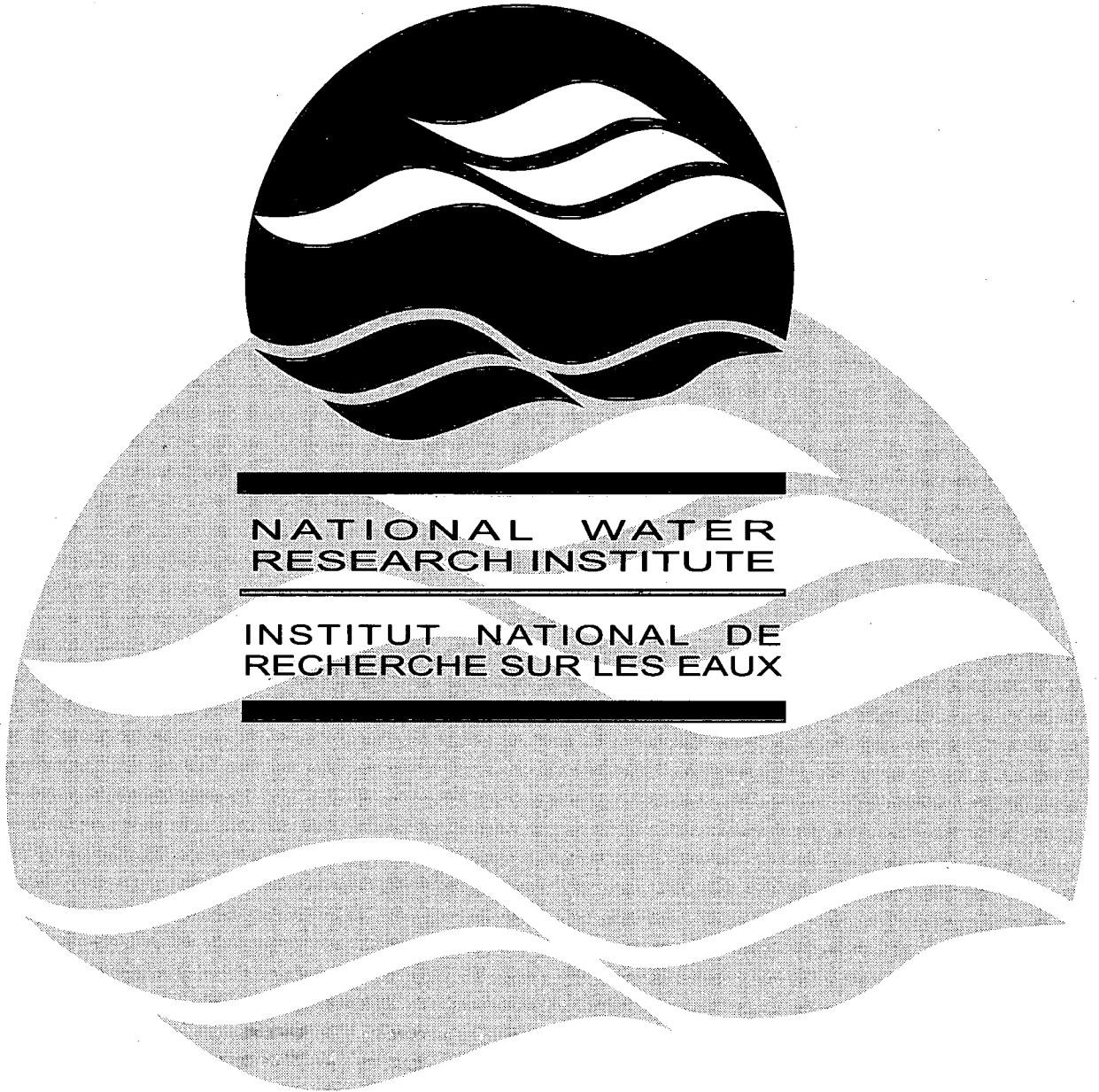


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**OCCURRENCE AND ELIMINATION OF  
NONYLPHENOL ETHOXYLATES AND  
METABOLITES IN MUNICIPAL WASTEWATER  
AND EFFLUENTS**

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**NWRI Contribution No. 98-032**

**Occurrence and elimination of nonylphenol ethoxylates and metabolites in  
municipal wastewater and effluents**

by

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## MANAGEMENT PERSPECTIVE

Industrial and domestic applications of detergents based on nonylphenol ethoxylates (NPEO) result in the generation of significant amounts of these compounds in municipal sewage. NPEO are transformed, by sewage treatment, into more toxic and estrogenic metabolites including nonylphenol, which is a PSL2 chemical along with NPEO. In this study, the occurrence and elimination of these surfactant-derived endocrine disrupting chemicals in a Canadian sewage treatment plant over a one-year period is reported. While over 80% of the incoming NPEO was removed, the overall elimination of total nonylphenolics was merely 53%. Conventional sewage treatment processes are ineffective in the biodegradation of NPEO since kilograms of these metabolites, with the alkylphenol moiety intact, in the final effluent are being released to the aquatic environment daily.

## SOMMAIRE À L'INTENTION DE LA DIRECTION

Les application industrielles et domestiques des détergents à base de nonylphénoléthoxylates (NPEO) font que les eaux usées municipales en renferment de fortes quantités. Les NPEO sont transformés par le traitement des eaux usées en métabolites plus toxiques et oestrogéniques dont le nonylphénol, qui est une substance PSL2, avec les NPEO. Dans cette étude, on traite de la présence et de l'élimination de ces substances chimiques dérivées de surfactants qui perturbent la fonction endocrinienne dans une usine canadienne de traitement des eaux usées sur une période d'un an. Bien que plus de 80 % des NPEO entrant dans l'usine ait été éliminé, l'élimination globale des substances nonylphénoliques totales n'a été que de 53 %. Les procédés classiques de traitement des eaux usées sont inefficaces pour la biodégradation des NPEO, des kilogrammes de ces métabolites, avec la fraction alkyphénolique intacte, dans l'effluent final étant libérés dans le milieu aquatique chaque jour.

## ABSTRACT

A survey of the concentrations of nonylphenol ethoxylates (NPEO) and their metabolites in wastewater samples collected from a Canadian sewage treatment plant using primary and secondary treatment is presented. 24-Hr composite raw sewage, primary effluent and final effluent samples were collected monthly over a one-year period. Levels of NP<sub>n</sub>EO (n=1 to 17) and their metabolites, nonylphenol (NP) and nonylphenoxy carboxylic acids (NPEC), in these samples were determined by HPLC and GC/MS methods. While ca. 85% of the total alkylphenolics in raw sewage are ethoxylates, the major component (nearly 80%) in the final effluent was in the form of carboxylic acids. During this study period, the median total alkylphenolic concentrations in raw sewage and final effluent were 526 and 248 nmol/L, respectively, representing an overall elimination rate of 53%. The estimated daily discharge of the nonylphenolics to the aquatic environment varied from 15 to 44 moles, with a median value of 20 moles. These data suggested that conventional sewage treatments are ineffective in the removal of the surfactant-derived metabolites.

## RÉSUMÉ

On présente une étude sur les concentrations de nonylphénoléthoxylates (NPEO) et de leurs métabolites dans des échantillons d'eaux usées recueillis dans une usine canadienne de traitement des eaux usées appliquant un traitement primaire et un traitement secondaire. On a recueilli chaque mois, sur une période d'un an, des échantillons composites de 24 heures des eaux brutes, de l'effluent primaire et de l'effluent final. On a déterminé par chromatographie liquide à haute performance et par CG/SM les niveaux de NP<sub>n</sub>EO (n = 1 à 17) et de leurs métabolites, de nonylphénol (NP) et d'acides nonylphénoxy-carboxyliques (NPEC) dans ces échantillons. Tandis que près de 85 % des substances alkylphénoliques totales dans les eaux brutes sont des éthoxylates, le composant majeur (près de 80 %) dans l'effluent final était sous la forme d'acides carboxyliques. Durant la période de l'étude, les concentrations médianes totales de substances alkylphénoliques dans les eaux brutes et dans l'effluent final étaient de 526 et 248 nmol/L, respectivement, ce qui donne un taux global d'élimination de 53 %. Le rejet quotidien estimé de substances nonylphénoliques dans le milieu aquatique variait de 15 à 44 moles, avec une valeur médiane de 20 moles. Ces données laissent penser que les traitements classiques des eaux usées sont inefficaces pour éliminer les métabolites dérivés de surfactants.

## INTRODUCTION

Nonylphenol ethoxylates (NPEO) and octylphenol ethoxylates (OPEO), to a smaller extent, are major non-ionic surfactants that have been used to produce many cleaning products. According to a study by Metcalfe et al. (1996), 11 sectors have been identified as the users of NPEO in Canada. The major users are the textile and pulp and paper industries, manufacturers for the petroleum and leather products as well as producers for household and industrial detergents.

As a result of the domestic and industrial applications of these detergents, NPEO with up to ca. 20 ethoxy units have been reported in river water, wastewater and sewage samples collected from many parts of Europe and North America (Ahel and Giger 1985a and b, Marcomini et al. 1987, Naylor et al. 1992, Ahel et al. 1994a and b, 1996, Blackburn et al. 1995). The fate of NPEO in sewage treatment is well established. They degrade to nonylphenol (NP) and the lower oligomers such as the mono- (NP1EO) and di-ethoxylates (NP2EO) under anaerobic conditions, and to nonylphenoxyacetic acid (NP1EC) and nonylphenoxy-ethoxyacetic acid (NP2EC) under aerobic conditions (Ahel et al. 1994a). Under the same conditions, OPEO follow similar biodegradation pathways to produce the corresponding metabolites (Ball et al. 1989). In addition to the parent compounds, monitoring of these metabolites in sewage samples is also essential because they are known to be lipophilic (Ahel and Giger 1993b) and have a tendency to bioaccumulate (Ekelund et al. 1990, Ahel et al. 1993). As well, NP/NPEC and OP/OPEC are relatively persistent (Ahel et al. 1987, Ball et al. 1989) and NP is more toxic than the parent compounds to some aquatic species (Granmo et al. 1989, Comber et al. 1993).

Some of them, including NP, OP, NP1EC and NP2EO, have also been shown to be weakly estrogenic using data developed by rainbow trout *in vitro* hepatocyte bioassay (Jobling and Sumpter, 1993).

Recently, the behaviour of NPEO surfactants in the aquatic environment has been reported (Ahel et al. 1994a and b, 1996). In one of these studies, the occurrence, transformation, and elimination of these surfactants and their metabolites in several Swiss sewage treatment plants was described (Ahel 1994a). Their results indicated that NPEO in untreated sewage and primary effluent are efficiently removed by biological treatment. However, the overall biodegradation rate for NPEO was limited by the formation of biorefractory metabolites, including NP, NP1EO, NP2EO, and NPEC.

There have been relatively few studies on the occurrence of NPEO and related compounds in Canada. Previously, the occurrence of NP, OP, and NP1EO, and NP2EO in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River has been reported (Bennie et al. 1997). Another study on the occurrence of the same compounds in sewage treatment plant waste streams has also been published (Bennie et al. 1998). However, there are no data on the effectiveness of sewage treatment processes in the removal of nonylphenolics. In this study, comprehensive analyses of all nonylphenolic compounds were conducted in the samples collected from a Canadian sewage treatment plant that uses both primary (mechanical) and secondary (biological with activated sludge) treatments. Using these data, the median percentage elimination of nonylphenolics and the daily discharge of these chemicals into the aquatic environment over a 12-month period were calculated.



## EXPERIMENTAL

### *Sampling*

Sewage samples from a southern Ontario STP were collected monthly from March 1997 to February 1998. At sampling time, one-litre, 24-hr composite samples of untreated raw sewage, primary effluent and final effluent were collected in brown glass bottles. Raw sewage was taken from the trunk sewer just before it entered the pumping station. The primary effluent was collected at the exit of the primary sedimentation tanks. The final effluent was taken at the exit of the final sedimentation tanks. No preservative was added to the sewage samples which were returned to the laboratory, kept at 4°C, and extracted within 24-hr.

### *Sample preparation*

Prior to extraction, each sample was filtered through a GF/C filter (1.2 µm pore) using an all-glass filtration apparatus with a sinter-glass base. A filter aid such as Celite 545 was also used to minimize plugging. From each filtered sample, two 250-mL aliquots were then measured. One aliquot was used for the determination of NP and OP. The other aliquot was used for the determination of the ethoxylates and carboxylates.

A previously published *in situ* acetylation procedure was used for the extraction and quantification of NP and OP in wastewater (Lee and Peart 1995). Briefly, 1 mL of acetic anhydride was added to the sample in the presence of potassium carbonate. The sample was then stirred with 30 mL of petroleum ether (b.p. 30 to 60°C) for 30 minutes. During this period of time, the phenols were acetylated and extracted into the organic layer. After phase separation, acetylation of the aqueous layer was repeated twice with

fresh acetic anhydride and petroleum ether. The combined organic layer was partitioned with 30 mL of 1%  $K_2CO_3$  to remove coextracted acetic acid, dried with anhydrous sodium sulfate, evaporated, and exchanged into 1 mL of iso-octane for GC/MS analysis.

The other aliquot was acidified to pH 2 with 1 N HCl. A solid phase extraction (SPE) procedure using a 1-g ODS cartridge was used for the preconcentration of APEO and APEC in the samples (Lee et al. 1998). Prior to extraction, the cartridge was conditioned with acetonitrile (5 mL), methanol (5 mL), and water (10 mL). The sample was then extracted at a flow rate of ca. 10 mL/min with a vacuum of 13-15 in. of mercury. The organics were eluted from the cartridge with 10 mL of methanol and the extract was equally split. One half was evaporated to dryness and redissolved in 1 mL of solvent A (see below) for high pressure liquid chromatography (HPLC) analysis of NPEO. The other half was also evaporated to dryness and reacted with 2 mL of 12%  $BF_3$ /methanol at 85°C for 30 min. The reaction mixture was then evaporated to ca. 0.5 mL and 3 mL of water was added. The methylated products were back extracted into three 2 mL aliquots of petroleum ether, dried with anhydrous sodium sulfate, evaporated, and exchanged into iso-octane (500  $\mu$ L) for GC/MS analysis for the carboxylates.

#### *Chemical analysis*

NPEO were analyzed by HPLC (Hewlett-Packard 1050) with a normal phase Hypersil APS column (100 x 2.1 mm i.d.) and a fluorescence detector operating at 230 nm (excitation) and 300 nm (emission) (Lee et al. 1997). For the separation of NPEO oligomers, the following solvent mixtures were used: solvent A, n-hexane/2-propanol (98:2, v/v) and solvent B, 2-propanol/water (9:1, v/v). The initial mobile phase, 97% A and 3% B, was kept constant for the first 3 min of each run. It was then linearly

programmed from this composition to 43% A and 57 % B in the next 22 min. A post-run equilibration time of 15 min between injections was used. The HPLC column was maintained at 40°C and a constant flow rate of 0.3 mL/min.

The acetylated NP and OP were analyzed by GC/MS using a Hewlett-Packard gas chromatograph (5890 Series II) equipped with a Mass Selective Detector (5972 MSD) and a HP-5MS column (30 m x 0.25 mm i.d.) (Lee and Peart 1995). The injection port and detector interface temperatures were 250 and 280°C, respectively. The GC oven temperature program was 70°C initial (kept for 1 min), increased to 160°C at 30°C/min and then to 280°C at 5°C/min. Carrier gas (helium) was held constant at 39.8 cm/s. The electron energy and electron multiplier voltages were 70 eV and 200 V above the autotune value, respectively. Ions at  $m/z$  107, 121, 135, 163, 191, and 262 were monitored for the quantitative determination of the acetyl derivatives of NP. For OP, the ions at  $m/z$  135, 177, and 248 were monitored. The same GC/MS conditions were used for the analysis of the APEC methyl esters except that the following ions were monitored:  $m/z$  207, 208, and 278 for OP1EC,  $m/z$  117, 251, and 322 for OP2EC,  $m/z$  207, 221, and 292 for NP1EC, as well as  $m/z$  117, 265, 307, and 336 for NP2EC.

## RESULTS AND DISCUSSION

### *Description of the sewage treatment plant*

The sewage treatment plant receives wastewater generated by the local industries and a municipality with a population of ca. 140,000. After the grit in raw sewage is removed, the sewage is pumped into one of the four primary sedimentation tanks. The

flow of the primary effluent exiting these tanks is split between six aeration tanks where it is further treated with activated sludge as a secondary treatment. The effluent then flows into a series of 12 final sedimentation tanks before discharging into the environment. At this plant, chlorination of the final effluent was only used in the warmer months (from May to October).

#### *Occurrence of nonylphenol ethoxylates*

The concentrations of NPEO found in the untreated raw sewage as well as the primary and final effluents samples collected in this study are tabulated in Table 1. For the sake of conciseness, the concentrations of NP1EO, NP2EO, and the sum for NP3EO through NP17EO were listed. In these samples, the raw sewage had the highest total NPEO concentrations and they varied from 123 to 415 (median 191)  $\mu\text{g/L}$  over the year. Lower NPEO levels, ranging from 43 to 167 (median 129)  $\mu\text{g/L}$  and from 3 to 32 (median 13)  $\mu\text{g/L}$ , were detected in the primary and final effluents, respectively. While the lowest NPEO concentrations were observed in the January samples, the highest ones were detected in the March and April samples. Hence, there was no obvious seasonal (or ambient temperature) dependence on the NPEO concentrations for these samples.

In consistent with previous reports (Ahel and Giger 1985b, Ahel et al. 1994a), the most abundant oligomers in the raw sewage and primary effluent were NP1EO/NP2EO as well as NP6EO/NP7EO. Since NP1EO and NP2EO are minor components in most commercial detergents, the presence of high levels of these oligomers are due to the aerobic and anaerobic biodegradation of NPEO in the sewer system and in the primary clarifiers. While long chain ethoxylates such as NP14EO through NP17EO were detected,

their occurrence in these samples was <50% and their concentrations were usually <20 and <10 µg/L in the raw sewage and the primary effluent, respectively.

The most abundant oligomers in the final effluent were NP1EO and NP2EO, with concentrations varying from 0.5 to 13 µg/L. The levels of NPEO with three to nine ethoxy units decreased rapidly and NPEO with ten or more ethoxy units were rarely detected in the final effluent.

The observation of OP and OPEC in the sewage (see later discussion) indicated the presence of OPEO in these samples. The results for NPEO in Table 2 are therefore biased high since NPEO and OPEO coelute under our HPLC conditions. Based on the relative concentrations of OP and NP as well as OP1EC and NP1EC in the same sample (see Tables 2 and 3), the estimated OPEO concentration in a sample is roughly 10% of NPEO. Therefore, this analytical error would not contribute a major bias to the NPEO results.

#### *Occurrence of nonyl- and octyl- phenols*

NP and OP were readily detected in all samples tested over the year (Table 2). The levels of OP varied from 0.16 to 1.55 (median 0.60) µg/L in the raw sewage, from 0.12 to 0.81 (median 0.54) µg/L in the primary effluent, and from 0.05 to 0.66 (median 0.14) µg/L in the final effluent. In contrast, the concentrations of NP in these samples were much higher. They ranged from 1.81 to 22.69 (median 6.91) µg/L in the raw sewage, from 1.59 to 10.92 (median 4.01) µg/L in the primary effluent, and from 0.56 to 2.12 (median 1.21) µg/L in the final effluent. For the samples collected at the same time, the lowest NP and OP concentrations were invariably found in the final effluent. In contrast, the highest concentrations of these compounds occurred in 50% of the raw

sewage and 50% of the primary effluent. Overall, there was a larger percentage decrease in the NP than the OP levels going from raw sewage or primary effluent to final effluent. This observation correlates well with their water solubility as NP is less soluble than OP (5.43 vs. 12.6 mg/L at 20.5°C) (Ahel and Giger 1993a) and is therefore more likely to be adsorbed by sludge.

#### *Occurrence of alkylphenol carboxylates*

Again, the carboxylate metabolites, NP1EC/NP2EC and OP1EC/OP2EC, were detected in all sewage samples (Table 3). Over the year, the concentrations of NP1EC varied from 2.2 to 71.3 (median 4.4) µg/L in the raw sewage, from 3.3 to 11.1 (median 6.6) µg/L in the primary effluent, and from 9.1 to 43.8 (median 22.8) µg/L in the final effluent. Similarly, the levels of NP2EC ranged from 1.4 to 15.4 (median 4.5) µg/L, from 4.3 to 16.4 (median 7.2) µg/L, and from 13.2 to 41.1 (median 25.6) µg/L for the respectively samples. For OP1EC, the concentrations varied from 0.20 to 8.39 (median 0.64) µg/L in the raw sewage, from 0.23 to 3.03 (median 0.73) µg/L in the primary effluent, and from 0.89 to 28.79 (median 4.36) µg/L in the final effluent. For OP2EC, the respective ranges varied from 0.10 to 3.81 (median 0.57) µg/L, from 0.30 to 3.13 (median 0.79) µg/L, and from 1.52 to 12.62 (median 4.91) µg/L.

For the samples collected at the same time, the highest level of APEC was always detected in the final effluent, with only one exception. (It is unclear why an extremely high NP1EC result was observed in the raw sewage collected in August.) As suggested by Ahel et al. (1994a), APEC are formed by aerobic degradation of the phenolics during the secondary sewage treatment with activated sludge.

The observation of NP/OP and NP<sub>n</sub>EC/OP<sub>n</sub>EC (n=1 and 2) in raw sewage (Tables 2 and 3) indicates that NPEO and OPEO have already undergone partial degradation in the sewer system before they reached the sewage treatment plant.

#### *Distribution of phenolic compounds in sewage*

Before the total alkylphenolic concentrations were calculated, concentrations of individual species with different molecular weights were first converted to molar basis (Table 4). Since there were substantial random variations in the levels of the nonylphenolics over the year, the median rather than the mean concentration for each component in sewage samples was used in the following calculations. Using these median values, the relative abundance of NPEO (total), NP, NPEC (NP1EC+NP2EC), OP, and OPEC (OP1EC+OP2EC), in raw sewage, primary and final effluents is shown in Figure 1. In raw sewage, nearly 85% of the total nonylphenolic content was in the ethoxylate form. In contrast, NP and NPEC were present at 6 and 7%, respectively, whereas OP and OPEC constituted <2% of the total. The relative abundance of NP, OP, and OPEC in the primary effluent was quite similar to that observed for raw sewage. The amount of NPEO dropped to 78% and that for NPEC increased to 14%. The composition of nonylphenolics in the final effluent was significantly different from the raw sewage and primary effluent. As reported by other authors, the most abundant component in the final effluent is NPEC (64%). The octyl derivatives, OPEC, constitute another 13%. NPEO, NP, and OP at 13, 1.5, and 0.3% respectively, were substantially reduced in comparison to the primary effluent. It should be noted that, the higher carboxylic acids (i.e. OP3EC, NP4EC, etc.) were likely to be present but were not monitored in the sewage samples. If

these compounds were also included, the relative abundance of APEC in the final effluent would have been even higher.

#### *Elimination of nonylphenolics in sewage treatment plant*

NPEO are very effectively removed by the sewage treatment processes as the annual median concentration decreased from 436 nmol/L in the raw sewage to 41 nmol/L in the final effluent, representing a >90% reduction. In terms of individual components, the higher NPnEO (n>8) are nearly entirely removed in the final effluent. Based on the median concentrations (on molar basis) in the influent and final effluent, the rates of elimination for the intermediate NPnEO (n=3 to 7) were mostly >90%. For the lipophilic NP1EO and NP2EO, the rates of elimination were 63 and 54%, respectively. These results were also consistent with the previously published report.

Net elimination for NP and OP was also observed in the sewage treatment processes. Again, based on their median concentrations (on molar basis) in the raw sewage and final effluent, the rates of elimination were 82 and 76% for NP and OP, respectively. Since AP are also produced by the anaerobic degradation of APEO in the plant, the actual elimination rates of these compounds should be even higher. In contrast, the median NP1EC and NP2EC concentrations in the final effluent increased by 418 and 468%, respectively, in comparison to the influent. The respective increases in OP1EC and OP2EC concentrations were 585 and 761%.

The median total alkylphenolic concentrations decreased from 526 to 355 nmol/L from raw sewage to primary effluent and further to 248 nmol/L in the final effluent. This overall reduction rate of 53% is very similar to the mean elimination rate for the nonylphenolics (59%) observed by Ahel et al. (1994a) for 11 sewage treatment plants in



Switzerland. Using the flow rates provided by the sewage treatment plant for the sampling dates, the number of moles of alkylphenolics in the raw sewage and final effluent per day as well as the % elimination have been calculated. As shown in Table 5, loading of these phenolics to the aquatic environment ranged from 15 to 44 moles/day, with a median value of 20.0 moles/day. It is rather surprising to note that % elimination of the alkylphenolics varied widely from 20 to 76 % (median 43%). The highest elimination rates for the alkylphenolics were observed in April and October and the lowest in September and December. Again, the efficiency in the removal of APEO and their metabolites in the sewage treatment plant did not seem to be ambient temperature dependent.

### *Conclusions*

While the use of detergents based on NPEO for domestic applications has recently been reduced, these ethoxylates and their metabolites are still readily detected in municipal sewage samples. Over 80% of the incoming NPEO and NP are eliminated in the sewage treatment plant, however, this number is deceptively high as the overall reduction of total nonylphenolics and octylphenolics is rather low (53%). A major reason for the latter is the formation of the carboxylates, in the final effluent, by the activated sludge-induced aerobic degradation of NPEO. Since extremely high levels of NP, NP1EO, NP2EO have been found in sewage sludge (Giger et al. 1984, Lee and Peart 1995, Lee et al. 1997), some or most of the nonylphenolics "eliminated" in the sewage treatment processes are undoubtedly bound to the sludge which was used for landfill applications, thus making the total environmental loading even higher. From a biodegradation standpoint, nonylphenol based surfactants are poorly degraded by conventional sewage treatment as most of them

are broken down into biorefractory molecules with the aromatic moiety intact. From an ecotoxicology standpoint, one should be more concerned about the environmental impact of the major NPEO degradation products, *i.e.* NP, NP1EO/NP2EO, NP1EC/NP2EC, since they are more toxic and estrogenic than the parent surfactant. The results of this study suggest that the biodegradation pathways and elimination of NPEO in a Canadian sewage treatment plant follow a pattern similar to that reported in Europe.

## REFERENCES

- Ahel, M., Conrad, T. and Giger, W. (1987). Persistent organic chemicals in sewage effluents. 3. Determinations of nonylphenoxy carboxylic acids by high-resolution gas chromatography/mass spectrometry and high-performance liquid chromatography. *Environ. Sci. Technol.* **21**, 697-703.
- 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. *Water Res.* **28**, 1131-1142.
- Ahel, M., McEvoy, J. and Giger, W. (1993). Bioaccumulation of the lipophilic metabolites of nonionic surfactants in freshwater organisms. *Environ. Poll.* **79**, 243-248.

- Ahel, M., Giger, W. and Schaffner, C. (1994b). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment - II. Occurrence and transformation in rivers. *Water Res.* **28**, 1143-1152.
- Ahel, M., Schaffner, C. and Giger, W. (1996). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment - III. Occurrence and elimination of their persistent metabolites during infiltration of river water to groundwater. *Water Res.* **30**, 37-46.
- Ball, H.A., Reinhard, M. and McCarty, P.L. (1989). Biotransformation of halogenated and nonhalogenated octylphenol polyethoxylate residues under aerobic and anaerobic conditions. *Environ. Sci. Technol.* **23**, 951-961.
- Blackburn, M.A. and Waldock, M.J. (1995). Concentrations of alkylphenols in rivers and estuaries in England and Wales. *Water Res.* **29**, 1623-1629.
- Bennie, D.T., Sullivan, C.A., Lee, H.-B., Peart, T.E. and Maguire, R.J. (1997). Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River, *Sci. Total Environ.* **193**, 263-275.
- Bennie, D.T., Sullivan, C.A., Lee, H.-B. and Maguire, R.J. (1998). Alkylphenol polyethoxylates metabolites in Canadian sewage treatment plant waste streams. *Water Qual. Res. J. Canada*, in press.
- Comber, M.H.I., Williams, T.D. and Stewart, K.M. (1993). The effects of nonylphenol on *Daphnia magna*. *Water Res.* **27**, 273-276.
- Ekelund, R., Bergman, A., Granmo, A. and Berggren, M. (1990). Bioaccumulation of 4-nonylphenol in marine animals - a re-evaluation. *Environ. Pollut.* **64**, 107-120.
- 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.
- Granmo, A., Ekelund, R., Magnusson, K. and Berggren, M. (1989). Lethal and sublethal toxicity of 4-nonylphenol to the common mussel (*Mytilus edulis* L.). *Environ. Pollut.* **59**, 115-127.
- 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. *Aquat. Toxicol.* **27**, 361-372.
- Lee, H.-B. and Peart, T.E. (1995). Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. *Anal. Chem.* **34**, 1976-1980.

- Lee, H.-B., Peart, T.E., Bennie, D.T. and Maguire, R.J. (1997). Determination of nonylphenol polyethoxylates and their carboxylic acid metabolites in sewage treatment plant sludge by supercritical carbon dioxide extraction. *J. Chromatogr.* **785**, 385-394.
- Lee, H.-B., Weng, J., Peart, T.E. and Maguire, R.J. (1998). Occurrence of alkylphenoxyacetic acids in Canadian sewage treatment plant effluents. *Water Qual. Res. J. Canada* **33**, 19-29.
- Marcomini, A., Capri, S. and Giger, W. (1987). Determination of linear alkylbenzenesulphonates, alkylphenol polyethoxylates and nonylphenol in waste water by high-performance liquid chromatography after enrichment on octadecylsilica. *J. Chromatogr.* **403**, 243-252.
- Metcalfé, C., Hoover, L., and Sang, S. (1996). Nonylphenol ethoxylates and their use in Canada. World Wildlife Fund report, December 1996. World Wildlife Fund Canada, 90 Eglinton Avenue East, Suite 504, Toronto, Ontario M4P 2Z7.
- 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. Amer. Oil Chemists' Soc.* **69**, 695-703.

Table 1. Concentrations ( $\mu\text{g/L}$ ) of NPnEO in sewage samples.

| Date     | NP1EO |      |       | NP2EO |      |       | NPnEO (n=3 to 17) |       |       | Total |       |       |
|----------|-------|------|-------|-------|------|-------|-------------------|-------|-------|-------|-------|-------|
|          | raw   | prim | final | raw   | prim | final | raw               | prim  | final | raw   | prim  | final |
| 97/3/10  | 2.8   | 4.5  | 5.7   | 23.8  | 7.6  | 13.4  | 237.6             | 154.7 | 13.3  | 264.2 | 166.9 | 32.4  |
| 97/4/7   | 5.5   | 7.5  | 3.1   | 6.5   | 7.1  | 9.4   | 402.9             | 120.5 | 6.9   | 414.9 | 135.1 | 19.4  |
| 97/5/5   | 9.2   | 7.6  | 5.4   | 5.2   | 5.5  | 8.2   | 147.2             | 79.5  | 6.6   | 161.6 | 92.6  | 20.2  |
| 97/6/18  | 11.9  | 11.4 | 1.1   | 5.3   | 5.0  | 1.5   | 152.5             | 89.5  | 0.9   | 169.7 | 105.9 | 3.5   |
| 97/7/7   | 16.8  | 13.3 | 4.0   | 5.7   | 10.0 | 3.9   | 168.8             | 117.2 | 5.0   | 191.3 | 140.6 | 12.9  |
| 97/8/11  | 23.6  | 21.2 | 5.7   | 10.8  | 11.9 | 4.7   | 155.7             | 114.2 | 2.3   | 190.2 | 147.2 | 12.7  |
| 97/9/16  | 37.3  | 21.5 | 8.9   | 17.9  | 16.4 | 10.8  | 121.2             | 98.9  | 4.1   | 176.4 | 136.7 | 23.8  |
| 97/10/27 | 20.9  | 14.6 | 5.2   | 10.1  | 7.0  | 4.0   | 226.9             | 83.0  | 2.2   | 257.9 | 104.5 | 11.4  |
| 97/11/14 | 15.0  | 18.3 | 4.8   | 8.4   | 9.0  | 3.8   | 303.4             | 124.7 | 1.2   | 326.8 | 152.0 | 9.8   |
| 97/12/9  | 16.7  | 16.7 | 6.5   | 18.7  | 8.1  | 4.5   | 164.5             | 97.5  | 1.7   | 199.8 | 122.4 | 12.7  |
| 98/1/13  | 12.2  | 4.5  | 1.8   | 8.2   | 6.5  | 1.5   | 103.0             | 32.2  | 0.0   | 123.4 | 43.1  | 3.3   |
| 98/2/10  | 11.7  | 2.8  | 0.5   | 14.8  | 7.2  | 3.8   | 98.5              | 109.1 | 7.6   | 125.0 | 119.1 | 11.9  |

Table 2. Concentrations ( $\mu\text{g/L}$ ) of OP and NP in sewage samples.

| Date     | raw  | primary | final | raw   | primary | final |
|----------|------|---------|-------|-------|---------|-------|
|          | OP   | OP      | OP    | NP    | NP      | NP    |
| 97/3/10  | 0.32 | 0.42    | 0.37  | 2.06  | 2.95    | 1.09  |
| 97/4/7   | 0.16 | 0.54    | 0.27  | 1.81  | 3.00    | 1.17  |
| 97/5/5   | 0.20 | 0.32    | 0.26  | 2.74  | 5.01    | 2.12  |
| 97/6/18  | 0.56 | 0.71    | 0.21  | 8.46  | 10.92   | 1.24  |
| 97/7/7   | 0.99 | 0.62    | 0.16  | 8.88  | 4.63    | 1.26  |
| 97/8/11  | 1.55 | 0.72    | 0.66  | 14.14 | 3.05    | 1.24  |
| 97/9/16  | 0.76 | 0.38    | 0.11  | 11.15 | 3.39    | 1.84  |
| 97/10/27 | 0.63 | 0.77    | 0.08  | 22.69 | 7.70    | 1.50  |
| 97/11/14 | 0.52 | 0.53    | 0.12  | 8.05  | 5.55    | 0.69  |
| 97/12/9  | 1.04 | 0.81    | 0.05  | 4.77  | 5.26    | 0.57  |
| 98/1/13  | 0.70 | 0.12    | 0.05  | 4.28  | 1.59    | 0.56  |
| 98/2/10  | 0.45 | 0.18    | 0.06  | 5.77  | 1.89    | 0.69  |

Table 3. Concentrations ( $\mu\text{g/L}$ ) of APEC in sewage samples.

| Date     | raw   | primary | final | raw   | primary | final |
|----------|-------|---------|-------|-------|---------|-------|
|          | OPIEC | OPIEC   | OPIEC | OP2EC | OP2EC   | OP2EC |
| 97/3/10  | 1.14  | 1.18    | 2.43  | 0.24  | 0.47    | 1.88  |
| 97/4/7   | 0.31  | 0.33    | 0.89  | 0.20  | 0.33    | 1.52  |
| 97/5/5   | 0.20  | 0.23    | 1.30  | 0.10  | 0.30    | 1.71  |
| 97/6/18  | 1.29  | 0.67    | 4.71  | 0.83  | 0.89    | 5.14  |
| 97/7/7   | 0.93  | 0.98    | 11.28 | 1.11  | 1.11    | 10.67 |
| 97/8/11  | 8.39  | 3.03    | 28.79 | 3.81  | 3.13    | 12.62 |
| 97/9/16  | 1.11  | 0.79    | 10.04 | 1.03  | 1.58    | 12.24 |
| 97/10/27 | 0.33  | 0.39    | 3.96  | 0.21  | 0.33    | 1.83  |
| 97/11/14 | 0.46  | 0.95    | 10.03 | 0.61  | 1.04    | 6.35  |
| 97/12/9  | 0.77  | 2.51    | 20.73 | 0.74  | 1.95    | 9.82  |
| 98/1/13  | 0.28  | 0.35    | 2.97  | 0.22  | 0.41    | 2.42  |
| 98/2/10  | 0.50  | 0.66    | 4.00  | 0.53  | 0.68    | 4.67  |
|          | NP1EC | NP1EC   | NP1EC | NP2EC | NP2EC   | NP2EC |
| 97/3/10  | 8.3   | 9.0     | 27.9  | 5.0   | 7.9     | 36.9  |
| 97/4/7   | 3.0   | 3.3     | 9.1   | 3.4   | 6.3     | 20.0  |
| 97/5/5   | 2.2   | 3.5     | 12.9  | 1.4   | 4.8     | 13.2  |
| 97/6/18  | 16.8  | 6.7     | 20.5  | 6.8   | 7.7     | 23.8  |
| 97/7/7   | 7.7   | 6.5     | 21.8  | 6.6   | 6.4     | 27.1  |
| 97/8/11  | 71.3  | 11.1    | 43.8  | 15.4  | 15.3    | 40.2  |
| 97/9/16  | 7.6   | 6.6     | 31.1  | 7.3   | 16.4    | 41.1  |
| 97/10/27 | 2.6   | 3.4     | 19.4  | 2.1   | 4.3     | 14.3  |
| 97/11/14 | 3.6   | 7.8     | 41.7  | 4.8   | 10.9    | 34.5  |
| 97/12/9  | 4.0   | 8.7     | 42.3  | 4.2   | 8.7     | 31.0  |
| 98/1/13  | 3.6   | 4.6     | 23.8  | 2.1   | 6.1     | 24.0  |
| 98/2/10  | 4.8   | 6.1     | 20.3  | 3.8   | 6.7     | 22.5  |

Table 4. Concentrations (nmol/L) of total nonylphenolics in sewage samples.

| Date     | NPnEO | NP    | NP1EC | NP2EC | OP  | OPIEC | OP2EC | Total |
|----------|-------|-------|-------|-------|-----|-------|-------|-------|
| raw      |       |       |       |       |     |       |       |       |
| 97/3/10  | 483.4 | 9.4   | 29.9  | 15.5  | 1.6 | 4.3   | 0.8   | 544.8 |
| 97/4/7   | 671.2 | 8.2   | 10.8  | 10.6  | 0.8 | 1.2   | 0.7   | 703.4 |
| 97/5/5   | 333.5 | 12.5  | 7.9   | 4.4   | 1.0 | 0.8   | 0.3   | 360.3 |
| 97/6/18  | 336.5 | 38.5  | 60.4  | 21.1  | 2.7 | 4.9   | 2.7   | 466.8 |
| 97/7/7   | 401.0 | 40.4  | 27.7  | 20.5  | 4.8 | 3.5   | 3.6   | 501.5 |
| 97/8/11  | 424.2 | 64.3  | 256.5 | 47.8  | 7.5 | 31.8  | 12.4  | 844.4 |
| 97/9/16  | 447.1 | 50.7  | 27.3  | 22.7  | 3.7 | 4.2   | 3.3   | 559.0 |
| 97/10/27 | 538.7 | 103.1 | 9.4   | 6.5   | 3.1 | 1.3   | 0.7   | 662.7 |
| 97/11/14 | 622.6 | 36.6  | 13.0  | 14.9  | 2.5 | 1.7   | 2.0   | 693.3 |
| 97/12/9  | 447.2 | 21.7  | 14.4  | 13.0  | 5.1 | 2.9   | 2.4   | 506.7 |
| 98/1/13  | 274.6 | 19.5  | 13.0  | 6.5   | 3.4 | 1.1   | 0.7   | 318.7 |
| 98/2/10  | 301.4 | 26.2  | 17.3  | 11.8  | 2.2 | 1.9   | 1.72  | 362.5 |
| Median   | 435.6 | 31.4  | 15.9  | 14.0  | 2.9 | 2.4   | 1.9   | 525.7 |
| primary  |       |       |       |       |     |       |       |       |
| 97/3/10  | 311.1 | 13.4  | 32.4  | 24.5  | 2.0 | 4.5   | 1.5   | 389.5 |
| 97/4/7   | 251.2 | 13.6  | 11.9  | 19.6  | 2.6 | 1.3   | 1.1   | 301.3 |
| 97/5/5   | 202.1 | 22.8  | 12.6  | 14.9  | 1.6 | 0.9   | 1.0   | 255.7 |
| 97/6/18  | 231.2 | 49.6  | 24.1  | 23.9  | 3.5 | 2.5   | 2.9   | 337.7 |
| 97/7/7   | 297.7 | 21.1  | 23.4  | 19.9  | 3.0 | 3.7   | 3.6   | 372.4 |
| 97/8/11  | 342.4 | 13.9  | 39.9  | 47.5  | 3.5 | 11.5  | 10.2  | 468.8 |
| 97/9/16  | 332.0 | 15.4  | 23.7  | 50.9  | 1.8 | 3.0   | 5.1   | 432.0 |
| 97/10/27 | 233.2 | 35.0  | 12.2  | 13.4  | 3.7 | 1.5   | 1.1   | 300.1 |
| 97/11/14 | 339.3 | 25.2  | 28.1  | 33.9  | 2.6 | 3.6   | 3.4   | 436.0 |
| 97/12/9  | 282.3 | 23.9  | 31.3  | 27.0  | 3.9 | 9.5   | 6.3   | 384.3 |
| 98/1/13  | 109.4 | 7.2   | 16.6  | 18.9  | 0.6 | 1.3   | 1.3   | 155.4 |
| 98/2/10  | 246.9 | 8.6   | 21.9  | 20.8  | 0.9 | 2.5   | 2.2   | 303.8 |
| Median   | 266.8 | 18.2  | 23.6  | 22.4  | 2.6 | 2.8   | 2.6   | 355.0 |
| final    |       |       |       |       |     |       |       |       |
| 97/3/10  | 96.7  | 5.0   | 100.4 | 114.6 | 1.8 | 9.2   | 6.1   | 333.7 |
| 97/4/7   | 58.9  | 5.3   | 32.7  | 62.1  | 1.3 | 3.4   | 4.9   | 168.7 |
| 97/5/5   | 63.1  | 9.6   | 46.4  | 41.0  | 1.3 | 4.9   | 5.6   | 171.9 |
| 97/6/18  | 11.4  | 5.6   | 73.7  | 73.9  | 1.0 | 17.8  | 16.7  | 200.2 |
| 97/7/7   | 38.1  | 5.7   | 78.4  | 84.2  | 0.8 | 42.7  | 34.6  | 284.6 |
| 97/8/11  | 43.1  | 5.6   | 157.6 | 124.8 | 3.2 | 109.1 | 41.0  | 484.4 |
| 97/9/16  | 79.6  | 8.4   | 111.9 | 127.5 | 0.5 | 38.0  | 39.7  | 405.8 |
| 97/10/27 | 37.7  | 6.8   | 69.8  | 44.4  | 0.4 | 15.0  | 5.9   | 180.1 |
| 97/11/14 | 33.8  | 3.1   | 150.0 | 107.1 | 0.6 | 38.0  | 20.6  | 353.3 |
| 97/12/9  | 43.8  | 2.6   | 152.2 | 96.3  | 0.2 | 78.5  | 31.9  | 405.5 |
| 98/1/13  | 11.7  | 2.6   | 85.6  | 74.5  | 0.2 | 11.3  | 7.9   | 193.7 |
| 98/2/10  | 34.9  | 3.1   | 73.0  | 69.9  | 0.3 | 15.2  | 15.2  | 211.5 |
| Median   | 40.6  | 5.5   | 82.0  | 79.4  | 0.7 | 16.5  | 15.9  | 248.0 |



Table 5. Elimination of total nonylphenolics in the sewage treatment processes.

| Date     | Flow rate           | Influent | Final effl. | Influent | Final effl. | % Elimination |
|----------|---------------------|----------|-------------|----------|-------------|---------------|
|          | m <sup>3</sup> /day | nmol/L   | nmol/L      | mol/day  | mol/day     |               |
| 97/3/10  | 114105              | 544.8    | 333.7       | 62.2     | 38.1        | 39            |
| 97/4/7   | 90355               | 703.4    | 168.7       | 63.6     | 15.2        | 76            |
| 97/5/5   | 91100               | 360.3    | 171.9       | 32.8     | 15.7        | 52            |
| 97/6/18  | 94996               | 466.8    | 200.2       | 44.3     | 19.0        | 57            |
| 97/7/7   | 72222               | 501.5    | 284.6       | 36.2     | 20.6        | 43            |
| 97/8/11  | 91541               | 844.4    | 484.4       | 77.3     | 44.3        | 43            |
| 97/9/16  | 70988               | 559.0    | 405.8       | 39.7     | 28.8        | 27            |
| 97/10/27 | 92941               | 662.7    | 180.1       | 61.6     | 16.7        | 73            |
| 97/11/14 | 80612               | 693.3    | 353.3       | 55.9     | 28.5        | 49            |
| 97/12/9  | 73251               | 506.7    | 405.5       | 37.1     | 29.7        | 20            |
| 98/1/13  | 99772               | 318.7    | 193.7       | 31.8     | 19.3        | 39            |
| 98/2/10  | 73251               | 362.5    | 211.5       | 32.0     | 18.7        | 42            |

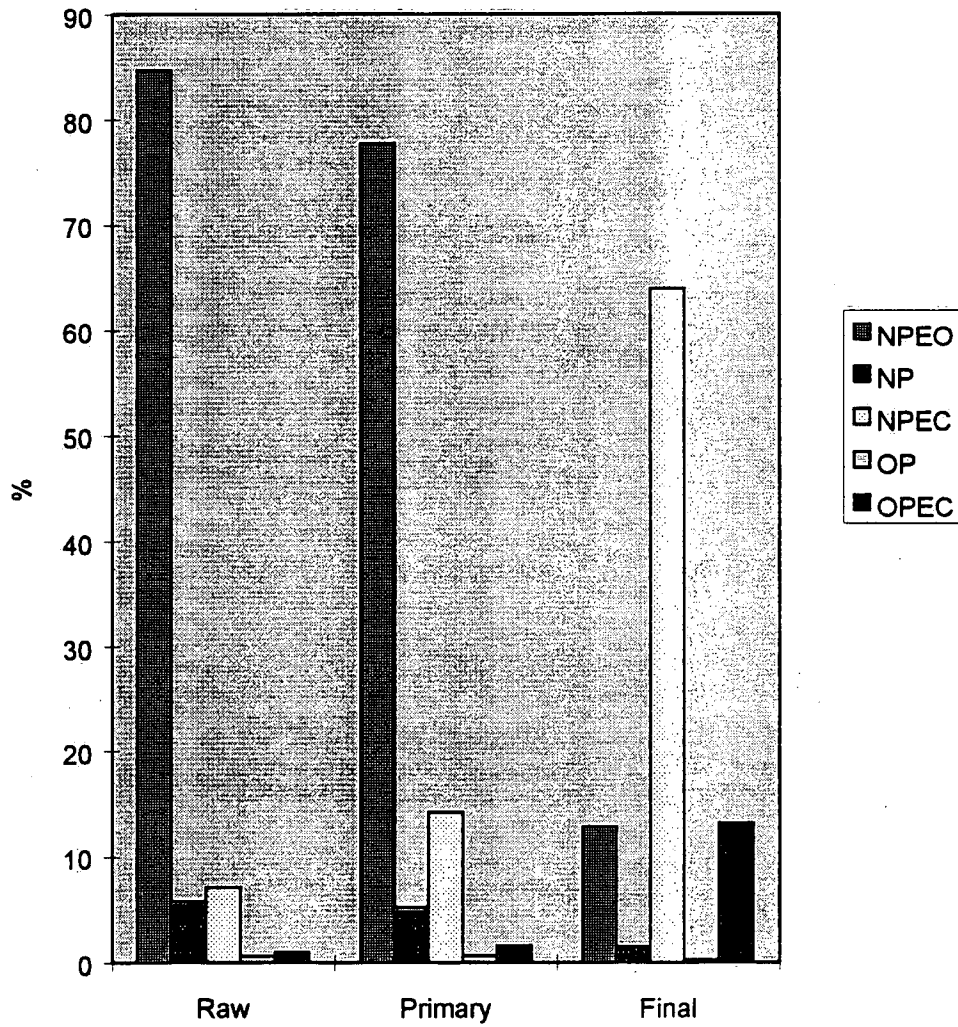
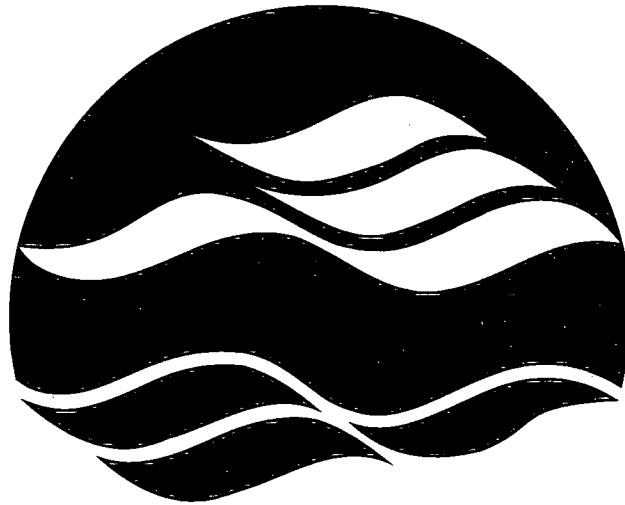


Figure 1. Distribution of alkylphenolic compounds in raw sewage, primary and final effluent.



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