

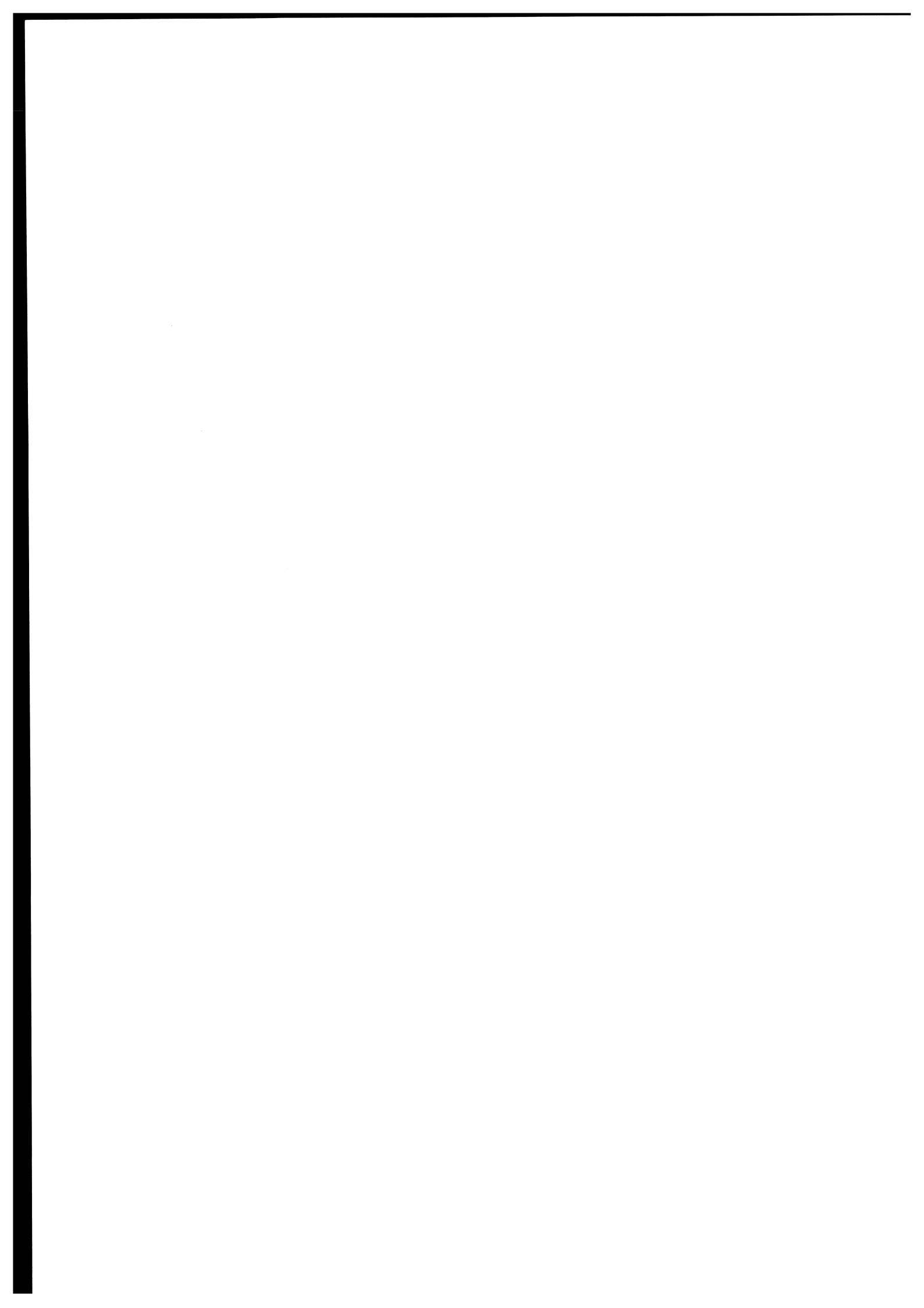
Ammonia removal mechanisms in a vertical  
up-flow treatment wetland and evaluation of  
the performance of the wetland under winter  
conditions

Kvävereducerande mekanismer i våtmark  
med vertikalt uppåt-flöde samt utvärdering  
av våtmarkens funktion under  
vinterförhållanden

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## ABSTRACT

Preem Oil Refinery constructed a treatment wetland in 1998. This was a pilot plant with vertical up-flow, planted with the common reed *Phragmites australis*. The purpose was to examine if a treatment wetland was a reliable method for removing ammonia from oil refinery effluent.

Cecilia Moreno carried out a study on the pilot plant during the summer 2000. The results showed an ammonia reduction of 80%. This thesis is a continuation of her study.

The purpose of this project was to get an understanding of ammonia removal mechanisms within the wetland bed. There are 45 sampling locations in the bed at three different depths. By continuously measuring the ammonia, nitrate and total-nitrogen concentrations in these locations, a three-dimensional picture of the wetland is gained. This gives an indication of how a full-scale treatment wetland will behave and if this is a suitable treatment method for the wastewater at Preem.

The second part of the study was dedicated to examining what results a treatment wetland could provide during winter. The treatment is partly based on biological processes and seasonal variations therefore influence the activities in the wetland.

The three-dimensional study was carried out during early fall. It showed that it is between 25 and 50 cm below ground that the ammonia reduction occurs. Most of the roots and rhizomes are located in this area and it is home for many microorganisms. Besides a reduction of ammonia, there was a net reduction of total-nitrogen. The removal of ammonia can therefore be attributed to adsorption of ammonia to the root surfaces or bacterial nitrification followed by plant uptake. A close study of the roots is necessary to evaluate which of these two mechanisms predominates.

Whichever mechanism is dominant, the removed nitrogen is concentrated in the roots. This means that harvesting of the plants, including the roots, will permanently remove nitrogen from the effluent waters.

During winter, an ammonia reduction of approximately 15% was obtained. The concentrations of nitrate on the other hand increased which left the amounts of total-nitrogen unchanged. This implies that there is nitrification of ammonia in winter but in a lesser extent than in summer. The plants however, do not take up nitrate.

In summer, a treatment wetland will effectively reduce the amounts of ammonia and nitrogen from wastewater. However, in winter the results are markedly impaired. If it is necessary with a constantly high reduction of ammonia a treatment wetland is not a sustainable treatment method. If on the contrary it is enough to even out concentration peaks, a treatment wetland is an efficient buffer.

## **ACKNOWLEDGEMENTS**

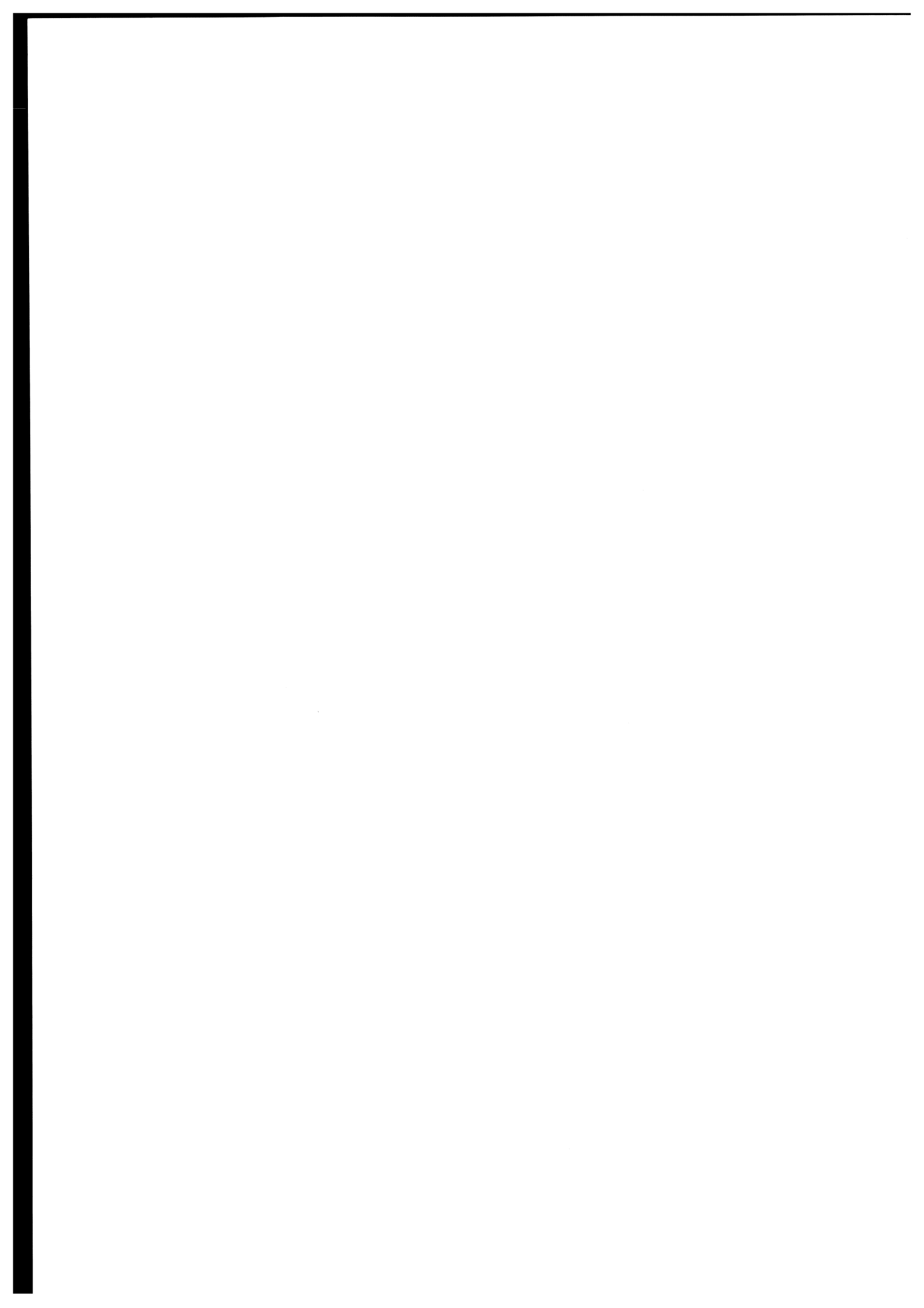
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Göteborg, June 2001  
Katarina Svensson

<b>INTRODUCTION.....</b>	<b>1</b>
<i>Wastewater from oil refineries.....</i>	<i>1</i>
<i>Preem Oil Refinery.....</i>	<i>2</i>
<b>AIMS AND OBJECTIVES.....</b>	<b>3</b>
<i>3-dimensional study.....</i>	<i>3</i>
<i>Winter conditions .....</i>	<i>4</i>
<b>BACKGROUND .....</b>	<b>5</b>
<b>NITROGEN.....</b>	<b>5</b>
<i>Nitrogen pollution .....</i>	<i>5</i>
<i>The nitrogen cycle .....</i>	<i>6</i>
<b>WETLANDS .....</b>	<b>8</b>
<i>Treatment wetlands .....</i>	<i>9</i>
<i>Substrate .....</i>	<i>10</i>
<i>Vegetation .....</i>	<i>10</i>
<i>Nitrogen removal mechanisms in wetlands .....</i>	<i>11</i>
<b>EXPERIMENTAL .....</b>	<b>13</b>
<b>SYSTEM DESIGN .....</b>	<b>13</b>
<i>Water flow.....</i>	<i>14</i>
<i>Substrate .....</i>	<i>15</i>
<i>Vegetation .....</i>	<i>15</i>
<i>Oxygen .....</i>	<i>15</i>
<i>Flotation unit.....</i>	<i>16</i>
<i>Heat exchanger .....</i>	<i>17</i>
<b>SAMPLING AND ANALYSIS.....</b>	<b>17</b>
<i>3-dimensional study.....</i>	<i>18</i>
<i>Winter conditions .....</i>	<i>19</i>
<b>SOURCES OF ERRORS .....</b>	<b>20</b>
<b>RESULTS AND DISCUSSION .....</b>	<b>22</b>
<b>THE 3-DIMENSIONAL STUDY .....</b>	<b>22</b>
<i>Ammonia.....</i>	<i>22</i>
<i>Nitrate.....</i>	<i>27</i>
<i>Total nitrogen.....</i>	<i>27</i>
<b>WINTER CONDITIONS.....</b>	<b>27</b>
<i>Cold water.....</i>	<i>28</i>
<i>Heat-exchanged water .....</i>	<i>29</i>
<b>CONCLUSIONS .....</b>	<b>31</b>
<b>THE POTENTIAL OF A CONSTRUCTED WETLAND.....</b>	<b>31</b>
<i>Problems that need solving.....</i>	<i>32</i>
<b>RECOMMENDATIONS .....</b>	<b>33</b>
<i>Preem.....</i>	<i>33</i>
<i>Further research.....</i>	<i>34</i>
<b>REFERENCES.....</b>	<b>36</b>



## **Introduction**

In recent years, the increased production and disposal of wastewaters have caused an accelerated eutrophication of fresh and coastal waters. The demand has therefore increased for removing the main nutrients, nitrogen and phosphorus, as well as the organic content of the wastewater, prior to disposal (Brix, 1987).

Under the North Sea Agreement, Sweden is committed to reducing the discharge of nutrients to the sea by 50% of calculated 1985 levels (Moreno *et al.*, 1998).

During the past two decades, treatment wetlands have become well established for the treatment of different classes of wastewater effluents. They are widely used for the treatment of stormwater, but also wastewater categories such as municipal and agricultural waste. Their use in treating industrial wastewater is however, less well developed (API, 1998).

### **Wastewater from oil refineries**

The petroleum industry is an important generator of wastewater as large amounts of water are used in the oil refining process. Water is for instance inserted to the distillation columns as steam, where it is used for heating, but it is also used for washing, as in the desalter (API, 1998). However, the largest part of the effluent water is usually stormwater that has fallen within the refinery area. This is collected and led to the wastewater treatment plant together with the process water.

Effluent wastewaters from oil refineries are rich in organic material, suspended solids and metals as well as nitrogen and phosphorous (API, 1998). Conventional treatment technology effectively reduces these pollutants but the methods are energy consuming, expensive and complicated (Brix, 1987).

Constructed treatment wetlands provide a cost-effective, low-technology, method for the removal of nutrients. Several large-scale wetland projects currently exist at oil refineries,

and numerous pilot studies of constructed treatment wetlands are being conducted. These are showing promising results when applied to wastes generated by the petroleum industry (API, 1998).

Wetland treatment is a relatively new technology and additional research is needed for definite results. The water cleansing mechanisms are complicated and have not yet been satisfactorily described. The role of external factors, such as climate, need to be investigated (Reddy *et al*, 1987).

### **Preem Oil Refinery**

The Preem Oil Refinery in Göteborg, Sweden, regularly reports elevated levels of ammonia in the effluent wastewaters. Nitrogen occurs naturally in crude oil as organic nitrogen, originating from organic material (API, 1998). This nitrogen reacts with hydrogen present in the process, and forms ammonia, which leads to the elevated values.

An experimental treatment wetland was constructed at Preem in the summer of 1998. This is a subsurface flow system and its purpose is to reduce the levels of nutrients, mainly ammonia.

## ***Aims and objectives***

The results reported in this thesis are part of a larger study where the main question is whether a constructed wetland with vertical up-flow is appropriate for removing nitrogen from petroleum industry wastewater.

A pilot plant was constructed at the Preem Oil Refinery in Göteborg, Sweden, in the summer 1998. A Chalmers exchange student, Cecilia Moreno, participated in the design process and carried out experiments on the pilot plant until the end of summer 2000. The purpose of her study was to investigate if any nitrogen removal could be expected from the wetland. There were many problems due to the quality of the process water. However, satisfying results were obtained during the last month of her study.

This study is a continuation of Cecilia Moreno's work. Its principal aim was to understand ammonia removal mechanisms in the wetland bed. A clear picture of what happens in the pilot plant would give an indication of how a full-scale constructed wetland will behave and if this would be a suitable treatment system for the wastewater at Preem.

The second part of the work was dedicated to investigating if the wetland gave similar results in winter as in summer. As nitrogen removal is partly based on biological processes, seasonal variations are expected to occur.

### **3-dimensional study**

Several possible ammonia removal mechanisms are known but it is not yet certain which of these is dominant in the experimental wetland. To get an understanding a 3-dimensional study of the wetland was carried out.

There are sampling locations throughout the bed. By continuously measuring the concentrations of ammonia, nitrate and total nitrogen, in these sampling locations, a picture of what is happening in each level of the bed is gained.

## **Winter conditions**

In the summer 2000, an average ammonia reduction of 80% was reported (Moreno, 2000). These results were very satisfying. However, it is important to know the performance under winter conditions before the final evaluation of the experimental wetland. Seasons are expected to play a role on the activities in the wetland, which makes this study important.

The ammonia reduction is registered for different inflow concentrations and different water temperatures. The purpose being to see what influence the amount of daylight and temperature has on the removal of ammonia.

## **Background**

### ***Nitrogen***

Many different nitrogen, N, species exist on earth. The largest nitrogen reserve is the atmosphere where nitrogen occurs as nitrogen gas, N<sub>2</sub>. In most soils, 90% of the nitrogen content is organic and originates from the biodegradation of dead plants and animals. In water systems, nitrogen mainly exists as ammonia-nitrogen, NH<sub>4</sub><sup>+</sup>, and nitrate-nitrogen, NO<sub>3</sub><sup>-</sup>, species.

Nitrogen is an essential component of proteins and other living matter. Together with phosphorus and potassium, it is a growth-limiting nutrient. It is a restricting factor, which means that plant growth, and absorption of nitrogen, increases while nitrogen is added. In agriculture, nitrogen is added as fertilizer, leading to higher yields and more nutritious plants and cereals.

Under natural conditions, nitrogen is supplied to the soil through nitrogen fixation. In the process, atmospheric nitrogen is converted to nitrogen compounds that are available to plants. Significant quantities of nitrogen can be added to the soil through nitrogen fixation. Most plants take up nitrogen as nitrate.

### **Nitrogen pollution**

Eutrophication is the main environmental problem associated with nutrient cycles. As nitrogen is a growth-limiting substance, increased amounts of nitrogen in waters and especially coastal waters, lead to increased production and algal growth. Excessive amounts lead to an exhaustion of oxygen and dead waters where neither plants nor animals can live.

Nitrate pollution is a problem that occurs in agricultural areas with widespread use of fertilizers. Excessive amounts of nitrate can be absorbed by the plants, which leads to poisoning of ruminant animals.

## The nitrogen cycle

The nitrogen cycle is the dynamic process through which nitrogen is interchanged between the atmosphere, organic matter and inorganic compounds (Figure 1). It is one of Nature's most vital processes, mainly mediated by microorganisms.

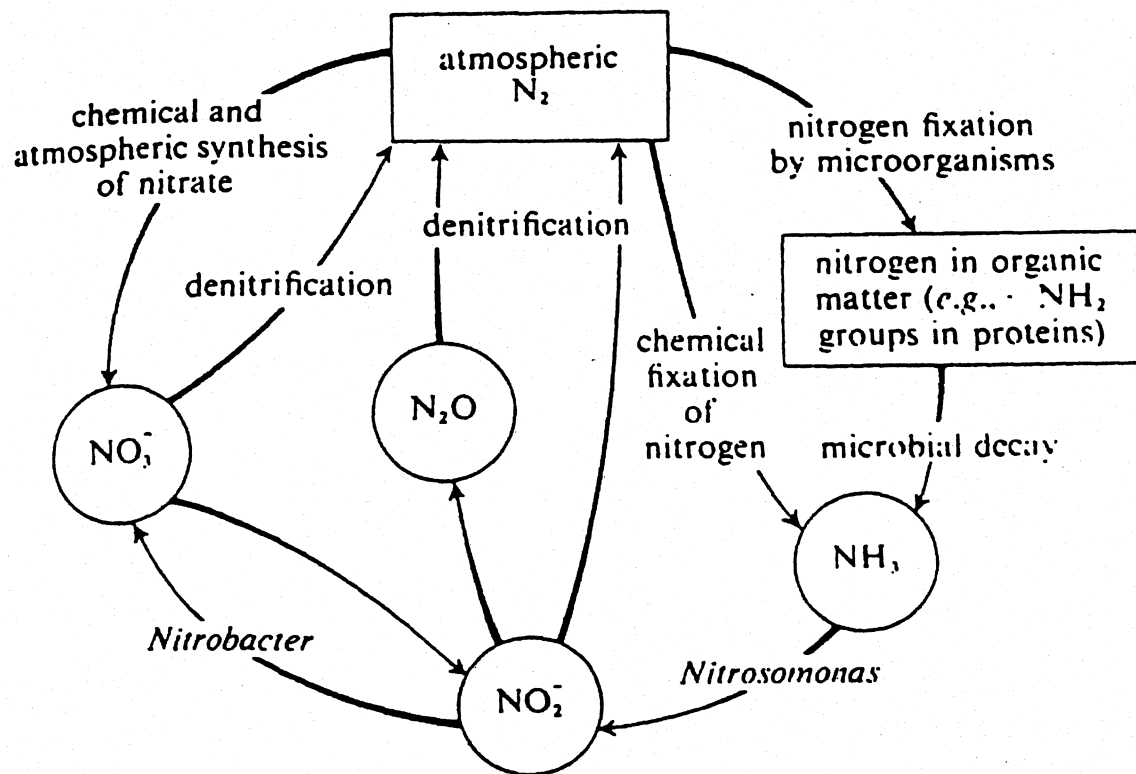
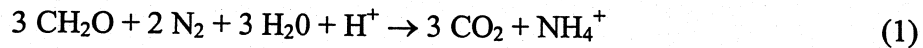
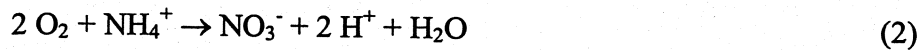


Figure 1. Through the nitrogen cycle, nitrogen is converted between the different nitrogen species.

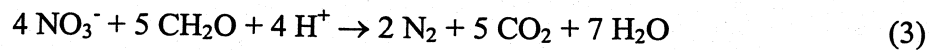
Nitrogen fixation is the process through which atmospheric nitrogen is converted from nitrogen gas to nitrogen compounds available to plants. The transformation is done by nitrogen-fixing bacteria that live in symbiotic relations with certain plants, for instance some kinds of legumes (Equation 1). The organisms live on the root structures of leguminous plants.



In aquatic environments that are in thermodynamic equilibrium with air, nitrogen occurs as nitrate. The process where ammonia is transformed into nitrate is called nitrification (Equation 2). It is led by microorganisms and is highly favored from a thermodynamic point of view. It is of great importance as nitrogen is primarily absorbed by the plants as nitrate. The condition for the process is that oxygen is available.



In environments poor in oxygen, some bacteria may use nitrate as an electron receptor and oxygen source for the synthesis of proteins. Denitrification is a specific kind of nitrate reduction where nitrate is reduced to nitrogen gas that can be released to the atmosphere (Equation 3). Denitrification allows growth of bacteria under anaerobic conditions.



(Kiely, 1997)

## **Wetlands**

Wetlands are ecosystems in areas where water conditions are intermediate between up-land and deep-water aquatic systems. The soils are saturated with water and the lands are colonised by adapted plants and animals (Brix, 1997). There are consequently numerous kinds of wetlands. These are characterised by the level of the water surface, the water depth and the direction of the water flow.

Wetlands have become well established during the past decades for cleansing different types of wastewaters. They are effective purification systems and nutrient sinks (Breen, 1990). Conventional treatment technologies provide good results but are expensive, energy consuming and complicated. Furthermore, they are usually located in sparsely populated areas so water to be treated has to be pumped over long distances. Economic reasons hinder an effective treatment of the water. Hope is placed on wetlands to provide a cost-effective and low-technology method for purification of wastewaters and removal of nutrients. They are ideal in land intensive areas where there is a minimum requirement for operation and maintenance (API, 1998).

Initial enthusiasm for the use of wetlands to remove nitrogen from domestic wastewaters arose from the potential that existed in the large variety of biological, physical and chemical transformations of nitrogen known to occur in natural systems (Rogers *et al*, 1991).

Constructed wetlands are man-made systems that imitate the functions of the natural systems but with a better chance for management and control. They can be placed close to and in connection with the generator of wastewater. Which system to adopt for treatment of wastewaters is dependent upon the treatment goals, the climatic conditions, the hydraulic load and the surface area available.

## Treatment wetlands

The surface flow wetland is a basin with a free water surface. Plants can either grow on the bottom or float on the surface. This kind is mainly used for primary treatment of water, which is removal of suspended solids and particles that settle on the bottom (API, 1998).

In a subsurface flow wetland, the water surface is below ground. If the treatment is based on wetland plants, it is called the root-zone method. These are best suited for secondary and tertiary treatment of wastewater, which reduces levels of organic material, nutrients and toxics. It is the rhizosphere, the area where the roots grow, that is active in the root-zone method (Brix, 1987).

Wastewater may be discharged into constructed subsurface wetlands with either horizontal or vertical flow regimes. Horizontal flow is the most widely adopted. It is appropriate for eliminating oxygen-demanding substances (Tchobanoglous, 1991). The organic material is removed quickly at the beginning of the wetland. It is, however, more difficult to obtain a satisfying removal of nutrients. As the rhizosphere is the active area, it is important that the water passes through these parts. In horizontal flow wetlands, the water flow is often unevenly distributed and the water-rootzone contact is reduced. Vertical flow systems have been reported to provide a better performance due to the effective water-rootzone contact (Breen, 1990). They have been in use for several years in Europe (Cooper *et al.*, 1997; Morris and Herbert, 1997; Von Felde and Kunst, 1997).

If the water that is led into the vertical flow wetland is introduced from the bottom, it is called a vertical up-flow system. This is the best way to obtain an even flow (Farahbakhshazad, 2000). The bed is filled before the water runs out at the top.

## **Substrate**

The choice of substrate determines the porosity of the bed and therefore makes it critical when constructing wetlands with subsurface flows. The water usually carries particles with it and these tend to clog the media. Not only does this give an unsatisfactory hydrologic distribution but it can also lead to flooding of the wetland.

In particular, the size of the particles is important. Using media with varying sizes is the best way to avoid clogging. The particles in the water are filtered off successively where a larger diameter, and thus porosity, is used in the beginning and a smaller at the end (Moreno, 2000).

## **Vegetation**

The role of plants in wetlands is a widely discussed topic. There is however, no doubt that the vegetation plays a crucial role. The plants decrease wind velocity and create a natural insulation in winter. This is necessary in a climate such as in Sweden (Brix, 1997).

Oxygen is transferred to the soil through the root system. This creates an optimum environment for the microbiological activities in the ground. This is especially important, where the effluent water is poor in oxygen. The roots also provide a large surface area for attached microbial growth (Brix, 1997).

A more questioned statement is the plants capacity to absorb nutrients. The plants do take up nutrients; the question is if the uptake is sufficient for reducing nutrient levels in wastewaters. The plants have to be regularly harvested and taken away from the wetland. Otherwise, the plant material and the nutrients will return to the soil while the plants die and decay. The plant material can later be used as fertiliser, taking advantage from its storage of nutrients (Farahbakhshazad and Morrison, 2000).

The rhizosphere is the area in the soil where the roots are located. It is home for many microorganisms. These are responsible for the biological activities in the ground such as the nitrogen cycle. The bacteria live in symbiosis with the plant roots.

### **Nitrogen removal mechanisms in wetlands**

There are mainly three, possibly competing alternatives known today. These are rhizosphere oxidation, plant uptake and soil adsorption (Breen, 1990; Brix, 1987; Reddy *et al.*, 1987; Rogers *et al.*, 1991; van Oostrom and Russel, 1994).

Whichever alternative, or combination of alternatives, is correct, the rhizosphere is the particularly active area in the wetland. It is a zone of increased biomass, strongly influenced by the plant roots and the microorganisms associated with plant roots. It is therefore crucial that the water passes through this region. This is not easily achieved in horizontal flow wetlands. Root biomass fills the pores and directs the water away from the rhizosphere. Vertical flow systems have been reported to provide a better performance. There is a more effective water-root zone contact, which enhances the nutrient removal (Moreno *et al.*).

The first theory states that water is cleaned by microbiological degradation in the rhizosphere. The roots and rhizomes provide a substrate for attached growth of microorganisms and oxygen is transferred to the rhizosphere by leakage from the roots. This increases aerobic degradation of organic matter and nitrification. It is only in surface flow systems that plant uptake are of importance. In subsurface flow systems, the amounts removed through plant uptake are insignificant (Brix, 1997; Wittgren and Maehlum, 1997).

The second theory states that the presence of plants inhibits microbial degradation and that plant uptake therefore is the dominant nitrogen removal mechanism. The oxygen transferred to the soil by the plants, hinders the denitrification processes. Plants compete with nitrifying/denitrifying microbiota for available nitrogen (Rogers *et al.*, 1991). Thus,

in the absence of plants, systems behaved much as would be expected of conventional activated sludge and trickling filter systems (Tchobanoglous, 1987).

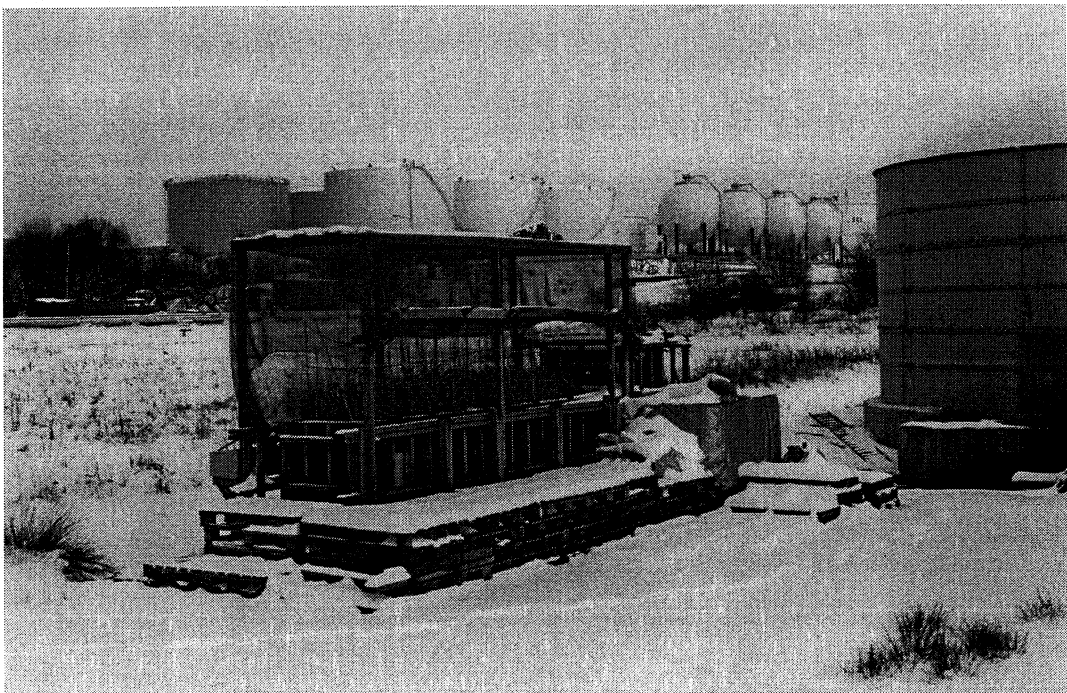
If plant uptake is the dominant mechanism, it is important to harvest the reeds to permanently remove the nutrients from the water and the wetland. The green parts above ground only constitute a fraction of the biomass of the plants; the major part is in the roots. The plants therefore have to be dug up. Harvesting need not be frequent. Plants remain in growing mode for three years. Furthermore, the high nutrient supply retards winter senescence even when exposed to frosts that kill natural established vegetation. The amount of dead plant material at the end of three years is small (Rogers *et al.* 1991; Reddy *et al.* 1987). Nutrients may be collected and recycled into the systems (Farahbakhshazad and Morrison, 2000). The root biomass can for instance, be used as fertiliser in agriculture. This would prevent a loss of valuable nutrients.

The ultimate removal mechanisms known today are physical and chemical processes, such as adsorption. These depend upon the substrate in the wetland. Gravel has a poor adsorption capacity. There is a progressive saturation of the adsorption sites, which limits the usefulness of the adsorption processes in these systems (Breen, 1990). Organic soils and clay minerals have higher exchange capacities. Ion exchange can remove significant amounts of positively charged ions, such as ammonia. Binding of nutrients to the soil particles is not a permanent removal mechanism. This means that there is no long-term effect on nitrogen removal; adsorbed nitrogen is later released into the water. The wetland however acts as a buffer and stabilizes the system (Brix, 1987).

## Experimental

### *System design*

The current wastewater treatment plant, at the Preem Oil Refinery, consists of two API-basins (American Petroleum Institute-basins), a sandfilter and a biological bed. After treatment, the process water is released into a coastal lagoon. The experimental wetland was constructed in May 1998. It was placed after the biofilter and intended to be an additional and last step in the wastewater treatment.



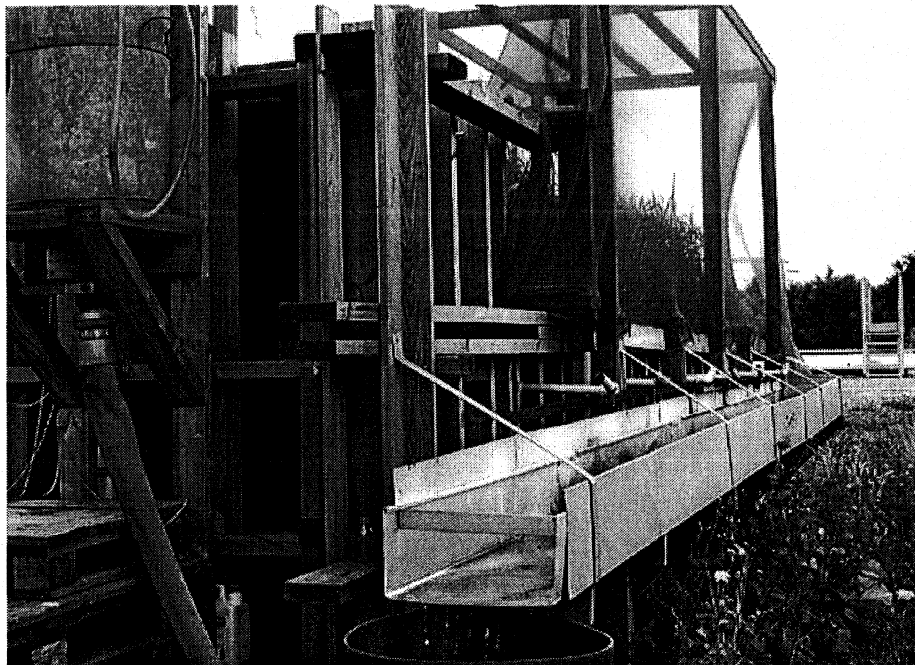
**Figure 2. Experimental wetland at the Preem Oil Refinery. The netting was to protect the young plants from wind during early spring growth.**

The effluent water is pumped from the biofilter into a well of 1.5 m<sup>3</sup>. The well is placed higher than the wetland giving the difference in pressure that drives the water flow into the wetland. The pilot plant has a surface area of 5 m<sup>2</sup> and a depth of 1.5 m. It is constructed above ground to facilitate its management and control.

### **Water flow**

The wetland at Preem is a vertical up-flow system, which means that the water enters the bed from the bottom and runs out at the top. The effluent water enters through pipes that cover the bottom of the bed. The pipes are perforated all along to give an even flow through the wetland.

Six outlet pipes are situated approximately 15 cm below ground. The outlets are adjustable to control the water flow and water level in the bed.



**Figure 3. The effluent pipes are adjustable to control the level of the water surface in the wetland.**

## **Substrate**

Substrate with varying sizes is used, as this is better for avoiding clogging of the wetland. The particles in the water are filtered off successively while a larger diameter, and thus porosity, is used in the beginning and a smaller at the end.

The wetland is divided into five layers each with a specific size of gravel. Gravel size decreases from bottom to top. The particles at the bottom have a diameter of 15-25 mm and those at the top a diameter of 2-3 mm.

The soil porosity was calculated to 50%, giving an operational volume of 3750 litres.

## **Vegetation**

The plant used at Preem is the common reed, *Phragmites australis*. This emergent macrophyte is widely used in experimental wetlands for purification of different types of wastewaters. It is famous for being tolerant and fast growing under difficult climatic conditions. It is resistant to low pH and high salinity and has deep growing roots, which creates a great volume of rhizosphere (Reddy *et al.* 1987). The rhizosphere is the layer of soil in which plant roots and microorganisms are particularly active.

## **Oxygen**

Oxygen is a crucial factor in wetlands. It is necessary for both plants and microorganisms. Microorganisms are active in the nitrification process where ammonia is transformed into nitrate. Nitrification directly depends upon the amount of oxygen available (Kiely, 1997).

The effluent water at Preem is very poor in oxygen. It is impossible to use alone for watering and the plants themselves cannot provide sufficient oxygen for the microbiologic activity. It is necessary to add air.

Early experiments were done using intermittent loading as an air supply. That was however not used during these experiments. Instead, compressed air was led through

slotted pipes straight into the bed. This had a very good effect, raising the concentrations of dissolved oxygen from approximately 1 to 7 mg / litre.



**Figure 4. Pipes through which pressurised air is inserted to the bed.**

### **Flotation unit**

Effluent waters from oil refineries are rich in suspended solids. Six months after the wetland at Preem was in operation, the wetland was totally clogged. The substrate had to be taken out and washed before being inserted again into the bed. After that, a flotation unit was placed before the wetland. Its purpose was to reduce the amounts of suspended solids. The flotation unit had to be backwashed daily, or it would be clogged.

## Heat exchanger

During winter, the effluent water generally held a temperature around 30° C. However, at several occasions the water had temperatures far above that. This killed the macrophytes on one occasion in 1998. After that, a heat exchanger was placed between the biofilter and the wetland. This kept the water at a steady temperature of approximately 20° C, which is close to the optimum temperatures for macrophytes.

In a full-scale wetland, this would probably not be necessary, as dilution of the water would even out the temperatures.

For further details on the construction of the experimental wetland, see Moreno (2000).

## Sampling and analysis

There are 45 sampling locations throughout the bed. The locations are arranged in fifteen parallel columns, numbered 1-15, at increasing distances from the well. There is approximately 30 cm between each column. In each column, there are three sampling locations located at depths of 75cm, 50cm and 25cm, respectively.

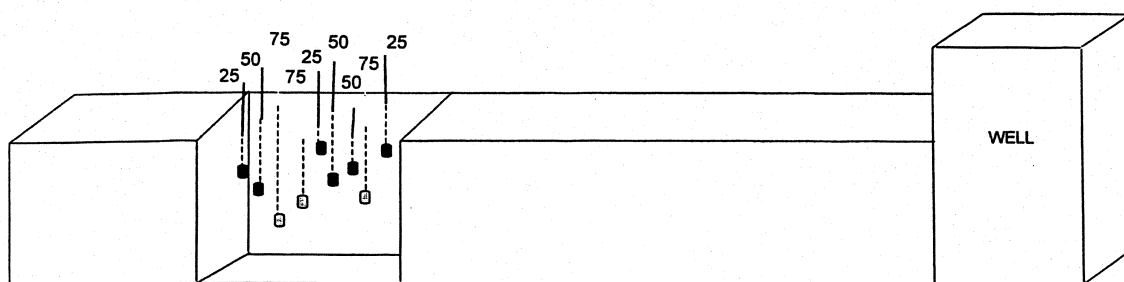


Figure 5. View of the sampling locations in the bed; 25, 50 and 75 are location depth in cm in the bed.

Ammonia was measured with a Dr Lange Photometer. The results are given in mg ammonia-nitrogen per litre.

Nitrate and total-nitrogen were measured using a Hach Photometer. The results are given in mg nitrate-nitrogen per litre and mg total-nitrogen per litre, respectively.

### **3-dimensional study**

The purpose of the study was to describe the wetland from a three-dimensional point of view using the many sampling locations throughout the bed. The results would give an understanding of the mechanisms that contribute to nitrogen removal. The study was carried out during the first days of November.

The bed was first thoroughly washed with firewater for two days. When all traces of nitrogen were eliminated, the experiment was started.

Ammonia was added to the ordinary inflow of process water raising its concentration from approximately 2 to 8 mg/litre. The aim was to keep the inflow concentration constant at this level but the pump broke down which gave a high initial level that was later diluted with ordinary process water. However, this did not hinder the experiment. Instead of a constant and high ammonia inflow level, the result became a constantly decreasing inflow concentration.

Retention time was set to eight hours but the experiment was stopped a little before the retention time had passed. Night fell at five o'clock and darkness made it impossible to take samples later than that. A shorter retention time would have made it difficult to continuously take samples from all sampling locations. When the experiment was stopped, the water had just reached the top of the bed but not yet the outflows. The picture of what happens within the bed is therefore complete but there is no result of the final outflow concentrations.

Samples were taken five times with approximately one hour and thirty minutes between each occasion. The sampling occasions are numbered "t1" to "t5". The samples were taken from all the sampling locations as well as from the well and the outflows. The concentrations of ammonia, nitrate and total nitrogen were analysed for each sample.

### **Winter conditions**

This part of the study was carried out during the months of January and February. The outdoor temperatures were constantly between  $-5^{\circ}$  and  $-10^{\circ}$  C. Daylight was restricted to seven to eight hours per day.

During the time of experiment, the wastewater treatment plant was under reconstruction. Several times the process water was led past some of the treatment steps. This led to strongly varying quantities and qualities of effluent process water. In order to avoid problems in the wetland due to these uncontrolled discharges, firewater was used instead of process water. In this way, it was easier to control both the flow and the concentrations entering the wetland.

The experiment was divided into two parts. In the first part, firewater was taken straight from the tap. Its temperature was between  $0^{\circ}$  and  $5^{\circ}$  C. In the second part, firewater was heat exchanged with process water to give a temperature of  $15^{\circ}$  C. This was done as process water generally holds a higher temperature and that could have an impact on the transformation of nitrogen. Process water holds a temperature of  $30^{\circ}$  C during winter but when entering a full-scale wetland it will be diluted and cooled down. The two parts of this study should together give a realistic picture of the performance under winter conditions.

Retention time was set to five hours. Ammonia was added in varying concentrations, ranging from 2 to 30 mg/l. Each concentration was kept for two or three days in order to get stable values.

The inflow samples were taken from the well one or two days after the new concentration of ammonia was inserted. The outflow samples were taken five hours later. The six outflow spots are located at different distances from the well and receive different amounts of pressurised air. The concentrations of ammonia and nitrate could therefore vary, as nitrification is dependent upon the oxygen available. At first, samples were taken from each of the outflow spots. They were analysed separately to see if the concentrations differed. This was however not the case. Firewater is almost saturated with oxygen and the oxygenation unit had minimal influence. The outflow samples were therefore mixed into one outflow sample.

### ***Sources of errors***

Both the retention time and the inflow concentrations depend upon the water flow, which makes the water flow very important. It was difficult to adjust an exact flow. The pressure of the process water is affected by the amounts of stormwater for the period and the pressure in the firewater system is set in town and impossible to control at Preem. This resulted in unsteady retention times and concentrations. The variations are relatively small and do not affect the overall results.

A bed's porosity determines the retention time of the water passing through the bed. The porosity of the wetland was measured by Moreno in 1998. The results obtained then were used in this study while calculating the retention time. These results may not be accurate today but they should have approximately the same magnitude as then and therefore do not alter the results significantly.

The method used for analysing ammonia is the same adopted by Preem. It is controlled every week and can be expected to be accurate. The analysis methods for nitrate and total nitrogen on the other hand are less well controlled. They do however seem rather exact while compared to the results given by the ammonia analysis.

Many samples were kept for a day or two in a fridge before being analysed. The temperatures in the fridge were below 8° C, which should keep the microbiological activities low. When the time between sampling and analysis exceeded two days, the samples were put in a freezer. The results obtained from a fresh sample and from an older sample can therefore differ, but the difference should be minimal.

## **Results and discussion**

### ***The 3-dimensional study***

The results show how the water flow is distributed through the wetland. It is fairly even but two of the outflow pipes have a reduced flow and the sampling spots next to these were almost totally blocked. These are situated at approximately one and two meters from the well, respectively.

Oxygen is added through pipes into the bed. Pressure is higher close to the well and lower further away which could lead to varying concentrations of dissolved oxygen in the bed. This would influence the transformation of ammonia to nitrate. However, no deviation that can be related to the distance from the well and the amounts of dissolved oxygen was noted.

### **Ammonia**

As the time of observation had to be limited due to darkness, no result of the total reduction of ammonia was obtained. However, there are indications that the reduction reaches approximately 65%. The removal of ammonia is lower in November than in summer. Best results were obtained in July 2000 when an ammonia reduction of 80% was observed (Moreno, 2000).

The following three diagrams show the evolution of ammonia concentrations during the experiment. There is one diagram for each depth: 75cm, 50cm and 25cm, with the concentrations given at five different sampling occasions. The fifteen sampling columns are represented on the X-axis. "1" is the row closest to the well and "15" is the row furthest away. On the Y-axis, the concentrations of ammonia are given in mg/l.

Figure 6. Ammonia concentrations at location depth 75 cm for the five sampling occasions.

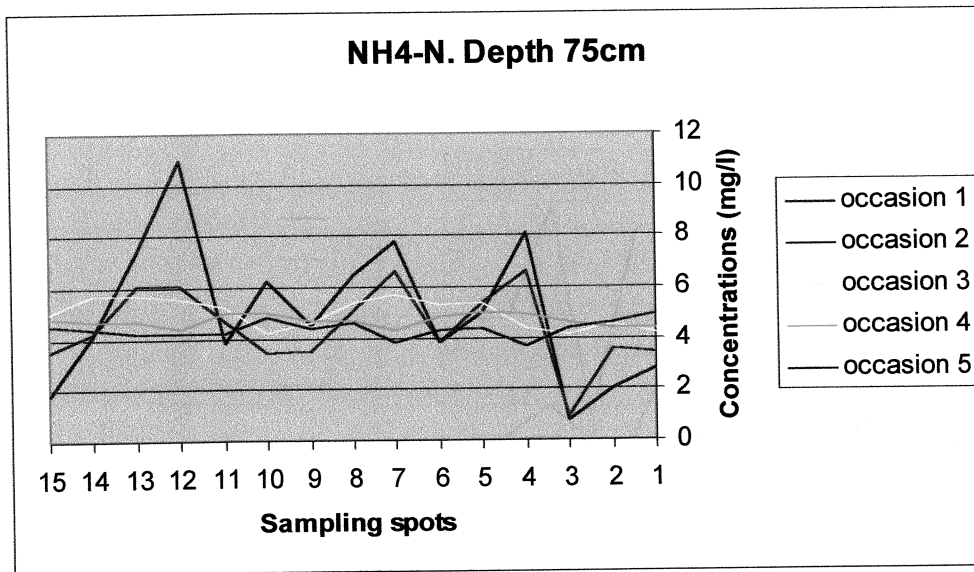


Figure 6 show that the concentrations of ammonia at 75 cm depth are relatively constant during the experiment. At the first sampling occasion, the concentrations of ammonia differ between the sampling locations. This indicates that the water flow is not perfectly even. However, the differences even out and soon, the levels are the same in the entire bed, as should be the case. The concentrations are the same as the ones that enter the bed, which means that no ammonia reduction occurs below 75 cm.

Figure 7. Ammonia concentrations at location depth 50 cm for the five sampling occasions.

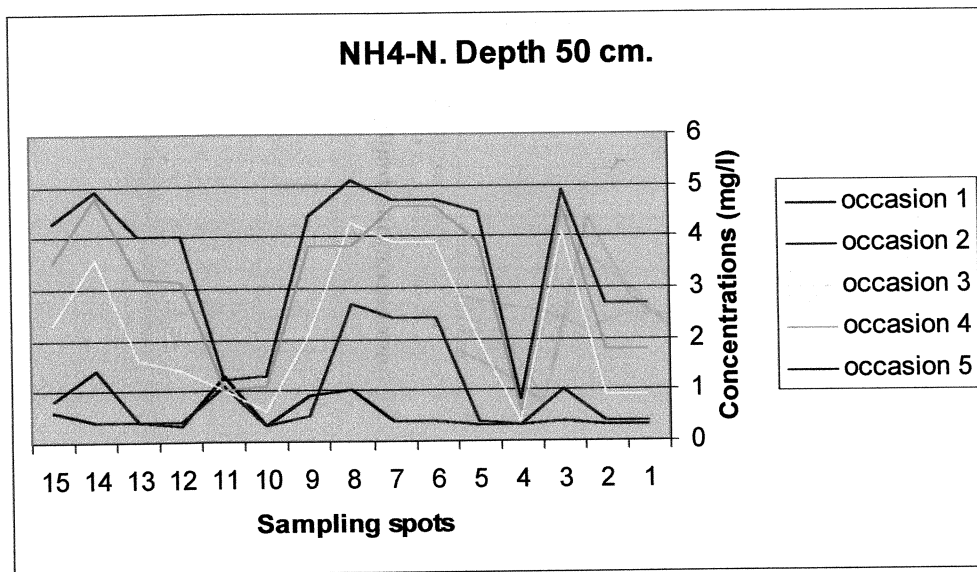


Figure 7 shows the evolution of ammonia concentrations at 50 cm depth. At the first sampling occasion, the concentration is zero. During the time of experiment, the concentration increases until it reaches approximately 5 mg/l. The levels are almost the same as at 75 cm, which means that there is hardly any reduction between 75 and 50 cm.

The curves are irregular with two distinct dips at sampling locations 4 and 10-11. Here the ammonia concentrations are very low. This is due to the diminished outflows through the pipes next to these locations. Decreased flow leads to longer retention time which in turn leads to increased reduction of ammonia.

Figure 8. Ammonia concentrations at location depth 25 cm for the five sampling occasions.

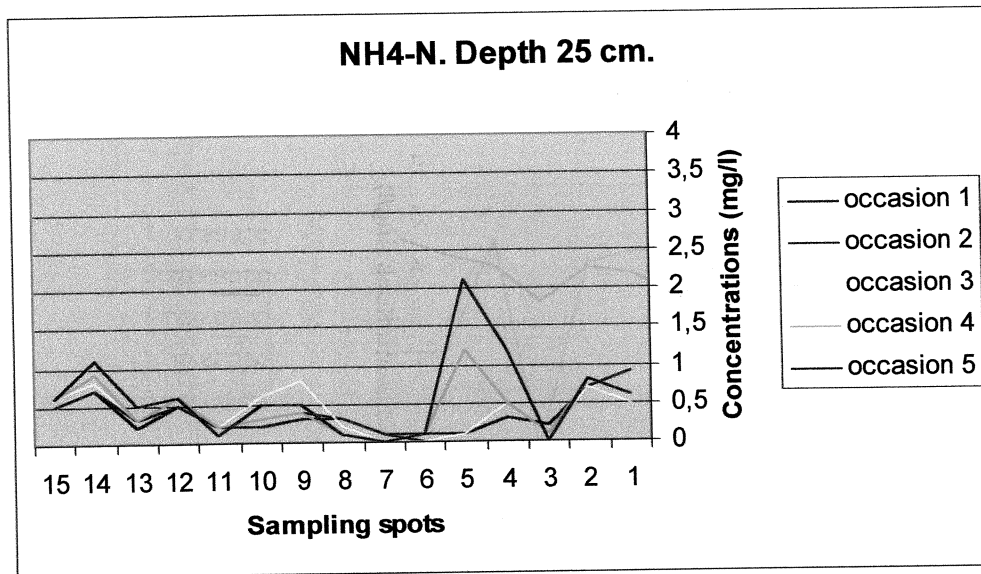
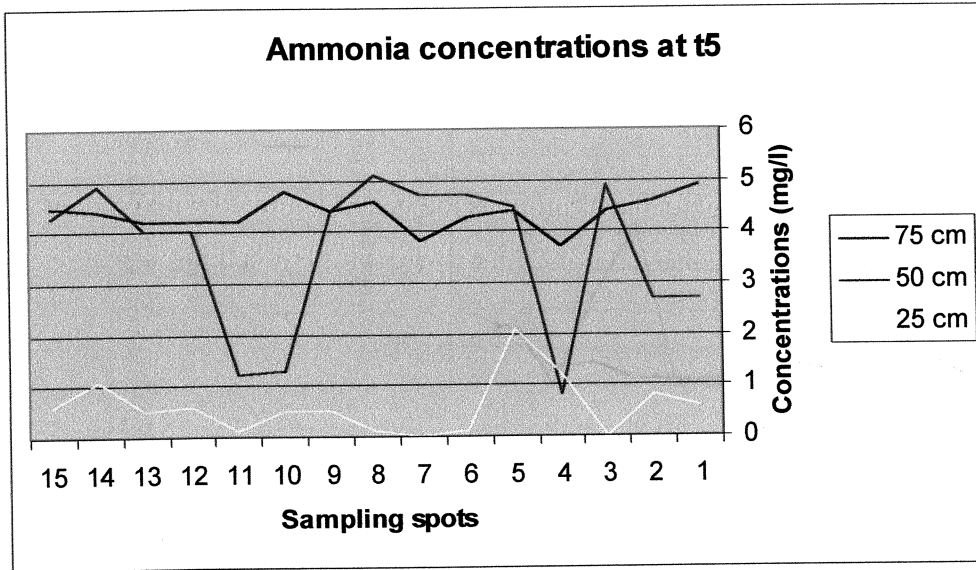


Figure 8 shows the concentrations over time at 25 cm. As the first diagram, it shows constant concentrations. However, this time they are constantly low instead of constantly high. The concentrations never reach above 1 mg/litre. This indicates that there is removal of ammonia and that it occurs below 25 cm. An exception is the sampling location "5". It shows a little peak, which reflects the irregular flow already noted in that area.

**Figure 9. Ammonia concentrations at each level of the bed, eight hours after the experiment was started.**



In Figure 9, the concentrations at the different depths, at the last sampling occasion, are placed next to each other. The sampling occasions are numbered “t1” to “t5”, “t5” being the last sampling occasion. This gives an instant picture of the concentrations in the bed, eight hours after the experiment was started. It clearly shows what zone and level is active in the wetland. It is between 50 and 25 cm that the ammonia reduction occurs.

The main part of the roots is located to this zone. These are not only responsible for plant uptake but also home for the nitrifying bacteria.

Beside nitrification, ammonia can be removed through chemical or physical adsorption to surfaces in the bed. If the adsorption would be to the substrate in the bed, the ammonia removal would be distributed over the entire bed. This is not the case. As is shown in the diagrams the reduction occurs in the rhizosphere. This implies that if there is adsorption it is adsorption to the roots and not to the substrate.

## **Nitrate**

The nitrate concentrations are constantly very low, for every location and every occasion. They are between 0.1 and 1.0 mg nitrate-nitrogen / litre and they exceed 1.5 only very few times.

There is no removal of nitrate through denitrification as the bed is saturated with oxygen. Denitrification only happens in anaerobic environments where nitrate functions as oxygen source.

The plants are able to take up large amounts of nitrate; even excessive amounts for limited periods. The low nitrate levels are therefore due to the plants ability to immediately take up this form of nitrogen. The rate-limiting step in ammonia reduction is the transformation of ammonia into nitrate.

## **Total nitrogen**

The concentrations of total nitrogen are slightly more irregular than the ammonia concentrations but still follow the latter closely. They generally lay one or two units above the ammonia levels. The difference between them corresponds to the amounts of nitrate and organic nitrogen in the bed.

## ***Winter conditions***

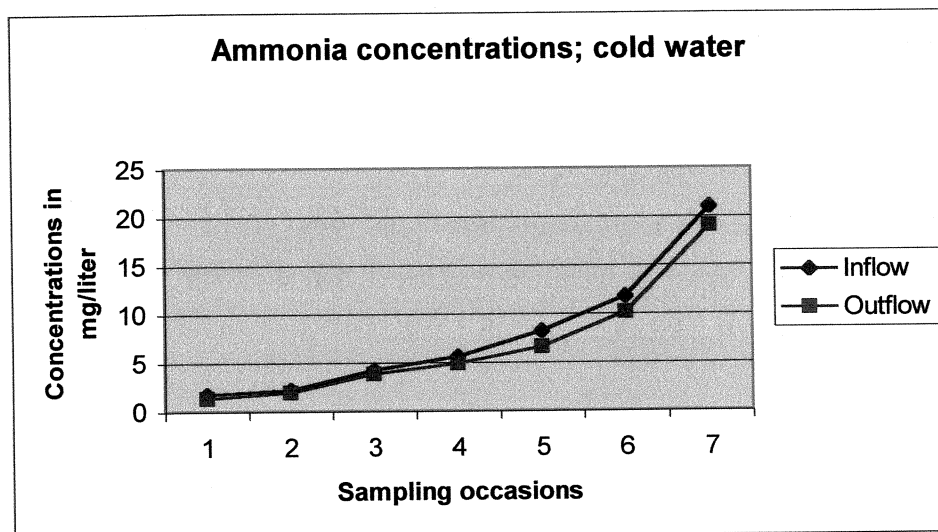
There was ammonia reduction with both cold and heat exchanged water. It was however, far lower than the reduction obtained during the summer 2000.

In this part of the study, firewater was used instead of process water. Firewater is saturated with oxygen, which made the aeration unit superfluous. It was anyway kept active. The concentrations were the same through all outlet pipes.

## Cold water

The reduction of ammonia nitrogen ranges from 0.3 to 2.0 mg / litre, which is equivalent to a reduction between 10 and 24 %.

**Figure 10. Concentrations of ammonia in inflow and outflow with cold water under winter conditions.**



In Figure 10, the inflow and outflow concentrations are plotted. The sampling occasions are represented on the X-axis and the ammonia concentrations on the Y-axis. The outflow concentrations closely follow the inflow concentrations.

Nitrate, on the other hand, increased with 0.1 to 0.6 mg /litre, which is hardly above the limit of detection. The final amounts of total nitrogen remained unchanged.

These results indicate that the removal mechanism for ammonia is bacterial nitrification and plant uptake. Microbiological activities are temperature dependent and start at temperatures around 5° C. Plant physiology is governed by both temperature and solar radiation (Wittgren and Maehlum, 1997). The ammonia levels have decreased while the nitrate levels have increased. This implies that there is nitrification in winter, but in a lesser extent, than in summer. The plants on the other hand are now resting and do not take up nutrients, which leaves the amounts of total-nitrogen unchanged. The ammonia

reduction can also be through adsorption. Nevertheless, since the total amount of nitrogen has not changed, adsorption is insignificant and nitrification is dominant.

### Heat-exchanged water

The results were similar when warmer water was used but the tendencies were slightly stronger.

Ammonia was reduced by 0.4 to 4.1 mg /litre, which corresponds to 14 to 29 %. This is a little higher than with colder water.

**Figure 11. Concentrations of ammonia in inflow and outflow with heat-exchanged water under winter conditions.**

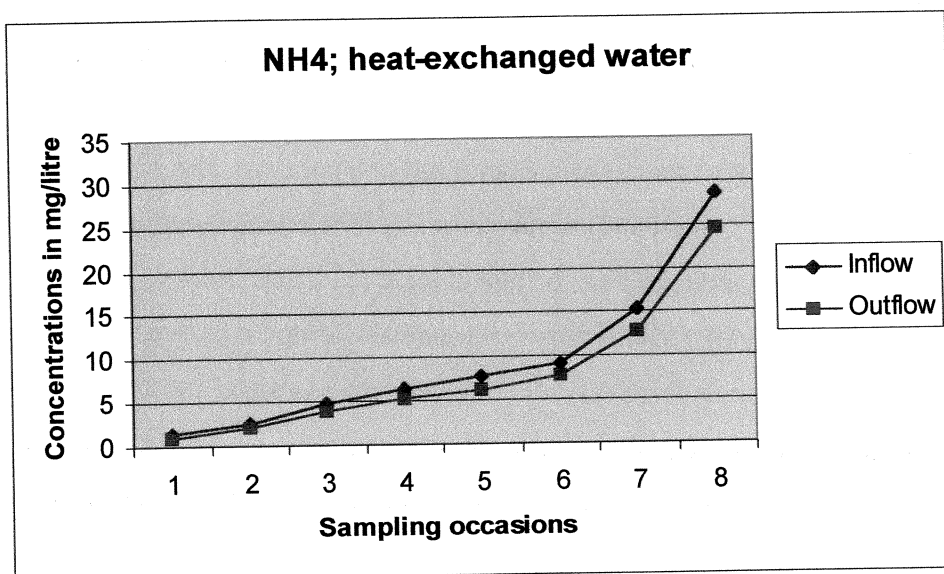


Figure 11 show the inflow and outflow concentrations. The sampling occasions are represented on the X-axis and the ammonia concentrations on the Y-axis. The outflow concentrations closely follow the inflow concentrations.

Nitrate increased with 0.2 to 1.8 mg /litre. On average there was a reduction of total nitrogen of 1.0 mg /litre.

The results obtained with heat-exchanged water support the conclusions made with cold water. There is nitrification in winter and it increases when temperatures are raised. The

amounts of total nitrogen have decreased a little. This indicates that either plant uptake or adsorption, or both, increases with temperature.

In this study, it is not possible to tell if the reduction of total nitrogen is due to plant uptake or to adsorption. It is necessary with a close study of the plants and their roots before drawing these conclusions. Whichever alternative is correct, the removed nitrogen is located to the surfaces of the roots or the inside of the plants. This means that a removal of the plants, including the roots, will permanently eliminate nitrogen from the effluent waters.

A study carried out by Breen (1989) partly supports these results. A mass balance method for assessing the potential of artificial wetlands for wastewater treatment is presented. The paper describes the partitioning of wetlands into a number of components (above ground parts, rhizomes, roots, organic films on the substratum and roots and the substratum) and the measurement of mass changes in these components. The systems had an up-flow hydraulic format and consistently removed 95% of the nitrogen influent load. The nutrient partitioning studies indicate that the plants were the major nutrient sinks for nitrogen. They were responsible for 55% of nitrogen removal. Complex films of microbial cells and organic materials form the interface between plant and substratum surfaces. These account for approximately 10% of the nitrogen removal, and represent a highly active nutrient pool. Bacterial denitrification is a significant removal mechanism, for both planted and unplanted systems.

## Conclusions

### *The potential of a constructed wetland*

Experiments on the pilot plant at the Preem Oil Refinery have given an idea of how a full-scale treatment wetland will behave. It has shown that there are several advantages with a treatment wetland, but also that a wetland is not easily run with the given conditions.

In summer, the wetland will reduce the amounts of total nitrogen very effectively. Ammonia is adsorbed to the roots or transformed into nitrate that is taken up by the plants. It is therefore not only the amount of ammonia but also the amount of total nitrogen that decreases. A wetland will also even out peaks and act as a buffer and stabiliser (Kadlec, 1999).

In wintertime, there is removal of ammonia but it is far lower than the reduction in summer. The ammonia is transformed into nitrate but the nitrate is not absorbed by the plants. This leaves the levels of total-nitrogen almost unchanged. Although there are no restrictions today on the discharge of nitrate into recipients, these are likely to come in the future. Solely relying on microbiological nitrification of ammonia into nitrate is therefore not a sustainable solution. The stabilising effects of the wetland however, remain during the winter and the bed will even out temporary peaks.

After being harvested, the roots are filled with nutrients. This has raised the idea that they could be used in agriculture as fertilizers. However, the roots probably also contain toxic chemicals that are not appropriate in agriculture. These need to be taken care of properly. Having them concentrated in the roots is convenient. They can easily be transported and be incinerated with municipal waste. The ashes are then disposed of together with the rest of the waste ashes.

## **Problems that need solving**

During the time of the study, many problems occurred with the operation of the wetland. These need to be solved before construction of a full-scale treatment wetland at Preem.

The greatest problem was suspended solids and particles in the effluent water. If not removed, these immediately lead to clogging of the wetland. This happened in 1998 and to avoid further complication a flotation unit was placed before the wetland. This worked satisfactorily as long as it was backwashed every day. A flotation unit is however not realistic for a full-scale wetland. It would be complicated and expensive. The question is whether a filter or a settling pond could replace it.

Another problem was uncontrolled discharge with the effluent waters. Many times elevated levels of phenols and aliphatic carbons were registered and on some occasions the water had a temperature above what the plants and microorganisms could tolerate. The discharges are not registered until the effluent water reaches the lagoon, which is too late and might lead to irreversible effects on the wetland. The quality of the process water must be controlled before the wetland and it must be possible to lead the water past the wetland in case of high levels of toxics. However, when led around, the water misses part of the treatment. These problems remain for every kind of biological treatment, as for instance nitrification/denitrification basins.

The microorganisms require oxygen for nitrification, which is the first step in biological treatment. The effluent waters are free from dissolved oxygen, which makes it necessary to add oxygen to the water before the biological step. In the pilot plant, this was done with pressurised air inserted into the bed through pipes. In a full-scale wetland, this is hardly possible. The installation of an aeration pond or similar will be a necessity.

## **Recommendations**

### **Preem**

Before considering building a treatment wetland, Preem has to define the goals of the treatment. Do the raised treatment requirements consider total nitrogen or only ammonia? Is it necessary to have a net reduction of nitrogen or ammonia or is it sufficient to even out the concentration peaks? Well-defined criteria have to be set together with the authorities.

Spread over the entire year, the average ammonia reduction is approximately 40%. Calculated from day-to-day the reductions vary between 10 and 90%, depending on the season. This study has shown that if it is necessary with a constant and high reduction of nitrogen all year round, a treatment wetland is not a sustainable solution for Preem. A treatment wetland effectively reduces the nitrogen concentrations in summer. In winter, it only slightly reduces the amounts of ammonia and leaves the amounts of total nitrogen unchanged. A different kind of treatment will therefore be needed if same results are necessary in winter as in summer. However, if it is only the ammonia concentrations that have to be reduced, and not the total amounts of nitrogen, and variations can be tolerated during the year, a treatment wetland will be a good last step in the wastewater treatment. It is also an efficient buffer.

If constructing a wetland, Preem has to take into account the problems encountered while operating the pilot plant. Suspended solids need to be removed from the wastewater, and the concentration of dissolved oxygen needs to be raised, before the water enters the wetland. Uncontrolled discharges of toxic chemicals with the effluent water cannot be tolerated, or the microorganisms will die. This is true whichever biological treatment is chosen.

Another problem that needs to be considered is how harvesting of the plants shall be performed effectively without hindering the wastewater treatment. It is not enough to

remove the green parts above ground; the roots have to be removed as well. New plants need time before they are capable of reducing significant amounts of ammonia. The wetland therefore needs to be over-dimensioned permitting areas under growth without full performance.

If Preem decides not to construct a treatment wetland, research must be put on finding a new alternative for additional treatment of the process waters. From 2002, the requirements are raised on the quality of the wastewaters and for the time being Preem is asked to actively search for new treatment alternatives.

The most sustainable solution is probably to choose a different treatment alternative for removing ammonia from the effluent waters. A constant and more reliable reduction of nitrogen can then be obtained. A treatment wetland is better suited for being a complement to traditional treatment.

### **Further research**

In this study, the effects of a treatment wetland, receiving wastewater with elevated concentrations of ammonia, were examined. The purpose being to see if ammonia was removed and to understand how it was done. Adsorption and plant uptake were identified as the main ammonia removal mechanisms. A similar study, using nitrate instead of ammonia, would help identify which of these two mechanisms is dominant. If nitrate is removed, plant uptake is probably dominant as nitrate is the nitrogen species that is taken up by plants. If, on the contrary, the nitrate concentration is the same in the outflow as in the inflow, adsorption is the dominant ammonia removal mechanism. Positive ions, such as ammonia, are adsorbed to a higher extent than negative ions, such as nitrate.

Due to the very low levels of dissolved oxygen in the process water, aeration is necessary before biological treatment of the water. In this study, aeration was carried out with pressurised air that was inserted straight into the bed. In this way, the entire wetland became saturated with oxygen. Using other aeration methods may alter the performance of the wetland and give different results. If both aerobic and anaerobic zones can be

obtained, favourable conditions for bacterial denitrification might appear. The results would be the same as in traditional nitrification/denitrification basins, which is a sustainable way of removing ammonia from wastewaters.

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