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THE OCCURRENCE OF ALKYLPHENOLS IN CANADA: A REPORT ON CONCENTRATIONS FOUND IN RIVERS, LAKES, INDUSTRIAL EFFLUENTS AND MUNICIPAL EFFLUENTS

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The Occurrence of Alkylphenol Polyethoxylates in Canada: A report on concentrations found in rivers, lakes, industrial effluents and municipal effluents

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Preamble

Prior to the placement of nonylphenol and its ethoxylates on the second Priority Substance List (PSL 2) under the Canadian Environmental Protection Act (CEPA), a large number of samples were collected from a wide variety of Canadian sources and matrices to be analyzed for their alkylphenolic content. The data show that effluents from municipal wastewater treatment plants (WWTPs) seem to have a high abundance of alkylphenolics present, with alkylphenoxy carboxylic acids (APnECs) being particularly high. Textile mill effluents presented extremely high levels of alkylphenol ethoxylate (APE) concentrations. Sludge samples from WWTPs showed high concentrations of 4-nonylphenol (4-NP) and the lower ethoxylate oligomers, nonylphenol ethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO). But levels in surface waters from lakes, rivers, creeks and harbours were relatively low except where sites were heavily impacted by WWTP discharges or high industrial inputs to the receiving environment.

Préambule

Avant l'inscription du nonylphénol et de ses dérivés éthoxylés sur la seconde liste de substances d'intérêt prioritaire (LSIP 2) selon les dispositions de la *Loi canadienne sur la protection de l'environnement* (LCPE), un grand nombre d'échantillons avaient été prélevés dans une vaste gamme de sources et de matrices canadiennes en vue de les analyser pour déterminer leur teneur en composés alkylphénoliques. Les données montrent que les effluents des stations municipales de traitement des eaux usées (SMTEU) semblent contenir de grandes quantités d'alkylphénoliques, celles d'acides alkylphénoxycarboxyliques étant particulièrement élevées. Les effluents d'usines textiles renfermaient des teneurs extrêmement fortes d'alkylphénol éthoxylé. Les échantillons de boue de SMTEU présentaient des concentrations élevées de 4-nonylphénol (4-NP) et d'oligomères éthoxylés inférieurs, soit le nonylphénol éthoxylé (NP1EO) et le nonylphénol diéthoxylé (NP2EO). Mais, les concentrations dans les eaux de surface de rivières, de lacs, de ruisseaux et de ports étaient relativement faibles, excepté aux endroits fortement soumis aux effets des rejets des SMTEU ou à d'importants déversements industriels dans le milieu récepteur.

Introduction

Alkylphenol polyethoxylate surfactants (APEs) are commonly used in various industrial, commercial, institutional and consumer applications. They are relatively inexpensive and efficient nonionic surfactants. Canadian consumption of these substances amounted to 19,000 tonnes in 1996 (Environment Canada and Health Canada, 2001). As a direct consequence of their widespread use patterns, these substances can be found in various effluent streams that enter municipal wastewater treatment plants (WWTPs) before entering the receiving environment. While these substances are being subjected to the various wastewater treatment processes, they are degraded to more recalcitrant and toxic metabolites - namely alkylphenols (APs), alkylphenoxy carboxylic acids (APnECs) and lower alkylphenol ethoxylates. Recent reports suggest that these substances will ultimately degrade to CO_2 under aerobic conditions (Staples et al., 2002).

There have been numerous studies in which data have been collected on the concentrations of the various alkylphenolics in aquatic life, natural surface waters, wastewater treatment plant (WWTP) influents and effluents, WWTP sludge (or biosolids) and sediments. A reasonably complete summary of these references and data can be found in Bennie (1999). Over the past ten years, there has been substantial interest in the levels of alkylphenolics and their effects on the health of aquatic organisms, terrestrial organisms and humans. Several papers have addressed the issue of endocrine disruption potential of 4-nonylphenol (4-NP), 4-*tert*-octylphenol (4-*t*-OP), and nonylphenol ethoxylates (NPEs) and nonylphenoxyacetic acid (NP1EC)

(Soto et al., 1991; Jobling and Sumpter, 1993; White et al., 1994; Sharpe et al., 1995; Jobling et al., 1996; Gray and Metcalfe, 1997; Ashfield et al.). To address the need for information on this topic and to discern if there were any toxicological concerns in Canada, nonylphenol and its ethoxylates were placed on the second CEPA Priority Substances List (PSL 2) by the Ministers' Expert Advisory Panel (1995). The data to be presented in this report had, for the most part, already been accumulated and formed the backbone of the data set used in the supporting document for the nonylphenol assessment (Servos et al., 2000) and the subsequent final assessment report entitled "Canadian Environmental Protection Act (1999), Nonylphenol and Its Ethoxylates (Priority Assessment List Report)" (Environment Canada and Health Canada, 2001). In this report, it was determined that "nonylphenol and its ethoxylates are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long term effect on the environment or its biological diversity." (Environment Canada and Health Canada, 2001, pp 14.). As such, these substances are designated as "CEPA toxic" and are subject to risk management steps which have yet to be determined.

Sample collection for this set of data started in 1991 and extended to 1998. It includes several groups of data which are to be the covered in more detail in upcoming reports and manuscripts. However, it was thought that since the data had already been used in the CEPA PSL 2 process and had been disseminated publicly through various presentations that the original material should be made available in a public report.

Materials and Methods

Chemicals and Standards

Acetic anhydride, 4-NP, 4-*t*-OP, and boron trifluoride/methanol complex (12%) were obtained from Aldrich (Milwaukee, WI, USA). A calibrated mixture of nonylphenol polyethoxylates with zero to seventeen ethoxy units was generously provided by Dr. C. Naylor of Huntsman Corp., Austin, TX. Standards of NP1EC and OP1EC were synthesized in-house as described in Lee et al. (1998). Formaldehyde solution (37-40%, AnalaR® grade) was obtained from BDH Laboratory Supplies (BDH Inc., Toronto, ON, Canada). All organic solvents used for extractions and cleanup were pesticide grade and high performance liquid chromatographic determinations were performed with HPLC grade solvents purchased from Caledon Laboratories (Georgetown, ON, Canada). HPLC grade water was purchased from Fisher Scientific (Nepean, ON, Canada). Organic-free water for extractions and blanks was obtained by purification of reverse osmosis-treated water through a Milli-Q water system (Millipore Canada Ltd., Nepean, ON, Canada).

Sampling Sites

Water and final effluent samples were collected from 26 natural water sources (i.e. lakes, harbours, creeks and rivers), 11 textile mills, 13 pulp and paper mills, one oil sands extraction plant and 28 municipal wastewater treatment plants (WWTPs) across Canada from 1991 to 1998. Sediment samples collection took place at 2 sites (Grand River and Hamilton Harbour). Digested sludge samples were also collected from some of the WWTPs at the same time as the effluent sampling. The 28 Canadian municipal

WWTPs represented a wide range of process types, and design loading rates for a given process.

Sample Collection

In the early stages of this study, grab sample collection was utilized to obtain an instantaneous snapshot of the conditions at a particular sampling location. Later in the study, daily 24-hour bulk composite samples were collected at WWTPs and industrial sources to obtain more relevant temporal trends in concentrations. Composite samples of final treated effluent were collected in pre-cleaned stainless steel canisters using Isco 6700FR refrigerated automatic samplers (Isco, Inc., Lincoln, Nebraska, USA) at all sites that utilized continuous flow conditions. Sample temperature in the automatic samplers was maintained at 4 °C during effluent collection. Single grab samples of wastewater were collected from the continuous discharge aerated lagoon system. All sludge samples were collected as single daily grab samples. Field duplicates were taken on occasion for QA/QC purposes and represented about 10% of the total number of samples analyzed. Water blanks were also collected periodically for chemical analysis and this involved the collection of reverse-osmosis filtered water into a pre-cleaned stainless steel canister using an automatic sampler and pre-cleaned tubing. Before the bulk samples were split into aliquots for preservation, the pH of the wastewater was measured. After thorough mixing of bulk composite sample, wastewater samples for organic analysis were immediately transferred to 1 L new, pre-cleaned amber glass bottles with Teflon-lined caps. Aliquots for alkylphenolic analysis were preserved by the addition of formaldehyde (1%, v/v). Sludge sample aliquots were preserved for

alkylphenolic analysis by the addition of formaldehyde (2%, v/v). In our laboratories, all water and wastewater samples were stored at 4 °C until extraction. Water and wastewater samples to be analyzed for alkylphenolics were then filtered using pre-cleaned glass fibre filters (nominal pore size 1 μm). The use of filtered samples is based on the assumption that the amount of alkylphenolics associated with suspended solids in raw sewage and treated final effluents is minor (Brunner et al., 1988). Sample aliquots for alkylphenol and alkylphenolic carboxylate analysis were acidified with sulphuric acid to pH 2. Sludge and sediment samples were air dried in a fume hood at ambient room temperature (~22 °C). After drying, the samples were ground using a Micro-Mill grinding mill (Bel-Art Products, Pequannock, New Jersey, USA) and passed through a 30-mesh sieve (600 μm). Dried and sieved sludge and sediment samples were then stored in amber glass jars with Teflon-lined caps in a freezer at -20 °C until extraction.

Alkylphenolic Extraction and Analysis

Alkylphenolic extractions, clean up steps and derivatizations for effluent and sludge samples were performed as outlined in Lee and Peart (1995), Lee et al. (1997), Lee et al. (1998) and Bennie et al. (1998). The less polar acetyl derivatives of 4-NP and 4-*t*-OP were used in our 4-NP/4-*t*-OP analysis for several reasons. First, the acetates offer better chromatographic separation of the 4-NP isomers than underivatized 4-NP, the acetate detection limit is about 4 times lower in SIM GC-MSD mode and, when dealing with highly contaminated sludge, the derivative is more readily

separated from more polar co-extractives by silica gel column clean up (Lee and Peart, 1995).

Derivatized sample extracts were analyzed for 4-NP and 4-*t*-OP using a Hewlett-Packard (HP) 5971 mass selective detector (MSD) interfaced to an HP 5890 Series II gas chromatograph (Hewlett-Packard (Canada) Ltd., Mississauga, ON, Canada). Samples were injected via splitless mode onto a 30 m x 0.25 mm id. x 0.25 mm DB5-MS fused silica capillary column (J&W Scientific Inc., Folsom, CA, USA). The GC oven temperature program was as follows: 70 °C for 1 min, 70 °C to 160 °C at 30 °C/min and thence to 240 °C at 5 °C per minute. The quantitative analysis for 4-NP acetates was carried out in the SIM mode by monitoring the ions at *m/z* 107, 121, 135, 163, 191 and 262. The monitored SIM ions for the determination of 4-*t*-OP acetate were *m/z* 135, 177 and 248. Calibration standards were produced by acetylation of 10 mg of 4-NP and 4-*t*-OP in 30 mL of K_2CO_3 in the presence of acetic anhydride in the same manner as described above for the water samples. The acetylated products were diluted to a concentration of 1 µg/mL 4-NP and 0.1 µg/mL 4-*t*-OP in hexane for SIM GC-MSD analysis and quantitation. Sample extracts were quantified by the external standard method using the response factors generated by the acetylated 4-NP and 4-*t*-OP standards. It had been determined that response factors for the 4-NP and 4-*t*-OP constituents were linear up to at least the level mentioned above. The observation of the *m/z* 262 ion was used for confirmation of the presence of 4-NP while *m/z* 248 was used for 4-*t*-OP confirmation.

With the exception of the ions monitored, the same GC/MS conditions were also utilized for the analysis of the derivatized APnEC sample extracts. These extracts were

analyzed for nonylphenoxyacetic acid (NP1EC), nonylphenoxyethoxyacetic acid (NP2EC), octyphenoxyacetic acid (OP1EC) and octylphenoxyethoxyacetic acid (OP2EC). The monitored ions for APnECs were as follows: *m/z* 207, 221 and 292 for NP1EC; *m/z* 117, 265, 307 and 336 for NP2EC; *m/z* 207, 208 and 278 for OP1EC; and *m/z* 117, 251 and 322 for OP2EC. External quantitation standard methods were used for the quantitation of APnECs. However, due the lack of authentic standards for NP2EC and OP2EC, response factors generated for NP1EC and OP1EC were used to estimate the concentrations of the AP2EC components. It had been determined that response factors for the APnEC constituents were linear up to at least the level of 1 μg/mL NP1EC and 0.1 μg/mL OP1EC.

Analyses for NPEs were performed with an HP 1050 normal phase high performance liquid chromatography system utilizing fluorescence detection (excitation λ = 230 nm; emission λ = 300 nm) and normal phase HP APS Hypersil column (100 mm x 2.1 mm id.). The NPEs that were characterized included nonylphenol ethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO) and nonylphenol polyethoxylates with 3 to 17 oligomer groups (NP3-17EO). Chromatographic conditions for the separation of the NPEs were derived from the methods published by Ahel and Giger (1985b) and Marcomini and Giger (1987). The following solvent mixtures were used to separate the NPE oligomers: solvent A was n-hexane/2-propanol (98:2, v/v) and solvent B was 2-propanol/water (9:1, v/v). The solvent gradient employed was 97% A and 3% B for the first three minutes of each run, linearly programmed to 43% A and 57% B over the next 22 minutes, followed by a post-run equilibrium of 15 minutes between injections. Quantitative results were obtained using the external standard method from response

factors generated from the NPE standard solutions. It was previously determined that the fluorescence detector response to NPE standard solutions were linear at concentrations up to and including that level.

Results and Discussion

A large number of hitherto unpublished Canadian alkylphenolic data can be found in Appendices 1 to 6 at the end of this report. The data has also been summarized and can be found in Tables 1, 2, and 3.

It can be concluded from looking at Table 1 that the 11 sampled textile mills are significant contributors of nonylphenol polyethoxylates to the Canadian environment and also contribute a significant loading to municipal wastewater treatment plants that receive these types of effluents. Levels of total APEs (sum of all AP + APnEC + NPnEO concentrations reported) in untreated effluents discharged directly to the environment ranged from about 1670 µg/L to 9400 µg/L. However, at plants where onsite secondary treatment is utilized, the amount of total APEs discharged is somewhat lower with levels ranging from 7.9 µg/L to ~2200 µg/L. The amount of 4-NP discharged is similar regardless of the treatment or lack of treatment utilized. Concentrations of 4-NP discharged directly to rivers ranged from <0.090 µg/L to13 µg/L. From this one can conclude that 4-NP is a significant component of the NPEs used as dye carriers. It is also noteworthy that, as expected, the average APnEC concentrations at the secondary-treated textile effluent sites are elevated relative to the untreated textile effluents. Secondary waste treatment processes are known to degrade APEs significantly, resulting in elevated levels of APnECs and APs. Levels of the known endocrine disrupting substance 4-*t*-OP discharged to the environment were one to two orders of magnitude lower in textile mill waste treated onsite relative to untreated discharged waste.

Data found in Appendix 2 and summarized in Table 1 show the contribution by effluents from 12 pulp and paper mills and one oil sands extraction plant to the Canadian environment. Most pulp and paper mills discharged little or no APE substances. There appear to be some anomalies in the NP1EO and NP2EO data where at times there are detectable levels of NP1EO but no detectable levels of NP2EO. An extreme example of this anomaly can be found in the data from the Malette Kraft mill at Smooth Rock Falls, ON where NP1EO levels are 1580 µg/L and 3780 µg/L but no NP2EO was detected. This is unusual and no explanation for this anomaly could be determined. Dramatically different day to day results have also been found at some mills. No viable explanation was found for this variance other than the fact that the samples collected were grab samples and offer just a very narrow snapshot in time of the effluent composition being discharged. Each sample result shown in the Appendix represents a different day's sampling so there may also be differences attributable to slight changes in the plants' day-to-day process operations. Significant levels of 4-NP were found in effluents from mills in Edmunston, NB, Hinton, AB, and Terrace Bay, ON. The elevated results at the Hinton mill cannot be totally attributable to the pulp and paper mill however as the mill's waste treatment facility also processes the municipal wastewater from the Town of Hinton.

The 9 municipal wastewater treatment plants (WWTPs) that use only primary treatment contribute significant concentrations of APEs to our lakes and rivers and the major constituent is NP3-17EO (see Table 2 and Appendix 3). Levels of total APEs in primary effluents ranged from 1.6 µg/L to 864 µg/L while NP3-17EO contributions ranged from 4.8 µg/L to 735 µg/L with a mean of 171 µg/L for the 19 samples. Analysis

of 4-NP was completed at every plant and results varied from <0.050 µg/L to 62 µg/L, APnEC analysis was not done on most of these samples since a viable methodology was not available at the time of sampling at the majority of the plants. Highest levels of APEs were found in municipalities that have significant textile mill industries contributing to their waste influent streams.

Fifteen municipal WWTPs utilizing secondary wastewater treatment were sampled over the years (Table 2 and Appendix 3). All plants except one (Winnipeg) use the secondary activated sludge process. Winnipeg's plant utilized rotating biological contactors for its secondary treatment. Concentrations of total APEs found in these final effluent streams ranged from 0.030 µg/L to 171 µg/L. However, many of the samples from lower level plants did not have NP3-17EO or APnEC analysis completed. The analysis of APnECs is critical to determining the loading of APEs to the environment, especially from secondary WWTPs, since these plants tend to increase the levels of APnECs in the sewage streams as the sewage goes through the treatment process. The activated sludge process in particular tends to break down APEs with the concomitant rise in APnEC concentrations. It is significant to note that the samples where APnEC analysis was completed show these substances to be the major alkylphenolic constituents in the discharged effluent.

The four tertiary WWTPs found in Table 2 and Appendix 3 also show similar results to the secondary activated sludge WWTPs mentioned previously. The data from the two frequently sampled plants show a remarkable consistency in their effluent quality. Total APE concentrations in effluents from Guelph and Edmonton ranged from 12 µg/L to 144 µg/L. The major constituents of these effluent streams were again the

APnECs with the NP2EC and OP2EC being the dominant oligomers. Levels of 4-NP discharged from these plants were all lower than 1 µg/L.

The NP1EO and NP2EO concentrations in all the WWTP effluents may be disturbing from an endocrine disruption point of view as well. Mean concentrations of NP2EO in primary, secondary and tertiary plants were 9.4 µg/L, 2.7 µg/L and 1.9 µg/L, respectively, while mean concentrations of NP1EO in the same plants were 12 µg/L, 3.5 µg/Land 2.5 µg/L, respectively. NP2EO has been found to have a similar endocrine disrupting potential as 4-NP (Jobling and Sumpter, 1993) and it is not unreasonable to assume that the NP1EO has a similar endocrine disrupting properties to NP2EO. Therefore the endocrine disrupting potential of these effluents may be more problematic than previously thought.

Concentrations found in the final effluents of these primary, secondary and tertiary WWTPS are comparable to those found in other studies by Ahel and Giger (1985a), Ahel et al. (1987), Brunner et al. (1988), Marcomini et al. (1988a), Kubeck and Naylor (1990), Di Corcia et al. (1994), Blackburn and Waldock (1995), and numerous other authors.

One WWTP that used lagoon treatment was sampled in the early years of this study. Data from this plant are found in Appendix 3. The 4-NP concentration in this one sample was 2.2 µg/L but due to the lack of corroborating sampling and more comprehensive analyses, the significance of this data is not known.

Data from 130 surface water samples can be found in Appendix 4 and are summarized in Table 2. Only 6 samples showed 4-NP concentrations of >1.0 µg/L, i.e. 2 samples from the Grand River in Cambridge, ON and the other 4 samples from the

Red Hill Creek in Hamilton, ON. The significance of the Red Hill Creek samples is questionable due to the lack of NP3-17EO and APnEC data. The two Grand River samples were taken very close to the Galt WWTP in Cambridge, ON, a plant with significant influent loadings from 4 textile mills. Most of the natural water samples were taken from the Grand River and the Athabasca River in Alberta. The Grand River samples are affected, as mentioned previously, by the Cambridge-Galt WWTP but these levels diminish to very close to background levels within 4 km of the WWTP discharge. The Athabasca River samples were collected during the same time frame as the 5 pulp/paper mill and oil sands extraction plant effluent samples in Alberta were taken. The purpose was to determine the alkylphenolic impacts of these plants on the river. There were no detectable levels of 4-NP and 4-*t*-OP in the Athabasca River at that time. Samples collected from harbours on the Great Lakes and rivers draining into those waters were sampled very early in the study. Consequently, several parameters were not analyzed due to lack of viable analytical methodologies. However, from the little data that is present, it appears that Hamilton Harbour and Toronto Harbour are the only areas of the Great Lakes that have any significant alkylphenolic concentrations. Both of these harbours are drainage areas for major metropolitan areas with numerous WWTPs and a large variety of commercial and industrial inputs. These surface water data are similar to that collected by Naylor et al. (1992) in their study of alkylphenolics in numerous American rivers.

Sediment samples are far more limited in numbers and sparse data are shown from just 2 geographic areas in Ontario: the Grand River downstream of the Galt WWTP and Hamilton Harbour. These data are found in Appendix 5 and are

summarized in Table 3. One Hamilton Harbour site which was located at the effluent discharge pipe for the Burlington Skyway WWTP showed elevated APE concentrations. The Grand River sites show the influence of the effluent discharge from the Galt WWTP but only for the hydrophobic substance, 4-NP.

Also found in Table 3 is a summary of the sludge data generated from the 9 WWTPs, the raw data for which can be found in Appendix 6. With the exception of Granby, all the plants utilize secondary activated sludge treatment for their wastewater. The Granby plant uses only primary clarification. From the data, it can be seen that significant levels of APEs are discharged in the watery sludge material that is hauled away from these plants. Total APE levels range from 154 µg/g to over 1100 µg/g of which the major component is 4-NP. Average and median levels for 4-NP in dried sludge samples were 279 µg/g and 212 µg/g, respectively. Data from these Canadian WWTPs is comparable to data collected from Swiss STPs (Marcomini et al. 1988a), German STPs (Jobst, 1995) and UK STPs (Waldock and Thain, 1986). These elevated levels of 4-NP raise questions about the methods used to dispose of sludge and the potential for this substance to find its way into the environment. The levels of lower ethoxylate oligomers in sludge could also be significant. Concentrations of NP1EO ranged from 3 µg/g to 332 µg/g with mean and median concentrations of 97 µg/g and 80 µg/g, respectively. The levels of NP2EO were somewhat lower with a range of 4.8 µg/g to 297 µg/g and mean and median concentrations of 31 µg/g and 20 µg/g, respectively. The levels of these substances beg the questions: when these materials are applied to agricultural land as an amendment, will the lower ethoxylate oligomers

degrade further into the more toxic 4-NP and how long will these substances remain in soils before being completely degraded?

In conclusion, a large number of samples were collected from a wide variety of sources and matrices to be analyzed for their alkylphenolic content. Effluents from WWTPs seem to have a high abundance of alkylphenolics present, with APnECs being particularly high. Textile mill effluents presented extremely high levels of APE concentrations. Sludge samples from WWTPs showed high concentrations of 4-NP and the lower ethoxylate oligomers, NP1EO and NP2EO. But levels in surface waters from lakes, rivers, creeks and harbours were relatively low except where sites were heavily impacted by WWTP discharges or high industrial inputs to the receiving environment.

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Table 1. Summary of alkylphenolic results in various industry effluent streams.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Textile mill effluents discharged directly to rivers									
n (number of samples analyzed)	5	5	5	5	2	2	5	2	2
Minimum	2.7	37	106	798	0.45	0.45	1.9	0.68	1.3
Median	10	58	489	7905	0.45	0.45	3.8	0.76	1.9
Maximum	13	257	592	8811	0.45	0.45	9.0	0.83	2.5
Average	8.2	99	362	6044	0.45	0.45	5.4	0.76	1.9
Textile mill effluents receiving onsite secondary treatment									
n (number of samples analyzed)	5	5	3	5	5	5	5	5	5
Minimum	<0.09	0.52	0.25	2.1	<0.45	<0.45	<0.015	<0.045	<0.045
Median	0.61	4.1	0.93	84	1.0	3.4	0.059	0.050	0.045
Maximum	3.6	1870	3.9	315	5.2	55	0.22	0.43	12
Average	1.1	635	1.7	122	2.2	13	0.090	0.16	2.4
Textile mill effluents discharged to municipal WWTPs									
n (number of samples analyzed)	15	15	15	15	9	9	15	9	9
Minimum	0.23	0.74	0.64	50	<0.45	<0.45	<0.015	<0.045	<0.045
Median	2.8	18	39	1828	0.45	0.45	0.18	0.045	0.045
Maximum	26	69	285	6848	2.8	6.9	1.2	0.15	0.95
Average	5	26	119	2478	1.0	1.5	0.31	0.061	0.15
Pulp/paper/other industrial effluents discharged directly to rivers									
n (number of samples analyzed)	33	32	33	0	0	0	29	0	0
Minimum	<0.050	0.020	<0.050				<0.005		
Median	0.050	3.9	0.050				<0.005		
Maximum	26	3780	68				<0.005		
Average	3.7	206	6.4				<0.005		

Table 2. Summary of alkylphenolic results in natural surface waters and wastewater treatment plant effluents.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-t-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Primary-treated final wastewater treatment plant effluents									
n (number of samples analyzed)	21	23	23	19	4	4	21	4	4
Minimum	<0.050	0.072	0.34	4.8	1.2	1.0	<0.015	0.15	0.20
Median	1.8	3.0	4.4	35.1	3.7	3.0	0.18	0.31	0.32
Maximum	62	56	36	735	11	5.2	1.2	0.46	0.37
Average	8.5	12	9.4	171	4.9	3.0	0.33	0.31	0.30
Secondary-treated final wastewater treatment plant effluents									
n (number of samples analyzed)	35	27	27	17	15	15	35	15	15
Minimum	<0.050	<0.020	<0.020	<2.0	9.0	10	<0.015	2.6	2.1
Median	0.58	1.1	1.1	6.4	16	23	0.060	5.8	5.8
Maximum	4.8	43	33	53	75	45	0.57	10	13
Average	1.0	3.5	2.7	12	25	24	0.12	6.2	5.7
Tertiary-treated final wastewater treatment plant effluents									
n (number of samples analyzed)	17	17	17	15	14	14	17	14	14
Minimum	<0.050	0.63	0.25	0.51	4.2	24	<0.015	0.49	3.2
Median	0.25	1.7	1.9	3.1	11	46	0.025	1.6	5.5
Maximum	0.85	6.9	5.4	13	49	82	0.28	29	9.0
Average	0.29	2.5	1.9	4.8	19	48	0.040	3.6	5.8
Natural surface waters from rivers and lakes									
n (number of samples analyzed)	130	84	84	35	46	46	130	46	46
Minimum	<0.010	<0.020	<0.020	0.11	0.44	0.65	<0.005	0.066	0.059
Median	0.074	0.15	0.14	0.50	2.3	2.5	0.005	0.35	0.21
Maximum	4.3	10	10	18	15	41	0.61	0.89	0.90
Average	0.23	0.60	0.36	1.3	2.8	5.2	0.027	0.36	0.23

Table 3. Summary of alkylphenolic results in sediments and wastewater treatment plant sludge.

Sampling Site		4-NP (µg/g)	NP1EO (µg/g)	NP2EO (µg/g)	NP3-17EO (µg/g)	NP1EC (µg/g)	NP2EC (µg/g)	4-*t*-OP (µg/g)	OP1EC (µg/g)	OP2EC (µg/g)
Sediments from rivers and lakes										
	n (number of samples analyzed)	12	5	5	4	0	0	10	0	0
	Minimum	<0.020	<0.020	<0.020	<0.020			<0.005		
	Median	0.16	0.033	0.020	0.026			0.020		
	Maximum	72	38	6.0	0.17			1.8		
	Average	9.0	7.6	1.2	0.060			0.24		
Sludge from municipal waste treatment plants										
	n (number of samples analyzed)	41	38	38	38	31	31	41	31	31
	Minimum	32	3.0	4.8	0.44	0.30	1.9	0.45	0.030	0.096
	Median	212	80	20	47	2.2	12	4.6	0.075	0.53
	Maximum	850	332	297	167	4.3	24	20	0.66	2.3
	Average	279	97	31	51	2.2	11	5.2	0.11	0.74

Appendix 1. Textile mill effluent concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1E (µg/L)C	OP2EC (µg/L)
Effluent directly discharged to river									
Bridgetown, NS - Britex mill final	11	257	592	798			9.0		
Bridgetown, NS - Britex mill final	13	37	115	4065			3.8		
Bridgetown, NS - Britex mill final	10	49	106	8638			3.8		
St-Victor, QC - Lainages Victor Ltee.	3.3	93	489	7905	0.45	0.45	8.5	0.83	2.5
St-Victor, QC - Lainages Victor Ltee.	2.7	58	506	8811	0.45	0.45	1.9	0.68	1.3
Onsite secondary treatment of effluent									
Caraquet, NB - Wink Industries	0.60	4.1	3.9	208	5.2	<0.45	<0.015	0.43	<0.045
Caraquet, NB - Wink Industries	3.6	1.1	0.93	2.1	3.7	55	0.059	0.24	11.8
Magog, QC - C.S. Brooks*	0.68	1870		315	0.74	5.2	0.22	<0.045	<0.045
Magog, QC - C.S. Brooks*	0.61	1301		84	<0.45	<0.45	0.14	<0.045	<0.045
Magog, QC - C.S. Brooks	<0.090	0.52	0.25	2.6	1.0	3.4	0.015	<0.050	<0.050
*: NP1EO and NP2EO were not resolvable due to high concentrations - number listed under NP1EO is the sum of both oligomers									
Effluent discharged to municipal treatment plant									
Cambridge, ON - Cambridge Towel (to Galt STP)	0.95	18	39	189	<0.45	<0.45	0.18	0.080	<0.045
Cambridge, ON - Cambridge Towel (to Galt STP)	0.23	5.4	12	210	0.45	<0.45	<0.015	<0.045	<0.045
Cambridge, ON - Montreal Woolens (to Galt STP)	26	65	219	4162	1.9	2.8	0.072	<0.045	<0.045
Cambridge, ON - Montreal Woolens (to Galt STP)	15	52	234	4834	0.74	0.77	0.12	<0.045	<0.045
Cambridge, ON - Penman's (to Galt STP)	0.58	69	252	4567	<0.45	<0.45	<0.015	<0.045	<0.045
Cambridge, ON - Penman's (to Galt STP)	2.8	26	171	3436	1.4	0.63	0.026	<0.045	<0.045
Cambridge, ON - Tiger Brand (to Galt STP)	0.58	18	204	6848	<0.45	<0.45	<0.015	<0.045	<0.045
Cambridge, ON - Tiger Brand (to Galt STP)	2.9	40	276	5768	<0.45	<0.45	0.027	<0.045	<0.045
Cookshire, QC - Cookshiretex (to Cookshire STP)	10	57	285	787	2.8	6.9	1.2	0.15	0.95
Moncton, NB - Tandem mill effluent (to Moncton STP)	1.1	2.3	2.3	50			0.65		
Moncton, NB - Tandem mill effluent (to Moncton STP)	1.5	0.74	0.64	148			0.46		
Moncton, NB - Tandem mill effluent (to Moncton STP)	2.1	1.5	0.97	320			0.59		
Truro, NS - Stanfields mill effluent (to Truro STP)	4.9	8.7	28	1459			0.26		
Truro, NS - Stanfields mill effluent (to Truro STP)	3.1	8.8	27	2559			0.40		
Truro, NS - Stanfields mill effluent (to Truro STP)	5.8	15	32	1828			0.63		

Appendix 2. Pulp/paper/other industrial effluent concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Boyle, AB Alberta-Pacific mill	< 0.050	0.84	< 0.050				< 0.005		
Boyle, AB Alberta-Pacific mill	< 0.050	1.57	< 0.050				< 0.005		
Boyle, AB Alberta-Pacific mill	< 0.050	2.4	< 0.050				< 0.005		
Edmunston, NB Fraser mill	6.9	1.07	< 0.050				< 0.005		
Edmunston, NB Fraser mill	6.0	1.89	< 0.050				< 0.005		
Edmunston, NB Fraser mill	9.8	160	68				< 0.005		
Edmunston, NB - Fraser mill	16	110	49				< 0.005		
Espanola, ON - E.B. Eddy mill	< 0.050	1.4	< 0.050				< 0.005		
Espanola, ON - E.B. Eddy mill	< 0.050	3.5	< 0.050				< 0.005		
Fort McMurray, AB - SunCor Plant	< 0.050	< 0.050	< 0.050				< 0.005		
Fort McMurray, AB - SunCor Plant	< 0.050	12	< 0.050				< 0.005		
Hinton, AB - Weldwood mill (combined with municipal effluent)	11	0.020	< 0.050				< 0.005		
Hinton, AB - Weldwood mill (combined with municipal effluent)	26	26	36				< 0.005		
Hinton, AB - Weldwood mill (combined with municipal effluent)	20	18	28				< 0.005		
Kamloops, BC - Weyerhauser mill	< 0.050	1.0	< 0.050				< 0.005		
Kamloops, BC - Weyerhauser mill	< 0.050	0.53	< 0.050				< 0.005		
Kamloops, BC - Weyerhauser mill	< 0.050	0.49	< 0.050				< 0.005		
La Tuque, QC - Cdn. Pacific Forest Products mill	< 0.050	2.2	< 0.050				< 0.005		
La Tuque, QC - Cdn. Pacific Forest Products mill	< 0.050	5.2	< 0.050				< 0.005		
Saint John, NB - Rothsay Paper mill	< 0.050		2.8				< 0.005		
Slave Lake, AB - Slave Lake Pulp mill	< 0.050	4.2	< 0.050				< 0.005		
Slave Lake, AB - Slave Lake Pulp mill	< 0.050	5.7	< 0.050				< 0.005		
Smooth Rock Falls, ON - Malette Kraft mill	0.38	1580	< 0.050						
Smooth Rock Falls, ON - Malette Kraft mill	1.1	3780	< 0.050						
Ste. Anne de Nackawic, NB - pulp mill	< 0.050	9.3	< 0.050				< 0.005		
Ste. Anne de Nackawic, NB - pulp mill	< 0.050	15	< 0.050				< 0.005		
Terrace Bay, ON - Kimberly-Clark mill	7.8	3.3	10						
Terrace Bay, ON - Kimberly-Clark mill	8.2	5.5	11						
Terrace Bay, ON - Kimberly-Clark mill	8.7	< 0.050	6.4				< 0.005		
Whitecourt, AB - A.N.C. mill	< 0.050	2.5	< 0.050				< 0.005		
Whitecourt, AB - A.N.C. mill	< 0.050	1.3	< 0.050				< 0.005		
Whitecourt, AB - Millar-Western mill	< 0.050	8.2	< 0.050				< 0.005		
Whitecourt, AB - Millar-Western mill	< 0.050	3.7	< 0.050				< 0.005		

Appendix 3. Wastewater treatment plant effluent concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-t-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Primary treatment facilities:									
Charlottetown, PE STP	2.5	3.3	1.7				0.37		
Cowansville, QC WWCP	18	26	23	35			0.40		
Cowansville, QC WWCP	25	35	29	50			0.81		
Cowansville, QC WWCP	1.2	43	36	50			0.88		
Cowansville, QC WWCP	0.37	1.5	2.1	18			<0.015		
Cowansville, QC WWCP	62	43	24	735			<0.015		
Elmira, ON WPCP	0.11	0.21	0.34	5.4			<0.015		
Elmira, ON WPCP	<0.050	0.64	0.94				<0.015		
Granby, QC WWCP	2.4	1.5	3.1	16			0.24		
Granby, QC WWCP	36	2.4	4.2	15			0.38		
Granby, QC WWCP	0.62	0.072	0.67	4.8			0.054		
Granby, QC WWCP	2.3	4.3	6.5	619			0.12		
Moncton, NB - Greater Moncton STP	1.4	2.3	3.3	293			0.12		
Moncton, NB - Greater Moncton STP	1.8	3.0	4.4	403			0.13		
Moncton, NB - Greater Moncton STP	1.1	3.2	5.0	388			0.16		
Montreal, QC - MUC STP	1.2	2.5	1.7				0.12		
Truro, NS STP - Colchester County Central STP	2.0	1.4	4.5	14			0.20		
Truro, NS STP - Colchester County Central STP	1.8	1.5	5.4	20			0.18		
Vancouver, BC - Annacis Island STP		15	25	21	11	5.2		0.42	0.28
Vancouver, BC - Annacis Island STP		2.5	4.3	5.6	5.8	4.8		0.46	0.20
Vancouver, BC - Annacis Island STP	13	5.3	2.4				0.55		
Windsor, ON - West Windsor PCP	3.8	31	11	158	1.6	1.0	1.2	0.15	0.36
Windsor, ON - West Windsor PCP	1.7	56	18	400	1.2	1.1	1.0	0.20	0.37
Secondary treatment facilities:									
Burlington, ON - Skyway STP	1.6	10	8.9	3.9	22	21	0.13	7.4	4.0
Burlington, ON - Skyway STP	0.93						< 0.015		
Burlington, ON - Skyway STP	0.58	0.21	0.20				0.040		
Burlington, ON - Skyway STP	0.50	0.13	0.25				0.050		
Burlington, ON - Skyway STP	0.38						0.030		
Hamilton, ON - Woodward Ave. STP	0.13	1.1	1.4	6.3	9.4	23	0.045	5.6	8.6
Hamilton, ON - Woodward Ave. STP	0.12	1.0	1.4	4.4	9.9	23	0.040	4.1	6.6
Hamilton, ON - Woodward Ave. STP	1.0						< 0.015		
Hamilton, ON - Woodward Ave. STP	0.83						< 0.015		
Hamilton, ON - Woodward Ave. STP	3.6						0.50		
Hamilton, ON - Woodward Ave. STP	1.4	1.1	1.1				0.17		

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Secondary treatment facilities continued:									
Hamilton, ON - Woodward Ave. STP	2.4						0.39		
Hamilton, ON - Woodward Ave. STP	0.60	3.8	1.1				< 0.015		
Kitchener, ON STP	0.34	1.9	1.7	21	44	35	0.087	2.6	2.1
Kitchener, ON STP	0.18	2.6	2.1	13	38	35	0.046	3.7	3.3
Mississauga, ON - Lakeview WPCP	0.15	1.7	1.5	6.1	11	18	0.054	4.6	9.0
Mississauga, ON - Lakeview WPCP	0.14	2.0	1.1	2.1	13	20	0.12	5.8	6.7
Niagara Falls, ON - Stanford WPCP	3.2	<0.020	<0.020				0.15		
Pickering, ON - Duffin Creek WPCP	1.6	5.6	2.8	27	75	38	0.57	10	6.0
Pickering, ON - Duffin Creek WPCP	1.3	3.4	2.0	53	64	33	0.53	9.0	5.4
Saint John, NB - Thorne Ave. STP	0.45	0.26	0.38				0.049		
Scarborough, ON - Highland Creek STP	0.17	0.92	0.69	11	9.0	11	0.19	7.3	5.8
Scarborough, ON - Highland Creek STP	0.26	1.5	2.2	5.9	11	14	0.32	8.1	7.0
St. Catharines, ON - Port Dalhousie WPCP	0.58	0.034	0.025				0.040		
St. Catharines, ON - Port Weller WPCP	0.60	0.021	< 0.020				0.060		
Toronto, ON - Humber STP	0.12	0.46	0.36	3.8	11	45	0.095	4.4	13
Toronto, ON - Main STP	2.2						0.11		
Toronto, ON - Main STP	1.7						0.070		
Toronto, ON - Main STP	1.1	0.092	0.099				< 0.015		
Toronto, ON - Main STP	0.30	1.9	1.1	8.0	21	12	0.14	8.0	2.8
Toronto, ON - Main STP	0.34	1.2	0.83	6.5	16	10	0.10	5.3	2.5
Toronto, ON - North Toronto STP	0.28	0.86	0.62	5.6	19	23	0.069	7.9	3.1
Waterloo, ON STP	<0.050	43	33	< 2.0			< 0.015		
Waterloo, ON STP	0.28	7.7	7.0	15			0.034		
Winnipeg, MB - North STP	4.8	1.0	1.8				< 0.015		
Tertiary treatment facilities:									
Cambridge, ON - Galt WWTP	0.85	5.7	5.4	11			0.025		
Edmonton, AB - Gold Bar WWCP	0.55	6.9	4.8				<0.015		
Edmonton, AB - Gold Bar WWCP	0.36	3.3	2.6	0.89	39	59	0.039	2.9	5.2
Edmonton, AB - Gold Bar WWCP	0.49	4.3	3.4	2.3	38	57	0.032	2.7	5.8
Edmonton, AB - Gold Bar WWCP	0.29	2.9	2.1	2.9	49	82	0.016	1.5	4.1
Edmonton, AB - Gold Bar WWCP	0.10	1.3	0.31	<2.0	32	47	0.017	2.7	4.8
Edmonton, AB - Gold Bar WWCP	0.22	1.7	1.2	5.6	9.7	45	<0.015	0.55	4.1
Edmonton, AB - Gold Bar WWCP	0.23	3.3	2.6	3.3	12	53	0.027	0.65	5.0
Edmonton, AB - Gold Bar WWCP	0.37	1.4	2.5	13	30	62	0.057	1.8	6.4
Guelph, ON - Guelph-Eramosa WWCP	0.25	2.2	0.29	0.51	6.6	45	0.016	0.69	6.7
Guelph, ON - Guelph-Eramosa WWCP	0.13	0.86	0.25	2.2	11	45	0.027	2.7	7.8
Guelph, ON - Guelph-Eramosa WWCP	0.31	2.2	2.5	3.9	4.2	27	0.027	0.49	3.2

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NPnEO 3-17 (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Tertiary treatment facilities continued:									
Guelph, ON - Guelph-Eramosa WWCP	0.18	1.7	1.4	7.2	12	24	0.28	29	5.2
Guelph, ON - Guelph-Eramosa WWCP	0.15	0.97	1.9	11	8.3	47	0.051	1.0	9.0
Regina, SK STP	<0.050	1.1	0.46				<0.015		
Lagoon treatment facility:									
Niagara-on-the-Lake, ON - Queenston WPCP	2.2	0.34	0.027				0.12		

Appendix 4. Surface water concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-t-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Athabasca R. at Calling R., AB	<0.050						<0.005		
Athabasca R. at Calling R., AB	<0.050						<0.005		
Athabasca R. downstream of Ft. McMurray, AB at Mile 11	<0.050						<0.005		
Athabasca R. downstream of Ft. McMurray, AB at Mile 11	<0.050						<0.005		
Athabasca R. downstream of Tar Sands Projects at Mile 33, AB	<0.050						<0.005		
Athabasca R. downstream of Tar Sands Projects at Mile 33, AB	<0.050						<0.005		
Athabasca R. downstream of Weldwood mill, Hinton, AB	<0.050						<0.005		
Athabasca R. downstream of Weldwood mill, Hinton, AB	<0.050						<0.005		
Athabasca R. downstream of Whitecourt, AB	<0.050						<0.005		
Athabasca R. downstream of Whitecourt, AB	<0.050						<0.005		
Athabasca R. near Smith, AB	<0.050						<0.005		
Athabasca R. north of Athabasca, AB	<0.050						<0.005		
Athabasca R. upstream of ANC, Whitecourt, AB	<0.050						<0.005		
Athabasca R. upstream of ANC, Whitecourt, AB	<0.050						<0.005		
Athabasca R. upstream of Ft. McMurray, AB	<0.050						<0.005		
Athabasca R. upstream of Ft. McMurray, AB	<0.050						<0.005		
Athabasca R. upstream of Millar-Western, Whitecourt, AB	<0.050						<0.005		
Athabasca R. upstream of Millar-Western, Whitecourt, AB	<0.050						<0.005		
Athabasca R. upstream of Weldwood mill, Hinton, AB	<0.050						<0.005		
Canagagigue Creek, downstream of Elmira, ON STP	<0.020	0.084	0.082	10			<0.005		
Canagagigue Creek, downstream of Elmira, ON STP	<0.020	<0.020	<0.020				<0.005		
Canagagigue Creek, upstream of Elmira, ON STP	<0.020	0.087	0.10	18			<0.005		
Canagagigue Creek, upstream of Elmira, ON STP	<0.020	0.13	0.054				<0.005		
Grand R. 0 km, at Galt STP outfall, east shore	0.62	0.75	0.85	1.1	3.7	19	0.19	0.23	0.27
Grand R. 0 km, at Galt STP outfall, east shore	1.2	1.4	0.86	1.0	8.0	28	0.025	0.55	0.78
Grand R. 0 km, at Galt STP outfall, east shore	1.5	1.5	0.74	0.97	15	41	0.028	0.89	0.90
Grand R. 0 km, at Galt STP outfall, midstream	0.13	0.12	0.16	0.22	2.7	2.4	0.077	0.37	0.16
Grand R. 0 km, at Galt STP outfall, midstream	0.13	0.24	0.28	0.30	2.2	3.2	0.007	0.35	0.27
Grand R. 0 km, at Galt STP outfall, midstream	0.069	0.17	0.17	0.58	2.2	2.2	<0.005	0.42	0.26
Grand R. 0.1 km downstream of Galt STP, east shore	0.46	0.55	0.57	0.50	3.3	14	0.16	0.26	0.23
Grand R. 0.1 km downstream of Galt STP, east shore	0.62				4.2	12	0.020	0.44	0.41
Grand R. 0.1 km downstream of Galt STP, east shore	0.23	1.1	0.57	1.0	9.4	25	<0.005	0.68	0.45
Grand R. 0.5 km upstream of Galt STP, control	0.19	0.12	0.14	0.19	2.5	1.9	0.11	0.35	0.11
Grand R. 0.5 km upstream of Galt STP, control	0.15	0.21	0.26	0.19	2.0	2.1	0.009	0.34	0.21
Grand R. 0.5 km upstream of Galt STP, control	0.11	0.20	0.20	0.58	2.4	2.3	0.007	0.45	0.27
Grand R. 1 km downstream of Galt STP, east shore	0.19	0.13	0.21	0.13	2.7	3.8	0.007	0.35	0.18
Grand R. 1 km downstream of Galt STP, east shore	0.18	0.37	0.29	0.90	2.3	3.5	0.008	0.37	0.21
Grand R. 1 km downstream of Galt STP, east shore	0.25				3.1	5.9	0.012	0.38	0.30

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-t-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Surface water sites continued:									
Grand R. 1 km downstream of Galt STP, midstream	0.19	0.21	0.21	0.12	3.2	3.4	0.007	0.42	0.20
Grand R. 1 km downstream of Galt STP, midstream	0.11	0.18	0.30	0.76	2.1	2.1	0.008	0.38	0.20
Grand R. 1 km downstream of Galt STP, midstream	0.13				2.3	2.2	0.009	0.41	0.26
Grand R. 1 km downstream of Galt STP, west shore	0.17	0.19	0.20	0.18	2.3	2.1	0.008	0.32	0.15
Grand R. 1 km downstream of Galt STP, west shore	0.12	0.22	0.26	0.49	1.9	2.1	0.009	0.34	0.20
Grand R. 1 km downstream of Galt STP, west shore	0.13				2.1	2.6	0.008	0.37	0.24
Grand R. 2 km downstream of Galt STP, east shore	0.20	0.18	0.21	0.14	2.5	4.3	0.008	0.31	0.18
Grand R. 2 km downstream of Galt STP, east shore	0.17	0.22	0.31	0.53	2.1	4.0	0.011	0.34	0.21
Grand R. 2 km downstream of Galt STP, east shore	0.42				2.6	4.3	0.009	0.35	0.24
Grand R. 2 km downstream of Galt STP, midstream	0.16				2.1	2.0	0.007	0.28	0.13
Grand R. 2 km downstream of Galt STP, midstream	0.092	0.17	0.21	0.37	0.44	0.65	<0.005	0.066	0.059
Grand R. 2 km downstream of Galt STP, midstream	0.13				2.5	2.5	0.012	0.45	0.29
Grand R. 2 km downstream of Galt STP, west shore	0.079	0.16	0.17	0.22	1.7	1.6	<0.005	0.23	0.12
Grand R. 2 km downstream of Galt STP, west shore	0.11	0.28	0.25	0.85	0.55	0.81	0.007	0.088	0.073
Grand R. 2 km downstream of Galt STP, west shore	0.14				2.8	2.8	0.009	0.51	0.28
Grand R. 4 km downstream of Galt STP, east shore	0.16	0.18	0.18	0.11	2.1	2.9	0.007	0.28	0.15
Grand R. 4 km downstream of Galt STP, east shore	0.17	0.32	0.27	0.66	2.3	3.5	0.011	0.35	0.19
Grand R. 4 km downstream of Galt STP, east shore	0.17				2.5	2.7	0.010	0.43	0.27
Grand R. 4 km downstream of Galt STP, midstream	0.13	0.11	0.14	0.16	2.8	3.0	<0.005	0.35	0.18
Grand R. 4 km downstream of Galt STP, midstream	0.14				0.69	1.1	0.010	0.10	0.081
Grand R. 4 km downstream of Galt STP, midstream	0.16						0.012		
Grand R. 4 km downstream of Galt STP, west shore	0.12	0.085	0.17	0.19	2.4	2.2	0.006	0.33	0.14
Grand R. 4 km downstream of Galt STP, west shore	0.60	0.17	0.22	0.64	2.0	2.2	0.037	0.33	0.20
Grand R. 4 km downstream of Galt STP, west shore	0.15				2.2	2.7	0.011	0.41	0.29
Grand R. 8 km downstream of Galt STP, east shore	0.17						0.011		
Grand R. 8 km downstream of Galt STP, east shore	0.14	0.10	0.17	0.12	2.4	2.7	0.007	0.31	0.16
Grand R. 8 km downstream of Galt STP, east shore	0.17	0.11	0.19	0.66	2.5	2.6	0.009	0.43	0.22
Grand R. 8 km downstream of Galt STP, midstream	0.12	0.11	0.11	0.39	2.1	2.4	0.005	0.24	0.14
Grand R. 8 km downstream of Galt STP, midstream	0.12	0.20	0.21	0.71	1.9	2.1	0.009	0.32	0.18
Grand R. 8 km downstream of Galt STP, midstream	0.12				1.9	2.0	0.009	0.34	0.21
Grand R. 8 km downstream of Galt STP, west shore	0.13	0.069	0.078	0.11	1.9	1.9	0.005	0.25	0.13
Grand R. 8 km downstream of Galt STP, west shore	0.16	0.22	0.20	1.0	1.6	1.9	0.010	0.26	0.16
Grand R. 8 km downstream of Galt STP, west shore	0.12				1.9	2.0	0.009	0.34	0.21
Hamilton Harbour, west harbour, Hamilton, ON	<0.010	0.18	0.14				<0.005		
Hamilton Harbour, Windermere Basin, Hamilton, ON	0.92	0.78	0.95				0.082		
Hamilton Harbour, at Burlington STP discharge, Hamilton, ON	0.12	0.36	0.40				0.013		
Hamilton Harbour, at Burlington STP discharge, Hamilton, ON	0.38						0.036		
Hamilton Harbour, near Burlington STP, Hamilton, ON	0.019	1.1	<0.020				0.021		
Hamilton Harbour, near Lax property, Hamilton, ON	0.24						0.023		

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-t-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Surface water sites continued:									
Hamilton Harbour, near Randle Reef, Hamilton, ON	0.30						0.028		
Hamilton Harbour, Windermere Basin near Dofasco, Hamilton, ON	0.86						0.082		
Hamilton Harbour, Windermere Basin, farthest, Hamilton, ON	0.98						0.096		
L. Erie, Niagara R. mouth, Fort Erie, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Van Wagner's Beach, Hamilton, ON	0.058						<0.005		
L. Ontario, Credit R. mouth, Port Credit, ON	<0.010	1.8	10				<0.005		
L. Ontario, Ganaraska R. mouth, Port Hope, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Humber R. mouth, Mississauga, ON	0.27	1.5	1.5				0.084		
L. Ontario, Humber R. mouth, Mississauga, ON	<0.010	0.19	0.29				<0.005		
L. Ontario, Kingston Harbour, Kingston, ON	<0.010	0.36	< 0.02				<0.005		
L. Ontario, Kingston Harbour, Kingston, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Kingston Harbour, Kingston, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Niagara R. mouth, Niagara-on-the-Lake, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Port Credit Harbour, Port Credit, ON	<0.010	0.11	0.13				<0.005		
L. Ontario, Whitby Harbour, Whitby, ON	<0.010	0.80	< 0.02				<0.005		
L. Ontario, Whitby Harbour, Whitby, ON	<0.010	<0.020	<0.020				<0.005		
L. Ontario, Whitby Harbour, Whitby, ON	<0.010	<0.020	<0.020				<0.005		
Lake St. Clair, Thames R. mouth, near Sarnia, ON	<0.010	<0.020	<0.020				0.009		
Lake Superior, Marathon Harbour, Marathon, ON	<0.010	<0.020	<0.020				<0.005		
Lake Superior, Mission Bay, Thunder Bay, ON	0.026	0.16	<0.020				<0.005		
Lake Superior, Nipigon Bay, Red Rock, ON	0.013	5.1	<0.020				<0.005		
Lake Superior, Thunder Bay, ON	<0.010	7.8	<0.020				0.047		
Lake Superior, Thunder Bay, ON	<0.010	10	<0.020				0.055		
Lake Superior, Thunder Bay, ON	<0.010	<0.020	<0.020				<0.005		
Lesser Slave R., downstream of Slave Lake mill, AB	<0.010						<0.005		
Lesser Slave R., downstream of Slave Lake mill, AB	<0.010						<0.005		
Lesser Slave R., upstream of Slave Lake mill, AB	<0.010						<0.005		
Red Hill Creek, Hamilton, ON	0.13	<0.020	0.055				<0.005		
Red Hill Creek, Hamilton, ON	0.16	<0.020	0.026				<0.005		
Red Hill Creek, Hamilton, ON	0.25	0.074	0.19				<0.005		
Red Hill Creek, Hamilton, ON	0.054	<0.020	0.031				<0.005		
Red Hill Creek, Hamilton, ON	0.088	<0.020	0.040				<0.005		
Red Hill Creek, Hamilton, ON	1.0	1.6	2.5				<0.005		
Red Hill Creek, Hamilton, ON	4.3						0.57		
Red Hill Creek, Hamilton, ON	2.7						0.39		
Red Hill Creek, Hamilton, ON	4.1						0.61		
Saint John R. - Downstream of Fraser mill, Edmunston, NB	<0.010	<0.020	<0.020				<0.005		
Saint John R. - Downstream of Fraser mill, Edmunston, NB	<0.010	<0.020	<0.020				<0.005		
St. Clair R., Sarnia, ON	<0.010	1.8	<0.020				<0.005		

Sampling Site	4-NP (µg/L)	NP1EO (µg/L)	NP2EO (µg/L)	NP3-17EO (µg/L)	NP1EC (µg/L)	NP2EC (µg/L)	4-*t*-OP (µg/L)	OP1EC (µg/L)	OP2EC (µg/L)
Surface water sites continued:									
St. Clair R., Sarnia, ON	<0.010	<0.020	<0.020				<0.005		
St. Lawrence R. @ Montreal, QC	<0.010	0.11	0.023				<0.005		
St. Lawrence R. @ Montreal, QC	<0.010	0.15	0.020				<0.005		
St. Lawrence R. @ Montreal, QC	<0.010	0.11	<0.020				<0.005		
St. Lawrence R., Cornwall, ON	<0.010	<0.020	<0.020				<0.005		
St. Lawrence R., Cornwall, ON	<0.010	<0.020	<0.020				<0.005		
St. Lawrence R., Cornwall, ON	<0.010	<0.020	<0.020				0.013		
St. Mary's R., Sault Ste. Marie, ON	<0.010	<0.020	<0.020				<0.005		
St. Mary's R., Sault Ste. Marie, ON	<0.010	<0.020	<0.020				<0.005		
Toronto Harbour near Main STP discharge, Toronto, ON	0.29	2.8	1.9				0.030		
Toronto Harbour near Main STP discharge, Toronto, ON	0.21	1.4	0.96				0.024		
Toronto Inner Harbour, Toronto, ON	<0.010	0.040	0.031				<0.005		
Toronto Inner Harbour, Toronto, ON	<0.010	0.036	0.027				<0.005		
Welland Canal Lock 7, Welland, ON	<0.010	0.32	<0.020				<0.005		

Appendix 5. Sediment concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/g)	NP1EO (µg/g)	NP2EO (µg/g)	NP3-17EO (µg/g)	NP1EC (µg/g)	NP2EC (µg/g)	4-t-OP (µg/g)	OP1EC (µg/g)	OP2EC (µg/g)
Grand R. 1 km downstream of Galt STP, west shore	2.5	<0.020	<0.020	<0.020			0.020		
Grand R. 2 km downstream of Galt STP, west shore	4.6	0.022	0.020	<0.020			0.083		
Grand R. 4 km downstream of Galt STP, midstream	1.0	0.033	<0.020	0.031			0.022		
Grand R. 8 km downstream of Galt STP, west shore	27	0.035	<0.020	0.17			0.41		
Hamilton Harbour - at Burlington WWCP discharge, Hamilton, ON	72	38	6.0				1.8		
Hamilton Harbour near Burlington WWCP discharge, Hamilton, ON	<0.020						<0.005		
Hamilton Harbour near Lax property, Hamilton, ON	<0.020						<0.005		
Hamilton Harbour near Randle Reef, Hamilton, ON	0.022						<0.005		
Hamilton Harbour Windermere Dofasco, Hamilton, ON	0.10						0.010		
Hamilton Harbour Windermere farthest, Hamilton, ON	0.22						0.020		

Appendix 6. Wastewater treatment sludge concentrations of alkylphenolic substances.

Sampling Site	4-NP (µg/g)	NP1EO (µg/g)	NP2EO (µg/g)	NP3-17EO (µg/g)	NP1EC (µg/g)	NP2EC (µg/g)	4-t-OP (µg/g)	OP1EC (µg/g)	OP2EC (µg/g)
Burlington, ON - Skyway WWCP	146						7.7		
Edmonton, AB - Gold Bar WWCP	159	332	297	7.4			5.3		
Edmonton, AB - Gold Bar WWCP	527	11	7.7	57	4.2	5.5	5.7	0.035	2.2
Edmonton, AB - Gold Bar WWCP	167	23	8.9	39	4.3	15	1.7	0.13	0.47
Edmonton, AB - Gold Bar WWCP	235	18	9.0	42	1.4	8.6	2.5	0.11	0.62
Edmonton, AB - Gold Bar WWCP	212	61	10	38	4.3	8.6	2.2	0.081	0.32
Edmonton, AB - Gold Bar WWCP	80	77	11	49	2.2	12	0.82	0.15	0.32
Edmonton, AB - Gold Bar WWCP	327	89	17	50	2.1	14	3.5	0.075	0.50
Edmonton, AB - Gold Bar WWCP	788	208	28	63	2.8	24	8.8	0.085	0.84
Edmonton, AB - Gold Bar WWCP	258	227	20	28	3.5	12	2.6	0.15	0.50
Edmonton, AB - Gold Bar WWCP	663	242	32	48	3.4	15	6.2	0.075	0.36
Edmonton, AB - Gold Bar WWCP	257	122	21	47	1.4	6.8	2.6	0.035	0.24
Edmonton, AB - Gold Bar WWCP	348	131	31	39	2.2	13	4.2	0.075	0.45
Edmonton, AB - Gold Bar WWCP	39	173	38	64	1.4	10	0.45	0.11	1.1
Granby, QC WWCP	32	88	45	11			1.7		
Granby, QC WWCP	63	122	51	19			1.1		
Guelph, ON - Guelph-Eramosa WWCP	850	36	23	2.5			20		
Guelph, ON - Guelph-Eramosa WWCP	451	26	10	24			8.1		
Guelph, ON - Guelph-Eramosa WWCP	381	30	6.4	117	2.4	17	9.0	0.11	0.75
Guelph, ON - Guelph-Eramosa WWCP	292	29	6.3	95	1.9	9.8	5.9	0.11	0.53
Guelph, ON - Guelph-Eramosa WWCP	360	24	4.8	89	3.1	14	8.7	0.13	0.96
Guelph, ON - Guelph-Eramosa WWCP	217	31	6.1	55	4.2	11	4.3	0.13	0.81
Guelph, ON - Guelph-Eramosa WWCP	149	104	20	167	2.4	12	3.3	0.13	0.75
Guelph, ON - Guelph-Eramosa WWCP	65	67	12	66	1.8	13	1.2	0.075	0.78
Guelph, ON - Guelph-Eramosa WWCP	201	63	16	70	2.1	12	6.7	0.27	0.84
Guelph, ON - Guelph-Eramosa WWCP	137	67	31	94	2.3	23	4.6	0.35	1.6
Guelph, ON - Guelph-Eramosa WWCP	174	83	30	42	3.4	15	7.2	0.66	1.2
Guelph, ON - Guelph-Eramosa WWCP	153	62	17	74	0.59	2.2	6.2	0.035	0.34
Guelph, ON - Guelph-Eramosa WWCP	202	83	30	35	1.3	5.4	7.1	0.075	0.56
Guelph, ON - Guelph-Eramosa WWCP	177	172	49	73	0.89	5.4	3.5	0.075	0.33
Guelph, ON - Guelph-Eramosa WWCP	170	143	42	42	1.4	3.0	5.3	0.075	0.28
Guelph, ON - Guelph-Eramosa WWCP dewatered sludge	675						14		
Guelph, ON - Guelph-Eramosa WWCP dewatered sludge	394						8.1		
Kitchener, ON STP	329	89	14	43	2.5	4.2	4.6	0.035	0.11
Kitchener, ON STP	444	69	12	46	0.30	2.6	5.1	0.030	0.096
Mississauga, ON - Lakeview WPCP	68	104	52	48	0.83	13	2.8	0.035	2.2
Mississauga, ON - Lakeview WPCP	62	90	43	29	0.35	15	2.8	0.035	2.3
Toronto, ON - Humber STP	126	38	14	31	0.30	1.9	3.5	0.030	0.26

Sampling Site	4-NP (µg/g)	NP1EO (µg/g)	NP2EO (µg/g)	NP3-17EO (µg/g)	NP1EC (µg/g)	NP2EC (µg/g)	4-*t*-OP (µg/g)	OP1EC (µg/g)	OP2EC (µg/g)
STP sludge sites continued:									
Toronto, ON - North Toronto STP	43	74	63	62	3.9	4.0	1.7	0.035	0.17
Waterloo, ON STP	630	68	25	0.44			7.6		
Waterloo, ON STP	404	242	16	17			3.4		

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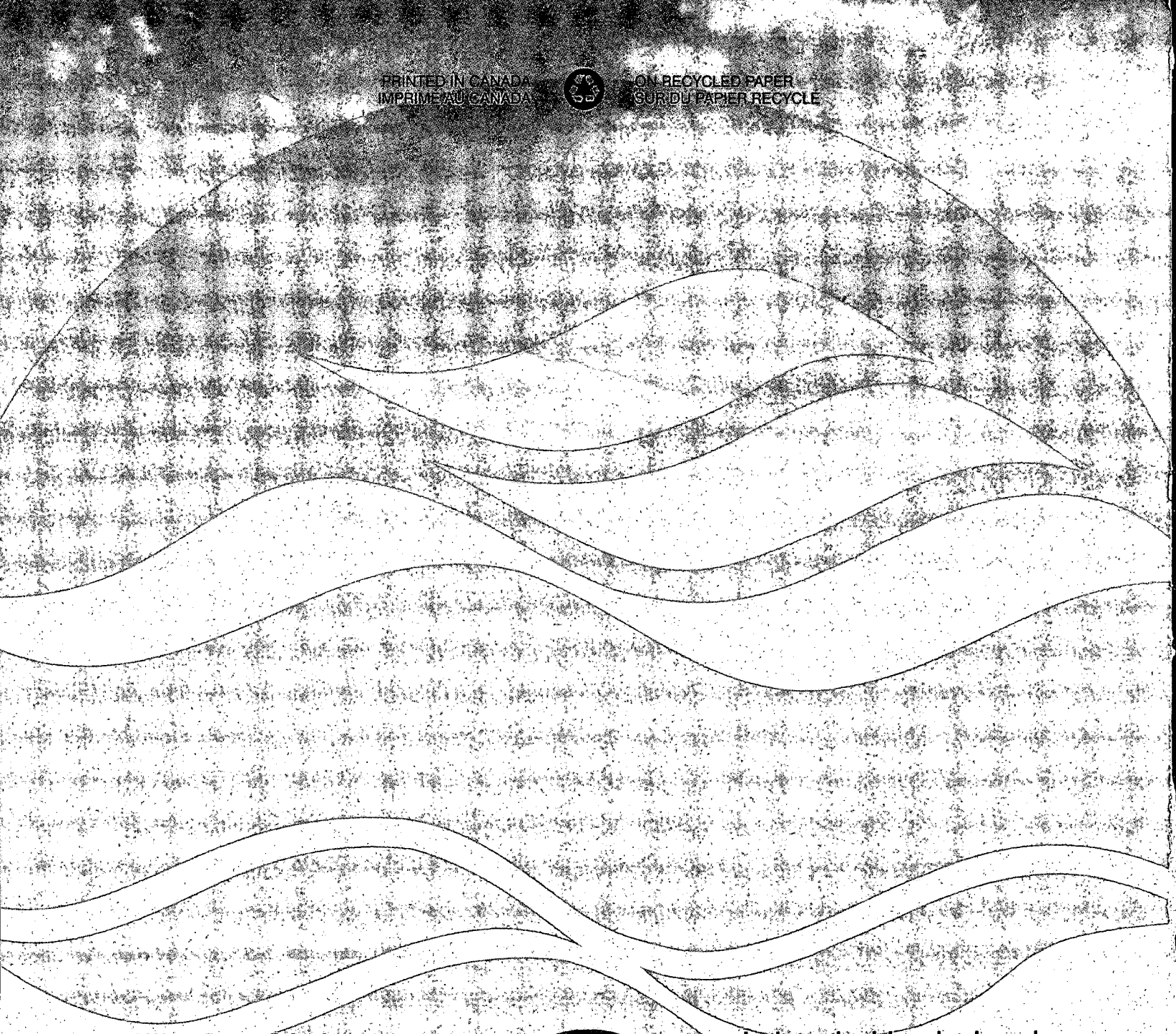

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