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OCCURRENCE OF ALKYLPHENOLS AND ALKYLPHENOL MONO-AND DIETHOXYLATES IN NATURAL WATERS OF THE LAURENTIAN GREAT LAKES BASIN AND THE UPPER ST. LAWRENCE RIVER

D.T. Bennie, C.A. Sullivan, H.-B. Lee,
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NWRI CONTRIBUTION NO. 96-164

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OCCURRENCE OF ALKYLPHENOLS AND ALKYLPHENOL MONO- AND DIETHOXYLATES IN NATURAL WATERS OF THE LAURENTIAN GREAT LAKES BASIN AND THE UPPER ST. LAWRENCE RIVER

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MANAGEMENT PERSPECTIVE

Nonylphenol and its ethoxylates are employed in formulations that are used as industrial detergents, emulsifiers, dispersants, antifoamers, dyeing assists and pesticide adjuvants. These chemicals are on PSL2 of CEPA. This study was undertaken to provide data on the occurrence of nonylphenol and its ethoxylates in surface waters and sediments in Canada, data which are required in order to determine exposure levels of such chemicals in the environment for the CEPA assessment. This study will be extended to include sewage treatment plant effluent and sludge from across Canada.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le nonylphénol et ses dérivés éthoxylés sont utilisés dans des formulations employées par l'industrie comme détergents, émulsifiants, dispersants, antimoussants, adjuvants de teintures ou de pesticides. Ces produits chimiques figurent dans la deuxième liste des substances d'intérêt prioritaire de la LCPE. La présente étude a été entreprise pour obtenir des données sur la présence du nonylphénol et de ses dérivés éthoxylés dans les sédiments et les eaux de surface au Canada, données qui sont requises pour déterminer les niveaux d'exposition à des produits de ce type dans le cadre de l'évaluation selon la LCPE. L'étude portera également sur les effluents et les boues de stations d'épuration d'eaux usées dans tout le Canada.

ABSTRACT

Nonylphenol and its ethoxylates are on the second Priority Substances List (PSL2) to determine if they are "toxic" as defined under the Canadian Environmental Protection Act. This study addresses the need for data on their occurrence in surface waters and sediments in Canada. Samples of surface water from thirty-five sites in the Laurentian Great Lakes basin and the upper St. Lawrence River were analyzed for 4-nonylphenol (4-NP), nonylphenol ethoxylate (NPE_1), nonylphenol diethoxylate (NPE_2) and 4-*tert*-octylphenol (4-t-OP). Bottom sediment samples from nine heavily industrialized sites were also analyzed for the same chemicals. Measurable quantities of 4-NP and 4-t-OP were found in 24% of all water samples. Values ranged from < 0.010 µg/L to 0.92 µg/L and from < 0.005 µg/L to 0.084 µg/L for 4-NP and 4-t-OP, respectively. Of the surface water samples, 58% were found to contain NPE_1 and 32% contained NPE_2. Their concentrations ranged from < 0.020 µg/L to 7.8 µg/L for NPE_1 and from < 0.020 µg/L to 10 µg/L for NPE_2. All nine sediment samples contained 4-nonylphenol, with values ranging from 0.17 µg/g to 72 µg/g (dry weight). The majority of sediment samples also contained detectable levels of the other contaminants: 66% of sediments had detectable amounts of NPE_1 and concentrations ranged from < 0.015 µg/g to 38 µg/g (dry weight); 66% of sediments had detectable amounts of NPE_2 and values ranged from < 0.015 µg/g to 6.0 µg/g (dry weight); and 89% of sediment samples had detectable amounts of 4-t-OP and values ranged from < 0.010 µg/g to 1.8 µg/g (dry weight). The highest concentrations of the analytes found are well below acute toxicity thresholds, but in some cases there may be cause for concern with regard to long-term effects on reproductive health of fish.

RÉSUMÉ

Le nonylphénol et ses dérivés éthoxylés figurent dans la deuxième liste de substances d'intérêt prioritaire, qui vise à déterminer s'ils sont toxiques selon la Loi canadienne sur la protection de l'environnement. L'étude permettra d'obtenir de l'information sur leur présence dans les sédiments et les eaux de surface au Canada. Les échantillons d'eaux de surface de 35 sites du bassin laurentien des Grands Lacs et du bassin supérieur du Saint-Laurent ont été analysés pour le 4-nonylphénol (4-NP), le nonylphénol (mono)éthoxylé (NPE_1), le nonylphénol diéthoxylé (NPE_2) et le 4-*tert*-octylphénol (4-t-OP). On a également analysé pour les mêmes composés chimiques les échantillons de sédiments de fond provenant de neuf sites très industrialisés. Vingt-quatre pour cent de tous les échantillons d'eau renfermaient des quantités mesurables de 4-NP et de 4-t-OP. Les valeurs variaient de < 0,010 µg/L à 0,92 µg/L, et de < 0,005 µg/L à 0,084 µg/L respectivement pour 4-NP et 4-t-OP. Dans le cas d'échantillons d'eaux de surface, 58% renfermaient du NPE_1 et 32% du NPE_2. Leurs concentrations variaient de 0,020 µg/L à 7,8 µg/L pour NPE_1, et de < 0,020 µg/L à 10 µg/L pour NPE_2. Chacun des neuf échantillons de sédiments renfermaient du 4-nonylphénol, les concentrations variaient de 0,17 µg/g à 72 µg/g (poids sec). la majeure partie des échantillons de sédiments contenaient également des teneurs décelables des autres contaminants: 66% des sédiments renfermaient des quantités décelables de NPE_1, soit <0,015 µg/g à 38 µg/g (poids sec); 66% des sédiments avaient des quantités décelables de NPE_2, soit < 0,015 µg/g à 6,0 µg/g (poids sec); enfin, 89% des échantillons de sédiments renfermaient des quantités décelables de 4-t-OP, soit <0,010 µg/g à 1,8 µg/g (poids sec). Les concentrations maximales de produits analysés décelés se situaient bien en dessous des seuils de toxicité aiguë, mais, dans certains cas, on pourrait craindre les effets à long terme sur la capacité de reproduction des poissons.

INTRODUCTION

Alkylphenol polyethoxylates are among the most widely used nonionic surfactants in the world (Talmage, 1994). These surfactants have been employed for decades in formulations used as detergents, emulsifiers, dispersants, antifoamers, dyeing assists and pesticide adjuvants. The most significant commercial alkylphenol ethoxylate surfactants are octylphenol polyethoxylates, nonylphenol polyethoxylates, dodecylphenol polyethoxylates and dinonylphenol polyethoxylates. Nonylphenol polyethoxylates (NPE_n, where n = 3 to > 20 ethoxylate units) possess the properties of good wetting, detergency, low foaming, applicability at low water temperatures and low cost. However, their use in household detergent formulations has been voluntarily discontinued in North America because of their slow biodegradability. In Canada, the demand for NPE_n surfactants was 6.0 kt in 1989 and was expected to rise to 7.0 kt by 1993 (CPI Product Profiles, 1989). The primary users are the textile and the pulp and paper industries. Up to 1 kt of NPE_n is also used annually as the emulsification agent for pesticide solutions. Nonylphenol polyethoxylates are biodegraded under anaerobic conditions (Stephanou and Giger, 1982; Giger *et al.*, 1984; Ahel *et al.*, 1994a), such as those found in most sewage treatment plants, to 4-nonylphenol (4-NP), nonylphenol mono- and diethoxylate (NPE_1 and NPE_2). The breakdown product, 4-NP, shows greater aquatic toxicity than the original surfactant, and is persistent and lipophilic. The compound 4-*tert*-octylphenol (4-t-OP) is a degradation product of octylphenol polyethoxylate surfactants and may also be found as a minor component in nonylphenol polyethoxylate preparations. Octanol/water partition coefficients (reported as log K_{ow}) for 4-nonylphenol, 4-*tert*-octylphenol and nonylphenol ethoxylate and diethoxylate have been determined experimentally to be in the range of 4.1 to 4.5 (Ahel and Giger, 1993b) (see Table 1). Nonylphenol 96

h LC_{50} values for juvenile Atlantic salmon (*Salmo salar*) and shrimp (*Crangon septemspinosa*) ranged from 0.13 to 0.30 mg/L (McLeese *et al.*, 1981). Comber *et al.* (1993) found acute 24 h and 48 h EC_{50} levels for *Daphnia magna* of 0.30 and 0.19 mg/L, respectively, for 4-NP, based on immobilization, while the chronic 21 day no observed effect concentration (NOEC) was found to be 0.024 mg/L of 4-NP. A 96 h NOEC of 0.098 mg/L and a 96 h LC_{50} of 0.135 mg/L were reported for fathead minnows (*Pimephales promelas*) exposed to nonylphenol by Holcombe *et al.* (1984). By contrast the acute toxicity of alkylphenol ethoxylates generally decreases with increasing number of ethoxylate groups attached to the alkylphenol moiety. Testing on Japanese killifish (*Oryzias latipse*) by Yoshimura (1986) resulted in 48 h LC_{50} values of 1.4 mg/L, 3.0 mg/L, 2.5 mg/L, 3.6 mg/L, 5.4 mg/L, 11.6 mg/L, 48 mg/L and 110 mg/L for NP, NPE_1, $NPE_{3.3}$, NPE_5, $NPE_{6.4}$, $NPE_{8.4}$, NPE_{13} and $NPE_{16.6}$, respectively. Other researchers have found similar results. Macek *et al.* (1975) reported 96 h LC_{50} results on bluegills (*Lepomis macrochirus*) of 6.4 - 9.8 mg/L for NPE_9, 2.4 - 2.8 mg/L for NPE_5 and 2.8 - 3.2 mg/L for OPE_{4-5}. The brown trout (*Salmo trutta*) was found to be very sensitive to NPE_{9-10} with a 96 h LC_{50} of 1.0 mg/L (Rieff *et al.*, 1979). Other species in the same study were less sensitive to the NPE_{9-10} formulation and the 96 h LC_{50} values ranged from 4.9 - 11.2 mg/L for goldfish (*Carassius auratus*), harlequin fish (*Rashora heteromorpha*) and the golden orfe (*Idus idus melanotus*).

Very little data on the occurrence of NPE_n and its refractory metabolites in natural waters have been generated in North America. One study conducted by Naylor *et al.* (1992) found that 60 to 75% of water samples from 30 river sites in the United States had no detectable levels of 4-NP, NPE_1 and NPE_2, and that most of the sediment samples collected contained detectable amounts of 4-NP and NPE_1. Canadian data on the occurrence and fate of nonionic surfactants are limited. Rutherford *et al.*

(1992) examined the effluent streams of three textile mills in Atlantic Canada and found surfactant concentrations ranging from 5.4 mg/L to 50 mg/L relative to Triton® X-100, a mixture of t-octylphenol polyethoxylates. Nonylphenol, octylphenol, octylphenol ethoxylate, nonylphenol ethoxylate and nonylphenol diethoxylate were identified in municipal wastewater and sludge from Vancouver, British Columbia, but were not quantified (Rogers *et al.*, 1986). Several Canadian researchers have studied the ecotoxicity of 4-nonylphenol, octylphenol and octylphenol polyethoxylates when used as an adjuvant in herbicide/pesticide formulations (Caux *et al.*, 1988; Holmes and Kingsbury, 1980; Kingsbury *et al.*, 1981; McLeese *et al.*, 1980a, 1980b, 1981; Sundaram *et al.*, 1980; Sundaram and Szeto, 1981; Weinberger, 1984; Weinberger *et al.*, 1987). However, these studies did not consider the presence of nonylphenol or octylphenol as degradation products of their respective parent polyethoxylate surfactants. One method development study (Sithole and Allen, 1989) did find a total nonylphenol polyethoxylate surfactant concentration of 0.31 mg/L in a single unbleached white water sample from a pulp and paper mill in eastern Canada. Quantitative results for 4-NP and 4-t-OP in primary effluent, final effluent and digested sludge were obtained from four sewage treatment plants in the Toronto area as well as levels in sediments from Hamilton Harbour, the Humber River in Metropolitan Toronto and Kaministiquia River at Thunder Bay, Ontario (Lee and Peart, 1995). All effluent samples and sediments were found to contain detectable amounts of 4-NP, and 4-t-OP was also detected in most of these samples. Both digested sludge samples were highly contaminated with 4-NP and concentrations were in excess of 135 μg/g.

There have been numerous studies on the occurrence of 4-NP and NPE_n in European countries. Most of these studies have focused on monitoring surface waters and sewage treatment plant (STP)

effluent and digested sludge. Reported levels in surface waters ranged from < 0.2 to 180 μg/L for 4-NP, < 0.5 to 18 μg/L for NPE_1 and < 0.5 to 16 μg/L for NPE_2 (Stephanou, 1985; Ahel and Giger, 1985a; Blackburn and Waldock, 1995). STP effluent concentrations ranged from 0.7 to 21000 μg/L of 4-NP, 0.65 to 133 μg/L of NPE_1, and < 10 to 230 μg/L of NPE_2. Since the log K_{ow} values of these substances are in the range of 4.1 to 4.5, it is expected that they should be adsorbed onto sediments and may be available for uptake and bioaccumulation by benthic organisms. Dried sludge samples from European sewage treatment plants have yielded concentrations of 0.47 to 4000 μg/g of 4-NP, 0.66 to 680 μg/g of NPE_1, and 0.04 to 280 μg/g of NPE_2 (Giger *et al.*, 1984; Ahel and Giger, 1985a; Waldock and Thain, 1986; Marcomini and Giger, 1987; Brunner *et al.*, 1988; Wahlberg *et al.*, 1990; Chalaux *et al.*,1994).

More recently, it has been claimed that nonylphenol is an estrogen mimic and can interfere with the reproductive success of fish. Jobling and Sumpter (1993) have found that nonylphenol at low μg/L levels can induce the production of vitellogenin in cultured rainbow trout hepatocytes. Vitellogenin is a lipoglycophosphoprotein and a precursor of the egg yolk. It is normally secreted by the liver of mature female fish after stimulation by estrogen. Utilizing a recombinant estrogen yeast screen, Routledge and Sumpter (1996) showed that alkylphenol polyethoxylate metabolites, namely: 4-octylphenol, 4-nonylphenol, nonylphenol diethoxylate and nonylphenolic carboxylic acid derivatives, possess estrogenicity. Previously, Soto *et al.* (1991) reported that 4-nonylphenol was capable of inducing cell proliferation in MCF-7 human breast tumour cells, which are estrogen-sensitive. It was also observed that the estrogenic potency of nonylphenol polyethoxylates appears to decrease with increasing ethoxylate chain length. However, the water solubility of the NPE_n increases with increasing chain

length (Ahel and Giger, 1993a) so that more NPE_n is bioavailable to aquatic organisms. Organisms that are exposed to these compounds for longer periods of time may therefore suffer the same or greater effects that are attributable to shorter exposures to 4-nonylphenol or 4-*tert*-octylphenol.

In 1995, Environment Canada added nonylphenol and nonylphenol polyethoxylates to the second Priority Substances List (PSL2) for assessment under the Canadian Environmental Protection Act (Environment Canada, 1995). These compounds are to be assessed from a Canadian perspective for their occurrence, transformation, bioavailability, bioaccumulation, and toxicity.

In this work, we determined the occurrence of 4-nonylphenol, 4-*tert*-octylphenol, nonylphenol ethoxylate and nonylphenol diethoxylate in natural waters and selected sediments from the Great Lakes basin and the upper St. Lawrence River for the purpose of providing Canadian data for the PSL2 assessment process. This study will later be extended to include sewage treatment plant effluent and sludge from across Canada.

METHODS

Materials

Acetic anhydride, 4-NP and triethylamine were obtained from Aldrich (Milwaukee, WI). The nonylphenol mono- and diethoxylate were purchased as a mixture called POE(1 to 2) nonylphenol from ChemService (West Chester, PA). The POE(1 to 2) nonylphenol mixture consisted mainly of nonylphenol mono-, di- and triethoxylates. The concentrations of each component were determined by

preparatory scale high performance liquid chromatography (HPLC) fractionation of components. Subsequent identification by full scan electron impact gas chromatography-mass spectrometry (EI GC-MS) confirmed the identity of each component. All organic solvents used for extractions and cleanup were pesticide grade and high performance liquid chromatographic determinations were done with HPLC grade solvents. Organic-free water was obtained by purification of reverse osmosis-treated water through a Milli-Q water system (Millipore Canada Ltd., Nepean, Ontario). The anhydrous sodium sulphate, potassium carbonate, silica gel, aluminum foil, glass fibre filters, and disposable pipettes used in the treatment of field samples and laboratory extractions were heated to 450 °C overnight before use. All glassware and field filtration equipment was rinsed with organic-free water and pesticide grade solvents before use. *AnalaR*™ grade sulphuric acid and formaldehyde solution (37% to 41% w/v) used in the field for sample preservation as well as the acetic anhydride, which was used for acetylation, were obtained from BDH Inc. (Toronto, Ontario). Non-acid-washed Celite 545 was purchased from Fisher Scientific Co. (Toronto, Ontario) and supercritical fluid extraction grade carbon dioxide was obtained from Air Products (Nepean, Ontario). Samples were stored in bottles and jars that were purchased pre-cleaned to American Society for Testing and Materials standards for organic samples (ASTM, 1986).

Sample Collection and Extraction

Water samples and duplicates were collected from 35 sites during the 1994-1995 period (Figure 1). Sediment collection occurred at nine selected sites during 1995 only. A list of the locations of sampling sites is shown in Table 2. In areas where there were industrial or municipal wastewater

discharges into the receiving waters, samples were usually collected from more than one site in the vicinity.

Two different extraction techniques were used for each sample matrix. Natural water samples were extracted by *in situ* acetylation for 4-NP and 4-t-OP while the nonylphenol polyethoxylates were extracted using liquid-liquid extraction with dichloromethane as the extracting solvent. Sediment samples for 4-NP and 4-t-OP were subjected to supercritical fluid extraction and on-line acetylation during the extraction stage. Nonylphenol polyethoxylates in sediments were Soxhlet extracted using dichloromethane.

(i) Water Samples

One litre samples were collected from a depth of 0.5 m, stored in a chest cooler until returned to shore and pressure-filtered through 1 μm Gelman type A/E glass fibre filters using compressed N_2 and modified pressurized beverage containers, pressure filters and Teflon transfer lines (Fox, 1986). Nonylphenol polyethoxylate samples were preserved in 1 L amber glass pre-cleaned bottles with 10 mL of formaldehyde solution while 4-NP/4-t-OP samples were preserved to a pH < 2 with 1 mL of concentrated sulphuric acid in 1 L amber glass pre-cleaned bottles. Samples were stored at 4 °C in the dark until returned to the laboratory in Burlington, Ontario for extraction.

Samples to be analyzed for 4-NP and 4-t-OP were acetylated *in situ* as outlined by Lee *et al.* (1984). The acid-preserved samples were adjusted to pH 10 using potassium carbonate, and acetylated directly in the extraction vessel with triple-distilled acetic anhydride. The resulting acetates were

extracted using hexane. Acetylation and extraction was performed three times and the combined extracts were dried through anhydrous sodium sulphate. Extracts were then concentrated to 1 mL in hexane and analyzed by electron impact gas chromatography-mass spectrometry in the selected ion monitoring (SIM) mode.

Nonylphenol polyethoxylate samples were extracted using liquid-liquid extraction techniques. Sample volumes of 500 mL to 1 L were extracted three times with 50 mL of dichloromethane and the combined extract was dried by passage through anhydrous sodium sulphate, concentrated and partitioned into hexane for normal phase high performance liquid chromatographic analysis.

(ii) Sediment Samples

Samples were collected by Ponar® dredge or Ekman dredge. In each case, only the top 2 cm of sediment was collected. The sediment was transferred to a pre-cleaned 500 mL glass jar with a Teflon-lined screw cap. Sediment jars were frozen and transported to the laboratory in Burlington for drying, extraction and analysis. In the lab, samples were thawed, air dried at 21 °C, ground using a mortar and pestle and passed through a 30 mesh sieve. The ground material was stored in a freezer at -20 °C until extraction.

For NPE_n extraction, 5 g aliquots of the sediments were mixed with anhydrous sodium sulphate and Soxhlet extracted with dichloromethane for at least 6 hours at 8 cycles/h. The extracts were dried by passage through anhydrous sodium sulphate, concentrated and partitioned into hexane for normal phase HPLC analysis.

The 4-NP/4-t-OP supercritical fluid extraction, cleanup and analysis is described by Lee and Peart (1995). Sediment aliquots of 250 mg to 1 g were added to the extraction thimble of the Hewlett-Packard (HP) 7680T supercritical fluid extractor which already contained Whatman GF/C filter paper and Celite. Triethylamine was then spiked onto the sample. Another layer of Celite was then added, followed by acetic anhydride and another layer of GF/C filter paper. The thimble void volume was then taken up by a suitable length of 1 cm diameter glass rod.

Supercritical carbon dioxide extraction then took place at 80 °C and 5096 psi with a flow rate of 2 mL/min. Extraction times were 15 min static and 10 min dynamic and the variable restrictor nozzle was kept at 50 °C. The acetyl derivatives of the subject compounds were adsorbed on an octadecyl-functionalized silica gel (ODS) trap during the extraction. They were later eluted from the ODS trap with hexane. Extracts were combined, partitioned with 1% potassium carbonate to remove coextracted acetic acid, dried with anhydrous sodium sulphate and concentrated to 1 mL for silica gel column cleanup. Samples were applied to a petroleum ether washed Pasteur pipette column containing 5 cm of 5% deactivated silica gel and 5 mm of anhydrous sodium sulphate. Sequential elution followed using (1) 5 mL of 5% dichloromethane in petroleum ether, (2) 10 mL of 50% dichloromethane in petroleum ether and (3) 10 mL of 1% methanol in dichloromethane. Fractions 2 and 3 were saved, solvent exchanged into iso-octane, and concentrated to a final volume of 1 mL for analysis.

Analysis

(i) 4-Nonylphenol and 4-*tert*-Octylphenol

All 4-NP/4-t-OP analyses on sample extracts were carried out utilizing EI GC-MS techniques, but two different instruments were used.

Analysis of extracts of water samples for 4-NP and 4-t-OP were done with a Hewlett-Packard 5989A MS Engine in the SIM mode. The Engine was interfaced to an HP 5890 Series II gas chromatograph and all injections were made by an H-P 7673A autosampler. Mass spectrometer conditions, gas chromatograph conditions and data acquisition were controlled by a UNIX-based HP MS ChemStation. Samples were injected in splitless mode onto a 30 m x 0.25 mm i.d. x 0.25 μm DB-5MS fused silica capillary column (J&W Scientific, Folsom, CA). The injector and GC-MS interface temperatures were both set at 250 °C. EI ion source and quadrupole mass filter temperatures were set at 200 °C and 100 °C, respectively. 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/min. Helium carrier gas flow was about 1 mL/min with a head pressure of 70 kPa. The electron energy was set at 70 eV while the electron multiplier voltage was determined during the instrument tuning process. 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. Confirmation of 4-NP and 4-t-OP was done in the full scan mode while scanning from *m/z* 40 to 300. Calibration standards were produced by acetylation of 10 μg of 4-NP and 4-t-OP in 30 mL of potassium carbonate in the presence of acetic anhydride in the same manner as described above for the water samples. The product was diluted to a concentration of 1 μg/mL in hexane for EI GC-MS

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. 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.

Sediment samples were analyzed for 4-NP and 4-t-OP using an HP 5972 mass selective detector (MSD) interfaced to an HP 5890 Series II gas chromatograph. Samples were injected via splitless mode using an HP 7673A autosampler onto a 30 m x 0.25 mm i.d. x 0.25 μm HP-5-MS column (Hewlett-Packard (Canada) Ltd, Mississauga, Ontario). The injector temperature was set at 250 °C while the GC-MSD interface temperature was 280 °C. The GC oven temperature program was the same as described for the HP MS Engine, but the carrier gas flow rate was held constant by electronic pressure sensing at 39.8 cm/sec. The electron multiplier voltage was 2000 V while the electron energy was 70 eV. Confirmation and quantitative analysis were carried out in the same manner as described for water samples.

(ii) Nonylphenol Mono- and Diethoxylates

Analysis for these parameters was performed with normal phase high performance liquid chromatography utilizing fluorescence detection.

The HPLC system consisted of a Hewlett-Packard 1050 Series pump, an HP 1050 Series autosampler and an HP 1046A programable fluorescence detector interfaced to an HP LC ChemStation. Chromatographic conditions for the separation of the nonylphenol polyethoxylates were

derived from the methods published by Ahel and Giger (1985b) and Marcomini and Giger (1987). The samples were chromatographed isocratically on a 100 mm x 2.1 mm i.d., 5 μm particle size HP Hypersil APS normal phase column (Hewlett-Packard (Canada) Ltd., Mississauga, Ontario). The mobile phase was composed of 98% hexane and 2% isopropanol (v/v) and was pumped at a rate of 0.3 mL/min. Sample injection volume was 20 μL. The HP 1046A fluorescence detector used an excitation wavelength of 230 nm and an emission wavelength of 300 nm. Quantitative results were obtained using the external standard method from response factors generated from the POE (1 to 2) nonylphenol standard solution at the 10 ng/μL level. Any samples that generated peak heights above that of the standard peaks were diluted until their response was less than or equal to that of the standard.

Recoveries for all analytes were in excess of 80% for water and sediment samples.

RESULTS AND DISCUSSION

Thirty-eight natural water samples and seven duplicates were collected from thirty-five sites in the Great Lakes basin and in the lower St. Lawrence River in 1994 and 1995 and analyzed for 4-NP, 4-t-OP, NPE_1 and NPE_2. Nine sediment samples and 2 duplicates were collected from some of the more industrialized areas in 1995 and analyzed for the same chemicals.

(i) Water Sample Results

The results for water samples (Table 3) show that measurable levels of 4-NP were found in nine of thirty-eight samples, 4-t-OP in nine samples, NPE_1 in twenty-two samples and NPE_2 in twelve

samples. The chemicals were found most frequently in areas of effluent discharge from pulp and paper mills, sewage treatment plants and industrial sources.

Levels of 4-NP ranged from < 0.010 μg/L to 0.92 μg/L and the mean of measurable samples (where detected) was 0.21 μg/L. Generally, Great Lakes sites yielded very low or non-detectable levels with the exceptions of the highly industrialized areas of Hamilton, Metropolitan Toronto and Detroit. Samples from sites on the St. Lawrence River, *i.e.* Cornwall and Montréal, did not yield any detectable amounts of 4-NP. The highest recorded value was found in the Windermere Basin of Hamilton Harbour (site 19) where the combined outflow from the Redhill Creek and the Hamilton-Wentworth sewage treatment plant is diluted by harbour waters. All of the reported 4-NP levels are substantially lower than the published NOEC for *Daphnia magna* and fathead minnows as well as being below the 96 h LC_{50} values for juvenile Atlantic salmon, shrimp and fathead minnows (Comber *et al.*, 1993; McLeese *et al.*, 1981; Holcome *et al.*, 1984). It appears that, in the most contaminated sample, there is a safety factor of about 25 times the NOEC value reported for *Daphnia magna* for dissolved 4-NP exposure. The highest concentration, 0.92μg/L, is also about twenty times less than the lowest concentration of 4-NP (20.3 μg/L) required to induce a significant elevation of the plasma vitellogenin concentration in maturing male rainbow trout (*Oncorhynchus mykiss*) in a three-week exposure (Jobling *et al.*, 1996). However, it is possible that the LOEC for this effect may be considerably lower with long-term exposure. The concentrations of 4-NP in this study are comparable to those obtained by Naylor *et al.* (1992) who reported concentrations of up to 0.64 μg/L of 4-NP in 30 rivers in the United States of America. When compared to European data from Lake Geneva (where [4-NP] = < 0.5 to 2.0 μg/L), the Glatt River (where [4-NP] = < 0.3 to 45 μg/L) and various rivers in England

(where [4-NP] = < 0.2 to 53 µg/L) (Stephanou, 1985; Ahel *et al.*, 1994b; Blackburn and Waldock, 1995), concentrations in the Great Lakes and St. Lawrence River samples are slightly lower.

Nonylphenol ethoxylate concentrations ranged from < 0.020 µg/L to 7.8 µg/L with a mean (where detected) of 1.3 µg/L. Results for nonylphenol diethoxylates varied from < 0.020 µg/L to 10 µg/L. The mean for the NPE_2 samples (where detected) was 1.4 µg/L. Measurable quantities of the ethoxylates were found mainly in heavily industrialized areas of the Great Lakes basin and the St. Lawrence River. A sample from Thunder Bay Harbour near the pulp and paper mill (site 1) yielded the highest NPE_1 concentration of 7.8 µg/L while a 1994 sample from the Credit River mouth (site 21) had 10 µg/L of NPE_2. Contributions to the Credit River may result from input to the local wastewater treatment plant from the manufacture of surfactants in the City of Mississauga. These ranges of NPE_1 and NPE_2 concentrations compare favourably with literature values cited in Naylor *et al.* (1992), Ahel and Giger (1985a), Ahel *et al.* (1994b) and Stephanou (1985). The measured concentrations are well below the 48 h LC_{50} results for the cladoceran *Ceriodaphnia dubia* of 1.04 mg/L for $NPE_{1\&2}$ reported by Ankley *et al.* (1990). Hall *et al.* (1989) stated that the 48 h LC_{50} test results for Mysid shrimp (*Mysidopsis bahia*) ranged from 0.11 mg/L for highly branched $NP_{1.5}$ to 1.66 - 3.34 mg/L for linear $NPE_{1.5}$. There are few chronic toxicity data with which to compare the NPE_1 and NPE_2 concentrations. However, it should be noted that the highest concentration found for NPE_2, 10 µg/L, is only three times lower than a nominal concentration of 30 µg/L which was found to produce a significant increase in plasma vitellogenin concentration, and decrease in gonadosomatic index, in maturing male rainbow trout (*Oncorhynchus mykiss*) in a three-week exposure (Jobling *et al.*, 1996)

Concentrations of 4-t-OP ranged from < 0.005 µg/L to 0.084 µg/L with a mean (where detected) of 0.038 µg/L. The highest reported 4-t-OP value was obtained from the Humber River mouth (site 22) in Etobicoke. Outside of the heavily industrialized urban areas mentioned previously, only the Thunder Bay site 1 sample had any significant amount of 4-t-OP. The concentrations of 4-t-OP found in these samples are very low in comparison to the data published by Sheldon and Hites (1979) in which octylphenol concentrations of about 2 µg/L were found in the Delaware river downstream of a sewage treatment plant that processed effluent from industrial chemical sources. The low values of 4-t-OP may be an indication that octylphenol polyethoxylate surfactants are not widely used in the subject areas. The highest concentration, 0.084µg/L, is about 13,000 times lower than the 96 h LC_{50} value of 1.1 mg/L for 4-t-OP (McLeese *et al.*, 1981). It is also about 60 times lower than the lowest concentration of 4-t-OP (4.8 µg/L) required to induce a significant elevation of the plasma vitellogenin concentration in fully mature or regressing male rainbow trout (*Oncorhynchus mykiss*) in a three-week exposure (Jobling *et al.*, 1996). Again, it should be noted that the LOEC for this effect may be considerably lower with long-term exposure.

Twenty-four percent of all water samples had measurable concentrations of 4-NP and 4-t-OP. The proportion of water samples with detectable concentrations of NPE_1 was 58% and this decreased to 32% for NPE_2. Results from locations sampled on more than one occasion displayed a significant level of variability. For example, concentrations of NPE_1 and NPE_2 from the Credit River mouth (site 21) and Humber River mouth (site 22) in 1994 were 5 to 75 times greater than concentrations in 1995. In 1995, both of these sites had no detectable levels of 4-NP and 4-t-OP but 1994 concentrations were well above the limit of detection, with the exception of 4-t-OP in the Credit River. Variability in these

results can be attributed to several factors: dispersion and dilution of contaminated effluents by the lakes and large rivers into which they are discharged and differences in loadings. Loadings from sewage treatment plant effluent discharges can be quite variable due to fluctuations in surfactant use by industries, the short hydraulic residence time of effluent within a treatment facility and, occasionally, overflow conditions during periods of heavy precipitation and runoff.

(ii) Sediment Sample Results

As 4-NP, 4-t-OP, NPE_1 and NPE_2 have low solubility in water and log K_{ow} values of greater than 4.0 (Table 1), it is expected that they would be adsorbed to the sediment particles. Consequently their concentrations in sediments were expected to be substantially higher than the aqueous levels. In fact, all nine sediment samples were found to be heavily contaminated with 4-NP while eight and six sites were contaminated with 4-t-OP and NPE_n, respectively. The results of these analyses are shown in Table 4. None of the sediment samples had analyte concentrations below the minimum detectable levels for all four parameters and six sites had detectable concentrations of all four contaminants.

Concentrations of 4-NP ranged from 0.17 μg/g to 72 μg/g on a dry weight basis with a mean of 10.6 μg/g. Seven of the nine sites had concentrations of ≤ 2.2 μg/g. The highest values, *i.e.* those > 10 μg/g, were found in sediments in close proximity to the two sewage treatment plant effluent discharge points in Hamilton Harbour (sites 19 and 20). Hamilton Harbour site 19 is located in the Windermere Basin which receives the effluent from the Hamilton-Wentworth sewage treatment plant and the Redhill Creek runoff. Site 20 in Hamilton Harbour is located close to the effluent discharge for the Burlington sewage treatment plant. The high values associated with Montréal site 33, near the Pointe du Moulin à

Vent, can also be attributed to sewage effluent discharges. Nonylphenol ethoxylate concentrations varied from < 0.015 μg/g to 38 μg/g and the diethoxylate concentrations from < 0.015 μg/g to 6.0 μg/g. The mean values of the measurable ethoxylates were 7.1 μg/g for NPE_1 and 1.2 μg/g for NPE_2. Eight of the nine sites had NPE_1 and NPE_2 concentrations of ≤ 2.6 μg/g and ≤ 0.48 μg/g, respectively. Concentrations of 4-t-OP, which was found in eight of the nine sediment samples, ranged from < 0.010 μg/g to 1.8 μg/g, and the mean of samples (where detected) was 0.41 μg/g. These results are comparable to the values obtained by Ahel *et al.* (1994b) where sediment samples taken downstream of sewage treatment plant effluent discharges ranged in concentration from 0.19 μg/g to 13.1 μg/g of 4-NP, from 0.10 μg/g to 8.85 μg/g for NPE_1 and from N.D. to 2.72 μg/g for NPE_2. Concentrations of the 4-NP and NPE_1 analytes in sediments are also similar to data generated by Naylor *et al.* (1992) in their 30 river study. The toxicological significance of these residues in sediments cannot be assessed because of the lack of data on toxicity to benthic organisms.

In conclusion, alkylphenol polyethoxylate degradation products were found frequently in natural water and sediments in the Great Lakes basin and the upper St. Lawrence River, especially in heavily industrialized or urbanized areas. In this study, concentrations of contaminants at sites in the Great Lakes basin and on the St. Lawrence River were most affected by sewage treatment plants, heavy industry and pulp mill inputs to the receiving waters. Twenty-four percent of the water samples had detectable levels of the two most toxic degradation products of nonylphenol polyethoxylates, namely 4-nonylphenol and 4-*tert*-octylphenol. Sediments from highly industrialized areas showed high levels of contamination of 4-nonylphenol, 4-*tert*-octylphenol, nonylphenol ethoxylate and nonylphenol diethoxylate in the majority of sites. When the results of both matrices are compared it is apparent that

these lipophilic analytes are more likely to be adsorbed to sediments than dissolved in water. However, the bioavailability of these contaminants to benthic fauna cannot be estimated at this time. Of the nonylphenolic compounds, 4-nonylphenol is the most toxic and has the greatest potential to bioaccumulate. The ethoxylates cannot be dismissed since they have the potential under anaerobic conditions, such as those found in sediments, to degrade into the more toxic 4-nonylphenol form. The mono- and diethoxylates have only slightly lower relative estrogenic potencies than 4-NP (Jobling and Sumpter, 1993). Therefore, in areas where there is continuous exposure, organisms may be subjected to endocrine disruption.

Further studies into a) the organic carbon content of the sediments to help assess the bioavailability of the alkylphenolics and b) the occurrence of 4-NP, NPE_1, NPE_2 and 4-t-OP in sewage treatment plant wastewaters and sludge from across Canada are also in progress.

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REFERENCES

Ahel, M. and Giger, W. (1985a). Determination of alkylphenols and alkylphenol mono- and diethoxylates in environmental samples by high-performance liquid chromatography. Anal. Chem. 57:1577-1583.

Ahel, M. and Giger, W. (1985b). Determination of nonionic surfactants of the alkylphenol polyethoxylate type by high-performance liquid chromatography. Anal. Chem. 57:2584-2590.

Ahel, M. and Giger, W. (1993a). Aqueous solubility of alkylphenols and alkylphenol polyethoxylates. Chemosphere 26:1461-1470.

Ahel, M. and Giger, W. (1993b). Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. Chemosphere 26:1471-1478.

Ahel, M., Giger, W. and Koch, M. (1994a). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment - I. Occurrence and transformation in sewage treatment. Wat. Res. 28:1131-1142.

Ahel, M., Giger, W. and Schaffner, C. (1994b). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment - II. Occurrence and transformation in rivers. Wat. Res. 28:1141-1152.

Ankley, G.T., Peterson, G.S., Lukasewycz, M.T. and Jensen, D.A. (1990). Characteristics of surfactants in toxicity identification evaluations. Chemosphere 21:3-12.

ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82. Standard practice for preparation of sample containers and for preservation. American Society for Testing and Materials, Philadelphia, PA, p 86, 1986.

Blackburn, M.A. and Waldock, M.J. (1995). Concentration of alkylphenols in rivers and estuaries in England and Wales. Wat. Res. 29:1623-1629.

Brunner, P.H., Capri, S., Marcomini, A. and Giger, W. (1988). Occurrence and behaviour of linear alkylbenzenesulphonates, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment. Wat. Res. 22:1465-1472.

Caux, P.Y., Weinberger, P. and Carlisle, D.B. (1988). A physiological study of the effects of Triton surfactants on *Lemna minor* L. Environ. Toxicol. Chem. 7:671-678.

Chalaux, N., Bayona, J.M. and Albaigé, J. (1994). Determination of nonylphenols as pentafluorobenzyl derivatives by capillary gas chromatography with electron-capture and mass spectrometric detection in environmental matrices. J. Chromatography A 686:275-281.

Comber, M.H.I., Williams, T.D. and Stewart, K.M. (1993). The effects of nonylphenol on *Daphnia magna*. Wat. Res. 27:273-276.

CPI Product Profiles (1989). Camford Information Services Inc. Don Mills, Ontario. 4 pp.

Environment Canada (1995). Report of the Minister's Expert Advisory Panel on the second Priority Substance List under the Canadian Environmental Protection Act (CEPA). Environment Canada, PSL2 Secretariat, Hull, Quebec.

Fox, M.E. (1986). A practical sampling and extraction system for the quantitative analysis of sub ng/L organochlorine contaminants in filtered water and suspended solids. In: *Methods for Analysis of Organic Compounds in the Great Lakes, Vol. II*, ed. W.C. Sonzogni and D.J. Dube, University of Wisconsin Sea Grant Institute, Madison, Wisconsin, U.S.A., Vol. II:27-34.

Giger, W., Brunner, P.H. and Schaffner, C. (1984). 4-Nonylphenol in sewage sludge: Accumulation of toxic metabolites from nonionic surfactants. Science 225:623-625.

Hall, W.S., Patoczka, J.B., Mirenda, R.J., Porter, B.A. and Miller, E. (1989). Acute toxicity of industrial surfactants to *Mysidopsis bahia*.. Arch. Environ. Contam. Toxicol. 18:765-772.

Holcombe, G.W., Phipps, G.L., Knuth, M.L. and Felhaber, T. (1984). The acute toxicity of selected substituted phenols, benzenes and benzoic acid esters to fathead minnows (*Pimephales promelas*). Environmental Pollution (Series A) 35:367-381.

Holmes, S.B. and Kingsbury, P.D. (1980). The environmental impact of nonyl phenol and the Matacil® formulation. Part I: Aquatic ecosystems. Canada Department of the Environment, Report FPM-X-35, Canadian Forestry Service, Forestry Pest Management Institute, Sault Ste. Marie, Ontario.

Jobling, S. and Sumpter, J.P. (1993). Detergent components in sewage effluent are weakly oestrogenic to fish: An *in vitro* study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes. Aquatic Toxicology 27:361-372.

Jobling, S., Sheehan, D., Osborne, J.A., Matthiessen, P. and Sumpter, J.P. (1996). Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environ. Toxicol. Chem. 15:194-202.

Kingsbury, P.D., McLeod, B.B. and Millikin, R.L. (1981). The environmental impact of nonyl phenol and the Matacil® formulation. Part 2: Terrestrial ecosystems. Canada Department of the Environment, Report FPM-X-36, Canadian Forestry Service, Forest Pest Management Institute, Sault Ste. Marie, Ontario.

Lee, H.-B., Weng, L.-D. and Chau, A.S.Y. (1984). Chemical derivatization analysis of pesticide residues. VIII. Analysis of 15 chlorophenols in natural water by *in situ* acetylation. J. Assoc. Off. Anal. Chem. 67:789-794.

Lee, H.-B. and Peart, T.E. (1995). Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. Anal. Chem. 67:1976-1980.

Macek, K.J. and Krzeminski, S.F. (1975). Susceptibility of bluegill sunfish (*Lepomis macrochirus*) to nonionic surfactants. Bull. Environ. Contam. Toxicol. 13:377-384.

Marcomini, A. and Giger, W. (1987). Simultaneous determination of linear alkylbenzenesulfonates, alkylphenol polyethoxylates, and nonylphenol by high-performance liquid chromatography. Anal. Chem. 59:1709-1715.

McLeese, D.W., Sergeant, D.B., Metcalfe, C.D., Zitko, V. and Burridge, L.E. (1980a). Uptake and excretion of aminocarb, nonylphenol, and pesticide diluent 585 by mussels (*Mytilus edulis*). Bull. Environ. Contam. Toxicol. 24:575-581.

McLeese, D.W., Zitko, V., Metcalfe, C.D. and Sergeant, D.B. (1980b). Lethality of aminocarb and the components of the aminocarb formulation to juvenile Atlantic salmon, marine invertebrates and a freshwater clam. Chemosphere 9:79-82.

McLeese, D.W., Zitko, V., Sergeant, D.B., Burridge, L. and Metcalfe, C.D. (1981). Lethality and accumulation of alkylphenols in aquatic fauna. Chemosphere 10:723-730.

Naylor, C.G., Mieure, J.P., Adams, W.J., Weeks, J.A., Castaldi, F.J., Ogle, L.D. and Romano, R.R. (1992). Alkylphenol ethoxylates in the environment. J. Am. Oil Chem. Soc. 69:695-703.

Rieff, B., Lloyd, R., How, M.J., Brown, D. and Alabaster, J.S. (1979). The acute toxicity of eleven detergents to fish: results of an interlaboratory exercise. Wat. Res. 13:207-210.

Rogers, I.H., Birtwell, I.K. and Kruzynski, G.M. (1986). Organic extractables in municipal wastewater, Vancouver, British Columbia. Water Poll. Res. J. Canada 21:187-203.

Routledge, E.J. and Sumpter, J.P. (1996). Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast strain. Environ. Toxicol. Chem. 15:241-248.

Rutherford, L.A., Hennigar, P.A., Doe, K.G., Nicol, M.L., Holmes, M.M.E., MacDonald, B.C. and Horne, W.H. (1992). Chemical characterization, aquatic toxicity and environmental impact of untreated effluent discharges from three textile mills in the Atlantic Region. Canada Department of the Environment, Environment Canada Report EPS-5-AR-93-1, Environmental Protection Branch, Atlantic Region, Dartmouth, Nova Scotia B2Y 2N6.

Sheldon, L.S. and Hites, R.A. (1979). Sources and movement of organic chemicals in the Delaware River. Environ. Sci. Technol. 13:574-579.

Sithole, B.B. and Allen, L.H. (1989). Determination of nonionic nonylphenol ethoxylate surfactants in pulp and paper mill process samples by spectrophotometry and liquid chromatography. J. Assoc. Off. Anal. Chem. 72:273-276.

Soto, A.M., Justica, H., Wray, J.W. and Sonnenschein, C. (1991). p-Nonyl-phenol: An estrogenic xenobiotic released from "modified" polystyrene. Environmental Health Perspectives 92:167-193.

Stephanou, E. and Giger, W. (1982). Persistent organic chemicals in sewage effluents. 2. Quantitative determinations of nonylphenols and nonylphenol ethoxylates by glass capillary gas chromatography. Environ. Sci. Technol. 16:800-805.

Stephanou, E. (1985). Environmental determination of alkylphenol polyethoxylate refractory residues using mass spectrometric techniques. Intern. J. Environ. Anal. Chem. 20:41-54.

Sundaram, K.M.S., Szeto, S., Hindle, R. and MacTavish, D. (1980). Residues of nonylphenol in spruce foliage, forest soil, stream water and sediment after its aerial application. J. Environ. Sci. Health B15(4):403-419.

Sundaram, K.M.S. and Szeto, S. (1981). The dissipation of nonylphenol in stream and pond water under simulated field conditions. J. Environ. Sci. Health B16(6):767-776.

Talmage, S.S. (1994). Environmental and human safety of major surfactants: alcohol ethoxylates and alkylphenol ethoxylates. A report to the Soap and Detergent Association, pp 191-364. Boca Raton, Florida: Lewis Publishers.

Wahlberg, C., Renberg, L. and Wideqvist, U. (1990). Determination of nonylphenol and nonylphenol ethoxylates as their pentafluorobenzoates in water, sewage sludge and biota. Chemosphere 20:179-195.

Waldock, M.J. and Thain, J.E. (1986). Environmental considerations of 4-nonylphenol following dumping of anaerobically digested sewage sludges: a preliminary study of occurrence and acute toxicity. International Council for the Exploration of the Sea Marine Environmental Quality Committee Report CM 1986/E:16.

Weinberger, P. (1984). Screening for potential ecotoxicity of solvents, surfactants and detergents. Canada Department of the Environment, Final contract report, Contract No. KN107-2-4304, Environment Canada, Hull, Quebec.

Weinberger, P., DeChacin, C. and Czuba, M. (1987). Effects of nonyl phenol, a pesticide surfactant, on some metabolic processes of *Chlamydomonas segnis*. Can. J. Bot. 65:696-702.

Yoshimura, K. (1986). Biodegradation and fish toxicity of nonionic surfactants. J. Am. Oil Chem. Soc. 63:1590-1596.

Table 1: Chemical identities and properties

Name	CAS No.[a]	Formula	Formula Weight	Water Solubility[b] (mg/L at 20.5 °C)	Log K_{ow}[c]
4-Nonylphenol (4-NP)	104-40-5	$C_{15}H_{24}O$	220.4	5.43	4.48
4-*tert*-Octylphenol (4-t-OP)	140-66-9	$C_{14}H_{22}O$	206.3	12.6	4.12
Nonylphenol ethoxylate (NPE_1)	27986-36-3	$C_{17}H_{28}O_2$	264.4	3.02	4.17
Nonylphenol diethoxylate (NPE_2)	9016-45-9 (NPE_n mixture)	$C_{19}H_{32}O_3$	308.5	3.38	4.21

[a]: Talmage, 1994
[b]: Ahel and Giger, 1993a
[c]: Ahel and Giger, 1993b

Table 2: Sampling Locations

Site No.	Location	Latitude (deg/min/sec N)	Longitude (deg/min/sec W)
1	Thunder Bay Harbour, near pulp mill, Thunder Bay, Ontario	48 27 12	78 10 09
2	Thunder Bay Harbour, near breakwall, Thunder Bay, Ontario	48 27 36	89 10 33
3	Mission Bay, Thunder Bay, Ontario	48 21 18	89 12 24
4	Nipigon Bay, near pulp mill effluent discharge, Red Rock, Ontario	48 56 24	88 13 33
5	Marathon Harbour, near pulp mill, Marathon, Ontario	48 43 21	86 23 40
6	St. Marys R., near museum (old OMNR Bldg.), Sault Ste. Marie, Ontario	46 30 10	84 19 30
7	St. Marys R., near power plant canal, Sault Ste. Marie, Ontario	46 30 43	84 20 40
8	Collingwood Harbour, Collingwood, Ontario	44 30 34	80 13 40
9	Owen Sound Harbour, Owen Sound, Ontario	44 35 06	80 56 05
10	St. Clair R., near Ethyl plant, Corunna, Ontario	42 53 40	82 27 19
11	St. Clair R., near Shell plant, Sarnia, Ontario	42 55 19	82 27 30
12	Detroit R., near Bois Blanc Island, at Amherstburg, Ontario	42 05 37	83 07 00
13	Detroit R., at Gross Ile, Michigan	42 06 48	83 10 36
14	Thames R. mouth, Lake St. Clair, Ontario	42 19 21	82 27 17
15	Niagara R., at Peace Bridge, Fort Erie, Ontario	42 54 09	78 54 19
16	Niagara R., at Niagara-on-the-Lake, Ontario	43 15 25	79 03 36
17	Welland Canal, near paper mill and Lock 7, Thorold, Ontario	43 07 45	79 11 40
18	Hamilton Harbour, in west harbour, Hamilton, Ontario	43 16 47	79 52 04

Continued on next page...

Table 2 cont'd

Site No.	Location	Latitude (deg/min/sec N)	Longitude (deg/min/sec W)
19	Hamilton Harbour, Windermere Basin, Hamilton, Ontario	43 16 08	79 46 04
20	Hamilton Harbour, near Burlington sewage treatment plant, Burlington, Ontario	43 18 22	79 48 28
21	Credit R. mouth, Mississauga, Ontario	43 33 03	79 34 46
22	Humber R. mouth, Etobicoke, Ontario	43 37 52	79 28 00
23	Toronto Harbour, near Ashbridges Bay sewage treatment plant, Toronto, Ontario	43 38 59	79 18 51
24	Toronto Inner Harbour, Toronto, Ontario	43 37 55	79 21 33
25	Whitby Harbour, Whitby, Ontario	43 51 10	78 56 02
26	Corbett Creek mouth, east of Whitby Harbour, near sewage treatment plant, Whitby, Ontario	43 51 09	78 53 07
27	Ganaraska R. mouth, Port Hope, Ontario	43 56 35	78 17 29
28	Kingston Harbour, near dry dock, Kingston, Ontario	44 14 11	76 28 49
29	Kingston Harbour, near sewage treatment plant, Kingston, Ontario	44 14 19	76 25 11
30	Cornwall Canal, near Domtar/ICI plant, Cornwall, Ontario	45 00 40	74 44 16
31	St. Lawrence R., mid-river near sewage treatment plant, Cornwall, Ontario	45 01 17	74 40 35
32	St. Lawrence R., 10 m offshore near sewage treatment plant, Cornwall, Ontario	45 01 37	74 40 40
33	St. Lawrence R., near Pointe du Moulin à Vent, Montréal, Québec	45 30 19	73 32 48
34	St. Lawrence R., under Pont Jacques Cartier, Montréal, Québec	45 31 37	73 32 08
35	St. Lawrence R., at Île Charron, Montréal, Québec	45 35 19	73 29 25

Table 3: Concentrations of 4-NP, 4-t-OP, NPE_1 and NPE_2 in water samples collected in 1994 and 1995.

Site No.	Sampling Location	Sampling Date	4-NP (µg/L)	4-t-OP (µg/L)	NPE 1 (µg/L)	NPE 2 (µg/L)
	Great Lakes Sites:					
1	Thunder Bay, pulp mill	Jun 8/94	N.D.	0.047	7.8	N.D.
2	Thunder Bay, breakwall	Jun 8/94	N.D.	N.D.	N.D.	N.D.
3	Mission Bay	Jun 8/94	0.026	N.D.	0.16	N.D.
4	Nipigon Bay	Jun 8/94	0.013	N.D.	5.1	N.D.
5	Marathon	Jun 9/94	N.D.	N.D.	N.D.	N.D.
6	St. Marys R., museum	Jun 9/94	N.D.	N.D.	N.D.	N.D.
7	St. Marys R., canal	Jun 9/94	N.D.	N.D.	N.D.	N.D.
8	Collingwood	May 30/94	N.D.	N.D.	1.6	N.D.
9	Owen Sound	May 31/94	N.D.	N.D.	N.D.	N.D.
10	St. Clair R., Corunna	May 31/94	N.D.	N.D.	1.8	N.D.
11	St. Clair R., Sarnia	May 31/94	N.D.	N.D.	N.D.	N.D.
12	Detroit R., Amherstburg	Jun 1/94	N.D.	N.D.	N.D.	N.D.
13	Detroit R., Gross Ile	Jun 1/94	0.12	0.045	2.3	0.61
14	Thames River mouth	Jun 1/94	N.D.	0.009	N.D.	N.D.
15	Niagara R., Fort Erie	Jul 6/94	N.D.	N.D.	N.D.	N.D.
16	Niagara R., N.O.T.L.	Jul 6/94	N.D.	N.D.	N.D.	N.D.
17	Welland Canal, Thorold	Jul 8/94	N.D.	N.D.	0.32	N.D.
20	Hamilton Harbour, Burl. STP	Jun 23/94	0.019	0.021	1.1	N.D.
21	Credit R. mouth	Jun 28/94	0.10	N.D.	1.8	10
22	Humber R. mouth	Jun 23/94	0.27	0.084	1.5	1.5
23	Toronto Harbour, STP	Jun 23/94	0.29	0.030	2.8	1.9
25	Whitby	Jun 28/94	N.D.	N.D.	0.80	N.D.
26	Corbett Creek mouth, Whitby	Jun 28/94	N.D.	N.D.	N.D.	N.D.

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Table 3 cont'd:

Site No.	Sampling Location	Sampling Date	4-NP (µg/L)	4-t-OP (µg/L)	NPE 1 (µg/L)	NPE 2 (µg/L)
	Great Lakes Sites cont'd:					
27	Ganaraska R., Port Hope	Jun 28/94	N.D.	N.D.	N.D.	N.D.
28	Kingston, dry dock	Jun 17/94	N.D.	N.D.	N.D.	N.D.
29	Kingston, STP	Jun 17/94	N.D.	N.D.	0.36	N.D.
18	Hamilton Harbour, west	Nov 14/95	N.D.	N.D	0.18	0.14
19	Hamilton Harbour, Windermere	Nov 14/95	0.92	0.082	0.78	0.95
20	Hamilton Harbour, Burl. STP	Nov 14/95	0.12	0.013	0.36	0.40
21	Credit R. mouth	Nov 7/95	N.D.	N.D.	0.11	0.13
22	Humber R. mouth	Oct 26/95	N.D.	N.D.	0.19	0.29
24	Toronto Inner Harbour	Oct 26/95	N.D.	N.D.	0.040	0.031
	St. Lawrence River Sites:					
30	Cornwall Canal	Jun 15/94	N.D.	0.013	N.D.	N.D.
31	St. Lawrence R., Cornwall	Jun 15/94	N.D.	N.D.	N.D.	N.D.
32	St. Lawrence R., Cornwall STP	Jun 15/94	N.D.	N.D.	N.D.	N.D.
33	St. Lawrence R., Moulin à Vent	Oct 4/95	N.D.	N.D.	0.15	0.020
34	St. Lawrence R., Pont J.C.	Oct 4/95	N.D.	N.D.	0.11	N.D.
35	St. Lawrence R., Île Charron	Oct 4/95	N.D.	N.D.	0.11	0.023
	Limit of Detection		0.010	0.005	0.020	0.020
	Frequency of Occurrence (total # of sites)		9 (38)	9 (38)	22 (38)	12 (38)
	Mean (where detected)		0.21	0.038	1.3	1.4

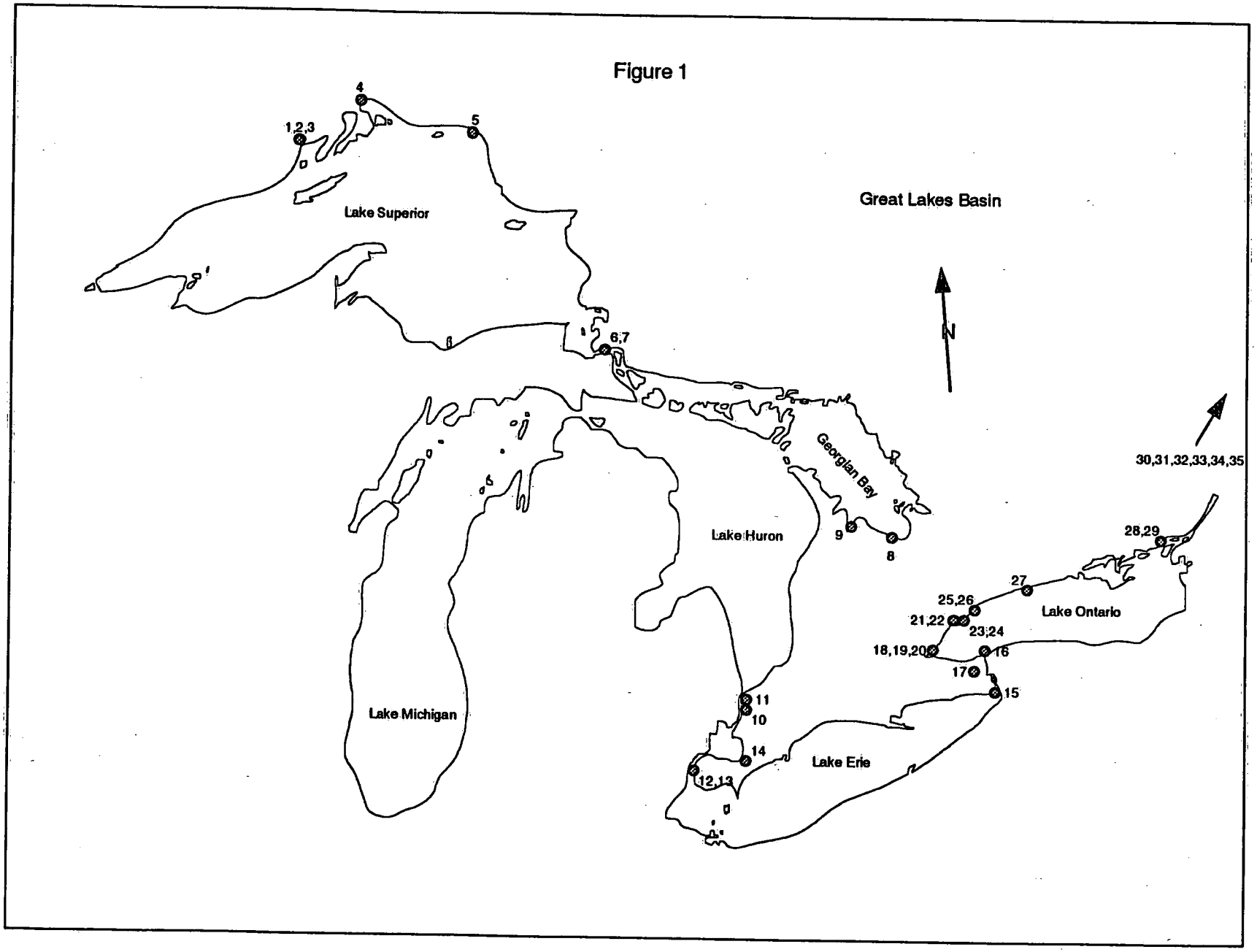
Table 4: Concentrations of 4-NP, 4-t-OP, NPE_1 and NPE_2 in sediments (based on dry weight)

Site No.	Sampling Location	Sampling Date	4-NP (µg/g)	4-t-OP (µg/g)	NPE 1 (µg/g)	NPE 2 (µg/g)
	Great Lakes Sites					
18	Hamilton Harbour, west	Nov 14/95	0.82	0.050	0.28	0.063
19	Hamilton Harbour, Windermere	Nov 14/95	18	1.0	1.2	0.35
20	Hamilton Harbour, Burl. STP	Nov 14/95	72	1.8	38	6.0
21	Credit R. mouth	Nov 7/95	0.43	0.010	N.D.	N.D.
22	Humber R. mouth	Oct 26/95	0.17	0.020	N.D.	N.D.
24	Toronto Inner Harbour	Oct 26/95	0.85	0.050	0.45	0.075
	St. Lawrence River Sites:					
33	St. Lawrence R., Moulin à Vent	Oct 4/95	2.2	0.28	2.6	0.48
34	St. Lawrence R., Pont J.C.	Oct 4/95	0.36	0.070	0.026	0.052
35	St. Lawrence R., Île Charron	Oct 4/95	0.72	N.D.	N.D.	N.D.
	Limit of Detection		0.100	0.010	0.015	0.015
	Frequency of Occurrence (total # of sites)		9 (9)	8 (9)	6 (9)	6 (9)
	Mean (where detected)		10.6	0.41	7.1	1.2

LIST OF FIGURES

Figure 1. Map of the Great Lakes basin showing sampling locations for 1994 and 1995.

Figure 1


Great Lakes Basin
N
Lake Superior
Lake Huron
Georgian Bay
Lake Michigan
Lake Erie
Lake Ontario
1,2,3
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