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**OCCURRENCE OF NONYLPHENOL  
ETHOXYLATES AND THEIR METABOLITES IN  
CANADIAN PULP AND PAPER MILL EFFLUENTS  
AND SLUDGE**

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**Occurrence of nonylphenol ethoxylates and their metabolites in  
Canadian pulp and paper mill effluents and sludge**

by

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## **MANAGEMENT PERSPECTIVE**

This survey is the first detailed report on the concentrations of nonylphenol ethoxylates and their metabolites found in Canadian pulp and paper mill primary and secondary treated effluents and sludge. The database is representative of the entire industry because of the number of mills involved and the types of process and waste treatment methods employed by the participants. The observation of these chemicals in many of the samples indicated that the surfactant is a component of products that have been used by nearly all mills in the production of pulp and paper. In comparison to the same type of samples in an American study, the median levels of surfactants found in the secondary effluent is much lower in this study.

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Cette étude est le premier rapport détaillé sur les concentrations d'éthoxylates de nonylphénol et de leurs métabolites trouvés dans les effluents et les boues de traitement primaire et secondaire des usines canadiennes de pâtes et papiers. La base de données est représentative de toute l'industrie en raison du nombre d'usines impliquées et des types de procédés et de méthodes de traitement des déchets employés par les participants.

L'observation de ces substances chimiques dans de nombreux échantillons indiquait que l'agent tensio-actif, ou surfactant, est une composante des produits qui ont été utilisés par presque toutes les usines lors de la production des pâtes et papiers. Comparativement au même type d'échantillons dans une étude américaine, les concentrations médianes d'agents tensio-actifs trouvées dans l'effluent secondaire sont beaucoup plus faibles dans la présente étude.

## ABSTRACT

A survey of the concentrations of nonylphenol ethoxylates (NPnEO) and their metabolites in the primary and secondary treated effluent and sludge samples collected from pulp and paper mills was conducted. Through the coordination of the Pulp and Paper Research Institute of Canada (PAPRICAN), nineteen Canadian and one U.S. mill of various process types and waste treatment methods supplied samples in this study. Previously developed solid-phase extraction, supercritical fluid extraction, high performance liquid chromatography and gas chromatography/mass spectrometry methods were used for the determination of NPnEO and their metabolites, nonylphenol (NP) and the carboxylates (NPEC), in effluent and sludge samples. The levels of NPnEO ranged from <2 to 129 (median 4.5)  $\mu\text{g/L}$  and from <2 to 71.3 (median 5.8)  $\mu\text{g/L}$  for the primary and secondary effluents, respectively. The concentrations of NP varied from <0.1 to 1.32 (median 0.35)  $\mu\text{g/L}$  in the primary effluent and from <0.1 to 4.32 (median <0.1)  $\mu\text{g/L}$  in the secondary effluent. NPECs were found in only one primary and four secondary effluent samples with an overall concentration range from <1 to 32  $\mu\text{g/L}$ . These results are lower than those reported for paper mill effluents discharged into the lower Fox River, WI, USA. For the pulp and paper mill sludge, the levels of NPnEO and NP, on a dry weight basis, varied from <1 to 90.8 (median 21)  $\mu\text{g/g}$  and from <0.05 to 121 (median 1.3)  $\mu\text{g/g}$ , respectively. While NPnEO and NP were detected in nearly all sludge, their concentrations were lower than those observed for digested sewage sludge. Again, NPEC were found in only four samples, with an overall range from <1 to 18.5  $\mu\text{g/g}$ . No relationship between the nonylphenolic levels in the effluent samples and the process and waste treatment types of the mill was found.

## RÉSUMÉ

On a fait une étude sur les concentrations d'éthoxylates de nonylphénol (NPnEO) et de leurs métabolites trouvées dans les effluents et les boues de traitement primaire et secondaire des usines canadiennes de pâtes et papiers. Par le biais de l'Institut canadien de recherches sur les pâtes et papiers (PAPRICAN), dix-neuf usines canadiennes et américaines utilisant différents types de procédés et de méthodes de traitement diverses ont fourni des échantillons pour cette étude. On s'est servi des méthodes existantes d'extraction de la phase solide, d'extraction du fluide supercritique, de chromatographie liquide à haute performance et chromatographie en phase gazeuse/spectrométrie de masse pour déterminer les NPnEO et leurs métabolites, le nonylphénol (NP) et les carboxylates (NPEC), dans les échantillons d'effluent et de boue. Les concentrations de NPnEO variaient respectivement de < 2 à 129 (médiane 4,5) µg/L et de < 2 à 71,3 (médiane 5,8) µg/L pour les effluents primaire et secondaire. Les concentrations de NP variaient de < 0,1 à 1,32 (médiane 0,35) µg/L dans l'effluent primaire, et de < 0,1 à 4,32 (médiane < 0,1) µg/L dans l'effluent secondaire. On n'a trouvé de NPEC que dans un échantillon d'effluent primaire et dans quatre échantillons d'effluent secondaire, avec une concentration globale variant de < 1 à 32 µg/L. Ces résultats sont inférieurs à ceux signalés pour les effluents des usines de papiers rejetés dans le cours inférieur de la rivière Fox, WI, aux É.-U. En ce qui a trait à la boue des usines de pâtes et papiers, les concentrations de NPnEO et de NP, en poids sec, variaient respectivement de < 1 à 90,8 (médiane 21) µg/g et de < 0,05 à 121 (médiane 1,3) µg/g. Bien que l'on ait décelé des NPnEO et des NP dans presque tous les échantillons de boue, leurs concentrations étaient inférieures à celles observées dans les échantillons de boues d'égout digérées. Là encore,

on n'a trouvé de NPEC que dans quatre échantillons, avec une variation globale de < 1 à 18,5 µg/g. On n'a pas observé de rapport entre les concentrations de nonylphénol dans les échantillons d'effluent et les types de procédé et de traitement des déchets de l'usine.

## **MOTS CLÉS**

éthoxylates de nonylphénol, usine de pâtes et papiers, effluents, boue, occurrence

## INTRODUCTION

Alkylphenol ethoxylates are a major class of non-ionic surfactants that have been used extensively in Europe and North America. Nonylphenol ethoxylates (NPnEO) and, to a smaller extent, octylphenol ethoxylates (OPnEO) are the two major members in this family of chemicals. Metcalfe et al. (1996) reviewed the use of NPnEO (domestic demand estimated to be 4.5 kilotonnes in 1990) in Canada. They identified 11 sectors which use NPnEO as detergents, emulsifiers, wetting and dispersing agents. Discharges coming from the textile, pulp and paper, petroleum, and leather industries as well as municipal sewage treatment plants are believed to be the five major sources of these surfactants in the environment.

As a result of their wide applications, NPnEO and their metabolites have been detected in nearly all wastewater samples such as raw sewage, primary and final effluents, as well as digested sludge collected from the municipal sewage treatment plants in Canada (Bennie et al. 1997, Lee and Peart, 1995, Lee et al. 1997, 1998, Lee and Peart, 1998). They have also been found, at high levels, in the wastewater samples originating from textile mills (Bennie, unpublished results). According to the pioneering work by Ahel et al. (1994a and b), NPnEO degrade to the monoethoxylate (NP1EO), diethoxylate (NP2EO) and nonylphenol (NP) under anaerobic sewage treatment conditions. These lipophilic metabolites are usually adsorbed by sludge so that their concentrations are greatly reduced in the final effluent. In contrast, nonylphenoxyacetic acid (NP1EC) and nonylphenoxyethoxyacetic acid (NP2EC) are formed under aerobic conditions of the secondary waste treatment employing activated sludge. For this reason, the carboxylates are the major metabolites occurring in the final effluents.



NP and NPnEO are one of the substances in CEPA Priority Substances List 2 (PSL2), due to their widespread occurrence as well as their persistence in the environment, toxicity to aquatic organisms, and endocrine disrupting potentials. In particular, NP, OP, NP1EO, NP2EO, and NP2EC have been shown to cause a number of estrogenic responses developed by rainbow trout *in vitro* hepatocyte bioassay (Nimrod and Benson, 1996). In preparation of the supporting document for the environmental assessment of NP and NPnEO under CEPA, review articles on the analytical methodologies (Lee 1999), persistence (Maguire 1999), occurrence (Bennie 1999), and aquatic toxicity (Servos 1999) of NPnEO and their metabolites have recently been prepared.

Nonylphenol ethoxylates can be components of products used for a variety of different applications at pulp and paper mills. They can be employed as, disclosed or non-disclosed, constituents of formulations used as pitch dispersants, felt washers and cleaners, defoamers, wetting agents, deinking agents, and industrial detergents. They may also be present as the non-active ingredient in herbicides, pesticides, and industrial microbiocides in wood. The use of products (pitch dispersants, etc.) containing NPnEO will be mill specific and the application rates will undoubtedly vary depending on the situation and chemical supplier. To date, some mills are looking into the removal of NPnEO in their process, however, there is no official timetable for the voluntary phase-out by the pulp and paper industry.

While the occurrence of NPnEO and their metabolites in sewage and textile mill effluent is well documented, very little data are available for the same compounds in pulp and paper mill effluents. Recently, Naylor (1992, 1995) has reported the environmental

fate and safety of alkylphenol ethoxylates. The levels of NPnEO and NP in a wood pulp mill and a paper mill have been described in the latter publication. Naylor et al. (1996) have also reported the concentrations of NPnEO and NP in the effluents of 15 pulp and paper mills and six sewage treatment plants that discharged into the Fox River near Green Bay, WI. In a related study, Field and Reed (1996) have also reported the occurrence of NPnEC (n=1 to 4) in effluents collected from the paper mills and sewage treatment plants in the same location. The total NPnEC concentrations in those samples varied from below detection to 1300 µg/L and NP2EC was always the most abundant oligomer. However, information regarding the levels of NPnEO and NP in the same samples was not available. To date, there were no published data on the occurrence of NPnEO and their metabolites in Canadian pulp and paper mill effluent and sludge. In this study, a survey of 20 pulp and paper mills (19 Canadian and one US) for NPnEO and NP was conducted in order to provide the baseline information on the levels of nonylphenolic compounds in the paper mill effluents and sludge required for the CEPA assessment.

## **EXPERIMENTAL**

### **Chemicals and Standards**

NP, OP, acetic anhydride, and boron trifluoride/methanol complex (12%) were purchased from Aldrich (Milwaukee, WI). A calibrated mixture of NPnEO (n=1 to 17) was supplied by Carter Naylor of Huntsman Corp. (Austin, TX). NP1EC and OP1EC were synthesized by the reactions of NP and OP with chloroacetic acid, respectively (Lee et al., 1998).

Stock solutions of NP and OP at 1000 µg/mL were prepared individually in acetone. A diluted mixture of the phenols, at concentrations of 10 (NP) and 1 (OP) µg/mL, was also prepared in acetone for spiking and calibration standards. Similarly, stock solutions of NP1EC and OP1EC were made up in methanol. A diluted mixture of these acids, at 50 (NP1EC) and 5 (OP1EC) µg/mL, was also prepared in methanol. A mixture of NPnEO at 12 µg/mL was prepared in hexane/isopropanol (98:2, v/v).

### **Collection of samples**

Through the coordination of Pulp and Paper Research Institute of Canada (PAPRICAN), participating mills were asked to collect 24-h composite samples of effluents from the outlet of their primary clarifier (from hereon, they are called primary effluent) and secondary treatment system (from hereon, they are called secondary effluent). A total of 19 pulp and paper mills located across Canada and one from the United States supplied samples in this survey. Once collected the samples were kept at 4°C, stored in 2 x 1L glass bottles and shipped in coolers to PAPRICAN within 24-hr of collection. After addition of 10 mL of a 37% formalin solution to each litre of effluent as a preservative at PAPRICAN, the samples were then forwarded to the National Water Research Institute (NWRI) for analysis.

Grab samples of final dewatered sludge from the wastewater treatment plants were also collected from the mills and shipped to PAPRICAN where they were air dried, ground and put through a 2 mm sieve before shipment to NWRI for analysis.

While their identities have never been revealed to NWRI, these mills are a good representation of the Canadian pulp and paper industry as they comprised of various process and waste treatment types. A brief description of these mills is given in Table 1.

### **Sample preparation**

#### *A. Effluent samples*

Prior to extraction, each effluent sample was filtered through a GF/C filter (47 mm diameter, 1.2  $\mu\text{m}$  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 samples, two 250-mL aliquots were measured. One aliquot was used immediately for the preconcentration of ethoxylates and carboxylates. The other aliquot was used for the determination of NP and OP.

A solid-phase extraction (SPE) procedure using a 1-g ODS cartridge (Supelco) was used for the extraction of the ethoxylates and carboxylates. Prior to preconcentration, the sample was acidified to pH 2 with 1 N HCl and the cartridge was conditioned with acetonitrile (5 mL), methanol (5 mL) and water (10 mL). The sample was then siphoned through the cartridge at a flow rate of ca. 10 mL/min with a vacuum of 10 to 15 inches 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 the subsequent HPLC analysis for NPnEO. The other half was also evaporated to dryness and reacted with 2 mL of boron trifluoride/methanol at 85°C for 30 min. The reaction products were 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 1 mL of iso-octane for GC/MS analysis of the carboxylates.

A previously published *in situ* acetylation procedure was employed for the extraction and derivatization of nonylphenol in effluent samples. Briefly, 1 g of  $K_2CO_3$ , 1 mL of triple distilled acetic anhydride, and 30 mL of petroleum ether (b.p. 30 to 60°C) were added to 250 mL of a sample. The mixture was then stirred for 30 min to convert nonylphenol into its acetyl derivative. After phase separation in a separatory funnel, acetylation of the aqueous layer was repeated twice with fresh acetic anhydride (100  $\mu$ L) and petroleum ether (30 mL). After three extraction, the aqueous layer was discarded and the combined organic layer was partitioned with 30 mL of 1%  $K_2CO_3$  to remove the acidic coextractives, dried with anhydrous sodium sulfate, and evaporated to 1 mL.

The derivatized products were transferred to a 5 cm 5% deactivated silica gel column prepared in a Pasteur pipet pre-rinsed by 3 mL of petroleum ether. The column was sequentially eluted by 5 mL of 5% DCM in petroleum ether and 10 mL of 50% DCM in petroleum ether. The latter fraction was collected, evaporated, and exchanged into 1 mL of iso-octane for GC/MS analysis.

#### *B. Sludge samples*

Each sludge sample was extracted by two previously published supercritical fluid extraction (SFE) procedures using carbon dioxide. One extraction procedure was employed for the determination of NPnEO and NPnEC. The other procedure was used specifically for the *in situ* acetylation of NP and OP in solid samples.

For the SFE of NPnEO and NPnEC, a freeze-dried sample (250 mg) was placed in an extraction thimble in the presence of 500  $\mu\text{L}$  of water as a modifier for  $\text{CO}_2$ . The sample was then extracted with supercritical  $\text{CO}_2$  at  $80^\circ\text{C}$  and 5100 psi (density = 0.79 g/mL) and a flow rate of 2 mL/min using a Hewlett-Packard 7680T extractor. The extraction times were 15 min static and 15 min dynamic. Sample extract was adsorbed onto an octadecylsilane (ODS) trap and was eluted, at the end of the extraction, by three aliquots of 1.5 mL of methanol at  $60^\circ\text{C}$ . The combined extract was equally split. One fraction was solvent exchanged into isopropanol/hexane (2/98, v/v) for the HPLC determination of NPnEO.

The other fraction was evaporated to ca. 250  $\mu\text{L}$  and then it was methylated at  $85^\circ\text{C}$  in the presence of 2 mL of 12%  $\text{BF}_3$ /methanol complex. At the end of the reaction, the solvent was reduced to ca. 500  $\mu\text{L}$ . Water (3 mL) was then added and the mixture was extracted three times with 2 mL aliquots of petroleum ether. After the combined organic extract was passed through a 5 cm column of anhydrous sodium sulfate prepared in a Pasteur pipet, it was again evaporated and exchanged into 1 mL of iso-octane for the GC/MS analysis of OP1EC, NP1EC, OP2EC, and NP2EC.

For the in situ acetylation of NP and OP in sludge, 250 to 500 mg of a sample was placed in an extraction thimble in the presence of 100  $\mu\text{L}$  of acetic anhydride and 30  $\mu\text{L}$  of triethylamine. The extraction was carried out at  $80^\circ\text{C}$  using  $\text{CO}_2$  at 5100 psi (density = 0.79 g/mL) and a flow rate of 2 mL/min. The extraction times were 15 min static and 10 min dynamic. The acetyl derivatives of NP and OP were eluted from the ODS trap by two 1.5 mL aliquots of hexane. The volume of the combined hexane extract was reduced to

ca. 1 mL and was subsequently cleaned up on a silica gel column as described above. The cleaned extract was exchanged into 1 mL of iso-octane for GC/MS analysis.

#### **High pressure liquid chromatography (HPLC) analysis for NPnEO**

All analyses were carried out with a Hewlett-Packard system consisting of a 1050 quaternary pump, a 1050 autosampler, a 1046A fluorescence detector, a 35900 multichannel interface, an APS Hypersil (NH<sub>2</sub>, 5 μm) 100 x 2.1 mm I.D. column equipped with a 20 x 2.1 mm I.D. ODS guard column. The detector was operated at wavelengths of 230nm (excitation) and 300 nm (emission). For the separation of NPnEO (n=1 to 17), the following solvent mixtures were used: A, hexane/isopropanol (98/2, v/v), B, isopropanol/water (90/10, v/v). The initial mobile phase, 97% A and 3 % B, was kept constant for three minutes. It was then linearly programmed to 43% A and 57% B in the next 22 min. A post-run equilibration of 15 min was used between injections. The HPLC column was maintained at 40°C and a flow rate of 0.3 mL/min. Ten μL injections of standards and samples were made.

#### **Gas chromatography/mass spectrometry (GC/MS) analysis of NPEC/OPEC and NP/OP derivatives**

All GC/MS analyses were performed with a Hewlett-Packard system consisted of a 5890 Series II gas chromatograph, a 7673 autosampler, and a 5972 Mass Selective detector (MSD), and a 30 m x 0.25 mm I.D., 0.25 μm thickness HP-5-MS column. One μL splitless injections were made. Injection port and detector interface temperatures were 250 and 280°C, respectively. Carrier gas (helium) linear velocity was held constant at 40

cm/s by means of an electronic flow controller. The electron energy and electron multiplier voltage were 70 eV and 200 V above the autotune value, respectively.

For the analyses of the methyl esters of NP1EC and OP1EC, the GC oven initial temperature, 70°C, was kept constant for 1 min. It was then programmed to 160°C at 30°C/min and then to 280°C at 5°C/min. Identification and quantitation of the NP1EC and OP1EC in sample extracts were achieved by selected ion monitoring (SIM). The following characteristic ions, m/z 207, 221, and 292 (for the NP1EC methyl ester isomers) and m/z 207, 208, and 278 (for the OP1EC methyl ester), were monitored.

Ions at m/z 107, 121, 135, 163, 191, and 262 were monitored for the acetyl derivatives of NP. For the OP derivative, ions at m/z 135, 177, and 248 were used.

## RESULTS AND DISCUSSION

### *Levels of total NPnEO and their metabolites in the primary and secondary effluents*

The concentrations of nonylphenolics in pulp and paper mill effluents are tabulated in Table 2. NPnEO were not detected (detection limit, 2 µg/L) in 12 samples, of which 8 of them were primary effluent and 4 were secondary effluent. The overall NPnEO concentration ranged from <2 to 128.8 µg/L (median, 4.5 µg/L) for the primary effluent and from <2 to 71.3 µg/L (median 5.8 µg/L) for the secondary effluent (Table 3). For comparison, the levels of NPnEO found in the effluents of 15 U.S. paper mills in the study by Naylor et al.(1996) were higher, with ranges from 3.13 to 729 µg/L (winter 1995) and from 1.28 to 712 µg/L (summer 1995) and medians of 90.4 and 56.3 µg/L, respectively. Meanwhile, the concentrations of NPnEO in the secondary effluent in this study were similar to those in the final effluent collected from two municipal sewage treatment plants



over a one year period (Di Corcia et al. 1994, Lee and Peart, 1998). In the latter case, the NPnEO concentrations ranged from 3.3 to 32.4  $\mu\text{g/L}$  with a median of 12.7  $\mu\text{g/L}$ .

For samples collected from the same mill, many of them had very similar NPnEO levels, with either a slight increase or decrease in the surfactant concentration between the primary effluent and secondary effluent. A significant (>50%) drop in the NPnEO level between the primary effluent and secondary effluent samples was only observed in four mills (D, F, G, and I). In contrast, a significant (>50%) *increase* in NPnEO concentration in the secondary effluent in comparison to the primary was noted in three mills (A, L, and P).

As far as the ethoxylate oligomer distribution in the effluent samples are concerned, NPnEO with ten or less ethoxy units were commonly found. Ethoxylates with 12 or more ethoxy groups were seldom detected in any samples. Many of the pri samples had higher levels of NP5EO through NP9EO, such as those from mills G1 and I as shown in Table 4. However, there was also an example where the major ethoxylates observed in the pri sample were the di- and tri- ethoxylates (mill L, Table 4). The discrepancy in this case may be due to the use of a surfactant with a formulation rich in the lower ethoxylates. The NPnEO in the pri and sec samples collected from the same mill generally exhibited a similar oligomeric pattern, regardless of the waste treatment process.

The NP concentration ranged from <0.1 (detection limit) to 1.32  $\mu\text{g/L}$  (median 0.35  $\mu\text{g/L}$ ) for the primary effluent and from <0.1 to 4.32  $\mu\text{g/L}$  (median <0.1  $\mu\text{g/L}$ ) for the secondary effluent (Table 3). Again, the effluent NP levels in the study by Naylor et al. (1996) were significantly higher, with ranges from non-detected to 21.2  $\mu\text{g/L}$  (winter 1995) and from 0.08 to 28.3  $\mu\text{g/L}$  (summer 1995) as well as medians of 1.09 and 1.20

$\mu\text{g/L}$ , respectively. The NP levels in the secondary effluent in this study were quite close to those observed for the final effluents collected from two sewage treatment plants over a 12-month period (Di Corcia et al. 1994, Lee and Peart, 1998). In the latter case, the NP concentrations ranged from 0.56 to 2.12  $\mu\text{g/L}$  with a median value 1.21  $\mu\text{g/L}$ .

Among the 17 samples of which NP was not detected, 13 of them were secondary effluents. Moreover, for the samples collected from the same mill, the level of NP in the secondary effluent was significantly (>50%) lower than the primary effluent, with only three exceptions (mills I and M, as well as the US mill). In general, higher NP concentrations were associated with the samples that were more contaminated with NPnEO, with the primary effluent samples from mills B and S as the major exceptions. Since NP is a persistent metabolite of NPnEO, the occurrence of nonylphenol in the effluent samples further confirms the presence of parent surfactant in the same samples.

While OP was detected (detection limit 0.01  $\mu\text{g/L}$ ) in 24 out of the 48 primary and secondary effluent samples, its level was very low (<0.05  $\mu\text{g/L}$ ) in all but eight samples. Only one sample, the primary effluent from mill D, showed a relatively high OP concentration of 0.40  $\mu\text{g/L}$ . In all samples, the level of OP rarely exceeded one-tenth of the concentration of NP. Since oligomers of OPnEO and NPnEO at each level of ethoxylation coelute under our HPLC conditions, it may create a biased high result for NPnEO. As OP was derived from OPnEO, low levels of OP observed in the same samples suggested that OPnEO was only a minor component (or an impurity) in the surfactants used by the paper mills. Therefore the coelution problem should not create a significant error to the quantification of NPnEO concentration in the primary and secondary effluents.

Approximately 75% of the effluent samples were also analyzed for the carboxylates. In those samples, OP1EC, NP1EC, OP2EC, and NP2EC were only detected in the secondary effluents from mills I, L, M, and S, as well as the primary effluent from mill S. Of the four secondary effluents which the carboxylates were detected, the concentrations varied from <0.1 to 3.95  $\mu\text{g/L}$  (OP1EC), from 2.65 to 10.1  $\mu\text{g/L}$  (NP1EC), from <0.1 to 3.22  $\mu\text{g/L}$  (OP2EC), and from 8.12 to 32.3  $\mu\text{g/L}$  (NP2EC). The results of carboxylates in our study contrast from those reported by Field and Reed (1996) in the following respects. While the carboxylates were detected in 14 out of 15 U.S. paper mill effluents, the same acids were detected in 4 out of 18 secondary effluents in this study. Due to the presence of a very contaminated sample, the overall concentration ranges for NP1EC (from <0.2 to 140.0  $\mu\text{g/L}$ ) and NP2EC (from <0.4 to 931.0  $\mu\text{g/L}$ ) in the paper mill effluents were much wider in the U.S. study. The observation of higher levels of the carboxylates in the study by Field and Reed is consistent with the occurrence of NPnEO and NP at higher concentrations in the samples collected at the same location (Naylor et al., 1996). However, the median concentrations of NP1EC (3.7  $\mu\text{g/L}$ ) and NP2EC (16.9  $\mu\text{g/L}$ ) in the U.S. study were not substantially different from the levels of the carboxylates found in the four Canadian pulp and paper mill secondary effluents .

The results of the carboxylates in the secondary effluent in this study also differ from those observed for the final effluent of a sewage treatment plant. In the latter case, the carboxylates were readily detected in all samples since they are invariably the most abundant component among all nonylphenolics in the final effluent (Ahel et al. 1994a, Lee

and Peart, 1998). In this study, this was true in only three cases (mills I, M, and S). For the majority of the secondary effluent tested, the carboxylates were undetected.

*Levels of total NPnEO and their metabolites in pulp and paper mill sludge*

The concentrations of nonylphenolics found in the pulp and paper mill sludge are tabulated in Table 5. Except for mills B and O, NPnEO were found in the sludge samples obtained from all mills, with a concentration range from 3.3 to 96.1  $\mu\text{g/g}$  and a median of 20.6  $\mu\text{g/g}$  on dry weight basis. Of the 18 samples with detected NPnEO, the levels of ten of them were less than 25  $\mu\text{g/g}$ , four were between 25 and 50  $\mu\text{g/g}$ , and four were over 50  $\mu\text{g/g}$ . The concentrations of NPnEO in pulp and paper mill sludge are considered to be much lower than what have been found in digested sludge originated from municipal sewage treatment plants; many of the latter have total NPnEO concentrations in excess of 100  $\mu\text{g/g}$  (Lee and Peart, 1997, Bennie, 1999). An example of a sewage sludge is included in Table 5, with the code MUNIA.

In order to illustrate the distribution of the ethoxylate oligomers in sludge, the results for four mills are summarized in Table 6. Mills F, G, K, and L were selected since they employed different waste treatment types and also their total NPnEO concentrations were among the highest. With the exception of the sludge from Mill F which has a very high concentration of NP1EO, all sludge samples including those not listed in Table 6 generally displayed the highest ethoxylate concentrations in the NP8EO and NP9EO region. This oligomeric distribution pattern is consistent with some common commercial preparations of NPnEO such as Surfonic N-95 and Triton N-101 which have an average of ca. 9 ethoxy units. It also suggests that the NPnEO in pulp and paper mill sludge has

not undergone an extensive degradation, regardless of which waste treatment type the mill is employing. This is in marked contrast to a typical sewage sludge (also included in Table 6 for comparison) which is heavily enriched in the lower, lipophilic ethoxylates from NP1EO to NP3EO.

NP was found in all pulp and paper mill sludge except the one from mill N (Table 5). The concentrations of NP in sludge varied from  $<0.05$  to  $121 \mu\text{g/g}$ , with a median value of  $1.28 \mu\text{g/g}$  (Table 3). Although the two samples collected from mill I were found to have NP as high as  $121 \mu\text{g/g}$ , the levels of NP in the other 18 samples were  $<5 \mu\text{g/g}$ . The latter number is again much lower than the NP level found in digested sewage sludge (typically in the range of a few hundred  $\mu\text{g/g}$ ) due to its lipophilic nature and affinity to solids (Giger et al., 1984, Ahel and Giger, 1985, Lee and Peart, 1995). OP were undetected in five samples of paper mill sludge (detection limit  $0.005 \mu\text{g/g}$ ). Of the other samples which OP was detected (range  $0.006$  to  $0.225 \mu\text{g/g}$ ), ten were  $<0.1 \mu\text{g/g}$  and the other five were between  $0.1$  and  $0.25 \mu\text{g/g}$ .

Presumably because of their higher water solubility, the carboxylates were rarely detected in sewage sludge at high concentrations (Lee et al., 1997). Of the four samples which NP1EC and NP2EC were detected (mills D, F, G, and K), only one sample (mill K) had carboxylate concentrations  $>5 \mu\text{g/g}$  (Table 5). Concentrations of these acids ranged from  $<1$  to  $5.78 \mu\text{g/g}$  (NP1EC) and from  $<1$  to  $18.5 \mu\text{g/g}$  (NP2EC). Similarly, the octylphenoxy acids were only observed in the sludge obtained from mills D, F, and K, with concentrations ranging from  $<0.1$  to  $0.39 \mu\text{g/g}$  (OP1EC) and from  $<0.1$  to  $1.64 \mu\text{g/g}$  (OP2EC) (Table 3).

*Relationship between NPnEO levels and process/treatment types*

Prior to the collection of samples, this survey was designed in such a way that Canadian mills representative of various process types such as bleached kraft, deinking, thermomechanical and newsprint would be included. The purpose was to determine if there is any correlation between process type and the occurrence of NPnEO in pulp and paper mill effluents. A careful examination of the information given in Table 1 and the data summarized in Table 2 suggested that such a correlation did not exist. For example, while the highest level of NPnEO was observed in the primary treated effluent collected from mill D, a deinking mill, very low levels of ethoxylates were observed for the same type of samples from the other deinking mills (E, F, and H). Similarly, both high and low NPnEO concentrations were observed for the primary treated effluent for the kraft mills (A, B, G, I, J, L, M, N, and R).

The lack of any observed trend or relationship between the levels of NPnEO in the primary effluents and the mills' process types may not be surprising since pulp and paper production is a very complicated operation. There are simply no two mills of the same process type (e.g. kraft) that have identical operating conditions such as wood species used, daily pulp production, water usage, the amount of defoamer used, and the amount of NPnEO surfactant in the defoamer formulation, etc. There are even more variation for mills of different process types for a valid comparison.

Again, no pattern between the NPnEO levels in the secondary effluent and the waste treatment technique used by the mills seems to exist. Based on a very limited number of effluent samples collected from each mill, it is impossible to estimate the efficiency for the removal of the ethoxylates. Although various NPnEO elimination rates

between the primary and secondary treated effluents were observed from mills using the same waste treatment process (e.g. activated sludge), they may not be a true indication of their operating efficiency because the retention time of the effluent in the treatment system was not accounted for. Because of this, the reader is cautioned not to use the effluent data in this report to estimate the elimination efficiency for NPnEO and their metabolites in the waste treatment process employed by each mill.

For the sludge, samples collected from the deinking mills (D, E, F, and H), as a group, tended to have higher NPnEO concentrations (range 15.6 to 96.1  $\mu\text{g/g}$ ). In contrast, both high and low NPnEO concentrations have been observed for samples of all kraft mills, i.e. A, B, G, I, L, and N (range  $<1$  to 88.2  $\mu\text{g/g}$ ) and thermomechanical mills O and Q ( $<1$  and 20.8  $\mu\text{g/g}$ , respectively). The levels of NP in sludge obtained from the deinking mills were also slightly higher than the rest, although it is not clear why very high concentrations of NP was found in the samples from mill I, a bleached kraft mill.

### *Summary*

The secondary effluents of four pulp and paper mills (C, H, O, and R) were completely free from the contamination of nonylphenol ethoxylates and their metabolites. For most of the other mills, the major nonylphenolic component detected in the secondary effluents were NPnEO, with an overall concentration range from  $<2$  to 71.3  $\mu\text{g/L}$  and a median value of 5.8  $\mu\text{g/L}$ . While NP was detected in the secondary effluents from eight mills (G, I, K, L, M, P, S, and the U.S. mill), its level was below 1  $\mu\text{g/L}$  except for mills I and M. The NPnEO and NP concentrations in the secondary effluent in this study were much lower than those reported for the effluents of 15 paper mills discharged into Fox

River, MI, USA. They were, however, quite similar to those observed for the final effluent collected from municipal sewage treatment plants. While the carboxylates are the major nonylphenolic component in the final effluent of a municipal sewage treatment plant, NP1EC and NP2EC were not detected in many pulp and paper mill secondary effluents. In those few cases where they were observed, their levels were much lower than those found in sewage final effluent. While there was a notable decrease in NP concentrations between the primary and secondary treated effluents collected from the same mill, the same was not observed for NPnEO. Low concentrations of OP detected in these samples suggested that OPnEO was only a minor component in the surfactants used by the Canadian mills. Although NPnEO and NP were readily detected in nearly all pulp and paper mill sludge, their concentrations were much lower than those found in digested municipal sewage sludge.

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**Table 1. Process and treatment types for the pulp and paper mills included in this study.**

<b>Mill</b>	<b>Process <sup>a</sup></b>	<b>Treatment <sup>a</sup></b>
A	Kraft	Activated sludge
B	Kraft, TMP	UNOX
C	GW, SCMP	Activated sludge
D	DIP	Activated sludge
E	GW, TMP, DIP	Sequential batch reactor
F	DIP	Activated sludge
G	Kraft	Activated sludge
H	DIP, TMP	UNOX
I	Kraft	Aerated lagoon
J	Kraft	Aerated lagoon
K	TMP, DIP	Aerated lagoon
L	Kraft	UNOX
M	Kraft	Aerated lagoon
N	Kraft	Activated sludge
O	TMP	Activated sludge
P	Recycled	Not available
Q	TMP	Activated sludge
R	Kraft	UNOX
S	GW, UHYS	Activated sludge
U.S.	Not available	Not available

**DIP:** Deinked pulp  
**GW:** Groundwood  
**SCMP:** Semicheical mechanical pulp  
**TMP:** Thermomechanical pulp  
**UHYS:** Ultra high yield sulphite  
**UNOX:** Oxygen activated sludge

Table 2. Levels ( $\mu\text{g/L}$ ) of OP, NP, NPnEO, OP1EC, NP1EC, OP2EC, and NP2EC found in the pulp and paper mill effluent samples.

Mill	Date received	Total NPnEO	OP	NP	OP1EC	NP1EC	OP2EC	NP2EC
A pri <sup>a</sup>	9-Sep-97	3.5	<0.01	0.30	<0.1	<1.0	<0.1	<1.0
A sec <sup>a</sup>	9-Sep-97	47.5	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
B pri	9-Sep-97	<2	<0.01	1.32	<0.1	<1.0	<0.1	<1.0
B sec	9-Sep-97	6.6	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
C pri	9-Sep-97	<2	0.05	0.18	<0.1	<1.0	<0.1	<1.0
C sec	9-Sep-97	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
C pri	23-Apr-98	<2	<0.01,<0.01	<0.1,0.107	<0.1	<1.0	<0.1	<1.0
C sec	23-Apr-98	4.9	<0.01,<0.01	<0.1,<0.1	<0.1	<1.0	<0.1	<1.0
D pri	18-Sep-97	128.8	0.40	1.03	NA <sup>d</sup>	NA	NA	NA
D sec	18-Sep-97	5.8	<0.01	<0.1	NA	NA	NA	NA
E pri	18-Sep-97	<2	0.03	0.30	NA	NA	NA	NA
E sec	18-Sep-97	5.3	<0.01	<0.1	NA	NA	NA	NA
F pri	18-Sep-97	9.9	0.08	0.51	NA	NA	NA	NA
F sec	18-Sep-97	3.8	0.01	<0.1	NA	NA	NA	NA
G1 pri <sup>b</sup>	1-Dec-97	112.5	0.08	0.78	NA	NA	NA	NA
G1 sec	1-Dec-97	6.1	0.00	0.18	NA	NA	NA	NA
G2 pri	1-Dec-97	84.1	0.08	0.47	NA	NA	NA	NA
G2 sec	1-Dec-97	3.3	0.02	0.23	NA	NA	NA	NA
G3 pri	1-Dec-97	12.9	0.06	0.45	NA	NA	NA	NA
G3 sec	1-Dec-97	10.0	0.00	0.18	NA	NA	NA	NA
H pri	4-Feb-98	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
H sec	4-Feb-98	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
I pri	23-Apr-98	59.7	<0.01	0.91	<0.1	<1.0	<0.1	<1.0
I sec	23-Apr-98	16.3	0.06	3.73	0.22	7.48	0.55	32.32
I midpoint	23-Apr-98	7.0	0.04	2.05	NA	NA	NA	NA

J pri	24-Jun-98	<2	<0.01	0.34	<0.1	<1.0	<0.1	<1.0
J sec	24-Jun-98	2.9	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
K pri	29-May-98	4.4	0.03	0.19	<0.1	<1.0	<0.1	<1.0
K sec	29-May-98	6.7	<0.01	0.25	<0.1	<1.0	<0.1	<1.0
L news pri <sup>c</sup>	29-May-98	18.5	0.03	0.51	<0.1	<1.0	<0.1	<1.0
L news sec	29-May-98	34.3	<0.01	0.28	0.29	2.65	0.15	11.73
L kraft pri <sup>c</sup>	29-May-98	74.3	0.02	1.29	<0.1	<1.0	<0.1	<1.0
L kraft sec	29-May-98	71.3	0.01	0.56	<0.1	<1.0	<0.1	<1.0
M pri	29-May-98	27.9	0.01	0.35	<0.1	<1.0	<0.1	<1.0
M sec	29-May-98	20.9	0.02	4.32	<0.1	6.84	<0.1	14.64
N pri	24-Jun-98	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
N sec	24-Jun-98	3.7	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
O pri	12-May-98	3.6	0.14	<0.1	<0.1	<1.0	<0.1	<1.0
O sec	12-May-98	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
P pri	29-May-98	11.0	0.00	0.10	<0.1	<1.0	<0.1	<1.0
P sec	29-May-98	23.5	0.02	0.14	<0.1	<1.0	<0.1	<1.0
Q pri	29-May-98	<2	<0.01	0.12	<0.1	<1.0	<0.1	<1.0
Q sec	29-May-98	5.8	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
R pri	12-May-98	3.9	0.03	0.42	<0.1	<1.0	<0.1	<1.0
R sec	12-May-98	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
S pri	12-May-98	4.7	0.10	0.93	0.97	6.74	0.44	6.36
S sec	12-May-98	4.7	0.00	0.16	3.95	10.13	3.22	8.12
US pri	24-Jun-98	24.5	<0.01	0.08	<0.1	<1.0	<0.1	<1.0
US sec	24-Jun-98	26.2	<0.01	0.32	<0.1	<1.0	<0.1	<1.0

<sup>a</sup> pri refers to the primary treated effluent, sec refers to secondary treated effluent.

<sup>b</sup> Since the first set of samples had high levels of NPnEO and NP in the primary effluent, three more sets of samples were collected from this mill for confirmation.

<sup>c</sup> Mill L has a newsprint mill and a kraft mill on-site each having its own treatment system.

<sup>d</sup> Not analyzed.

Table 3. Minimum, maximum, and median concentrations of nonylphenolics in effluent ( $\mu\text{g/L}$ ) and sludge ( $\mu\text{g/g}$ ) samples<sup>a</sup>.

	Total NPnEO	OP	NP	OP1EC	NP1EC	OP2EC	NP2EC
<i>Primary treated effluent</i>							
No. of samples analyzed	24	24	24	18	18	18	18
No. of samples above detection limit	16	15	21	1	1	1	1
Minimum concentration	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
Maximum concentration	128.8	0.40	1.32	0.97	6.74	0.44	6.36
Median concentration	4.5	0.02	0.35	<0.1	<1.0	<0.1	<1.0
<i>Secondary treated effluent</i>							
No. of samples analyzed	24	24	24	18	18	18	18
No. of samples above detection limit	20	9	11	3	4	3	4
Minimum concentration	<2	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
Maximum concentration	71.3	0.06	4.32	3.95	10.13	3.22	32.32
Median concentration	5.8	<0.01	<0.1	<0.1	<1.0	<0.1	<1.0
<i>Sludge</i>							
No. of samples analyzed	20	20	20	19	19	19	19
No. of samples above detection limit	18	15	19	3	3	4	4
Minimum concentration	<1	<0.005	<0.05	<0.1	<1	<0.1	<1
Maximum concentration	90.8	0.255	120.9	0.39	5.78	1.64	18.5
Median concentration	20.6	0.019	1.28	<0.1	<1	<0.1	<1

<sup>a</sup> In cases where there were two results for the same sample, the average was used for the determination of minimum, maximum, and median values.

Table 4. Levels ( $\mu\text{g/L}$ ) of individual NPnEO oligomers in pulp and paper mill effluents.

	Mill G1 Pri	Mill G1 Sec	Mill I Pri	Mill I Sec	Mill L Kraft Pri	Mill L Kraft Sec
Waste treatment	Activated sludge	Activated sludge	Aerated lagoon	Aerated lagoon	UNOX	UNOX
NP1EO	5.5	0.1	<0.2	1.3	<0.1	6.9
NP2EO	4.4	0.1	2.9	5.1	49.4	35.6
NP3EO	3.5	0.2	6.0	2.4	14.2	12.4
NP4EO	5.6	0.2	2.4	1.2	3.0	9.4
NP5EO	10.7	0.4	4.5	1.3	2.9	4.2
NP6EO	18.6	0.6	8.4	1.5	2.2	2.0
NP7EO	23.9	0.8	9.5	0.9	0.9	0.6
NP8EO	18.6	0.8	8.9	1.3	0.2	0.4
NP9EO	13.0	0.7	7.1	0.6	<0.2	<0.2
NP10EO	6.5	0.6	4.5	0.4	<0.2	<0.2
NP11EO	1.9	0.5	3.3	0.2	<0.2	<0.2
NP12EO	0.3	0.4	1.2	0.2	0.2	<0.2
NP13EO	<0.2	0.3	0.5	<0.2	1.4	<0.2
NP14EO	<0.2	0.2	<0.2	<0.2	<0.2	<0.2
NP15EO	<0.2	0.2	<0.2	<0.2	<0.2	<0.2
NP16EO	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
NP17EO	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
<b>Total NPnEO</b>	<b>112.5</b>	<b>6.1</b>	<b>59.7</b>	<b>16.3</b>	<b>74.3</b>	<b>71.3</b>

**Table 5. Levels ( $\mu\text{g/g}$ ) of OP, NP, NPnEO, OPIEC, NP1EC, OP2EC, and NP2EC found in pulp and paper mill sludge samples. Second value was obtained from a duplicate analysis.**

Mill	Date received	Total NPnEO	OP	NP	OPIEC	NP1EC	OP2EC	NP2EC
A	Nov-97	20.3	0.164	0.69	NA <sup>c</sup>	NA	NA	NA
B	Dec-97	<1, <1	<0.005	1.78	<0.1	<1	<0.1	<1
C	Apr-98	5.4, 6.2	<0.005, <0.005	0.14, 0.16	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1
D (sample 1)	Sep-97	25.7, 31.1	0.032, 0.033	0.75, 0.69	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1
D (sample 2)	Dec-97	15.6	0.255	2.53	0.39	<1	0.74	1.16
E	Dec-97	7.4, 5.2	0.006	0.34	<0.1	<1	<0.1	<1
E (DEINK)	Dec-97	26.5, 28.2	0.041	2.22	<0.1	<1	<0.1	<1
F	Dec-97	85.5, 96.1	0.065	1.62	0.17	0.91	0.32	2.00
G	Dec-97	84.3	0.008, 0.010	1.34, 1.36	<0.1, <0.1	1.86, 2.60	<0.1, 0.11	3.34, 4.30
H	Feb-98	21.6	0.109	3.55	<0.1	<1	<0.1	<1
I (TOP) <sup>a</sup>	Jun-98	4.8, 6.9	0.225, 0.215	119.0, 122.8	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1
I (BOTTOM) <sup>a</sup>	Jun-98	32.7	0.094, 0.140	62.74, 43.77	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1
J	no sample							
K	Jun-98	69.6	0.052	4.36	0.29	5.78	1.64	18.5
L	Jun-98	88.2	0.013	2.15	<0.1	<1	<0.1	<1
M	no sample							
N	Jun-98	4.6	<0.005	<0.05	<0.1	<1	<0.1	<1
O	Jun-98	<1	0.025	0.49	<0.1	<1	<0.1	<1
P	Jun-98	3.3	0.048	1.09	<0.1	<1	<0.1	<1
Q	Jun-98	20.8	0.009	0.50	<0.1	<1	<0.1	<1
R	Jun-98	32.8, 35.6	<0.005, <0.005	1.18, 1.25	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1
S	Jun-98	17.5	<0.005	0.29	<0.1	<1	<0.1	<1
U.S.	no sample							
MUNIA <sup>b</sup>	Apr-98	173.1, 148.4	0.470, 0.516	17.20, 18.25	<0.1, <0.1	<1, <1	<0.1, <0.1	<1, <1

<sup>a</sup> The top sample was sludge skimmed off the top of the aeration pond. The bottom sample was sludge dredged from the bottom.

<sup>b</sup> A sludge collected from a municipal sewage treatment plant with no secondary treatment.

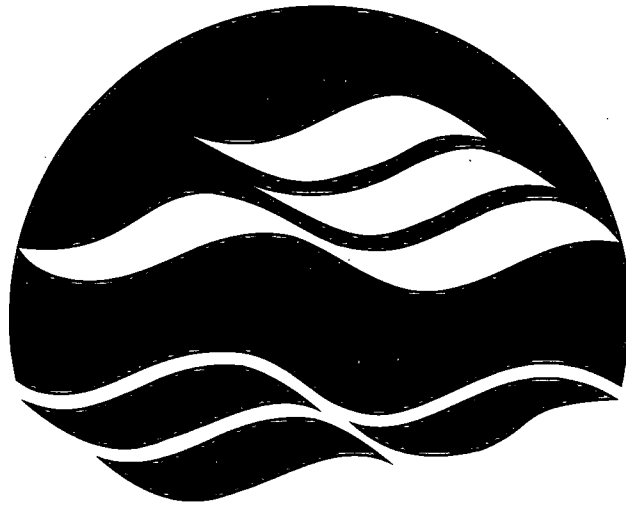
<sup>c</sup> Sample not analyzed.



Table 6. Levels ( $\mu\text{g/g}$ ) of individual NPnEO oligomers in several sludge samples.

Waste treatment	Mill F	Mill G	Mill K	Mill L	Munia (sewage sludge)
	Activated sludge	Activated sludge	Aerated lagoon	UNOX	No secondary treatment
NP1EO	13.7	2.8	0.9	1.9	54.5
NP2EO	4.1	2.2	1.7	2.2	29.1
NP3EO	8.0	4.9	2.3	3.6	17.1
NP4EO	4.7	3.9	1.8	2.5	11.0
NP5EO	6.2	1.8	4.5	3.7	7.0
NP6EO	4.9	2.9	7.6	6.3	8.7
NP7EO	7.5	5.2	9.0	8.4	7.0
NP8EO	8.7	6.3	8.8	15.1	5.7
NP9EO	6.6	7.6	8.4	7.9	6.3
NP10EO	5.4	8.1	*	*	5.0
NP11EO	4.4	7.9	5.7	6.4	3.8
NP12EO	3.7	7.7	5.6	6.8	3.0
NP13EO	3.1	7.4	5.3	5.9	2.5
NP14EO	2.0	6.1	2.9	3.1	2.0
NP15EO	1.4	5.5	2.4	2.6	1.9
NP16EO	1.1	4.1	2.6	2.5	2.3
NP17EO	<1	<1	<1	9.5	5.9
<b>Total NPnEO</b>	<b>85.4</b>	<b>84.3</b>	<b>69.6</b>	<b>88.2</b>	<b>173.1</b>

\* A very large peak with an obvious sign of interference was observed.



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