The profile of contamination with alkylphenol ethoxylates of some Israeli watercourse rivers and their sediment layers
M. Houshan and U. Zoller

ABSTRACT

The ‘hard’ non-biodegradable alkylphenol ethoxylates (APEOs) nonionic surfactants are environmentally persistent and widely used worldwide. The aim of this work is to determine the total concentration and the homological distribution in rivers and there sediments, in central Israel. The concentrations of APEOs in the water of these rivers and in their sediments were found to be 11.83–55.32 μg/L, and 99.68–1,176.61 μg/kg, respectively. The APEOs’ concentration level decreases as the sample is taken from a deeper layer of the sediment. A possible explanation for this is that in APEOs molecules, the hydrophilic fraction (CH2-CH2-O) increases the APEOs’ absorption into sediment layers close to water, being saturated with water. In addition, the organic biofilm in the sediment layers used as schmutzdecke can reduce the concentration levels of APEOs that penetrates the deep layers of the sediment. The dominant homologues of APEOs in the river watercourse were those with 9–15 units of ethylene oxide (EO). Homologues with 1–12 units of ethylene oxide were found to be the dominant ones in the sediment layers of Hadera and Alexander rivers.

Key words | alkylphenol ethoxylats (APEOs), endocrine disrupting chemicals (EDCs), environmentally persistent, homological distribution, rivers’ water and sediments

HIGHLIGHTS

- The importance of this study stems from a number of facts. Firstly, APEOs have been widely used in the world and in Israel in the past.
- In addition, the biodegradation of APEOs is slow and prolonged, so they survive in the environment.
- Finally, APEOs as well as their breakdown products have endocrine activity on animals in both freshwater and seawater.

INTRODUCTION

There is a continuing concern world-wide regarding the biological effects on human health with endocrine disrupting chemicals (EDC) because of their presence in the aquatic ecosystems resulted from wastewater treatment plants (WWTPs), agricultural irrigation, industrial and household wastewater. These EDCs potentially affect the reproductive health of aquatic organisms (Söffker & Tyler 2012; Aris et al. 2014). Alkylphenol ethoxylates (APEOs) are a group of the most studied EDCs; they are a class of non-ionic surfactants – nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs) – which are commonly used in industrial, agricultural and domestic applications (Gao et al. 2017). ‘They are widely used in agriculture, industry, laundry, cleaning and production of pulp and paper’ (Chen et al. 2014) with ‘high production volumes’ (OECD 2004). ‘The most extensively used APEO products are nonylphenol ethoxylates (NPEOs), representing 80–85% of the total use’ (Loyo-Rosales et al. 2010). These contaminants are discharged into aquatic ecosystems from sewage
plants’ (Stasinakis et al. 2012). APEOs show an estrogenic activity and it is considered to be EDCs (Pan et al. 2015; Noorimotlagh et al. 2018), moreover, their metabolites exhibit higher toxicity than their precursors, and have been identified as xenoestrogens. NPEOs have been detected at high concentrations in the atmosphere and waterways in many countries around the world, as well (Ahel et al. 2013; Pryor et al. 2002; Johnson et al. 2005; Barber et al. 2003; Maruya et al. 2005).

Reported concentration levels of APEOs in the surface of the watercourse range from tens of ng/L to tens of μg/L (Petrovic et al. 2004; Loos et al. 2007; Mayer et al. 2007; Ribeiro et al. 2007; Chen et al. 2010; Berge et al. 2012; Gong et al. 2012).

APEOs undergo both aerobic (Giger et al. 1984; Soares et al. 2008) and anaerobic biodegradation (Lu et al. 2008a, 2008b) and are expected to be removed to a high degree. However, APEOs are found to be degraded into some persistent organic pollutants (POPs) and estrogenic substances such as nonylphenol (NP), octylphenol (OP), and mono- or di-ethoxylated alkyl phenols, which have been widely detected in both sediment and surface water (Michael & Joseph 2009). This degradation starts by 1-β-decarboxylation and shortening the ethylene oxide chain and leads to short chain that contains one or two ethylene oxide (Ahel et al. 1994; Guang-Guo 2004; Cladière et al. 2014). Complete decarboxylation to produce alkylphenols (Aps) was observed only under anaerobic conditions (Giger et al. 1984; Shibata et al. 2006; Chang et al. 2007).

APEOs are recalcitrant depending on polymer size and environmental conditions (e.g. the presence of nutrients or cofactors) (Hayashi et al. 2005; Ying 2006; Paterakis et al. 2012); ‘their degraded products are more hydrophobic, which can partition into sediments and become more permanent’ (Huang et al. 2007; Li et al. 2007; Zhou et al. 2010).

Under anaerobic conditions, APEOs degrade more slowly than in the presence of oxygen through the stepwise shortening of the terminal ethoxylate chain pathway (Frings et al. 1992).

### MATERIALS AND METHODS

Two rivers in the center of the Israel (Hadera and Alexander) underwent on a grab sample, as described in Figure 1, in order to determine the long-range concentration level and homologous distribution of the APEOs in the river watercourse and in the sediment layers (at a depth of 0–50 cm) of these above mentioned rivers.

The determination of the total concentration levels of APEOs (Marcomini & Giger 1987) was done using high performance liquid chromatography (HPLC) – reversed phase. The analytical method was somewhat modified in accordance with the local constraints:


The total concentration of APEOs in the river water is determined according to the reference curve of the Marlophen 810 industrial/commercial mixture (made by Hüls), in the concentration range 10.23–70.56 μg/L. The total concentration of APEOs in the river sediments is determined according to the reference curve of the Marlophen 810 industrial/commercial mixture (made by Hüls), in the concentration range 205.23–1,010.55 μg/L.

Homologous distribution of APEOs was done using HPLC – Normal Phase (Kubeck & Nayler 1990). The analytical method was somewhat modified in accordance with the local constraints:

- **Column:** (RP-18 pre column) Lichrospher 100 CN (5 mm).
- **Eluent A:** Tetrahydrofuran – hexane 20:80 (v/v); Eluent B: Isopropanol – water 90:10 (v/v).
The homologous distribution of APEOs in river water was determined according to the reference curve of the Marlophen 810 industrial/commercial mixture (made by Hüls), in the concentration range 10.23–70.56 μg/L. The homologous distribution of APEOs in river sediments is determined by the reference curve of the Marlophen 810 industrial/commercial mixture (made by Hüls), in the concentration range 205.23–1,010.55 μg/L.

**SAMPLING**

**Water samples**

Samples, 4 L each one, were taken from different ‘stations’ along Hadera and Alexander rivers from the top 20 cm of their water at five close points with a radius of 1 m, about 2 m from the riverbed. A 1% formalin solution of the total volume was added to each sample (to suppress any biological activity). These were kept in the refrigerator at about 4 °C for one night to stop the biological degradation of APEOs.

**Sediment samples**

The samples were collected at the sampling stations and they were taken from the river water at depths of 0–15, 15–30 and 30–50 cm below their surface at five close points with a radius of 1 m. A sample was prepared at each sampling station by mixing samples from the five sampling points at each station. For each sample it was added 1% formalin solution to the total volume. These were kept in the refrigerator at about 4 °C overnight, similar to the water samples. Every sediment sample was dried in Bachner Funnel at room temperature for 2 h, and 5 g of the dry sediment was dissolved in 50 mL of methanol (CH3OH) for chromatography (Merck). After sonication at 40–50 °C for 30 min, we performed centrifugation at 3,000 rpm for 10 min.

**RESULTS AND DISCUSSION**

The chromate grams that we have received include three peaks, two peaks for octylphenol ethoxylates with retention time – RT at about 13 and about 15 min, and one peak for nonylphenol ethoxylates with RT at about 19 min. The total concentrations of APEOs are given in Table 1.

APEOs concentrations levels of Alexander river’s watercourse are higher than those in Hadera river’s water. This finding can be attributed to the fact that domestic and industrial wastewater from Nablus and Tul Karm flows directly into the Shechem river channel, and from there it makes its way to Alexander river. At station 3 of the Hadera river, the concentration level of APEOs is relatively low. In this section, which is located near the ‘Orot Rabin’ power station, seawater flows all the time. Dilution of water in the river causes a decrease in the concentration level of APEOs. In contrast, the concentration level of APEOs at station 1 is relatively high. This sampling station is close to the industrial zone of Hadera. Hadera Paper Mills is located in the above mentioned area. Paper mills use APEOs for cleaning and whitening, so the water of Hadera river near the industrial zone contains high concentration levels of APEOs in analogy to other parts of the river.

A comparison of these results with the results obtained in our laboratory in 2000 showed that was a decrease in APEOs concentration levels in the water of Hadera and Alexander rivers by 17% and 8%, respectively. This finding might indicate a decrease in the amount of APEOs levels in these river basins reaching to the rivers from WWTPs or factories that use formulation based on APEOs in their production processes or it might be an improvement in the level of removal of APEOs from their wastewater. Another explanation could be a significant decreasing use of APEOs in Israel.

<table>
<thead>
<tr>
<th>River</th>
<th>Station</th>
<th>Concentration (μg/L)</th>
</tr>
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<tbody>
<tr>
<td>Hadera</td>
<td>1</td>
<td>35.65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.35</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11.83</td>
</tr>
<tr>
<td>Alexander</td>
<td>1</td>
<td>50.03</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>42.48</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>46.57</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>50.10</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>47.15</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>55.32</td>
</tr>
</tbody>
</table>
APEOs concentrations were also determined in the sediments of the rivers at the upper 50 cm. The total concentrations are given in Table 2.

The results in Table 2 indicate that the concentration of APEOs level decreases as the sample is taken from a deeper layer of sediment. A possible interpretation for this is that in APEOs molecules, the hydrophilic fraction (CH2-CH2-O groups) increases the APEOs’ absorption into sediment layers close to water, saturated with water. In addition, the organic biofilm in the sediments used as schmutzdecke can reduce the concentration levels of APEOs that penetrate through the deep layers of the sediment (Hwang et al. 2014).

The homological distribution of the APEOs was determined in the water of Hadera and Alexander rivers in the sampling stations, as shown in Figure 1. The chromatograms obtained for the APEOs included eighteen peaks whose RT ranged from 2 to 22 min, respectively.

Figure 2 summarizes the average relative concentrations of the APEOs in the water of the Hadera and Alexander rivers.

The results in Figure 2 indicate that the dominant homologues of APEOs in river water (in Israel) are homologues with 9 to 15 units of ethylene oxide (EO). The low concentration levels of homologues with 16 to 18 units of EO, which dissolve more in water, and therefore dissipate, indicate that in the process of decomposition of high homologues, homologues with a moderate number of ethylene or oxide units are produced as intermediate products of the decomposition.

The homological distribution of the APEOs in the sediment layers of the Hadera and Alexander rivers is shown in Figure 3, where the average relative concentration levels of APEOs are summarized in the sediment layers of these two rivers.

Homologues with 1–12 units of EO are dominant in the sediment layers of the Hadera and Alexander rivers. A possible explanation might be the high concentration levels of short homologues in sediment layers, compared to their concentration levels in the river water in that these homologues

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Total concentrations of Alkylphenol Ethoxylates (APEOs) in Hadera and Alexander rivers’ sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Hadera river (μg/Kg)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Station 1</strong></td>
</tr>
<tr>
<td>layer 1*</td>
<td>711.30</td>
</tr>
<tr>
<td>layer 2</td>
<td>569.41</td>
</tr>
<tr>
<td>layer 3</td>
<td>283.25</td>
</tr>
</tbody>
</table>

*: depth of the layers:
– layer 1: 0–15 cm.
– layer 2: 15–30 cm.
– layer 3: 30–50 cm.
are hydrophobic so their solubility in water is low and for this reason they are accumulated in the sediment layers in a preferred manner. In contrast, the longer homologues are hydrophilic and therefore their solubility in water is high, so their total concentration is divided between the liquid phase and the precipitation phase - in favor of the river water. The number of hydrophilic lipophilic balance (HLB) of the long homologues is higher and is more soluble in water. In addition, the high homologues break down in the classical process of β-decarboxylation while creating more short homologues. Another possible explanation is that under anaerobic conditions found in sediments, the short homologues are more stable than the long homologues, so the long homologues break down into average homologues, and these continue to decompose into short homologues.

CONCLUSIONS

The results presented in this paper indicate that the concentration levels of APEOs in the water of the Hadera and Alexander rivers and in their sediments (at the upper 50 cm) are in the ranges 11.83–55.52 μg/L, and 99.68–1,176.61 μg/kg, respectively. These results indicate also that the concentration level of APEOs decreases as the sample is taken from a deeper layer of the sediment.

Homologues with 9 to 15 units of EO are the dominant homologues of APEOs in the river water and homologues with 1–12 units of EO are dominant in the sediment layers of the Hadera and Alexander rivers.

APEOs are ‘hard’ organic surfactants whose biological decomposition is slow and prolonged, and therefore survives in the environment. APEOs and their degradation products have estrogenic properties and an endocrine activity for animals both in freshwater and in seawater. Therefore, the survival, the homologous distribution and the accumulation of APEOs in river water and their sediment layers is a serious environmental problem.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


OECD. 2004 The 2004 OECD List of High Production Volume Chemicals.


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