Environmental behaviour of onylphenol ethoxylates in coastal waters

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General discussion, conclusions and recommendations
Chapter 8

In this chapter, the main findings described in the previous chapters will be used to answer the research questions posed in the general introduction (Chapter 1). The results of both laboratory, field and modeling studies will be linked. In addition, the most important remaining uncertainties related to each question are discussed, conclusions are drawn and recommendations for further research are made.

8.1. General discussion

The first research question in this thesis was:

• What is the most suitable method to sample and analyze A₃PEO in the aquatic environment?

Sampling issues
Depending on their hydrophobicity, compounds in the environment will be mainly present in either the dissolved or sorbed phase. With $K_{ow}$ values below 3, compounds are expected to be mainly present in the dissolved phase, while compounds with $K_{ow}$ higher than 5 will be sorbed to suspended particulate material (SPM) and sediment to a large extent [1]. The $K_{ow}$ values of 4.2 for A₃PEO₂ and 4.5 for NP [2] indicate that these analytes may be present in the environment in both the water and sediment compartments. This is confirmed by the field data presented in chapters 4 and 5. For environmental monitoring purposes, both types of samples could be chosen. The extraction methods employed in this thesis are easiest for water samples, resulting in higher recoveries and smaller standard deviations compared to the sample pretreatment procedures for sediments (see table 6.1). In addition, extracts of water samples are usually cleaner and therefore cause less matrix effects in LC-MS analysis, again improving the reliability of A₃PEO quantification.

In surface sediments, analyte concentrations are present which often have equilibrated over several years, and are therefore representative of the location over a long period. For estuarine water, a representative description of dissolved concentrations and processes occurring in the area can be obtained when water samples are taken along the salinity gradient. By keeping track of the conservatively behaving salinity, the mixing of fresh and marine water as well as tidal processes can be accounted for.
General discussion and conclusions

Figure 8.1: Profile of salinities and concentrations of dissolved total A9PEO along the Rhine estuary at 3 different depths (October 2002). Black bars: water from surface; grey bars: water at 1.5 m depth; white bars: water at maximum depth (3-7 m).

A complicating factor with water samples (investigated in more detail in chapter 6.3.2, p. 146) is that a vertical stratification of A9PEO over the water column is often present. This phenomenon has been demonstrated for dissolved A9PEO in marine and estuarine water in chapters 5 and 6. To a lesser extent, the metabolites NP and A9PEC also show this behaviour. As an example, the dissolved A9PEO concentrations at different depths in the Rhine estuary from the sampling campaign of 2002 are shown in figure 8.1. The intrusion of saline water from the sea is stronger in the deepest layer, leading to a vertical stratification of salinity. Stratification of A9PEO is observed both in the freshwater and saline part of the
Chapter 8

estuary. The fact that stratification of A₉PEO was also observed in completely saline water columns of the Dutch coastal zone indicates that the stratification is not a result of salting out processes. The data of figure 8.1 were used to construct the fate model of the Rhine estuary as described in chapter 7. For an adequate description of the occurrence of A₉PEO (and probably all surface active agents), water samples should be taken both at the surface and at several meters depth, and more attention should be given to their occurrence in the surface microlayer of the water.

Finally, the stratification of A₉PEO in water columns may also complicate the interpretation of aquatic toxicity tests. Even when working with actual instead of nominal concentrations, the tests do not take into account possible stratification of dissolved analyte concentrations in a laboratory set up. Therefore concentrations measured may not be representative for the whole water body, resulting in incorrect no-effect concentrations. Due to the difference in scale between an estuarine and a laboratory test water column, the stratification may be quite different for the two systems.

Sample treatment methods

In the present study, water samples were extracted using Solid Phase Extraction (SPE) cartridges with C₁₈-material. This is the method most often encountered in literature, because of its simplicity and efficiency. An advantage of our water sample handling method compared to those of other studies is that in the present studies most water samples were filtered and extracted on board the sampling ship, within several hours after sampling. In this way, possible problems with conservation of the samples were prevented, as in some water matrices, degradation of A₉PEO occurs within a few days [3]. Although our filtration/SPE equipment could be transported without many problems, the commercial availability of a portable SPE device in the future would be advantageous for many environmental chemists.

During our studies, the possibilities of the automation of SPE extraction of A₉PEO from water samples was investigated using the Prospekt I instrument (Spark Holland, Emmen, The Netherlands). Due to several practical problems, this method never developed into an official standard operating procedure in our laboratory. Disadvantages of the method were possible clogging of solvent/sample tubes (careful filtration of the water sample was necessary), an insufficient reproducibility of the sample load volume, and a reproducibility of the complete method which was not better than the manual SPE method [4].

In addition, we made several attempts at applying Solid-Phase Microextraction (SPME) for the extraction of A₉PEO from water. The main practical problem of this method was that during the desorption of the SPME fiber in the SPME-LC interface (filled with methanol), the coating was stripped from the fiber, after which the fiber became useless. Although unsuccessful in our studies, SPME remains a promising technique, which may have more
success in future studies if a different desorption interface or system is used in which the sensitive fibers are protected [5].

For the extraction of \( A_9\text{PEO} \) from sediments, the Soxhlet method was applied. The main advantage is that this method is robust and can be used for virtually all solid samples. The disadvantages include the relatively large amount of glassware and solvents necessary, and the relatively long extraction time, which was 16 hours (overnight) in our studies. Other methods which have recently gained in popularity are Accelerated Solvent Extraction (ASE) and sonication extraction, which eliminate most of the disadvantages occurring with Soxhlet. In the future, the use of ASE and sonication is expected to surpass that of Soxhlet methods [6].

**LC-MS analysis**

LC-ESI-MS analysis using a reversed phase column and the electrospary interface in positive mode is very suitable for the analysis of \( A_9\text{PEO} \) in environmental samples. As demonstrated in chapter 2, several adduct signals are observed for most oligomers. The stabilities of single sodium monomer adducts \([A_9\text{PEO}+\text{Na}]^+\) and \([A_9\text{PEO}_2+\text{Na}]^+\) as well as dimer adducts \([2\times A_9\text{PEO}+\text{Na}]^+\) and \([2\times A_9\text{PEO}_2+\text{Na}]^+\) were calculated by molecular dynamics. In all cases, adduct formation energies were negative and the adducts were stable with respect to the reagents. The calculated higher stability of \([A_9\text{PEO}_5+\text{Na}]^+\) compared to \([A_9\text{PEO}_2+\text{Na}]^+\) was in agreement with LC-MS observations, but the calculated higher stabilities of the dimer adducts compared to the corresponding monomer was not. In addition, the calculated higher stability of \([2\times A_9\text{PEO}_5+\text{Na}]^+\) compared to \([2\times A_9\text{PEO}_2+\text{Na}]^+\) was not in agreement with LC-MS observations. Further molecular dynamics calculations in which the role of the solvent is taken into account may give more insight into the adduct formation processes occurring for \( A_9\text{PEO} \) during LC-ESI-MS analysis.

The formation of several adducts per oligomer does not compromise the quantification of \( A_9\text{PEO} \) mixtures as long as the oligomer composition of the standard is similar to that of the sample. When the compositions strongly differ, especially when both long-chain oligomers \((\sim A_9\text{PEO}_{10})\) and short-chain oligomers are present \((A_9\text{PEO}_1 \text{ and } A_9\text{PEO}_2)\), the reliability of the quantification decreases and often an overestimation will occur. This situation can occur for samples in which partial biodegradation has taken place, and both the original long-chain \( A_9\text{PEO} \) and the metabolites \( A_9\text{PEO}_1 \) and \( A_9\text{PEO}_2 \) are present. An example of a sediment extract showing this pattern is shown in figure 8.2.

A comparison of calibrations using different \( A_9\text{PEO} \) mixtures revealed that when only \( A_9\text{PEO}_{12} \) are present in the sample and standard, a difference in average oligomer chain length between sample and standard does not lead to errors in quantification. A molar
calibration must be used, followed by a correction for the actual average molar weight of the A₉PEO in the sample.

Figure 8.2: Mass spectrum of a sediment extract from the Rhine estuary analyzed by LC-ESI-MS, showing two apexes in the A₉PEO oligomer distribution at high and low ethoxylate chain length.

The availability of A₉PEO and NP standards containing $^{13}$C in the aromatic ring, which can be used as internal standards, has greatly improved the reliability of the quantitative determination of A₉PEO in environmental samples. However, matrix effects can still cause underestimations of up to 30% (as shown in chapter 2.3.3), possibly due to the fact that the internal standard (IS) elutes some minutes later than the A₉PEO analytes, because the IS has a linear alkyl chain, while common A₉PEO is branched. $^{13}$C-A₉PEO with branched alkyl chains would be the ideal internal standard, and has been specially synthesized and used in one other study [7].

The application of hyphenated techniques such as LC-MS has several advantages over more classical spectrophotometric techniques such as fluorescence detection (LC-Flu). Both selectivity and sensitivity are higher for LC-MS techniques. In addition, the analysis is simplified, as with LC-Flu two analyses are required for each sample (using a normal phase column for the determination of the average ethoxylate chain length and a reversed phase column for the quantification), while one analysis is sufficient when using LC-MS techniques [8, 9].
As technology progresses, an increasing number of publications report the application of tandem mass spectrometry (LC-MS/MS) for the environmental analysis of A9PEO. With this technique, detection limits are often significantly improved compared to LC-MS. However, all of the quantitative analytical issues addressed in this thesis are equally applicable to LC-MS/MS analysis of A9PEO. For these applications, the advantages of LC-MS/MS over LC-MS are only limited.

**Which are the main metabolites of A9PEO and what is their relative persistence in the environment?**

In the laboratory biodegradation experiments described in chapter 3, the main metabolites formed in freshwater under aerobic conditions proved to be the alkylphenoxy ethoxy acetic acids (A9PEC), with ethoxylate chain lengths of 1 to 15. This process is called the oxidative hydrolytic degradation mechanism. Within this metabolite group, the A9PE2C oligomer accumulated to the highest degree and was relatively persistent compared to A9PEO. However, after 10 days, the A9PEC metabolites were further oxidized to form the metabolite group named CAPEC, with both the ethoxylate and alkyl chain oxidized. This metabolite group reached a maximum concentration of around 5% of the total metabolite concentration present, and was further degraded to unidentified metabolites.

The mass balance in the degradation experiments was not complete. Although all samples were screened for many logical oxidation and hydrolysis products, other metabolites (too polar for extraction by C18-SPE or non detectable by LC-MS) may have been formed. Alternatively, a large fraction of the A9PEO may have been mineralized to CO2 and water without the accumulation of any metabolites.

A recent study by Ferguson et al. shed some more light on the possible biodegradation processes of A9PEO [10]. Biodegradation studies of radioactive 14C-labeled A9PEO1.9 in sediment under both aerobic and anaerobic conditions showed that after 120 days, only a few percent of the A9PEO was transformed to CO2. Metabolites formed in both the aerobic and anaerobic study were mainly short-chain A9PE1.3C, and to a lesser degree A9PEO1. A relatively large part of the 14C activity originating from the spiked A9PEO1.9 was found as non-extractable dissolved or sediment-bound material. Ferguson suggested that this fraction may include additional metabolites such as CAPEC, or 14C which has been metabolized and incorporated into biomass.

The field data of chapter 5 are largely in accordance with the degradation processes observed in our laboratory studies. In the Rhine and Scheldt estuaries, the metabolites present at the highest dissolved concentrations were A9PE1.8C. The CAPEC metabolite group could not be detected in any of the field samples. The non-availability of CAPEC
standards makes reliable identification of these compounds rather difficult, as in our analyses only an extract from the biodegradation studies could be used as CAPEC reference. However, this metabolite group has been detected in environmental samples in some other studies [11, 12].

During the laboratory studies the nonoxidative hydrolytic degradation mechanism occurred only to a minor degree. This mechanism, involving a simple shortening of the ethoxylate chain, resulted in a minor increase in the A₉PEO₂ oligomer. Complete de-ethoxylation, which would result in the metabolite nonylphenol, was not observed in the experiments. The field results of the Scheldt and Rhine estuaries also showed the nonoxidative hydrolytic mechanism to be of minor importance for the water phase of the investigated estuaries. The oligomer distribution of dissolved A₉PEO showed an average around A₉PEO₃, and did not vary when going downstream. However, this result also indicates that probably nonoxidative degradation has already occurred to a certain extent before the A₉PEO entered the study area, as commercial A₉PEO mixtures usually have oligomer distributions with an average around A₉PEO₁₀ or longer.

In the marine environment, concentrations of A₉PEC observed were relatively low, while dissolved concentrations of A₉PEO were sometimes very high. Therefore, the nonoxidative hydrolytic mechanism is probably more important for degradation of dissolved A₉PEO in the marine environment than in estuarine or freshwater environments.

In sediments, a number of samples contained maxima in the oligomer distribution at both long (A₉PEO₁₀) and short-chain oligomers (A₉PEO₂). This is an indication that in sediments, the non-oxidative hydrolytic mechanism is an important degradation route, resulting in accumulation of A₉PEO₂.

According to our studies and other literature, nonylphenol is not formed out of A₉PEO under aerobic conditions. For the formation of NP under anaerobic conditions, the proof provided in literature is rather thin. An actual increase in NP concentration during the degradation of A₉PEO has been reported only once in the literature [13]. Other evidence for this formation is indirect, such as increasing NP/A₉PEO concentration ratios during degradation of A₉PEO, while in fact both concentrations decreased [14]. Also in the recent experiments by Ferguson et al., NP was not found to accumulate during the anaerobic biodegradation of A₉PEO₁₉ in sediment [10]. However, it could not be excluded that over longer time scales in anoxic sediment, NP may be formed out of A₉PEO. Further research on the possible formation of NP in anaerobic environments is necessary.

Nonylphenol was detected in our field studies in most of the water and sediment samples. In both water and sediments, NP concentrations were usually somewhat lower but in the same order of magnitude as those of A₉PEO. Only in marine water collected at the surface in the Dutch coastal zone, concentrations of A₉PEO were much higher than those of NP.
If the formation of NP out of A₉PEO is not the main explanation of the environmental occurrence of NP, other sources must be considered. NP may be present as impurity in some A₉PEO formulations. Another source which may contribute significantly to the environmental load of NP, is the degradation of the hydroperoxide decomposer tris(nonylphenyl)phosphite (TNPP), which is added to polymers as an antioxidant. In addition, NP is used for the production of phenolic resins, used in applications such as protective coatings, laminates, insulation and molding compounds [15].

*Which are the main possible sources of A₉PEO to the Dutch coastal zone?*

For A₉PEO in surface sediment and water in the Dutch coastal zone, different spatial distributions are observed. From these distributions it is concluded that the main sources of A₉PEO to the surface sediment and water of the Dutch coastal zone are different. Concentrations of A₉PEO in surface sediments are relatively high at the locations where the main freshwater sources reach the Dutch coastal zone, and decrease sharply with distance from these locations. Therefore it is concluded that the main routes of A₉PEO to sediments of the Dutch coastal zone are the Rhine and Scheldt estuaries and the North Sea canal (see figure 8.3). In addition, the dump site for harbour dredge and in some cases production platforms are sources of A₉PEO to the sediment.

In the water phase, a different spatial pattern was observed, as relatively high dissolved concentrations of A₉PEO were found far from the shore. The locations with the highest dissolved concentrations coincided with the main shipping routes in this area. This suggests that shipping is an important source of A₉PEO to the Dutch coastal zone. The main application of surfactants on ships is for cleaning cargo holds. Some of the cleaning products are known to contain A₉PEO. However, exact data on A₉PEO use in shipping activities are not available. Another possible source of surfactants to the marine environment is their application as oil spill dispersants. In addition, some types of oil are transported in the form of oil/surfactant/water emulsions, such as the Orimulsion® product [16]. In some cases, this surfactant is A₉PEO, which may end up in marine waters during cleaning of these tankers (even when A₉PEO is not present in the cleaning agent) [16].

It can be expected that part of the dissolved A₉PEO will adsorb to SPM off shore, and will be transported to the coastal region before it sedimentates [17, 18].

From the current results we suspect shipping to be a more significant source of A₉PEO to the marine water phase than the freshwater discharges into the Dutch coastal zone. Additional research on this subject is necessary, as the exact role of shipping as a source of A₉PEO to the marine environment is far from clear yet.
From the results of fate model exercises described in chapter 7 it was concluded that additional sources of $A_9$PEO are present in the investigated estuaries. For the Rhine estuary, the observed concentration profiles could only be described when sources at the Oude Maas river and one of the Rotterdam harbours were included. Confirmation of the presence of these suspected sources was provided recently from the analysis of $A_9$PEO in rain water of this region [19]. For the Scheldt estuary, the canal Gent-Terneuzen is a significant additional source of $A_9$PEO.

- **Which processes mainly govern the fate of $A_9$PEO in the estuarine environment?**

In the laboratory studies, it was shown that primary biodegradation of $A_9$PEO can occur relatively easily in freshwater. During the field campaigns, metabolites were usually present at higher concentrations than the surfactant itself. These findings suggested that biodegradation is the main process in the environmental fate of $A_9$PEO.
In a more quantitative way, the contribution of different environmental processes was studied using a hydrodynamic fate model, as described in chapter 7. For the fate model of the Scheldt estuary, variations in biodegradation rates caused a more significant difference in the modeled dissolved concentration profiles than variations in sorption coefficients, additional A<sub>9</sub>PEO sources or dispersion coefficients did. Therefore, this fate model confirms biodegradation to be the main process governing the fate of A<sub>9</sub>PEO in the environment.

From the Scheldt fate model, field biodegradation rates of A<sub>9</sub>PEO and its metabolites could be derived, which is valuable information for the risk assessment of these compounds. Biodegradation rates of A<sub>9</sub>PEO previously reported in literature were mostly determined in laboratory experiments, and are difficult to extrapolate to the real environment [14, 20, 21, 22]. In our laboratory biodegradation experiments, a half-life of 0.4 days was determined for A<sub>9</sub>PEO<sub>3.15</sub>. These experiments were performed at room temperature, at saturated oxygen concentrations and with a high microbial activity on the glass beads of the test filter. The biodegradation rates derived from our fate models were considerably lower, corresponding to half-lives of 10-11 days. These values are in agreement with half-lives reported in literature for laboratory experiments using estuarine water (2.5-69 days for A<sub>9</sub>PEO<sub>1.18</sub> [20, 21]), laboratory shake-flask experiments (1.9-69 days for A<sub>9</sub>PEO<sub>1.2</sub> [22]) and in situ in estuarine water (<30 days for A<sub>9</sub>PEO<sub>1.3</sub> [23]).

In the Scheldt estuary fate model, the employment of higher degradation rates at the freshwater side and lower rates at the saline end of the estuary resulted in further improvement of the fit of the dissolved concentration profiles. This suggests that in the Scheldt estuary biodegradation rates are salinity dependent. This is in accordance with a study of Kveštak et al., who reported salinity dependent biodegradation of A<sub>9</sub>PEO in the Krka estuary (Croatia) [20].

In the fate model of the Rhine estuary, the dissolved concentration profiles were mainly influenced by the additional A<sub>9</sub>PEO sources of the Rotterdam harbours and the Oude Maas river. A relatively short water residence time in this estuary (2-3 days for the Rhine estuary compared to 2-3 months for the Scheldt estuary) may be an explanation why biodegradation is not found to be of high importance in the Rhine estuary.

Sorption does occur for A<sub>9</sub>PEO, as in most SPM samples, A<sub>9</sub>PEO and NP are detected at significant concentrations. In the entire water column, on average 20-40% of A<sub>9</sub>PEO and NP is present sorbed to SPM. No salting out effects were observed, as sorption coefficients were fairly constant along the salinity gradients.

The environmental fate model was able to describe the dissolved concentration profiles of A<sub>9</sub>PEO, A<sub>9</sub>PEC and NP in the estuaries in a satisfactory way. For sediments and SPM, the model predicted concentrations in the correct order of magnitude. As detailed processes concerning the movement of SPM (tides, currents, turbulence, biological processes) were
not included in the model, the variations of concentrations in sediments and SPM along the estuary could not be modeled. For sediment and SPM, additional uncertainties include the sedimentation and erosion rates in the estuaries, which strongly vary in different parts of the estuary.

**Do A9PEO form a potential environmental risk to the Dutch coastal zone?**

Of the compounds investigated in this thesis, nonylphenol has the highest toxicity (at equal concentrations) both for the general narcosis and endocrine disruption endpoints (see figure 1.3, general introduction). For the A9PEC metabolite group, LC50 values range from 1000 to 17000 μg L⁻¹, which signifies a toxicity about an order of magnitude less than that of A9PEO [24]. The toxicological importance of CAPEC is probably not very high, as the compounds are very polar and water soluble, and will probably not bioaccumulate. No actual toxicological data for CAPEC are available yet. Recently, Maximum Permissible Concentrations (MPC) in water and sediments for A9PEO₁₂, A9PEO₃₈, A9PEO₇₈, A9PE₁₂C and NP have been proposed for the Netherlands by RIVM, as shown in table 8.1 [25]. The current field results show that at some locations in the Rhine and Scheldt estuaries, these target concentrations are exceeded in water and sediments. However, the maximum estuarine concentrations observed in our studies remain below levels at which endocrine disruption or other toxic effects may occur (threshold level for vitellogenin induction is 10 μg L⁻¹ for NP, an order of magnitude higher for A9PEO [26]). In the coastal zone, A9PEO are sometimes present at relatively high dissolved concentrations at the water surface, for example in the shipping route to and from the Rhine estuary (Maasgeul). These concentrations exceed MPC values by far. However, also in these cases concentrations are below levels at which endocrine disruption or other toxic effects could be expected.

In other studies, endocrine disruptive effects have been observed in the form of vitellogenin induction in the Scheldt estuary [27]. While A9PEO concentrations were below levels at which these effects could be expected, apparently the cumulated effects of A9PEO, NP and other endocrine disruptors present in those surface waters, could still cause endocrine disruption to occur in Dutch surface waters.

Organisms are especially sensitive to endocrine disruptive effects in their larval/embryonal stadium. As certain fish species produce eggs which float at the water surface, these organisms may be at increased risk of endocrine effects caused by surface active compounds such as APEO [28].
Table 8.1: Proposed Maximum Permissible Concentrations (MPC) for A₉PEO and metabolites for the Netherlands [25], and maximum observed concentrations in the Dutch estuaries and coastal zone (this thesis).

<table>
<thead>
<tr>
<th>compound</th>
<th>MPC in water (µg L⁻¹)</th>
<th>maximum observed concentration in water (µg L⁻¹)</th>
<th>factor by which MPC is exceeded</th>
<th>MPC in sediment (µg g⁻¹ dry weight)</th>
<th>maximum observed concentration in sediment (µg g⁻¹ dry weight)</th>
<th>factor by which MPC is exceeded</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₉PEO₈₋₁₂</td>
<td>0.12</td>
<td>1.0ᵃ</td>
<td>8</td>
<td>0.15</td>
<td>0.16ᵇ</td>
<td>1.1</td>
</tr>
<tr>
<td>A₉PEO₃₋₈</td>
<td>14</td>
<td>35ᵇ</td>
<td>2.5</td>
<td>4.5</td>
<td>7.3ᵇ</td>
<td>1.6</td>
</tr>
<tr>
<td>NP</td>
<td>0.33</td>
<td>1.7ᵈ</td>
<td>5</td>
<td>0.105</td>
<td>1.08ᵇ</td>
<td>10</td>
</tr>
<tr>
<td>A₉PE₁₂₋₁₂</td>
<td>1.0</td>
<td>9.2ᵇ</td>
<td>9</td>
<td>0.086</td>
<td>0.17ᵇ</td>
<td>2</td>
</tr>
</tbody>
</table>

ᵃ: Scheldt, near Antwerp (1999); ᵇ: North Sea, location N1 (2000); ᵈ: North Sea, location R2 (1999); ᵉ: North Sea, location SW5 (1999); ᵊ: Scheldt, location S10 (1999); ᵫ: Scheldt, location SCs (2000); *: value for A₉PEO₈₋₁₅. Long chain oligomers (A₉PEO₈₋₁₅) constitute only a minor fraction of the total.

From table 8.1 it is clear that concentrations of A₉PEO and metabolites exceed the MPC at a number of locations in the Dutch estuarine and marine environment. Therefore, a potential environmental risk is present, and action should be taken to reduce emissions of these compounds to the environment.

With the new EU Directive on the restrictions of the use of NP and APEO [29], the voluntary ban on A₉PEO in household cleaning agents in the Netherlands [30] will be expanded to many industrial detergents and other applications. As a result, the environmental presence of A₉PEO is expected to decrease. The A₉PEO concentrations upstream of the Scheldt estuary, which were the highest observed in the Dutch estuarine environment, indicate that international regulations on a catchment level are indeed necessary.

If policy initiatives regarding A₉PEO in the Dutch coastal zone will be taken in the future, it is advised to specifically include regulations on waste water discharges from ships at open sea and offshore platforms. This would only be possible through international regulations, issued by organizations such as the Oslo Paris Convention (OSPAR), European Union or the International Maritime Organization (IMO).
8.2. Conclusions

The answers to the research questions of this thesis, as provided in the general discussion, can be summarized in the following conclusions:

- LC-MS is a suitable method for the analysis of A₉PEO in environmental samples. Several adduct signals per oligomer are observed. This formation of adducts can partly be explained by the relative stabilities of adducts as calculated by molecular dynamics.

- A reliable quantification of A₉PEO in environmental samples is possible with commercially available standards, despite the formation of different types of adducts during LC-MS analysis. A separate quantification of A₉PEO₁ and A₉PEO₂ is necessary, due to the relatively low response of short chain A₉PEO oligomers.

- The degradation of A₉PEO in surface water occurs relatively fast in laboratory experiments. The main metabolites are A₉PEC, CAPEC and A₉PEO₂. Of these metabolites, A₉PE₂C is the most persistent, but all metabolites are eventually further degraded. The formation of NP out of A₉PEO does not occur under the test conditions.

- In the Rhine and Scheldt estuaries, the main biodegradation route of A₉PEO in water is the oxidative hydrolytic pathway. In the Dutch coastal zone, both the oxidative and nonoxidative hydrolytic degradation occurs. Biodegradation of A₉PEO in sediments, if occurring, seems to follow the nonoxidative hydrolytic pathway.

- Degradation is the main process governing the fate of A₉PEO in the aquatic environment. Metabolites are often present at higher concentrations than the surfactant itself. Sorption does occur for A₉PEO and NP, as these compounds are detected in most fresh, estuarine and marine sediments and suspended particulate material samples.

- Due to the surface active properties of A₉PEO, dissolved concentrations are often an order of magnitude higher at the water surface than at several meters depth.

- Spatial profiles of A₉PEO and metabolites in the Dutch coastal zone differ for sediment and water. Sediments show relatively high concentrations close to the shore. These concentrations decrease rapidly with distance from shore. The water compartment shows relatively low concentrations close to the shore, while concentrations in offshore samples are often higher.
• Maximum estuarine and marine dissolved concentrations of A9PEO are found in the upstream part of the Scheldt estuary, and in the coastal zone at 30-70 km from the shore. These relatively high marine concentrations coincide with the main shipping routes in the Dutch coastal zone.

• The main sources of A9PEO to the Dutch coastal zone are different for sediment and water. For sediments, the main sources are the Scheldt and Rhine estuary, the North Sea Canal, the harbour dredge dump site near Noordwijk and in some cases production platforms. In the water phase, A9PEO mainly originates from off shore sources, e.g. shipping activities.

• In the Dutch estuarine and marine waters and sediments, concentrations of A9PEO and their metabolites are in several cases above Maximum Permissible Concentrations.

• A hydrodynamic fate model was able to describe the behaviour of A9PEO and its metabolites in two Dutch estuaries. Satisfactory model fits were obtained for the dissolved concentration profiles. From the model, biodegradation constants of A9PEO and metabolites in the field were derived, which were in agreement with values from literature.

8.3. Recommendations

As a starting point for further research on surfactants in the aquatic environment, the following issues deserve attention in the future:

• The current results indicate shipping as a relevant source of A9PEO to the marine environment, while in the Rhine estuary, the Rotterdam harbours were identified as an additional source. Further investigation of the importance of these sources is desirable. An inventory should be made of exactly which cleaning agents and other surfactants are used in shipping activities. In addition, field studies in which the main shipping lanes of the Dutch coastal zone (and other intensively used shipping lanes) are extensively sampled should be performed.

• As the results of this thesis indicate that dissolved A9PEO is vertically stratified in the water column, the surface microlayer of the water deserves specific attention in the
investigation of all surface active compounds. The potential risk of A9PEO to organisms dwelling at the surface microlayer (especially in juvenile life-stages) should be re-evaluated.

- The validity of aquatic toxicity tests of surface active compounds should be investigated, as it is possible that in experimental set ups a stratification of the analytes is present as well, which would lead to incorrect determinations of the concentration. The difference in scale between an estuarine ecosystem and a laboratory aquarium may result in stratifications which are quite different for the two systems. Additional processes such as the movement of the organisms during the toxicity tests may disturb the possible stratification of analyte concentrations.

- Surfactants will often be present in the environment in combination with a number of other contaminants (e.g. during their application as oil spill dispersants). Due to their surface active properties, the surfactants may increase the solubility of apolar contaminants, thereby increasing their bioavailability and possibly the uptake by organisms. This interaction between surfactants and apolar contaminants should be studied further.

- Further toxicity data is needed for the A9PEC metabolites. During risk assessment, the current incomplete toxicity data set leads to relatively large safety factors, resulting in relatively low Maximum Permissible Concentration values. Possibly, the MPC could be adjusted when more toxicity data is available.

- The results in this thesis show that the current state of the art of analytical chemistry permits detailed studies of the environmental fate of polar contaminants. Further studies could focus on other polar contaminants in the Dutch aquatic environment, such as other surfactants, pharmaceuticals or perfluorinated compounds.

References


