Fate of Nonylphenol in lakes:
Case study modelling of two small lakes
in Stockholm, Sweden

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Summary

Nonylphenol is a widely used organic compound which has been reported to have potential risk to aquatic environment. According to the result of recent studies, it has been detected in many lakes in Stockholm, Sweden, which raised great concern. In this thesis, a dynamic fate model was adopted and modified from literature in order to study the distribution and concentration of nonylphenol in small lakes, guide the field sampling and provide information for corresponding decision making. Two lakes in Stockholm, Lake Trekanten and Lake Drevviken, were selected as case studies. Another model was included for comparison purpose.

Based on the model result, the most important nonylphenol removal process in both lakes was the transformation in water. A sensitivity analysis showed that the model results were most sensitive to the process of nonylphenol water inflow. In terms of sediment concentration of nonylphenol, satisfactory agreements were obtained from the comparison between model results and field data. However, problems, such as the simultaneous handling of nonylphenol and nonylphenol ethoxylates, may cause uncertainties on the model performance. The result of the analysis about scenario load change and the seasonal variation showed that the sediment nonylphenol content is more stable to the seasonal change compare to nonylphenol water content, but the response times to load change of nonylphenol content in these two compartments are quite close and somewhat lower than the water residence time.

Key words: nonylphenol, fate, modelling, lake.
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## Symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Physical entities</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area</td>
<td>[m²]</td>
</tr>
<tr>
<td>bd</td>
<td>Bulk density</td>
<td>[g/m³]</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
<td>[g/m³]</td>
</tr>
<tr>
<td>D</td>
<td>Empirical divided value</td>
<td>[-]</td>
</tr>
<tr>
<td>f</td>
<td>Fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>F</td>
<td>Flow</td>
<td>[kg/year]</td>
</tr>
<tr>
<td>G</td>
<td>Rate</td>
<td>[kg/year]</td>
</tr>
<tr>
<td>H</td>
<td>Henry’s Law Constant</td>
<td>[Pa.m³/mol]</td>
</tr>
<tr>
<td>h</td>
<td>Depth</td>
<td>[m]</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss on ignition</td>
<td>[%]</td>
</tr>
<tr>
<td>K</td>
<td>Rate constant in ET-A Model</td>
<td>[year⁻¹]</td>
</tr>
<tr>
<td>K_A</td>
<td>Air side mass transfer coefficient</td>
<td>[m/h]</td>
</tr>
<tr>
<td>K_{aw}</td>
<td>Air-water partition coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>K_i</td>
<td>Water side mass transfer coefficient</td>
<td>[m/h]</td>
</tr>
<tr>
<td>K_{OC}</td>
<td>Organic carbon-water partition coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>K_{ow}</td>
<td>Octanol-water partition coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>K_p</td>
<td>Water to particle partition coefficient</td>
<td>[L/kg]</td>
</tr>
<tr>
<td>K_T</td>
<td>Sediment-water diffusion mass transfer coefficient</td>
<td>[m/h]</td>
</tr>
<tr>
<td>K_V</td>
<td>overall water side mass transfer coefficient</td>
<td>[m/h]</td>
</tr>
<tr>
<td>M</td>
<td>Mass</td>
<td>[kg]</td>
</tr>
<tr>
<td>R</td>
<td>Rate constant in the base-case lake model</td>
<td>[year⁻¹]</td>
</tr>
<tr>
<td>Temp</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>T_A</td>
<td>Age of A sediment</td>
<td>[year]</td>
</tr>
<tr>
<td>T_{ET}</td>
<td>Age of ET sediment</td>
<td>[year]</td>
</tr>
<tr>
<td>T_{HLS}</td>
<td>Half life in sediment</td>
<td>[h]</td>
</tr>
<tr>
<td>T_{HLW}</td>
<td>Half life in water</td>
<td>[h]</td>
</tr>
<tr>
<td>T_W</td>
<td>Water retention time</td>
<td>[year]</td>
</tr>
<tr>
<td>T'</td>
<td>Response time</td>
<td>[year]</td>
</tr>
<tr>
<td>v</td>
<td>Particulate settling velocity</td>
<td>[m/year]</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>[m³]</td>
</tr>
<tr>
<td>V_d</td>
<td>Volume development</td>
<td>[-]</td>
</tr>
<tr>
<td>W</td>
<td>Sediment water content</td>
<td>[-]</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
<td>[g/cm³]</td>
</tr>
</tbody>
</table>
Subscript:

A Accumulation area
bur Burial
dep Deposition
diff_A Diffusion from A area to water
DW Dissolved in water
DS Dissolved in sediment
equ Equivalents
ET Erosion and transport area
in Going in to the lake
OCS Organic carbon in sediment
OCW Organic carbon in water
out Going out from the lake
PS Particles in sediment
PW Particles in water
res Resuspension
res_ETA Resuspension from ET area to A area
res_ETW Resuspension from ET area to water
S Sediment
sed_A Sedimentation on A area
sed_ET Sedimentation on ET area
SS Sorbed in sediment
SW Sorbed in water
trans_A Transformation in A sediment
trans-ET Transformation in ET sediment
trans_W Transformation in water
vol Volatilization process
W Water
1. Introduction

1.1 Background

There are huge amounts of chemicals existing in the world, and more and more are being synthesized nowadays for use in different sectors including manufacturing, building, transportation and household. Stimulated by these demands, the global chemical industry has developed rapidly during the past few decades. Nowadays, it represents one of the biggest economic sectors worldwide with 10 million employees and a combined turnover (excluding pharmaceuticals) of 1300 billion Euros (Jenck et al., 2004). Among all the regions, European Union plays an important role. According to ICCA (2009), 30% of the world chemical turnover was generated by European chemical industry.

However, at the same time various kinds of chemicals are produced to fulfill different demands from human activities, they also cause problems. One of the most worrisome problems is that some of the chemicals may pose potential risk to aquatic environment and human health. European Union has attached great importance to this issue and a number of measures have been taken to deal with this problem. In 2000, the Water Framework Directive (WFD, 2000/60/EC) entered into force, aiming to achieve a good (both ecologically and chemically) overall quality of all the water bodies in EU by the year 2015. In Annex X of this directive, 32 chemicals were listed as priority substances, 11 out of which were classified as hazardous priority substances, representing a significant risk to aquatic environment. It was required that all the emissions of those compounds must cease within 20 years.

As one of the synthetic chemicals, nonylphenol (NP) is on the list of hazardous priority substances. Ever since the first concern of nonylphenol emerged in the 1980s (Giger et al., 1984), numerous efforts have been focused on determining its physical-chemical properties, sources and environmental risks. In the past, most of the nonylphenol emission was contributed by industrial point sources, but diffuse sources are believed to play a more important role after a voluntary phase-out of nonylphenol production within EU countries (Hansson et al., 2008). Moreover, nonylphenol is getting more and more attention nowadays due to its proved toxicity to aquatic environment and endocrine disrupting effects to wildlife (Ying et al., 2002).

As one of the member countries of EU, Sweden has to achieve the requirement of the WFD. According to the results of recent monitoring reports, nonylphenol was detected in sediments of lakes and was found to be enriched in the urban region of Stockholm (Strömberg & Sternbeck, 2004). Under this situation, some studies have been carried out to address this problem in Sweden. Björklund (2009) identified the emission sources and amount of nonylphenol in urban storm water. Andersson (2008) analyzed the sources and showed a static distribution of nonylphenol within different compartments of River Viskan. However, none of these studies provided the dynamic change rates of different processes and the system response time before it reached the steady state, which are very
important for a better understanding of nonylphenol’s behavior and changing trends in aquatic environments and corresponding decision making.

1.2 Aim and objectives

This master thesis aims to develop a dynamic, environmental fate model of nonylphenol in lakes and to observe the distribution and concentration of nonylphenol within different environmental compartments with respect to time. This information is important to guide the field sampling and to serve as a basis of corresponding environmental decision making.

In order to build the fate model, a comprehensive grasp of the physical-chemical properties of nonylphenol is a prerequisite. Also, a wise choice of modeling methods and tools are essential to ensure the model quality while maintaining its simplicity. Moreover, a test of model performance is needed before its application. Therefore, this study has the following working objectives:

• Compile literature information and construct a conceptual model of nonylphenol in a lake.
• Quantify and implement the model in two different modeling tools, and apply it to selected lakes in Stockholm.
• Test the performance of the fate models of nonylphenol with field data.
• Identify dominant processes by carrying out a model sensitivity analysis and analyze the uncertainty of key variables.
• Investigate the model prediction about the response time of the system to nonylphenol load changes.
2. Methodology

The chemical behavior in aquatic environments after its release can be very complex, and it is determined by both the substance’s properties and the environment conditions it resides in. Environmental fate modelling as a scientific method has been widely used to address this problem (SOCOPSE, 2009). Figure 2.1 shows the schematic of the environmental fate model. With the properties of studied chemical and corresponding environmental properties given, the concentrations of this chemical in different environmental compartments and the timescales to change them can be estimated by making use of the environmental fate model.

![Diagram of environmental fate modeling](image)

In this thesis, a conceptual model was developed from a literature study and modified to be suitable for Swedish conditions. Two lakes of Stockholm were selected to run the model in real cases with available lake specific data from different sources. Then a model quality test was carried out by comparison of model results and available field data. Sensitivity and uncertainty analysis were also conducted to evaluate influence of different processes and variables on the model performance.
3. Nonylphenol

Nonylphenol is an organic compound of the alkylphenol group. With a nine carbon alkyl chain attached on the phenol ring, nonylphenol has a variety of isomers, depending on attaching positions and branching degree of the C-9 group. It has been reported that these nonylphenol isomers may have different toxicity and estrogenicity (Lalah et al., 2003).

According to the EU Risk Assessment (2002) report, nonylphenol is used as the generic name for para substituted\(^1\) compounds with either a straight alkyl chain (CAS nr: 25154-52-3) or with a branched alkyl chain (CAS nr: 84852-15-3), and all the properties of nonylphenol are given for both types of isomers in this report. In order to keep in agreement with the EU system, “nonylphenol” in this study means the para substituted nonylphenols, including both straight and branched alkyl isomers. The chemical structures of these two isomers are shown in Figure 3.1.

![Figure 3.1. Structure of nonylphenols (one example of branched 4-nonylphenol is shown among several possible types).](image)

3.1 Physical-chemical properties

The molecular formula of nonylphenol is C\(_{15}\)H\(_{24}\)O. Nonylphenol appears to be a clear to pale yellow liquid with a slight phenolic odour under standard temperature and pressure (EU Risk Assessment, 2002). A range of values can be found from different literature due to differences in test methods and production processes, as listed in Table 3.1. All selected values are given for nonylphenol with CAS number 84852-15-3 and 25154-52-3, which is in agreement with the object of study in this thesis.

As shown in Table 3.1, great difference can be seen in the vapor pressure of nonylphenol among different literatures. In the EU Risk Assessment (2002) report, the vapor pressure of 0.3 Pa at 25 °C was estimated by extrapolation of data at high temperature (from 149.7 °C to 301.9 °C). This value was adopted by Environmental Quality Standards (EQS) but with an annotation that the actual value may be lower (EQS, 2005). As closely related to the vapor pressure, the corresponding Henry’s Law Constant of these two literatures was calculated by the equation (EU Risk Assessment, 2002):

\[^1\] the substituents occupy the opposite ends of the benzene
\[
H = \frac{\text{Vapor Pressure (Pa)} \times \text{Molar Mass (g/mol)}}{\text{Water Solubility (mg/L)}}
\]

(1)

### Table 3.1 Properties of nonylphenol in literatures.

<table>
<thead>
<tr>
<th>Vapor pressure (Pa)</th>
<th>Water solubility (mg/L)</th>
<th>Henry’s Law Constant (Pa.m³/mol)</th>
<th>Log K_{ow} *</th>
<th>Comments</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.55 x 10^{-3} (±3.54x10^{-3})</td>
<td>4.6 (pH 5) 6.24 (pH 7) 11.9 (pH 9)</td>
<td>3.8-4.77</td>
<td></td>
<td>Water solubility is pH and temperature dependent</td>
<td>1</td>
</tr>
<tr>
<td>0.008</td>
<td>6</td>
<td>11.02</td>
<td>4.48</td>
<td>The vapor pressure is the arithmetical mean value of nonylphenol with CAS nr 84852-15-3 and 25154-52-3</td>
<td>2</td>
</tr>
<tr>
<td>0.3 (25°C)</td>
<td>6 (20°C)</td>
<td>11.02</td>
<td>4.48</td>
<td>Vapor pressure is extrapolated from the data at high temperature</td>
<td>3</td>
</tr>
<tr>
<td>0.3 (25°C)</td>
<td>6 (20°C)</td>
<td>11.02</td>
<td>4.48</td>
<td>Some evidence has proved that the actual value of vapor pressure may be lower</td>
<td>4</td>
</tr>
</tbody>
</table>

* Logarithm of the n-octanol-water partition coefficient

1. USEPA, 2005
2. Andersson, 2008
3. EU Risk Assessment, 2002
4. EQS, 2005

A much lower vapor pressure of 0.008 Pa, which is the mean value of the vapor pressures of two nonylphenol isomers, was used by Andersson (2008) in her study about the distribution of nonylphenol within different compartments of River Viskan. However, the Henry’s Law Constant she used was still 11.02 Pa.m³/mol, which is confusing, since the corresponding value should be in accordance with the vapor pressure and much lower.

In this thesis, the vapor pressure value given by the United States Environmental Protection Agency (USEPA), i.e. 4.55 x 10^{-3} (± 3.54 x 10^{-3}) Pa, is used in the fate modeling. The vapor pressure used by Andersson (2008), 0.008 Pa.m³/mol, also lies within the ranges of this value. Moreover, from the result of first sensitivity analysis (see Section 7.1.1), the process related to vapor pressure, i.e. the volatilization, has low impact on model results. So the choice of vapor pressure seems acceptable. Other physical-chemical values of nonylphenol are adopted from the EU Risk Assessment (2002) report unless
annotated specifically. Since no value of Henry’s Law Constant was given by USEPA, it was calculated based on Eq. 1. All the parameters used in the models are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>220.34</td>
<td>g/mol</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>-8</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Relative density</td>
<td>0.95</td>
<td></td>
<td>at 20 °C</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>0.00455</td>
<td>Pa</td>
<td>USEPA, 2005</td>
</tr>
<tr>
<td>Water solubility</td>
<td>6</td>
<td>mg/l</td>
<td>at 20 °C and pH 7</td>
</tr>
<tr>
<td>Log K&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>4.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Henry’s law constant</td>
<td>0.17</td>
<td>Pa·m&lt;sup&gt;3&lt;/sup&gt;/mol</td>
<td>calculated</td>
</tr>
</tbody>
</table>

### 3.2 Production and application areas

Nonylphenol is industrially produced by the reaction of phenols and mixed nonenes under certain conditions (presence of catalyst or ion exchange resins) in either batch or continuous processes, depending on the producer (EU Risk Assessment, 2002). Further purification by distillation is needed before it can be sold. However, the final product of nonylphenol for industrial use is still a mixture of different isomers, which normally contains around 85-90% of 4-nonylphenol (KEMI, 2009).

According to the EU risk Assessment (2002) report, nonylphenol can be used for the production of resin plastics and stabilizers, and for phenolic oximes production in rare cases. However, a greater part of the manufactured nonylphenol is used as an intermediate to produce surfactants, above all nonylphenol ethoxylates (NPEs). In EU, nonylphenol has been produced in large amounts. In 1997, 78500 tons of nonylphenol was consumed within EU, 60% of which was used for the production of NPEs (EU Risk Assessment, 2002).

### 3.3 Nonylphenol ethoxylates

As produced by the ethoxylation process of nonylphenol, NPEs is one of the most widely used non-ionic surfactants, which gains its applications in both residential and industrial fields. Many consumer goods such as detergents, shampoo, pesticides and surface cleaners contain NPEs. Industrial uses of NPEs are as detergents, emulsifier, wetting agents, and also they serve as auxiliary in pulp and paper industry, oil extraction, metal processing, etc (Hansson et al., 2008). The chemical structure of NPEs is shown in Figure 3.2.
The physical and chemical properties of NPEs vary significantly depending on the number of ethoxylate groups that are attached. This number can vary from just a few to about a hundred, and different groups of NPEs with different ethoxy chain length are involved in different products (Hansson et al., 2008). By the stepwise loss of ethoxy groups, NPEs can be biodegraded to its congeners with shorter ethoxylate chain, nonylphenol ethoxycarboxylates (NPECs) and nonylphenol (Ying et al., 2002). According to the study of Giger et al. (1984), in which a complete deethoxylation from NPEs to nonylphenol was observed, nonylphenol is therefore considered as the final metabolite of NPEs degradation under anaerobic condition.

Concerns have emerged along with the worldwide use of NPEs. As the majority of NPEs are used in aqueous solutions, they tend to be discharged within municipal and industrial wastewater (Gabriel et al., 2005). Also, it has been revealed that the metabolites of NPEs, such as nonylphenol, are more persistent and toxic than the parent substances (Ying et al., 2002). So the NPEs degradation has been considered as a main source of nonylphenol emission, which is believed to possess a great risk to the aquatic environment.

### 3.4 Sources

Nonylphenol emission during industrial production can be seen as a point source of nonylphenol. However, due to a voluntary ban on the NP/NPEs in chemical products by major manufacturers, there has been a great decrease in the direct emissions of these substances in EU countries (Hansson et al., 2008).

In Stockholm, Sweden, the point sources are estimated to have low contribution to the nonylphenol emission in water bodies, since there is no direct production of nonylphenol in Sweden now (Hansson et al., 2008). Nevertheless, products containing NPEs are still widely manufactured outside EU. Therefore these products can enter Swedish market through import of end products. So instead of point sources, other diffuse sources, including degradation from NPEs, leakage from commercial goods, municipal and industrial wastewater, and wastewater treatment plants, etc, play a more important role nowadays in nonylphenol emission to aquatic environment (Hansson et al., 2008).
3.5 Environmental risks

According to the Annex 1 of Directive 67/548/EEC, the main environmental risks of nonylphenol can be summarized as follows:

- Can cause long-term reverse effect to the aquatic environment
- Very toxic to aquatic organisms
- Possible risk of impaired fertility

Since nonylphenol possesses potential risks to the environment, a calculation was carried out by the European Chemicals Bureau based on nonylphenol’s properties and toxicity data to predict the no effect concentration in aquatic environment in Environment Quality Standards (EQS) of EU. The result is listed in Table 3.3.

Table 3.3 Predicted no effect concentrations of nonylphenol in aquatic environment (data from EQS, 2005).

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>0.33 μg/l</td>
</tr>
<tr>
<td>Sediment</td>
<td>0.039 mg/kg wet weight</td>
</tr>
</tbody>
</table>

3.6 Environmental fate

It is desirable to understand the behavior and fate of nonylphenol before assessing its environmental risks. The environmental fate of an organic chemical depends both on its internal physical-chemical properties and the external environment it resides in. The environmental fate of nonylphenol is dominated by sorption and various degradation processes following its release into the environment (Ying et al., 2002).

3.6.1 Volatilization and precipitation

As shown in Table 3.2, the Henry's Law constant of nonylphenol is 0.17 Pa.m^3/mol. A low air-water partitioning coefficient can be derived from the low Henry's Law constant, indicating a relatively weak volatilization from surface water to air. So it is not likely that large amounts of nonylphenol enter atmosphere. Therefore the removal of nonylphenol from the atmosphere by precipitation is negligible (EU Risk Assessment, 2002). However, some other studies reported that volatilization may be an important removal of semivolatile organic pollutants, such as nonylphenol, from the water column in shallow aquatic environments (Van Ry et al., 2000).

3.6.2 Sorption

The octanol-water partition coefficient, known as K_{ow}, is one of the most frequently used parameters describing the chemical’s behavior in the environment. For nonylphenol, its comparatively low water solubility and a log K_{ow} value of 4.48 (EU Risk Assessment,
suggest that it partitions to organic matters favorably in aquatic environment, which has already been proved by many studies (Huang et al., 2007; EU Risk Assessment, 2002). According to the experiment carried out by Huang et al. (2007), nonylphenol showed a strong affinity to aquatic particles and the sediment served as an important sink of nonylphenol in the aquatic environment.

### 3.6.3 Degradation

In the atmosphere, nonylphenol is likely to react with hydroxyl radicals and therefore to be degraded. The half-life\(^2\) of nonylphenol for this reaction was calculated as 0.3 days (EU Risk Assessment, 2002), which means nonylphenol is not likely to be transported far from its original emission site by air.

Abiotic degradation of nonylphenol occurs in water through both photolysis and hydrolysis. A half-life of 10 to 15 hours was reported by Ahel et al. (1994) for the photolysis of nonylphenol on top layer of water with plenty of sunlight, whilst the hydrolysis of nonylphenol is believed to be negligible (EU Risk Assessment, 2002).

It is also reported that nonylphenol can be biodegraded in aquatic environment and the aerobic condition is more preferable. Its degradation in the water pillar is faster than in water filled pores of the sediment, and the rates are temperature depended (Ying et al., 2002). Various results of half-lives can be found from different studies depending on the prevailing conditions. In Sweden, the half-life of nonylphenol undergoing biodegradation may be longer than reported for many other geographic locations due to the low ambient temperature. Andersson (2008) summarized the half lives of nonylphenol in different environmental compartments, which are considered to be valid under Swedish conditions, as shown in Table 3.4.

<table>
<thead>
<tr>
<th>Environmental compartment</th>
<th>Half-lives (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.3</td>
</tr>
<tr>
<td>Surface water</td>
<td>150</td>
</tr>
<tr>
<td>Sediment</td>
<td>3013</td>
</tr>
</tbody>
</table>

### 3.7 Model review

Various kinds of models have been used to study the fate of nonylphenol in different environmental conditions. A kinetic model was employed by Manzano et al. (1999) to analyze the biodegradation process of nonylphenol in river water. However, the model only served as a testing method of the experimental data. Van Ry et al. (2000) devised a box-model to estimate the input and removal fluxes of nonylphenol from Hudson River.

---

\(^2\) The time by when half of the chemical will have been degraded (Mackay, 2001).
estuary. Many processes were considered with the emphasis on the wind influence on the nonylphenol occurrence in shallow aquatic environment, such as estuary system. However, these models were focused on either a certain process or nonylphenol concentration in a single compartment. Comprehensive models are needed in order to have an overall knowledge about the environmental fate of nonylphenol and provide reliable prediction about the change of concentration in response to environmental changes.

In Sweden, some more comprehensive studies about environmental fate modeling of nonylphenol have been conducted. In the study of Andersson (2008), QWASI (Quantitative Water Air Sediment Interaction; Mackay et al., 1983) was used to identify the distribution and concentration of nonylpheol in the contaminated section between Borås and Rydboholm. According to the model output, 98% of the nonylphenol emission was transported downstream with the water outflow, and 78% of nonylphenol residing in the system was found in the sediment after the equilibrium state has been reached. A further simulation using the Sediment model (CEMC, 2008) was also carried out to analyze the maximum and minimum sediment concentrations of nonylphenol under two scenarios. Björklund et al. (2009) applied a modified QWASI model to study the catchment area of Gårda sedimentation facility. The model results showed that the sediment is a very important sink for nonylphenol in urban areas.

However, nonylphenol fate in lakes has not been assessed previously. Moreover, only steady state results were provided in the above mentioned studies. The time span to reach equilibrium state of the system, and the response time to load changes are thus still unknown. Therefore, in this master thesis, a dynamic fate model of nonylphenol in lake system under natural environmental conditions is built to get a comprehensive understanding of nonylphenol’s behavior within different environmental compartments in respect to time and to predict the possible consequence of certain implemented measures.
4. Case studies

Stockholm, located in Sweden’s south central-east coast, is the capital and biggest city of Sweden. Stockholm is situated on 14 islands and on the banks to the archipelago where Lake Mälaren meets the Baltic Sea. With 30% of its inner city area being water, Stockholm government attaches great importance on water quality monitoring and management. Different measures have been taken to deal with problems caused by heavy metals, nutrients, and other organic chemical pollutants in order to improve the water quality. However, according to the result of recent monitoring report, nonylphenol was still detected in sediments of lakes and was found to be enriched in the urban region of Stockholm (Strömberg & Sternbeck, 2004).

Two lakes, Lake Trekanten and Lake Drevviken in Stockholm, Sweden, were selected as case studies in this thesis. Both of these two lakes are located in the urban, residential areas of Stockholm, but have different characteristics. Lake Trekanten is a small park lake with engineered water inflow and outflow. It has been a focus of many studies since the concentration of nutrients and heavy metals in the lake is high (Stockholm Vatten, 2000a). Compared to Lake Trekanten, the Lake Drevviken is much larger, with relatively higher water flow rate and a lower residence time (Stockholm Vatten, 2000b). Moreover, according to the sampling result, the nonylphenol concentration in the sediment of Trekanten is much higher than in that of Drevviken (Sternbeck et al., 2003). Therefore, the simulation of these two different lakes can provide more comprehensive understanding about the fate of nonylphenol, and forward different environmental decisions to deal with nonylphenol contamination problem under different lake conditions.

4.1 Lake Trekanten

With its 13.5 hectares surface area and mean depth of 4.4 m, Lake Trekanten is a small lake located in a park in southern-central Stockholm, which is popular for bathing and fishing. Lake Trekanten and its surrounding areas have diversified flora and fauna, and thus it is considered as of great recreational value to the local environment. However, it is reported that the lake is heavily eutrophied and the sediment contains various pollutants (Stockholm Vatten, 2000a).

4.1.1 Catchment area

The catchment area of Lake Trekanten is around 60 hectares. Since Lake Trekanten is located in a park on a flat terrain, the area along the shore of lake is mainly comprised of open land and forest, which account for 28% and 20% of the total catchment area, respectively. Residential areas take another 18% of the catchment area, followed by high density traffic area that covers around 14% including tram ways and roads. Other land uses such as industry and workplace can also be found but only in small fractions. Figure
4.1 shows the components of the catchment area of Lake Trekanten (Stockholm Vatten, 2000a).

There used to be many small scale industries, e.g. tanneries, dye and creosote works, along the lake shore until early 1960s, which caused contamination of the lake water and sediment. Nowadays, only a timber trade is still operating in the industrial area to the north of the lake. As can be seen in Figure 4.1, four stormwater discharge points are located at four corners of the lake as indicated by blue arrows. Also, there is a tributary (drinking water) to Lake Trekanten on its south bank and pumped water outflow from the north.

**Figure 4.1. Catchment area of Lake Trekanten (modified from Stockholm Vatten, 2000a).**

### 4.1.2 Lake quality

Many studies have been carried out about Lake Trekanten since it is reported to be heavily eutrophied and have relatively high concentration of heavy metals in the sediment (Stockholm Vatten, 2000a). As a remedy measure, the bottom water of the lake is pumped out and replaced by drinking water from nearby reservoir. This effort greatly reduced the amount of nutrients in the lake and at the same time cut the water retention time from 3.1 years to 1.6 years (Lindström and Håkanson, 2001). However, the copper concentration in sediment was still classified as high (Cui et al., 2009).

Compared to the problems of eutrophication and heavy metal, nonylphenol has not been extensively studied for Lake Trekanten. In a recent monitoring program in May and June 2002, Lake Trekanten was selected as one of the sampling sites in Stockholm. At least eight sediment cores from each station were sampled and mixed in the field and a high concentration of nonylphenol (3200 ng/g dw) was detected in the sediment of Lake Trekanten (Sternbeck et al., 2003).
4.1.3 Source and load of nonylphenol

Due to the wide use of nonylphenol, it has diffusive sources in the environment. According to an earlier study of Björklund (2009), traffic is considered as one of the most important sources of nonylphenol in urban stormwater. As mentioned before, high density roads and tram ways take a great part of the catchment area of Lake Trekanten. As a result of wear and tear during driving, NP/NPEs used as additives in lubricants and fuel can be released to the environment. Also, being widely used in washing and degreasing agents of car care products, NP/NPEs emission can happen by the release of these materials from cars to the parking area (Björklund, 2009).

Building material in the catchment area of Lake Trekanten is another potentially important source of nonylphenol; here nonylphenol is mainly used as additives in concrete and in roofing and cladding materials. In addition, atmospheric deposition of NP/NPEs to the lake and surrounding area is a possible source as well. Moreover, as 18% of the catchment is residential area, other human activities causing wear and tear of NP/NPEs containing products, such as shoes, strollers, etc, can also contribute to the total load of nonylphenol (Björklund, 2009).

A Substance Flow Analyses of NP/NPEs has recently been carried out by Djurberg (2010a) in parallel with this work, and a preliminary estimated load of NP/NPEs of Lake Trekanten is 3.58 kg/year, which is adopted in this thesis for the fate modeling of nonylphenol. All the following sensitivity and uncertainty analysis and discussion are based on this load.

Just before the final draft of this report, an updated estimate of the load of NP/NPEs is derived as 0.535 kg/year (Djurberg, 2010b). Simulation based on the new load is conducted in Chapter 10.

4.1.4 Lake specific parameters

In order to apply the fate model to selected case studies, values of several lake specific parameters are needed for the model quantification. In the case of Lake Trekanten, both the base-case lake model (see Section 5.1.1 and 5.1.2) and the ET-A lake model (see Section 5.2) are used to simulate the distribution and concentration of nonylphenol in different compartments. The data of Lake Trekanten involved in these models are listed in Table 4.1.
### Table 4.1 Lake specific parameters of Lake Trekanten.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water surface area</td>
<td>$A_W$</td>
<td>m²</td>
<td>130000</td>
<td>Stockholm Vatten, 2000a</td>
</tr>
<tr>
<td>Sediment area</td>
<td>$A_S$</td>
<td>m²</td>
<td>130000</td>
<td>assumed the same as water</td>
</tr>
<tr>
<td>Mean water depth</td>
<td>$h_W$</td>
<td>m</td>
<td>4.4</td>
<td>Stockholm Vatten, 2000a</td>
</tr>
<tr>
<td>Water volume</td>
<td>$V_W$</td>
<td>m³</td>
<td>570000</td>
<td>Stockholm Vatten, 2000a</td>
</tr>
<tr>
<td>Sediment active depth</td>
<td>$h_S$</td>
<td>m</td>
<td>0.02</td>
<td>Sternbeck et al., 2003</td>
</tr>
<tr>
<td>Fraction of erosion and transportation (ET) sediment</td>
<td>$D_{ET}$</td>
<td></td>
<td>0.71</td>
<td>Lindström &amp; Håkanson 2001</td>
</tr>
<tr>
<td>Age of ET-sediment</td>
<td>$T_{ET}$</td>
<td>year</td>
<td>1</td>
<td>Håkanson, 2004</td>
</tr>
<tr>
<td>Fraction of accumulation (A)sediment</td>
<td>$D_A$</td>
<td></td>
<td>0.29</td>
<td>Lindström &amp; Håkanson 2001</td>
</tr>
<tr>
<td>Volume development</td>
<td>$V_d$</td>
<td>-</td>
<td>1.78</td>
<td>Lindström &amp; Håkanson 2001</td>
</tr>
<tr>
<td>Particle settling velocity</td>
<td>$v$</td>
<td>m/year</td>
<td>210</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Burial velocity</td>
<td>$v_{bur}$</td>
<td>m/year</td>
<td>0.001</td>
<td>assumed (See Appendix I)</td>
</tr>
<tr>
<td>Water retention time</td>
<td>$T_W$</td>
<td>year</td>
<td>1.6</td>
<td>Lindström and Håkanson, 2001</td>
</tr>
<tr>
<td>Suspended solids concentration</td>
<td>$C_{PW}$</td>
<td>g/m³</td>
<td>3</td>
<td>Lithner et al. 2003</td>
</tr>
<tr>
<td>Sediment water content</td>
<td>$W$</td>
<td>-</td>
<td>0.95</td>
<td>Sternbeck et al., 2003</td>
</tr>
<tr>
<td>Sediment bulk density</td>
<td>$b_{ds}$</td>
<td>g/cm³</td>
<td>1.03</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Volume fraction of solids in sediment</td>
<td>$f_{PS}$</td>
<td>m³/m³</td>
<td>0.021</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Sediment solids density</td>
<td>$\rho_{PS}$</td>
<td>g/cm³</td>
<td>2.4</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Temperature</td>
<td>$Temp$</td>
<td>K</td>
<td>281.5</td>
<td>SCB, 2010</td>
</tr>
<tr>
<td>Air side mass transfer coefficient (MTC)</td>
<td>$K_A$</td>
<td>m/h</td>
<td>1</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Water side MTC</td>
<td>$K_L$</td>
<td>m/h</td>
<td>0.01</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Sediment-water diffusion MTC</td>
<td>$K_T$</td>
<td>m/h</td>
<td>0.0004</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>$G_{dap}$</td>
<td>kg/year</td>
<td>81900</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Resuspension rate</td>
<td>$G_{res}$</td>
<td>kg/year</td>
<td>70762</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Burial rate</td>
<td>$G_{bur}$</td>
<td>kg/year</td>
<td>6552</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Fraction of organic carbon in water</td>
<td>$f_{OCW}$</td>
<td></td>
<td>0.3</td>
<td>Håkanson, 2006</td>
</tr>
<tr>
<td>Fraction of organic carbon in sediment</td>
<td>$f_{OCS}$</td>
<td></td>
<td>0.16</td>
<td>Sternbeck et al., 2003</td>
</tr>
</tbody>
</table>

### 4.2 Lake Drevviken

As located in the southern part of Stockholm, Sweden, Lake Drevviken is shared by Stockholm, Huddinge, Tyresö and Haninge municipalities, and the Stockholm part
covers the northern and western areas of its northern basin, as shown in Figure 4.2. Lake Drevviken is the largest lake in Tyresån's lake system with a surface area of 571 hectares. Lake water mainly comes from two large tributaries: Lissmaån in the south and Forsån in the north of the catchment, and the primary outflows are Gudö å and Långsjön (Stockholm Vatten, 2000b). The water retention time is 11 months (Sternbeck et al., 2003). As a part of the nature reserve of Lake Flaten, the lake and green space to its north are of great natural and recreational value to its surrounding environment (Stockholm Vatten, 2000b).

### 4.2.1 Catchment area

The catchment area of Lake Drevviken is around 4897 hectares and it is largely occupied by residential buildings, mostly one-family houses. Three major industrial areas are located in Handen, Länna and Larsboda, as shown in Figure 4.2. Besides the residential and industrial areas, the rest of the catchment is dominated by forests and open grasslands (Stockholm Vatten, 2000b).
Some activities in this area have been classified as environmentally hazardous, including a petrol station at Nynäsvägen to the west, an asphalt works and concrete industry in Larsboda industrial area, some other small industries in Skrubba and a closed stock pile containing landfill and construction dump to the east of the lake. Also, a subway track to Farsta runs through the catchment area and there are around 8 km roads with heavy traffic load located to the west and east sides of the lake (Stockholm Vatten, 2000b).

### 4.2.2 Lake quality

Historically, the phosphorous and nitrogen concentration in the lake water were very high in early 1970’s, but the situation is better nowadays since efforts have been made to improve the management of sewage discharge from Huddinge. There is little literature available about the nonylphenol concentration in Lake Drevviken. However, at least eight sediment cores been sampled and mixed in the field, a sediment nonylphenol concentration of 1500 ng/g dw was reported for Lake Drevviken as monitoring result of the study in May and June 2002 (Sternbeck et al., 2003). In a more recent program about the surface water quality of Stockholm, 9 samples of the water of Lake Drevviken were tested, and a mean nonylphenol concentration of 0.91 mg/l was detected (Österås and Sternbeck, 2010).

### 4.2.3 Source and load of nonylphenol

All the potential sources identified for Lake Trekanten (see Chapter 4.1.3) can also be found in the catchment area of Lake Drevviken. As for Lake Trekanten, several traffic roads with high vehicle density lie around Lake Drevviken. These roads can be important sources of nonylphenol emission in the area. Building materials, human activities and atmospheric deposition can also contribute to the total load as mentioned before. According to Djurberg (2010b), private sewers within the catchment area might be another important source of NP/NPEs to Drevviken.

A rough estimation of the total load of NP/NPEs, which is around 3.75 kg/year, was derived in the study of Djurberg (2010b) for the Lake Drevviken. However, due to lack of information, the part of NP/NPEs that came from building material was missing in this estimate, but might be an important source and thus cannot be ignored. In this report, the roughly estimated load is used in the following fate modeling, and the influence of the missing part on the model result is discussed in Section 6.2.

### 4.2.4 Lake specific parameters

The data of Lake Drevviken used in the base-case lake model are listed in Table 4.2. The conceptual model of the base-case lake model and its quantification will be introduced in Section 5.1.1 and 5.1.2 respectively.
Table 4.2 Parameters of Lake Drevviken used in the lake model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water surface area</td>
<td>$A_W$</td>
<td>m²</td>
<td>5710000</td>
<td>Stockholm Vatten, 2000b</td>
</tr>
<tr>
<td>Sediment area</td>
<td>$A_S$</td>
<td>m²</td>
<td>5710000</td>
<td>assumed the same as water</td>
</tr>
<tr>
<td>Mean water depth</td>
<td>$h_W$</td>
<td>m</td>
<td>6.5</td>
<td>Stockholm Vatten, 2000b</td>
</tr>
<tr>
<td>Water volume</td>
<td>$V_W$</td>
<td>m³</td>
<td>37000000</td>
<td>Stockholm Vatten, 2000b</td>
</tr>
<tr>
<td>Sediment active depth</td>
<td>$h_S$</td>
<td>m</td>
<td>0.02</td>
<td>Sternbeck et al., 2003</td>
</tr>
<tr>
<td>Water retention time</td>
<td>$T_W$</td>
<td>year</td>
<td>0.917</td>
<td>Stockholm Vatten, 2000b</td>
</tr>
<tr>
<td>Suspended solids concentration</td>
<td>$C_{PS}$</td>
<td>g/m³</td>
<td>3</td>
<td>assumed (see text)</td>
</tr>
<tr>
<td>Sediment water content</td>
<td>$W$</td>
<td>-</td>
<td>0.942</td>
<td>Sternbeck et al., 2003</td>
</tr>
<tr>
<td>Sediment bulk density</td>
<td>$b_{dS}$</td>
<td>g/cm³</td>
<td>1.04</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Volume fraction of solids in sediment</td>
<td>$f_{PS}$</td>
<td>m³/m³</td>
<td>0.025</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Sediment solids density</td>
<td>$\rho_{PS}$</td>
<td>g/cm³</td>
<td>2.4</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Temperature</td>
<td>$\text{Temp}$</td>
<td>K</td>
<td>281.5</td>
<td>SCB, 2010</td>
</tr>
<tr>
<td>Air side mass transfer coefficient (MTC)</td>
<td>$K_A$</td>
<td>m/h</td>
<td>1</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Water side MTC</td>
<td>$K_L$</td>
<td>m/h</td>
<td>0.01</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Sediment-water diffusion MTC</td>
<td>$K_T$</td>
<td>m/h</td>
<td>0.0004</td>
<td>SOCOPSE, 2009</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>$G_{dep}$</td>
<td>kg/year</td>
<td>2226900</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Resuspension rate</td>
<td>$G_{res}$</td>
<td>kg/year</td>
<td>1558830</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Burial rate</td>
<td>$G_{bur}$</td>
<td>kg/year</td>
<td>342600</td>
<td>calculated (see Appendix I)</td>
</tr>
<tr>
<td>Fraction of organic carbon in water</td>
<td>$f_{OCW}$</td>
<td>_</td>
<td>0.3</td>
<td>Håkanson, 2006 Mackay, 2001 (see Appendix I)</td>
</tr>
<tr>
<td>Fraction of organic carbon in sediment</td>
<td>$f_{OCS}$</td>
<td>_</td>
<td>0.11</td>
<td>Sternbeck et al., 2003 Mackay, 2001 (see Appendix I)</td>
</tr>
</tbody>
</table>

Since no data is available for the suspended solid concentration in Lake Drevviken, it is assumed the same as in Lake Trekanten, which is 3mg/l (Lithner et al. 2003). Section 7.2 shows that the uncertainty of model results caused by this variable is rather low. So here this assumed value is considered acceptable and used in the fate modeling.
5. Model description

During the last two decades, many models, developed based on the mass balance principle, have been widely used to study the fate of chemicals in the aquatic environment. The basic idea of these studies is to establish the linkage between the load of specific chemicals and the resulting concentrations of these chemicals in different environmental compartments, such as water and sediment (Mackay et al., 1994; Van Ry et al., 2000; Lindström and Håkanson, 2001). Environmental fate modelling has been proofed to be useful for providing opportunity to investigate systems that could otherwise not be studied due to scales of time or size or due to financial reasons, and thus it is very helpful to guide the field sampling and to support environmental decision making.

A rate constant model (referred to as the base-case lake model in this thesis) based on mass balance principle is employed in this thesis to study the fate of nonylphenol in lakes. This model was developed by Mackay et al. (1994), and was originally applied to simulate the fate of Polychlorinated biphenyls (PCBs) in Lake Ontario. As written in a “rate constant” form, it is a simple model without requiring complex input data and extensive computation.

In order to carry out a comparison between different modeling methods, another model developed by Lindström and Håkanson (2001), which divided the lake sediment into erosion and transport (ET) area and accumulation (A) area, is taken as a second type of model (referred as ET-A Model) to quantify the fate of nonylphenol in Lake Trekanten. This model follows the same principle as the one by Mackay et al. (1994), with somewhat different process conceptualization as shown below (Section 5.3).

5.1 The base-case lake model

5.1.1 Conceptual model

The basic structure of the base-case lake model consists of two compartments: water and sediment. The lake water is assumed to be well-mixed and homogeneous in composition. Similarly, the bottom sediment is assumed to be a well-mixed layer of defined depth, with inaccessible, buried sediments underneath. These two assumptions are key simplifications in this model, and make further horizontal and vertical compartmentalization unnecessary, and reduce the data requirement in the model quantification. As defined as the sediment accumulation zone, the horizontal area of sediment is equal or less than the surface water area (Mackay et al., 1994).

Processes, such as volatilization, wet and dry atmospheric deposition, absorption, water inflow and outflow, transformation in water and sediment, diffusion, sediment deposition, resuspension and burial are considered in this model, as shown in Figure 5.1.
After being released into the lake system, part of the dissolved nonylphenol will be evaporated into atmosphere, and this process is called volatilization. The reverse process, i.e. the incorporation of free nonylphenol vapor in the air to water, is called absorption. However, there is no available data of nonylphenol's atmospheric concentration, so the absorption from air to water is assumed negligible in this study. Besides, nonylphenol associated with aerosol particles can be transferred from air to water by dry deposition, i.e. the particles fall under the influence of gravity, and wet deposition, in which the particles are swept out from the air by rain drops. According to the result of a recent substance flow analysis of Lake Trekanten and Lake Drevviken, the part of nonylphenol emission from atmospheric deposition on the catchment area and on lakes’ surface is already included in the total load (Djurberg, 2010a). Therefore in order to avoid double counting, the nonylphenol transfer from air to water by atmospheric deposition (both dry and wet) is not considered as separate processes in the fate model, but to be incorporated into the total load within the inflow water.

For water-sediment exchange, particles in water play a very important role. They serve as vehicles to transport sorbed nonylphenol from water to bottom sediment; this process is called deposition. The reverse process, resuspension, is caused by currents, which bring the settled particles back to water, or by biotic activity, in which the organic carbon in particles is mineralized resulting in release of nonylphenol to solution (Mackay et al., 1994). Also, the bioturbation by benthic fauna or flora can directly (e.g. direct interception of the animal with particles) or indirectly (e.g. changes of physical properties

![Conceptual model of the fate of nonylphenol in the base-case lake model.](image)
of the sediments) influence both the resuspension and deposition (Graf and Rosenberg, 1997). Finally, particles will be conveyed out from the well mixed layer of the sediment and become inaccessible by the process of sediment burial. Diffusion of dissolved nonylphenol between the water column and the pore water in sediment will take place due to the gradient in concentration.

Also degradation of nonylphenol can take place in water and sediment including photolysis, hydrolysis and biodegradation. These different mechanisms are considered together as one process in water and in sediment, respectively, as transformation in water and transformation in the sediment in this model.

5.1.2 Model quantifications

The load of NP/NPEs from a recent study of Djurberg (2010a) is employed as the input data in this thesis, and it is treated as direct emission \( F_{in} \) to lake water. All processes mentioned above are assumed to be first order, each of which is treated by a first order rate constant with units of reciprocal time (year\(^{-1}\) in this study), as follows:

- Volatilization of nonylphenol from water to air, \( R_{vol} \)
- Water outflow from the lake, \( R_{vol} \)
- Transformation of nonylphenol in water, \( R_{trans,W} \)
- Deposition, \( R_{dep} \)
- Diffusion from water to sediment, \( R_{diff,WS} \)
- Resuspension, \( R_{res} \)
- Diffusion from sediment to water, \( R_{diff,SW} \)
- Transformation of nonylphenol in sediment, \( R_{trans,S} \)
- Sediment burial, \( R_{bur} \)

These rate constants depend on both chemical properties and lake conditions, and they can be used to compare different processes. Generally speaking, a larger rate constant means a faster and more important process in determining the behavior of the chemical in the aquatic environment (Mackay et al., 1994). Table 5.1 shows the quantification of the rate constants used in this model.

Based on the mass balance principle, the mass balance equations for the amount of chemical in water \( (M_w, \text{kg}) \) and sediment \( (M_s, \text{kg}) \) can be expressed as follows, in units of kg/year:

For water compartment:

\[
\frac{dM_w}{dt} = F_{in} + (R_{res} + R_{diff,SW})M_s - (R_{vol} + R_{out} + R_{dep} + R_{diff,WS} + R_{trans,W})M_w
\] (2)

For sediment compartment:
\[
\frac{dM_S}{dt} = (R_{dep} + R_{diff_{WS}}) M_W - (R_{res} + R_{diff_{SW}} + R_{trans_{S}} + R_{bur}) M_S
\]

(3)

Based on above mentioned equations, the mass of chemical in water \((M_W, \text{ kg})\) and sediment \((M_S, \text{ kg})\) can be obtained as the direct model output. The chemical concentrations in different compartments can be calculated by following formulas:

The chemical concentration in water \((C_W, \text{ ng/l})\):

\[
C_W = \frac{M_W}{V_W} \times 10^9
\]

(4)

This equation is based on the assumption that the water density is 1 kg/L.

The chemical concentration in sediment on a dry weight (dw) basis \((C_S, \text{ ng/g dw})\):

\[
C_S = \frac{M_S}{A_S \cdot h_S \cdot f_{ps} \cdot \rho_{ps}} \times 10^6
\]

(5)

Where \(A_S\) is the sediment area \((\text{m}^2)\); \(h_S\) is the sediment mean depth \((\text{m})\); \(f_{ps}\) is the volume fraction of solids in sediment \((\text{m}^3/\text{m}^3)\); \(\rho_{ps}\) is the density of sediment solids \((\text{g/cm}^3)\).

<table>
<thead>
<tr>
<th>Processes</th>
<th>Quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatilization</td>
<td>(R_{vol} = K_V \cdot f_{DW} \cdot 8760 / h_W)</td>
</tr>
<tr>
<td></td>
<td>(K_V = \frac{1}{K_L + \frac{1}{K_A \cdot K_{AW}}})</td>
</tr>
<tr>
<td></td>
<td>(K_{AW} = \frac{H}{8.314 \cdot \text{Temp}})</td>
</tr>
<tr>
<td></td>
<td>(f_{DW} = \frac{1}{1 + 10^{-6} \cdot K_P \cdot C_{PW}})</td>
</tr>
<tr>
<td></td>
<td>(K_P = K_{OC} \cdot f_{OC})</td>
</tr>
<tr>
<td></td>
<td>(K_{OC} = 0.41 \cdot K_{OW})</td>
</tr>
<tr>
<td>Outflow</td>
<td>(R_{out} = \frac{1}{T_W})</td>
</tr>
</tbody>
</table>

Table 5.1 Quantification of the rate constants treated in the base-case lake model
Water Transformation

\[ R_{\text{trans}_W} = 8760 \cdot \frac{0.693}{T_{HLW}} \]

Deposition

\[ R_{\text{dep}} = \frac{1000 \cdot G_{\text{dep}} \cdot f_{SW}}{V_W \cdot C_{PW}} \]

Diffusion from water to sediment

\[ R_{\text{diff}_WS} = \frac{8760 \cdot K_T \cdot A_S \cdot f_{DW}}{V_W} \]

\[ f_{SW} = \frac{10^{-6} \cdot K_p \cdot C_{PW}}{1 + 10^{-6} \cdot K_p \cdot C_{PW}} \]

Resuspension

\[ R_{\text{res}} = \frac{1000 \cdot G_{\text{res}} \cdot f_{SS}}{V_S \cdot C_{PS}} \]

\[ C_{PS} = 10^6 \cdot f_{PS} \cdot \rho_{PS} \]

Diffusion from sediment to water

\[ R_{\text{diff}_ SW} = \frac{8760 \cdot K_T \cdot A_S \cdot f_{DS}}{V_S} \]

\[ f_{DS} = \frac{1}{1 + 10^{-6} \cdot K_p \cdot C_{PS}} = 1 - f_{SS} \]

Sediment Transformation

\[ R_{\text{trans}_S} = 8760 \cdot \frac{0.693}{T_{HLs}} \]

Sediment Burial

\[ R_{\text{bur}} = \frac{1000 \cdot G_{\text{bur}} \cdot f_{SS}}{V_S \cdot C_{PS}} \]

*See Mackay et al., 1994

*See Karickhoff, 1981

Nomenclature and explanation:

- AS-sediment area (m²);
- CPW, CPS-concentration of particles in water, sediment (g/m³);
- fDW, fDS-fraction of nonylphenol dissolved in water, sediment; fPS-volume fraction solids in sediment (m³/m³).
- fSW, fSS-fraction of nonylphenol sorbed to particles in water, sediment; fOCS-organic carbon fraction in sediment; Gbur, Gdep, Gres-particle burial, deposition, resuspension rate (kg/year); H-Henry’s Law Constant (Pa.m³/mol); hW-mean water depth (m);
- KA-air side MTC, (m/h);
- KL-water side MTC, (m/h);
- KAW-air-water partition coefficient;
- KOC-organic carbon-water partition coefficient;
- KOW-octanol-water partition coefficient;
- KP-water to particle partition coefficient, (L/kg);
- KT-sediment-water diffusion MTC, (m/h);
- KV-overall water side MTC,
With the chemical-physical properties of nonylphenol (see Table 3.2) and values of lake specific parameters (see Table 4.1 and Table 4.2) given, the quantification of the base-case lake model can be achieved using above mentioned equations in selected modeling tools.

5.1.3 Model implementation

5.1.3.1 The modeling tool - Simile

Simile is a generic visual modeling environment which is designed to simulate complex dynamic systems in the earth, environmental and life science. As derived from traditional agro-ecological simulation models, Simile inherited the familiar System Dynamics (Compartment-flow) paradigm and combined it with the object-based paradigm. The extended applicability enables its handling of different forms of disaggregation, as well as spatial modeling and individual based modeling (Muetzefeldt and Massheder, 2003). Moreover, the graphical user interface makes it accessible to non-programmers, and it could also represent interactions within complex system in a clear structured and intuitive way.

With these above mentioned characteristics, Simile has already been widely used as a tool in some research programs and to develop various demonstration models in different fields (Muetzefeldt and Massheder, 2003). Different models have been constructed in Simile to study the fate of copper in Swedish lakes (Cui et al., 2009; Sinha, 2009). In order to have a comprehensive understanding of the fate of nonylphenol, the modeling tool of this thesis work should be able to reflect the response time of nonylphenol concentrations to load variations. Therefore, the easy accessibility and the dynamic characteristic of Simile make it a good choice for this study.

5.1.3.2 Model implementation in Simile

The model is implemented in Simile in this study. In Simile, each compartment is a state variable, and each flow contributes to the rate of change expression for the associated state variable(s). Different rate constants are calculated from above mentioned equations and treated as variables of corresponding flows. The flow diagram of the model implemented in Simile is shown in Figure 5.2.

In Figure 5.2, two blocks, i.e. the upper and lower ones, stand for the water and the sediment compartment, respectively. Also, ten different flows in this figure correspond to previous mentioned ten processes in the conceptual model (see Figure 5.1). Except for the water inflow (Fin), each flow has a corresponding rate constant. These rate constants can be quantified follow the equations provided in Table 5.1 with given chemical properties and lake specific data. Therefore, the modeler can run the model in Simile to
get the model results.

Figure 5.2 The flow diagram of the base-case lake model in Simile. The upper and lower blocks, stand for the water and the sediment compartment, respectively. Ten different flows in this figure correspond to previous mentioned ten processes in the conceptual model. Except for the water inflow ($F_w$), each flow has a corresponding rate constant (see Figure 5.1). The meaning of the subscripts can be found at Page VIII.

5.1.4 Sensitivity and uncertainty analysis

A sensitivity analysis is a study of how and to what extent the model's outputs are influenced by changes of model inputs. By carrying out a sensitivity analysis, the user can be knowledgeable of the relative importance of processes and parameters in the model. It provides the possibility for modelers to further simplify the model on the least important processes, as well as to enable decision makers to take effective measures on the dominant processes. Moreover, the sensitivity analysis is related to model uncertainty, and it demonstrates how uncertainty in a model output can be systematically apportioned to different sources of uncertainty in the model input.

In this study, Lake Trekanten is selected to conduct the sensitivity analysis, which will focus on the rate constants of different processes with the following steps. Firstly, change the nine rate constants to 0.1 times and 10 times of their original value, respectively, while keep others remain unchanged, and then compare the change of the model outputs, i.e. the concentration of nonylphenol in water and sediment. By carrying out such a rough analysis, processes with relatively big influence on the model results can be identified. Secondly, a detailed sensitivity analysis with smaller steps will be conducted
on the rate constants selected from the first step, and to further analyze the influence of relevant parameters.

The uncertainty of the base-case lake model will be analyzed based on the result of sensitivity analysis. Results of sensitivity and uncertainty analysis will be given in Chapter 7.

5.2 The ET-A lake model

As developed by Lindström and Håkanson (2001), the ET-A lake model was used to study the heavy metal load in lakes. The most prominent feature of this model is that the sediment is differentiated into two interactive parts, i.e. the erosion and transport (ET) area and accumulation (A) area, according to the criteria provided by Håkanson and Jansson (1983). Affected by the wind speed and water current, resuspension can happen from the relatively shallow ET-area to the water body and to the A-area, and therefore interrupt the particle sedimentation on this area. A-area prevails where the fine particles can deposited continuously, and gradually be buried under newly deposited ones and transferred to inaccessible bottom sediments. Also, the process of diffusion of chemicals from A-area to water is considered in this model (Lindström & Håkanson, 2001).

![Figure 5.3. Conceptual model of the ET-A lake model.](image)

However, as the model was designed to simulate the fate of heavy metal in lakes, it is not suitable to be used on nonylphenol directly. Processes including volatilization, water and sediment transformation are added to the model in order to make the model applicable to nonylphenol, which is classified as semivolatile and biodegradable (Van Ry et al., 2000). The conceptual model is shown in Figure 5.3.
Same as in the base-case lake model, all the processes considered in the ET-A lake model are also treated by first order rate constants. In order to quantify the added processes for nonylphenol, i.e. the volatilization, and transformation in water and in sediment, the corresponding rate constants are borrowed from the base-case lake model. For the calculation of water outflow rate constants, the base-case lake model just calculated it as the simply hydrological flushing, i.e. \( R_{\text{out}} = \frac{1}{T_W} \). In the original work about the ET-A lake model, Lindström and Håkanson (2001) proposed different equations to calculate the water outflow rates based on the sizes and water turnover times of different lakes. However, in this thesis, the equation of water outflow rate is set the same as in the base-case lake model, in order to make these two models comparable and to highlight the effect caused by separated sediment compartments. Moreover, since there is no consensus on the diffusion constant of nonylphenol, the overall rate constant of the sediment to water diffusion process is employed from the base-case lake model and be used in the ET-A lake model. The quantification of processes of the ET-A lake model is shown in Table 5.2.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Quantification</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatilization</td>
<td>( K_{\text{vol}} = R_{\text{vol}} )</td>
<td>See Table 5.1</td>
</tr>
<tr>
<td>Outflow</td>
<td>( K_{\text{out}} = \frac{1}{T_W} )</td>
<td>Modified in order to be comparable with the base-case model.</td>
</tr>
<tr>
<td>Water Transformation</td>
<td>( K_{\text{trans}<em>W} = R</em>{\text{trans}_W} )</td>
<td>See Table 5.1</td>
</tr>
<tr>
<td>Sedimentation on ET-area*</td>
<td>( K_{\text{sed}<em>ET} = D</em>{ET} \cdot K_{\text{sed}} )</td>
<td>( f_{SW} ) see Table 5.1</td>
</tr>
<tr>
<td></td>
<td>( K_{\text{sed}} = f_{SW} \cdot v / h_W )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D_{ET} = 1 - D_A )</td>
<td></td>
</tr>
<tr>
<td>Sedimentation on A-area*</td>
<td>( K_{\text{sed}<em>A} = D_A \cdot K</em>{\text{sed}} )</td>
<td></td>
</tr>
</tbody>
</table>
Resuspension from ET-area to water
\[ K_{\text{res \_ETW}} = K_{\text{res}} \cdot (1 - \frac{V_d}{3}) \]
\[ K_{\text{res}} = \frac{1}{T_{\text{ET}}} \]

Resuspension from ET-area to A-area
\[ K_{\text{res \_ETA}} = K_{\text{res}} \cdot \frac{V_d}{3} \]

Diffusion from A-area to water
\[ K_{\text{diff \_A}} = R_{\text{diff \_SW}} \quad \text{See Table 5.1} \]

ET-area transformation
\[ K_{\text{trans \_ET}} = R_{\text{trans \_S}} \quad \text{See Table 5.1} \]

A-area transformation
\[ K_{\text{trans \_A}} = R_{\text{trans \_S}} \quad \text{See Table 5.1} \]

Sediment Burial
\[ K_{\text{bur}} = \frac{1}{T_A} \]
\[ T_A = \frac{h_S}{v_{\text{bur}} \cdot \frac{V_d}{3}} \]

*See Lindström & Håkanson, 2001

Nomenclature and explanation:
\( D_{\text{ET}}, D_A \)-empirical value of ET-area, A-area; \( f_{\text{SW}} \)-fraction of nonylphenol sorbed to particles in water; \( h_w \)-mean water depth (m); \( h_S \)-sediment active depth (m); \( T_{\text{ET}}, T_A \)-Age of ET-sediment, A-sediment (year); \( T_W \)-water retention time (year); \( v \)-particle settling velocity (m/year); \( v_{\text{bur}} \)-sediment burial velocity (m/year); \( V_d \)-volume development;

The differential mass balance equations for the amount of nonylphenol in water \( (M_W, \text{kg}) \), ET-sediment \( (M_{\text{ET}}, \text{kg}) \) and A-sediment \( (M_A, \text{kg}) \) are, in units of \( \text{kg/year} \):

For water compartment:
\[ \frac{dM_W}{dt} = E_{\text{in}} + K_{\text{diff \_A}} \cdot M_A + K_{\text{res \_ETW}} \cdot M_{\text{ET}} - (K_{\text{volat}} + K_{\text{sed \_ET}} + K_{\text{sed \_A}} + K_{\text{out}} + K_{\text{trans \_W}}) \cdot M_W \]

For ET-sediment compartment:

(6)
\[
\frac{dM_{ET}}{dt} = K_{sed\_ET} \cdot M_W + (K_{res\_ETW} + K_{res\_ETA} + K_{trans\_ET}) \cdot M_{ET}
\]

(7)

For A-sediment compartment:

\[
\frac{dM_A}{dt} = K_{sed\_A} \cdot M_W + K_{res\_ETA} \cdot M_{ET} - (K_{diff\_A} + K_{trans\_A} + K_{bur}) \cdot M_A
\]

(8)

Corresponding concentrations in these compartments are calculated as follows.

Nonylphenol concentration in water (\(C_W\), ng/l):

\[
C_W = \frac{M_W}{V_W} \times 10^9
\]

(9)

Nonylphenol concentration in ET-sediment (\(C_{ET}\), ng/g dw)

\[
C_{ET} = \frac{M_{ET}}{A_S \cdot h_S \cdot f_{PS} \cdot \rho_{PS} \cdot D_{ET}} \times 10^6
\]

(10)

Nonylphenol concentration in A-sediment (\(C_A\), ng/g dw)

\[
C_A = \frac{M_A}{A_S \cdot h_S \cdot f_{PS} \cdot \rho_{PS} \cdot D_A} \times 10^6
\]

(11)

### 5.3 Comparison between the base-case lake model and the ET-A lake model

#### 5.3.1 Similarities

Firstly, both of the base-case lake model and the ET-A model are built based on the mass balance principle. Secondly, these two models are designed to study the fate of chemicals in a lake, especially their behavior in water and in the sediment and the interaction between these two compartments. Thirdly, all processes considered in these two models are assumed to be first order. This treatment can greatly simplify these two models and make them easy to understand.

#### 5.3.2 Differences

First of all, the most predominant difference is that the ET-A lake model separates the sediment into two interactive areas, i.e. the erosion and transport (ET) area and accumulation (A) area. This may have a better reflection of the real situation since different layers of the sediment have different characteristics. However, it requires more data to quantify the ET-A lake model.

Secondly, these two models have different application objects. The base-case lake model...
was firstly used to study the fate of Polychlorinated biphenyls (PCBs) in Lake Ontario, while the ET-A lake model was originally applied to simulate the fate of heavy metals in lakes. Therefore, the original ET-A lake model is not readily to be used to study the fate of organic compounds, such as nonylphenol in this work. To make the ET-A lake model applicable in this study, several processes and variables are just borrowed from the base-case lake model. However, according to Sinha (2009), who carried out a similar comparison between different models in his study, to use values of variables compatible to one model directly to a different model may not be appropriate.

Thirdly, as originally designed for heavy metal modeling, the ET-A lake model treats the diffusion process as from sediment to water, since concentrations of heavy metals are usually much higher in interstitial water of the sediment than in the overlying lake water (Lindström and Håkanson, 2001). In the base-case lake model, diffusion is considered both from water to sediment and from sediment to water. Without clear explanation from the original paper, it is supposed that the net diffusion can happen in either direction depending on the chemical’s properties and environmental conditions.

Besides the above mentioned differences in the conceptualization of these two models, some differences in the model quantifications can also be observed. For example, in the ET-A lake model, a form factor, $V_{da}$, is introduced as a correction to obtain a lake-typical sedimentation. This form factor is not used in the quantification of the base-case lake model.

Considering above mentioned differences in both model conceptualization phase and the quantification phase of the base-case lake model and the ET-A lake model, different model results can be expected from these two models. However, it is difficult to say which one is better. Since the base-case lake model is readily to be used for organic compounds such as nonylphenol, it is selected as the main model in this work. The sensitivity and uncertainty analysis in this work are also focused on the base-case lake model. Due to time limitation and availability of data, the ET-A lake model is only applied for the Lake Trekanten for comparison purpose.
6. Results

6.1 Lake Trekanten

As adopted from personal communication with Djurberg (2010a), a preliminary NP/NPEs load of 3.58 kg per year from the catchment area is treated as the emission with the inflow water to Lake Trekanten. The results of the fate modeling in this chapter are based on the assumption that the entire load is pure nonylphenol. A discussion about the mixed load of NP/NPEs is carried out in Chapter 9.

6.1.1 Results of the base-case lake model

The result of nonylphenol’s distribution and concentration in Lake Trekanten at steady-state is shown in Figure 6.1. The transformation of nonylphenol in water is the most important nonylphenol removal process followed by the water outflow in the second place.

![Figure 6.1. Mass balance of nonylphenol at steady state in Lake Trekanten from the base-case lake model. The conceptual model is shown in Figure 5.1.](image)

About 0.89 kg nonylphenol goes to the downstream system with the water outflow every year while around 2.40 kg (67% of the total load) of nonylphenol is transformed by biodegradation, hydrolysis and photolysis in water, even though its half-life in water is 150 days in this model. This can be explained as a result of the small water inflow and outflow rate of the Lake Trekanten (a corresponding water retention time of 1.6 years; Lindström and Håkanson, 2001), which means nonylphenol can have enough retention time in the water body for transformation to take place to a considerable extent. Only a
small part of the nonylphenol is removed from the water body by the volatilization process. This is in good agreement with nonylphenol’s low vapor pressure and a corresponding low Henry’s Law Constant.

Moreover, the nonylphenol removed by transformation in the sediment is only a little more than 0.05 kg per year, which can be explained by the very long half life (3013 days) of nonylphenol in the sediment mainly caused by the low ambient temperature. Also, a small fraction of nonylphenol is subjected to the burial process, which is due to the typically slow burial velocity of 1mm per year used in the simulation. As shown in Figure 6.1, about 1.43 kg of nonylphenol will stay in a dynamic mass exchange between water and sediment as a result of deposition, resuspension and diffusion processes.

The overall residence time of nonylphenol, defined as the mass of nonylphenol within the lake (both in water and in sediment) divided by the sum of all removal flows, is around 0.58 years. Of the 2.07 kg nonylphenol in the lake system at steady state, 1.43 kg stays in the water body while the rest 0.638 kg is in the sediment. Theoretically, with a logKow value of 4.48, nonylphenol is expected to adsorb strongly to the sediment in the aquatic environment. But this doesn’t necessarily mean that there should be more nonylphenol in sediment than in water column. As in this case, the volume of sediment is much smaller compared to the volume of the water body, and the volume fraction of solids in sediment is only 0.021. That’s why less nonylphenol is found in sediment than in water in Lake Trekanten, even though it is favorable for nonylphenol to partition to organic matters in the sediment.

6.1.2 Comparison of the base-case lake model results with field data

According to the model results, the concentration of nonylphenol in the water body is around 2.5 μg/l. This value is higher than 0.33 μg/l, which is the predicted no-effect value of nonylphenol concentration in surface water as given in Table 3.3. However, there is no field data on the nonylphenol concentration in the water of Lake Trekanten available for comparison with the model result. Also, the concentration in lake water may be variable due to seasonal changes, different weather conditions, etc. So it is more reliable and practically useful to compare the measured and simulated concentrations in the sediment.

A concentration of nonylphenol in Lake Trekanten of 3200 ng/g dw was detected by Swedish Environmental Research Institute in 2003 (Sternbeck et al., 2003). The modeling result, i.e. 4870 ng/g dw, is in good agreement with the field data. From both the field data and model results, it is obvious that the load of nonylphenol is rather high if we take the small size of Lake Trekanten into account, and thus it results in a high nonylphenol concentration in the sediment. However, there are always uncertainties associated with model results. An analysis of the model uncertainty is carried out in Section 7.2.
6.1.3 Results of the ET-A lake model

With the same nonylphenol load (3.58 kg/year) applied to the ET-A lake model as in the base case model (Chapter 6.1.1), its concentration and distribution in Lake Trekanten under steady state is shown in Figure 6.2.

Figure 6.2. Mass balance of nonylphenol at steady state in Lake Trekanten from the ET-A lake model. The conceptual model is shown in Figure 5.3.

The result obtained from the ET-A lake model is similar with that of the base-case lake model. The dominant nonylphenol removal process is the transformation in water, and then comes the outflow. However, in the ET-A lake model, the amount of nonylphenol removed by sediment burial is much smaller than that in the base-case lake model. For the mass exchange between water and sediment, these two models have obvious differences in their conceptual models, as previously mentioned in Section 5.3.2. Therefore, the amount of nonylphenol that participate in the dynamic mass exchange between water and sediment in the base-case lake model (ca. 1.45 kg/year) is higher than the corresponding amount of nonylphenol in the ET-A lake model (ca. 0.37 kg/year). Also, the net sedimentation (water sediment exchange) of nonylphenol in the ET-A lake model is 0.039 kg/year, while in the base-case lake model a higher value of 0.082 kg/year was derived.

According to the results of the ET-A lake model, about 1.86 kg of nonylphenol stays within the lake system after the steady state has been reached. In the water column, there is 1.44 kg of nonylphenol which is very close to the results from the base-case lake model. However, the amount of nonylphenol in sediment (ET area plus A area) in the ET-A lake model, i.e. 0.42 kg, which is 35% lower than the amount in the base-case lake model (0.64 kg). This may due to the differences in the conceptualization of these two models, especially the ET-A model only consider the diffusion from sediment to water while the base-case lake model considers diffusion on both directions (see Section 5.3.2).
Therefore the sediment nonylphenol content of ET-A lake model can be lower. The mass of nonylphenol in the A-sediment is 0.150 kg, and the corresponding concentration is 3950 ng/g dw. Since the surface sediment samples of the field sampling were collected within the areas defined as the accumulation area (A-sediment) in ET-A lake model (Lindström and Håkanson, 2001), the field data should be compared with the nonylphenol concentration in A-sediment of this model.

Compared with results of the base-case lake model, the sediment concentration of nonylphenol of the ET-A lake model is closer to the field data (3200 ng/g dw). However, this does not necessarily mean that the ET-A lake model is better than the base-case lake model. Firstly, according to Djurberg (2010a), the load is actually a mixture of nonylphenol and nonylphenol ethoxylates. This means an overestimation about the concentration is expected for the model output, which is derived under the assumption of a pure nonylphenol load (a further discussion about this issue is in Section 9.2). So without knowing the load composition, it is difficult to judge which model output is a better fit to the field data. Secondly, since the ET-A lake model was originally used for heavy metals, many processes, such as volatilization, the transformation in water and in sediment, are just added to adapt to organic chemicals in this case with parameters borrowed from the base-case lake model. It is unknown whether these modifications are appropriate or not (see Section 5.3). So there are still many uncertainties on the model performance of ET-A lake model.

6.2 Lake Drevviken

A rough estimate of the NP/NPEs load of 3.75 kg/year is adopted here as a direct emission to Lake Drevviken (Djurberg, 2010b). The load is assumed to be pure nonylphenol. Without counting in the emission from building materials, which was not possible in the study of Djurberg (2010b), this load will be much lower than the real one, and it may cause great uncertainty on the model results. However, this data is used in the fate modeling in order to provide an indicative model result of Lake Drevviken, which can still reflect certain characteristics of nonylphenol distribution in lakes with similar properties.

6.2.1 Results of the base-case lake model

Figure 6.3 shows the model results for Lake Drevviken in the base-case lake model. Same as for Lake Trekanten, transformation in water is the most important nonylphenol removal process (58% of the total load) from the system. After that, 1.41 kg nonylphenol is transferred to the downstream area per year by water outflow, and it takes 37.5% of the total load. This proportion is higher than that in the case of Lake Trekanten, since the water retention time of Lake Drevviken, i.e. 11 months (0.92 years), is shorter than 1.6 years of Lake Trekanten. This result also provides an insight that for lakes with short water residence time, a great part of nonylphenol may go further to the downstream area. Therefore, if the half life of nonylphenol in water is much longer than the water
residence time and transportation time, water outflow from upstream lakes can be a potential nonylphenol load to downstream lakes.

According to Figure 6.3, volatilization still takes a minor fraction (3.3% of total removal) in the case of Lake Drevviken, and this is mainly due to the low vapor pressure of nonylphenol itself, same as in the case of Lake Trekanten.

![Figure 6.3. Mass balance of nonylphenol at steady state in Lake Drevviken from the base-case lake model. The conceptual model is shown in Figure 5.1.](image)

In the sediment compartment, typical rather than site specific deposition rate and burial rate were employed for Lake Drevviken during parameterization due to lack of information (see Table 4.2). Only 0.7% (0.027 kg/year) of total nonylphenol is removed by transformation process in the sediment, which can be explained by its very long half life in sediment in the Swedish environment. The overall residence time of nonylphenol in Lake Drevviken can be calculated as 0.43 years.

As previously mentioned, an underestimated load of NP/NPEs is used in the fate modeling of Lake Drevviken. As can be seen later in the sensitivity analysis section, the amount of nonylphenol within each process is directly proportional to the load while the proportion taken by each part will keep unchanged. So in this case, the proportion of the total removal covered by each process is much more meaningful than absolute numbers. For mass of nonylphenol in water and sediment under steady state and their corresponding concentrations, it can only be concluded that the real values will be higher than the model results, depending on the actual nonylphenol load with the part from building materials.
7. Sensitivity and uncertainty analysis

7.1 Sensitivity analysis

As mentioned in Section 5.1.4, a sensitivity analysis is conducted to reveal the sensitivity of model results with respect to different processes and variables and their corresponding importance in the base-case lake model. Lake Trekanten is selected to conduct the sensitivity analysis of the base-case lake model in this thesis. Between two case studies in this work, Lake Trekanten has a better lake specific data availability compared to Lake Drevviken. To select one lake as the representative to do the sensitivity and uncertainty analysis can save the time and space in repeating the same procedures.

7.1.1 A first sensitivity analysis

As can be seen in Table 5.1, a lot of parameters, both chemical specific and lake specific ones, are involved in the quantification of the base-case lake model. In order to save time and efforts, a rough sensitivity analysis with big steps (i.e. 0.1 and 10 times of the run reference value) based on the process level is carried out firstly to identify processes with relatively high impact on the model outputs. All processes are treated with their corresponding rate constants as the representative parameters in the analysis. Moreover, the load of nonylphenol is of great importance to the model output, which is also considered in the analysis. The steady state values of these parameters in the model results are treated as the run reference values as shown in Table 7.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run reference value</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{\text{in}}$ (kg/year)</td>
<td>3.58</td>
<td>The load of nonylphenol</td>
<td>Djurberg, 2010a</td>
</tr>
<tr>
<td>$R_{\text{vol}}$</td>
<td>0.143</td>
<td>Rate constant of volatilization</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{out}}$</td>
<td>0.625</td>
<td>Rate constant of outflow</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{trans,W}}$</td>
<td>1.686</td>
<td>Rate constant of water transformation</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{dep}}$</td>
<td>0.283</td>
<td>Rate constant of deposition</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{diff,WS}}$</td>
<td>0.794</td>
<td>Rate constant of water to sediment diffusion</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{res}}$</td>
<td>0.535</td>
<td>Rate constant of resuspension</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{diff,SW}}$</td>
<td>1.737</td>
<td>Rate constant of sediment to water diffusion</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{trans,S}}$</td>
<td>0.084</td>
<td>Rate constant of sediment transformation</td>
<td>Calculated*</td>
</tr>
<tr>
<td>$R_{\text{bur}}$</td>
<td>0.050</td>
<td>Rate constant of sediment burial</td>
<td>Calculated*</td>
</tr>
</tbody>
</table>

*From the simulation results of base case lake model with parameter values from Table 4.1

By changing the representative parameters one at a time, the corresponding changing
range of nonylphenol concentration in water and in sediment can be achieved respectively. The results of the first sensitivity analysis are shown in Figure 7.1 and Figure 7.2.

It is obvious that the processes have different influence on the nonylphenol concentration in water and in sediment. The nonylphenol load is the most dominant process for both nonylphenol in water and in sediment. In the water body, the transformation process in the water comes in the second place, which possesses relatively large influence on the nonylphenol concentration, followed by the water outflow process. The rest of the processes are considered as having low impact on the model results.

In the sediment compartment, after the nonylphenol load, the diffusion process from...
water to sediment shows a relatively high influence on the model output. Diffusion from sediment to water, deposition and the transformation process in water show similar results with minor differences and these processes occupy the third to fifth place. The rest of the processes are considered to have low impact on the nonylphenol concentration in the sediment.

### 7.1.2 Detail sensitivity analysis

After identifying the processes with relatively high impact on the model outputs, a detailed sensitivity analysis is needed to further clarify the relationship between these processes and the model results. Smaller steps with 0.1, 0.25, 0.5, 1, 2, 4, 10 times of the run reference values are used in this detailed sensitivity analysis. The results of this sensitivity analysis for water and sediment are shown in Figure 7.3.

![Figure 7.3 Nonylphenol concentration as function of normalized process rate (a) in water; (b) in sediment. Both simulated nonylphenol concentrations (C_w and C_s at the steady state) and the parameters (Z) are normalized for the base-case and shown as C/C_0 and Z/Z_0.](image)

As can be seen from Figure 7.3, the nonylphenol concentrations in water and sediment are directly proportional to the load of nonylphenol. In the water column, the water concentration has a negative and nonlinear correlation with \( R_{\text{trans, w}} \) and \( R_{\text{out}} \) representing their corresponding processes of nonylphenol transformation in water and water outflow, respectively. The nonylphenol transformation process in water is enhanced by increasing \( R_{\text{trans, w}} \), thus the concentration of nonylphenol in water decreases, since more nonylphenol is consumed by transformation. A similar trend can also be observed on water outflow process but with smaller change range of nonylphenol concentration, which suggests a lower impact to the model result of this process.

On the variables level, both the transformation process in the water and the water
outflow process have only one variable involved. Those processes are inversely proportional to their corresponding characteristic rate constant (see Table 5.1). These variables are nonylphenol half life in water (THLW) and the water retention time (TW), respectively. Therefore, the same type of relation between these two variables and the nonylphenol concentration in water is expected, and the same conclusion about sensitivity can be applied to these variables as in the process level, i.e. THLW has a bigger impact on water concentration than TW.

The nonylphenol concentration in the sediment is sensitive to Fin and the other four rate constants as representative for the corresponding processes, as shown in Figure 7.3b. The diffusion from water to sediment and the deposition processes (represented by R_{diff,WS} and R_{dep} respectively) are both in a positive and linear correlation with the sediment concentration, since these two processes will transfer nonylphenol from water to sediment. In contrary, negative and nonlinear influence on sediment concentration by sediment to water diffusion and water transformation processes can be observed from Figure 7.3b. With more nonylphenol being consumed by transformation in water, the concentration gradient between sediment and water will be increased, which can enhance the diffusion from sediment to water and therefore cause the drop of sediment concentration.

### 7.2 Uncertainty analysis

An uncertainty analysis is a very important step of the model testing, which can not only enable the user to have an idea about the model performance, but can also provide a direction for modeler to further improve the model parameterization or even to guide the field sampling. Two kinds of model uncertainties, conceptual uncertainty and parametric uncertainty, will be discussed in this section.

#### 7.2.1 Conceptual uncertainty

The conceptual uncertainty mainly comes from the assumptions made when building the base-case lake model. During the conceptualization of the lake system, lake water and sediment are assumed to be well-mixed, which is not the case in reality. For water compartment, the temperature will change along with the water depth, and there is more turbulence in up layer water than in deep water, etc. For sediment, surface layer is much involved in the particles exchange with water pillar while the bottom sediment is more stable and subject to the sediment burial process. Due to this conceptual uncertainty, the simulated concentrations of nonylphenol in the water and in the sediment are average values of the whole compartment. However, the field data about the concentration may vary a lot depending on different sampling positions and depths. Therefore, this conceptual uncertainty can cause discrepancy between the model results and field data.

Although the above mentioned assumptions can greatly simplify the conceptual model
and alleviate the difficulty of model quantification, they will cause uncertainty in the
test performance, which should be kept in mind when analyzing the model
uncertainty.

### 7.2.2 Parametric uncertainty

For parametric uncertainty analysis, a well known and widely used method is Monte
Carlo simulation, which is a technique to forecast the entire range of model output
change under certain situation, and to provide the confidence limits for a given event
(Håkanson, 2000). However, due to a large amount of random numbers of each variable
that is required to conduct this simulation, and the restriction of the modeling tool
Simile, which cannot handle this method by the software itself, the Monte Carlo
simulation is difficult to be conducted in this thesis work.

Therefore, another more convenient approach is adopted in this thesis. The uncertainty
of a variable is reflected by its coefficient of variation (CV) value for model output,
deﬁned as the ratio of standard derivation (SD) and the mean. Normal frequency
distributions of random values of these variables are needed here to derive the CV values.
This approach has been proofed adequate in a previous study under situations with few
data available (Håkanson, 2000).

Based on the sensitivity analysis, ﬁve processes are identiﬁed as of relatively high
importance to the model outputs. It can be summarized that thirteen variables are
involved in the quantiﬁcations of these processes (see Table 5.1). Among these variables,
four lake variables, i.e. water depth \(h_W\), sediment active depth \(h_S\), water volume \(V_W\)
and sediment solid density \(\rho_{PS}\) are easy to measure and one chemical property, i.e. the
octanol-water partition coefﬁcient \(K_{ow}\), is reliable and has been used in many studies
(Chiou et al., 1982; Ahel and Giger, 1993; EU Risk Assessment, 2002). Therefore the
uncertainties of these variables are neglected in this analysis. The rest of variables, as
listed below, are included in the test, which will quantify their uncertainty for
coresponding model output. The CV values are selected with reference to a similar
study carried out by Håkanson (2004).

1. \(F_{in}\) the nonylphenol inflow to Lake Trekanten, which is calculated by Djurberg
   (2010a) from a Substance Flow Analysis of diffusive sources of NP/NPE using
   emission factors. Both the emission factors and mixed result of NP/NPE are of
   great uncertainty. The CV value of \(F_{in}\) is set to 0.5.

2. \(T_W\) the water retention time of Lake Trekanten. In this special case, bottom water
   of the lake was pumped out and replaced by drinking water from nearby reservoir
   (Stockholm Vatten, 2000a), which means the water outflow is relatively stable and
   controllable. So the CV value is set to 0.1 in this test.

3. \(T_{HLW}\) the nonylphenol half life in water. Since many different values of this variable
   can be found in different literatures and no speciﬁc data available for Swedish
   condition, therefore its CV is set to 0.5.
4. \( G_{\text{dep}} \), sediment deposition rate. This data is from the study of Sternbeck (1998), in which the sedimentation rate was detected using \(^{210}\text{Pb} \) with a CV value of 0.1.

5. \( K_T \), the sediment-water diffusion mass transfer coefficient. This data is adopted as the recommended value in environmental fate modeling in water management of Decision Support System (SOCOPSE, 2009). The uncertainty of this variable was qualitatively marked as medium among three levels. So in this test, its CV value is set to 0.25.

6. \( f_{\text{OCS}} \), the organic carbon fraction in sediment. The organic matter fraction in sediment is estimated as the loss on ignition, of which 50% was assumed to be organic carbon according to Mackay (2001). This CV value is set to 0.5.

7. \( C_{\text{pg}} \), the particle concentration in water. A range of 2-4 mg/l was provided by Lithner et al. (2003), and the mean value was adopted for in the fate modeling. Due to the relatively high uncertainty, the CV value is set to 0.5.

8. \( f_{\text{PS}} \), the volume fraction of particles in sediment. This is calculated from water content in the sediment, water and particle density. Since the uncertainty of water and particle density is neglected here, \( f_{\text{PS}} \) will have the same CV as water content. Håkanson (2004) used a CV value of 0.1 for the water content sediment, which is adopted here in this test.

The target of this uncertainty analysis is to get the uncertainty that each of these variables can cause on model outputs, and it is reflected by the CV value of each variable for nonylphenol concentration in water/sediment. Based on the sensitivity of model results on their corresponding processes, \( F_{\text{in}}, T_W \) and \( T_{\text{HEW}} \) will be involved in the analysis for water concentration, while \( F_{\text{in}}, T_{\text{HEW}}, G_D, K_p, f_{\text{OCS}}, C_{\text{pg}}, \) and \( f_{\text{PS}} \) will be analyzed for sediment concentration.

All the base case values of these variables are taken as the mean values and ten random numbers of each variable have been generated by the website of Wessa (2010) with given SD and mean. By changing a variable with the generated random numbers once at a time and keeping all other variables unchanged, ten corresponding concentrations (either in water or in sediment) can be obtained. Then the CV value (named as ‘CV for water concentration’ or ‘CV for sediment concentration’ in Table 7.2) of the ten concentrations can be calculated, and thus it can reflect the uncertainty of the original variable can pose on the model output. The result of the parametric uncertainty analysis is shown in Table 7.2.
Table 7.2 Coefficient of variation for different entities.

<table>
<thead>
<tr>
<th>Physical entity</th>
<th>Symbols</th>
<th>Own CV*</th>
<th>CV for water concentration#</th>
<th>CV for sediment concentration#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon fraction in sediment</td>
<td>fOCS</td>
<td>0.5</td>
<td>–</td>
<td>0.522</td>
</tr>
<tr>
<td>Load of nonylphenol within inflow water</td>
<td>F_in</td>
<td>0.5</td>
<td>0.430</td>
<td>0.430</td>
</tr>
<tr>
<td>Nonylphenol half life in water</td>
<td>T_HLW</td>
<td>0.5</td>
<td>0.300</td>
<td>0.300</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>G_dep</td>
<td>0.1</td>
<td>–</td>
<td>0.047</td>
</tr>
<tr>
<td>Water retention time</td>
<td>T_W</td>
<td>0.1</td>
<td>0.025</td>
<td>–</td>
</tr>
<tr>
<td>Volume fraction of particles in sediment</td>
<td>f_PS</td>
<td>0.1</td>
<td>–</td>
<td>0.006</td>
</tr>
<tr>
<td>Sediment-water diffusion mass transfer coefficient</td>
<td>K_T</td>
<td>0.25</td>
<td>–</td>
<td>0.004</td>
</tr>
<tr>
<td>Particle concentration in water</td>
<td>C_PW</td>
<td>0.5</td>
<td>–</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* Model input.  # Model result  –Not involved

According to Table 7.2, the ranking of variables contributing to the uncertainty of nonylphenol concentration in water is: F_in > T_HLW > T_W. That is to say, in order to improve the model prediction about nonylphenol concentration in water, a more accurate measurement of the load is essential, as well as a better estimation of its half life in the Swedish aquatic environment.

From Table 7.2, the ranking of variables contributing to the uncertainty of nonylphenol concentration in sediment is: f_OCS > F_in > T_HLW > G_dep > f_PS > K_T > C_PW. Besides above mentioned F_in and T_HLW, f_OCS turns out to be of great uncertainty for nonylphenol sediment concentration. High accuracy of data collection of these variables can therefore greatly reduce the model uncertainty. Also, the parametric uncertainty on model outputs caused by these variables can be a reason for the disagreement of model results and field observations.

There is should be noted that the level of uncertainty indicates that one significant figure at best is appropriate for the model results. Nevertheless, this thesis uses 2 to 3 significant figures in the presentation of results in the sake of clarity.
8. Dynamic model prediction on nonylphenol levels in lakes

Besides the application of the base-case lake model to predict the concentration and distribution of nonylphenol in lakes, it can also be used reversely to do backcasting prediction, which starts from existing policy to estimate how much change is needed in order to fulfill the requirements. Two such regulations can be found as the Water Framework Directive (WFD, 2000/60/EC) in 2000 and the Environmental Quality Standard (EQS, 2005) in 2005.

According to WFD, all the pollutants of priority substances (including nonylphenol) into surface water should cease by the year of 2025 (WFD, 2000/60/EC), while the EQS provided the predicted no effect concentration (PNEC) of nonylphenol in aquatic environment, as shown in Table 3.3. Based on these regulations, the estimated load and dynamic response of nonylphenol concentrations in Lake Trekanten and Lake Drevviken to the corresponding change of the load will be analyzed in this chapter.

As shown in Table 3.3, the PNEC of nonylphenol in water is 0.33 μg/l, while the PNEC value in sediment is 0.039 mg/kg on a wet weight basis (EQS, 2005). Based on the calculation in Appendix II, to meet this requirement, the critical load of Lake Trekanten is 0.473 kg/year. For Lake Drevviken, the nonylphenol concentration in water and sediment is underestimated due to the missing load from building materials. However, the model result shown in Figure 6.3 is still used here just to illustrate its response time to load change. The nonylphenol concentration in water and sediment is well below the PNEC value. So only a cut off of total load on 2025 will be analyzed for Lake Drevviken (see Appendix II).

The simulation is set to start from 2005 with the steady state concentration of the original base-case lake model as the initial concentration, assuming an instantaneous load drop from initial condition to the critical value at year 2010 (marked with subscript ‘1’ in Table 8.1 and Figure 8.1), and a cutoff of the entire nonylphenol load at 2025 (marked with subscript ‘2’ in Table 8.1 and Figure 8.1) according to WFD regulation. The dynamic concentrations of nonylphenol in these two lakes are shown in Figure 8.1. The response time of water (T_w) and sediment (T_s) is defined as the time taken to achieve 95% of the concentration difference between adjacent steady states. The results are summarized in Table 8.1.

<table>
<thead>
<tr>
<th></th>
<th>Water response time (years)</th>
<th>Sediment response time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_w1</td>
<td>T_w2</td>
</tr>
<tr>
<td>Lake Trekanten</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Lake Drevviken</td>
<td>---</td>
<td>1.2</td>
</tr>
</tbody>
</table>
From Table 8.1, it can be observed that for both of the two lakes, the response time in sediment is longer than that in water, but the difference is not large. This result is different from previous study on the copper fate in lakes, which concluded that the response of sediment copper content is much slower than that of water content (Cui et al., 2009). This means that the effect of certain measures taken to reduce the nonylphenol load can be reflected by the concentration drop in both water and sediment within a relatively short time. However, it also means that both water and sediment nonylphenol concentrations may fluctuate due to temporal load variation, which will cause uncertainty to field sampling data. Under this situation, a more frequent sampling of the concentration is recommended to have a better monitoring on the real load of nonylphenol.

![Figure 8.1](image.jpg)

*Figure 8.1. Modeled nonylphenol concentration versus time [year] (a) in water, Lake Trekanten; (b) in the sediment, Lake Trekanten; (c) in water, Lake Drevviken; (d) in the sediment, Lake Drevviken. In year 2010 the load was in this scenario changed to the critical load to reach PNEC and in year 2005 the load ceased completely. T’ is the response time defined as the time taken to reach 95% of the total change in concentration.*

As shown in Table 8.1, Lake Drevviken has a shorter response time than Lake Trekanten, which can be explained by the smaller overall residence time of nonylphenol in Lake Drevviken (0.43 years, while 0.58 years of Lake Trekanten, see Chapter 6). A small nonylphenol residence time in the lake means a rapid substance replacement, which means fast reach of the steady state.
9. Discussion

Any model has its uncertainties, which may come from different aspects. In the uncertainty analysis section (Chapter 7.2), the characteristic CV values for the model outputs of selected key model variables are analyzed to show the uncertainty in model parameterization. However, uncertainties may also be caused by basic concept of modeling and the availability of desirable data, such as the annual average outputs and undesirable mixed load of NP/NPEs in this case. A preliminary discussion about these aspects as well as the relation of the model results of this work to other fate studies of nonylphenol will be conducted in this chapter.

9.1 Seasonal change of nonylphenol concentration

Since the base-case lake model in this thesis is a mass balance model built on annual basis, and all the values of lake specific variables are treated as annual average values, this model cannot reflect the seasonal change of the nonylphenol concentration in different compartments. However, obvious seasonal characteristics can be observed in the study area of this report. For lakes in Stockholm, Sweden, one dominant characteristic of seasonal change is the ice covered period, which is caused by low temperature during the winter time.

Lake Trekanten is selected for an indicative analysis of the effects of seasonal change on the nonylphenol concentration. An ice covered period of 134 days is employed in this analysis based on a study of Nyberg and Wass (2009) on Lake Eckarfjärden, since no data is available for Lake Trekanten. Many variables will be affected by the ice covered period. There will be no volatilization from water to atmosphere since the lake surface is covered by ice. It is also assumed that there will be no water inflow and outflow during this period. According to Niemistö and Horppila (2007), wind-driven waves and currents are considered the main factors causing sediment resuspension in shallow lakes, and their research showed that the ice coverage can have great influence on both the resuspension and deposition rate, but to different extent. Other variables, such as the half life of nonylphenol in water and sediment, may change due to the low temperature during the winter time.

Based on the results of sensitivity analysis, the nonylphenol half life in the sediment has minor impact on the model outputs, so a change of nonylphenol half life in the sediment is not considered here. However, the model results are sensitive to nonylphenol half life in water, yet no information of the relation between nonylphenol half life in water and temperature is available in the literature. Therefore this change is also not considered here. Without considering the half life increase caused by low temperature during the winter time, an underestimation of both nonylphenol concentrations in water and in the sediment is expected, since less nonylphenol would be transformed under the real situation. So in this analysis, seasonal changes are only considered on water inflow and
outflow, volatilization, deposition, resuspension and related burial processes, while other variables are remain unchanged (see Appendix III).

Since the concentrations of nonylphenol in water and in sediment have different units (i.e. ng/L and ng/g dw, respectively), the mass (kg) of nonylphenol in these two compartments are selected as the target parameter instead of their concentration in this study in order to make the result comparable. With the steady state of the original base-case lake model being the initial state in this analysis, the result of the analysis of seasonal change of mass of nonylphenol in three years time span is shown in Figure 9.1.

The ice covered period of Lake Trekanten is assumed to be from late November to early April the next year (see Appendix III). During this period, an obvious decrease of the nonylphenol content in water can be observed from Figure 9.1, while the change of nonylphenol content in sediment is relatively small. This is mainly because the cutoff of the nonylphenol load within the inflow water can pose a direct influence on the nonylphenol content in water, which is decreased since no nonylphenol is transferred to the lake during this period. Other changes such as no volatilization and no water outflow can somehow offset this trend. However, according to the results of sensitivity analysis (see Chapter 7), the nonylphenol inflow is the dominant process while the influence of water outflow and volatilization processes are relatively small. So the overall trend of nonylphenol water content during the ice-covered period is still decreasing. Moreover, the ice covered period has higher influence on the drop of resuspension rate than the drop of deposition rate (see Appendix III). This effect can increase the net sedimentation and contribute to the decrease of nonylphenol amount in water. It can also cause increase of nonylphenol in the sediment, and offset the influence from the cutoff of nonylphenol load, therefore helps to maintain a stable nonylphenol content in

Figure 9.1. Modeled mass of nonylphenol in water and sediment as function of time over three years when seasonal variations of lake characteristics were considered.
the sediment.

In the open period, all the variables, including the water inflow and outflow, rate constants of volatilization, deposition, resuspension and burial processes, are changed back to their original values. So an increasing trend of nonylphenol in water can be seen from the ice break up date in Figure 9.1, but still the change in sediment is very small.

In general, it can be concluded from this indicative analysis that the nonylphenol sediment content is more stable to seasonal variation compare to the nonylphenol water content. The same conclusion is also valid for the corresponding nonylphenol concentrations in these two compartments. The water concentration of nonylphenol will decrease during the ice covered period in winter and increase in the open period. Similar results can also be found in some other literatures (Derbalah et al., 2003; Xu et al., 2006).

9.2 Mixed NP/NPEs load

Mixed NP/NPEs load from the recent study of Djurberg (2010a) was adopted in this thesis as direct emission in the fate modeling of nonylphenol in the base-case lake model, in which it was assumed to be pure nonylphenol. This assumption will cause great uncertainty in the model performance. Månsson et al. (2008) proposed a way to transform NPEs to NP equivalents (NPequ) by using the molar weights of the substances. Different NPEs (each group has a similar length of ethoxy chain) are used in different products. Based on the average molar weight of a certain NPEs group, a corresponding ratio is summarized to transform NPEs to NP equivalents. Several examples of the transformation from NP to NPEs are shown in Table 9.1. Therefore, to treat mixed NP/NPEs load as pure NP can cause an overestimation of the nonylphenol concentration in water and in the sediment since the molar weights of NPEs are higher than that of nonylphenol.

<table>
<thead>
<tr>
<th>Products</th>
<th>Number of ethoxy groups</th>
<th>NP:NPequ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning agents; decreasing products</td>
<td>&lt;10</td>
<td>NP:NPEs ≈ 2:5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 kg NPEs ~ 4 kg NPequ</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>10-30</td>
<td>NP:NPEs ≈ 1:5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 kg NPEs ~ 2 kg NPequ</td>
</tr>
<tr>
<td>Paint, biocides</td>
<td>30-80</td>
<td>NP:NPEs ≈ 1:10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 kg NPEs ~ 1 kg NPequ</td>
</tr>
</tbody>
</table>

Table 9.1 Examples of ratios of the transformation from NPEs to NP equivalents (from Månsson et al., 2008)

As nonylphenol is one of the metabolites of NPEs, most existing literature about nonylphenolic compounds do not distinguish NP and NPEs with different length of ethoxy chain (Björklund, 2009). According to Djurberg (2010a), the emission of NP/NPEs is calculated based on different sources, from where part of the emission is
transferred to the lake by storm water. If the half lives of NPEs are much smaller than NP and the transportation time, then it can be assumed that pure NP will reach the lake. In this case, a literature search about the half lives of NP and NPEs in surface water is carried out to try to verify if the assumption of pure NP load is acceptable. However, different literature provided different half lives, as summarized in Table 9.2. Moreover, the half lives of NP and NPEs may very much depend on the environment conditions and also the length of ethoxy chain may be an influential factor. Therefore, there is no solid evidence that NPEs can be transformed into NP before it reaches the lake.

Table 9.2 Summary of half lives of NP and NPEs from literature.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Study object</th>
<th>Half life (d)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water (aerobic)</td>
<td>NPE_{4,15}</td>
<td>0.42</td>
<td>Jonkers et al., 2001</td>
</tr>
<tr>
<td>River die-away</td>
<td>NPE_{9}</td>
<td>18.6</td>
<td>Serak and Yan, 2007</td>
</tr>
<tr>
<td>Estuarine water (aerobic)</td>
<td>NP; NPE_{1,3}</td>
<td>&lt;30</td>
<td>Ferguson et al., 2001</td>
</tr>
<tr>
<td>Surface water</td>
<td>NP</td>
<td>150</td>
<td>EU Risk Assessment, 2002</td>
</tr>
<tr>
<td>Sediment slurry (aerobic)</td>
<td>NP</td>
<td>178</td>
<td>Ferguson and Brownawell, 2003</td>
</tr>
<tr>
<td></td>
<td>NPE_{1,8}</td>
<td>45-204</td>
<td></td>
</tr>
<tr>
<td>Sediment slurry (anaerobic)</td>
<td>NP</td>
<td>231</td>
<td>Ferguson and Brownawell, 2003</td>
</tr>
<tr>
<td></td>
<td>NPE_{1,9}</td>
<td>165-301</td>
<td></td>
</tr>
</tbody>
</table>

So it is very possible that the actual load reaches the lake is a mixture of both NP and NPEs. According to Månsson et al. (2008), given the composition of the total load corresponding to different products, an overall NP equivalent can be roughly estimated by using the transformation ratios listed in Table 9.1. Another more accurate solution is to add a step before the water inflow in the lake model, dealing with the transformation process of each type of NPEs oligomers from emission source to the lake. For this method, more data is required, including composition of load, half life of each oligomer of NPEs and the corresponding transportation time to the lake, etc. However, in the case studies of this thesis, without knowing the composition of the total load to these two lakes, the problem of mixed load still cannot be solved.

The long physical residence time of the load in water, which provides enough time for the transformation from NPEs to NP to take place, motivates field determination of only nonylphenol. Here, the physical residence time is defined as the time before the mass in water been physically (without considering the removal by water transformation) taken out from the water body. From the modeling result, it can be calculated that the physical residence time of mass in water for Lake Trekanten is 441 days, while it is for Lake Drevviken 299 days. The residence time is much longer than the reported half life of NPEs in surface water from different literature, which is summarized as from 0.42 days to 69 days (Kvestak & Ahel, 1999; Potter et al., 1999; Jonkers et al., 2001). So in the water compartment, there is enough time for the transformation from NPEs to NP or to even further metabolites and this is why field data for only nonylphenol may be considered sufficient.
9.3 Relation to other fate studies of nonylphenol

Van Ry et al. (2000) used a box model to study the fate of nonylphenol in the Lower Hudson River Estuary (LHRE). According to their model results, the volatilization accounted for 40% of the total removal of nonylphenol from the water column of the LHRE. This figure is much higher than the model results of this work, i.e. 5.6% of Lake Trekanten and 3.3% of Lake Drevviken (see Chapter 6). This can be explained by the geographical features of the LHRE, which is a rather shallow tidal estuary and vulnerable to the influence of wind. Besides the volatilization, the water outflow and degradation of nonylphenol were also pointed out as important nonylphenol removal processes. This is in good agreement with the model results of this work.

Several studies of the fate of nonylphenol in the Swedish environment have been conducted recently. Andersson (2008) studied the fate of nonylphenol in the section of River Viskan by using the QWASI model (Quantitative Water Air Sediment Interaction; Mackay et al., 1983). It was reported in her study that 98% of the nonylphenol entering the system was transported further downstream by water outflow while the same process in this work accounted for 25% of the total nonylphenol removal from Lake Trekanten. This is because of the big difference between the water residence times of these two systems, i.e. 33.6 hours of the section of River Viskan and 1.6 years of Lake Trekanten. Moreover, under such short water residence times, the degradation of nonylphenol and volatilization from water to air would not have time to take place to a considerable extent. Therefore, these processes only accounted for small fractions of the total nonylphenol removal (Andersson, 2008).

Björklund et al. (2009) employed a modified QWASI model to simulate the fate of nonylphenol in the Gårda sedimentation facility of a stormwater treatment system, Sweden. It was reported that 59% of the nonylphenol removal from the system was through sediment burial, due to the characteristics of the sedimentation facility (low disturbance, long water residence time and high burial rate). Only 2.1% of nonylphenol was removed by volatilization (Björklund et al., 2009). The proportion is quite close to the model results in this thesis work (5.6% of Lake Trekanten and 3.3% of Lake Drevviken). The rest of 39% nonylphenol removal was taken by the degradation process (Björklund et al., 2009). Although higher proportions of transformation (68% of Lake Trekanten and 59% of Lake Drevviken) were obtained from this thesis work, both of the two studies reflected that the transformation process played an important role in the fate of nonylphenol in aquatic environments.
10. Model result of updated load of Trekanten

An updated and improved estimated load of 0.525 kg/year of NP/NPEs was derived for Lake Trekanten from a Substance Flow Analysis by Djurberg (2010b). The modeling result in the base-case lake model for this is shown in Figure 10.1.

By comparing Figure 10.1 with Figure 6.1, it is obvious that the amount of nonylphenol within each flow decreases to around 1/6.7 of the preliminary result, which is the same as the ratios of the loads in the first rough and the later improved Substance Flow Analysis, because the model output is directly proportional to the load. Then the percentage of each process taken of the total nonylphenol removal is still unchanged. So the biggest removal of nonylphenol is done by water transformation, and followed by the water outflow. Processes such as volatilization, sediment transformation and burial only take small fraction of the total removal of nonylphenol from the system.

The nonylphenol concentrations in water and sediment also decreased according to this ratio. The concentration in water is now 0.367 μg/l, which is quite close to the 0.33 μg/l PNEC (Predicted No Effect Concentration) of nonylphenol in surface water shown in Table 3.3 as the no effect concentration. If we take the possible overestimation caused by the mixed NP/NPEs load, this concentration might be even lower in reality. This indicates that even though around 25% (0.131 kg/year) of nonylphenol will be transferred to the downstream area, the corresponding influence will not be severe, since the concentration of nonylphenol in the outflow water is relatively low.

In sediment, the modeled concentration of nonylphenol is 717 ng/g dw, which agrees
with the field data of 3200 ng/g dw (Sternbeck et al., 2003) within a factor of 5. For an uncalibrated model, such as the base-case lake model in this thesis work, it is generally a satisfactory agreement between the field data and the model outputs. Similar ratios between measured/modeled concentrations can be observed from other relevant studies (Mackay et al., 1994; Björklund et al., 2009). However, there might be uncertainties in both the model results and the field observations. As previously mentioned in Section 7.2, the conceptual uncertainties and parametric uncertainties of the base-case lake model can cause uncertainty in model outputs. Moreover, the field data may also vary a lot depending on different sampling positions.

Finally, it is worth noting that since the proportion of each flow taken up of the total nonylphenol removal remains unchanged, the results of the previous sensitivity analysis, relative stability to seasonal load variation of water and sediment, and the response time of Lake Trekanten will not change no matter how the nonylphenol load changes. That is to say, the previous results based on the preliminary load of nonylphenol are still valid for the updated load of Lake Trekanten on a general level.
11. Conclusion

Nonylphenol is a widely used organic compound which was reported to possess potential risk to aquatic environment (Giger et al., 1984; EU Risk Assessment, 2002). It has been detected in many lakes in Stockholm, Sweden, according to the result of recent studies, which also raised great concern over this problem (Strömberg & Sternbeck, 2004). This thesis work made an attempt to develop a dynamic, environmental fate model of nonylphenol in lakes and to predict the distribution and concentration of nonylphenol within different compartments with respect to time. After a review of relevant literatures, a conceptual model for the fate of nonylphenol in lakes was constructed based on the method from Mackay et al. (1994). Two lakes in Stockholm, i.e. Lake Trekanten and Lake Drevviken were selected as case studies to run the model. Another modeling method, using separated ET and A sediment, was also included for comparison purpose.

In both of the lakes, the most important nonylphenol removal was predicted to be from the transformation process in water, followed by the water outflow. The contribution of other processes such as volatilization, transformation in sediments and the burial process are considered to be small. Field observations from a recent monitoring program were used to test the model performance (Sternbeck et al., 2003). For Lake Trekanten, the model prediction (for updated load) of nonylphenol concentration in sediment agrees with the field data within a factor of 5. The discrepancy might be caused by the uncertainties from both modeling and field sampling processes. For Lake Drevviken, a load of nonylphenol is adopted from the study of Djurberg (2010b) without counting in the emission from the building materials, which might be an important contribution to the total load. Therefore, underestimated simulation results of the nonylphenol concentrations both in water and in the sediment are expected for Lake Drevviken.

In a sensitivity analysis, the nonylphenol water inflow ($F_{in}$) is identified as the most dominant process, and is directly proportional to water and sediment nonylphenol concentration. The nonylphenol water concentration showed high sensitivity to the transformation process in water and water outflow process; while water to sediment diffusion, sediment to water diffusion, sediment deposition and water transformation are identified to have high impact on the sediment nonylphenol concentration.

Moreover, in the uncertainty analysis, the nonylphenol load and the half life of nonylphenol in water ($T_{HLW}$) are identified to cause high uncertainty in both the nonylphenol concentrations in water and in the sediment, while the organic carbon fraction in sediment ($f_{OCS}$) can cause great uncertainty of the sediment nonylphenol concentration. Model uncertainties may be greatly reduced by improving the measurement of these variables.

From the scenario of change of the nonylphenol load and the seasonal variation in lake characteristics, it can be concluded that the sediment nonylphenol content is more stable to seasonal change compare to nonylphenol water content, but the response times to
load change of nonylphenol content in these two compartments are quite close to each other. Especially for sediment, the response time of nonylphenol content is much shorter than in the case of heavy metal, such as copper (Cui et al., 2009). This indicates that in order to have a better monitoring of the actual nonylphenol load, a more frequent sampling of the sediment concentration is required.
References


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Appendices

Appendix I. Calculations of lake parameters

Lake Trekanten

Sediment bulk density & volume fraction of solids in sediment

The bulk density of sediment is estimated according to the equations provided by Håkanson & Bryhn (2008) in their study:

\[ bd_s = \frac{\rho_{ps} \cdot \rho_{ws}}{\rho_{ws} + (\rho_{ps} - \rho_{ws}) \cdot W} = 1.03 \text{ g/cm}^3 \]

with the approximation that the density of water in sediment (\(\rho_{ws}\)) is 1 g/cm\(^3\). Then the volume fraction of solids in sediment can be calculated as:

\[ f_{ps} = \frac{(1 - W) \cdot bd_s}{\rho_{ps}} = 0.021 \text{ m}^3/\text{m}^3 \]

Fraction of organic carbon in water and sediment

Based on particulate organic matter of 60% as a standard value recommended by Håkanson (2006), and the assumption that half of the organic matter is organic carbon (Mackay, 2001), the fraction of organic carbon in water (\(f_{OCW}\)) is estimated to be 0.3 in this study. Moreover, the loss of ignition (LOI) of sediment of Lake Trekanten is 31% (Sternbeck et al., 2003), which also represents the organic matter fraction in sediment (Mackay, 2001). Likewise, half of the LOI, 0.16, is used as the estimation of fraction of organic carbon in sediment.

Deposition, resuspension and burial rate

According to Sternbeck (1998), the deposition rate (\(R_{dep}\)) of Lake Trekanten is 0.063 g/cm\(^2\)/year. Then convert the unit to kg/year:

\[ G_{dep} = 10 \cdot R_{dep} \cdot A_s = 81900 \text{ kg/year} \]

Corresponding particle settling velocity (\(v\)) is:

\[ v = \frac{10000 \cdot R_{dep}}{C_{pw}} = 210 \text{ m/year} \]

A typical value of the burial velocity (\(v_{bur}\)) of 1 mm/year recommended by Mackay (2001) is adopted in this study. Since the sensitivity of sediment burial process is rather low in the base-case lake model (see section 7.1), this value is acceptable to be used in this model. Then convert the unit to kg/year:
\[ G_{bur} = v_{bur} \cdot \rho_{PS} \cdot A_S \cdot f_{PS} / 1000 = 6552 \text{ kg/year} \]

A carbon mass balance calculation is needed to get the resuspension rate, as shown in Table A.1. The amount of organic matter was estimated to be twice as much as the amount of organic carbon (Mackay, 2001). The difference in organic carbon content of the deposition (30\%) and the burial solids (16\%) is used as an estimation of organic matter conversion.

| Table A.1 Illustrative sediment-water mass balance of Lake Trekanten (kg/year) |
|-------------------|-------------------|-------------------|-------------------|
|                   | Mineral matter    | Organic matter    | Total             |
| Deposition        | 32760             | 49140             | 81900             |
| Resuspension      | 28304.6           | 42457.4           | 70762             |
| Organic matter    | Na                | 4586              | 4586              |
| conversion        |                   |                   | 2293              |
| Burial            | 4455.4            | 2096.6            | 6552              |
|                   |                   |                   | 1048.3            |

\[ G_{res} = 70762 \text{ kg/year} \]

**Lake Drevviken**

**Sediment bulk density & volume fraction of solids in sediment**

The bulk density of sediment is estimated according to the equations provided by Håkanson & Bryhn (2008) in their study:

\[ bd_s = \frac{\rho_{PS} \cdot \rho_{WS}}{\rho_{WS} + (\rho_{PS} - \rho_{WS}) \cdot W} = 1.04 \text{ g/cm}^3 \]

with the approximation that the density of water in sediment (\( \rho_{WS} \)) is 1 g/cm\(^3\). Then the volume fraction of solids in sediment can be calculated as:

\[ f_{PS} = \frac{(1 - W) \cdot bd_s}{\rho_{PS}} = 0.025 \text{ m}^3/\text{m}^3 \]

**Fraction of organic carbon in water and sediment**

Based on particulate organic matter of 60\% as a standard value recommended by Håkanson (2006), and the assumption that half of the organic matter is organic carbon (Mackay, 2001), the fraction of organic carbon in water (\( f_{OCW} \)) is estimated to be 0.3 in this study. Moreover, the loss of ignition (LOI) of sediment of Lake Trekanten is 22\% (Sternbeck et al., 2003), which also represents the organic matter fraction in sediment (Mackay, 2001). Likewise, half of the LOI, 0.11, is used as the estimation of fraction of organic carbon in sediment.
Deposition, resuspension and burial rate

A settling velocity \( v \) of 130 m/year of nine Swedish lakes summarized by Lindström and Håkanson (2001) is employed in this study. After converting the unit to kg/year:
\[
G_{\text{dep}} = \frac{v \cdot A_s \cdot C_{PW}}{1000} = 2226900 \text{ kg/year}
\]

A typical value of burial velocity \( v_{\text{bur}} \) of 1 mm/year is adopted recommended by Mackay (2001) is adopted in this study. Then convert the unit to kg/year:
\[
G_{\text{bur}} = v_{\text{bur}} \cdot \rho_{PS} \cdot A_s \cdot f_{PS} = 342600 \text{ kg/year}
\]

A carbon mass balance calculation is needed to get the resuspension rate, as shown in Table A.2. The amount of organic matter was estimated to be twice as much as the amount of organic carbon (Mackay, 2001). The difference in organic carbon content of the deposition (30%) and the burial solids (11%) is used as an estimation of organic matter conversion.

| Table A.2 Illustrative sediment-water mass balance of Lake Drevviken (kg/year) |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|
| Mineral matter                   | Organic matter  | Total           | Organic carbon  |                  |
| Deposition                        | 890760          | 1336140         | 2226900         | 668070          |
| Resuspension                      | 623532          | 935298          | 1558830         | 467649          |
| Organic matter conversion        | Na              | 325470          | 325470          | 162735          |
| Burial                            | 267228          | 75372           | 342600          | 37686           |

\( G_{\text{rec}} = 1558830 \text{ kg/year (see Table 4.2) } \)
Appendix II. Calculation of nonylphenol levels in lakes

Lake Trekanten

As shown in Table 3.3, the PNEC of nonylphenol in water is 0.33 μg/l, while the PNEC value in sediment is 0.039 mg/kg on a wet weight basis (EQS, 2005). Based on the proportional relationship between nonylphenol load and its concentration in water and sediment, the load of nonylphenol should be smaller than 0.473kg/year in order to fulfill the PNEC value in water, and the corresponding mass of nonylphenol in sediment is 0.084 kg.

The wet weight concentration \( (C_{S,\text{wet}}, \text{mg/kg ww}) \) can be calculated by the following formula:

\[
C_{S,\text{wet}} = \frac{M_S}{A_s \cdot h_s \cdot b d_s} \times 10^3 = 0.031 \text{mg/kg ww} = 31 \text{ng/g ww}
\]

which is lower than the PNEC value in sediment. So the nonylphenol load of 0.473kg/year is used as the critical load of Lake Trekanten in section 8.1.

Lake Drevviken

It is obvious that nonylphenol water concentration in Lake Drevviken, i.e. 34.9ng/l, is lower than the PNEC in surface water. The wet weight concentration in sediment is:

\[
C_{S,\text{wet}} = \frac{M_S}{A_s \cdot h_s \cdot b d_s} \times 10^3 = 0.0027 \text{mg/kg ww} = 2.7 \text{ng/g ww}
\]

Which is also much lower than the PNEC value of nonylphenol in sediment.
Appendix III. Quantification of variables in the analysis of the effects of seasonal variations in lake characteristics on model predicted concentrations

Several assumptions are made for the seasonal ariation analysis:

1. According to Nyberg and Wass (2009), the lake freeze-up started from 26th Nov. 2008 to 9th April 2009 for the ice to break up, which lasted for a period of 134 days. The same ice covered period is employed in the quantification.

2. According to the study of a Finnish lake, the deposition rate decreased from 30 to 1.4 g(dw)m²/d, and the resuspension rate decreased from 27 to 1 g(dw)m²/d during ice covered periods (Niemistö & Horppila, 2007). The same decreasing rate is assumed to be valid for the Lake Trekanten for the seasonal change, and a corresponding burial rate can be calculated as shown in Table A.1.

3. No volatilization from water to atmosphere during the ice covered period.

4. No water inflow and outflow.

5. Assume an instantaneous lake freeze-up and break up.

Based on these assumptions, the quantification of relevant variables for the seasonal change analysis is listed in Table A.3, while all other variables are remain unchanged as in the original base-case lake model.

<table>
<thead>
<tr>
<th>Variables (Unit)</th>
<th>Ice covered period</th>
<th>Open period</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{in} ) (kg/year)</td>
<td>0</td>
<td>3.58</td>
</tr>
<tr>
<td>( R_{vol} )</td>
<td>0</td>
<td>As in Table 5.1</td>
</tr>
<tr>
<td>( R_{out} )</td>
<td>0</td>
<td>As in Table 5.1</td>
</tr>
<tr>
<td>( G_{dep} ) (kg/year)</td>
<td>3822</td>
<td>81900</td>
</tr>
<tr>
<td>( G_{res} ) (kg/year)</td>
<td>2609</td>
<td>70762</td>
</tr>
<tr>
<td>( G_{bur} ) (kg/year)</td>
<td>714</td>
<td>6552</td>
</tr>
</tbody>
</table>