Environmental behaviour of onylphenol ethoxylates in coastal waters

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Citation for published version (APA):
Sources and fate of nonylphenol ethoxylates and their metabolites in the Dutch coastal zone of the North Sea

Submitted to Marine Chemistry

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Abstract

Results are presented of a field study in the Dutch coastal zone of the North Sea on the environmental fate of nonylphenol ethoxylates (A₉PEO). The goal of this field study was to determine the sources of these nonionic surfactants to the Dutch coastal zone, and their subsequent fate.

Surface waters, sediments and suspended particulate material were analyzed on A₉PEO, nonylphenol (NP) and the carboxylated metabolites (A₉PEC), using Soxhlet extraction, Solid Phase Extraction and liquid chromatography - electrospray ionization mass spectrometry (LC-ESI-MS).

Unusually high dissolved concentrations of A₉PEO were observed in a number of offshore samples. Maximum dissolved concentrations of 36, 1.7 and 0.63 μg L⁻¹ were observed, respectively, for A₉PEO, NP and A₉PEC. Dissolved concentrations of A₉PEO at the water surface were roughly one order of magnitude higher than several meters below the surface. In sediments, maximum concentrations of 277 and 86 ng g⁻¹ for A₉PEO and NP were observed, whereas A₉PEC were only found sporadically. Relatively high concentrations of A₉PEO and NP were observed in sediments near the shore, which decreased until below 50 ng g⁻¹ d.w. at about 10 km off shore. In the sediments, mainly the short chain A₉PEO₂₋₃ are detected, indicating that extensive biodegradation has occurred.

Both the oxidative and non-oxidative hydrolytic biodegradation mechanisms occur in the Dutch coastal zone, although the oxidative route is less important than in the adjacent Scheldt and Rhine estuaries.

More than 25% of the A₉PEO present in marine water is sorbed to suspended particulate material.

The main sources of A₉PEO in sediments in the Dutch coastal zone were identified as the Rhine and Scheldt estuaries, dump sites for harbour dredge and in some cases production platforms. For the water phase, the most likely sources of A₉PEO seem to be discharges from ships at open sea.

6.1. Introduction

Along the North Sea, some of the most densely populated and industrialized regions in the world are situated, including the Scheldt, Rhine Meuse, Elbe and Thames basins. The North Sea has some of the most crowded shipping routes (to the harbours of Rotterdam, Antwerp and Hamburg) as well as one of the world’s most intensive fisheries. Understandably, pollution of the North Sea has been of major environmental concern for decades.
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Generally, river discharges of the major contaminants to the North Sea have decreased over the last decade [1]. In addition, measures such as the cessation of sewage sludge dumping have resulted in decreasing concentrations of PAH and PCB [2, 3]. These phenomena logically shift the attention slightly towards other sources of contaminants, e.g. compounds which are used in shipping and offshore industry. Surfactants (surface active agents) belong to this type of compounds.

One of the main nonionic surfactant groups consists of the alkylphenol ethoxylates (APEO), which are used in e.g. the textile and paper industry, and are present in many types of products, such as cleaning agents, paints and pesticides. APEO have an annual global production of around 700,000 tons [4]. Especially this surfactant group is environmentally relevant, as some of their possible metabolites (nonylphenol (NP), A_9PEO\textsubscript{1} and A_9PEO\textsubscript{2}, see figure 6.1) are weak endocrine disruptors [5, 6]. Recently, NP was identified as a major contributor to endocrine disrupting effects observed in the Dutch aquatic environment, in a large study including analysis of phthalates, bisphenol-A, brominated flame retardants and estrogenic hormones [7].

![Figure 6.1: Biodegradation routes of A_9PEO: the oxidative hydrolytic pathway (A) and the non-oxidative hydrolytic pathway (B).](image-url)
Although a reasonable amount of data is now available on the occurrence of APEO in fresh waters of Europe, North America and Asia [8, 9], the knowledge about their subsequent fate in saline waters is still limited. Typical estuarine and marine maximum concentrations reported in literature are around 1 µg L\(^{-1}\) [10-12] with occasional maximum values around 10 µg L\(^{-1}\) in Spain [13] and 25 µg L\(^{-1}\) in Israel [14]. In general, A\(_9\)PEO concentrations in saline environments are found to be roughly one order of magnitude lower than those in fresh water [15-17].

A study on NP and A\(_9\)PEO in British estuaries reaching the North Sea showed that in over 80% of the estuarine water samples, total NP concentrations were below 0.1 µg L\(^{-1}\). However, in some cases exceptionally high concentrations were found due to local sources [15]. In a field study performed near the mouth of the river Elbe and the German Bight of the North Sea, maximum dissolved estuarine concentrations of 84 ng L\(^{-1}\) for NP and 135 ng L\(^{-1}\) for A\(_9\)PEO\(_{1,2}\) were reported, and maximum concentrations of NP and A\(_9\)PEO\(_{1,2}\) in marine water amounted to 63 and 32 ng L\(^{-1}\), respectively [18]. Another publication reports lower concentrations of NP and A\(_9\)PEO in the same region, with maximum dissolved NP concentrations of 33 ng L\(^{-1}\) in the estuary and below 1 ng L\(^{-1}\) in the North Sea, while A\(_9\)PEO concentrations were all below 10 ng L\(^{-1}\) [19].

Studies on sorption of A\(_9\)PEO to marine sediments have shown that once the surfactants have entered the sediment, further degradation will be very slow, and the ethoxymer distribution does not change substantially anymore [20].

De Voogt et al. reported concentrations of 20-400 ng g\(^{-1}\) dry weight (d.w.) for A\(_9\)PEO\(_{1,3}\) in estuarine sediments from several countries along the North Sea [21]. In the German Bight of the North Sea, maximum concentrations of NP in sediment were 153 ng g\(^{-1}\) d.w. near the coast, and 55 ng g\(^{-1}\) at open sea. A\(_9\)PEO concentrations were below 10 ng g\(^{-1}\) in all sediment samples [19]. Lye et al. observed high maximum NP and A\(_9\)PEO\(_1\) concentrations in British estuarine sediment of 9050 and 3970 ng g\(^{-1}\), respectively [22]. North Sea fish samples taken off shore did not contain detectable levels of APEO metabolites in liver or muscle tissue [22, 23]. Recently, Jonkers and De Voogt reviewed the occurrence of A\(_9\)PEO and metabolites in the estuarine and marine environment [24].

For the Netherlands, recently Maximum Permissible Concentrations (MPC) in water and sediments have been proposed of 0.12 µg L\(^{-1}\) and 0.15 µg g\(^{-1}\) d.w. for A\(_9\)PEO\(_{1,2}\) and 0.33 µg L\(^{-1}\) and 0.105 µg g\(^{-1}\) d.w. for NP [25]. From the field data available in literature, it is concluded that these MPC are exceeded at several locations.

Although the biodegradation of A\(_9\)PEO\(_n\) is a matter of ongoing scientific debate, it is generally believed that two degradation routes are possible (see figure 6.1). In the oxidative-hydrolytic route, an \(\omega\)-oxidation of the ethoxylate chain produces alkylphenoxy ethoxy acetic acids (A\(_9\)PEC), which is followed by a stepwise shortening of the ethoxylate chain. Then, the alkyl chain is oxidized, leading to doubly carboxylated metabolites (CAPEC) [26,
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This degradation route occurs only under aerobic conditions. In the nonoxidative hydrolytic route, the first step is a shortening of the ethoxylate chain, leading to A₉PEO₂ and A₉PEO₁. Under aerobic conditions, these compounds can be oxidized to form A₉PEC, and under anaerobic conditions, NP may be formed [28, 29].

The present study focuses on the environmental fate of A₉PEO and its metabolites in the Dutch coastal zone. The main objective was to study the occurrence of these compounds in marine water, suspended particulate material (SPM) and sediments, using sophisticated LC-MS methods. In addition, a detailed comparison was made of different marine water sampling techniques. To our knowledge, no previous publications exist which comprehensively study A₉PEO and all their metabolites in the three marine compartments. With the results, the main sources and routes of A₉PEO to the Dutch coastal zone of the North Sea could be assessed. The analysis of A₉PEO metabolites gives insight into biodegradation processes occurring in this area, while sorption processes could be quantified from the analysis of suspended particulate material.

6.2. Experimental Section

Study area
The semi-enclosed, epi-continental North Sea is relatively shallow, with an average depth of 90 m. The highly developed industry and agriculture in its watershed produce a large load of contaminants and nutrients which are transported to the North Sea. In addition, the North Sea is a major navigation route to some of the world’s biggest harbours: Rotterdam, Antwerp and Hamburg. Oil and gas exploitation in the North Sea results in the presence of over 500 production platforms in the North Sea [3]. Flushing time for the entire North Sea was estimated at one year to 500 days [30].

In this study, the Dutch coastal zone in the Southern Bight of the North Sea was investigated. Most water in this section of the North Sea is flowing in from the English Channel, resulting in a south-north net water current. Total run-off of freshwater into the Southern Bight from the Netherlands and Belgium (Scheldt, Meuse, Rhine and Dutch Wadden Sea) is estimated to be 91 km³ per year [3].
Chapter 6

Figure 6.2: Study area: the Dutch coastal zone. Sampling locations are shown along transects from anticipated A₈PEO sources: 2 platforms (P), Wadden Sea (W), North Sea canal (N), Scheveningen waste water discharge (SW), Rhine (R), Haringvliet (H) Scheldt estuary (SE). Locations D1 and D2 are harbour dredge dump sites. The dotted lines indicate the main shipping routes.

Sampling campaigns
Two sampling campaigns were carried out in the Dutch coastal zone of the North Sea in November 1999 and June 2000, with the research ship Mitra of the Directorate North Sea of the Dutch Ministry of Transport, Public Works and Water Management. Sampling locations at the North Sea were chosen with the aim to trace possible important sources and the fate of A₈PEO and metabolites in the Dutch coastal zone (see figure 6.2). In most marine field studies on A₈PEO reported in the literature, fresh water sources and harbours are considered the main sources of surfactants to the marine environment, and consequently the sampling locations are limited to only several miles off shore. In the present study, other possible sources were specifically included in the sampling strategy,
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namely production platforms and shipping. As a consequence, sampling locations further off shore were included.

Samples were collected in a series of transects, starting at the following suspected sources (see figure 6.2): the mouth of the Scheldt estuary, the two exits of the Rhine (Nieuwe Waterweg and Haringvliet), the Scheveningen waste water effluent pipe, the mouth of the North Sea canal, the entrance of the Wadden Sea as well as two production platforms. Finally, samples were taken at two coastal dumping sites for harbour dredge.

Samples of surface sediments were collected using a box core sampler, with average box core depths of 30 cm. From the work of Laane et al. it was concluded that no vertical concentration gradients are present in the top 30 cm of the sediments in the study area [2]. To ensure that the samples obtained were representative of the location, three box cores were collected at each location and the complete cores were mixed.

During the campaign of 1999, the water samples were taken from the water surface (at a depth of approximately 0.5 m) using a stainless steel bucket. In the campaign of 2000, water samples were taken at approximately 3 m depth, using a sampling torpedo. Both water and sediment samples were taken at each location.

Initial biodegradation of A₉PEO is known to occur easily in some aqueous matrices [27]. To avoid any chance of changes in their integrity, all water samples were treated immediately after sampling on board the ship, thereby avoiding any potential conservation problems. From the mixed sediment cores, subsamples of approximately 150 g were taken and stored immediately after sampling at -20 °C.

Characterization of the surface sediments was done by determining the organic carbon content, grain size distribution (fraction of particles smaller than 63 μm) and water content. In addition, the ¹³C/¹²C stable isotope ratios (δ¹³C) of the organic matter were determined using an element analyzer and isotope ratio – mass spectrometry (IR-MS). The stable carbon isotope ratio gives an indication of the origin of the sediment, as this ratio is lower for sediment from terrestrial origin than for sediment from marine origin [31]. For the characterization of the water samples, the suspended particulate material (SPM), chlorophyll-a and dissolved organic carbon (DOC) concentrations were determined.

In July 2001, an additional sampling trip was performed, in order to make a detailed comparison between different water sampling techniques, at two locations in the North Sea. A location far (70 km, C1) from and a location close (2 km, C2) to the shore were chosen (see figure 6.2). To this end, water samples were taken with a bucket at six positions around the ship. In addition, a Rosette sampler was used to take three samples at depths of 3 m, at half the water depth, and at maximum depth, respectively. Another sample was taken using the sampling torpedo at about 3 m depth. Finally, one water sample was taken with a bucket from a life boat at 300 m from the research ship, resulting in a total of 11 samples per location. Waste water from the research ship was sampled as well.
Sample treatment
Sample treatment procedures were modified from methods published previously (see p. 108-110) [12].
Briefly, total sediment samples were extracted using Soxhlet devices, which were prerinseed by refluxing with methanol for 5 hours. Between 5 and 25 g of wet sediment was extracted overnight with 250 mL of basic methanol, depending on the grain size of the sample. The raw extract was concentrated to 15 mL, then 80 mL of nanopure water was added and this mixture was acidified to pH=2. For further clean up, the mixture was passed over a C\textsubscript{18}-SPE cartridge as described below.

One L of water sample was filtered using a GF/C glass fiber filter. The filters (SPM samples) were then stored at -20 °C, and extracted later according to the method for sediments. Filtered water was immediately acidified to pH=2 with HCl and extracted using Solid-Phase Extraction (SPE). C\textsubscript{18}-SPE cartridges were conditioned with 10 mL of methanol and then 10 mL of nanopure water. Subsequently the cartridge was loaded with 500 mL water sample or with the diluted sediment extract. The cartridge was then dried by a stream of nitrogen, and eluted with 10 mL of methanol. The extract was evaporated with nitrogen until dryness, and redissolved in 1 mL of methanol/nanopure water 1:1 (v:v). Finally, the extract was filtered through a 0.2 μm Acrodisc filter.

LC-MS analysis
Analysis was performed with reversed phase liquid chromatography coupled to electrospray mass spectrometry detection (LC-ESI-MS), using methods described previously [12]. A Thermoquest Navigator LC-MS system was used with a Lichrospher RP-C\textsubscript{18} column (dimensions 125 x 2 mm, 3μm) and a mobile phase flow rate of 0.25 mL min\textsuperscript{-1}. Gradient elution was performed with pure methanol (A) and a water-methanol 3:1 (v:v) buffer (B) as mobile phases. The ethoxylates and metabolites were analyzed separately in different runs, using positive ionization with a sodium acetate buffer (0.1 mM) for the ethoxylates, and negative ionization with an ammonium acetate buffer (2 mM) for all metabolites. A potential problem of the use of nonvolatile buffers such as sodium acetate is salt precipitation on the MS entrance cone, leading to decreased sensitivity of the system. This problem was eliminated by inserting a programmable 6-way valve between the LC-column and the MS interface, which diverted the mobile phase from the MS to the waste during the first and the last minutes of the analysis (when buffer concentrations are highest, and no compounds of interest elute). The reproducibility of the signals was not affected by this procedure.

All analyses were performed in SIM mode, using the deprotonated molecular ions of NP, A9PEC and CAPEC during negative ionization, and the sodium adducts of A9PEO in positive mode. For A9PEO\textsubscript{1}, an additional mass of the [A9PEO\textsubscript{1}+methanol+Na]\textsuperscript{+} adduct
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(m/z = 319) was selected [12]. The probe temperature was set at 220 °C, and probe and cone voltages were +4.0 kV and +20 V in positive ionization mode, and −3.8 kV and −20 V in negative ionization mode, respectively.

For the quantification of A₉PEO₁ and A₉PEO₂, pure standards were available, while the higher oligomers were quantified using a commercial mixture with an average ethoxylate chain length of 10 units (in which A₉PEO₁ or A₉PEO₂ are present below 0.5%). For NP, A₉PE₁C and A₉PE₂C, pure standards were used, and for higher A₉PE₂C, the A₉PE₂C calibration was used, assuming the response of A₉PE₂C to be equal to that of A₉PE₂C. All standards were analyzed in every sequence, from which 8-point quadratic calibration curves were constructed.

For the CAPEC metabolites, only a qualitative identification was possible, as no standards are available. Extracts from previously performed biodegradation experiments, in which CAPEC were identified using LC-ESI-MS/MS [27], were used as reference.

A₉PEO₂ and NP containing ¹³C-labeled aromatic rings were added as internal standards to the extracts prior to injection, in order to correct for matrix effects or variations in sensitivity of the LC-MS.

### Table 6.1: Quality parameters of the analytical method for the determination of A₉PEO and metabolites in sediment and water.

<table>
<thead>
<tr>
<th></th>
<th>Sediment</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>recovery (%) + STD</td>
<td>blank value (ng/sample)</td>
</tr>
<tr>
<td>A₉PEO₁</td>
<td>83 ± 11</td>
<td>0.3</td>
</tr>
<tr>
<td>A₉PEO₂</td>
<td>83 ± 11</td>
<td>2.2</td>
</tr>
<tr>
<td>A₉PEO₃₋₁₅</td>
<td>83 ± 11</td>
<td>7.7</td>
</tr>
<tr>
<td>NP</td>
<td>63 ± 10</td>
<td>14</td>
</tr>
<tr>
<td>A₉PE₁C</td>
<td>44 ± 14</td>
<td>0</td>
</tr>
<tr>
<td>A₉PE₂C</td>
<td>44 ± 14</td>
<td>0</td>
</tr>
</tbody>
</table>

**Quality control**

Sediment samples were extracted in batches of 4, one of which was either a procedural blank or a spiked sediment. Sediments were spiked with NP, A₉PE₁₋₂C and either A₉PEO₁₋₂ or A₉PEO₃₋₁₅ at environmental levels of 100-200 ng g⁻¹ (wet weight). Recoveries calculated from these spiked samples could be somewhat higher than for actual environmental sediments, in which the analytes can be bound more strongly to the sediments. The low recoveries of A₉PEC from sediments inevitably led to higher variations in recovery, and
therefore these results could suffer from some inaccuracy. The quality parameters of the analytical method are shown in table 6.1.

As the water samples were extracted on board the sampling ship, water blanks were also extracted on board. Small blank signals were observed for NP in most cases, while for the other analytes blank signals were mostly absent in both water and sediment. Reported concentrations have been corrected for both the blank value and recovery (shown in table 6.1). Detection limits were calculated as three times the noise level.

6.3. Results

6.3.1. \(A_9\)PEO and metabolites in surface sediments

\(A_9\)PEO concentrations in sediments

Standard parameters were determined to characterize each sediment sample (composition, origin), and are shown in tables 6.2 and 6.3. Organic carbon contents of sediments from both sampling campaigns were generally low (below 0.5% in 80% of the samples), with a range from below 0.05 to 8.3%. Most sediments were very sandy, as is expressed in the median value of 0.012 (range 0.002 – 0.57) for the fraction of sediment particles smaller than 63\(\mu\)m. Isotope ratios \(\delta^{13}C\) ranged from –34.0 to –19.5‰. Both organic carbon content and the particle fraction <63\(\mu\)m decreased with distance from the shore, while \(\delta^{13}C\) showed no spatial trend.

The sediments from the campaign of 1999 generally showed low analyte concentrations, with ranges of <1.6-32, <0.6-225 and <0.6-45 ng g\(^{-1}\) dry weight (d.w.) for \(A_9\)PEO\(_{1,2}\), \(A_9\)PEO\(_{2-2}\) and NP, respectively. The concentrations are listed in table 6.2.

The highest concentrations were observed at the mouths of the North Sea canal, Haringvliet and Scheldt estuary (see figure 6.3). Relatively high concentrations were also observed in all four sediments collected along the transect near the K12 production platform. This 10 km long transect did not show a decreasing spatial trend with distance from the platform. In contrast, the sediments sampled near a second platform showed relatively low concentrations in all four sediments.

For both \(A_9\)PEO and NP, a clear decreasing concentration trend was observed with distance from the shore. At about 10 km from the shore, sediment concentrations had dropped below 50 ng g\(^{-1}\) d.w. for both \(A_9\)PEO and NP, and decreased even further to around the detection limits. In addition, a south to north trend could be distinguished, with higher concentrations in the south, near the mouth of Rhine and Scheldt, and the lower concentrations in the north. In most sediments (32 out of 39), concentrations of \(A_9\)PEC were below the limit of detection.
Table 6.2: Sediment characteristics and concentrations of A$_0$PEO, NP and A$_0$PEC in surface sediments from the Dutch coastal zone, collected during the campaign of 1999.

<table>
<thead>
<tr>
<th>location (see figure 6.2)</th>
<th>organic carbon (%)</th>
<th>fraction $&lt;63\mu m$</th>
<th>$\delta^{13}C$ (%)</th>
<th>A$_0$PEO$_1$ (ng g$^{-1}$ d.w.)</th>
<th>A$_0$PEO$_2$ (ng g$^{-1}$ d.w.)</th>
<th>A$<em>0$PEO$</em>{15}$ (ng g$^{-1}$ d.w.)</th>
<th>A$<em>0$PEO$</em>{total}$ (ng g$^{-1}$ d.w.)</th>
<th>NP (ng g$^{-1}$ d.w.)</th>
<th>A$_0$PEC (ng g$^{-1}$ d.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.3</td>
<td>0.067</td>
<td>-25.7</td>
<td>&lt;1.3</td>
<td>1.2</td>
<td>21</td>
<td>22</td>
<td>29</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P2</td>
<td>0.16</td>
<td>0.049</td>
<td>-26.8</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>18</td>
<td>18</td>
<td>4.9</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P3</td>
<td>0.23</td>
<td>0.059</td>
<td>-25.4</td>
<td>20</td>
<td>&lt;0.3</td>
<td>23</td>
<td>43</td>
<td>6.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P4</td>
<td>0.41</td>
<td>0.207</td>
<td>-22.7</td>
<td>24</td>
<td>0.5</td>
<td>15</td>
<td>40</td>
<td>23</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P5</td>
<td>&lt;0.05</td>
<td>0.004</td>
<td>-31.4</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.8</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P6</td>
<td>&lt;0.05</td>
<td>0.002</td>
<td>-32.4</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>2.2</td>
<td>2.5</td>
<td>2.1</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P7</td>
<td>&lt;0.05</td>
<td>0.006</td>
<td>-32.6</td>
<td>&lt;1.3</td>
<td>0.64</td>
<td>&lt;0.6</td>
<td>0.64</td>
<td>2.6</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>P8</td>
<td>0.1</td>
<td>0.008</td>
<td>-22.1</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>&lt;0.6</td>
<td>&lt;0.3</td>
<td>0.6</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>W1</td>
<td>&lt;0.05</td>
<td>0.002</td>
<td>-34.0</td>
<td>&lt;1.3</td>
<td>0.37</td>
<td>&lt;0.6</td>
<td>0.37</td>
<td>3.9</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>W2</td>
<td>&lt;0.05</td>
<td>0.005</td>
<td>-30.3</td>
<td>3.4</td>
<td>0.62</td>
<td>1.4</td>
<td>5.4</td>
<td>1.8</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>W3</td>
<td>8.3</td>
<td>0.522</td>
<td>-29.3</td>
<td>16</td>
<td>0.3</td>
<td>2.0</td>
<td>18</td>
<td>6.4</td>
<td>6.8</td>
</tr>
<tr>
<td>W4</td>
<td>&lt;0.05</td>
<td>0.006</td>
<td>-30.1</td>
<td>9.7</td>
<td>0.3</td>
<td>1.7</td>
<td>12</td>
<td>1.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>N1</td>
<td>1.4</td>
<td>0.568</td>
<td>-24.3</td>
<td>&lt;1.3</td>
<td>14</td>
<td>225</td>
<td>239</td>
<td>14</td>
<td>&lt;0.4</td>
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<tr>
<td>N2</td>
<td>3.5</td>
<td>0.568</td>
<td>-27.5</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>5.1</td>
<td>5.1</td>
<td>4.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>N3</td>
<td>0.34</td>
<td>0.034</td>
<td>-24.9</td>
<td>&lt;1.3</td>
<td>0.99</td>
<td>19</td>
<td>20</td>
<td>6.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>N4</td>
<td>&lt;0.05</td>
<td>0.006</td>
<td>-21.4</td>
<td>&lt;1.3</td>
<td>0.52</td>
<td>0.88</td>
<td>1.4</td>
<td>0.89</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>N5</td>
<td>&lt;0.05</td>
<td>0.004</td>
<td>-28.5</td>
<td>&lt;1.3</td>
<td>0.42</td>
<td>&lt;0.6</td>
<td>0.42</td>
<td>3.0</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>N6</td>
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<td>0.008</td>
<td>-22.2</td>
<td>3.8</td>
<td>&lt;0.3</td>
<td>&lt;0.6</td>
<td>3.8</td>
<td>1.0</td>
<td>&lt;0.4</td>
</tr>
<tr>
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<td>&lt;0.4</td>
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<td>-24.6</td>
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<td>19</td>
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<td>10</td>
</tr>
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<td>6.8</td>
<td>3.9</td>
<td>&lt;0.4</td>
</tr>
<tr>
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<td>0.012</td>
<td>-23.2</td>
<td>4.0</td>
<td>&lt;0.3</td>
<td>&lt;0.6</td>
<td>4.0</td>
<td>4.0</td>
<td>&lt;0.4</td>
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<tr>
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<td>&lt;0.3</td>
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<td>&lt;0.6</td>
<td>3.1</td>
<td>&lt;0.6</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

Sources and fate of nonylphenol ethoxylates and their metabolites in the Dutch coastal zone.
Figure 6.3: Spatial distribution of A₉PEO and NP concentrations in surface sediments of the Dutch coastal zone from the campaign of 1999 (ng g⁻¹ d.w.). A₉PEO₁₋₂ and A₉PEO₃₋₁₅ are shown separately. Bar length in the legend corresponds to concentration given between brackets. The ~ signifies that the total concentration exceeds the scale used in the figure. In all cases, the A₉PEO₁₋₂ / A₉PEO₃₋₁₅ ratio is shown.
Table 6.3: Sediment characteristics and concentrations of A₉PEO, NP and A₉PEC in surface sediments from the Dutch coastal zone, collected during the campaign of 2000.

<table>
<thead>
<tr>
<th>Location (see figure 6.2)</th>
<th>Organic carbon &lt;63μm (%)</th>
<th>δ²³C (‰)</th>
<th>A₉PEO₁ (ng g⁻¹ d.w.)</th>
<th>A₉PEO₂ (ng g⁻¹ d.w.)</th>
<th>A₉PEO₂₁₅ (ng g⁻¹ d.w.)</th>
<th>A₉PEO total (ng g⁻¹ d.w.)</th>
<th>NP (ng g⁻¹ d.w.)</th>
<th>A₉PEC total (ng g⁻¹ d.w.)</th>
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<tr>
<td>W1</td>
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<td>0.015</td>
<td>-28.5</td>
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<td>7.8</td>
<td>&lt;0.6</td>
<td>7.8</td>
<td>12</td>
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<td>0.004</td>
<td>-24.6</td>
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<td>&lt;0.3</td>
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<td>17</td>
<td>1.6</td>
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<td>&lt;0.6</td>
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<td>&lt;1.3</td>
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<td>9.6</td>
<td>9.9</td>
<td>3.4</td>
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<td>70⁺</td>
<td>87⁺</td>
<td>7291⁺</td>
<td>7448</td>
<td>617⁺</td>
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<td>&lt;0.3</td>
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<td>7.4</td>
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<td>9.7</td>
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<td>0.80</td>
<td>0.92</td>
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<td>1.5</td>
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</table>

⁺: Sample taken at the freshwater side of the lock.

*: Concentration exceeds Dutch MPC value (the sum of A₉PEO₁ and A₉PEO₂ is considered for the MPC of A₉PEO₁₂) (Van Vlaardingen et al., [25]).
Figure 6.4: Spatial distribution of A₉PEO and NP concentrations in surface sediments of the Dutch coastal zone from the campaign of 2000 (ng g⁻¹ d.w.). A₉PEO₁₋₂ and A₉PEO₃₋₁₅ are shown separately. Bar length in the legend corresponds to concentration given between brackets. The ~ signifies that the total concentration exceeds the scale used in the figure. In all cases, the A₉PEO₁₋₂ / A₉PEO₃₋₁₅ ratio is shown.
A₉PEO and NP concentrations in sediments collected during the campaign of 2000 were similar to those of 1999, with concentration ranges of <1.6-28 (A₉PEO₁₂), <0.6-249 (A₉PEO₁₂) and 0.3-86 (NP) ng g⁻¹ d.w.. Concentrations are listed in table 6.3, and the spatial distribution of concentrations is shown in figure 6.4.

Elevated concentrations were found at the mouth of the Scheldt estuary, at a dumping site for harbour dredge and at the fresh water side of the locks at the mouth of Haringvliet. Of all sediments sampled, the highest concentrations were observed just inside the North Sea canal (at the fresh water side of the locks) at 157 and 7448 ng g⁻¹ d.w. for A₉PEO₁2 and A₉PEO₁₂, and for NP at 617 ng g⁻¹ d.w.. In 10 out of 32 sediments of the campaign of 2000, low concentrations of A₉PEC were observed, with one higher concentration of 118 ng g⁻¹ d.w. at location R2.

When concentrations in sediment were normalized to organic carbon content, the spatial profiles in the Dutch coastal zone showed a less obvious pattern for both campaigns. As the sediments further off shore were quite sandy and have lower organic carbon contents than those close to the shore, the normalized analyte concentrations expressed in ng per g organic carbon showed smaller differences between areas close to and far from the shore.

**Ethoxymer distribution patterns in sediments**

The A₉PEO ethoxylate (EO) distribution pattern provides information on the degree of biodegradation that has occurred. One of the possible degradation mechanisms of A₉PEO is a shortening of the EO chain, and therefore an average EO chain length of 1-3 indicates that extensive biodegradation has occurred, while the presence of longer chains would indicate no or slow degradation. Some caution is necessary, as commercial products vary in average EO chain length between 5 and 25, depending on their application. Therefore, samples showing an average EO length of 7 may already have undergone some biodegradation. Average EO lengths higher than 12 are seldomly observed in environmental samples.

In North Sea sediments, A₉PEO concentrations were sometimes so low that the EO distribution pattern was difficult to distinguish. In general, average EO chain lengths of 1-3 units were present. The EO distribution patterns of the samples of 1999 and 2000 showed many similarities. In offshore sediments and sediments at the entrance of the Wadden Sea, average A₉PEO chain lengths were low (between 1 and 3). In about 25% of the sediment samples, patterns with higher average EO chain lengths were observed. Higher average EO chain lengths (5 to 10) were observed in both campaigns at the mouths of the North Sea canal, Haringvliet and Scheldt, as well as in all sediments of the Scheveningen transect. This was also the case for the sediments near the K12 production platform, and at the harbour dredge dumping sites. In some of these samples, two distribution maxima were observed in the EO patterns: both the original longer chain A₉PEO and short chain A₉PEO₁₂ metabolites were present. An example of this type of EO distribution is shown in figure 6.5.
In the sediments collected in 1999, this pattern was observed close to the shore (locations N1, R1, SE1 and SE3), and at one location near a platform (P3). In 2000, this EO distribution was found along the Scheveningen transect (SW1-SW5).

Figure 6.5: Mass spectrum of surface sediment SW2 (campaign of 2000) analyzed by positive LC-ESI-MS (sodium adducts), showing an A9PEO oligomer distribution with two apaxes at high and low ethoxylate chain length.

6.3.2. A9PEO and metabolites in water

Concentrations in marine water

The samples of the campaign of 1999 contained unusually high dissolved A9PEO concentrations, with maximum concentrations of 0.73 and 35 μg L⁻¹ for A9PEO₁₂ and A₉PEOₙ₂, respectively. NP and A₉PEC were present at concentrations of 1.7 and 0.63 μg L⁻¹, respectively. For A₉PEO₁₂, A₉PEOₙ₂ and NP, all concentrations were above the detection limits, and median concentrations were calculated of 0.13, 2.5 and 0.077 μg L⁻¹, respectively. The spatial distribution of these concentrations is presented in figure 6.6, with the exact values listed in table 6.4.
The highest surfactant concentrations were found in the coastal area adjacent to the Rhine estuary, up until 40 km off shore. Relatively high concentrations were also observed outside the Scheldt estuary, continuing until 70 km from its mouth. As can be seen in figure 6.6, most of the locations with high dissolved A₉PEO concentrations are in or close to the main shipping lanes in the Dutch coastal zone.

Some of the water samples collected near the platforms also contained relatively high A₉PEO concentrations. The lowest dissolved A₉PEO concentrations were observed in the north, in the samples taken at the entrance of the Wadden Sea.

In the campaign of 2000, A₉PEO were detected in 26 out of the 30 coastal zone water samples, with maximum concentrations of 0.14 and 0.27 µg L⁻¹ for A₉PEO₁₂ and A₉PEO₂₂, respectively. When corresponding locations of 2000 and 1999 are compared, dissolved concentrations of A₉PEO were lower in 2000 at all but one locations, often by more than an order of magnitude. Concentrations of metabolites were relatively low as well, with maximum concentrations of 0.031 (NP) and 0.11 µg L⁻¹ (A₉PEC) in the coastal zone. On the freshwater side of the locks at the mouth of the North Sea canal, slightly higher metabolite concentrations were observed of 0.042 (NP) and 0.31 µg L⁻¹ (A₉PEC).

Figure 6.7 shows the spatial distribution of the compounds analyzed in the water phase. The exact concentrations are given in table 6.5. The highest dissolved concentrations in the 2000 campaign were observed relatively far off shore, in the North Sea Canal transect (locations N4, N5 and N6). These locations again coincide with the main shipping routes in the North Sea.

The doubly oxidized CAPEC metabolites could not be detected in any of the samples collected in 1999 or 2000.

*Ethoxymer distribution patterns in water*

All water samples of 1999 showed similar ethoxylate patterns with EO chain lengths from 1 to 10 units present. Relatively high average EO chain lengths of around 5 were observed. This pattern indicates a lack of biodegradation, and therefore suggests that these surfactants were recently discharged in this area.

In the campaign of 2000, most marine water samples displayed an EO distribution pattern with an average around 1 or 2 EO units, while the samples just outside Scheveningen, Rhine, Haringvliet and Scheldt showed slightly higher average EO chain lengths. At the three furthest offshore locations of the North Sea canal transect (N4, N5 and N6) in summer, dissolved A₉PEO showed a high average EO length of 5, suggesting a surfactant source other than the North Sea canal.
Table 6.4: Concentrations of A<sub>9</sub>PEO, NP and A<sub>9</sub>PEC in water samples from the Dutch coastal zone, collected during the campaign of 1999.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;1&lt;/sub&gt; (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;2&lt;/sub&gt; (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;3-15&lt;/sub&gt; (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;total&lt;/sub&gt; (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>NP (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PE&lt;sub&gt;1&lt;/sub&gt;C (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PE&lt;sub&gt;2&lt;/sub&gt;C (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PE&lt;sub&gt;3&lt;/sub&gt;C (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
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<td>&lt;0.015</td>
<td>0.044</td>
<td>1.4</td>
<td>1.4</td>
<td>0.14</td>
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<td>&lt;0.013</td>
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<td>P2</td>
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<td>0.044</td>
<td>1.2</td>
<td>1.3</td>
<td>0.082</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
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<td>1.4</td>
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<td>0.11*</td>
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<td>3.8</td>
<td>0.24</td>
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<td>&lt;0.013</td>
<td>&lt;0.013</td>
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<td>2.6</td>
<td>0.060</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
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<tr>
<td>P7</td>
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<td>0.17*</td>
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<td>0.088</td>
<td>0.013</td>
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<td>0.17</td>
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<td>15.9*</td>
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<td>0.94*</td>
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<td>0.091*</td>
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<td>0.24</td>
<td>0.11</td>
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<td>0.041</td>
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<td>0.018</td>
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<tr>
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<td>1.4</td>
<td>0.13</td>
<td>0.098</td>
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<td>0.075</td>
</tr>
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<td>0.13*</td>
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<td>12.7</td>
<td>0.70*</td>
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<td>&lt;0.013</td>
<td>0.055</td>
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<td>0.11*</td>
<td>3.6</td>
<td>3.8</td>
<td>0.26</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE1</td>
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<td>0.11*</td>
<td>2.9</td>
<td>3.0</td>
<td>0.039</td>
<td>0.12</td>
<td>0.082</td>
<td>0.055</td>
</tr>
<tr>
<td>SE2</td>
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<td>0.47*</td>
<td>21.4*</td>
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<td>0.061</td>
<td>0.10</td>
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<tr>
<td>SE3</td>
<td>0.033*</td>
<td>0.17*</td>
<td>2.9</td>
<td>3.1</td>
<td>0.040</td>
<td>0.060</td>
<td>0.033</td>
<td>0.058</td>
</tr>
<tr>
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<td>7.1</td>
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<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>0.014</td>
</tr>
<tr>
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<td>0.19*</td>
<td>5.1</td>
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<td>0.047</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
</tbody>
</table>

<sup>a</sup>: sample taken inside harbour; <sup>b</sup>: sample taken at the freshwater side of the lock.

*: concentration exceeds Dutch MPC value (the sum of A<sub>9</sub>PEO<sub>1</sub> and A<sub>9</sub>PEO<sub>2</sub> is considered for the MPC of A<sub>9</sub>PEO<sub>1,2</sub>) (Van Vlaardingen et al., [25]).

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Figure 6.6: Spatial distribution of $A_9\text{PEO}$, NP and $A_9\text{PEC}$ concentrations in water from the campaign of 1999 ($\mu$g L$^{-1}$). $A_9\text{PEO}_{1-2}$ and $A_9\text{PEO}_{3-15}$ are shown separately. Bar length in the legend corresponds to concentration given between brackets. The $\sim$ signifies that the total concentration exceeds the scale used in the figure. In all cases, the $A_9\text{PEO}_{1-2} / A_9\text{PEO}_{3-15}$ ratio is shown. The dotted lines indicate the main shipping routes.
## Table 6.5: Concentrations of A₉PEO, NP and A₉PEC in water samples from the Dutch coastal zone, collected during the campaign of 2000.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>A₉PEO₁ (µg L⁻¹)</th>
<th>A₉PEO₂ (µg L⁻¹)</th>
<th>A₉PEO₃,1₅ (µg L⁻¹)</th>
<th>A₉PEO_{total} (µg L⁻¹)</th>
<th>NP (µg L⁻¹)</th>
<th>A₉PE₁C (µg L⁻¹)</th>
<th>A₉PE₂C (µg L⁻¹)</th>
<th>A₉PE₂₂C (µg L⁻¹)</th>
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<td>&lt;0.006</td>
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<td>0.21</td>
<td>&lt;0.011</td>
<td>0.030</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
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<td>&lt;0.030</td>
<td>0.066</td>
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<td>&lt;0.006</td>
<td>&lt;0.030</td>
<td>0.046</td>
<td>0.019</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
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<td>0.030</td>
<td>0.014</td>
<td>0.032</td>
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<td>&lt;0.013</td>
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<td>0.042</td>
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<td>0.016</td>
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<td>&lt;0.030</td>
<td>0.059</td>
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<td>0.018</td>
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<tr>
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<tr>
<td>H1*</td>
<td>&lt;0.015</td>
<td>0.0063</td>
<td>0.039</td>
<td>0.050</td>
<td>0.024</td>
<td>0.074</td>
<td>0.052</td>
<td>0.042</td>
</tr>
<tr>
<td>H2</td>
<td>&lt;0.015</td>
<td>0.012</td>
<td>0.23</td>
<td>0.24</td>
<td>0.031</td>
<td>0.053</td>
<td>0.031</td>
<td>0.030</td>
</tr>
<tr>
<td>H3</td>
<td>&lt;0.015</td>
<td>&lt;0.006</td>
<td>0.036</td>
<td>0.039</td>
<td>0.019</td>
<td>0.025</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>H4</td>
<td>0.059</td>
<td>&lt;0.006</td>
<td>0.030</td>
<td>0.091</td>
<td>0.019</td>
<td>0.031</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>H5</td>
<td>0.036</td>
<td>&lt;0.006</td>
<td>&lt;0.030</td>
<td>0.036</td>
<td>&lt;0.011</td>
<td>0.014</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>H6</td>
<td>&lt;0.015</td>
<td>&lt;0.006</td>
<td>&lt;0.030</td>
<td>&lt;0.015</td>
<td>0.0047</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>H7</td>
<td>0.060</td>
<td>0.011</td>
<td>&lt;0.030</td>
<td>0.071</td>
<td>0.015</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE1</td>
<td>0.049</td>
<td>0.011</td>
<td>&lt;0.030</td>
<td>0.088</td>
<td>0.012</td>
<td>0.041</td>
<td>0.022</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE3</td>
<td>0.031</td>
<td>&lt;0.006</td>
<td>&lt;0.030</td>
<td>0.061</td>
<td>&lt;0.011</td>
<td>0.022</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE4</td>
<td>0.021</td>
<td>0.006</td>
<td>0.031</td>
<td>0.057</td>
<td>0.014</td>
<td>0.021</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE5</td>
<td>0.051</td>
<td>0.015</td>
<td>0.042</td>
<td>0.11</td>
<td>&lt;0.011</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
<tr>
<td>SE6</td>
<td>0.068</td>
<td>0.014</td>
<td>0.046</td>
<td>0.13</td>
<td>0.016</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
<td>&lt;0.013</td>
</tr>
</tbody>
</table>

*: sample taken at the freshwater side of the lock.

*: concentration exceeds Dutch MPC value (the sum of A₉PEO₁ and A₉PEO₂ is considered for the MPC of A₉PEO₁,₂) (Van Vlaardingen et al., [25]).
Figure 6.7: Spatial distribution of A₉PEO, NP and A₉PEC concentrations in water from the campaign of 2000 (µg L⁻¹). A₉PEO₁-₂ and A₉PEO₃-₁₅ are shown separately. Bar length in the legend corresponds to concentration given between brackets. The dotted lines indicate the main shipping routes.
Comparison of water sampling techniques

In the 2001 sampling trip, similar ethoxylate and concentration patterns were observed at both sampling locations (C1 and C2). The observed EO distributions varied somewhat from sample to sample, but the prevailing pattern showed an average of 6 EO units.

As shown in table 6.6, a clear difference was observed between samples from different sampling depths, although relatively high standard deviations were obtained. A₉PEO concentrations were around one order of magnitude higher in the surface water samples taken with a bucket than in the samples taken at greater depth, with averages of 0.49 and 0.044 μg L⁻¹, respectively. Between bucket samples taken at different sides of the ship and from the life boat at 300 m from the ship, no systematic differences in concentrations were observed. A₉PEO concentrations in the samples taken with the Rosette sampler invariably were less than in the samples from the surface.

In the sampling trip of 2001, no systematic differences were observed between NP concentrations in surface samples and samples from greater depth. NP concentrations varied between 0.028 and 0.082 μg L⁻¹, with an overall average of 0.052 μg L⁻¹. Apparently, the surface-active properties of A₉PEO are responsible for an accumulation of A₉PEO at the water surface, while the less surface active NP does not show this effect.

Average A₉PEC concentrations in the surface water samples amounted to 0.4 μg L⁻¹, and were on average 5 times lower in the samples from greater depth. However, due to the large standard deviations these differences are not significant.

Table 6.6: Comparison of analyte concentrations in water using different water sampling techniques. For further explanation see paragraph 6.2, p. 131.

<table>
<thead>
<tr>
<th>sampling technique used</th>
<th>sampling depth (m)</th>
<th>concentration (μg L⁻¹) + standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A₉PEO₁₂</td>
</tr>
<tr>
<td>location C1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bucket (n=6)</td>
<td>0.5</td>
<td>0.073 (0.046)</td>
</tr>
<tr>
<td>torpedo</td>
<td>3</td>
<td>0.011</td>
</tr>
<tr>
<td>Rosette (n=3)</td>
<td>3-27</td>
<td>0.009 (0.002)</td>
</tr>
<tr>
<td>life boat</td>
<td>0.5</td>
<td>0.033</td>
</tr>
<tr>
<td>location C2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bucket (n=6)</td>
<td>0.5</td>
<td>0.056 (0.030)</td>
</tr>
<tr>
<td>torpedo</td>
<td>3</td>
<td>0.023</td>
</tr>
<tr>
<td>Rosette (n=3)</td>
<td>3-10</td>
<td>0.040 (0.053)</td>
</tr>
<tr>
<td>life boat</td>
<td>0.5</td>
<td>0.064</td>
</tr>
</tbody>
</table>
Two wastewater streams of the research ship were analyzed (normal sink and washing machine). Both contained A₉PEO at concentrations of 1.5 µg L⁻¹. In the sample from the normal sink, short ethoxylates were present, while the washing machine water contained mainly long ethoxylates. The washing machine water contained in addition a high NP concentration of 3.8 µg L⁻¹. No A₉PEC metabolites were detected in the waste water.

If the waste water of the research ship had had a significant influence on the composition of the bucket water samples, an elevated NP concentration would have to be present. However this was not the case. The fact that A₉PEC were detected in the marine water and not in the wastewater suggests that the A₉PEO in the marine water must have been there long enough to allow some biodegradation to occur, and therefore do not originate from the research ship.

6.3.3. Concentrations in suspended particulate material

Concentrations of SPM in the Dutch coastal zone ranged from 2 to 134 mg L⁻¹, with a median value of 7 mg L⁻¹.

Analyte concentrations in SPM were around two orders of magnitude higher than those in sediments. In samples of SPM from the campaign of 1999, concentrations ranged from <87 to 95·10³ ng g⁻¹ (A₉PEO₁₂), 458 to 247·10³ ng g⁻¹ (A₉PEO₁₂) and 76 to 127·10³ ng g⁻¹ (NP). Organic carbon normalized SPM/water partition coefficients values (log KᵦC) were calculated for A₉PEO and NP. The values calculated for both A₉PEO and NP ranged between 4.3 and 7.7. Average log KᵦC values (+ standard deviations) amounted to 5.9 ± 0.4, and 5.4 ± 0.5 and 6.5 ± 0.7 for A₉PEO₁₂, A₉PEO₁₂ and NP, respectively. The average contributions of the analytes sorbed to SPM to the total water concentrations (dissolved + sorbed) were 14% for A₉PEO and 52% for NP. Only those results in which both water and SPM showed concentrations above detection limits were used for calculating these average values.

In the samples collected in 2000, A₉PEO and NP were observed in 23 and 16 out of 30 filter residues respectively. Concentrations were observed between <87 and 88·10³ ng g⁻¹ (A₉PEO₁₂), <40 and 65·10³ ng g⁻¹ (A₉PEO₁₂) and <20 and 20·10³ ng g⁻¹ (NP). Average contributions of SPM associated analytes to the total water concentrations (dissolved + sorbed) amounted to 40% for A₉PEO and 35% for NP, using only results for which both phases were above detection limits. Clearly, for A₉PEO and NP, the sorbed fraction in marine water samples is significant. For both A₉PEO and NP, similar ranges of log KᵦC between 4.5 and 7.1 were observed. Average log KᵦC values (+ standard deviations) amounted to 6.1 ± 0.6, and 5.9 ± 0.9 and 5.7 ± 0.7 for A₉PEO₁₂, A₉PEO₁₂ and NP, respectively.
Although the dissolved concentrations were considerably higher in the campaign of 1999 than in 2000, the log $K_{oc}$ values were not significantly different. This suggests that a sorption equilibrium is established relatively fast for these compounds.

$A_9$PEO oligomer distribution patterns in the SPM samples were similar to those of the corresponding water samples: in the campaign of 1999, oligomers with EO chain lengths from 1 to 10 were present (average 4-5), while in the campaign of 2000, only short chain $A_9$PEO$_{1-4}$ were observed (average 2-3).

In both sampling campaigns, concentrations of $A_9$PEC were below the detection limit in all SPM samples (<20 ng g$^{-1}$).

6.3.4. Relationship between analyte concentrations and sample characteristics

For all sediment characteristics, correlation coefficients with analyte concentrations were calculated. Concentrations in sediment correlated strongly with organic carbon content, with correlation coefficients of 0.71 (p<0.0001) and 0.64 (p<0.0001) for $A_9$PEO and NP, respectively (pooled data of the 1999 and 2000 sampling campaigns). This behaviour is observed for most organic contaminants, where mainly hydrophobic interactions determine the degree of sorption.

The correlation between the fraction of particles <63 μm and organic carbon content (oc%) was strong. This is not surprising, as almost all of the organic carbon of the sediment is present in the silt and clay fraction. As a consequence, strong correlations between analyte concentrations and the fraction <63 μm were observed as well: $r=0.85$ (p<0.0001) for $A_9$PEO$_{total}$ and 0.66 for NP (p<0.0001). Low correlation coefficients were found between analyte concentrations in sediment and carbon stable isotope ratio ($\delta^{13}C$) for both organic carbon normalized and non normalized concentrations ($r<0.3$ for each of the analytes).

In the water phase, both dissolved organic carbon and chlorophyll-a concentrations were relatively low, with concentration ranges of 0.74-4.7 (median 1.2) and 1.0-2.6 (median 1.8) mg DOC L$^{-1}$, and 0.8-3.8 (median 2.0) and 1.3-33.4 (median 8.6) μg chlorophyll-a L$^{-1}$ in during the winter (1999) and summer (2000) cruises, respectively. Correlations of dissolved analyte concentrations with dissolved organic carbon in both seasons were weak. The parameters chlorophyll-a and phaeopigment-a (a degradation product of chlorophyll-a) both indicate the presence of algae. In both seasons, chlorophyll-a or phaeopigment-a concentrations did not correlate with dissolved analyte concentrations, indicating that the presence of the surfactants was not related to algae.

For the suspended particulate material samples of both seasons, organic carbon contents in the range 2.3-17.0% were observed with a median value of 5.0%. For the $A_9$PEO and NP concentrations in SPM samples, no correlation was found with the organic carbon content of the SPM. When $K_d$ values of $A_9$PEO and NP are compared to organic carbon content of the
SPM, correlations are weak as well. This lack of correlation seems to suggest that the binding of A₉PEO and NP to SPM is not mainly governed by hydrophobic interactions. This is in contrast with the strong correlation found between analyte concentrations and organic carbon content in sediments.

6.4. Discussion

Comparison between summer and winter concentrations
As the water samples in the summer campaign (2000) were taken using a different technique than in the winter campaign of 1999 (surface water with a bucket in the winter campaign, and water from 1.5 m depth taken with the sampling torpedo in the summer campaign), a detailed comparison between the two seasons based on these results is not justified.

A comparison of dissolved concentrations in winter and summer for every location individually showed that A₉PEO₁₂, A₉PEO₂₂, NP and A₉PEC concentrations were on average respectively a factor 5, 82, 10 and 6 higher in the winter campaign than in the summer campaign (calculated only for locations at which both concentrations were above the detection limit). From the sampling exercise with different sampling techniques (2001) it was found that samples taken from the surface always have A₉PEO concentrations higher by about a factor of 10 than water from greater depth. Therefore, the differences in sampling depths are probably mainly accounting for the concentration differences observed between 1999 and 2000. However, the differences for A₉PEO₂₂ were larger than can be explained by the difference in sampling techniques. In addition, the higher average concentrations of NP and A₉PEC in water of 1999 compared to 2000 cannot be explained by the surface-active properties of the analytes, as no significant differences between concentrations at the surface and at greater depth were found in 2001.

One possible explanation for the high A₉PEO₂₂ concentrations in water is a lower bacterial activity, and therefore lower biodegradation rates during the winter season. Evaporation processes which occur to a larger extent in summer than in winter may account for some of the seasonal differences. However, it would then be expected that the differences in concentration for the more volatile NP would be larger than for A₉PEO, which is not the case.

A final explanation is that the high dissolved concentrations of 1999 may have been caused by incidental recent discharges of A₉PEO. The relatively high average EO chain lengths and the relatively low concentration ratios of metabolites/A₉PEO in 1999 compared to 2000 indicate a low degree of biodegradation and therefore recent discharges.
For concentrations in the sediments, a comparison between the seasons shows many similarities. When all locations are compared individually, sediment concentrations of A₉PEO and NP are of the same order in both seasons. Maximum concentrations in marine sediments were observed at the same sampling locations in both seasons (i.e. N1, H2 and SE1). Spatial trends of concentrations in sediments were the same in summer and winter. Similar A₉PEO ethoxylate distribution patterns in the sediments and SPM were observed, and in both seasons, A₈PEC was only sporadically detected in marine sediments.

**Transformation routes**

Jonkers *et al.* have shown that concentration ratios of metabolite to ‘parent’ surfactant (M/P) can be used to evaluate biodegradation processes (cf. introduction) in estuarine waters [12]. Table 6.7 lists three different M/P ratios calculated from the present data for the Dutch coastal zone, as well as the ratios for two Dutch estuaries, taken from Jonkers *et al.* [12]. From these ratios it can be concluded that in particular the formation of A₉PEC is different in the estuaries compared to the coastal zone, and that oxidative hydrolytic transformation occurs to a much lower extent in marine than in estuarine waters. The smaller differences in the ratios NP/ΣA₉PEO and A₉PEO₁₋₂/ΣA₉PEO between the two systems indicate that degradation via the non-oxidative hydrolytic pathway occurs slightly less in marine than in estuarine environments.

<table>
<thead>
<tr>
<th></th>
<th>salinity range</th>
<th>NP/ΣA₉PEO</th>
<th>A₉PEO₁₋₂/ΣA₉PEO</th>
<th>A₉PEC/ΣA₉PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhine + Scheldt estuariesᵃ</td>
<td>0.5 – 30</td>
<td>0.67</td>
<td>0.40</td>
<td>7.7</td>
</tr>
<tr>
<td>Dutch coastal zoneᵇ</td>
<td>27 – 35</td>
<td>0.19</td>
<td>0.28</td>
<td>0.37</td>
</tr>
</tbody>
</table>


In one of the few comparable studies, which was performed in the Venice lagoon (Italy), similar results were found. In river water (salinity below 1%), A₉PEC/A₉PEO ratios of 2-3 were found in that study, while in the lagoon (salinity between 24 and 31%) lower ratios of 0.5 were reported [16]. In a field study performed along the Spanish Mediterranean coast, A₉PEC was not detected in any of the samples, although A₉PEO were present at several μg L⁻¹ [13]. Longer chain A₉PEₙC were not analyzed in that study.

In the current study, the presence of metabolites in the water phase clearly shows that biodegradation occurs in this compartment. For the sediments, two possible scenarios could account for the presence of short EO chain A₉PEO metabolites. Either biodegradation
occurs in the water phase, and afterwards the metabolites settle with precipitating SPM to the sediment, or SPM-bound undegraded A₉PEO are deposited and biodegradation takes place in the sediment. The current results do not permit unambiguous conclusions in this respect.

The relatively low average EO chain lengths observed in SPM samples collected at 3 m depth indicate that biodegradation of A₉PEO starts in the water/SPM phase. This suggests that A₉PEO₁,₃ in sediments result not from degradation in the sediments but from deposition of SPM-bound A₉PEO₁,₃. Other studies have shown that in marine sediment, further degradation of A₉PEO is very slow [20, 32]. However, the presence of two distinct ethoxylate chain length maxima (one at EO = 1 or 2, and one at higher chain length, see figure 6.5) in some of the sediments in our study suggests that non-oxidative hydrolytic degradation is occurring at those locations. The non-oxidative hydrolytic mechanism seems to prevail. Although formation of A₉PEC metabolites in the sediment cannot be ruled out entirely, the absence of A₉PEC in the sediments strongly suggests that the oxidative-hydrolytic degradation does not occur in this (mainly anaerobic) compartment.

Comparison to literature data
The spatial trend observed for A₉PEO and NP concentrations in sediments with decreasing concentrations when going north is in agreement with the general trends in concentrations of organic contaminants observed along the Dutch coast, due to a north-bound net transport/advection [2]. Concentration ranges of A₉PEO and NP in sediments are in agreement with those observed in previous studies in the Dutch coastal zone [7, 21, 33], and in the German Bight of the North Sea [19]. Along the Spanish coast, higher concentrations in sediments were found (in the ranges 10-620 ng g⁻¹ for A₉PEO and <10-1000 ng g⁻¹ for NP) [13]. Only sporadically, estuarine or marine dissolved concentrations of A₉PEO comparable to those of the current study (1999 values) have been reported. In all those cases, a specific point source could be identified to account for these high local maxima: a river containing high concentrations of A₉PEO [14], a wastewater discharge [13] or industrial activities [15]. Spatial concentration profiles from those studies (with sharply decreasing concentrations with distance from the point source) differ strongly from the present results, where high dissolved concentrations are observed in offshore samples in a relatively large area, but not in the main fresh water streams flowing into the coastal zone.

In a field survey on endocrine disruptors (including A₉PEO and NP) in the Dutch coastal zone, water samples were taken using stainless steel buckets in the same time period as in the present study (but on different sampling cruises) [7]. In some cases the results of that study showed unusually high marine A₉PEO concentrations up to 87 µg L⁻¹ as well (samples
collected in April 1999). In other marine water samples from that study, concentrations were below 0.18 µg L\(^{-1}\).

In two studies in the German Bight of the North Sea, dissolved concentrations of A\(_9\)PEO were slightly lower than in the water samples collected in 2000 of the present study [18, 19]. In those studies, samples were taken at 3 m and 5 m depth, respectively, and therefore no comparison is possible with the high concentrations at the water surface found in this study. In the literature, some values for SPM/water distribution coefficients (K\(_{oc}\)) of A\(_9\)PEO are available. Ferguson et al. determined field logK\(_{oc}\) values in an estuary of 5.4, 5.5, 5.2 and 4.9 for NP, A\(_9\)PEO\(_1\), A\(_9\)PEO\(_2\) and A\(_9\)PEO\(_3\) [11]. In another study, field log K\(_{oc}\) values were reported of 5.9, 5.6 and 6.4 for NP, A\(_9\)PEO\(_1\) and A\(_9\)PEO\(_2\) [18]. These literature values agree well with the logK\(_{oc}\) values found in the present study.

For the water samples, the lack of correlation between dissolved A\(_9\)PEO concentrations and chlorophyll-a concentrations is not in agreement with the findings of Marcomini et al. [34]. In that field study, 3-10 times higher A\(_9\)PEO concentrations were observed in sediments covered with algae than in sediments free from algae in the Venice lagoon.

Conclusively, the comparison with literature shows that concentrations found in sediments and SPM in this study are comparable to those of other studies, while the dissolved concentrations of the 1999 campaign reported here are higher than those usually found in the marine environment.

The Maximum Permissible Concentrations (MPC, cf. introduction), which were recently proposed for the Netherlands [25] were exceeded in a number of water samples from the current study (outside the Rhine and Scheldt estuaries in 1999, and at location D1 in 2000, cf. the values with asterisks in tables 6.2-6.5). For sediments, only at location N1 (2000), the Dutch MPC was exceeded.

**Sources of A\(_9\)PEO to the Dutch coastal zone**

Although the analyte concentrations and \(\delta^{13}\)C in sediments did not show a high correlation, the spatial trends of decreasing concentrations in sediments with distance from the shore, in combination with the absence of such a trend for the water phase do suggest a transport of particle-bound analytes of mainly terrestrial origin.

Evaluation of the sediment concentration profiles reveals several possible sources of A\(_9\)PEO and NP to the Dutch coastal zone. The relatively high coastal zone sediment concentrations just outside the Rhine estuary, Scheldt estuary and North Sea canal show that these are all sources of A\(_9\)PEO and metabolites to the coastal zone.

Another significant source is the dumpsite for harbour dredge west of Scheveningen (location D2, only sampled in the campaign of 2000). At this ‘hot spot’ the highest concentrations of both A\(_9\)PEO and NP in coastal zone surface sediment were observed. An
even higher concentration was observed at location N1 (North Sea canal, inside the locks), which is considered a freshwater environment hot spot.

All of the land-based sources mentioned have only a limited spatial influence, as in all cases concentrations in sediments more than 10 km distance from the shore drop to almost the open sea background level.

Of the two platforms investigated, one showed elevated A9PEO and NP concentrations in the surface sediments. Production platforms must therefore be considered as a possible source of A9PEO to the North Sea, which can cause elevated A9PEO and NP sediment concentrations at least 10 km downstream of the platform.

In most cases, the sediment samples with elevated A9PEO concentrations mentioned above show average EO chain lengths which are relatively high (5 to 10 EO units). These EO patterns confirm that the A9PEO sources are nearby.

In sediments from the entrance of the Wadden Sea, concentrations were only slightly elevated compared to those from open sea. Apparently, the Wadden Sea does not contribute significantly to the total load of A9PEO to the Dutch coastal zone. This is in agreement with the fact that the Wadden Sea is a sedimentation area of material transported from the Dutch coastal zone into the Wadden Sea [3]. Likewise, the contribution from the Scheveningen sewage effluent outlet is minor, as sediment concentrations near the outlet were not significantly higher than those in open sea sediments.

In the water samples of the campaign of 1999, very high concentrations were present at the water surface of the shipping route to Rotterdam, as well as at the locations furthest off shore from the Scheldt estuary and one location (SE2) in the mouth of the Scheldt estuary (see figure 6.6). Water samples of the North Sea canal and Wadden Sea transects collected closer to the shore but further from the main shipping routes showed lower concentrations.

A similar situation is observed in the 2000 campaign, with the highest concentrations in water samples taken further off shore (locations N4-N6), and in the shipping route to Rotterdam (locations R2, R3, D1). These spatial concentration profiles strongly suggest that the main sources of A9PEO to the marine water are at sea and not freshwater or land based. The intensive shipping activities in the Dutch coastal zone would be a likely source of A9PEO.

The different spatial profiles of concentrations in sediments and water illustrate that the dissolved A9PEO at the water surface have little interaction with the underlying sediments in this area. This is in agreement with the fact that no net sedimentation occurs in the Dutch coastal zone.

It is interesting to note that A9PEO concentrations in coastal water samples taken in 1999 were on average one order of magnitude higher than in samples taken inside the Rhine and Scheldt estuaries in the same period (and sampled by the same technique), which did not exceed 0.8 and 2.3 µg L\(^{-1}\) in the respective estuaries [12]. Dissolved concentrations in the
coastal zone samples collected in 2000 were on average a factor 2.3 (total $A_9$PEO) and 3.6 (NP) lower than estuarine dissolved concentrations found inside the Scheldt and Rhine estuary in 2000 [35].

If shipping is a major source of surfactants to the coastal environment, it seems surprising that the surfactant concentrations inside the Rhine estuary (leading to the Rotterdam harbours) were lower than dissolved marine concentrations in 1999 [12]. However, ships are not allowed to release their waste water from cargo hold cleaning into the harbours and the Rhine estuary, but are under certain conditions allowed to release this water at open sea. This could explain the observed increase in concentrations further off shore. It is known that $A_9$PEO are used in ship cleaning products. Unfortunately, data on exact consumption amounts are not available.

In addition to the application of surfactants during cargo hold cleaning, the transported products themselves sometimes contain considerable amounts of $A_9$PEO. It is known that certain types of oil are transported in the form of oil/surfactant/water emulsions, such as the Orimulsion® product. This product contains approximately 0.5% $A_9$PEO, and is transported to the Rotterdam harbour at estimated amounts of 2.5 million tonnes per year [36, 37]. In some of the Orimulsion® formulations, $A_9$PEO have been replaced recently by alcohol ethoxylates [38].

Another possible source of surfactants to the marine environment is their application after oil spills. The use of surfactants as oil spill dispersants is somewhat controversial, and reports on the actual use of this oil remediation method are contradictory. However, in a recent publication the application of oil spill dispersants was reviewed, indicating that this method is indeed widely used [39].

The large differences between the present sampling campaigns themselves, and the fact that other literature data of $A_9$PEO in the North Sea report relatively low concentrations suggests that the high dissolved concentrations in the 1999 campaign do not reflect the ‘normal’ situation in this area, but rather represent a temporary ‘worst case’ situation. This further suggests that the $A_9$PEO do not originate from a constant source like river water, but rather from an ‘incidental’ source such as application in ship cargo hold cleaning or as oil spill dispersant.

Another possible source of $A_9$PEO to the Dutch coastal zone would be the presence of $A_9$PEO in precipitation. A recent publication reports median $A_9$PEO and NP concentrations of 91 and 82 ng L⁻¹ with maxima of 924 and 256 ng L⁻¹, respectively, in precipitation in the Netherlands [40]. In an earlier study, $A_9$PEO and NP concentrations in rain water from the Netherlands were found to be below the detection limit of 100 ng L⁻¹ (for both $A_9$PEO and NP) [7].

A quantitative estimation of the $A_9$PEO sources to the Dutch coastal zone is given in table 6.8. Dissolved concentrations at 3 m depth are used, and the elevated concentrations at the
water surface are not taken into account. It is interesting to note that the contribution of the Scheldt estuary as a source of A9PEO is relatively low, although A9PEO concentrations in the Scheldt river are relatively high [12]. In addition to the relatively low discharge of the Scheldt, the extensive biodegradation of A9PEO in the Scheldt estuary is mainly responsible for the low flux of A9PEO to the Dutch coastal zone. In the Rhine estuary, the water residence time is too short for significant biodegradation to occur. For the possible contribution of ship cleaning activities to the total load of A9PEO to the Dutch coastal zone, a quantitative estimation cannot be made at this time, as data on the usage of A9PEO on ships are not available.

As a comparison, the estimated annual consumption of A9PEO in the Netherlands was 1500 tons per year [41], indicating that about 1% of the A9PEO used in the Netherlands ends up in the Dutch coastal zone.

Table 6.8: Estimated contributions of the freshwater sources of A9PEO to the Dutch coastal zone. Concentrations of the campaign of 2000 are used for the calculations.

<table>
<thead>
<tr>
<th>source</th>
<th>freshwater discharge (10^9 m^3 year^-1)</th>
<th>dissolved concentration (ng L^-1)</th>
<th>concentration in SPM (ng g^-1)</th>
<th>concentration SPM in water (mg L^-1)</th>
<th>dissolved load (kg year^-1)</th>
<th>load sorbed to SPM (kg year^-1)</th>
<th>total load (kg year^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wadden Sea</td>
<td>10</td>
<td>66^b</td>
<td>3228</td>
<td>17</td>
<td>660</td>
<td>549</td>
<td>1209</td>
</tr>
<tr>
<td>North Sea canal</td>
<td>2.7</td>
<td>80^c</td>
<td>6355</td>
<td>3</td>
<td>216</td>
<td>51</td>
<td>267</td>
</tr>
<tr>
<td>Nieuwe Waterweg d</td>
<td>44</td>
<td>94^a</td>
<td>5356</td>
<td>13</td>
<td>4108</td>
<td>3043</td>
<td>7151</td>
</tr>
<tr>
<td>Haringvliet</td>
<td>22</td>
<td>50^d</td>
<td>10437</td>
<td>4</td>
<td>1105</td>
<td>923</td>
<td>2028</td>
</tr>
<tr>
<td>Scheldt estuary</td>
<td>4.3</td>
<td>88^g</td>
<td>3023</td>
<td>14</td>
<td>378</td>
<td>182</td>
<td>560</td>
</tr>
<tr>
<td>deposition (rain)</td>
<td>8.0^h</td>
<td>91^f</td>
<td>-</td>
<td>-</td>
<td>727</td>
<td>-</td>
<td>727</td>
</tr>
<tr>
<td><strong>total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>12·10^3</strong></td>
</tr>
</tbody>
</table>

^a: discharge data taken from [42]. ^b: median concentration of W1-W3. ^c: concentration at location N1 (freshwater side of the lock). ^d: this is the main exit of the Rhine estuary. ^e: median concentration in Rhine estuary, taken from [35]. ^f: concentration at location H1 (freshwater side of the lock). ^g: concentration at location SE1. ^h: deposition is calculated for an area of 150*70 km (average rainfall in the Dutch coastal zone is 751 mm year^-1). ^i: data taken from [40].
6.5. Conclusions

The present results provide several insights into the sources and environmental fate of A9PEO surfactants in the Dutch coastal zone of the North Sea. A9PEO are ubiquitous in the Dutch coastal zone, and are observed in marine water and sediments up to at least 80 km off shore. As there is little exchange between those two compartments, the spatial profiles and A9PEO sources differ for sediment and water.

In sediments close to the shore, A9PEO is present in relatively high concentrations, but concentrations decrease sharply with distance from the shore. The Rhine and Scheldt estuaries are the main sources of A9PEO in sediments of the Dutch coastal zone. Additional sources of A9PEO are production platforms and harbour dredge dumping sites. A seasonal influence on sediment concentrations was not observed.

While in many water samples longer ethoxymers are observed, most sediments contain ethoxymers with an EO chain length between 1 and 3 units. This indicates that biodegradation is a major process occurring in the Dutch coastal zone and that ethoxymers with 1 to 3 EO units are relatively stable intermediates. The A9PEO metabolites A9PEO1, A9PEO2, NP and A9PEC are all detected in the Dutch coastal zone. In the marine as well as in the adjacent estuarine environments, A9PEC are the main metabolites present in the dissolved phase. However, while in estuarine water A9PEC are more abundant than the A9PEO, in marine water the A9PEO are present at higher concentrations than A9PEC.

High dissolved A9PEO concentrations are sometimes observed in the upper seawater surface layer of 20 cm. The highest dissolved concentrations are observed relatively far off shore. The most likely sources of these surfactants seem to be discharges from ships at open sea, possibly due to the use of surfactants to clean cargo holds.

In the marine water column, more than 25% of the A9PEO is sorbed to SPM, and therefore the suspended particulate material is certainly of significance for the marine fate of A9PEO. Dissolved A9PEO concentrations at the water surface are roughly one order of magnitude higher than several meters below the surface, and therefore in reports on dissolved surfactant concentrations in the environment, it is essential to specify water sampling depths. From a risk evaluation point of view, both the concentrations at and below the water surface are relevant.

Further research is necessary to investigate the relevance of shipping activities as a source of surfactants to the marine system.
Sources and fate of nonylphenol ethoxylates and their metabolites in the Dutch coastal zone

Acknowledgments

The authors wish to express their gratitude to the crew of the research ship Mitra, for making the sampling campaigns possible, and to the colleagues of MTC for their assistance in sampling. The scientists at the RIKZ laboratory in Middelburg are gratefully acknowledged for performing the analyses of the standard parameters. This work was financially supported by the RIKZ institute of the Dutch ministry of Transport, Public Works and Water Management, project SURTRANS, and the European Union, project PRISTINE (ENV4-CT97-0494).

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