Environmental behaviour of onylphenol ethoxylates in coastal waters
Jonkers, C.C.A.

Citation for published version (APA):
Fate modeling of nonylphenol ethoxylates and their metabolites in the Dutch Scheldt and Rhine estuaries: validation with new field data

Submitted to Estuarine, Coastal and Shelf Science

Niels Jonkers¹, Remi W.P.M. Laane², Chris de Graaf¹, Pim de Voogt¹

¹ Department of Environmental and Toxicological Chemistry, Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam
² National Institute for Coastal and Marine Management/RIKZ, The Hague
Abstract

The environmental behaviour of nonylphenol ethoxylates (A₉PEO) in the Rhine and Scheldt estuaries (The Netherlands) was investigated using a hydrodynamic advection-dispersion fate model (ECoS 3). The model was validated with the results of field studies, in which A₉PEO as well as the metabolites nonylphenoxy ethoxy acetic acids (A₉PEC) and nonylphenol (NP) were analyzed in sediment, water and suspended particulate material (SPM) samples using LC-MS methods.

Maximum actual concentrations observed in surface sediments were 620, 560 and 1100 ng g⁻¹ d.w. for A₉PEO, A₉PEC and NP, respectively. In the dissolved phase, maximum observed concentrations amounted to 1100 ng L⁻¹ (A₉PEO), 6500 ng L⁻¹ (A₉PEC) and 960 ng L⁻¹ (NP). Clear spatial trends were observed for dissolved A₉PEO and metabolites in the Scheldt estuary, with decreasing concentrations going downstream. This concentration decrease was steeper than for conservatively behaving compounds. This trend was not visible in the Rhine estuary.

The fate model was applied to A₉PEO and metabolites in both estuaries. Transport of chemicals in the water column was considered as a longitudinal one-dimensional process through a number of estuary segments. For the Rhine estuary, to cope with the stratification observed, a model structure was chosen consisting of two water layers above each other, between which exchange was possible. Sedimentation/erosion processes were included in the model. A biodegradation scheme was incorporated, and rates were adjusted to fit the calculated concentration profiles with the actual profiles of both A₉PEO and its metabolites. In this way, field biodegradation rates for A₉PEO, A₉PEC and NP could be derived, which were in agreement with values from literature.

The measured dissolved concentration profiles as well as salinity and concentrations of SPM could be described successfully by the model. The concentrations calculated in SPM and sediment were of the same order of magnitude as the actual concentrations.

In the Rhine estuary, additional sources of A₉PEO had to be included to account for the relatively high concentrations in the middle of the estuary. The fate model for the Scheldt estuary could be slightly improved by using salinity dependent biodegradation rates.

A sensitivity analysis of the model showed that in the Scheldt estuary, the environmental process with the strongest influence on the dissolved concentration profiles of A₉PEO and metabolites is biodegradation. In the Rhine estuary, the water residence time is too short for significant biodegradation to occur, and in this estuary the dissolved concentration profiles were mainly influenced by the additional A₉PEO sources.
7.1. Introduction

The nonionic surfactants nonylphenol ethoxylates ($A_9\text{PEO}$) receive a lot of scientific attention, because of their excellent surface active properties as well as their potential environmental risk. With a worldwide production of around 700,000 tons annually, they are applied in many fields ranging from industrial cleaning agents to paints and pesticides [7]. Although the environmental behaviour of $A_9\text{PEO}$ has been extensively studied in recent years, the environmental risk of these compounds is still a subject of debate. The environmental concern for these compounds is mainly because of the endocrine disrupting effects of two short chain $A_9\text{PEO}$ oligomers ($A_9\text{PEO}_1$ and $A_9\text{PEO}_2$) and the metabolite nonylphenol (NP) [2, 3].

The environmental presence of $A_9\text{PEO}$ and NP has been established in both sediment, water and suspended particulate material in freshwater [4], marine [5, 6] and estuarine environments [7-10]. Field sorption coefficients show log$K_{oc}$ ranges of 5.4-6.0 (NP) and 4.9-6.4 ($A_9\text{PEO}$) [6, 8, 10].

![Figure 7.1: Biodegradation routes of $A_9\text{PEO}$: the oxidative hydrolytic pathway (A) and the non-oxidative hydrolytic pathway (B).](image-url)
One of the uncertainties in the environmental fate of $A_9$PEO is their biodegradation behaviour. Two biodegradation routes are known for these compounds, as shown in figure 7.1. In the oxidative-hydrolytic pathway, the main metabolites are the alkylphenoxy ethoxy acetic acids ($A_9$PEC), followed by the doubly oxidized CAPEC metabolites [11, 12]. This degradation route is mainly observed in freshwaters [12]. The nonoxidative hydrolytic pathway results in short-chain $A_9$PEO and NP. This route is mainly followed in marine waters and sediments. Shang et al. reported that biodegradation rates in marine sediments are extremely slow [13]. In another study, both short and long chain $A_9$PEO were reported in marine sediments, indicating that biodegradation does occur to some extent in this compartment [14]. In estuarine environments, biodegradation by both the oxidative and the nonoxidative route have been reported [9, 10].

In a field study in the Scheldt estuary (The Netherlands), $A_9$PEO concentration profiles showed a faster than conservative concentration decrease during transport through the estuary [10]. In addition, the ratios of metabolites over surfactant gradually increased when going downstream, indicating that biodegradation is proceeding in the estuary. However, from those results it is not possible to directly derive field biodegradation rate constants for $A_9$PEO, as it is difficult to quantitatively determine the contribution of dilution, biodegradation and sorption processes.

Application of an environmental fate model can provide a more quantitative insight into the importance of the different environmental processes which influence the fate of $A_9$PEO in estuaries. To the best of our knowledge, the few fate modeling studies on surfactants in literature are limited to the anionic linear alkylbenzene sulfonates (LAS) [15, 16]. A generic mathematical fate model applied to LAS in a Japanese estuary showed that biodegradation is by far the most important removal process in summer, while in winter, biodegradation and sedimentation processes had an equal contribution to the disappearance of LAS from the water column [15]. For Tokyo Bay and Osaka Bay (Japan), two hydraulic mass balance models were constructed for LAS, showing that the dominating removal processes were biodegradation and tidal transport out of the area [16].

No previous studies exist in which environmental fate models are applied to nonionic surfactants. Only for the metabolite nonylphenol, a box model using a mass balance approach was constructed for its fate in the Hudson estuary (USA) [17].

In the present study, a fate model is constructed for $A_9$PEO in the Scheldt and Rhine estuaries, two heavily industrialized areas in the Netherlands (see figure 7.2). This study makes use of the ECoS modeling software (version 3.0, Plymouth Marine Laboratory, UK), which has been applied to several other estuarine systems. In the Tamar estuary (UK), the distribution of Zn and Ni in the dissolved and suspended particulate phase was described.
Fate modeling of nonylphenol ethoxylates and their metabolites in Dutch estuaries

[18], while in the Gironde estuary (France) the distribution of dissolved Cd was modeled [19].

Figure 7.2: Map of the study areas Rhine (A) and Scheldt (B) estuary, with sampling locations.
\(x\) = water 2000, \(\Delta\) = sediment 2000, \(o\) = water 2002.

Fate models for the Scheldt and Rhine estuaries have been used in the past for other compounds. A one-dimensional hydrological model using ECoS3 software was able to describe the general movement of water masses in the Scheldt estuary, as well as the dissolved concentration profiles of a number of pesticides [20]. The model was based on the
earlier SAWES model (Systems Analysis WEstern Scheldt), which was developed by Van Gils et al. [21]. The SAWES model was used by Zwolsman to describe the concentration profiles and speciation of some trace metals in the Scheldt estuary [22]. For the fate modeling of PCB in the Scheldt estuary, a general water quality model named WASP has been used [23]. According to that model, the distribution of PCB was mainly regulated by hydrophobic sorption and suspended sediment transport.

In the Rhine estuary, hydrological fate models have been used for the study of trace metals, benzo[a]pyrene and oil in harbour sediments [24]. In that study, important contaminant sources besides the Rhine river itself were industrial discharges for the metals and oil, and shipping activities for benzo[a]pyrene and oil.

Objective
This research aims to describe the sources, fate and distribution of A₉PEO surfactants and their metabolites in the two Dutch estuaries Rhine and Scheldt by using a hydrological fate model. New field data is presented which, combined with already published results, were used for validation of the model.

A main objective in this model study was to obtain a quantitative estimate of A₉PEO biodegradation rates, as it is difficult to estimate this environmental process directly from field data or laboratory experiments. By fitting the biodegradation rate constants to the concentration profiles observed for both A₉PEO and its metabolites, a quantitative estimation could be made of the biodegradability of these compounds in the field.

7.2. Experimental Section

Study areas
The two investigated areas are both situated in the south of The Netherlands, as shown in figure 7.2.

The first study area is the Western Scheldt estuary, which is 100 km long with a strong curvature, and has a width of 500 m at Antwerp and 6500 m at Vlissingen. The mesotidal estuary has a freshwater input from the Scheldt river of on average 104 m³ s⁻¹. The water in the estuary has a residence time of two to three months and is vertically well-mixed. An additional source of freshwater to the estuary is the canal Gent-Terneuzen (on average 15 m³ s⁻¹). The main industrial areas are the harbours of Antwerp and Vlissingen [25].

A strong exchange of material between sediment and suspended particulate material (SPM) occurs in the Scheldt estuary. It is estimated that a sediment surface layer of 0.5 m in the entire estuary is mixed into the water column every 0.5 year [26]. Terrestrial SPM which
enters the Scheldt estuary is retained there for about 90% [25]. The most important sedimentation area is the tidal marshland Saeftinge. The shipping channel of the Scheldt estuary is heavily dredged, and the dredged material is dumped elsewhere in the estuary. The other investigated area is the Rhine estuary, which passes the harbours of Rotterdam. The length of the estuary is 40 km, with an average width of around 500 m. The freshwater input is around 800 m$^3$ s$^{-1}$ at the head of the estuary, while halfway the estuary the river Oude Maas provides another large freshwater input of 700 m$^3$ s$^{-1}$. The residence time of the water in the estuary is between one and three days, and the water column is vertically stratified. It is estimated that the retention of riverine SPM in the Rhine estuary is about 50% (Laane, unpublished results). The whole estuary is heavily industrialized, and has intensive shipping traffic. Due to heavy dredging activities and strong tidal currents in the estuary, the surface sediment layer is well-mixed [27].

**Sampling strategy**

Two sampling campaigns were performed in the Scheldt estuary, in November 1999 and June 2000. In the Rhine estuary, three sampling campaigns were conducted, in December 1999, September 2000, and October 2002. Results of both campaigns of 1999 were previously reported [10].

Sampling locations for surface sediments were evenly distributed over the entire estuary (see figure 7.2). Three box cores (average core depth 30 cm) were collected at each location and the complete cores were mixed, in order to obtain a sample representative of the location. Water samples were taken along the salinity gradient, at 2% salinity intervals (monitored on-line during the sampling campaigns). As a consequence, water sampling locations are different from those of the sediments. In the Scheldt estuary, additional water, SPM and sediment samples were collected just inside the canal Gent-Terneuzen.

Water sampling techniques were different for the different sampling campaigns. In both campaigns of 1999, samples were taken from the water surface (at a depth of approximately 0.5 m) using a stainless steel bucket. In the campaigns of 2000, a water sampling torpedo was used, which obtained water at 1.5 m depth.

For the 2002 campaign in the Rhine estuary, both sampling techniques were used at each sampling location, with one water sample taken with a bucket from the water surface, a second sample taken at 1.5 m depth using the sampling torpedo, and a third sample taken at the maximum depth the sampling torpedo could reach (between 2.7 and 6.7 m). The goal of this extensive sampling was to obtain insight into the vertical distribution of A$_9$PEO in the salinity stratified water column of this estuary. In addition to the samples taken along the salinity gradient, in the 2002 campaign samples were also collected in (locations R27, R29 and R30) and between (R26, R28 and R31) the exits of the main harbours of the Rhine.
estuary, to investigate the contribution of the harbours to the concentration profiles observed in the estuary. No sediments or SPM samples were collected during that campaign.

**Analysis**

The extraction procedures and LC-MS analysis of the water, SPM and sediment samples have been described in detail elsewhere [10].

Briefly, water samples were filtered and the glass fiber filters were extracted separately. Filtered water was acidified and extracted using Solid-Phase Extraction (SPE) with a C_{18}-SPE cartridge. Cartridges were eluted with methanol. Water samples were extracted immediately on board the sampling ship to avoid any possible conservation problems. Sediment samples were frozen until further treatment in the laboratory.

Wet sediment samples and filters (SPM samples) were Soxhlet extracted overnight with basic methanol. The extract was concentrated, nanopure water was added and this mixture was acidified and cleaned up using SPE as described above. A_9PEO_2 and NP labeled with ^{13}C-labeled aromatic rings were added as internal standards. Analysis was performed using reversed phase liquid chromatography coupled to electrospray mass spectrometry detection, as described previously [10]. Analyses were done in SIM mode, using positive ionization for A_9PEO, and negative ionization for A_9PEC and NP. The oligomers A_9PEO_1 and A_9PEO_2 were quantified separately with pure standards, while the longer oligomers were quantified together using a commercial standard mixture of on average 10 ethoxylate units. For NP, A_9PE_1C and A_9PE_2C pure standards were available (see structures in figure 7.1), and for longer A_9PE_{>2}C oligomers, the calibration of A_9PE_2C was used [10].

**Fate model structure**

The field data showed the analytes to be present in relevant concentrations in both the water, suspended particulate material and sediment compartments. Therefore, all three compartments are incorporated into the fate model. It is assumed that no atmospheric exchange takes place in the estuaries. For A_9PEO (Henry coefficient of 0.0003 Pa.m^3 mole^{-1} for A_9PEO_2) and A_9PEC, this seems reasonable. NP (Henry coefficient 0.6 Pa.m^3 mole^{-1}) is more volatile, and therefore it cannot be completely ruled out that some atmospheric exchange occurs for this compound [28]. A study of the estuarine fate of alkylphenols in the Hudson Bay by Van Ry et al. did suggest that atmospheric exchange is a relevant process for NP [17]. However, due to a complete lack of data on the atmospheric presence of NP in the investigated estuaries, this process was not yet incorporated into the model.

The description of the water movement was based on the actual geographies of the estuaries and on actual hydrological data. Exchange processes of analytes between water and SPM (sorption) and of SPM with sediment (sedimentation/erosion) were incorporated. For the
stratified Rhine estuary, exchange of dissolved analytes and SPM between the upper and lower water layer was included as well. In addition, biodegradation was incorporated into the model.

For modeling purposes, A₉PEO and their metabolites were divided into the following groups: A₉PEO₂, A₉PEO₁₂, A₉PEO₂C, A₉PE₁₂C and NP. One reason for this division was the fact that the short chain A₉PEO₁₂ are considered as metabolites of the long chain A₉PEO₂ in the non-oxidative hydrolytic pathway. In addition, it is interesting to consider the fate and behaviour of these two oligomers separately from a toxicological point of view, as these short chain A₉PEO₁₂ are the only endocrine disrupting oligomers.

The software used in this study is the ECoS 3.0 modeling framework. This software is specifically designed to model physical, chemical and biological processes in estuaries. The scheme in figure 7.3 shows the structure and input parameters of the model.

![Diagram of ECoS model](image)

**Figure 7.3:** Scheme of the ECoS model, showing the required input data.
Optimization of the model was first done using the data of the sampling campaign in the Scheldt estuary of 1999, as those results showed the smoothest dissolved concentration profiles and were therefore easiest to work with. Then, the model was adjusted to optimize it for the data sets of the other campaigns.

In the ECoS modeling framework, it is necessary to define boundary conditions of the model space (analyte concentrations, salinity and SPM at the river and open sea end of the estuary). These boundaries were fixed at the actual concentrations measured in the field samples. In order to fit the data of the different sampling campaigns, the model scenarios were run separately, using boundary concentrations corresponding to the actual concentrations at the time of sampling. It was assumed that the fluctuation of the analyte concentrations at the boundaries is relatively small.

### 7.3. Results and discussion

#### 7.3.1 Model optimization

**Hydrology**

For both the Scheldt and Rhine estuary, data on actual freshwater input at the head of the estuaries were provided by the Dutch Ministry of Transport, Public Works and Water Management. Ten day average values were used in the Scheldt model, while in the Rhine estuary 5 day averaged input values were used. For the Rhine estuary, actual data on the input of the additional freshwater source the river Oude Maas were also incorporated into the model using 5 day average values. In the Scheldt estuary, the additional freshwater input of the canal Gent-Terneuzen was fixed at the average value of 10 m$^3$ s$^{-1}$.

To describe the actual shape of the estuaries, they were divided into a number of segments, each with their known depth, width and cross-sectional area. Transport of chemicals in the water column is considered as a longitudinal one-dimensional process described by the advection-dispersion equation proposed by Pritchard [29]. For the derivation of the dispersion coefficients ($K_x$) between the water segments, the dilution profile of the conservatively behaving salinity was used. The assumption is made that the salinity gradient is in steady state, that is the advection and dispersion balance each other. With an integrated version of the advection-dispersion equation, $K_x$ values can be determined for any position in the estuary from the slope of the plot of salinity against distance [20].

The Scheldt estuary was divided into 19 segments of around 5 km and treated as vertically well-mixed [21, 25]. These data were taken from the study by Steen et al. [20], and were originally derived from the SAWES model [30].
The optimized dispersion coefficients for the segments of the Scheldt estuary ranged from 86 to 335 m$^2$ s$^{-1}$, and are in the same range as values reported in literature for this estuary [20, 23, 31]. Figure 7.4a shows the calculated salinity curve obtained with this method. When the $K_x$ values optimized for the 1999 sampling campaign were used to describe the salinity curve of the 2000 sampling campaign, an acceptable fit was obtained as well. The description of salinity in time was also modeled correctly, as can be seen in figure 7.4b, which shows the calculated and actual salinities at three locations in the Scheldt estuary over a period of 700 days.

![Figure 7.4: a) Calculated and actual salinity profiles for the Scheldt estuary data of 1999. ◆ = actual salinities; striped line = calculated salinity profile. b) Calculated and actual salinities at three locations in the Scheldt estuary during 700 days (day 1 is January 1st, 1999). ■ = actual salinity at x=95 km; full line = calculated salinity at x=95 km; ◆ = actual salinity at x=70 km; dotted line = calculated salinity at x=70 km ▲ = actual salinity at x=37 km; striped line = calculated salinity at x=37 km.](image)

The segmentation and segment geometries of the Rhine estuary were based on the DELWAQ model [24]. This estuary was divided into 42 segments of approximately 1 km length each. The vertical stratification of the water column was incorporated into the model by horizontally dividing all segments of the Rhine estuary into equal surface and bottom layers, between which exchange of matter was possible. As the field data (see section 3.2.3) showed that the concentrations in the surface layer were on average higher by a factor of 2.5 than in the bottom layer, the exchange between the two layers was programmed to be at equilibrium when this ratio was reached. In addition, as the
field data showed a stronger stratification of analyte concentrations in the saline region, the equilibrium ratio was made salinity dependent. Stratification of A9PEO and NP in an estuarine water column was previously reported for the Krka estuary (Croatia) by Kveštak et al. [7].

Water dispersion coefficients for the Rhine estuary were again determined from the salinity profiles in the estuary. Two separate series of $K_x$ values were optimized, because the salinity profiles of the surface and bottom water layers were different. As the salinities in the upstream part of the estuary were close to 0, in that region moderate $K_x$ values of 250 m$^2$ s$^{-1}$ were chosen. At the saline end of the estuary, for some segments relatively high $K_x$ values (up to 800 m$^2$ s$^{-1}$) were necessary to describe the salinity profiles. With moderate $K_x$ values, the modeled salt intrusion would be significantly smaller than observed in the field. A comparison of the calculated and actual salinities during the 2002 sampling campaign in the Rhine estuary (surface and maximum depth samples only) is shown in figure 7.5.

![Figure 7.5: Calculated and actual salinity profiles for the Rhine data of 2002.](image)

$\bullet$ = actual salinities in surface water layer; striped line = calculated salinity profile surface layer; $\Delta$ = actual salinities in bottom water layer; dotted line = calculated salinity profile bottom layer.

Suspended particulate material

The movement of SPM in the horizontal direction was described by advection and dispersion, while for movement in the vertical direction, sedimentation and erosion were incorporated into the model. Downstream movement of SPM is the result of advective movement with the water, and therefore increases with water velocity ($U_w$). A contrary process occurs due to the
asymmetry between the rise and fall of the tide caused by frictional dissipation of tidal energy, causing a more rapid flood and a slower ebb in the estuary, which results in an upstream transport of SPM. Therefore, the velocity of SPM ($U_{x,spm}$) was simulated to increase with water velocity, and decrease with tidal range ($R$) and salinity ($S$), according to the equation $U_{x,spm} = a_1U_w - b_1R*S$ [32].

Dispersion of the SPM ($K_{x,spm}$) increased with both water velocity, the tidal range and salinity, via the equation $K_{x,spm} = a_2U_w + b_2R*S$.

With these equations, a turbidity cloud is present when $U_{x,spm}=0$, or when $a_1U_w = b_1R*S$. The location of this maximum can be shifted by changing coefficients $a_1$ and $b_1$. In the Scheldt estuary model, $a_1$ and $b_1$ are adjusted so that $U_{x,spm}=0$ at $x=20$ km, as it is known from literature the turbidity cloud in the Scheldt estuary occurs in that region at average river discharge [23].

For the Scheldt estuary, the sedimentation and erosion rates of SPM were fitted to both the observed SPM concentration profile in the estuary and the average analyte concentrations in both compartments. Exchange of SPM with the surface sediment was estimated by Van Maldegem et al. to be between 0.1 and 1 kg m$^{-2}$ day$^{-1}$ for the whole Scheldt estuary [26]. In this study, a default value of 0.17 kg m$^{-2}$ day$^{-1}$ (0.002 g m$^{-2}$ s$^{-1}$) was chosen for both sedimentation and erosion. To optimize the fit of the SPM concentration profile, sedimentation or erosion fluxes were adjusted in certain areas of the estuary [26]. According to Van Maldegem et al., the net sedimentation is highest at Saeftinge ($x=35$-$45$ km), and close to zero around Antwerp [26]. In the downstream section of the estuary, an area with net resuspension is present. In the current model, the adjusted maximum sedimentation rate was 0.247 kg m$^{-2}$ day$^{-1}$ at $x=45$ km (keeping the local erosion rate at 0.17 kg m$^{-2}$ day$^{-1}$), and the maximum erosion rate was 0.251 kg m$^{-2}$ day$^{-1}$ at $x=60$ km (keeping the local sedimentation rate at 0.17 kg m$^{-2}$ day$^{-1}$).

In the Scheldt campaigns of 1999 and 2000, the field data for SPM showed a turbidity cloud (relatively high SPM concentration) of respectively 27 and 35 mg L$^{-1}$ around Hansweert ($x=55$ km). In the campaign of 2000 only, a second SPM maximum (127 mg L$^{-1}$) situated near Antwerp (at the location where the salinity starts to increase, $x=15$ km) was observed. The maximum near Antwerp is considered a ‘classical’ maximum turbidity zone occurring because the advection and dispersion of SPM are in equilibrium in that region, while the other SPM maximum occurs due to local net resuspension [26].

The SPM boundary concentrations in the model were fixed at the values of the actual samples. Consequently, the SPM concentration for the campaign of 1999 at $x=0$ km was set low (10 mg L$^{-1}$), resulting in only one SPM maximum at $x=55$ km, the one near Antwerpen being absent. Results for the calculated and actual SPM concentrations at the 1999 and 2000 sampling days are shown in figure 7.6. Due to the increased sedimentation rate near Saeftinge and the increased erosion further downstream used in the model, the resulting
calculated SPM maximum is not situated at the location where the velocity of SPM \( (U_{x,spm}) \) is 0 \( (x=20 \text{ km}) \) but more downstream \( (x=55 \text{ km}) \).

For the Rhine estuary, an exchange of SPM between the surface and bottom water layer was incorporated, and exchange of SPM between water and sediment was only possible for the bottom layer. For lack of detailed data on sedimentation rates in the Rhine estuary, the SPM exchange rates between both the surface and bottom water layer and the bottom water layer and sediment were taken to be equal to the default exchange rates of SPM between sediment and water in the Scheldt estuary \( (0.17 \text{ kg m}^{-2} \text{ day}^{-1}) \).

![Figure 7.6: Calculated and actual suspended particulate material concentrations in the Scheldt estuary at the two sampling times. □ = actual SPM concentration 1999; dotted line = calculated SPM concentration 1999; ▲ = actual SPM concentration 2000; striped line = calculated SPM concentration 2000.](image)

**Biodegradation**

After the hydrology of the estuaries had been modeled, biodegradation processes were optimized. The reason to optimize biodegradation before the sorption processes was that the field data suggested biodegradation to be the main environmental process in the estuary \([10]\). Sorption was neglected in this procedure.

In the fate model, biodegradation is assumed to occur only in the dissolved phase. The oxidative hydrolytic pathway is assumed to be followed, resulting in the following modeled degradation routes: \( \text{A}_9\text{PEO}_{12} \rightarrow \text{A}_9\text{PE}_{12}C \rightarrow \text{A}_9\text{PE}_{1,2}C \rightarrow \text{X}; \text{A}_9\text{PEO}_{1,2} \rightarrow \text{A}_9\text{PE}_{1,2}C \rightarrow \text{X} \); and \( \text{NP} \rightarrow \text{X} \) (X signifies subsequent metabolites, e.g. CAPEC, see figure 7.1 \([12]\)).
Biodegradation rates were adjusted to optimize the fits of the calculated dissolved concentration profiles of \( A_9\text{PEO} \) and metabolites to the actual profiles. The optimization of the biodegradation rates for \( A_9\text{PEO}_{-2}, A_9\text{PEO}_{1,2}, \text{NP}, A_9\text{PE}_{-2}\text{C} \) and \( A_9\text{PE}_{1,2}\text{C} \) was performed for the Scheldt data of the 1999 and 2000 sampling campaigns separately. Evidently, the rates for \( A_9\text{PEO} \) must be fitted before \( A_9\text{PEC} \), as the degradation of the surfactant results in formation of \( A_9\text{PEC} \), and therefore influences the fit of the subsequent degradation of \( A_9\text{PEC} \). The optimum biodegradation rates are shown in table 7.1.

In addition to the optimum biodegradation rates, validity intervals were defined, based on the quality of the analytical method for the field samples. After running the model with an adjusted biodegradation rate, for each model segment the percentual deviation between the concentration calculated with the new scenario and that of the optimum scenario was determined. These values were averaged, and compared to the relative standard deviation of the recovery of the analytical method (14, 5 and 13% for \( A_9\text{PEO}, A_9\text{PEC} \) and \( \text{NP} \), respectively [10]). When the former value is lower than the latter, the biodegradation rate lies within the validity interval.

As an example, when a biodegradation rate of 0.049 is chosen for \( A_9\text{PEO}_{-2} \) (1999 data, see table 7.1), the concentrations of the dissolved profile calculated are higher than those obtained with the optimum biodegradation value (0.061). When for each segment in the estuary the concentrations are compared with the optimum profile, the differences in concentrations are on average 14%. This value is equal to the relative standard deviation of the recovery of the analytical method for this compound, and therefore this biodegradation rate is defined to be the minimum value of the validity interval.

For \( A_9\text{PEO} \), the half-life corresponding to the optimum biodegradation rate is 10-11 days (1999 data), which lies within the range of values reported in literature (ranging from 1.9 to 69 days [33-35]).

No metabolites of \( \text{NP} \) were analyzed in the field studies, and therefore, the biodegradation rates are slightly less reliable than those of \( A_9\text{PEO} \). Due to the relative volatility of \( \text{NP} \) (compared to \( A_9\text{PEO} \)), a portion of the disappearance of \( \text{NP} \) from the water column may have been caused by volatilization instead of degradation.

For \( A_9\text{PEC} \) and \( \text{NP} \), biodegradation rates were smaller during the 1999 campaign, which was performed in winter. Biodegradation rates of \( A_9\text{PEO}_{1,2} \) were not significantly different for the two campaigns, while biodegradation of \( A_9\text{PEO}_{-2} \) proceeded more slowly in summer than in winter. Oxygen concentrations did not deviate significantly between the two sampling campaigns (both measured at 1.5 m depth).

For the Rhine estuary model, the same biodegradation rates as optimized for the Scheldt campaign of 1999 were employed.
Table 7.1: Process constants with validity intervals for the optimum model scenarios of the Scheldt estuary.

<table>
<thead>
<tr>
<th></th>
<th>biodegradation rate constant (day⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1999 data</td>
<td>2000 data</td>
</tr>
<tr>
<td>A₉PEO₂</td>
<td>0.061 (0.049-0.077)</td>
<td>0.000 (0-0.007)</td>
</tr>
<tr>
<td>A₉PEO₂₄</td>
<td>0.070 (0.060-0.085)</td>
<td>0.057 (0.047-0.072)</td>
</tr>
<tr>
<td>A₉PE₂C</td>
<td>0.017 (0.015-0.019)</td>
<td>0.030 (0.028-0.033)</td>
</tr>
<tr>
<td>A₉PE₁₂C</td>
<td>0.018 (0.016-0.020)</td>
<td>0.049 (0.046-0.053)</td>
</tr>
<tr>
<td>NP</td>
<td>0.032* (0.024-0.043)</td>
<td>0.056* (0.046-0.070)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>sorption coefficient K_d (L kg⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1999 data</td>
<td>2000 data</td>
</tr>
<tr>
<td>A₉PEO₂</td>
<td>47000 (18800-89300)</td>
<td>47000 (31500-70500)</td>
</tr>
<tr>
<td>A₉PEO₂₄</td>
<td>33700 (10110-67400)</td>
<td>33700 (0-84300)</td>
</tr>
<tr>
<td>A₉PE₂C</td>
<td>645 (0-5160)</td>
<td>645 (0-10320)</td>
</tr>
<tr>
<td>A₉PE₁₂C</td>
<td>645 (0-4580)</td>
<td>645 (0-13545)</td>
</tr>
<tr>
<td>NP</td>
<td>24900 (7221-52290)</td>
<td>24900 (0-72210)</td>
</tr>
</tbody>
</table>

*: this rate includes the possible disappearance from the water phase by volatilization. For the relatively volatile NP (compared to A₉PEO), this process may be of significance.

Sorption

After the biodegradation rates of all analytes had been fitted, sorption was introduced into the model. Average distribution coefficients between SPM and water (sorption coefficients, K_d) of the analytes were used as calculated from the analyses of the water and SPM samples of both estuaries. The calculated K_d values were in agreement with other literature data [6, 8]. As for none of the field data a salinity dependence of the K_d was observed, no salting out effects were incorporated into the model. Although in most SPM samples A₉PEC concentrations were below detection limits, sorption was incorporated in the model for these compounds, with a K_d value based on the few SPM samples in which A₉PEC were detected [10].

Resulting analyte concentrations in SPM and sediment as calculated by the model were of the same order of magnitude as the field data, and therefore no further optimization of sorption coefficients was performed. Again, validity intervals with minimum and maximum sorption coefficients were determined (see table 7.1) as described in the previous section (Biodegradation, p. 174).

After the introduction of sorption into the model, the biodegradation rates were again slightly adjusted, as the sorption processes will have some influence on the fit. Degradation
rates had to be slightly increased, as the analytes sorbed to the SPM are ‘shielded’ from degradation.

**Additional sources**
To obtain acceptable model fits of the concentration profiles in the Rhine estuary, it was necessary to incorporate two additional point sources. These were the Oude Maas tributary (x=18 km) and a source in the Rotterdam harbour area (x=12 km). Input concentrations were fitted to the concentration profiles in the estuary, as the actual analyte concentrations were unknown for these sources. The values are shown in table 7.2 (see also p. 185-187). A recent report on the analysis of A9PEO in rain water of this region confirms the presence of these suspected sources [36].

For the additional water source in the Scheldt estuary (canal Gent-Terneuzen, x=81 km), initially the actual A9PEO, A9PEC and NP concentrations were fixed in the model. As a final optimization step, these values were also fitted to the observed concentration profiles in the estuary, and the adjusted concentrations used in the optimum scenario are shown in table 7.2 (2-10 times the actual concentrations in the canal for the different analytes).

Table 7.2: Final input values of dissolved concentrations and loads of the sources used in the optimum model scenarios for the Scheldt estuary (1999) and Rhine estuary (2002).

<table>
<thead>
<tr>
<th>source</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A9PEO_{2}</td>
</tr>
<tr>
<td>Scheldt estuary</td>
<td></td>
</tr>
<tr>
<td>canal Gent-Terneuzen (ng/L)</td>
<td>1540</td>
</tr>
<tr>
<td>total input canal Gent-Terneuzen (kg/day)</td>
<td>2.3</td>
</tr>
<tr>
<td>total input at head of estuary (kg/day)</td>
<td>11.4</td>
</tr>
<tr>
<td>Rhine estuary</td>
<td></td>
</tr>
<tr>
<td>Oude Maas surface layer (ng/L)</td>
<td>0</td>
</tr>
<tr>
<td>Oude Maas bottom layer (ng/L)</td>
<td>0</td>
</tr>
<tr>
<td>total input Oude Maas (kg/day)</td>
<td>0</td>
</tr>
<tr>
<td>harbour surface layer (ng/L)</td>
<td>4000</td>
</tr>
<tr>
<td>harbour bottom layer (ng/L)</td>
<td>5500</td>
</tr>
<tr>
<td>total input harbour (kg/day)</td>
<td>8.2</td>
</tr>
<tr>
<td>total input at head of estuary (kg/day)</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Chapter 7

7.3.2 Comparison to field results

A short description of the results of the several sampling campaigns will be given, followed by the comparison of model results and field data. The results of the sampling campaigns of 1999 (next section) were reported previously by Jonkers et al. (Chapter 5) [10].

Sampling campaigns of 1999

The dissolved concentration profiles in the Scheldt estuary showed a stronger than conservative decrease in $A_9$PEO from Antwerp to Vlissingen, while the $A_9$PEC metabolites concentration decreased more slowly. The $\Sigma A_9$PEC/$\Sigma A_9$PEO concentration ratio therefore increased going downstream, suggesting the formation of $A_9$PEC out of $A_9$PEO in the estuary. The dissolved $A_9$PEC/$A_9$PEO ratio reached a maximum near Terneuzen, followed by a decrease further downstream. The water inside canal Gent-Terneuzen showed a high $A_9$PEC/$A_9$PEO ratio as well.

For the Rhine estuary, the profiles of the water concentrations appeared to be less pronounced, probably due to more complicated water flows and point sources in the Rotterdam harbour area. Dissolved $A_9$PEC/$A_9$PEO ratios were fairly constant with values between 2 and 3. These findings indicate that biodegradation is only limited in this estuary, which is not surprising because of the high water flow and short residence time. Maximum dissolved estuarine concentrations amounted to of 1.3, 1.0, 0.9 and 8.1 $\mu$g L$^{-1}$ for $A_9$PEO$_{22}$, $A_9$PEO$_{1,2}$, NP and $\Sigma A_9$PEC, respectively.

In sediments, concentrations normalized to the fraction with particle sizes <63$\mu$m showed a maximum of 4500 ($A_9$PEO$_{22}$), 998 ($A_9$PEO$_{1,2}$) and 2600 (NP) ng g$^{-1}$, whereas $A_9$PEC were only present sporadically. No gradients were observed for the sediment concentrations. Concentrations in estuarine SPM varied strongly from 690 to 115,000 ng g$^{-1}$ for $A_9$PEO and from 190 to 30,400 ng g$^{-1}$ for NP.

Sampling campaign of 2000

The concentrations of $A_9$PEO, NP and $A_9$PEC observed in the sampling campaign of 2000 are listed in tables 7.3 and 7.4. In general, dissolved concentrations were about half of those observed in the first sampling campaigns. The highest dissolved concentrations of $A_9$PEO were observed near Antwerp, with values of 450 ng L$^{-1}$ for $A_9$PEO$_{22}$ and 680 ng L$^{-1}$ for $A_9$PEO$_{1,2}$. In the Rhine estuary, dissolved $A_9$PEO concentrations were invariably below 250 ng L$^{-1}$. The concentrations of NP observed in water were mostly below the level of 100 ng L$^{-1}$. Only in the upper Scheldt estuary, dissolved concentrations of NP were higher, with a maximum of 960 ng L$^{-1}$ near Antwerp. The highest dissolved estuarine $\Sigma A_9$PEC concentrations were found near Antwerp as well. An overall maximum value of 6500 ng L$^{-1}$ was observed inside the canal Gent-Terneuzen.
Table 7.3: Concentrations of A<sub>9</sub>PEO and their metabolites measured in surface sediment and suspended particulate material in the Rhine and Scheldt estuary, 2000.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>organic carbon (%)</th>
<th>fraction &lt;63μm</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;1&lt;/sub&gt; (ng/g d.w.)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;2&lt;/sub&gt; (ng/g d.w.)</th>
<th>A&lt;sub&gt;9&lt;/sub&gt;PEO&lt;sub&gt;2&lt;/sub&gt; total (ng/g d.w.)</th>
<th>NP (ng/g d.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhine sediments, 2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1s</td>
<td>0.15</td>
<td>0.048</td>
<td>&lt;1.3</td>
<td>1.3</td>
<td>3.9</td>
<td>7.1</td>
</tr>
<tr>
<td>R2s</td>
<td>0.17</td>
<td>0.036</td>
<td>&lt;1.3</td>
<td>1.3</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>R3s</td>
<td>0.06</td>
<td>0.005</td>
<td>&lt;1.3</td>
<td>1.4</td>
<td>14</td>
<td>3.9</td>
</tr>
<tr>
<td>R4s</td>
<td>1.5</td>
<td>0.35</td>
<td>8.7</td>
<td>16</td>
<td>121</td>
<td>124</td>
</tr>
<tr>
<td>R5s</td>
<td>0.46</td>
<td>0.32</td>
<td>3.7</td>
<td>3.6</td>
<td>22</td>
<td>54</td>
</tr>
<tr>
<td>R6s</td>
<td>2.3</td>
<td>0.50</td>
<td>19</td>
<td>25</td>
<td>123</td>
<td>223</td>
</tr>
<tr>
<td>R7s</td>
<td>0.09</td>
<td>0.012</td>
<td>&lt;1.3</td>
<td>1.2</td>
<td>26</td>
<td>16</td>
</tr>
<tr>
<td>R8s</td>
<td>0.11</td>
<td>0.004</td>
<td>3.5</td>
<td>1.4</td>
<td>16</td>
<td>5.7</td>
</tr>
<tr>
<td>Scheldt sediments, 2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1s</td>
<td>0.2</td>
<td>0.028</td>
<td>&lt;1.3</td>
<td>1.4</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>S2s</td>
<td>0.18</td>
<td>0.024</td>
<td>&lt;1.3</td>
<td>0.6</td>
<td>13</td>
<td>3.7</td>
</tr>
<tr>
<td>S3s</td>
<td>0.06</td>
<td>0.009</td>
<td>&lt;1.3</td>
<td>&lt;0.3</td>
<td>2.0</td>
<td>3.6</td>
</tr>
<tr>
<td>S4s</td>
<td>2.1</td>
<td>0.59</td>
<td>33</td>
<td>34</td>
<td>554</td>
<td>1014</td>
</tr>
<tr>
<td>S5s</td>
<td>0.07</td>
<td>0.007</td>
<td>&lt;1.3</td>
<td>0.8</td>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>S6s</td>
<td>&lt;0.05</td>
<td>0.009</td>
<td>&lt;1.3</td>
<td>1.0</td>
<td>7.1</td>
<td>6.9</td>
</tr>
<tr>
<td>S7s</td>
<td>0.2</td>
<td>0.045</td>
<td>&lt;1.3</td>
<td>1.5</td>
<td>11</td>
<td>44</td>
</tr>
<tr>
<td>S8s</td>
<td>0.09</td>
<td>0.008</td>
<td>4.5</td>
<td>1.6</td>
<td>24</td>
<td>-</td>
</tr>
<tr>
<td>S9s</td>
<td>2.9</td>
<td>0.52</td>
<td>36</td>
<td>32</td>
<td>332</td>
<td>1057</td>
</tr>
<tr>
<td>S10s</td>
<td>7.8</td>
<td>0.44</td>
<td>5.3</td>
<td>10</td>
<td>49</td>
<td>375</td>
</tr>
<tr>
<td>SCs</td>
<td>1.4</td>
<td>0.41</td>
<td>32</td>
<td>38</td>
<td>293</td>
<td>1026</td>
</tr>
<tr>
<td>Rhine SPM, 2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R11f</td>
<td>1.3</td>
<td>&lt;88</td>
<td>264</td>
<td>1576</td>
<td>437</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R12f</td>
<td>5.5</td>
<td>&lt;88</td>
<td>&lt;19</td>
<td>5205</td>
<td>2319</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R13f</td>
<td>5.3</td>
<td>&lt;88</td>
<td>831</td>
<td>4840</td>
<td>2158</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R14f</td>
<td>5.0</td>
<td>&lt;88</td>
<td>776</td>
<td>4227</td>
<td>1993</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R15f</td>
<td>5.8</td>
<td>&lt;88</td>
<td>960</td>
<td>4548</td>
<td>1387</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R16f</td>
<td>5.3</td>
<td>&lt;88</td>
<td>566</td>
<td>13605</td>
<td>6105</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R17f</td>
<td>5.0</td>
<td>&lt;88</td>
<td>78</td>
<td>7616</td>
<td>1550</td>
<td>&lt;24</td>
</tr>
<tr>
<td>R18f</td>
<td>4.2</td>
<td>513</td>
<td>97</td>
<td>1965</td>
<td>1230</td>
<td>&lt;24</td>
</tr>
<tr>
<td>Scheldt SPM, 2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S11f</td>
<td>10.8</td>
<td>2344</td>
<td>177</td>
<td>2808</td>
<td>11025</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S12f</td>
<td>2.8</td>
<td>196</td>
<td>26</td>
<td>509</td>
<td>8694</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S13f</td>
<td>4.6</td>
<td>&lt;88</td>
<td>66</td>
<td>1022</td>
<td>5943</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S14f</td>
<td>5.7</td>
<td>1270</td>
<td>309</td>
<td>2752</td>
<td>1856</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S15f</td>
<td>4.0</td>
<td>&lt;88</td>
<td>154</td>
<td>2294</td>
<td>764</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S16f</td>
<td>4.8</td>
<td>&lt;88</td>
<td>305</td>
<td>1641</td>
<td>1052</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S17f</td>
<td>5.7</td>
<td>&lt;88</td>
<td>313</td>
<td>4279</td>
<td>2553</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S18f</td>
<td>6.3</td>
<td>&lt;88</td>
<td>319</td>
<td>5977</td>
<td>2464</td>
<td>&lt;24</td>
</tr>
<tr>
<td>S19f</td>
<td>5.9</td>
<td>191</td>
<td>194</td>
<td>1208</td>
<td>1762</td>
<td>1812</td>
</tr>
<tr>
<td>S20f</td>
<td>4.3</td>
<td>386</td>
<td>225</td>
<td>1059</td>
<td>1233</td>
<td>702</td>
</tr>
<tr>
<td>S21f</td>
<td>-</td>
<td>448</td>
<td>280</td>
<td>1093</td>
<td>1651</td>
<td>1424</td>
</tr>
<tr>
<td>S22f</td>
<td>7.6</td>
<td>1171</td>
<td>731</td>
<td>2028</td>
<td>2480</td>
<td>6986</td>
</tr>
<tr>
<td>SCf</td>
<td>25.7</td>
<td>1231</td>
<td>3784</td>
<td>8176</td>
<td>16637</td>
<td>6056</td>
</tr>
</tbody>
</table>
Table 7.4: Dissolved concentrations of A$_2$PEO and their metabolites measured in the Rhine and Scheldt estuary, 2000.

<table>
<thead>
<tr>
<th></th>
<th>salinity (‰)</th>
<th>temperature (°C)</th>
<th>oxygen concentration (mg L$^{-1}$)</th>
<th>SPM (mg L$^{-1}$)</th>
<th>A$_2$PEO$_1$ (ng L$^{-1}$)</th>
<th>A$_2$PEO$_2$ (ng L$^{-1}$)</th>
<th>A$<em>2$PEO$</em>{2,15}$ (ng L$^{-1}$)</th>
<th>NP (ng L$^{-1}$)</th>
<th>A$<em>2$PE$</em>{2,C}$ (ng L$^{-1}$)</th>
<th>A$<em>2$PE$</em>{3,C}$ (ng L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhine estuary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R11w</td>
<td>29.0</td>
<td>17.7</td>
<td>7.6</td>
<td>20</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>&lt;30</td>
<td>15</td>
<td>64</td>
<td>&lt;13</td>
</tr>
<tr>
<td>R12w</td>
<td>19.0</td>
<td>19.1</td>
<td>8.2</td>
<td>6</td>
<td>&lt;15</td>
<td>8.4</td>
<td>36</td>
<td>13</td>
<td>110</td>
<td>75</td>
</tr>
<tr>
<td>R13w</td>
<td>14.0</td>
<td>19.9</td>
<td>8.2</td>
<td>6</td>
<td>&lt;15</td>
<td>7.9</td>
<td>185</td>
<td>18</td>
<td>60</td>
<td>&lt;13</td>
</tr>
<tr>
<td>R14w</td>
<td>11.5</td>
<td>20.3</td>
<td>8.0</td>
<td>6</td>
<td>&lt;15</td>
<td>11</td>
<td>225</td>
<td>38</td>
<td>83</td>
<td>40</td>
</tr>
<tr>
<td>R15w</td>
<td>7.5</td>
<td>17.9</td>
<td>8.6</td>
<td>6</td>
<td>&lt;15</td>
<td>23</td>
<td>66</td>
<td>88</td>
<td>188</td>
<td>116</td>
</tr>
<tr>
<td>R16w</td>
<td>5.3</td>
<td>18.1</td>
<td>9.2</td>
<td>6</td>
<td>&lt;15</td>
<td>9.5</td>
<td>62</td>
<td>38</td>
<td>177</td>
<td>144</td>
</tr>
<tr>
<td>R17w</td>
<td>2.9</td>
<td>18.1</td>
<td>9.3</td>
<td>7</td>
<td>&lt;15</td>
<td>23</td>
<td>68</td>
<td>48</td>
<td>77</td>
<td>&lt;13</td>
</tr>
<tr>
<td>R18w</td>
<td>1.0</td>
<td>18.3</td>
<td>9.1</td>
<td>26</td>
<td>&lt;15</td>
<td>12</td>
<td>196</td>
<td>12</td>
<td>109</td>
<td>&lt;13</td>
</tr>
<tr>
<td>Scheldt estuary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S11w</td>
<td>32.6</td>
<td>17.0</td>
<td>7.8</td>
<td>4</td>
<td>&lt;15</td>
<td>6.8</td>
<td>&lt;30</td>
<td>50</td>
<td>37</td>
<td>&lt;13</td>
</tr>
<tr>
<td>S12w</td>
<td>30</td>
<td>18.3</td>
<td>8.4</td>
<td>50</td>
<td>&lt;15</td>
<td>29</td>
<td>42</td>
<td>62</td>
<td>82</td>
<td>47</td>
</tr>
<tr>
<td>S13w</td>
<td>27.5</td>
<td>18.7</td>
<td>8.1</td>
<td>15</td>
<td>&lt;15</td>
<td>8.4</td>
<td>34</td>
<td>58</td>
<td>49</td>
<td>&lt;13</td>
</tr>
<tr>
<td>S14w</td>
<td>23.8</td>
<td>19.2</td>
<td>7.8</td>
<td>13</td>
<td>&lt;15</td>
<td>9.9</td>
<td>55</td>
<td>28</td>
<td>77</td>
<td>66</td>
</tr>
<tr>
<td>S15w</td>
<td>21.1</td>
<td>19.5</td>
<td>7.9</td>
<td>35</td>
<td>19</td>
<td>16</td>
<td>144</td>
<td>55</td>
<td>329</td>
<td>488</td>
</tr>
<tr>
<td>S16w</td>
<td>17.9</td>
<td>19.9</td>
<td>8.0</td>
<td>27</td>
<td>18</td>
<td>43</td>
<td>175</td>
<td>81</td>
<td>150</td>
<td>212</td>
</tr>
<tr>
<td>S17w</td>
<td>15.2</td>
<td>20.1</td>
<td>7.2</td>
<td>21</td>
<td>22</td>
<td>27</td>
<td>55</td>
<td>92</td>
<td>200</td>
<td>267</td>
</tr>
<tr>
<td>S18w</td>
<td>11.9</td>
<td>20.5</td>
<td>6.5</td>
<td>19</td>
<td>56</td>
<td>73</td>
<td>193</td>
<td>105</td>
<td>321</td>
<td>499</td>
</tr>
<tr>
<td>S19w</td>
<td>9.0</td>
<td>20.9</td>
<td>5.5</td>
<td>27</td>
<td>81</td>
<td>88</td>
<td>195</td>
<td>184</td>
<td>359</td>
<td>691</td>
</tr>
<tr>
<td>S20w</td>
<td>6.0</td>
<td>21.6</td>
<td>3.2</td>
<td>127</td>
<td>49</td>
<td>48</td>
<td>111</td>
<td>282</td>
<td>360</td>
<td>598</td>
</tr>
<tr>
<td>S21w</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>145</td>
<td>99</td>
<td>186</td>
<td>394</td>
<td>905</td>
<td>1163</td>
</tr>
<tr>
<td>S22w</td>
<td>0.53</td>
<td>22.5</td>
<td>0.33</td>
<td>99</td>
<td>443</td>
<td>234</td>
<td>447</td>
<td>962</td>
<td>644</td>
<td>1042</td>
</tr>
<tr>
<td>SCw</td>
<td>4.3</td>
<td>23.0</td>
<td>5.1</td>
<td>3</td>
<td>73</td>
<td>200</td>
<td>543</td>
<td>272</td>
<td>1030</td>
<td>2339</td>
</tr>
</tbody>
</table>

Chapter 7
### Table 7.5: Dissolved concentrations of A₉PEO and metabolites measured in the Rhine estuary at different sampling depths, 2002.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Salinity (%)</th>
<th>SPM (mg L⁻¹)</th>
<th>A₉PEO₁ (ng L⁻¹)</th>
<th>A₉PEO₂ (ng L⁻¹)</th>
<th>A₉PEO₂₂ (ng L⁻¹)</th>
<th>NP (ng L⁻¹)</th>
<th>A₉PE₁C (ng L⁻¹)</th>
<th>A₉PE₂C (ng L⁻¹)</th>
<th>A₉PE₂₂C (ng L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water Rhine estuary surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R21w1</td>
<td>15.9</td>
<td>8</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>48</td>
<td>38</td>
<td>184</td>
<td>92</td>
<td>132</td>
</tr>
<tr>
<td>R22w1</td>
<td>11.6</td>
<td>14</td>
<td>&lt;15</td>
<td>9.4</td>
<td>108</td>
<td>58</td>
<td>219</td>
<td>116</td>
<td>167</td>
</tr>
<tr>
<td>R23w1</td>
<td>8.8</td>
<td>13</td>
<td>&lt;15</td>
<td>7.4</td>
<td>82</td>
<td>80</td>
<td>256</td>
<td>143</td>
<td>185</td>
</tr>
<tr>
<td>R24w1</td>
<td>6.0</td>
<td>13</td>
<td>&lt;15</td>
<td>16</td>
<td>84</td>
<td>34</td>
<td>293</td>
<td>194</td>
<td>248</td>
</tr>
<tr>
<td>R25w1</td>
<td>4.4</td>
<td>14</td>
<td>15</td>
<td>8.4</td>
<td>95</td>
<td>115</td>
<td>229</td>
<td>139</td>
<td>142</td>
</tr>
<tr>
<td>R26w1</td>
<td>0.37</td>
<td>26</td>
<td>&lt;15</td>
<td>64</td>
<td>299</td>
<td>67</td>
<td>283</td>
<td>170</td>
<td>187</td>
</tr>
<tr>
<td>R27w1</td>
<td>0.25</td>
<td>28</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>42</td>
<td>102</td>
<td>263</td>
<td>143</td>
<td>172</td>
</tr>
<tr>
<td>R28w1</td>
<td>0.32</td>
<td>16</td>
<td>24</td>
<td>17</td>
<td>126</td>
<td>66</td>
<td>284</td>
<td>175</td>
<td>174</td>
</tr>
<tr>
<td>R29w1</td>
<td>0.26</td>
<td>18</td>
<td>21</td>
<td>28</td>
<td>203</td>
<td>134</td>
<td>367</td>
<td>247</td>
<td>327</td>
</tr>
<tr>
<td>R30w1</td>
<td>0.18</td>
<td>20</td>
<td>32</td>
<td>8.2</td>
<td>95</td>
<td>113</td>
<td>264</td>
<td>143</td>
<td>178</td>
</tr>
<tr>
<td>R31w1</td>
<td>0.16</td>
<td>20</td>
<td>22</td>
<td>13</td>
<td>136</td>
<td>136</td>
<td>192</td>
<td>92</td>
<td>101</td>
</tr>
<tr>
<td>R32w1</td>
<td>0.16</td>
<td>22</td>
<td>&lt;15</td>
<td>7.1</td>
<td>59</td>
<td>123</td>
<td>278</td>
<td>181</td>
<td>183</td>
</tr>
<tr>
<td>R33w1</td>
<td>0.16</td>
<td>28</td>
<td>&lt;15</td>
<td>9.8</td>
<td>74</td>
<td>82</td>
<td>220</td>
<td>138</td>
<td>139</td>
</tr>
<tr>
<td><strong>Water Rhine estuary 1.5 m depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R21w2</td>
<td>23.3</td>
<td>8</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>38</td>
<td>30</td>
<td>90</td>
<td>53</td>
<td>45</td>
</tr>
<tr>
<td>R22w2</td>
<td>12.2</td>
<td>18</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>40</td>
<td>40</td>
<td>224</td>
<td>131</td>
<td>136</td>
</tr>
<tr>
<td>R23w2</td>
<td>9.0</td>
<td>15</td>
<td>&lt;15</td>
<td>6.0</td>
<td>38</td>
<td>48</td>
<td>265</td>
<td>170</td>
<td>179</td>
</tr>
<tr>
<td>R24w2</td>
<td>6.8</td>
<td>15</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>33</td>
<td>100</td>
<td>225</td>
<td>145</td>
<td>131</td>
</tr>
<tr>
<td>R25w2</td>
<td>4.6</td>
<td>16</td>
<td>&lt;15</td>
<td>9.1</td>
<td>43</td>
<td>92</td>
<td>225</td>
<td>125</td>
<td>110</td>
</tr>
<tr>
<td>R26w2</td>
<td>0.50</td>
<td>35</td>
<td>&lt;15</td>
<td>13</td>
<td>70</td>
<td>77</td>
<td>284</td>
<td>194</td>
<td>184</td>
</tr>
<tr>
<td>R27w2</td>
<td>0.70</td>
<td>61</td>
<td>&lt;15</td>
<td>13</td>
<td>66</td>
<td>94</td>
<td>201</td>
<td>100</td>
<td>73</td>
</tr>
<tr>
<td>R28w2</td>
<td>0.30</td>
<td>18</td>
<td>&lt;15</td>
<td>16</td>
<td>70</td>
<td>80</td>
<td>261</td>
<td>169</td>
<td>188</td>
</tr>
<tr>
<td>R29w2</td>
<td>0.30</td>
<td>22</td>
<td>21</td>
<td>40</td>
<td>178</td>
<td>105</td>
<td>316</td>
<td>203</td>
<td>193</td>
</tr>
<tr>
<td>R30w2</td>
<td>0.20</td>
<td>22</td>
<td>&lt;15</td>
<td>11</td>
<td>51</td>
<td>78</td>
<td>255</td>
<td>156</td>
<td>132</td>
</tr>
<tr>
<td>R31w2</td>
<td>0.16</td>
<td>24</td>
<td>&lt;15</td>
<td>6.8</td>
<td>42</td>
<td>162</td>
<td>330</td>
<td>216</td>
<td>202</td>
</tr>
<tr>
<td>R32w2</td>
<td>0.16</td>
<td>29</td>
<td>&lt;15</td>
<td>9.8</td>
<td>47</td>
<td>93</td>
<td>200</td>
<td>125</td>
<td>99</td>
</tr>
<tr>
<td>R33w2</td>
<td>0.16</td>
<td>29</td>
<td>&lt;15</td>
<td>6.3</td>
<td>43</td>
<td>152</td>
<td>285</td>
<td>202</td>
<td>203</td>
</tr>
<tr>
<td><strong>Water Rhine estuary maximum depth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R21w3</td>
<td>28.5</td>
<td>7</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>&lt;30</td>
<td>17</td>
<td>61</td>
<td>27</td>
<td>&lt;13</td>
</tr>
<tr>
<td>R22w3</td>
<td>23.6</td>
<td>13</td>
<td>&lt;15</td>
<td>&lt;6</td>
<td>&lt;30</td>
<td>28</td>
<td>104</td>
<td>63</td>
<td>42</td>
</tr>
<tr>
<td>R23w3</td>
<td>11.2</td>
<td>15</td>
<td>&lt;15</td>
<td>9.4</td>
<td>51</td>
<td>37</td>
<td>226</td>
<td>154</td>
<td>176</td>
</tr>
<tr>
<td>R24w3</td>
<td>10.6</td>
<td>15</td>
<td>&lt;15</td>
<td>7.1</td>
<td>40</td>
<td>36</td>
<td>213</td>
<td>130</td>
<td>141</td>
</tr>
<tr>
<td>R25w3</td>
<td>4.7</td>
<td>18</td>
<td>&lt;15</td>
<td>7.7</td>
<td>54</td>
<td>148</td>
<td>256</td>
<td>169</td>
<td>144</td>
</tr>
<tr>
<td>R26w3</td>
<td>0.86</td>
<td>36</td>
<td>&lt;15</td>
<td>12</td>
<td>54</td>
<td>59</td>
<td>273</td>
<td>194</td>
<td>209</td>
</tr>
<tr>
<td>R28w3</td>
<td>0.36</td>
<td>27</td>
<td>&lt;15</td>
<td>12</td>
<td>85</td>
<td>130</td>
<td>322</td>
<td>193</td>
<td>208</td>
</tr>
<tr>
<td>R31w3</td>
<td>0.16</td>
<td>25</td>
<td>&lt;15</td>
<td>14</td>
<td>76</td>
<td>123</td>
<td>211</td>
<td>124</td>
<td>106</td>
</tr>
<tr>
<td>R32w3</td>
<td>0.16</td>
<td>28</td>
<td>&lt;15</td>
<td>7.1</td>
<td>39</td>
<td>75</td>
<td>316</td>
<td>213</td>
<td>223</td>
</tr>
<tr>
<td>R33w3</td>
<td>0.16</td>
<td>33</td>
<td>&lt;15</td>
<td>11</td>
<td>42</td>
<td>121</td>
<td>197</td>
<td>122</td>
<td>99</td>
</tr>
</tbody>
</table>
In the Scheldt estuary, the dissolved concentration gradients along salinity reported for the campaign of 1999 could be observed again, with a faster than conservative decrease of both A$_9$PEO and metabolite concentrations. However, the decrease of A$_9$PEO was less steep than in the first campaign. Dissolved $\Sigma$A$_9$PEC/$\Sigma$A$_9$PEO ratios varied between 1.3 and 6.9, and did not show a clear maximum as observed during the 1999 campaign.

In the Rhine estuary, dissolved A$_9$PEC/A$_9$PEO ratios were determined between 0.3 and 5.4. Dissolved NP/A$_9$PEO ratios varied in both estuaries between 0.05 and 1.8. No clear spatial trends could be observed.

Normalizing the surface sediment data to the fraction $<63\mu$m resulted in maximum concentrations of 4000 (A$_9$PEO$_{>2}$, location R8s), 1200 (A$_9$PEO$_{1,2}$, R8s) and 2000 ng g$^{-1}$ (NP, S9s). Concentrations were in the same range as in the campaigns of 1999. A$_9$PEC were detected in half the number of sediments collected, at a maximum normalized concentration of 3200 ng g$^{-1}$. No spatial trends were observed for concentrations in sediment.

The median contributions of the analytes sorbed onto SPM to the total water concentrations (dissolved + sorbed) calculated for both estuaries amounted to 35, 20, 37 and 16% for A$_9$PEO$_{>2}$, A$_9$PEO$_{1,2}$, NP and A$_9$PEC, respectively. For this calculation, only those samples were used for which both phases had concentrations above detection limits.

$K_{OC}$ values were calculated for A$_9$PEO and NP. For both analytes values were found to vary between log $K_{OC}$ = 4.2 and 7.1. Average log $K_{OC}$ values (+ standard deviations) were 5.8 ± 0.5 (A$_9$PEO$_{>2}$), 5.5 ± 0.7 (A$_9$PEO$_{1,2}$) and 6.0 ± 0.5 (NP). For the five SPM samples in which A$_9$PEC were detected, a log $K_{OC}$ was calculated of 4.5 ± 0.3.

**Sampling campaign of 2002**

Table 7.5 shows the analytical results for the 2002 water sampling campaign in the Rhine estuary. At locations R21 to R24, the salinity values illustrate the vertical stratification of the water column. At the locations upstream, salinities were close to 0 both at the surface and at greater depth.

Maximum concentrations amounted to 300 (A$_9$PEO$_{>2}$), 70 (A$_9$PEO$_{1,2}$), 160 (NP) and 940 ng L$^{-1}$ (A$_9$PEC). A$_9$PEC were usually present at higher concentrations than A$_9$PEO, with a median dissolved $\Sigma$A$_9$PEC/$\Sigma$A$_9$PEO concentration ratio of 7.3.

At all sampling locations except one (location R27), A$_9$PEO concentrations were higher in the water samples taken from the surface than those taken at greater depth. This vertical stratification of A$_9$PEO was present both in the saline part of the estuary and in the part where the complete water column consists of freshwater. The stratification did increase at higher salinities, with dissolved ratios of A$_9$PEO$_{surface}$/A$_9$PEO$_{max, depth}$ increasing from 1.5 at a bottom water salinity of 0.16 to 3.9 at a bottom water salinity of 28. Apparently, the vertical stratification of A$_9$PEO in the water column is not only caused by the stratification
of the water, but also by the surface active properties of A9PEO itself. For the metabolites A9PEC and NP, a vertical stratification is only observed at the saline end of the estuary. Concentration ratios of A9PEC\(_{\text{surface}}/A9PEC_{\text{max, depth}}\) and NP\(_{\text{surface}}/NP_{\text{max, depth}}\) are around one at most locations, and increase at locations R21 to R24 to 2.2 (A9PEC) and 4.3 (NP). The fact that these compounds are hardly surface active explains the absence of a stratification in the freshwater part of the estuary.

The lowest dissolved A9PEO concentrations in the Rhine estuary were found at both the river and the sea end boundaries of the estuaries (at all sampling depths). Maximum concentrations were observed around the harbours of Rotterdam. Apparently, local sources such as the harbours or the river Oude Maas play a more important role in the distribution of A9PEO in the estuary than the input from the Rhine and the North Sea. For NP and A9PEC, concentrations were lowest at the sea end of the estuary, and fairly evenly distributed in the rest of the area.

Validation procedure
As mentioned above, the analytical results yielded smooth spatial concentration profiles for the dissolved analytes in most sampling campaigns [10]. Therefore, it was possible to interpolate the data points, and obtain a curve of concentration vs. distance which could be directly compared to the output curves of the model. In this way, the quality of the fit could be determined by calculating the percentual deviations between the points of the model curve and those of the curve of the actual data. The average of these (absolute) values will be referred to as the quality of the fit (with a decrease in this number signifying an increase in quality of the fit). Results of this procedure are listed in table 7.6 for different model scenarios (described in the following sections). This table facilitates a quantitative comparison of the model scenarios.

To determine the significance of the deviation between two calculated concentration profiles, a method was used similar to the determination of the validity intervals of the process constants (see p. 175). Two profiles are considered to deviate significantly from each other when the average percentual deviation between the concentrations of the two profiles is higher than the standard deviation of the recovery of the analytical method.

For the A9PEO and metabolites concentrations in SPM and sediment, smooth curves could not be constructed, as no clear spatial trends were present. Therefore, only a general quality of the fit could be determined by checking if the calculated curve passed through the middle of the scatter of field data points.

The calculated sediment concentrations were compared to the analyzed sediment concentrations normalized to the particle size fraction <63\(\mu\)m, as it was assumed that this is the sediment fraction which has actual exchange with the SPM.
Table 7.6: Quality of fit of the calculated dissolved concentration profiles for the different model scenarios. For each scenario, the difference with the corresponding optimum scenario is described. A smaller value indicates a better fit. For further explanation see p. 183.

<table>
<thead>
<tr>
<th>model scenario</th>
<th>Scheldt 1999</th>
<th>Rhine 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NP</td>
<td>A₉PEO₂</td>
</tr>
<tr>
<td>I optimum scenario</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>II dispersion coefficients 100 m² s⁻¹</td>
<td>42</td>
<td>52</td>
</tr>
<tr>
<td>III dispersion coefficients 200 m² s⁻¹</td>
<td>34</td>
<td>44</td>
</tr>
<tr>
<td>IV dispersion coefficients 300 m² s⁻¹</td>
<td>33</td>
<td>48</td>
</tr>
<tr>
<td>V no sorption</td>
<td>39</td>
<td>48</td>
</tr>
<tr>
<td>VI sorption coefficients 5x optimum value</td>
<td>33</td>
<td>37</td>
</tr>
<tr>
<td>VII concentrations in canal Gent-Terneuzen zero</td>
<td>31</td>
<td>39</td>
</tr>
<tr>
<td>VIII concentrations in canal Gent-Terneuzen 3x optimum values</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>IX no biodegradation</td>
<td>129</td>
<td>179</td>
</tr>
<tr>
<td>X biodegradation rates 0.5x optimum values</td>
<td>53</td>
<td>62</td>
</tr>
<tr>
<td>XI biodegradation rates 2x optimum values</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>XII salinity dependent biodegradation</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>XIII optimum scenario</td>
<td>21</td>
<td>33</td>
</tr>
<tr>
<td>XIV optimum scenario</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>XV concentrations additional sources zero</td>
<td>34</td>
<td>51</td>
</tr>
<tr>
<td>XVI no sorption</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>XVII no biodegradation</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>XVIII biodegradation rates 5x optimum values</td>
<td>24</td>
<td>23</td>
</tr>
</tbody>
</table>

**Calculated concentration profiles**

For the Scheldt estuary, the model runs were started at January 1st, 1999. Concentration profiles for the day of sampling (November 17th, 1999, day 321) were calculated in the optimum scenario as shown in figures 7.7a-d. Satisfactory fits of the dissolved concentration profiles were obtained. The quality of the fits of the optimum scenario are given in table 7.6, model scenario I. For concentrations in SPM and sediment, deviations between the model and actual data were larger, but calculated and actual concentrations were of the same order of magnitude. This was considered the best possible result with the current model type.
For the additional source canal Gent-Terneuzen, the total input amounted to 8-33% of the input at the head of the estuary for the different compounds (see table 7.2). For the Scheldt data of 2000 (June 20th, 2000, day 536 in the model), calculated and actual concentration profiles are shown in figures 7.8 a-d (scenario XIII in table 7.6).

Figure 7.7a-d: Calculated and actual concentrations for the 1999 Scheldt data: a) dissolved concentrations; b) ratio of dissolved A₈PEC and A₈PEO; c) concentrations in SPM; d) concentrations in sediment. × = actual A₈PE₁₂C, + and dotted line = calculated profile; ▲ = actual A₈PEₓ₂C, △ and solid line = calculated profile; ○ = actual NP, ◆ and dotted line = calculated profile; ■ = actual A₈PEOₓ₂, ◇ and striped line = calculated profile; ♦ = actual A₈PEO₁₂, ◊ and striped/dotted line = calculated profile; * = actual A₈PEC/A₈PEO ratio, striped line = calculated ratio. CGT=position of canal Gent-Terneuzen; NS=North Sea side of the estuary.
Figure 7.8a-d: Calculated and actual concentrations for the 2000 Scheldt data: a) dissolved concentrations; b) ratio of dissolved $A_9$PEC and $A_9$PEO; c) concentrations in SPM; d) concentrations in sediment.

$x$ = actual $A_9$PE$_{1,2}$C, + and dotted line = calculated profile; ▲ = actual $A_9$PE$_{2,2}$C, △ and solid line = calculated profile; ● = actual NP, ○ and dotted line = calculated profile; ■ = actual $A_9$PEO$_{2,2}$, □ and striped line = calculated profile; ♦ = actual $A_9$PEO$_{1,2}$, ◊ and striped/dotted line = calculated profile; * = actual $A_9$PEC/$A_9$PEO ratio, striped line = calculated ratio.
Fate modeling of nonylphenol ethoxylates and their metabolites in Dutch estuaries

The fate model for the Rhine estuary was compared to the results of the 2002 sampling campaign, in which samples at different depths were taken. In this comparison, only the analytical results of the samples taken at the water surface and those taken at maximal depths were considered. Initially, the fits were not entirely satisfactory (table 7.6, scenario XV), as the actual concentration ‘humps’ in the middle of the estuary could not be modeled without additional A9PEO sources in the estuary. As it is likely that the harbours of Rotterdam constitute additional sources of A9PEO, a point source was added into the model [37]. The location of this source was chosen to be at 12 km, which was suggested by the maxima in the observed concentration profiles. This source would correspond to the Eem Harbour of Rotterdam. Another likely additional source is the river Oude Maas, which discharges into the estuary at x=18 km. Optimized input concentrations for both sources are shown in table 7.2. With these additional sources, satisfactory dissolved concentration profiles for the surface and bottom water layers were obtained with the optimum scenario, as shown in figure 7.9. The quality of the fits are listed in table 7.6 (scenario XIV).

For some analytes, the inputs of these additional sources are relatively high. For the harbour, the inputs range from 20 to 100% of the input at the head of the estuary for the different analytes, and for the Oude Maas these values range from 0 to 84%. This illustrates the importance of additional discharges in this area.

![Figure 7.9a-b](image.png)

Figure 7.9a-b: Calculated and actual concentrations for the final 2002 Rhine data: a) dissolved concentrations in the surface layer; b) dissolved concentrations in the bottom layer. x = actual A9PE12C, + and dotted line = calculated profile; ▲ = actual A9PE22C, △ and solid line = calculated profile; ● = actual NP, ○ and dotted line = calculated profile; ■ = actual A9PEO22, □ and striped line = calculated profile; ♦ = actual A9PEO12, ○ and striped/dotted line = calculated profile. H and OM=position of the additional sources: harbour and river Oude Maas; NS=North Sea side of the estuary.
Figure 7.10a-d: Calculated and actual concentrations for the 2000 Rhine data: a) dissolved concentrations (surface water layer); b) ratio of dissolved $A_9$PEC and $A_8$PEO; c) concentrations in SPM; d) concentrations in sediment. 

$x$ = actual $A_8$PE$_{1.2}C$, + and dotted line = calculated profile; $\triangle$ = actual $A_9$PE$_{>2}C$, $\Delta$ and solid line = calculated profile; $\bullet$ = actual NP, $\circ$ and dotted line = calculated profile; $\blacksquare$ = actual $A_9$PEO$_{>2}$, $\Box$ and striped line = calculated profile; $\blacklozenge$ = actual $A_9$PEO$_{1.2}$, $\Diamond$ and striped/dotted line = calculated profile; $*$ = actual $A_9$PEC/$A_8$PEO ratio, striped line = calculated ratio.

With the analytical results of the water samples from the 1999 and 2000 campaigns in the Rhine estuary, it was more difficult to evaluate the fit of the fate model. Most of those water samples were taken along the salinity gradient, which intrudes only several km into the estuary (see figure 7.2a). Therefore, for the major part of the estuary, no data on
concentrations in water are available from those campaigns. However, when the model was applied to the concentration data in this limited part of the estuary for the campaign of 2000, with the corresponding boundary concentrations and river discharge data, a satisfactory fit was obtained for the dissolved phase (water samples, taken at 1.5 m depth, were compared to the surface layer in the model, see figure 7.10a-b). The sediment and SPM data can be used to get an idea of the validity of the sorption coefficients and sedimentation/erosion rates that were used. As is shown in figure 7.10c-d, the calculated concentrations in SPM compare favorably with the field data, while the calculated concentrations in sediments were roughly an order of magnitude higher than the actual concentrations. This indicates that the sorption coefficients used in the model were correct, and that the exchange between SPM and sediment was overestimated for the Rhine estuary. Alternatively, degradation in the sediment could explain the relatively low actual concentrations in the sediments.

7.3.3 Sensitivity analysis

Several parameters in the optimized model scenarios were subjected to a sensitivity analysis. The influence of four parameters on the calculated concentration profiles was investigated: dispersion, sorption, additional sources and biodegradation.

For the Rhine estuary model, it was found that variation of both sorption and biodegradation had little influence on the dissolved concentration profiles. For example, when sorption is neglected in the model, the concentration profiles change only marginally, with average deviations from the optimum scenario from 0.03 to 1.5% for the different analytes (table 7.6, scenario XVI). When the biodegradation rates were set to 0, the average deviations from the optimum scenario ranged from 0.7 to 6.3% for the different analytes (scenario XVII). When increasing the biodegradation rates, the increase must be as much as a factor 5 to obtain significant deviations (see section 3.2.4) from the optimum curves (table 7.6, scenario XVIII). A likely explanation of this limited influence of biodegradation and sorption on the fate of A₉PEO in the Rhine estuary is the relatively short residence time of A₉PEO in the Rhine estuary (several days, compared to 2-3 months for the Scheldt estuary). As already mentioned in section 3.2.5, the parameter to which the model appeared to be the most sensitive was the insertion of additional A₉PEO sources. When this input was set to 0, a significant deviation from the optimum curve of 27-48% for the different analytes was calculated (table 7.6, scenario XV).

The sensitivity analysis of the model for the Scheldt estuary of 1999 will be discussed in more detail in the following paragraphs.
Figure 7.11: a) Actual and calculated dissolved concentration profiles of A₈PEO₂ using different sorption coefficients for the 1999 Scheldt model: ♦ and solid line = actual concentration profile; ◊ and striped line = optimum model scenario (Kₐ=47000); × = sorption coefficient set to 0; + = sorption coefficient 5 times the optimum value (Kₐ=235000).

b) Actual and calculated dissolved concentration profiles using different biodegradation rate constants for the 1999 Scheldt model for A₈PEO₂: ♦ and solid line = actual concentration profile; ◊ and striped line = optimum model scenario; × = biodegradation rate set to 0; + = biodegradation rate x1.5 (0.092 day⁻¹); - = biodegradation rate x0.5 (0.031 day⁻¹); Δ = salinity dependent biodegradation rate (0.001-0.183 day⁻¹).
Sensitivity towards dispersion coefficients

The implementation of different sets of dispersion coefficients in the Scheldt model of 1999 resulted in qualities of fit as shown in table 7.6 (scenarios II-IV). Variation of the dispersion coefficients appeared to have some influence on the concentration profiles. However, when using dispersion coefficients of 200 m² s⁻¹ for each segment of the estuary (scenario III), the deviation of the calculated A₉PEO and NP profiles from the optimum scenario was not significant. For model scenarios with dispersion coefficients of 100 or 300 m² s⁻¹ for each segment (scenarios II and IV, respectively), the deviations from the optimum scenario became significant.

Sensitivity towards sorption

As figure 7.11a illustrates for A₉PEO₂₂, relatively large changes in sorption coefficients were necessary in order to obtain significant deviations of the dissolved concentration profiles from the optimum scenarios. In other words, the concentration profiles were relatively insensitive towards sorption. This insensitivity is also illustrated with the sorption coefficient validity intervals in table 7.1, which are large compared to those of the biodegradation rates.

As examples, the quality of the fits of concentration profiles for scenarios with the sorption coefficient set to 0 or to 5 times the optimum value are shown in table 7.6 (scenarios V and VI, respectively).

Sensitivity towards an additional A₉PEO source

As a high ratio of dissolved concentrations of A₉PEC/A₉PEO was observed in both the water of the canal Gent-Terneuzen and near its discharge point in the estuary, it was hypothesized that the canal Gent-Terneuzen could be a relevant point source of A₉PEO and metabolites to the Scheldt estuary [10]. Therefore, the significance of this additional source was evaluated.

When concentrations in the canal were set to 0, the decrease in the fit of the dissolved profiles was significant for all analytes (table 7.6, scenario VII). When concentrations in the canal were increased, a 3-fold increase was necessary to obtain a significant deviation from the optimum scenario was obtained for all analytes. (table 7.6, scenario VIII).

It is concluded that the canal discharge does have a significant influence on the concentration profiles in the estuary.

Sensitivity towards biodegradation

Different biodegradation rates were tested to evaluate the influence of this process on the calculated concentration profiles of 1999 in the Scheldt estuary. The results in figure 7.11b show that for A₉PEO₂₂ changes in the biodegradation rates had a relatively strong effect on...
the profiles. In table 7.6, the quality of the fits are listed for scenarios with the degradation rates for all compounds changed to 0, 0.5 or 2 times the optimum values (scenarios IX, X and XI, respectively).

For all concentration profiles of the optimum scenario, the calculated concentrations were higher than the actual values in the upper part, and lower than the actual values in the lower part of the estuary. This may indicate that for each analyte, the biodegradation rate used in the model was too low in the relatively fresh part and too high in the saline part of estuary, and that the biodegradation rate is salinity dependent. A model scenario was tested with salinity dependent biodegradation rates, according to an empirically derived formula:

\[
\text{degradation rate} = \text{optimum rate} \times \left(3 - 3.07 \times \sqrt{\frac{\text{salinity}}{35}}\right)
\]

With this formula, biodegradation rates are 3 times the “optimum value” at the river end, and 0.01 times the “optimum” at the sea end of the estuary. This resulted in a slight but significant improvement of the fits, as shown in figure 7.11b and table 7.6 (scenario XII).

Salinity dependent biodegradation of A₉PEO has been reported before by Kvešták et al. [34]. For a stratified estuary, they observed that biodegradation rates can be up to 8.5 times higher in the surface water layer than in the lower saline layer.

### 7.4. Conclusions

The present study investigated the behaviour of A₉PEO in two estuaries with different hydrological characteristics. The field data indicated biodegradation to be an important process in the Scheldt estuary, showed that A₉PEO is vertically stratified in the Rhine estuary and suggested that relevant additional sources of A₉PEO were present in the latter estuary.

These findings were investigated in a more quantitative way by using different model scenarios. The hydrodynamic model was able to describe the movement of water and SPM satisfactorily for both estuaries. The sorption coefficients applied in the model yielded concentrations in SPM and sediment in the same order of magnitude as the field data. By fitting the calculated dissolved concentration profiles to the profiles observed in the field, an estimation of the field biodegradation rate constants for A₉PEO and metabolites could be made. The model calculations suggest an additional input of A₉PEO and metabolites from sources in the Rotterdam harbour area amounting to 20-100% of the input from that at the head of the estuary for the different analytes.
The model revealed that the main factors governing the fate of $A_9$PEO in the two investigated estuaries were biodegradation in the Scheldt estuary, and the input from additional sources in the Rhine estuary.

The accumulation of $A_9$PEO at water surfaces deserves more attention in future risk assessment studies, as the exposure to these compounds will be either considerably higher or lower than predicted from average concentrations for different organisms dwelling at or below the water surface.

**Acknowledgments**

The Dutch Ministry of Transport, Public Works and Water Management (RIKZ) is acknowledged for arranging the availability of the research ships. The crew of the research ships Argus and Cygnus are thanked for making the sampling campaigns possible, and the colleagues and students of the MTC department for their assistance during sampling. The authors want to thank the scientists at the RIKZ laboratory Middelburg for performing the analyses of the standard parameters of all water and sediment samples, and Dik Ludikhuize (RIZA), Koos Doekes (RIKZ) and dr. Ruud Steen for providing hydrological data on the Scheldt and Rhine estuaries.

$A_9$PEO and $A_9$PEC standards were kindly provided by Dr. Francesc Ventura, AGBAR, Spain, and the Shell laboratory Amsterdam, The Netherlands.

This work was financially supported by the RIKZ institute of the Dutch ministry of Transport, Public Works and Water Management, project MONOS, and the European Union, project PRISTINE (ENV4-CT97-0494).

**References**


Fate modeling of nonylphenol ethoxylates and their metabolites in Dutch estuaries


