BEHAVIOUR OF ALKYLPHENOL POLYETHOXYLATE SURFACTANTS IN THE AQUATIC ENVIRONMENT—III. OCCURRENCE AND ELIMINATION OF THEIR PERSISTENT METABOLITES DURING INFILTRATION OF RIVER WATER TO GROUNDWATER

MARIJAN AHEL1*, CHRISTIAN SCHAFFNER2 and WALTER GIGER2

1Center for Marine Research, Rudjer Bošković Institute, P.O. Box 1016, 41001 Zagreb, Croatia and
2Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600 Dübendorf, Switzerland

(First received November 1994; accepted in revised form April 1995)

Abstract—The behaviour of various persistent metabolites derived from nonylphenol polyethoxylate (NPnEO) surfactants was studied during infiltration of river water to groundwater at two field sites situated in the northern part of Switzerland (Glatt River and Sitter River). Nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenoxy acetic acid (NP1EC) and nonylphenoxy(ethoxy) acetic acid (NP2EC) were observed in the two investigated rivers at relatively high concentrations with average values of the individual types of nonylphenolic compounds ranging from 1.8 to 25 μg/l. The average concentrations of NP, NP1EO and NP2EO in groundwater were significantly lower (range < 0.1–1 μg/l) suggesting an efficient elimination of these compounds during infiltration. In contrast, the elimination of nonylphenoxy carboxylic acids was less efficient. Most of the observed elimination occurred in the first 2.5 m of the aquifer, while further decrease in concentration was rather slow. In one sampling period, residual concentrations of nonylphenolic compounds up to 7.2 μg/l were detected in a pumping station used for drinking water supply which is situated 130 m from the Glatt River bed. Concentrations of NP, NP1EO and NP2EO in both river water and groundwater showed a pronounced seasonal variability with higher values observed during winter. The data suggest that low temperatures, which prevail in winter, significantly reduce the elimination efficiency of NP and to a lesser extent of NP1EO, while the behaviour of NP2EO was not affected. Such a behaviour indicates biogical transformation as the responsible elimination process. A comparison of average elimination efficiencies of nonylphenolic compounds with those of pentachlorophenol (PCP) and nitrilotriacetate (NTA) gives the following sequence: NTA > NP2EO > NP1EO > NP > PCP > NP1EC = NP2EC.

Key words—surfactants, nonylphenol polyethoxyxylates, metabolic products, nonylphenol, river water, groundwater, infiltration

INTRODUCTION

Non-ionic surfactants of the alkylphenol polyethoxylate (APnEO) type (Fig. 1) have a significant share in the total surfactant market with annual production rate exceeding 350 thousand tons (Richler and Knaut, 1988). In contrast to most of the other types of surfactants, APnEOS are biotransformed starting at the hydrophilic part of their molecules (Swisher, 1987). Such a biotransformation pathway results in formation of a number of stable metabolic products including nonylphenol (NP), short-chain nonylphenol polyethoxylates (NP1EO, NP2EO) and nonylphenoxy carboxylic acids (NPnECs) (Reinhard et al., 1982; Giger et al., 1984; Giger et al., 1987; Ahel, 1987; Ball et al., 1989; Holt et al., 1992) (Fig. 1). Some of these metabolites, notably NP, are more lipophilic and consequently much more toxic than the parent compounds themselves (Granmo et al., 1989; Naylor et al., 1992a). Therefore, increasing attention has been focused on the ecotoxicological effects of APnEO in the aquatic environment. A significant bioaccumulation of the lipophilic metabolites in various species of aquatic organisms has been observed (Ekelund et al., 1990; Ahel et al., 1993). In addition, in vitro studies reported recently indicate that AP, APnEO and APnEC are weakly estrogogenic in fish, birds and mammals (White et al., 1994).

Comprehensive field studies conducted in Switzerland have shown that degradation of nonylphenol polyethoxylates (NPnEOs) in sewage treatment plants (STPs) can be incomplete (Ahel, 1987; Brunner et al., 1988; Ahel et al., 1994a). It was estimated that about 40% (calculated on a molar basis) of the total NPnEO load in STP influents can reach natural waters via secondary effluents, predominantly in the form of
metabolic products (Ahel et al., 1994a). Consequently, rather high concentrations of surfactant-derived nonylphenolic compounds were observed in Swiss rivers that receive secondary effluents (Ahel et al., 1984; Ahel et al., 1994b). The concentrations reported for 30 American rivers were comparatively lower (Naylor et al., 1992b).

Since groundwater represents one of the most important reservoirs for drinking water supplies in many European countries, the problem of its contamination by numerous organic pollutants represents a major concern. To date, only a few publications have reported on APnEOs and their metabolites in groundwater (Schaffner et al., 1987; Barber et al., 1988; Ahel, 1991; Field et al., 1992). Barber et al. (1988) have studied transport of NP in an aquifer that was contaminated by rapid infiltration of secondary sewage effluent. Their field data suggested that NP was retarded during subsurface transport which was in agreement with its predicted retardation factor of 3.4. Field et al. (1992) were able to identify at the same field site carboxylated residues of APnEO surfactants. Ahel (1991) has reported on the occurrence of NP, NP1EO, NP2EO and NP2EC in groundwater from three different field sites in the alluvial aquifer of the Sava River, Croatia. Apart from two rather preliminary reports (Schaffner et al., 1987; Ahel, 1991), systematic studies on the behaviour of the surfactant-derived nonylphenolic compounds during
Table 1. Concentrations of nonylphenol polyethoxylate-derived compounds in the Glatt River and in groundwater at Glattfelden field site

<table>
<thead>
<tr>
<th>Compound</th>
<th>Glatt River</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>2.7 ± 2.2</td>
<td>0.96 ± 0.94</td>
<td>0.40 ± 0.43</td>
<td>0.44 ± 0.46</td>
<td>0.20 ± 0.32</td>
</tr>
<tr>
<td>NP1EO†</td>
<td>(0.7–26)</td>
<td>(&lt;0.1–29)</td>
<td>(&lt;0.1–4.4)</td>
<td>(&lt;0.1–3.4)</td>
<td>(&lt;0.1–33)</td>
</tr>
<tr>
<td>NP2EO†</td>
<td>7.8 ± 5.2</td>
<td>0.91 ± 1.3</td>
<td>0.18 ± 0.25</td>
<td>0.09 ± 0.12</td>
<td>0.04 ± 0.09</td>
</tr>
<tr>
<td>NP1EC‡</td>
<td>14.7 ± 8.9</td>
<td>10.9 ± 3.1</td>
<td>9.7 ± 0.2</td>
<td>2.9 ± 0.1</td>
<td>4.5 ± 6.3</td>
</tr>
<tr>
<td>NP2EC‡</td>
<td>24.7 ± 5.7</td>
<td>22.4 ± 1.1</td>
<td>15.3 ± 6.6</td>
<td>14.5 ± 2.5</td>
<td>5.1 ± 7.1</td>
</tr>
</tbody>
</table>

| Distance (m)$|$ | 0  | 2.5 | 5  | 7  | 13 |

*Arithmetic mean ± standard deviation and range of 16 determinations.
†Exceptionally high concentration values obtained in December 1984 and February 1985 were not included in the calculation of the average values.
‡Arithmetic mean and range of 2 determinations.
§Distance of the observation wells (G1–G4) from the river bed; NP, nonylphenol; NP1EO, nonylphenol monoethoxylate; NP2EO, nonylphenol diethoxylate; NP1EC, (nonylphenoxy) acetic acid; (NP2EC), (nonylphenoxy (ethoxy)) acetic acid.

infiltration of river water to groundwater are completely lacking.

The present paper has therefore two goals. First, being the third paper in a series of closely related papers (Ahel et al., 1994a,b) it aims at improving our understanding of the environmental fate of nonylphenolic compounds as an important prerequisite for a better ecotoxicological assessment of these compounds. More generally, it aims to extend our knowledge about the behaviour of organic compounds in groundwater which are more polar than those which had been reported on in a previous study performed at the same field site (Schwarzenbach et al., 1983).

**EXPERIMENTAL**

**Description of investigated field sites and sample collection**

The behaviour of nonylphenolic compounds during the infiltration was investigated at two locations: (a) Glatt River near Glattfelden (Canton of Zürich; Glattfelden field site) and Sitter River near Engelburg (Canton of St Gall; Engelburg field site) (Fig. 2). The Glattfelden field site is located in the lower part of the Glatt Valley where the Glatt River infiltrates into a quaternary glaciofluvial valley-fill aquifer. The Glatt River (average discharge rate of 8 m³/s) is a rather heavily contaminated perialpine river. The major source for organic pollutants, including nonylphenol polyethoxylates and their metabolites, in the river are treated wastewaters from publicly-owned mechanical and biological STPs (Abel, 1987). At the Engelburg field site, the river is classified as moderately polluted Swiss river (Ahel, 1987). The original procedure was modified by applying isocratic conditions to separate NP, NP1EO and NP2EO and a spectrofluorimetric detector (Perkin Elmer LS-3; 277 nm/300 nm) for their quantitative determination (Ahel, 1987). The detection limit based on 2 litre-water samples was 10 ng/l.

Nonylphenol carboxylic acids (NP1EC and NP2EC) were extracted with chloroform from acidified water samples (pH 2) using a separatory funnel. Extracts were treated with anhydrous sodium sulphate, evaporated to dryness and purified using a column filled with deactivated silica gel (15% water). The NPnECs which eluted in the methanol fraction were methylated by 1 N HCl/methanol and were analysed using normal-phase HPLC. Details of the analytical procedure are described elsewhere (Ahel et al., 1987). The detection limit using a spectrofluorimetric detector (277 nm/300 nm) was 100 ng/l.

**Analytical methods**

Lipophilic nonylphenol ethoxylates (NP1EO and NP2EO) and nonylphenol (NP) were extracted from water samples using a combined steam distillation/solvent extraction procedure. After addition of 2,4,6-trimethylphenol as an internal standard, the extracts were analysed without any further purification by normal-phase HPLC as described elsewhere (Ahel and Giger, 1985). The original procedure was modified by applying isocratic conditions to separate NP, NP1EO and NP2EO and a spectrofluorimetric detector (Perkin Elmer LS-3; 277 nm/300 nm) for their quantitative determination (Ahel, 1987). The detection limit based on 2 litre-water samples was 10 ng/l.

Nonylphenoxycarboxylic acids (NP1EC and NP2EC) were extracted with chloroform from acidified water samples (pH 2) using a separatory funnel. Extracts were treated with anhydrous sodium sulphate, evaporated to dryness and purified using a column filled with deactivated silica gel (15% water). The NPnECs which eluted in the methanol fraction were methylated by 1 N HCl/methanol and were analysed using normal-phase HPLC. Details of the analytical procedure are described elsewhere (Ahel et al., 1987). The detection limit using a spectrofluorimetric detector (277 nm/300 nm) was 100 ng/l.
Nitrilotriacetate (NTA), pentachlorophenol (PCP) and 1,4-dichlorobenzene were determined by methods based on the procedures described by Schaffner and Giger (1984), Renberg and Lindström (1981) and Grob and Zürcher (1976), respectively.

RESULTS AND DISCUSSION

Occurrence and behaviour of nonylphenolic compounds in groundwater

Average values and ranges of concentrations for NP, NP1EO, NP2EO, NP1EC and NP2EC, obtained during a 1-year study at the location of Glattfelden are shown in Table 1. These compounds are the major metabolic products of nonylphenol polyethoxylates and comprise more than 95% of the surfactant-derived nonylphenolic compounds present in the river (Ahel et al., 1994b). Moreover, nonylphenolic compounds are among the most abundant micropollutants at Glattfelden field site. Their individual concentrations in the river water have been found to be one order of magnitude higher than the concentrations of tetrachloroethylene, 1,4-dichlorobenzene, 1,3-dimethylnenzene and pentachlorophenol (Schwarzenbach et al., 1983), while their total concentrations are similar to the concentration of NTA (Schaffner et al., 1987). This indicated that nonylphenolic compounds are of great concern with respect to their potential impact on groundwater quality in the investigated aquifer. The concentrations observed in the Glatt River and groundwater varied in space and time. The average concentration values, however, were considerably lower in groundwater suggesting an efficient elimination of nonylphenolic compounds during the most of the year. However, the maximum concentrations in river water and groundwater are quite similar, indicating that a breakthrough of these compounds into the aquifer can occur occasionally.

Fig. 3. Concentrations of NP, NP1EO and NP2EO in the Glatt River and in groundwater at the Glattfelden field site in relation to distance from the river bed in four different seasons: (A) October 1984; (B) January 1985; (C) June 1985; and (D) August 1985.
The groundwater concentrations of nonylphenolic compounds measured in this study are significantly higher than those reported for other alluvial aquifers (Ahel, 1991) reflecting the comparatively high concentrations in the Glatt River.

Figure 3 presents the typical concentration profiles of NP, NP1EO and NP2EO for the aquifer at Glattfelden field site during four different seasons. As can be seen, the concentration profiles are characterized by strong reduction in the concentrations of NP, NP1EO and NP2EO in the first 2.5 m of the aquifer, while further decrease in concentration was much slower. The concentration profiles of various individual nonylphenolic compounds are not identical indicating their different behaviour during infiltration. This is particularly true if concentration profiles of lipophilic nonylphenolic compounds (NP, NP1EO and NP2EO) are compared with the more hydrophilic ones (NP1EC, NP2EC) (Fig. 4). In contrast to the rather fast elimination of NP1EO and NP2EO in the first several meters of the aquifer, NP1EC and NP2EC showed a much slower elimination (Fig. 4A). However, the results from the second sampling (Fig. 4B) suggested that despite the low elimination of NPnECs in the first part of the aquifer, a later elimination may take place. Unfortunately, determination of NP1EC and NP2EC was not included in the investigations which were carried out for the period of a full year, therefore, only two data series from May 1986 are available for these compounds. There are two reasons why NPnECs should be regarded as potentially very important groundwater contaminants at river water infiltration sites. Analyses of the river water samples in this study (Table 1) confirmed our previous observations which showed that NP1EC and NP2EC were the predominant nonylphenolic compounds in the Glatt River (Ahel et al., 1994b). Moreover, the higher solubility of NP1EC and NP2EC and their resistance to biodegradation in aerobic conditions (Ahel, 1987) are possible reasons for their higher mobility in the aquifer compared to NP1EO and NP2EO. However, additional investigations are necessary to draw firm conclusions about the behaviour of NPnECs during infiltration.

In addition to the nonylphenolic compounds, the concentrations of other pollutants such as PCP and NTA were determined in the same samples (Schaffner et al., 1987). In Fig. 5, a comparison is given between the average elimination efficiencies of the mentioned organic pollutants during infiltration of river water to groundwater. The efficiencies for different observation wells have been obtained during a 1-year study at
Fig. 6. Distribution of NP, NP1EO and NP2EO in groundwater at the Glattfelden field site showing a major breakthrough of nonylphenolic compounds into the aquifer: (A) December 1984 and (B) February 1985.

Glattfelden field site and are expressed as a percentage of the river water concentration. As can be seen, the following sequence of the elimination efficiencies is obtained: NTA > NP2EO > NP1EO > NP > PCP > NP2EC. NP2EO is eliminated as efficiently as highly biodegradable NTA, while NP2EC exhibits a rather persistent behaviour comparable to the behaviour of PCP. Obviously, nonylphenolic compounds exhibit a wide range of different behaviours in groundwater which is in agreement with previously reported studies in sewage (Ahel et al., 1994a) and rivers (Ahel et al., 1994b).

Despite the generally very efficient elimination, in some sampling periods high concentrations of nonylphenolic compounds reached locations > 100 m from the river. Two different examples are shown in Fig. 6. In both cases, large fluctuations in the concentrations were observed in the first 5 m of infiltration, while further concentration changes were rather small. There are two possible mechanisms to explain these results: (a) breakthrough the actual adsorption capacity of the aquifer material close to river bed by a heavily polluted “package” of river water and (b) biological transformations by which particular nonylphenolic compounds are formed in situ from available precursors. Although available knowledge on microbial transformations of nonylphenolic compounds in groundwater does not allow us to be more specific about the processes involved in such events, a comparison with the behaviour of NTA (Kuhn et al., 1986) suggests the following scenario as a possible explanation. The aquifer part closest to the river bed, that was shown to be responsible for the most of the observed elimination, is characterized by a rather low concentration of dissolved oxygen (<1 mg/l) and in some situations becomes even anaerobic (denitrifying conditions) (Schwarzenbach et al., 1983). Changing from aerobic to denitrifying conditions in the aquifer can result in a temporary but strong reduction of the elimination efficiency of infiltrating pollutants (Kuhn et al., 1986). Moreover, anaerobic conditions are favourable for the formation of NP (Ahel, 1987).

As a consequence of nonylphenolic compound transport in the aquifer, detectable concentrations of NP (<0.1–7.2 μg/l), NP1EO (<0.1–3.4 μg/l) and NP2EO (<0.1–1.7 μg/l) were determined in a pumping station situated about 130 m from the Glatt River. Unfortunately, the samples from the pumping station were not analysed for NPnECs. However, NP2EC has been reported, in addition to other NPnECs and NPnEOs, to be present in finished drinking water of New Jersey at a concentration of 0.16 μg/l (Clark et al., 1992).

A summary of the results obtained at Engelburg field site is presented in Table 2. Concentrations of nonylphenolic compounds in the Sitter River are much lower than those in the Glatt River indicating a significantly lower organic load. Based on the concentration ratios between NP, NP1EO and NP2EO the major source of these compounds appear to be secondary effluents from STP. The diurnal fluctuations of nonylphenolic concentrations in the river (Fig. 7) do not suggest any regularity in their pattern that would possibly reflect diurnal loading dynamics to a sewage treatment plant. Moreover, the variations of concentrations in the river were not followed by similar variations in groundwater (Fig. 7). The residence time of the groundwater under pumping conditions is estimated to be 2–4 h (i.e. groundwater-flow velocity is 4–8 m/h). Despite such extremely high groundwater-flow velocities, the concentrations of nonylphenolic compounds in groundwater were found to be mainly in the range 0.01–0.1 μg/l with only two values higher than 0.5 μg/l. Consequently, the results indicate a very efficient elimination (>95%) of NP, NP1EO and NP2EO. For comparison, diurnal

<table>
<thead>
<tr>
<th>Sample</th>
<th>NP (μg/l)</th>
<th>NP1EO (μg/l)</th>
<th>NP2EO (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>1.8 ± 0.52</td>
<td>2.4 ± 0.34</td>
<td>1.8 ± 0.71</td>
</tr>
<tr>
<td>Groundwater</td>
<td>0.09 ± 0.05</td>
<td>0.12 ± 0.18</td>
<td>0.07 ± 0.14</td>
</tr>
<tr>
<td>Elimination (%)</td>
<td>94.8</td>
<td>96.9</td>
<td>96.2</td>
</tr>
</tbody>
</table>

*Arithmetic mean and standard deviation calculated from 12 measurements.
†Calculated as a ratio between the concentrations in groundwater and river.
dynamics of 1,4-dichlorobenzene is also presented (Fig. 7D). The elimination rate for this compound is only about 60–70% and there is a better agreement between the fluctuations in the river and groundwater. The findings for both classes of organic compounds are very similar to those obtained for the average situation found at Glattfelden field site confirming the general validity of the conclusions drawn from the present study.

Seasonal variations

It was shown that NP, NP1EO, and NP2EO concentrations in rivers are affected by seasonally-dependent factors such as temperature and light intensity (Ahel et al., 1994b) that strongly influence their biotic and abiotic transformation reactions. Because light can be excluded as a factor in subsurface processes, the main seasonal factor to be considered is temperature. The bulk of groundwater in the investigated aquifer is characterized by a rather constant temperatures between 10–12°C throughout the whole year, while only near the river (0–7 m) temperature fluctuations (4–20°C) were found to be similar to those in the Glatt River (Schwarzenbach et al., 1983). Figure 8 shows seasonal concentration variations of nonylphenolic compounds in the Glatt River and observation well G1 (2.5 m from the river bank). Despite the large variations of concentration in the river itself, a seasonal trend is observed for all nonylphenolic compounds, with the highest concentrations in winter (November–April; T = 3–10°C) and the lowest ones in summer (May–October; T = 10–20°C). Also, there is good agreement between general trends of the concentration changes in the river and groundwater.

It is important to note that the elimination efficiency of NP and NP1EO in the first 2.5 m of infiltration was significantly smaller in winter than in summer (Figure 8A, B). By contrast, NP2EO was rather efficiently eliminated even during the coldest part of the year (Fig. 8C). This comparison of different nonylphenolic compounds suggests a biological character of the ongoing elimination process. Consequently, these results show that winter represents the most critical part of the year with respect to the danger of polluting groundwaters by the investigated compounds.
Retardation factors

In addition to biological transformations, the impact of physicochemical processes, primarily interaction with the aquifer material, should be addressed when interpreting the behaviour of nonylphenolic compounds in the subsurface. Table 3 presents a comparison of retardation factors ($R_f$) of different nonylphenolic compounds and some other typical organic micropollutants detected at the Glattfelden field site. The retardation factors were estimated from the corresponding octanol/water partition coefficients ($K_{ow}$) by assuming hydrophobic partitioning between water and organic carbon in the fine fraction of the aquifer material as the responsible process (Schwarzenbach et al., 1983). $R_f$ values are of great importance for understanding transport of nonylphenolic compounds in the subsurface as well as for correlating river concentrations with those in groundwater.

The interpretation of the data obtained in an aquifer composed of three substantially different compartments is extremely difficult since predicted $R_f$ values vary in very wide ranges, especially for compounds with log $K_{ow}$ values > 4 (Table 3). However, the relative $R_f$ ratios between different micropollutants can be very useful in understanding the ongoing processes in subsurface. For example, $R_f$s of NP1EO and NP2EO are approx. 2 times lower than $R_f$ of NP but our field observations suggested better transport of...
Alkylphenol polyethoxylates in groundwater

Table 3. Comparison of retardation factors calculated for nonylphenolic compounds (NP, NP1EO, NP2EO) and some typical hydrophobic organic micropollutants detected in groundwater at Glattfelden field site

<table>
<thead>
<tr>
<th>Compound</th>
<th>log ( K_{ow} )</th>
<th>River sediment (0.1 m)</th>
<th>Aquifer close to river bed (&lt; 5 m)</th>
<th>Aquifer far from river bed (&gt; 5 m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>4.48</td>
<td>109-430</td>
<td>11.7-216</td>
<td>1-11.7</td>
</tr>
<tr>
<td>NP1EO, NP2EO</td>
<td>4.20</td>
<td>60-237</td>
<td>6.9-119</td>
<td>1-6.9</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>2.88</td>
<td>9-31</td>
<td>1.8-16</td>
<td>1-1.8</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>3.38</td>
<td>18-70</td>
<td>2.7-35</td>
<td>1-2.7</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>5.24</td>
<td>&lt; 100&lt;sup&gt;0&lt;/sup&gt;</td>
<td>&lt; 50&lt;sup&gt;0&lt;/sup&gt;</td>
<td>&lt; 10&lt;sup&gt;0&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

*Equation: \( R_f = 1 + 3.2 f_{oc}(K_{ow}p^{1/2})/(1 - \varepsilon) \) (Schwarzenbach et al., 1983); \( f \), fraction of the aquifer material in the grain size range \( f < 125 \) mm; \( f_{oc} \), organic carbon content of the fine fraction; \( p \), density of the aquifer material (2.5 g/cm<sup>3</sup>); \( \varepsilon \), total porosity (0.2-0.4); \( K_{ow} \), octanol/water partition coefficient; \( \gamma_{oc} = 0.01-0.02; f = 0.2-0.4; \gamma_{oc} = 0.001-0.01, f = 0.2-0.4; \gamma_{oc} < 0.001, f < 0.2; \) Ahel and Giger (1993); Schwarzenbach et al. (1983); Schellenberg et al. (1984) and Schwarzenbach (1986).

NP into groundwater. This comparison infers that biological elimination of the former compounds must play an important role in their distribution in the aquifer. Unfortunately, \( R_f \) values of NPnECs cannot be reliably estimated since their \( K_{ow} \) values are not available. However, a rough comparison with corresponding NPnEOs suggests that their \( K_{ow} \)s and consequently \( R_f \)s are expected to be significantly lower due to their higher solubility in water (Ahel, 1987).

Rather high \( R_f \) values up to 430 were estimated for NP, which is an order of magnitude higher than \( R_f \) of tetrachloroethylene and 1,4-dichlorobenzene. This difference means that the time available for elimination reactions in the biologically most active zone of the aquifer, situated close to the river bed, is about 10 times higher. This should be considered an important factor determining the fate of a given chemical in groundwater. The residence time of NP in the aquifer close to the river is estimated to be > 10 days. Moreover, due to favourable partitioning of NP and NPnEOs into the organic phase, the organic rich river sediment can be considered an important reservoir of these pollutants. We hypothesize that these accumulated compounds could be desorbed into the adjacent groundwater. The concentration profiles shown in Fig. 6 possibly reflect such a hypothetical situation. However, more investigations are required to elucidate physicochemical behaviour as well as biological transformations of nonylphenolic compounds in groundwater.

**CONCLUSIONS**

Elimination of the persistent surfactant-derived alkylphenolic compounds during infiltration of river water into groundwater is highly dependent on their predominant chemical form present in the river and specific conditions in the aquifer. For NP1EO and NP2EO, the elimination seems to be rather efficient (> 90%) in all seasons, while for NP it can be strongly reduced during winter. Comparison of the predicted retardation factors of NP and NPnEOs with their concentration profiles observed in the aquifer indicates biological elimination as the predominant mechanism. One of the results from the present study suggests, however, that biodegradation capacity of the involved bacterial consortium can collapse at low temperatures, leading to a significant breakthrough of nonylphenolic compounds into the groundwater.

Currently on-going developments for the remediation of contaminated soils and aquifers include the suggestion of applying surfactants. Such activities should, however, seriously consider possible problems caused by the applied surfactants. The results described in this publication can be used to evaluate the fate of nonylphenol polyethoxylate surfactants in the subsurface environment.

**Acknowledgements**—This project was supported in part by the Swiss National Science Foundation (Nationales Forschungsprogramm 7D, research project on "Organic Pollutants in Sewage Sludge"). Financial support of the Ministry of Science and Technology of the Republic of Croatia is also acknowledged. We are grateful to Eduard Hoehn and Meg David for critically reading the manuscript.

**REFERENCES**


