using this method yielded very low TEQ values. The three highest median TEQs were for Hamilton Harbour, Still and Blanche River with values of 79.3, 52.4 and 51.1 ng/L respectively, which is very low, compared to the guideline value of 1000 ng/L. This is due to the use of a median value for all sampling dates at one particular site while the high values of 111 to 477 ng/L were the highest values measured on one sampling date at a site.

### **Comparison to other studies**

To properly compare the changes in concentrations of NP compounds over time, it is important to compare historical concentrations obtained at the same sampling locations that previously showed high concentrations of NP, NPEs and OP. In this regard, some of the same locations sampled as part of this study were also sampled in the past (Table 4). Generally, we found the range of concentrations of NP compounds have decreased 1-2 order of magnitude over time at several sampling sites (Table 3 and 5). The magnitude of decrease is intrinsically linked to the reduction in usage of these products in textile mills for the St Victor and Princeville (Blanche River) sites (Berryman et al. 2012) and a decrease of concentrations in the effluents discharged from MWWTPs (Galt River, Hamilton Harbour sites 1001 and 914, respectively). Interestingly, such declines were not as evident, if at all, at the sampling sites located on large rivers such as Lavaltrie and Niagara-on-the-Lake. This may be due to the lower historical concentrations and the larger volume of water flowing ( $>10\ 000\ \text{m}^3/\text{s}$ ) at these sites. Two sites (Lavaltrie and Princeville) had detections NP<sub>1</sub>EO and NP<sub>2</sub>EO in this study, while older studies did not detect concentrations. This may be explained by the lower detection limit in the current study in comparison to that of the historical studies.

Table 5. Concentration range or individual values of alkylphenols at Canadian sites with historical data. Abbreviations are as follows; QC; Québec, ON: Ontario).

Site Name (province)	Years	NP (ng/L)	NP <sub>1</sub> EO (ng/L)	NP <sub>2</sub> EO (ng/L)	OP (ng/L)	Reference
St Victor (QC)	1991-98	2700-3300	5800-9300	48900- 506000	1900-8500	Bennie et al. 1997, 1998, 2003
St Victor (QC)	2009-10	<100	n/a	n/a	20	Berryman et al .2012
Grand River (ON) (Galt WWTP)	1991-98	69-1500	120-1500	160-860	<5 - 77	Bennie et al. 1997, 1998, 2003
Hamilton Harbour 1001 (ON)	1991-98	19-380	360-1100	<20- 400	13-36	Bennie et al .1997, 1998, 2003
Niagara-on-the- Lake (ON)	1991-98	<10	<20	<20	<5	Bennie et al . 1997, 1998, 2003
Hamilton Harbour 914 (ON)	1991-98	860-980	780	950	82-96	Bennie et al. 1997, 1998, 2003
St Lawrence R. (QC)	1991-98	<10	110-150	<20 -23	<5	Bennie et al. 1997, 1998, 2003
St Lawrence R. Lavaltrie (QC)	2009-10	<100	n/a	n/a	11	Berryman et al. 2012
Credit River (ON)	1991-98	10-9430	110-1800	130-10000	<5-10	Bennie et al. 1997, 1998, 2003
Princeville (Rivière Blanche) (QC)	2009-10	100	n/a	n/a	10	Berryman et al. 2012

The St Victor site had samples analysed for NP and NPEs in two different periods in addition to our study (Table 5) and is the site where the largest decreases in concentrations were measured. NPs concentrations changed dramatically at this site, from 2700-3330 ng/L in 1991-1998 to a median of 0.4 ng/L in 2016 – 2018 (Table 5). NP<sub>1</sub>EO was not even detected at that site in our study while NP<sub>2</sub>EO and OPs showed similar large concentration decreases of multiple orders of magnitude (Table 3 and 5). These declines in alkylphenol concentrations since the 1990's are not surprising given that many textile

processing facilities in that time period discharged untreated liquid effluents directly to adjacent rivers and waterbodies.

Most Canadian and international studies measuring NP compounds in freshwater have historically involved industrial (textile) and/or municipal wastewater sampling with little few recent work in ambient rivers and streams (Table 5 and 6). The majority of studies show a sharp decline in all alkylphenolic compounds in the last 15 to 20 years. As summarized in Table 6, more recent international studies such as those of Tabe et al. (2016) and Gorga et al (2015) report much lower concentrations of alkylphenols than those reported in earlier studies (Komori et al. 1997). However there are still some studies presenting recent high levels of nonylphenol in China (Table 6). The reduction of nonylphenol in certain parts of the world may be a reflection of the multiple life-cycle approaches and risk-management strategies put in place by different governments (including Canada) to prevent or minimize their releases to the environment. Gorga et al. (2015) suggested that the significant decrease in levels of NP and OP in Spanish Rivers since 2000 stems from a gradual withdrawal and replacement of NPEOs by Spanish textile and tannery industries. Berryman et al. (2012) also opined that the decrease in NP concentrations was not due to better MWWTP processes, which would be indicated by a rise in partially degraded (shorter ethoxy chains) derivatives, but rather from a reduction in usage by industry.

**Table 6. Comparison of alkylphenol ranges, medians and maximums (ng/L) in Canadian and international studies.**

Sources	NP (ng/L)	NP <sub>1</sub> EO (ng/L)	NP <sub>2</sub> EO (ng/L)	OP (ng/L)	Reference
<b>Canada</b>					
Various	<10 – 1700				Bennie et al. 1997
MWWTP raw and (final)	1810 – 22 690 (560- 2120)			160 – 1550 (50 -660)	Lee and Peart 1995
Rivers	20 -4250 (25.9)	20 -2300 (12.51)	20 – 2450 (12,51)		EC 2001

Textile (2 <sup>nd</sup> treat)	90 -3560 (2,41)	1120 – 4100 (1,2)	930 – 3920 (1,2)		EC 2001
MWWTP - 1	<20 - 6208	70- 56130	340- 36330		EC 2001
MWWTP – 2	120- 4790	20 – 43370	<20 - 32620		EC 2001
MWWTP - 3	<20 - 3200	30 – 26 400	250- 12450		EC 2001
Upstream of MWWTP	<1	<2		<1 - 9	Sabik et al. 2003
Effluent of MWWTP	92	<2		<1	Sabik et al. 2003
Downstream of MWWTP	<1	<2		<1	Sabik et al. 2003
MWWTP effluents median (maximum)	203 (7080)	124 (5750)	<330 (4730)	<3.6 (7.67)	Shah and Smyth 2013
MWWTP effluents	255-282	28.5-72.2	8.86-152	1.3 – 16.1	Tabe et al. 2016
<b>International</b>					
MWWTP effluents, (Japan)	<10 - 900				Komori et al. 1997
Erren River, (Taiwan)	20-3940				Lee et al. 2013
Rivers (Portugal)	<0.1 - 391	<62	<0.01-882	<0.14-85	Gorga et al. 2015
Downstream of WWTP (US)	5 (0.5-3000)	159 (1-7800)	15 (1-11000)	3 (0.5-470)	Klecka et al. 2010
Yangtze River (China)	1.4-858				Liu et al. 2017
Liao River (China)	122.4-2065.7			2.3-52.2	Wang et al. 2011

## Conclusion

This study included 241 samples for the analysis of NP/NPEs from 35 locations throughout Canada. The high proportion of non-detect values of these substances (18-65%) might be attributed to the government of Canada's risk management strategies. None of the values exceeded the CCME TEQ guideline for the protection of aquatic life. Most detections that did occur were from sites downstream of MWWTP outfalls and in densely populated urban streams. The concentrations of NP at many sites have also significantly decreased compared with earlier studies at the same locations, and even over the 5-year period of this study.

Although the dataset for this study included only water samples, there are a few lines of evidence, which suggest that sediments are also a major sink of NP/NPEs in the environment. As the ethoxy chain decreases, the water solubility of NPEs decreases and its affinity to organic particles and sediment increases (EC 2001). In addition, both Lee et al. (2003) and Gong et al. (2016) had corroborating evidence of statistically significant positive relationships between organic carbon and NPEs. Historically, Bennett and Metcalfe (2000) and more recently Hull et al. (2015) even identified NPEs as of potential concern in sediment in Canadian and American areas of the Great Lakes Basin. At the present time, ECCC has sampled the sediments at four textile-associated site only once and it is hard to draw any conclusions from such a small dataset. Therefore, we recommend the additional sampling of sediment at the majority of the sites of this study over multiple years in order to evaluate these concerns.

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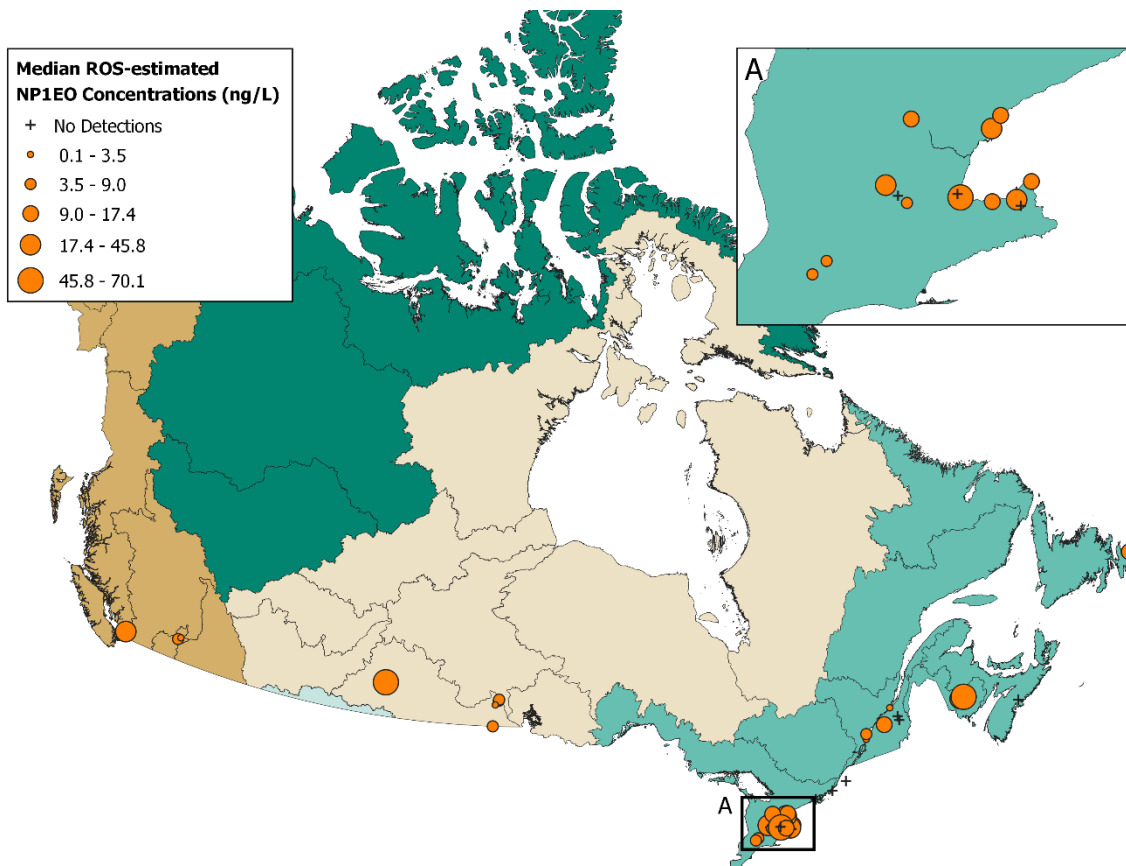
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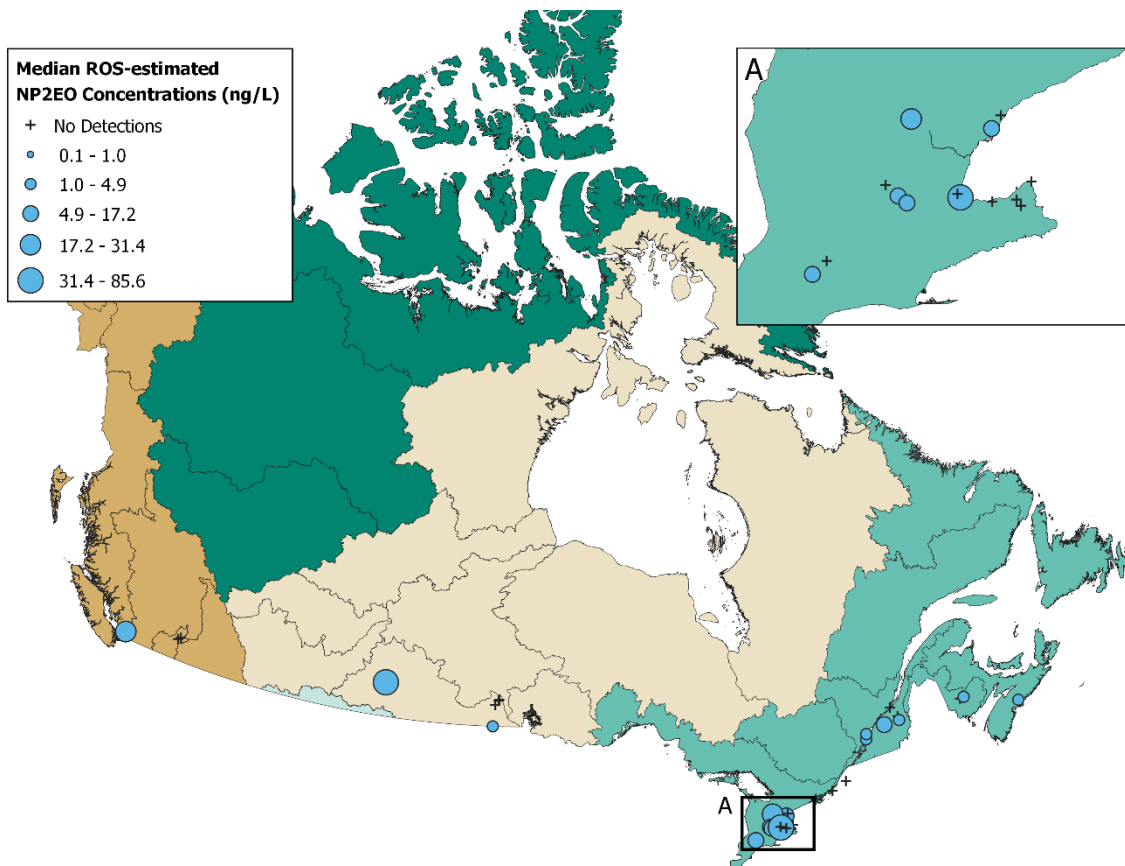
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### Supplemental Information

**Figures S1-S3. Median NP<sub>1</sub>EO, NP<sub>2</sub>EO and OP concentrations in Canadian major drainage areas and site type. ROS is the implementation of a regression on order statistics to utilise less than detection limit values without a substitution method.**





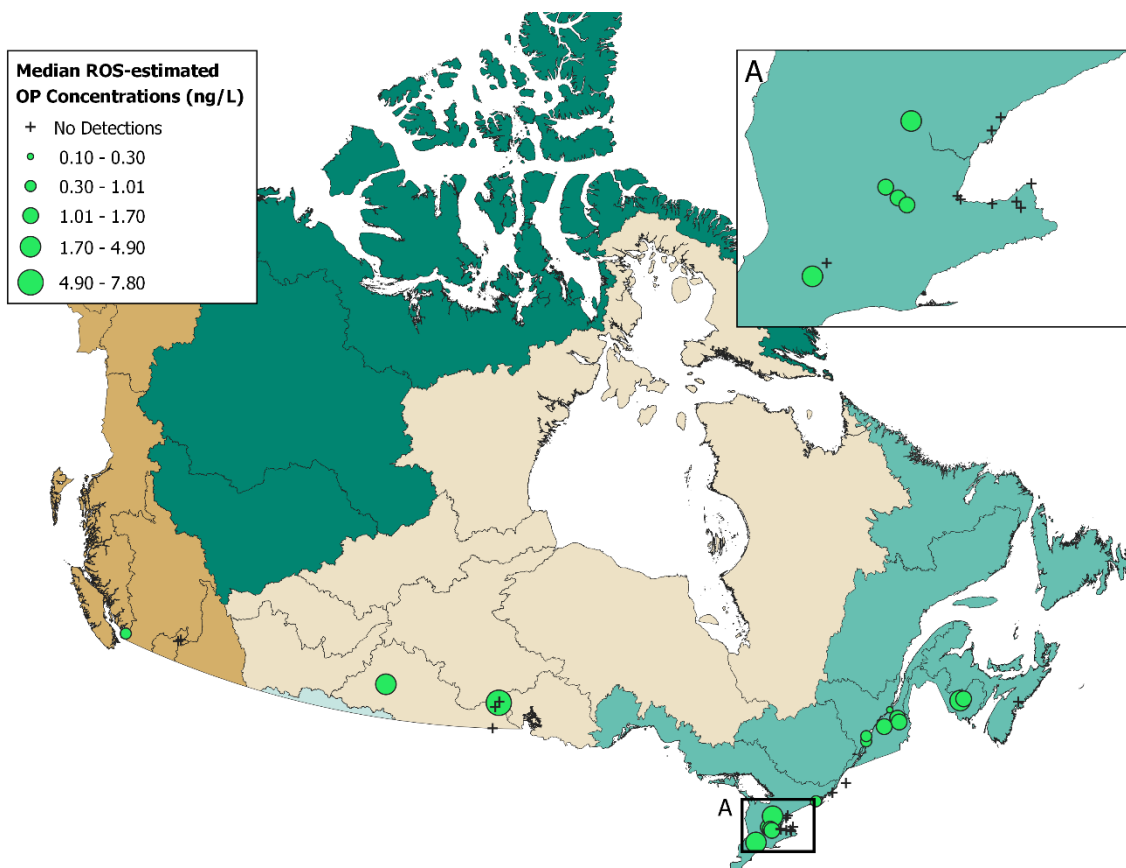


Table S1. Proportion of values that are uncensored (above the DL of the laboratory) separated by sampling sites and compounds (NP, NP<sub>1</sub>EO, NP<sub>2</sub>EO and OP). Color scheme is as follows. Green is for sites/compounds which had values of 0 to 50% of the values under the detection limit of the laboratory while red values were for sites/ compounds where 50 to 100% of the concentrations were below the DL.

Site Name	n	4NP	NP <sub>1</sub> EO	NP <sub>2</sub> EO	OP
Still Creek	19	0 of 19	2 of 19	7 of 19	11 of 19
Mill Creek (lower)	3	0 of 3	2 of 3	3 of 3	3 of 3
Mill Creek (reference)	3	3 of 3	2 of 3	3 of 3	3 of 3
Red River-Selkirk	9	3 of 9	6 of 9	8 of 9	8 of 9
Red River-Selkirk (down)	2	0 of 2	1 of 2	2 of 2	2 of 2
Red River-Winnipeg	4	2 of 4	3 of 4	4 of 4	4 of 4
Red River-Emerson	9	4 of 9	7 of 9	8 of 9	9 of 9
Waterford River	9	5 of 9	7 of 9	9 of 9	9 of 9
Little Sackville River	8	6 of 8	8 of 8	8 of 8	8 of 8
Grand River (down)	10	8 of 10	10 of 10	10 of 10	5 of 10
Grand River (up)	11	4 of 11	10 of 11	11 of 11	5 of 11
Grand River (Galt stp)	10	2 of 10	7 of 10	6 of 10	4 of 10
Thames River (up)	10	6 of 10	9 of 10	10 of 10	10 of 10
Thames River (down)	11	4 of 11	7 of 11	9 of 11	9 of 11
Niagara on the	2	1 of 2	1 of 2	2 of 2	2 of 2
Beaver Dam Creek	2	0 of 2	2 of 2	2 of 2	2 of 2
Dick's Creek	3	1 of 3	2 of 3	3 of 3	3 of 3
Hamilton Harbour-914	6	1 of 6	1 of 6	2 of 6	6 of 6
Hamilton Harbour-926	4	0 of 4	2 of 4	4 of 4	4 of 4
Hamilton Harbour-1001	2	0 of 2	2 of 2	2 of 2	2 of 2
Credit River	3	1 of 3	1 of 3	2 of 3	1 of 3
Highland Creek	3	0 of 3	1 of 3	3 of 3	3 of 3
Taylor Creek	3	0 of 3	1 of 3	0 of 3	3 of 3
Wolf Island	3	1 of 3	3 of 3	3 of 3	3 of 3
Berthierville	9	3 of 9	8 of 9	9 of 9	5 of 9

Site Name	n	4NP	NP <sub>1</sub> EO	NP <sub>2</sub> EO	OP
St Lawrence River (Lavaltrie)	24	6 of 24	15 of 24	23 of 24	9 of 24
St Lawrence River (Quebec)	5	2 of 5	4 of 5	5 of 5	4 of 5
Chaudière River	7	5 of 7	7 of 7	7 of 7	3 of 7
Saint-Victor arm	9	7 of 9	9 of 9	9 of 9	4 of 9
Rivière Blanche	8	1 of 8	2 of 8	6 of 8	3 of 8
Wascana Creek	18	0 of 18	2 of 18	6 of 18	11 of 18
Total % detection	241	77	37	20	31

Table S2. Summary statistics of the physico-chemical measurements obtained at sampling sites.

	Conductance (uS/cm)	Dissolved oxygen (mg/L)	pH (field)	Total dissolved solids (g/L)
Number of values	138	122	138	36
Minimum	58.900	1.940	5.610	0.055
Maximum	2 202.800	15.15	8.720	1.070
Median	473.750	10.605	7.640	0.395
Standard deviation	543.470	8.703	0.505	0.212