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

Benoit Lalonde[1] · Christine Garron[1]

Abstract

Nonylphenol, octylphenol, and nonylphenol ethoxylates are manmade compounds that 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_1EO), nonylphenol diethoxylate (NP_2EO), and octylphenols 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 to 2019. There were no exceedances of the Canadian Water Quality Guideline of 1000 ng/L.

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 also may occur as an impurity from 1 to 10% when manufacturing NP (OSPAR 2006).

NP, NPEs, and OP are not produced naturally, and their presence in the environment is 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

✉ Benoit Lalonde
Benoit.lalonde2@canada.ca

Christine Garron
Christine.garron@canada.ca

[1] Water Quality Monitoring and Surveillance Division, Water Science and Technology, Environment and Climate Change Canada, 45 Alderney Drive, Dartmouth, NS B2Y 2N6, Canada

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_1EO), and nonylphenol diethoxylate (NP_2EO) (EC and HC 2001). In aquatic environments, primary biodegradation of NPEs is rapid, but the resultant products, such as NP_1EO, NP_2EO, 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, whereas 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 nonlethal 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 2002). 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 more than 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 mills 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 measured a wide range in concentration of alkyphenol 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 past 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 also are 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 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.

Materials and Methods

Monitoring Approach

This study focusses on four alkylphenolic compounds: 4-nonylphenols (4-NP, CAS 84852-15-3); 4-nonylphenol monoethoxylates (NP_1EO); 4-nonylphenol diethoxylates (NP_2EO); 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 (Fig. 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 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. Because MWWTPs have been found previously to be the most likely sources of NP/NPEs

(Klecka et al. 2010; EC and HC 2001), 18 sites were selected immediately downstream of MWWTPs. Of those 18 sites, 4 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 1 year, whereas others were sampled up to 6 years (Table 1). During the course of this study, a total of 241 samples were collected and analysed for NP, NP_1EO, NP_2EO, and OP. Characteristics of the sampling sites are listed in Table 1, including population (either in the whole watershed or only
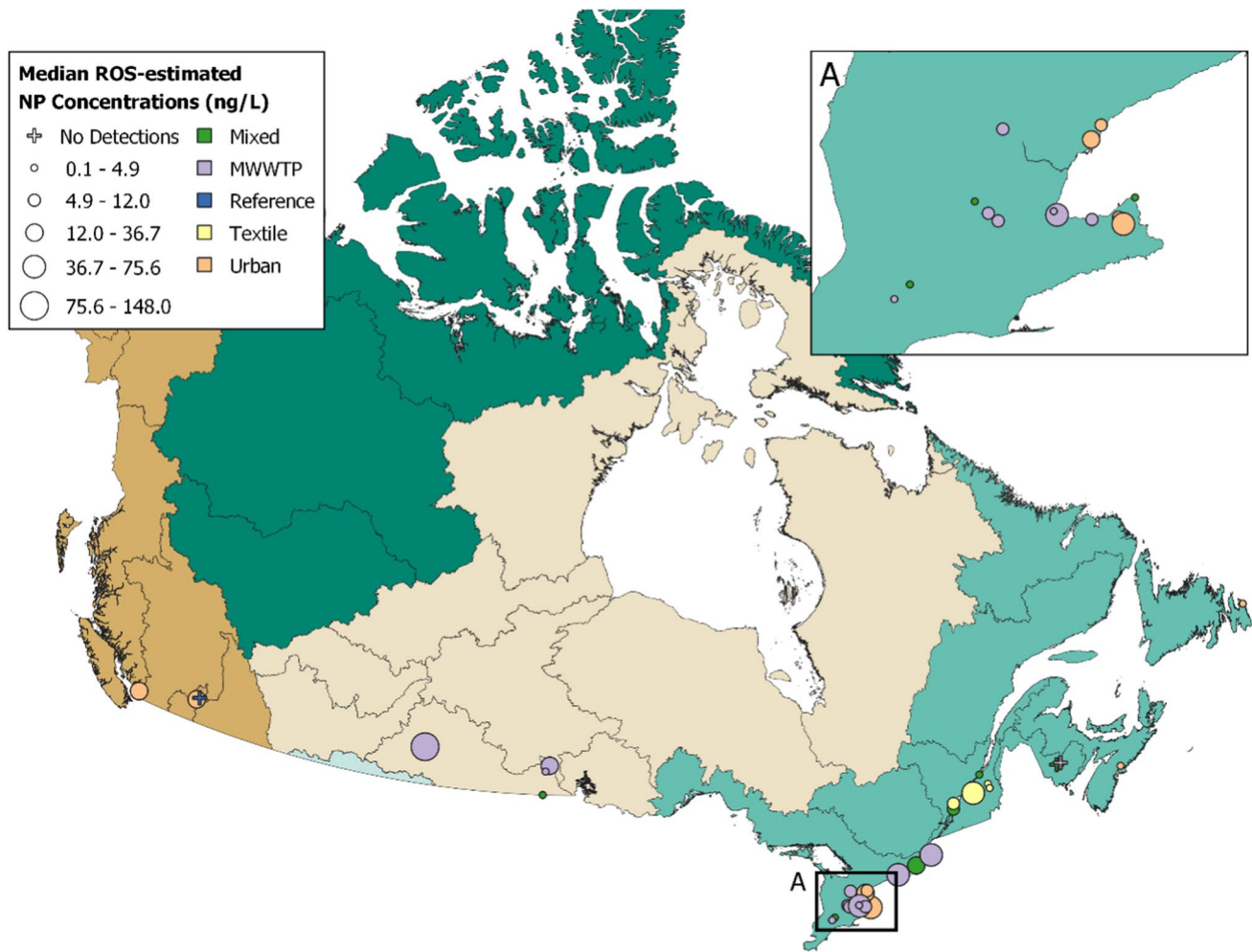
Fig. 1 Median NP concentrations in Canadian major drainage areas and site type. ROS is the implementation of a regression on order statistics to utilise less than detection limit values without a substitution method. Similar figures for NP_1EO, NP_2EO, and OP are included in the supplemental information

Table 1 List of monitored sites, years of sampling, and geographical characteristics

Site name (province)	Years	Latitude (DD)	Longitude (DD)	Watershed population	MWWTP (km)	River discharge (m^3/s)
Mixed development sites						
Saint John River (up), NB	2019	45.948	− 66.869	< 5000	36	350–6100
St. Lawrence River (Quebec), QC	2016–2019	46.806	− 71.187	538,238	13	> 12,000
St. Lawrence River (Lavaltrie), QC	2016–2019	45.875	− 73.281	3,824,221	29	> 10,000
St. Lawrence River (Wolfe I.), ON	2017–2019	44.211	− 76.237	11,000,000+	90	> 8000
Niagara River, ON	2017–2019	43.255	− 79.055	12,000,000+	15	> 5800
Thames River (up), ON	2014–2019	43.038	− 81.223	< 40,000	33	5–70
Grand River (up), ON	2014–2019	43.482	− 80.481	15,000	30	N/a
Red River—Selkirk (up), MB	2016–2019	50.141	− 96.869	633,450	28	> 3200
Red River—Emerson, MB	2016–2019	49.001	− 97.223	665	4.5	> 1200
Urban sites						
Waterford River, NFLD	2016–2019	47.529	− 52.741	24,284	None	1.1–3.3
Little Sackville River, NS	2016–2019	44.763	− 63.6888	21,379	None	0.017–8.52
Dicks Creek, ON	2017–2019	43.154	− 79.243	17,931	None	N/a
Beaver Dams Creek, ON	2017–2018	43.103	− 79.217	131,900	None	N/a
Taylor Creek, ON	2017–2018	43.701	− 79.312	N/a	None	N/a
Highland Creek, ON	2017–2018	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	2016–2018	49.259	− 122.969	100,000	None	0.04–0.4
Textile—associated sites						
Berthierville, QC	2016–2019	46.087	− 73.167	4091	0.25	N/a
Rivière Blanche, QC	2016–2019	46.205	− 71.902	5693	0.25	N/a
Chaudière River, QC	2017–2019	46.336	− 70.921	4722	0.25	12–1100
Saint Victor, QC	2016–2019	46.157	− 70.919	2509	0.25	< 5–60
MWWTP—associated sites						
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	30,729	0.75	0.75–10.25
Thames River (dn), ON	2014–2019	42.965	− 81.389	366,151	6	10 to > 500
Grand River (dn), ON	2014–2019	43.385	− 80.385	507,096	5	25–300
Grand River (Galt WWTP), ON	2016–2019	43.320	− 80.314	> 700,000	2	25–1100
Hamilton Harbour 914, ON	2014–2019	43.268	− 79.781	> 500,000	1.5	N/a
Hamilton Harbour 926, ON	2014–2017	43.183	− 79.483	> 175,000	0.25	N/a
Hamilton Harbour 1001, ON	2014–2017	43.297	− 79.802	> 700,000	1.5	N/a
Red River—Selkirk (dn), MB	2016–2017	50.191	− 96.844	9934	2.75	> 3200
Red River—Winnipeg, MB	2016–2017	49.950	− 97.098	633,450	0.1	N/a
Wascana Creek (dn), SK	2016–2018	50.499	− 104.800	193,100	8.5	< 5–60
Reference site						
Mill Creek (reference), BC	2012–2017	49.9835	− 119.352	< 50	None	N/a

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

the largest urban centre upstream of each site), distance to the closest MWWTP, and river discharge (range or annual average, if available).

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 1-L 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 h. 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 1-L glass bottle filled with ultra-pure water, which was exposed for 15 s 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}C-labelled surrogate standards ($^{13}C_6$-4-nonylphenol and $^{13}C_6$-4-nonylphenol diethoxylate) before 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 μL. 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 characteristics 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 20 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" sections.

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 and Lee 2006). To prevent this, nonparametric methods, included in the Nondetects 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 semiparametric 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 also were included in the assessments of differences in groups (nonparametric 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 ten 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_1EO, and 10% had detections of both NPE_2O 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.

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

	NP	NP$_1$EO	NP$_2$EO	OP
% 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

As described by Loos et al. (2008), Stottmeister et al. (2009), Salgueiro-Gonzales et al. (2012), and Vanderford et al. (2014), alkylphenols analyses often are 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. Salgueiro-Gonzales et al. (2012) suggested not performing filtration of the sample, because 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 8 days of refrigeration. Because 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; Salgueiro-Gonzales 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 Salgueiro-Gonzales 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.

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$_1$EO, NP$_2$EO, and OP). Nonylphenol had the highest detection frequency (77%), whereas NP$_2$EO had the lowest (20%) (Table S1). Because 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 with 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 and HC 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.

Of all the sampling sites in this study, Wascana Creek and Hamilton Harbour 914 had the highest median concentrations of NP, NP$_1$EO, and NP$_2$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

Table 3 Alkylphenol concentration range, median, and standard deviation (SD) for each site and each compound using the ROS* method

Site name (# of samples)	Median (SD) NP (ng/L)	Median (SD) NP$_1$EO (ng/L)	Median (SD) NP$_2$EO (ng/L)	Median (SD) OP (ng/L)
Mixed sites				
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)				
Urban sites				
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)			
Textile-associated sites				
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)
MWWTP-associated sites				
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			
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)				
Reference site				
Mill Creek (3)		1.1		

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

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, because there was only one OP detection out of nine 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.

All of 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 (Fig. 2). There was not enough data to represent the reference category in the boxplots.

The nonparametric Wilcoxon for NP, OP, and NPEs all revealed significant difference ($p < 0.001$) between the types of waterbodies sampled. For NP and NP_1EO, both MWWTP and urban sites had a statistically higher range of concentrations than that of the other types. For NP_2EO, 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 with the other types.

Temporal Analysis of Nonylphenol Concentrations

The nonparametric Wilcoxon was used to test for a statistically significant difference in alkylphenol concentrations
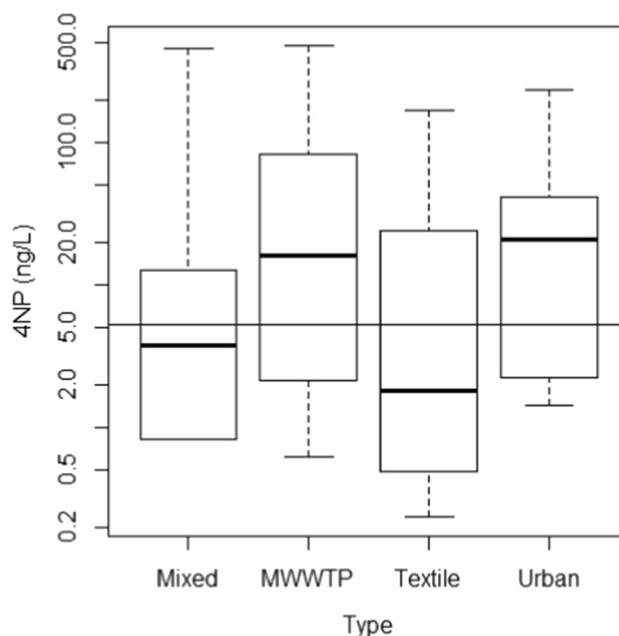
Fig. 2 NP concentration in surface waters as a function of watershed usage. The median is shown as the line in the middle of the boxes, while the first and third quartile are the end of both sides of the boxes. The minimum and maximum values are represented at the tip of each lines

by year, using both censored and uncensored data. The test revealed a significant difference ($p = 0.002$) between years for both NP and NP_1EO. The boxplots clearly show that the difference is due to a general decrease of 4-NP and NP_1EO concentrations over the period of this study (Fig. 3). The concentrations of NP_2EO 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-Kendal trend analysis could not be conducted at the present, because this study did not have enough years of data.

Because 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

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

Compounds	n	Equation	P value	R^2
NP	82	NP = 19.85 + 0.066 [Conductance]	< 0.001	0.199
NP_1EO	46	NP_1EO = 9.225 + 0.035 [Conductance]	< 0.001	0.295
NP_2EO	32	$Log_{10}(NP_2EO) = -0.873 + 0.782$ [Conductance]	0.004	0.251
OP	42	$Log_{10}(OP) = -0965 + 0.458$[Conductance]	< 0.001	0.364
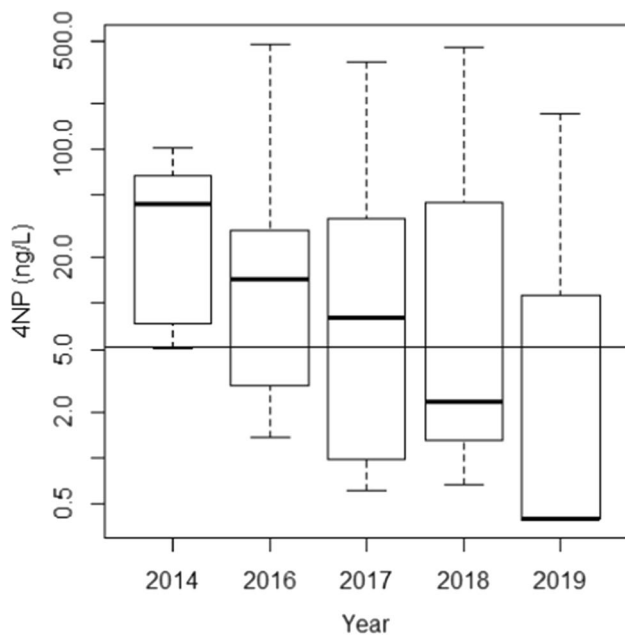
Fig. 3 Concentrations of NP in surface waters as a function of years. The median is shown as the line in the middle of the boxes, while the first and third quartile are the end of both sides of the boxes. The minimum and maximum values are represented at the tip of each lines. The straight line is the highest detection limit of the dataset (5 ng/L)

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 111–477 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 orders of magnitude over time at several sampling sites (Tables 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

Table 5 Concentration range or individual values of alkylphenols at Canadian sites with historical data

Site name (province)	Years	NP (ng/L)	NP_1EO (ng/L)	NP_2EO (ng/L)	OP (ng/L)	References
St Victor (QC)	1991–1998	2700–3300	5800–9300	48,900–506,000	1900–8500	Bennie et al. (1997, 1998, 2003)
St Victor (QC)	2009–2010	< 100	N/a	N/a	20	Berryman et al. (2012)
Grand River (ON) (Galt WWTP)	1991–1998	69–1500	120–1500	160–860	< 5–77	Bennie et al. (1997, 1998, 2003)
Hamilton Harbour 1001 (ON)	1991–1998	19–380	360–1100	< 20–400	13–36	Bennie et al. (1997, 1998, 2003)
Niagara-on-the-Lake (ON)	1991–1998	< 10	< 20	< 20	< 5	Bennie et al. (1997, 1998, 2003)
Hamilton Harbour 914 (ON)	1991–1998	860–980	780	950	82–96	Bennie et al. (1997, 1998, 2003)
St Lawrence R. (QC)	1991–1998	< 10	110–150	< 20–23	< 5	Bennie et al. 1997, 1998, 2003
St Lawrence R. Lavaltrie (QC)	2009–2010	< 100	N/a	N/a	11	Berryman et al. (2012)
Credit River (ON)	1991–1998	10–9430	110–1800	130–10,000	< 5–10	Bennie et al. (1997, 1998, 2003)
Princeville (Rivière Blanche) (QC)	2009–2010	100	N/a	N/a	10	Berryman et al. (2012)

QC Québec, *ON* Ontario

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 m^3/s) at these sites. Two sites (Lavaltrie and Princeville) had detections NP_1EO and NP_2EO 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.

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 to 3330 ng/L in 1991–1998 to a median of 0.4 ng/L in 2016–2018 (Table 5). NP_1EO was not even detected at that site in our study, whereas NP_2EO and OPs showed similar large concentration decreases of multiple orders of magnitude (Tables 3 and 5). These declines in alkylphenol concentrations since the 1990s 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 (Tables 5 and 6). The majority of studies show a sharp decline in all alkylphenolic compounds in the past 15–20 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.

Conclusions

This study included 241 samples for the analysis of NP/NPEs from 35 locations throughout Canada. The high proportion of nondetect values of these substances (18–65%) might be attributed to the government of Canada's risk

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

Sources	NP (ng/L)	NP_1EO (ng/L)	NP_2EO (ng/L)	OP (ng/L)	References
Canada					
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 (2nd treat)	90–3560 (2.41)	1120–4100 (1.2)	930–3920 (1.2)		EC (2001)
MWWTP-1	< 20–6208	70–56,130	340–36,330		EC (2001)
MWWTP-2	120–4790	20–43,370	< 20-32,620		EC (2001)
MWWTP-3	< 20–3200	30–26,400	250–12,450		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)
International					
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 (1–11,000)	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)

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 also have 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 and HC 2001). In addition, both Lee et al. (2013) 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.

Compliance with ethical standards

References

AXYS (2017) Summary of SGS AXYX method MLA-004 Rev 07 Ver05: analytical method for the determination of 4-n-octylphenol, 4-nonylphenol and 4-nonylphenolethoxylates by GC/MS. Sidney, BC

Bennett ER, Metcalfe CD (2000) Distribution of degradation products of alkylphenol ethoxylates near sewage treatment plants in the lower Great Lakes, North America. Environ Tox Chem 19(4):784–792

Bennie DT, Sullivan CA, Lee HB, Peart TE, Maguire RJ (1997) Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River. Sci Total Environ 193:263–275

Bennie DT, Sullivan CA, Lee HB, Maguire RJ (1998) Alkylphenol polyethoxylate metabolites in Canadian sewage treatment plant waste streams. Water Qual Res J Canada 33(2):231–252

Bennie DT, Sullivan CA, Maguire RJ (2003) Occurrence of alkylphenols in Canada: a report on concentrations found in rivers, lakes, industrial effluents and municipal effluents. Branch Tech Note. AEP-TN03-001

Berryman D, Sarrasin B, DeBlois C (2012) Diminution des concentrations de nonylphénols éthoxylés dans les cours d'eau du Québec méridional de 2000 à 2010. Ministère du Développement Durable, de l'Environnement et des Parcs. ISBN 978-550-65652-4

Canadian Council of the Ministers of the Environment (CCME) (2002) Canadian water quality guidelines for the Protection of Aquatic Life. Nonylphenol and its ethoxylates. http://ceqg-rcqe.ccme.ca/download/en/198. Accessed Oct 2020

Environment Canada (2004) Risk management strategy for nonylphenol and its ethoxylates under CEPA (1999). http://publications.gc.ca/site/eng/462251/publication.html. Accessed Oct 2020

Environment Canada (2007) Progress report—P2 planning and textile mills that use wet processing. https://ec.gc.ca/planp2-p2plan/default.asp?lang=En&n=3944D8AC-1. Accessed Oct 2020

Environment Canada (2016) Pollution prevention planning for nonylphenol and its ethoxylates in products: final evaluation report. https://www.ec.gc.ca/planp2-p2plan/default.asp?lang=En&n=54EE64B2. Accessed Oct 2020

Environment Canada and Health Canada (2001) Priority substances list assessment report for nonylphenol and its ethoxylates. ISBN: 0-662-29248-0. Cat. No.: En40-215/57E. https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/environmental-contaminants/canadian-environmental-protection-act-1999-priority-substances-list-assessment-report-nonylphenol-ethoxylates.html. Accessed Sept 2020

Environmental Protection Agency (EPA) (2006) Aquatic life ambiant water quality—Nonylphenol-Final. EPA-822-F05-003

Environmental Protection Agency (EPA) (2014) Significant new use rules: certain nonylphenols and nonylphenol ethoxylates. EPA-HQ-OPPT-2007-0490. Federal Register of October 1, 2014 [79 FR 59186] [FRL-9912-87]

Gauthier K, Berryman D, Dubreuil G, Sarrasin B, Deblois C, Van Coillie R (2013) Le nonylphénol et ses dérivés éthoxylés: une réussite dans leur élimination du milieu récepteur. http://www.mddelcc.gouv.qc.ca/eau/eco_aqua/nonylphenol/article-nonylphenol-derives-ethoxyles201301.pdf. Accessed Oct 2020

Gong J, Huang Y, Huang W, Ran Y, Chen D (2016) Multiphase partitioning and risk assessment of endocrine-disrupting chemicals in the Pearl River, China. Environ Toxicol Chem 35(10):2474–2482

Gorga M, Insa S, Petrovic M, Barcelo D (2015) Occurrence and spatial distribution of EDCs and related compounds in waters and sediments of Iberian rivers. Sci Total Environ 503–504:69–86

Helsel D (2005) Nondetects and data analysis: statistics for censored environmental data. Wiley, Hoboken

Helsel D (2012) Statistics for censored environmental data using Minitab and R, 2nd edn. Wiley, Hoboken

Helsel D, Lee L (2006) Analysis of environmental data with nondetects. In: Statistical methods for censored environmental data. ASA Workshop, Seattle, Washington. https://www.practicalstats.com/nada/downloads.html. Accessed Oct 2020

Hong Y, Feng C, Yan Z, Wang Y, Liu D, Liao W, Bai Y (2020) Nonylphenol occurrence, distribution, toxicity and analytical methods in freshwater. Environ Chem Lett 18:2095–2106

Hull RN, Kleywegt S, Schroeder J (2015) Risk-based screening of selected contaminants in the Great Lakes Basin. J Great Lakes Res 41:238–245

Klecka G, Persoon C, Currie R (2010) Chapter 1. Chemicals of emerging concern in the Great Lakes Basin: an analysis of environmental exposure. Rev Environ Contam Toxicol 207:1–93

Komori K, Okayasu Y, Yasojima M, Suzuki Y, Tanaka H (1997) Occurrence of nonylphenol ethoxylate surfactants and nonylphenol carboxylic acids in wastewater in Japan. Water Sci Technol 53(11):27–33

Lee HB, Peart TE (1995) Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. Anal Chem 67:1976–1980

Lee CC, Jiang LY, Kuo YL, Hsieh CY, Chen CS, Tien CJ (2013) The potential role of water quality parameters on occurrence of nonylphenol and BPA and identification of their discharge sources in the river ecosystems. Chemosphere 91:904–911

Liu YH, Zhang SH, Ji GX, Wu SM, Guo RX, Cheng J, Yan ZY, Chen JQ (2017) Occurrence, distribution and risk assessment of suspected endocrine-disrupting chemicals in surface water and suspended particulate matter of Yangtze River (Nanjing section). Ecotoxicol Environ Saf 135:90–97

Loos R, Wollgast J, Castro-Jiménez J, Mariani G, Huber T, Locoro G, Hanke G, Umlauf G, Bidoglio G, Hohenblum P, Moche W, Weiss S, Schmid H, Leiendecker F, Ternes T, Navarro Ortega A, Hildebrandt A, Barceló D, Lepom P, Dimitrova I, Nitcheva O, Polesello S, Valsecchi S, Boutrup S, Sortkjaer O, de Boer R, Staeb J (2008) Laboratory intercomparison study for the analysis of nonylphenol and octylphenol in river water. Trends Anal Chem 27(1):89–95

Mergel M (2014) Nonylphenol and nonylphenol ethoxylates. Toxipedia.org. N.p., 1 Nov 2011. Web. 27 Apr. 2014

OSPAR (2006) OSPAR background document on octylphenol. https://www.ospar.org/about/publications. Accessed June 2020

Sabik H, Gagné F, Blaise C, Marcogliese DJ, Jeanoot R (2003) Occurrence of alkylphenol polyethoxylates in the St Lawrence River and their bioconcentration by mussels (*Elliptio complanata*). Chemosphere 51:349–356

Salgueiro-Gonzales N, Concah-Grana E, Turney-Carou I, Muniategui-Lorenzo S, Lopez-Mahia P, Prada-Rodriguez D (2012) Blank and sample handling troubleshooting in ultra-trace analysis of alkylphenols and bisphenol A by liquid chromatography tandem mass spectrometry. Talanta 101:413–419

Servos MR, Maguire RJ, Bennie DT, Lee HB, Cuveton PM, Davidson N, Sutcliffe R, Rawn DFK (2000) Canadian Environmental Protection Act—priority substances list supporting document for the environmental assessment of nonylphenol and its ethoxylates. Commercial Chemicals Evaluation Branch, Hull, QC

Shah A, Smyth SA (2013) Alkylphenols in Canadian municipal wastewater and biosolids. Internal Report to Chemical Management Plan (CMP), Research and Monitoring Section, Science and Risk Assessment Directorate. Environment and Climate Change Canada, Ottawa

Soares A, Guieysse B, Jefferson B, Cartmell E, Lester JN (2008) Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ Int 34:1033–1049

Stottmeister E, Heemken OP, Hendel P, Donnevert G, Frey S, Allmendinger H, Sawal G, Jandel B, Geiss S, Donau R, Kock A, Heinz I, Ottaviani M, Veschetti E, Hartl W, Kubwabo C, Benthe C, Tobinski V, Woldmnn H, Spilker R (2009) Interlaboratory trial of the analysis of alkylphenols, alkylphenol ethoxylates, and bisphenol A in water samples according to ISO/CD 18857-2. Anal Chem 81:6765–6773

Tabe S, Pileggi V, Nowierski M, Kleywegt S, Yang P (2016) Occurrence, removal, and environmental impacts of emerging contaminants detected in water and wastewater in southern Ontario—part 1: occurrence and removal. Water Pract Technol 11(2):298–314

Vanderford BJ, Drewes JE, Eaton A, Guo YC, Haghani A, Hoppe-Jones C, Schluesener MP, Snyder SA, Ternes T, Wood CJ (2014) Results of an interlaboratory comparison of analytical methods for contaminants of emerging concern in water. Anal Chem 86(1):774–782

Wang L, Ying GG, Zhao JL, Liu S, Yang B, Zhou LJ, Tao R, Su HC (2011) Assessing estrogenic activity in surface water and sediment of the Liao River system in northeast china using combined chemical and biological tools. Environ Pollut 159:148–156