Organic micro pollutants:

Assessment on optimum treatment strategies in the water cycle

Judith van Tol

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TU Delft Delft University of Technology

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Assessment on optimum treatment strategies in the water cycle

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Executive summary

Introduction and problem definition

Since several decades organic micro pollutants (OMPs) have been detected in natural waters. Although appearing in very low concentrations (nanograms to micrograms per litre or even lower), the presence of more than 100.000 registered chemical substances in the European Union, of which 30.000-70.000 are in daily use, is a major reason for concern. Due to their persistent character the OMPs remain longer in the water cycle and can be transported over a longer distance than other pollutants. Current treatment facilities are not designed to remove those compounds, which causes them to end up in the environment and even in drinking water. The current problems on OMPs in the water cycle are not that the concentrations present in the water cycle are too high to guarantee the safety of drinking water, but are the long-term effects of these concentrations, the increase in concentrations (due to changing circumstances) and the unknown effect of OMPs in mixtures with other OMPs. In order to find a solution to this problem this project focusses on the following question:

What is the most sustainable, applicable and cost-efficient strategy to reduce concentrations of selected micro pollutants in surface water and drinking water in the Netherlands?

Methods

In this project various strategies to reduce the concentrations of OMPs are composed and scored by a Multi Criteria Analysis (MCA). The best strategy is tested on two case studies to see the influence of the strategy on the concentrations. The future situation regarding the emission of OMPs and discharge of river water is also taken into account. Whether the strategy is effective is determined based on limits of concentrations of OMPs. The scope of the project is on drinking water extraction areas in the Netherlands.

Firstly a literature study on current European and Dutch legislation and policy, future trends regarding population growth, consumer behaviour and climate change and the presence and behaviour of target compounds in the water cycle is conducted. Based on the Deltascenarios two future scenarios regarding emission of OMPs, river discharge and precipitation are selected: REST and STEAM. Scenario REST is a scenario of economic stagnation with moderate climate change. In scenario STEAM both the economic situation and climate change increases. Later in the report these scenarios are used to test the best strategy on, which reduces the concentrations of OMPs in the water cycle. Dutch limits on OMPs in the water cycle only exist for a few compounds. For other compounds target values of other organisations are used. The found limits and target values are in the order of 0.1-1.0 µg/L. The target compounds are selected based on an analysis of relevant compounds, which results in a limited number of compounds to elaborate on. Persistence of the compounds and availability of measurement data are important criteria in this analysis. The selected target compounds are carbamazepine, metformin, sulfamethoxazole (pharmaceuticals), iopromide (X-ray contrast agent), acesulfame-K, caffeine (domestic tracer compounds), MTBE (industrial chemical), AMPA, bentazone, glyphosate and N,N-DMS (pesticides). In surface water concentrations of the selected compounds between 0.025 and 83 µg/L are measured. Found removal efficiencies in WWTPs and DWTPs vary between 0 and 98%, highly depending on the type of OMP, the used treatment techniques and the composition of the influent. Different strategies with different approaches within the water cycle are discussed, which are divided in source approach *(use)*, mitigation approach *(emission)* and end-of-pipe approach *(drinking water)*.

Source approach

1. *Green pharmacy*
2. *Awareness in use and prescription*
3. *Legislation and policy*
4. *Green agriculture, greenhouse farming and cattle breeding*

Mitigation approach

5. *Separate collection of urine*
6. *Decentralised collection of wastewater in residential areas*
7. *Decentralised collection of wastewater in hospitals*
8. *Improvement of wastewater treatment plants*

End-of-pipe approach

9. *Improvement of drinking water treatment plants*

A MCA and sensitivity analysis are used to present the best strategy that is well balanced between all aspects of the water cycle and its users and which is sustainable, applicable, cost-efficient and which functions within European and Dutch legislation. The strategies are scored based on an expert judgement of the expert panel. The best two strategies are applied on water and mass balances of the two case studies to see the impact of the strategies. The first case study is the Bethunepolder between Amsterdam and Utrecht. This is a groundwater system. The second case study is the IJsselmeer area at Andijk, which is a surface water system. Both areas are partly fed by water originating from the river Rhine and serve as a drinking water extraction area. A water balance and, by multiplying the discharges by the measured concentrations, a mass balance of OMPs is composed. The results from the mass balances show whether or not the strategies are sufficient to decrease the concentrations to below the limits. Finally, a comparison between the two types of water systems (groundwater and surface water) is made.

Results

The MCA results in a highest score for the strategy 'legislation and policy'. However, this strategy only holds when incorporating other measures to reduce the emission of OMPs into the water cycle (implementing stricter regulations results in the need for solution at the use or emission of OMPS, WWTP or DWTP). For this reason also a second best strategy is determined. Strategies 1, 2, 4, 8 and 9 are in the same range and score moderately, where strategies 1 and 2 score higher than the remaining three strategies. Although without a big difference with the third best strategy, the second best strategy is 'green pharmacy'. All strategies with (de)centralised collection and treatment of urine or total wastewater score poor, due to a poor score on all three aspects: sustainability, applicability and cost-efficiency.

Although, the systems in the two case studies are both partly fed by the river Rhine (via the groundwater and via the river IJssel), the measured concentrations and exceedance of limits and target values are not the same. In the Bethunepolder the calculated concentrations exceed the limits for six compounds, while none of the measured concentrations exceed the limits. In the Andijk case the calculated concentrations of five compounds exceed the limits, while for the measured concentrations these are only three substances. The future scenarios regarding the emission of OMPs and the discharge of river water are not influencing the (non-) exceedance of the limits. After applying the strategies on the models in the Bethunepolder case concentrations of most compounds decrease to below the limits, where this decrease is in the Andijk case not enough to go below the limits. For both case studies the results show that 'legislation and policy' is a better strategy, because concentrations of all compounds are reduced, while for 'green pharmacy' only the concentrations of pharmaceuticals decrease.

Conclusion and recommendation

From these results it is concluded that 'legislation and policy' is the most sustainable, applicable and cost-efficient strategy to reduce concentrations of selected compounds in surface water and drinking water in the Netherlands. With this strategy governmental regulations regarding the emission of OMPs into the water cycle are improved. Comparing the two case studies with each other it can be concluded that in a groundwater driven system the influence of OMPs seems to be less acute than in a surface water system. However, in the groundwater system the effects of the presence of OMPs will be noticeable after a longer period, which makes this system more unpredictable and it takes more time till measures are resulting in a decrease in concentrations.

In this project the MCA is performed without exact numbers for the criteria 'sustainability', 'applicability' and 'cost-efficiency'. Further research on these aspects and the addition of more criteria improves the reliability of the MCA and thus of the winning strategy. Regarding the composed models of the case studies more attention needs to be paid to the assumptions on mixing and decay. In a system with high residence times (like the groundwater system of the Bethunepolder) decay could play an important role in the modelling.

Preface

Recently many news items are on the increasing concerns about the presence of pharmaceuticals and other organic micro pollutants (OMPs) in drinking water. Population growth, aging and climate change are only a few explanations for this. Research has been done on new innovative treatment technologies, but still not much knowledge of the behaviour of OMPs in water and the toxicological effects is known. Integral strategies have to be implemented to decrease the amount of OMPs in the environment and drinking water.

This report is the result of my master thesis at the department Watermanagement of Delft University of Technology. The research was commissioned by Witteveen+Bos, where I performed my daily activities. Especially the integral approach on the water cycle and the link between water quantity and water quality are the reasons why I chose this subject. During my research I visited various conferences and meetings with professionals in the water sector. This was an exciting and educational experience.

In this way I would like to sincerely thank the people that made my graduation thesis possible and an unforgettable experience for me. First of all, I would like to thank Raphaël van der Velde and Arjen van Nieuwenhuijzen for all their help as my daily supervisors. Furthermore I would like to thank Jan Peter van der Hoek for his involvement and knowledge. Also Astrid Fisher’s knowledge was of great value, especially her toxicological background. I would like to thank her for approachability and enthusiastic comments. I hope she can use some parts of my thesis in her own PhD-research. I would like to thank Ron van der Oost and Jan Willem Voort with their help and involvement on the case study Bethunepolder. Finally, I would like to thank my other colleagues at Witteveen+Bos for their interesting and entertaining conversations.

Utrecht, December 2013

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List of abbreviations

ADI	*Acceptable Daily Intake*
AMPA	*Animomethylphosphonic Acid*
AN	*Case study Andijk IJsselmeer*
ARK	*Amsterdam Rijnkanaal*
BQ	*Benchmark Quotient*
BP	*Case study Bethunepolder*
DBP	*Disinfection-by-Product*
DMR	*Danube, Meuse and Rhine Memorandum*
DWTP	*Drinking Water Treatment Plant*
EMS	*Ecological Main Structure*
ES	*Emerging Substances*
EQS	*Environmental Quality Standard*
GCC	*Global Climate Change*
HDSR	*Hoogheemraadschap De Stichtse Rijnlanden*
HWL	*Het Water Laboratorium*
IAWR	*International Association for Water Works in the Rhine Basin*
KNMI	*Koninklijk Nederlands Meteorologisch Instituut (Royal Dutch Meteorological Institute)*
LOEC	*Lowest Observed Effect Concentration*
MCA	*Multi Criteria Analysis*
MTBE	*Methyl-tert-butyl-ether*
NOAEL	*No Observed Adverse Effect Level*
N,N-DMS	*N,N-dimethylsulfamide*
NOEC	*No Observed Effect Concentration*
OMP	*Organic Micro Pollution*
PCPs	*Personal Care Products*
PNEC	*Predicted No Effect Concentration*
PS	*Priority Substances*
PSA	*Pumping Station Andijk*
PWN	*Drinking Water Company of Noord-Holland*
RBD	*River Basin District (WFD)*
REACH	*Registration, Evaluation, Authorisation and Restriction of Chemical substances*
RIWA	*Association of River Water Supply Companies*
RO	*Reverse Osmosis*
RWS	*Rijkswaterstaat*
WFD	*Water Framework Directive*
WPJ	*Water Intake Station Prinses Juliana*
WWTP	*Wastewater Treatment Plant*

1 Introduction

Issues concerning organic micro pollutants

Since several decades organic micro pollutants (OMPs) have been detected in natural waters. These organic compounds occur in very low concentrations (nanograms to micrograms per litre or even lower). Due to their persistent character the OMPs remain longer in the water cycle and can be transported over a longer distance (Houtman, 2010). Already in 1967 (Malaney *et al.*, 1967) presented an article about the presence of OMPs in drinking water and the impact on human health. More research has been done and awareness towards OMPs has increased, but after an environmental disaster in 1986 it was clear that OMPs could cause a serious problem for human health and aquatic life. In November 1986 a fire in a storehouse of Sandoz AG in Basel took place. During the fire water contaminated with pesticides was discharged into the river Rhine, which resulted in massive fish kill (Urk van *et al.*, 1993). The first detection of pesticides in Dutch drinking water was in 1988 in Amsterdam (Smeenk *et al.*, 1988). Nowadays, more advanced analytical techniques are available and lower concentrations can be measured (EINECS, 2002). This is one of the reasons why there is a growing concern regarding 'new substances', such as pharmaceuticals, endocrine disrupting compounds, personal care products (PCPs), drugs of abuse and carcinogenic compounds which have entered the ecosystem mostly by human activities. These emerging compounds can be toxic and may cause adverse effects on aquatic life, which include feminisation and kidney, gill and liver damage of fish (Smeenk *et al.*, 1988; U.S. Department of the Interior Bureau of Reclamation, 2009). Research of the past decade shows that there are no acute adverse health effects in (sources of) drinking water in the Netherlands (Hoeger *et al.*, 2005; Johnsona *et al.*, 2008; RIZA, 2003).

OMPs are found in all parts of the water cycle: groundwater, surface water, wastewater treatment plant influent and effluent and drinking water (Carlsson *et al.*, 2006; Loos *et al.*, 2009; RIZA, 2003). A major part of OMPs end up in the wastewater, which makes the effluent one of the main constant emission sources of OMPs. Discharges and spills from industrial companies and runoff of pesticides from agricultural lands are also conventional sources of OMPs. Research showed that OMPs can also be formed by a reaction during disinfection, called disinfection by-products (DBPs) (Jongh de *et al.*, 2012). Demographic trends, extreme rainfall and droughts caused by climate change increase the emission of OMPs to the environment, while the safety of intake water for the production of drinking water must be guaranteed (RIVM, 2008b; 2012). This increases the complexity of OMPs in the water cycle. Currently, the concentrations of pharmaceuticals measured in drinking water are about 10-50 ng/L (Cardador *et al.*, 2011; Loos *et al.*, 2010; RIVM, 2007a; b; c). This is a factor 1000 lower than the therapeutic dose (RIVM, 2012). Usually, in surface water the concentrations of OMPs are measured in the order of 0.1-1 µg/L, but also higher concentrations occur (RIVM, 2003). Although appearing in low concentrations, the presence of more than 100.000 registered chemical substances in the European Union, of which 30.000-70.000 are in daily use, is a major reason for concern (RIVM, 2007a). The long-term effects are in most cases unknown, as well as the behaviour of the substances in mixtures with other substances (Hoek van der *et al.*, 2013).

Problem definition and research questions

Together with the knowledge of the presence of OMPs in the water cycle and the impact of these compounds on human health and aquatic life the need grows for new strategies to decrease the emission of emerging substances (ES) into the environment. The complexity of the situation, caused by the many different sources, demographic trends, climate change and awareness on environmental challenges, results in the need for an integral approach to the decrease of OMPs in the water cycle and reduce the risks for human health and aquatic life. This leads to the objective of the project, which is to develop an integral strategy to decrease the concentration of target compounds in the water cycle and with that, the risk for human health and aquatic life. This approach will be a consideration between different strategies, including the decision between end-of-pipe or source-based solutions and cost-efficiency, sustainability and applicability. The research question is:

What is the most sustainable, applicable and cost-efficient strategy to reduce concentrations of selected micro pollutants in surface water and drinking water in the Netherlands?

In order to answer this question four sub-questions are drawn:

1. What are the target compounds, what is their impact on aquatic life and human health and what concentrations are accepted?
2. What are the sources of origin of the pollution?
3. Which treatment techniques are available and what is known about the removal of organic micro pollutants by these techniques?
4. Which strategies are possible to reduce the amount of organic compounds in the surface and drinking water?

Scope

To obtain an insight in the origin and impact of OMPs and to find applicable strategies to decrease the amount of emerging substances in surface and drinking water an integral approach is required, where the focus is on the water cycle as a whole: wastewater treatment, drinking water production, water management, ecology and human interaction. To include all effects on a water system it seems appropriate to use a river basin scale. However, to analyse a river basin is beyond the time scope of this project and thus the project focuses on the Netherlands only. It was decided to use two cases studies, which are both partly fed by the river Rhine: 1) the Bethunepolder (Waternet) and 2) water intake at Andijk (PWN). The Bethunepolder (BP) near Utrecht, bordering the Loosdrechtse Plassen, is used as a drinking water extraction area solely driven by groundwater seepage and is managed by Waternet, the water cycle company of the city of Amsterdam and the water board Amstel, Gooi en Vecht (Waternet, 2010). The water intake at Andijk (AN) is managed by PWN, the drinking water company of Noord-Holland. It is a surface water system where water from the IJsselmeer, partly fed by a river originating from the Rhine, is used. The focus of the project is on drinking water extraction areas during normal pollution (no accidental spills or other extreme situations occur).

Organic compounds can be separated in two groups: 1) synthetic organic compounds and 2) natural organic compounds. Synthetic (or anthropogenic) organic compounds are those compounds that have been created by man, while natural organic compounds exist naturally in nature (Happily Healthy, 2011). This project only deals with synthetic organic compounds.

Research method in brief

The project consists of a literature study on current and future European and Dutch legislation and policy, future trends regarding population growth, consumer behaviour and climate change and the presence and behaviour of target compounds in the water cycle. The target compounds are selected based on an analysis of relevant compounds, which results in a limited number of compounds to elaborate on. Different strategies with different approaches within the water cycle are discussed, of which: source approach, mitigation approach and end-of-pipe approach. Source approach strategies are focussing on decreasing the *use* of chemical compounds, where mitigation approach strategies are focussing on decreasing the *emission* of chemical compounds and end-of-pipe approach strategies are focussing on improving the quality of *drinking water*. A Multi Criteria Analysis and sensitivity analysis is used to present a strategy that is well balanced between all aspects of the water cycle and its users and which is sustainable, applicable and cost-efficient and which functions within European and Dutch legislation. The best two strategies are applied on water and mass balances of the two case studies to see the impact of the strategies.

Thesis outline

First the methodology is discussed in chapter 2, whereafter this methodology is applied to two case studies. In order to compose durable measures to reduce the risk for human health and aquatic life it is important to approach the current and future situation regarding legislation and policy, climate change and changes in human behaviour. This is done in chapter 3 by discussing legislation, trends and future scenarios. In chapter 4 the sources and pathways of OMPs entering the water cycle are discussed. Also (precautionary) standards are given for concentrations of compounds in different types of water. Finally a selection of OMPs is made and the selected OMPs are discussed in more detail. Possible strategies to reduce OMPs in the water cycle are discussed in chapter 5. By a Multi Criteria Analysis in chapter 6 different strategies are ranked. Chapters 7 and 8 discuss two case studies in which the methodology composed in the first chapters is applied. A water and mass balance of OMPs is composed, in which the future trends are incorporated. The selected best strategies are applied on these two case studies to see the effects of the strategies. Chapter 7 deals with the case Bethunepolder and in chapter 8 the case Andijk is presented. The discussion of the methodology and results and the recommendations are presented in chapter 9. Finally, conclusions are presented in chapter 10.

2 Methodology

In this chapter the methodology of the research is discussed. It consists of a literature review, elaboration part and the case studies. The relation between these aspects shows that knowledge from literature is combined with analytical techniques to determine the best strategy and to find an answer to the research question. In order to test this strategy, two case studies are used and the influence of this strategy is determined.

Literature review

The first part of the literature review consists of information about current and future European and Dutch legislation and policy. This is done in order to get an insight in the political situation of the member state in context with the European Union. The strategies, which are proposed in this project, must fit within European and Dutch legislation and policy. Another aspect is that limits must be determined for concentrations of compounds in the water cycle. Based on these limits it is determined whether a proposed strategy is a success in combating OMPs. The next part of the literature review consists of a study on future trends regarding the emission of OMPs into the water cycle. This incorporates (future) population growth and consumer behaviour. It is important to take possible future situation into account, because the strategies to reduce OMPs in the water cycle are required on long-term basis. Also the assumed climate change has an influence on this, because it causes the river discharge to change, and with that the concentration of OMPs in surface water and groundwater. Sources and pathways of OMPs in the water cycle are determined to compose strategies that are most possibly effective.

Elaboration

The elaboration consists of selecting OMPs, composing strategies and determining the best strategy based on a Multi Criteria Analysis. In this part the found literature is used to select OMPs and compose strategies. Also the criteria in the MCA are composed based on the found literature. First of all, a selection of OMPs is made based on relevance of the compounds for drinking water and the availability of measurement data. Also some attention is paid to the toxicology of the compounds on humans and aquatic life. Combined with the limits found in literature the lowest target value is determined. Thereafter, strategies are composed, which are inspired by the literature review. Different strategies that are composed are based on a source approach, a mitigation approach or an end-of-pipe approach. Source approach strategies are focussing on decreasing the *use* of chemical compounds, where mitigation approach strategies are focussing on decreasing the *emission* of chemical compounds and end-of-pipe approach strategies are focussing on improving the quality of *drinking water*. These strategies are scored and weighted by an expert panel. The best strategy is determined, which is well balanced between all aspects of the water cycle and its users, which is sustainable, applicable and cost-efficient and which functions within European and Dutch legislation. This gives the answer to the research question.

Case studies

In the case studies the found literature and the elaboration are combined to test the best strategies. Of both case studies a water balance and a mass balance is composed. The combined model represents the transport of the OMPs in the water system and results in certain concentrations of the selected OMPs. The future scenarios from the literature review are incorporated in these models to simulate the assumed future situation. The success of the strategy is determined by the (non) exceedance of the limits by the concentrations of the selected OMPs, which result from water and mass balances of the case studies.

Discussion and conclusions

Finally, a comparison is made between the two case studies (groundwater and surface water system) and the results of the strategies tested on the case studies are discussed. In the conclusion the answer to the research question is presented, as well as other outcomes.

3 Trends influencing OMPs

The implementation of strategies to reduce the amount of OMPs in the water cycle requires long-term projects, which are very costly. In order to respond to current legislation and policy and changes in usage patterns and climate, this chapter is concerned with the most influential legislation and trends that are related to the emission of OMPs. Based on these trends and other studies two future scenarios are chosen and described. These future scenarios will be applied on the water and mass balances of OMPs of the two case studies later in the report. Other legislation, policy and trends that are only indirectly related to water and the emission of OMPs in the water cycle are summarised in appendix 3-1.

3.1 Legislation and policy

European legislation – Drinking Water Directive (DWD)

In 1998 the Drinking Water Directive came into force. This law ensures the quality of water intended for the production of drinking water. The DWD is translated into Dutch legislation, whereby the standards set in the DWD may not be lowered (European Union, 1998). More detailed information can be found below.

Dutch legislation - Drinking Water Directive, Drinking Water Decree and Drinking Water Regulation (Drinkwaterwet, Drinkwaterbesluit en Drinkwaterregeling)

In 2009 the Drinking Water Directive came into force. In this law everything around drinking water is regulated: organisation, quality, supply, monitoring and public health (Aa van der *et al.*, 2011). In the Drinking Water Decree these aspects are explained in more detail. For example the price of drinking water and prevention of legionella (IIASA, 2002). In this Decree limits for specific compounds are set. More detailed information on these limits can be found in section 4.2. Based on the Drinking Water Decree the Drinking Water Regulation is composed, which is more specified and deals with the supply of drinking water and hot tap water (Dutch Government, 2011b).

European legislation – Water Framework Directive (WFD)

The Water Framework Directive is an European guideline to improve the ecological and chemical water quality in designated water bodies by monitoring and regulating the concentrations of various OMPs in the surface water and groundwater (Balbus *et al.*, 2013; Vewin, 2013b). In the context of this directive a list of Priority Substances (PS) is composed. The substances on this list have to be monitored and if the standards are exceeded, measures have to be taken to lower the concentration and meet the standards. In April 2013 the European Parliament, the European Commission and the Member States have reached an agreement on new substances on this list, in which three proposed pharmaceuticals are not included (KWR, 2012; Waterforum, 2013a). The compounds on the PS-list are considered to be harmful to the aquatic environment in particular, and most substances do not form a risk for drinking water.

European policy - Precautionary limits

The International Association for Water Works in the Rhine Basin (IAWR) is an organisation which aims at protecting the water quality in order to produce safe drinking water in this basin. In cooperation with RIWA Rijn[a], RIWA Maas[b] and IAWD[c] the IAWR composed the Danube, Meuse and Rhine Memorandum 2008 (DMR). This document contains precautionary limits for water quality (IAWR, 2008). The limits are further explained in section 4.2.

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[a] *RIWA Rijn is the Dutch River Waterworks Association - Rhine*

[b] *RIWA Maas is the River Waterworks Association - Meuse*

[c] *IAWD is the International Association of Waterworks in the Danube Catchment Area*

3.2 Game changers

3.2.1 Climate change

Changing river discharge influences the concentrations of OMPs in the water. Global climate change (GCC) induces the world becoming warmer in general. This can be seen in short-term weather extremes and long-term shifts in weather characteristics. The temperature increase is greatest over land and at high northern latitudes and least over the Southern Ocean and northern North Atlantic. GCC causes sea and mountain ice to melt, precipitation to increase in many regions at higher altitudes, and decrease in most subtropical land regions. Higher altitudes will be subject to flooding rains more frequently, while in many currently semiarid areas the expectation is that more prolonged periods of droughts will occur (Grave *et al.*, 2010). A shift in wind, precipitation and temperature patterns probably results in more extreme weather: longer droughts and heavier rainfall.

Global climate change is an important issue for the production of drinking water in the Netherlands. A relatively high amount of drinking water is produced from surface water (40%), which will be influenced by climate change (Sanchez *et al.*, 2011). Groundwater will only be influenced on a long-term scale, because of the high residence time of compounds in the groundwater. When the discharge of rivers decreases in periods of drought the intake of water may be at risk. The amount of water cannot be guaranteed and the water can be of lower quality, because the discharges of WWTPs and industry will remain the same, while the relatively clean (with regards to OMPs) rain water will be less. This is especially the case in rivers with lower average discharge, such as the rivers Meuse and Drentse Aa (Larsson *et al.*, 2002). In cases of heavy rainfall more sewer overflows will occur, which cause more pathogens entering the surface water system (Olivares *et al.*, 2010; RIVM, 2007a). Not only negative consequences of GCC are experienced: during droughts when the river discharge is low, the residence time of substances in the water increases and the oxygen levels decrease.

3.2.2 Social trends

OMPs are introduced to the environment by human activities. Demographic trends and changes in human behaviour influence the consumption of pharmaceuticals and the emission of other OMPs into the environment. A demographic aspect of great concern is the aging of the world population and in the Netherlands. This will result in an increasing use of pharmaceuticals. Also the population is expected to become older on average (figure 3-1). The reason for this is the birth of the so-called ‘baby-boomers’ just after the Second World War. After the period where the baby-boomers were born, the birth rate decreased. By 2025 the baby-boomers will reach an age of 60+ (Kelly *et al.*, 2009; Larsson *et al.*, 2002).

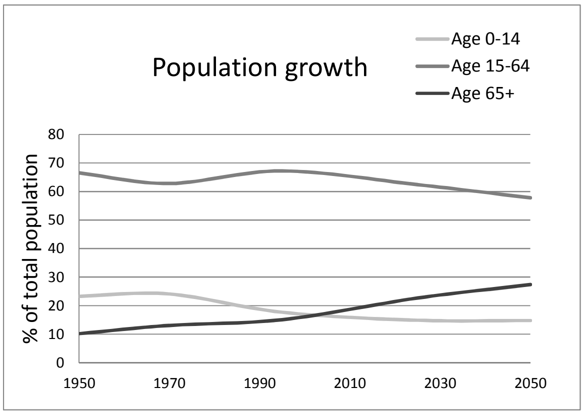

Figure 3-1 Population composition in western Europe as percentage of total population (IIASA, 2002)

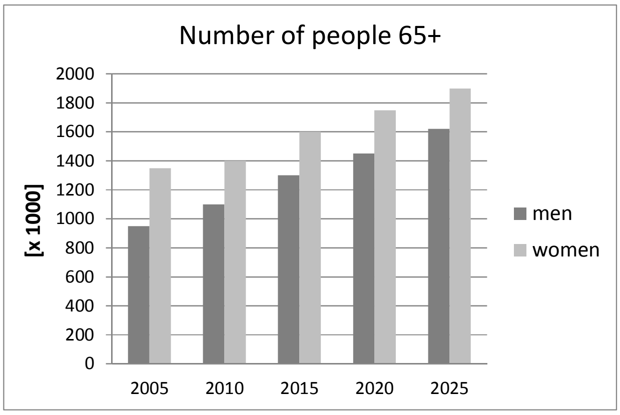

Figure 3-2 Number of people in the age of 65+ in the Netherlands (STOWA, 2010c)

In general elderly people consume more pharmaceuticals and more emerging pollutants of this nature will enter the water system. Most of the people of the age of 65+ are women (figure 3-2), who are generally using more pharmaceuticals than men. Currently, the population in the Netherlands is growing with about 65 people per day. From 2038 the population will decrease instead of growing (STOWA, 2010c). The expected population growth till 2060 in the whole Rhine river basin is -8%, mostly caused by the negative population growth in Germany (Kelly *et al.*, 2009). Another cause of the increase in use of pharmaceuticals is the decreasing age from which chronic diseases occur. There is also a trend in prescriptions from physicians. Since 1991 the average days for which one prescription holds, increased by 26% to 48 days in 2007 (STOWA, 2010c). The prognosis is that the consumption of pharmaceuticals will increase from 500 tons in 2007 to 600 tons in 2020 (20% growth) and with 37% till 2050 (RIVM, 2008b). Estrogens (contraceptives) are the only substances that are decreasing in usage, since the population under 50 is declining the coming decades (Brooks *et al.*, 2009; RIVM, 2008b; 2011).

3.3 Future scenarios on emission of OMPs

Besides the discussed trends there are various studies on future scenarios. Two important scenarios are the WLO-scenarios (Centraal Planbureau) and the climate scenarios from the Royal Dutch Meteorological Institute (KNMI) (Brooks *et al.*, 2009; RIVM, 2011). The WLO-scenarios are concerned with demographic, national and international economic and ecological changes. Estimations for temperature rise and the increase in precipitation in summer and winter are given in the KNMI-scenarios (appendix 3-2). Aspects of these two scenario studies are combined in the Deltascenarios of the Deltaprogram. The Deltaprogram has been started to function as a tool in important decision making regarding water management. Globally, the Deltaprogram is concerned with two aspects: flood prevention and insuring freshwater facilities, such as dike reinforcement and river widening. The aim is to approach a period till 2100, but future expectations are uncertain over a longer period. It has been decided to divide the period in two parts, with the first period from now till 2050 with more certain expectations, and the second more uncertain period from 2050 till 2100 (Deltaprogramma, 2011).

Within the scope of this project it has been decided to select two out of four Deltascenarios. These are the scenarios REST and STEAM, where REST represents a stand-still situation with socio economic contraction and moderate climate change and STEAM represents a 'worst case' with high socio economic growth and rapid climate change (figure 3-3). These scenarios reflect climate change, population growth, emission of OMPs, consumption of tap water, and economical and ecological issues within a horizon till 2050 and will be used to apply the water balance and mass balance of OMPs on for the cases Bethunepolder and Andijk. The results will be used to translate the strategies to other systems.

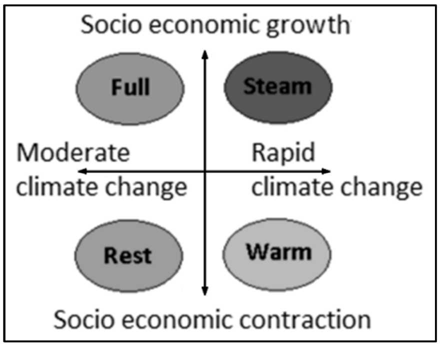

Figure 3-3 Deltascenarios (Bruggeman *et al.*, 2011)

REST

In this scenario only limited international trading takes place. International agreements concerning environmental issues remain unchanged. Due to the stagnation in trading and economy moderate or no immigration takes place, which means only moderate increase in water consumption and emission of OMPs due to small population growth. Limited economic growth results in small scale production and regional independency in the Netherlands, which is called 'regional communities' in the socio economic scenarios of the WLO. The northern, eastern and southern part of the Netherlands develops into high-tech and knowledge areas, which results in a decrease in urbanisation. Agriculture decreases and the focus is on regional production and independency. Only greenhouse farming intensifies, but from a very water efficient perspective. Nature areas increase, just as the Ecological Main Structure[d] (EMS). Due to regional independency cargo traffic by road and water decreases, from which less discharge of OMPs from these sources into the water cycle is a result. The climate changes only moderately, so river discharges and sea level remain equal. This corresponds to climate scenario G (Bruggeman *et al.*, 2011).

The influence of the described trends and the scenario REST on the water balance and mass balance of OMPs is described below (also appendix 3-3). These are estimations based on literature. At Lobith an increase by 5% in concentrations of all substances is caused by limited international trading and no changes in international agreements concerning environmental issues. At all locations there is a decrease in concentrations of pharmaceuticals by 37%, due to moderate or no immigration and a decrease in agricultural practise (veterinary pharmaceuticals decrease additionally by about 7%). The concentrations of pesticides decrease by 2.5% related to a decrease in agricultural practise. Humane tracer compounds increase in concentration by 5% at all locations due to the trend of artificial sweetener and caffeine consumption. Industrial compounds used in cargo traffic by road and water decrease in concentration by 4.4% and 10% respectively, which is caused by a decrease in cargo traffic. The river discharge of the Rhine at Lobith increases to 3100 m^3/s during winter and to 2000 m^3/s during summer. The precipitation increases by 4% and by 3% in winter and summer respectively. This is caused by the assumed climate change.

STEAM

Within the limits of acceptability, this scenario represents the most extreme scenario, with regard to climate change and socio economic growth. The national and international market grows, but there are no international agreements concerning environmental issues. Growth of the international economy and the stable position of the Dutch harbours leads to economic immigrants, which results in increasing water consumption and emission of OMPs. Production is based on international trading. In the WLO-scenarios this is called ‘global economy’. Immigration leads to increasing urbanisation and at the same time the increasing prosperity enables more people to move to nature areas or close to water bodies, which creates a greater risk for pollution by OMPs. Agriculture decreases due to increasing urbanisation. Greenhouse farming increases and becomes more efficient. Nature area increases, but there is also an increase in recreation and living in these areas. Some vulnerable nature areas are subject to good management. The stable position of the Dutch harbours leads to an increase in cargo traffic by water, which negatively influences the water quality. There is an extreme climate change with wet winters and dry summers; climate scenario W+. The maximum river discharges increases, with the risk of flooding. The dry summers enable intrusion of saline water into the groundwater and surface water, which results in salination. A rising sea level disables discharging of surplus water into the sea at times of high tide (Bruggeman *et al.*, 2011).

The influence of the described trends and the scenario STEAM on the water balance and mass balance of OMPs is described below (also see appendix 3-3). These are estimations based on literature. At Lobith the assumed increase in concentration of all compounds by 5% is caused by a growing international economy, in which no international agreements concerning environmental issues are made, and another increase by 5% due to the fact that more people live closely to water bodies. The concentrations of pharmaceuticals increase by an additional 5% at Lobith. At all locations the concentration of pharmaceuticals increases by 37% and additionally the concentration of veterinary pharmaceuticals decrease by 12%. Human tracer compounds increase in concentration by 5% at all locations. Pesticide concentrations decrease by 4% at all locations because of the decrease in agricultural area. Concentrations of industrial compounds used in cargo traffic by water increase by 50%, road cargo remains unchanged. The discharge of the river Rhine at Lobith increases in winter to 3400 m^3/s and decreases in summer to 1300 m^3/s. Precipitation increases in winter by 14% and decreases in summer by 19% due to the assumed climate change.

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[d] *The Ecological Main Structure (Ecologische Hoofdstructuur, EHS) is a network of connected nature areas, which aims at increasing the biodiversity.*

4 Emerging compounds

This chapter is concerned with the selection of target OMPs for further research. First the sources of origin are described followed by the standards and precautionary limits of concentrations of OMPs in surface water. The selection procedure for target compounds is described and thereafter the selected OMPs are discussed in detail.

4.1 Sources of organic micro pollutants

The sources of emission of OMPs into the water cycle can be classified by type of source and by origin of the source. The type of source is classified as:

- Accidental point spills. These are a result of a calamity or unforeseen event. Characteristic for this group of spills is that it is a single discharge that in most cases could not be prevented. The influence of the spill on the water quality can be enormous on local scale, but because of mixing the concentration will dilute (Schwarzenbach *et al.*, 2006).
- Structural point spills. These are continuous discharges, which are sometime licensed. The effect on the water quality of the receiving water body is more or less constant.
- Line sources. These are similar to point sources, but occur in a line.
- Diffuse sources. These are sources that spread over a wide area. Characteristic for this group of sources is the difficulty to trace the original sources of the spills and the seasonal variation in occurrence in the water (Schwarzenbach *et al.*, 2006).

The sources of origin can be divided in domestic, agricultural and industrial origin. Combining all sources results in figure 4-1. It shows all possible pathways by which emerging contaminants are introduced in the surface water and groundwater. The next subparagraphs explain the different sources of origin.

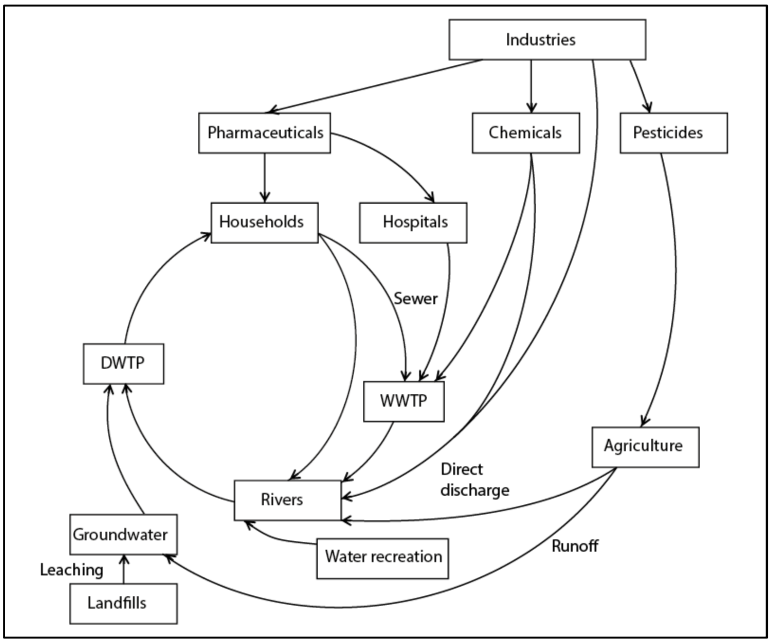

Figure 4-1 Sources of OMPs in the environment (RIWA, 2007)

4.1.1 Domestic origin of OMPs

OMPs of domestic origin are pharmaceuticals, PCPs and other chemicals used by humans. It concerns the emission of OMPs originating from residential areas, hospitals and health care centres. The emission of OMPs of this origin into the water cycle is mainly by sewerage and WWTPs, but a small part of the houses is not connected to the sewer system and discharges its wastewater directly on the surface water. The emission of pharmaceuticals per person measured in wastewater in residential areas is about 10% of the emission measured in hospital wastewater (figure 4-2). From this figure it can be seen that the emission of pharmaceuticals per person in health care centres is much lower than in hospitals. A cause of this is that the proportion of people who have incontinence is much higher in health care centres (elderly people) than in hospitals, whereby the faeces and urine is not discharged onto the sewage system (Kumar *et al.*, 2010). However, the contribution of hospitals and health care centres to the total emission of pharmaceuticals is relatively small compared to the emission of residential areas: respectively 20% and 80% (RIVM, 2012). The reason for this is that much more people live in residential areas than in hospitals and health care centres.

Not only pharmaceuticals and PCPs enter the water cycle by human activity, but also different types of biocides. In recreational water sports antifouling is used to prevent algae to grow on boats. This antifouling is in contact with the surface water (Waternet, 2010). Municipal landfills are typical sources of domestic origin, where the OMPs are not entering the water cycle by the pathway of the WWTP. Several studies report municipal landfills contributing for a substantial part (5%) of the total non-volatile organic carbon found in landfill leachates (Daughton *et al.*, 1999; Richardson, 2012).

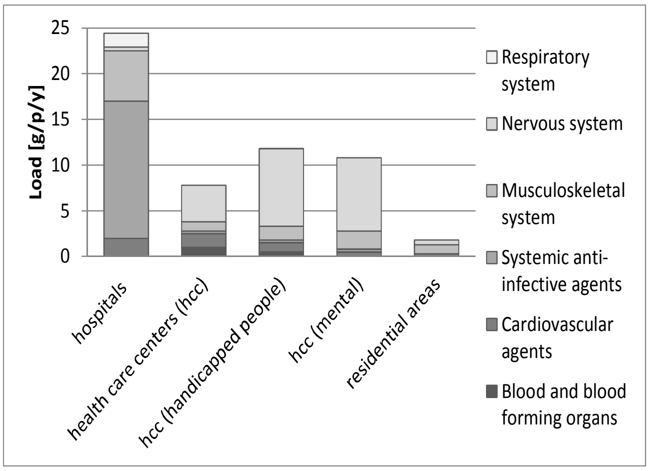

Figure 4-2 Indication of load per person per year (Kumar *et al.*, 2010)

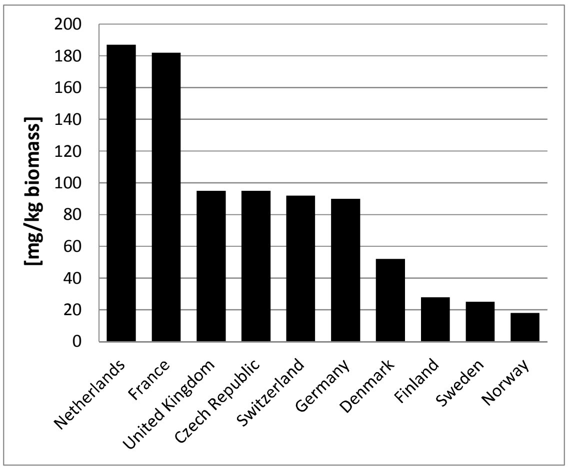

Figure 4-3 Amounts (mg) of veterinary antibacterial agents sold in 2007 per kg biomass (Dutch Government, 2011a)

4.1.2 Agricultural origin of OMPs

In agriculture different types of pesticides are used to protect crops. By runoff and leaching pesticide residues can enter the water cycle. Pesticides are not only applied in agriculture, but a substantial part of all used pesticides are applied on paved areas to remove weed by municipalities and water boards (Grontmij, 2010). Some paved areas are connected to the sewer system; from others rainwater transporting pesticides and other OMPs present on the paved areas can runoff to the surface water. This is not directly connected to agriculture, but the process is similar and is thus categorised as agricultural origin. In cattle breeding veterinary pharmaceuticals, mostly antibiotics, are preventively used. The Netherlands is biggest consumer of veterinary antibiotics (figure 4-3) (Dutch Government, 2011a). Those substances finally end up in the environment by leaching of pasture or manuring arable land.

4.1.3 Industrial origin of OMPs

The last group consists of OMPs with an industrial origin. Direct point spills from industries contribute to the presence of OMPs in the surface waters. Industries and municipalities are responsible for about 10% of the total accessible runoff and generate a stream of wastewater, which flows or seeps into the water cycle (Hoek van der *et al.*, 2013; ICBR, 2012). Some of the effects detected in fish are caused by discharges in the surface water by the pharmaceutical industry (Dutch Government, 2011b), paper industry (Dutch Government, 2009a), chemical industry and mining activities (Loos *et al.*, 2009; Waterforum, 2013a). The industry is connected to the domestic and agricultural origin of OMPs by producing products for daily use by humans and in agriculture.

Figure 4-4 shows the composition of the Rhine water at Lobith, where it crosses the border between Germany and the Netherlands. It should be noted that not all of the substances in this figure are of industrial origin, but the figure gives an idea of the impact of this category on the total composition of the Rhine water. It shows that the majority of the total concentration of OMPs in the Rhine at Lobith originates from industrial sources (compared to the previously discussed domestic and agricultural sources, which include pharmaceuticals, beverages, flavours, fragrances, detergents and pesticides).

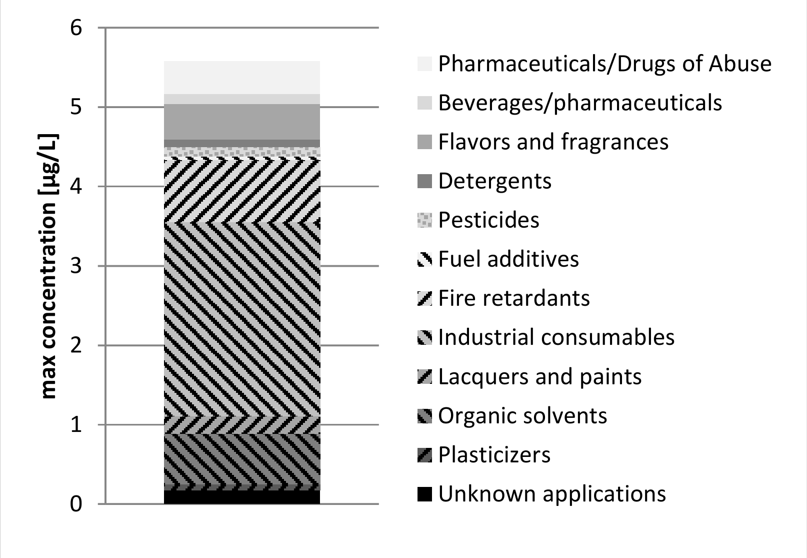

Figure 4-4 Composition of incoming Rhine water at Lobith in 2010 (IAWR, 2008)

4.2 Standards and guidelines

Not for all compounds limits are determined by law. For that reason precautionary limits and the Benchmark Quotient (BQ) are used. In this project the lowest limit of either official standards, the precautionary limits or the Benchmark Quotient is used to test the strategies on in the two case studies. In this section all three mentioned limits are discussed.

Standards regulated by law

The environmental quality standards (EQS) for organic compounds in surface waters intended for the production of drinking water, finished drinking water and groundwater exist only for pesticides: 0.1 µg/L for every single compound and the total concentration of pesticides must not exceed 0.5 µg/L (IIASA, 2002) (Balbus *et al.*, 2013). Additionally, for finished drinking water the precautionary standard is 1.0 µg/L for MTBE and other anthropogenic compounds that may be a risk for consumers of drinking water (IIASA, 2002).

Target values not regulated by law

For compounds that are not mentioned in the standards of the Dutch government for maximum concentrations in surface waters, another list with precautionary target values is used. This list is the Danube, Meuse and Rhine Memorandum 2008, composed by RIWA Rijn, RIWA Maas, IAWD and IAWR (section 3.1) (IAWR, 2008). In the Memorandum the target value for pesticides and their metabolites and pharmaceuticals is 0.1 µg/L. For compounds with a low biodegradability the target value is 1.0 µg/L (IAWR, 2008).

Benchmark Quotient for drinking water

A method to present the toxicity of a compound in context of the measured concentration is by using the Benchmark Quotient (BQ) (European Environment Agency, 2011). In this method a toxicological BQ is calculated and based on this it can be determined whether the compound is present in water sources in concentrations that should give rise to concern. The BQ is calculated by:

BQ = C_{max} water/pGLV

🟩 BQ < 0.01 🟨 BQ = 1-0.01 🟥 BQ > 1

Where;
C_{max} = maximum measured concentration of compound in source.
pGLV (provisional drinking water guideline value) = (TDI*70 kg (adult weight)*0,1)/(2L/day)
TDI (Tolerable Daily Intake)= µg/kg/day

If BQ is > 1 the compound potentially poses a risk for human health to the drinking water produced from this water. At a BQ value between 1 and 0.01 the concentration of the compound in the water source is equal or close to the pGLV. A potential increase in the concentration in the future could pose a risk for humans. In this range a future increase of the concentration by a factor 10 is taken into account. No or negligible risk is only assumed at a BQ of < 0.01 where an increase in concentration by a factor 100 is required before the compound poses a potential risk to public health. Not for all selected compounds a BQ value can be calculated due to missing ADI or NOAEL values.

Target values for aquatic life
The effect of anthropogenic micro pollutants on aquatic life is determined by the predicted no effect concentration (PNEC) (Huerta-Fontela *et al.*, 2008). This value represents a concentration which does not lead to negative effects in certain organisms it is tested on such as daphnia, algae, fish, bacteria, invertebrates and lemna (Bandyopadhyay *et al.*, 2008; Lange *et al.*, 2012; Manãs *et al.*, 2009; Satyavani *et al.*, 2011; Schulz *et al.*, 1999). When the concentration of the selected compounds in the water does not exceed the PNEC, it is assumed that no negative effects occur on the species it is related to. Not for all selected compounds a PNEC is found.

4.3 Selection procedure

Several articles and reports can be found in which detection of OMPs in the environment and the influence on human health and aquatic life are discussed (Carlsson *et al.*, 2006; Loos *et al.*, 2009; RIVM, 2012; RIZA, 2003; Stander, 1980). The presence of OMPs in the water cycle and their impact depends strongly on the type of OMP. Therefore, a selection of 11 compounds is made based on various criteria:

- Criterion 1: physical relevance for drinking water quality. This criterion is based on persistence and mobility of the compound in (ground) water (polar). Compounds that are not persistent and/or mobile in water will be degraded partly or completely before reaching the drinking water treatment facility.
- Criterion 2: potential effect on human health and aquatic life. This is determined by the presence on the list of Priority Substances (Water Framework Directive, WDF) or on a watch list of Waternet, Riwa-Rijn, STOWA, GWCR or the list of Rhine substances of ICBR.
- Criterion 3: availability of measurement data. It is only possible to elaborate on compounds of which measurement data are available at different locations within the target areas of the case studies. The limited budget and time for additional analyses is the reason for this.

From all compounds that meet the criteria the final selection is made consisting of compounds that are present on more than one watch list, that are measured by more than one institution or that are measured at more than one location. Special attention is paid to substances that are often found in literature or need special attention because of their assumed pathway of distribution in the environment, presence in high concentrations, impact on human health or aquatic life or potential risk in the future.
In cooperation with the Waternet research ‘KRW-spagaat[e]’ the following substances are selected based on the selection method and selection criteria described above (KWR, 2012; Waternet, 2010):

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[e] *KRW-spagaat is a research of Waternet on OMPs in surface water, where the different functions of the company (wastewater, drinking water and water management) are combined.*

- Pharmaceuticals: carbamazepine (CARB), metformin (METF), sulfamethoxazole (SULF) (also veterinary)
- X-ray agents: iopromide (IOPR)
- Domestic tracers: acesulfame-K (ACEK), caffeine (CAFF)
- Industrial chemicals: methyl *tert*-butyl ether (MTBE)
- Pesticides: bentazone (BENT), glyphosate (GLYF) and its metabolite aminomethylphosphonic acid (AMPA), *N*,*N*-dimethylsulfamide (NDMS)

No substances from the Priority Substances list of the WFD are selected. The reason for this is that those substances are especially toxic for aquatic life and in most cases not relevant for drinking water. The WFD has as goal to increase the condition of surface water and groundwater with regard to aquatic life, where the subject of this project is on the reduction of concentrations of compounds in water bodies intended for the production of drinking water (European Union, 2000).

Table 4-1 provides an overview of all concentrations found in literature, the removal efficiencies in WWTPs, log k_{ow} values and the toxicological parameters for each selected compound. The selected compounds will be discussed in more detail in the following paragraphs.

4.4 Selected compounds

For acesulfame-K, AMPA, bentazone, carbamazepine, glyphosate, iopromide, metformin, MTBE and N,N-DMS the trend of the concentration measured at Lobith is given (figure 4-5). Concentrations of most OMPs vary over time. A decrease in concentration can be seen during winter for acesulfame-K, AMPA and carbamazepine. Bentazone, glyphosate, iopromide, metformin, MTBE and N,N-DMS do not show a clear trend over the seasons. None of the selected OMPs show a clear increase or decrease over the past seven years (not all represented in the figure). Compounds that are not represented in the figure have either too low measurement values to show in the graph or no data are available in this period at this location. All selected OMPs are explained in this paragraph and the removal efficiency in a conventional WWTP is given. Also removal efficiencies of a DWTP are given, but these are not found for all substances. More detailed information on the substances can be found in appendix 4-1.

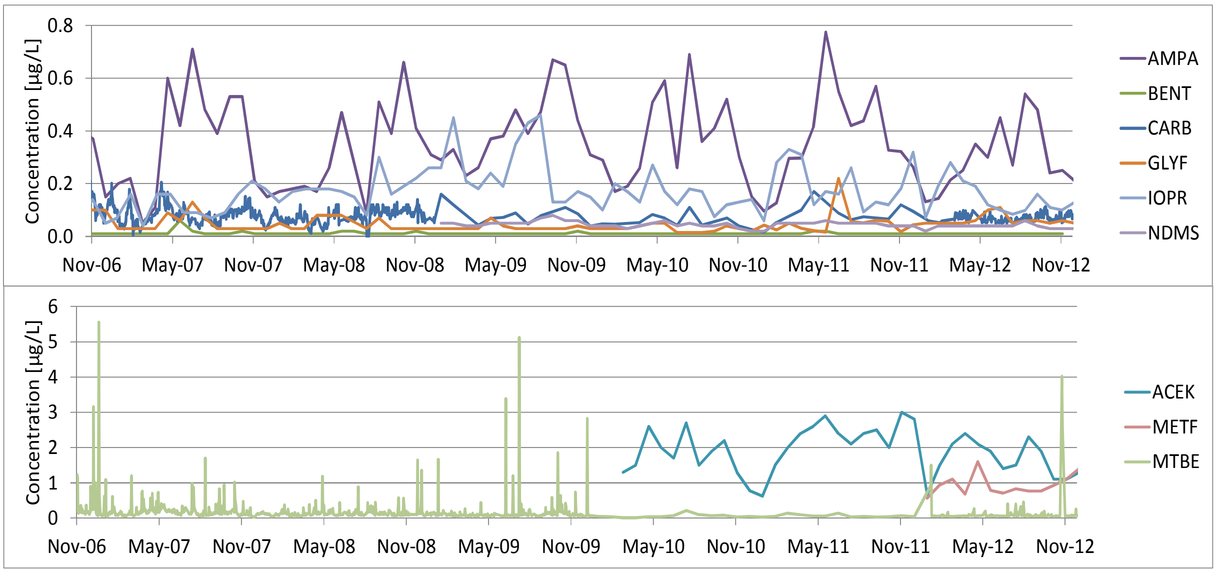


Figure 4-5 Concentrations in time measured at Lobith

Table 4-1 Properties of selected compounds

	Technical info	Measurements					Toxicity			Removal				Other	
	Molecular mass	Ground water	Surface water	Influent (WWTP)	Effluent (WWTP)	Drinking water	PNEC	ADI	NOAEL	Excretion rate un-changed	Removal efficiency (ww)	Removal efficiency (dw)	Log K_{ow}	Practice	Metabolite
	[g/mol]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[mg/kg bw/day]	[mg/kg bw/day]	[%]	[%]	[%]	[-]		
Acesulfame-K	201.24	6.9 [1,2,3,4,5]	0.7-6.9 [2,3]	15-43 [3,4]	15-46 [3,4]	0.02-0.07 [3]	*	5-50 [3]	*	100 [3]	40 [3]	*	-1.33	sweetener	*
AMPA	186.17	0.01-8 [6]	0.14-83 [7,8,9,10,11]	1.5-15 [9]	1.9-28 [7,9]	1.1 [10]	*	0.3 [10]	*	*	14-63 [9,12]	*	0.76	metabo-lite of glyphosate	*
Bentazone	240.28	0.116-11 [6,13]	0.014 [10,14,15]	*	*	0.28 [10]	*	0.1 [10]	10 [16,17]	91 [18]	*	*	2.5 to 3.8	herbicide	*
Caffeine	194.19	0.013-0.23 [13,19,20,21]	0.01-0.2 [15,19,20,22]	2-300 [19,20]	0.06-2 [19,20]	0.125 [22]	182 (A) [23]	3 [24,26]	*	3 [21]	60-80 [19,20]	60-80 [22,25]	-0.07	domestic tracer	paraxanthine, theobromine, theophylline
Carbamazepine	236.27	0.012-0.39 [13,20,26]	0.025-11.6 [15,20,26-29]	0.33-1.4 [9,20,28,30,31]	0.157-6.3 [9,20,27,28,32]	0.025 [26]	0.42 (A) [33,34]	0.016 [35]	*	1-2 [32,36]	7-30 [9,28,30,37-42]	30-96 [26]	2.45	anti-eleptic	carbamazepine-10,11-epoxide
Glyphosate	169.08	0.01-0.5 [6,43]	1.2-77 [7,9-11]	0.19-5.3 [9]	0.12-23 [9]	0.46 [10]	*	0.3 [10]	175 [16]	97.5 (C) [44]	40 [9,41,45]	*	-4.6 to -1.6	herbicide	AMPA
Iopromide	791.12	0.01-0.21 [36]	0.017-0.91 [10,36,46]	0.18-7.5 [46]	0.14-11 [36]	0.01-0.086 [10,36]	256 (A) [47]	0.021 [48]	*	97 [40,49]	0-73 [36]	*	-2.05	x-ray agent	*
Metformin	129.16	9.9 [50,51]	0.06-3.1 [36,50,51]	0.1-105 [50]	1.3-6 [50]	*	511 (B) [52]	0.0794 [53]	*	50-60 [54]	80-98 [2,42,50]	80-98 [50]	-2.64	anti-diabetic	guanylurea
MTBE	88.15	0.1-27 [10,55-57]	0.1-28 [56-58]	0.03-120 [56]	0.02-120 [56]	0.06-0.11 [10,55,56,58]	2600 (A) [59]	0.3 [10]	*	50-80 (C) [60]	*	*	0.94	gasoline additive	tert-butyl alcohol
N,N-DMS	124.16	0.1-6 [13,61-64]	0.05-0.14 [61-64]	*	*	0.18 [61-63]	140 (D) [69]	*	*	*	*	*	-0.2	antifouling	NDMA
Sulfamethoxazole	253.28	0.002-0.47 [13,36]	0.05-4.1 [10,15,26,27,36]	0.68 [30,65]	0.02-1.1 [27,31,36,65]	0.012-0.025 [10,26,36,66]	0.118(B) [67]	0.13 [10]	*	15-30 [32,36]	8-85 [30,40-42,65,68]	44-85 [26,36]	0.89	antibiotica human/ veterinary	nitroso sulfamethoxazole

** Data not found, A: invertebrates, B: algae, C: rats, D: species unknown*

[1] *(Buerge et al., 2009)*
[2] *(Scheurer et al., 2009)*
[3] *(Lange et al., 2012)*
[4] *(Scheurer et al., 2011)*
[5] *(Stempvoort van et al., 2011)*
[6] *(Fronhoffs et al., 2007)*
[7] *(Botta et al., 2009)*
[8] *(Landry et al., 2005)*
[9] *(Grontmij, 2010)*
[10] *(Schriks et al., 2010)*
[11] *(Battaglin et al., 2005)*
[12] *(Grontmij, 2009)*
[13] *(Loos et al., 2010)*
[14] *(Köck-Schulmeyer et al.)*
[15] *(Loos et al., 2009)*
[16] *(Younos et al., 2005)*
[17] *(Spencer, 1998)*
[18] *(Network, 1992)*
[19] *(Buerge et al., 2003)*
[20] *(Rabiet et al., 2006)*
[21] *(Seiler et al., 1999)*
[22] *(Huerta-Fontela et al., 2008)*
[23] *(Comber et al., 2003)*
[24] *(Happily Healthy, 2011)*
[25] *(EINECS, 2002)*
[26] *(RIVM, 2003)*
[27] *(Hernando et al., 2006)*
[28] *(Kim et al., 2007)*
[29] *(RIWA, 2012)*
[30] *(Buttiglieri et al., 2008)*
[31] *(STOWA, 2008)*
[32] *(Huschek et al., 2004)*
[33] *(Bandyopadhyay et al., 2008)*
[34] *(Ferrari et al., 2003)*
[35] *(RIZA, 2003)*
[36] *(Monteiro et al., 2010)*
[37] *(Daughton et al., 1999)*
[38] *(Joss et al., 2005)*
[39] *(Murray et al., 2010)*
[40] *(STOWA, 2009a)*
[41] *(Ruel et al., 2012)*
[42] *(STOWA, 2011b)*
[43] *(Sanchís et al., 2012)*
[44] *(Miller et al., 2010)*
[45] *(Grontmij, 2009)*
[46] *(Fent et al., 2006)*
[47] *(Orias et al., 2013)*
[48] *(NYC Environmental Protection, 2011)*
[49] *(ICBR, 2011)*
[50] *(Scheurer et al., 2012)*
[51] *(Vulliet et al., 2011)*
[52] *(Carlsson et al., 2006)*
[53] *(Cunningham et al., 2010)*
[54] *(RIVM, 2008b)*
[55] *(Achten et al., 2002)*
[56] *(Rosell et al., 2006)*
[57] *(Wezel van et al., 2009)*
[58] *(Baus et al., 2005)*
[59] *(Comber et al., 2003)*
[60] *(Benson et al., 2003)*
[61] *(Kowal et al., 2009)*
[62] *(KWR, 2009)*
[63] *(Schmidt et al., 2008)*
[64] *(Sharma, 2012)*
[65] *(Camacho-Muñoz et al., 2012)*
[66] *(Richardson et al., 2011)*
[67] *(Manãs et al., 2009)*
[68] *(Göbel et al., 2007)*
[69] *(NIVA, 2012)*

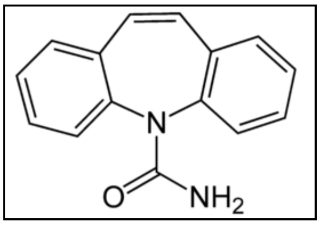
4.4.1 Pharmaceuticals

Dutch surface waters contain different types of pharmaceuticals and X-ray agents (Houtman, 2010; IAWR, 2008; Johnsona *et al.*, 2008; RIVM, 2012). Pharmaceuticals enter the environment due to the insufficient treatment of a wastewater treatment plants (WWTP), since the WWTPs are not designed for the removal of OMPs.

A large quantity of pharmaceuticals (inflammatory drugs and antibiotics) does not enter the wastewater treatment plant, because they are used as veterinary pharmaceutical to treat cattle feedlot and directly contaminate the environment (RIVM, 2007b; WHO, 2011b). Veterinary pharmaceuticals applied in livestock are in most cases preventively dosed and in some cases to cure diseases. An interview with pastoralists from the sectors poultry farming, (calve) dairy farming and pig farming showed that none of the farmers selected their pharmaceuticals based on the criterion of effects on the environment (Snijdelaar *et al.*, 2006).

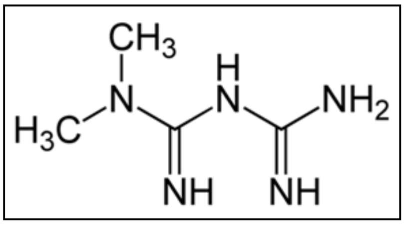
Although, no causal relation between human health effects and drinking water that contains trace concentrations of pharmaceuticals have been discovered yet, and most of the Lowest Observed Effect Concentrations (LOECs) are substantially higher than the environmental concentrations that have been observed, concerns about exposure to pharmaceuticals in drinking water are expressed by the scientific community, regulators and consumers (EINECS, 2002; Richardson *et al.*, 2011). For this reason, pharmaceuticals are investigated in this project.

Carbamazepine



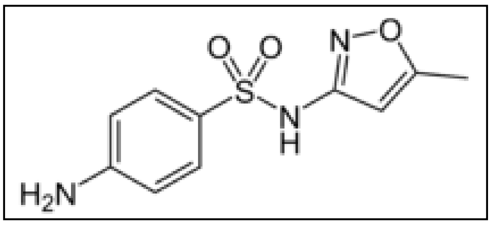
Carbamazepine is an anti-epileptic drug, which is designed to reduce rapid and excessive firing of neurons of the brain. It is also prescribed to patients with manic depressions. Only 1-2% of the ingested carbamazepine is excreted unchanged by human urine (Huschek *et al.*, 2004; RIVM, 2003). In several studies carbamazepine is the most frequently occurring pharmaceutical in groundwater and surface water (Carlsson *et al.*, 2006; Rabiet *et al.*, 2006; Sacher *et al.*, 2001). Carbamazepine is very toxic for bacteria, algae, and most of the tested invertebrates species (Bandyopadhyay *et al.*, 2008; Lange *et al.*, 2012).

Metformin



Metformin is an anti-diabetic drug and is one of the most frequently prescribed drugs of all pharmaceuticals worldwide (Santos *et al.*, 2007). In the human body metformin is excreted unchanged for 50-60% in urine (RIVM, 2008b). In WWTPs it is biologically degraded into its metabolite guanylurea. Due to its high influent concentrations and incomplete degradation, considerable amounts of metformin and guanylurea end up in the environment (Carson, 1962). Lack of data of metformin in drinking water in literature could suggest that metformin is not present in drinking water above the detection limit (Carson, 1962).

Sulfamethoxazole

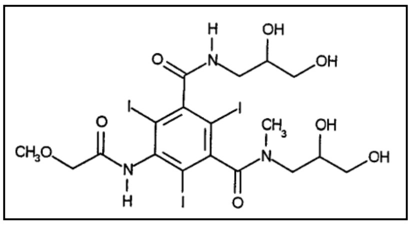


Sulfamethoxazole is an antibiotic drug, which can be used both as a human and a veterinary pharmaceutical (Carlsson *et al.*, 2006). The highest concentrations of sulfamethoxazole from human use in wastewater discharge originate from hospitals, because a high amount of antibiotics is used there (Thomaidis *et al.*, 2012; WHO, 2011b). In veterinary use sulfamethoxazole is applied in calve dairy farming, pig farming and broiler farming (RIVM, 2007b). This pharmaceutical is used in veterinary practice from an economic perspective: control of economic damage by preventing infectious diseases (Snijdelaar *et al.*, 2006).

4.4.2 X-ray agents

X-ray agents are used for medical diagnosis. The agent absorbs more X-radiation than normal soft tissue, which is not treated with X-ray agent. This process reveals the treated tissue. Iodinated substances (like iopromide) are mostly excreted in the hospital, while substances containing metals (like barium sulphate and gadolinium) are mostly excreted at home (Thomaidis *et al.*, 2012). X-ray agents leave the human body unchanged (Dutch Government, 2009b; Grontmij, 2010; Huschek *et al.*, 2004). Depending on the type of X-ray agent, hospitals or households are the main source of X-ray agents in WWTPs (Thomaidis *et al.*, 2012). Iodinated substances are most used as contrast agents and are found in raw water of drinking water companies and often also in drinking water. These substances are extremely persistent and thus not removed at bank infiltration. Biodegradation processes decrease the concentration, but other iodinated substances are formed. In literature no health effects on humans are discovered with respect to genotoxicity, potential neurotoxicity or damage to gametes (Haan de, 2013).

Iopromide

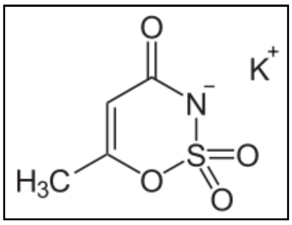


Iopromide is an iodinated contrast agent, which is used in CT-scans. It increases contrast in veins, urinary tract, veins in limbs, joints and uterus (Grontmij, 2010). The excretion rate by human urine is 97% within the first six hours after exposure (Haan de, 2013; Thomaidis *et al.*, 2012). It is a substance found in water with one of the highest concentration and therefore selected in this project *(Haan de, 2013)*.

4.4.3 Domestic tracers

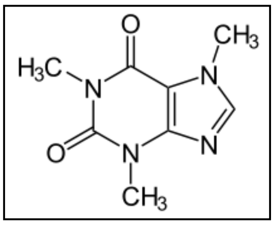
Artificial sweeteners are one of the latest groups of emerging compounds and are consumed as low-calorie sugar alternatives in food and drinks (Richardson *et al.*, 2011). Certain sweeteners are very persistent in liquids and are not degraded by the human body and excreted unchanged. This makes sweeteners the next class of compounds that proved to end up widespread in surface waters (Berghahn *et al.*, 2012). Due to their recalcitrance to transformation artificial sweeteners are viewed as an ideal marker for domestic wastewater (AGV, 2012). Besides artificial sweeteners also caffeine is used as a tracer compounds. In monitoring programs more often non-controlled stimulatory compounds, such as caffeine from coffee, tea, and soft drinks, nicotine and Drugs of Abuse (DoA) are included. In a Spanish study it is concluded that during the production of drinking water concentrations of illicit drugs were decreased to undetectable levels and that only traces of caffeine survived treatment *(Witteveen+Bos, 2011)*.

Acesulfame-K



Acesulfame-K is an artificial sweetener. It is heat-stable and therefore often used for baking purposes. It is very persistent in liquids, and therefore applied in soft drinks with long expiry dates *(Houtman, 2010)*. Acesulfame-K is excreted from the human body unchanged. Combined with its persistent character acesulfame-K is suitable as domestic tracer *(Richardson et al., 2011)*. In general, no harmful effects to the environment are found, which could also be caused by the fact that studies on the environmental effects of sweeteners are relatively recent (Cunningham *et al.*, 2010; Huerta-Fontela *et al.*, 2008; Waternet, 2013).

Caffeine

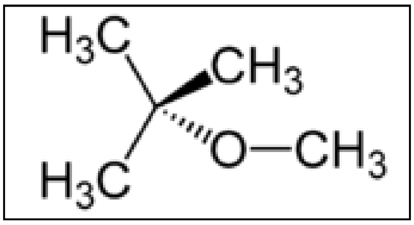


Caffeine is a persistent compound that occurs in more than 60 plant species and is a constituent of a variety of beverages (coffee, tea, caffeinated soft drinks) and of numerous food products (chocolate, pastries, dairy desserts). An estimation of about 80% of the daily caffeine consumption is coming from coffee (Loos *et al.*, 2009; Prince, 2000). Furthermore it is of importance in pharmaceuticals and considering its uptake with beverages and food, caffeine is probably the most widely consumed drug in the world (AGV, 2012; Rabiet *et al.*, 2006; Waterbase, 2013). Due to its clearly anthropogenic origin and numerous amount of detections, caffeine is marked as a potential indicator of domestic wastewater (AGV, 2012; Houtman, 2010; Loos *et al.*, 2009; Rijkswaterstaat, 2013; RIWA, 2013; Witteveen+Bos, 2011). About 97% of the ingested caffeine is metabolised in the human body; only 3% is excreted as caffeine (Rijkswaterstaat, 2013).

4.4.4 Industrial chemicals

Solvents are chemicals, which have the ability to dissolve, suspend or extract other materials. They are used in pharmaceuticals, microelectronics, industrial paint, gasoline additives and detergents (Ministerie van Verkeer en Waterstaat, 2006).

Methyl tertiary-butyl ether (MTBE)



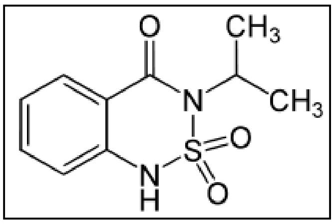
MTBE is an organic solvent, which is used as a gasoline additive that is low biodegradable and therefore persistent. Due to its high solubility and volatility, it disperses rapidly in the environment (Rijkswaterstaat, 2012b). MTBE can originate from gasoline used by shipping. A major part of groundwater pollution by MTBE is possibly caused by spills at gas stations.

4.4.5 Pesticides

Pesticides are substances to stimulate plant growth by reducing disturbing factors, like insects and other organisms, fungus or certain plant species. Pesticides can be subdivided into herbicides, fungicides, insecticides, plant growth regulators, bactericides and defoliants and have been a topic of concern for surface water quality for decades *(Houtman, 2010)*. Pesticides enter the environment by extensive use in agricultural practice, industrial emission during their production and due to runoff from urban practice. Pesticides applied on the field degrade and contaminate surface waters by drift, runoff, drainage and leaching. Introduction of relatively non-polar and very persistent pesticides enabled impressive increases in food production and crop security after the Second World War, but the use of these pesticides let to detrimental effects on the environment *(Carson, 1962)*. Pesticides used today are more polar and less persistent *(Kuster et al., 2009)*.

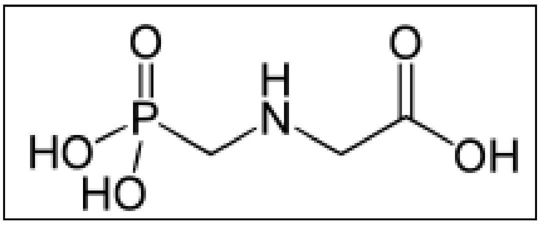
The use of pesticides can lead to harmful effects upon non-target organisms in the wider environment, including freshwater biota. Several studies showed the potential for oestrogenic effects, mortality of fish on expired pesticides and mortality of macro invertebrate species *(Berghahn et al., 2012; Satyavani et al., 2011; Schulz et al., 1999; Tyler et al., 2000)*. Knowledge of ecotoxicological effects of products formed by transformation of the parent pesticide and about the risk of additive or synergistic effects that may arise from the use of agricultural pesticides in combination with one another still remains limited *(European Environment Agency, 2011)*.

Bentazone



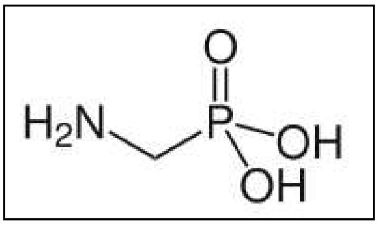
Bentazone is a herbicide used for a variety of crops. It is the first pesticide that is detected in drinking water in the Netherlands in 1988 (Smeenk *et al.*, 1988). This was the reason for the application of ozonation-activated carbon in the drinking water treatment plant in Amsterdam. It is very mobile in soil and moderately persistent in the environment *(WHO, 2011a)*. Because bentazone is used in agriculture, information about removal of bentazone in a WWTP is not found.

Glyphosate



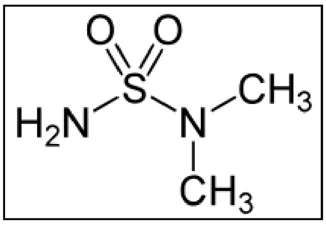
Glyphosate is an herbicide used in both agriculture and forestry and for aquatic weed control. After the detection of bentazone in drinking water, the use of glyphosate increased. Its main emission route is runoff of paved urban environments, where emissions from abroad are an important contribution *(Dutch Government, 2009b; European Solvents Industry Group, 2010; Grontmij, 2010; WHO, 2011a)*. Its most common metabolite is aminomethyl phosphonic acid (AMPA). Glyphosate only has a low acute toxicity towards animals. From all pesticides used for other purposes than agriculture, glyphosate is the most used (ca 50% of total used pesticides) (Grontmij, 2010).

Aminomethyl phosphonic acid (AMPA)



AMPA is a primary degradation product of glyphosate, with a higher persistence in ground water and often found in higher concentrations than glyphosate (Botta *et al.*, 2009; Manãs *et al.*, 2009).

N,N-dimethylsulfamide (N,N-DMS)



N,N-DMS is a pesticide that is used as an antifouling agent in shipping, to prevent growth of algae (Carlsson *et al.*, 2006). It is also a metabolite of tolylfluanid and of dichlofluanid. Although, the outdoor application of tolylfluanid is banned since 2007, N,N-DMS is still found. This approves the high persistence and polarity of N,N-DMS (Kowal *et al.*, 2009). The low toxicity of N,N-DMS (PNEC 140 µg/L) suggest no risk for drinking water production. However, DMS is the parent substance of its carcinogenic metabolite N-Nitrosodimethylamine (NDMA), which is formed with the treatment step ozonation and is regulated at very low levels in drinking water (10 ng/L) (Kowal *et al.*, 2009; Puijker *et al.*, 2009; Schatz, 2012).

5 Strategies

Strategies to reduce the amount of OMPs in the water cycle are proposed in this chapter. In the coming paragraphs different strategies will be discussed and a global cost estimation is given if possible. It should be taken into account that the strategies are based on the situation in the Netherlands and that the measures will be more effective if all countries upstream of the river Rhine are taking measures too.

5.1 Different strategies

Climate change, population growth and increasing emission of pharmaceuticals and other substances into the environment increases the need for more effective strategies to prevent OMPs entering the water cycle. Several strategies are possible, which intervene at different location in the water cycle. In this project a distinction is made between three types of strategies:

1. Source approach. This type of measures are taken at the user-side, where a polluter can either be a user of manufacturer of chemical compounds that finally end up in the water cycle as OMPs. Measures are intended to decrease the *use* of chemical compounds.
2. Mitigation approach. This type of measures are taken at the wastewater treatment facility. Several strategies are proposed, which all (partly) result in an improved effluent quality. Measures are intended to decrease the *emission* of chemical compounds.
3. End-of-pipe approach. This type of measures are taken at the drinking water consumption side and are only focussing on human health. Measures are intended to increase the *drinking water quality*.

Currently, in Europe several programs on OMPs are initiated. These programs focus on the presence of OMPs in the water cycle and on strategies to reduce the emission of OMPs. These initiatives are not discussed in detail, but an idea is given of current developments (appendix 5-1). In the following sections possible strategies will be discussed, as well as reference strategies applied in the Netherlands and other countries.

5.1.1 Source approach

1. Green pharmacy

The environmental impact of manufacturing 1 kg of product in the pharmaceutical industry is much higher than in other chemical industries. This is an important reason to apply ‘green pharmacy’ (European Environment Agency, 2010). Green pharmacy is based on both the sustainable production of pharmaceuticals and the production of sustainable pharmaceuticals. The pharmaceutical industry plays an important role in this (Hoek van der *et al.*, 2013; RIVM, 2012; Waterforum, 2013b). Recently the pharmaceutical industry has started to pay more attention to sustainability and in which way the impact on the environment can be decreased to a minimum. This is especially the case for X-ray agents and anti-epileptic medicines (RIVM, 2008b).

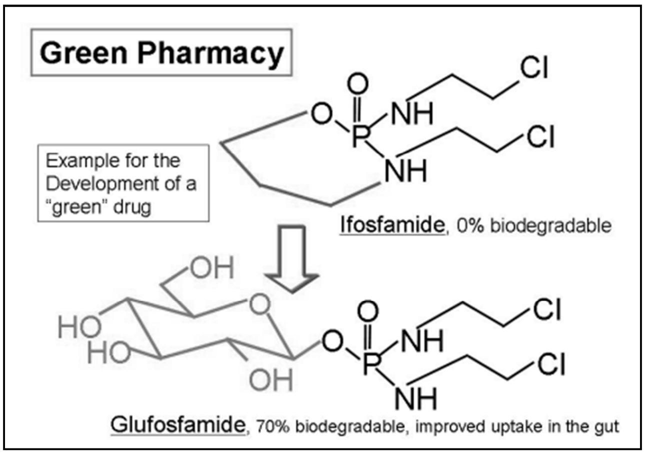


Figure 5-1 Example of green pharmacy (European Environment Agency, 2010)

So, improvements can be made, not only on the production of pharmaceuticals but also on packaging material and package size (European Environment Agency, 2010). Figure 5-1 shows an example of the advantages of green pharmacy. Not only is the compound more biodegradable, improvements are also made on the uptake in the human body. Green pharmacy focuses on production, use and disposal of pharmaceuticals. In several countries, like the U.S., Canada and Spain, pharmaceutical return programs already have been set up to safely dispose time-expired or unused medicines (Khetan *et al.*, 2007). Important to note is that this strategy only decreases the emission of (veterinary) pharmaceuticals into the environment.

2. Awareness (in pharmaceutical use)

Hardly any information dealing with awareness could be found on OMPs other than pharmaceuticals. For that reason this section is only about the awareness on human pharmaceutical use. Use of veterinary pharmaceuticals will be discussed in '4. Green agriculture and cattle breeding'. Besides improvement on the sustainability of pharmaceuticals, it is also important for doctors to be more critical towards the pharmaceuticals they prescribe. Less prescription of preventive pharmaceuticals and restraint in antibiotics prescription could result in lower concentrations in the water cycle, but the focus still needs to be on the patients' health (Eckstein *et al.*, 2011; Hoek van der *et al.*, 2013; RIVM, 2012). MEDUWA is an example of an initiative targeting awareness of pharmaceutical use (MEDUWA, 2013). Doctors and patients should be stimulated to use environmentally friendly pharmaceuticals, such as ibuprofen instead of diclofenac, which is much more difficult to remove from the water. This is not yet possible for all pharmaceuticals. Sotalol and metoprolol for instance, do not yet have an alternative that is easier to remove from the water. Another important aspect is the information from the doctors and pharmacists to the patient. Patients need to be even better informed about the right use of the medicines (Eckstein *et al.*, 2011; Hoek van der *et al.*, 2013; RIVM, 2012). At last, the approach for tackling the problem of pharmaceuticals in the water cycle needs to be regulated from the European Union. International standards on concentration in water and production of pharmaceuticals are essential since the river basins are transboundary (Gunnarsson *et al.*, 2008).

3. Legislation and policy

As mentioned previously, an international approach is essential for good results in decreasing the concentrations of pharmaceuticals, personal care products, industrial chemicals and pesticides in the water cycle. This strategy results in a decrease of OMPs by different types of legislation and policy: 1) legal ban on certain chemicals, 2) legal limits on concentrations of OMPs in the discharge water on surface water (factories and WWTPs), 3) policy on increasing awareness of consumers and users. Implementation of this strategy in some cases incorporates implementation of other strategies as well. For legal limits on concentrations in discharge water incorporating other strategies is essential ('1. green pharmacy', '4. green agriculture' and '8. improvement of WWTP'). Policy with the goal to increase awareness of consumers and users of chemicals incorporates the strategy '2. awareness'.

Some (international) environmental protection regulations and policies already exist, for example:

- Water Framework Directive, which is composed to decrease the load of OMPs entering the water cycle and to improve the quality of surface water and groundwater. Also on national and local scale new policies are important. Some European countries, such as Sweden, Germany and Great Britain, are currently achieving good results from their effort. Sweden has developed a pioneer environmental information and classification scheme for pharmaceuticals, while Germany and Great Britain concentrate more on research to support further action (Kampa *et al.*, 2008). Measures on pharmaceuticals have already been discussed previously (human) or will be discussed below (veterinary).
- Legal ban on some highly toxic pesticides that used to be applied on agricultural fields in the past. This is the case for chlorfenvinphos, diuron, isoproturon, dichlorvos, dicofol and quinoxyfen, of which all pesticides are on the WFD priority list and the last three have just recently been added (April 2013)

(CTGB, 2013). Although banned, some substances are still present in the water cycle due to their persistent character or illegal use (Compendium voor de Leefomgeving, 2013a).

- The implementation of a decision tree for the admission of pesticides possibly affecting the surface and drinking water quality *(Ministerie van Verkeer en Waterstaat, et al., 2009)*. This tool on European scale helps to determine whether the use of a certain new pesticide should be permitted or not.
- The introduction of certification for the use of glyphosate and other pesticides used on paved areas (mainly for gardeners) (Ministerie van Verkeer en Waterstaat *et al.*, 2009).
- An agreement on ship waste (oil, gasoline and other chemicals) between the Netherlands, Belgium, France, Germany, Switzerland and Luxembourg to decrease the MTBE leakage from ships (Ministerie van Verkeer en Waterstaat *et al.*, 2009).

Limiting factors in further legislation and policy development are limited knowledge on the fate and effects, low-level effects, long-term effects and effects of mixtures of OMPs in the environment and the behaviour of OMPs in a WWTP (Kampa *et al.*, 2008). With already over 100,000 registered chemicals in the European Union, for every banned chemical a new alternative will be found.

4. Green agriculture, greenhouse farming and cattle breeding

The strategies described previously are all focussed on human pharmaceuticals and other substances used in human practise and the measures are relatively clear to understand and apply. In agriculture this is different. The routes by which pesticides and veterinary pharmaceuticals enter the environment are runoff and leaching of agricultural land, where no WWTP interacts. The only way to prevent pesticides and veterinary pharmaceuticals entering the water cycle is to stop using them. Since agriculture, greenhouse farming or cattle breeding is the income for farmers, they are not willing to simply stop the application of pesticides and veterinary pharmaceuticals, which makes this a difficult matter. There are several alternatives to the current pesticide and pharmaceutical use, but they will only effectively work when regulated by law or policy. Examples are the introduction of the WFD priority list, pesticides control by regulations, banning of certain pesticides and legislation regarding the use of veterinary pharmaceuticals (chapter 3 and 4). In greenhouse farming the effluent water is in some cases already treated before discharged. Greenhouses consist of a closed system, where it is relatively easy to include a treatment step. Hereafter two small scale initiatives to stimulate sustainable use of pesticides are presented.

Squall is a tank mixing additive for pesticides, which enhances the protection of the crops by better attachment and divisibility on the leaves of the crops. This results in less pesticide needed and less often application (no new application after a rain event needed). It performs also as an anti-drift agent to prevent drops of pesticide to be blown away by the wind (Squall). Another method to reduce pesticide discharge into the environment is by application of floating cultivation of crops and flowers. Instead of being planted in the soil the crops and flowers are floating in a water system. Fewer pesticides are needed and nutrients can be provided in the water. This is a closed system, where all the water is reused (Haan de, 2013).

From an interview with farmers it appeared that most farmers do not have the knowledge to make a good indication of the impact of the applied veterinary pharmaceuticals on the water cycle. They were willing to choose an alternative pharmaceutical when it is proved that certain veterinary pharmaceuticals are harmful to the environment or human health. The most important criteria to choose a certain medicine is costs and effectiveness; impact on environment is a less important criterion (Snijdelaar *et al.*, 2006). For veterinary pharmaceuticals it is assumed that more animal friendly stables will reduce the occurrence of skin diseases and thus the amount of applied veterinary antibiotics. This is directly linked to a decrease in emission of veterinary pharmaceuticals into the water cycle (Ministerie van Verkeer en Waterstaat *et al.*, 2009).

5.1.2 Mitigation approach

5. Separate collection of urine in residential areas and hospitals

Separate collection of urine is based on the fact that about 80% of the pharmaceuticals applied on humans are excreted via urine and about 20% by faeces. The urine will be more concentrated, because less flushing water is used (Grontmij, 2011). There are two types of approaches: i) decentralised treatment at home, the effluent will be discharged into the sewer system, ii) centralised treatment at the WWTP. Figure 5-2 shows a toilet with separate urine collector. To apply this method the toilets need to be improved and either each house needs a treatment facility, or the whole sewer system needs to be replaced (STOWA, 2010a). Because of the huge costs, it is not realistic to do this at once. In new housing estates it is possible and more cost-efficient to construct a separate system, but the total implementation in the Netherlands will then take about 100 years with a replacement of 1% of all houses per year (Grontmij, 2011). For both in-house treatment and treatment at the WWTP the techniques conventional denitrification-nitrification (by means of a MBR), ozonation and activated carbon are suitable. It is also a possibility to recover nitrogen and phosphorus with struvite precipitation (STOWA, 2010a). Separate collection and decentralised treatment of urine costs about 304 €/m^3 of total diluted urine. This is an estimation and it includes investment costs (STOWA, 2010a).

Figure 5-2 Toilet with separate urine collector (Praktisch Duurzaam, 2011)

The principle of separate urine collection and treatment in hospitals is the same as described above, with the difference that the total load of pharmaceuticals in hospital wastewater is higher than that of residential areas. A study has shown that the total load of human pharmaceuticals excreted per person in hospitals is circa 24 g/p/y, in a care institution about 10 g/p/y and in a residential area about 1.8 g/p/y. This is not the case for X-ray agents and anti-diabetic pharmaceuticals, which are mainly excreted at home (Kumar *et al.*, 2010). The total costs of decentralised urine treatment in hospitals are lower compared to the costs in residential areas, due to the lower investment costs.

Other small-scale initiatives of separate collection and treatment of urine are the application of activated carbon in toilets and a special urine bag, which should be used after treatment with an X-ray agent.

6. Decentralised collection and treatment of total wastewater in residential areas

Decentralised collection and treatment of wastewater reduces the emission of OMPs into the water cycle by the effluent. These treatment facilities are new to build and in this way the most advanced and newly developed treatment steps can be applied, which are specialised on the removal of OMPs. Higher costs on small scale treatment facilities is compensated by saving money on lower transport costs. Decentralised collection and treatment of household wastewater needs a good approach, in which specific treatment techniques and infrastructural works are combined, and the safety of the residents must be guaranteed at all times. An example of a project, which is cost-efficient, is Nieuwe Sanitatie Noorderhoek in Sneek. After a pilot period a whole new housing estate consisting of about 230 houses is established with the new concept. The concept exists of a system where black water (kitchen and toilet, vacuum system) and grey water (washing machine and shower) are separately collected and treated (figure 5-3). A vacuum system for toilet and sink shredder results in less use of water (1L against 7L of a conventional toilet). From the black water biogas can be produced and nutrients can be recovered. The grey water is a source of heat recovery. The effluent is discharged on a nearby canal (Nieuwe Sanitatie Noorderhoek, 2013). The total costs of the project are about €2.5 million, of which 1% of the total costs are covered by the production of biogas and recovery of heat. The total water savings per households are 20-25% (Nieuwe Sanitatie Noorderhoek, 2013). No information on reducing of costs for households at implementation of this project could be found.

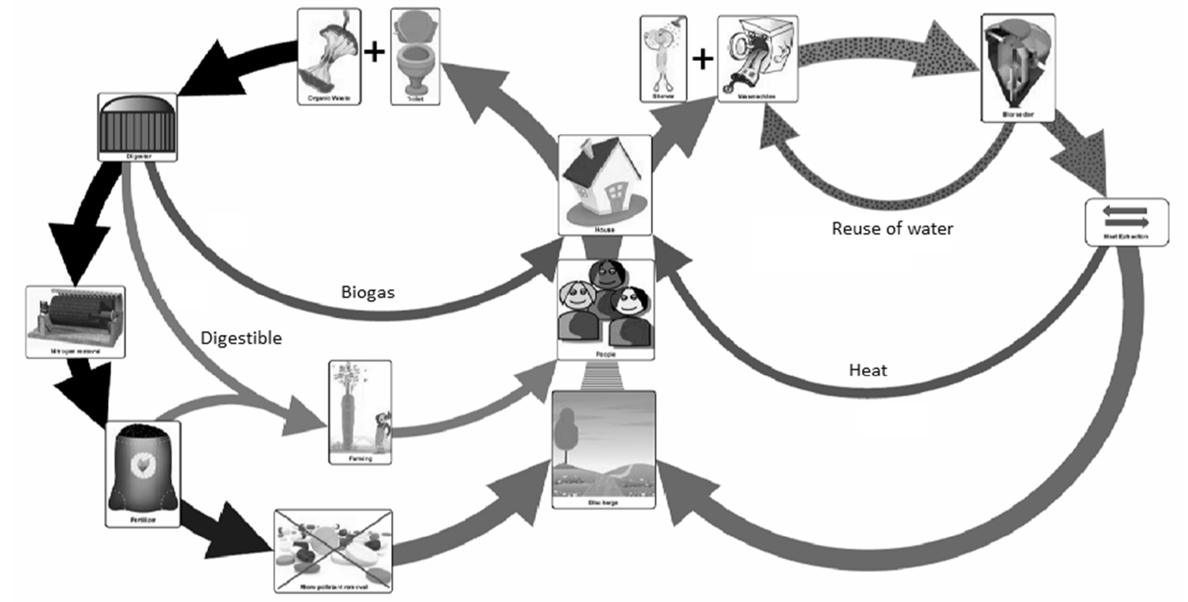


Figure 5-3 Principle of new sanitation at Noorderhoek Sneek (Nieuwe Sanitatie Noorderhoek, 2013)

7. Decentralised collection and treatment of total wastewater in hospitals

Decentralised collection and specific treatment of hospital wastewater can reduce the load of OMPs on a conventional WWTP and thus the discharge into the environment (Kumar *et al.*, 2010; STOWA, 2009a; 2010c; 2011b). In this strategy there is a difference between the collection and treatment of all hospital wastewaters or only the black water from hospitals, which contains the highest load of pharmaceuticals. Just like in the previous strategy the implementation incorporates adjustments on the (internal) sewer, selection of the specific treatment techniques, municipal licenses on the effluent discharge and safety regarding the hospital staff and patients. Biological treatment of hospital wastewater at a special treatment plant at the hospital costs about 2.00 €/m^3, which is about twice as much as at a conventional biological WWTP. Additional treatment with ozone and activated carbon to remove pharmaceuticals costs about 0.50 €/m^3, which is 2.50 €/m^3 in total. An example of a system where hospital wastewater is collected and treated is Pharmafilter at the Reinier de Graaf Hospital at Delft. The system is based on disposable bedpans made of bio plastics. The filled bedpan is disposed into a shredder and flushed with water into the internal sewer of the hospital. The water and shredded bedpans flow to the nearby treatment plant, which is designed to remove pharmaceuticals and other hospital specific compounds from the influent (figure 5-4). In this way not only the pharmaceuticals are removed efficiently, but also the working conditions of nurses are improved. About 70% of the effluent water is reused as process water in the hospital. In some other countries, like Dubai, effluent water of such installations can be used as drinking water, but in the Netherlands that is still prohibited (Pharmafilter, 2013). A similar project is SLIK, which is initiated by water board Groot Salland, ISALA klinieken (hospitals), municipality of Zwolle, drinking water company Vitens and STOWA. Within this project the water board closely co-operates with different companies to decrease the emission of pharmaceuticals into the water cycle to increase the surface water quality (STOWA, 2013).

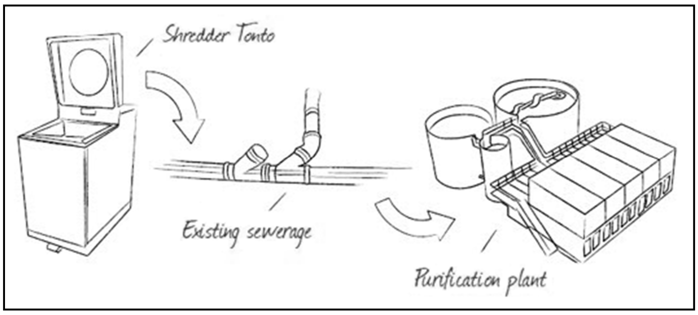
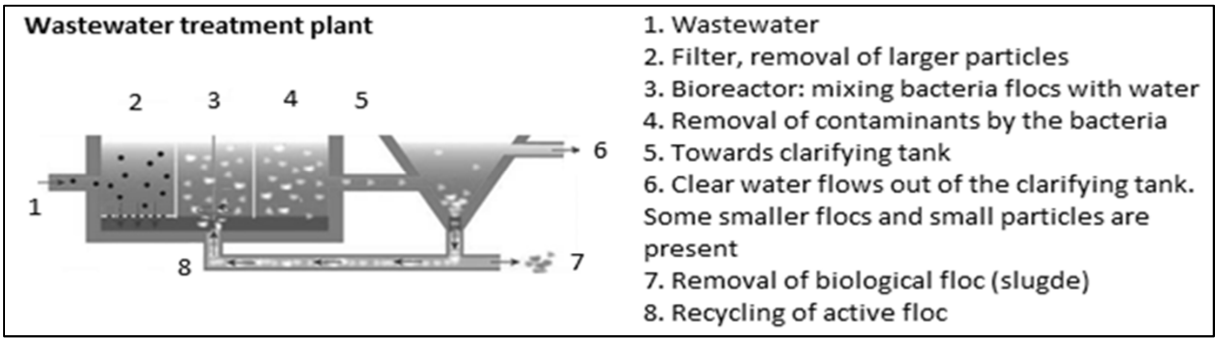


Figure 5-4 Schematic conceptual drawing of Pharmafilter (Pharmafilter, 2013)

8. Improvement of wastewater water treatment plants and effluent treatment

Conventional WWTPs for domestic wastewater are designed for the removal of particulate matter, aerobic degradation of dissolved organic compounds, nitrogen removal and removal of phosphate from wastewater (C, N and P) (figure 5-5). The produced sludge can be digested (anaerobic), where biogas is produced. This can be used as energy supply for the WWTP. Metals are primarily removed due to their fixation to the sludge. Some WWTPs are supplemented with a tertiary treatment step to protect receiving waters from any excess nutrients (Comber *et al.*, 2003). The past decades have shown that the conventional processes are inadequate in removing most of the (synthetic) organic compounds (Houtman, 2010). The elimination of OMPs in primary and secondary treatment processes depends on their ability to adsorb to solid particles or to biodegrade.



1. Wastewater
2. Filter, removal of larger particles
3. Bioreactor: mixing bacteria flocs with water
4. Removal of contaminants by the bacteria
5. Towards clarifying tank
6. Clear water flows out of the clarifying tank. Some smaller flocs and small particles are present
7. Removal of biological floc (slugde)
8. Recycling of active floc

Figure 5-5 Indication of a treatment scheme for conventional wastewater treatment (RIWA, 2007)

By improvement of WWTPs or additional effluent treatment, the effluent quality can be improved. This measure can be applied relatively easily, because due to aging of the system, most WWTPs must be upgraded anyway after a certain period of time. Drawback of this measure is that the new or improved treatment steps are expensive, because they have to be implemented at a large scale. It would be more cost-efficient if a more concentrated stream is treated, than a diluted stream. In an existing WWTP it is easier to implement additional effluent treatment and those treatment steps can be designed only for removing OMPs, because all other pollution is already removed.

Treatment techniques that are plausibly effective in the treatment of OMPs and that are well-accepted in the field of water treatment are combined and described in detail in appendix 5-2, and summarised in appendix 5-3. Techniques that are best suitable for improved micro pollutant removal of conventional WWTPs and effluent treatment are adsorption (activated carbon), advanced oxidation processes (Ozone and UV, preferably in combination with H_2O_2), nanofiltration and reverse osmosis (STOWA, 2005). Other described techniques are: coagulation/ flocculation, membrane bioreactor, microfiltration, ultrafiltration, ion exchange, chlorination, ozone and UV disinfection and constructed wetlands. Not for each selected compound the removal efficiency is found and for the found removal efficiencies it must be taken into account that this is only an indication, since the removal efficiency highly depends on the exact type of treatment and influent quality (Moel de *et al.*, 2006). Also a list of promising new techniques is provided (appendix 5-4). Those technologies are not widely applied yet and only very limited information is available of full-scale operation or efficacy on the removal of the selected compounds. Some treatment techniques, especially for effluent treatment, overlap with techniques used in drinking water treatment.

5.1.3 End-of-pipe approach

9. Improvement of drinking water treatment plants

Drinking water treatment plants are usually able to (partly) remove OMPs from the water (Compendium voor de Leefomgeving, 2013a; RIVM, 2008b). Nevertheless, not all types of OMPs are removed equally well. The design of a DWTP is more complex and differs per type of source water. In general a DWTP consists of aeration, if necessary coagulation and flocculation, sand filtration, and one or more techniques like activated carbon, ozone and UV disinfection/oxidation (also in combination with H_2O_2, AOP), chlorination, ultrafiltration, nanofiltration and reverse osmosis and additionally pH correction (figure 5-6) (Moel de *et al.*, 2006). The elimination of OMPs depends on their ability to adsorb to solid particles or to biodegrade.

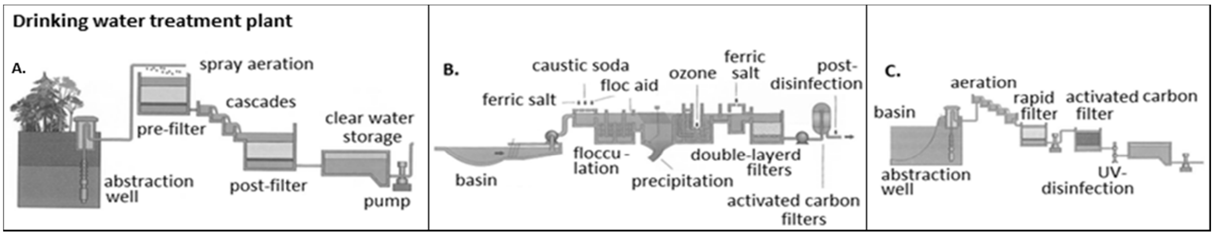


Figure 5-6 Indication of a treatment scheme for A. consumable water production from groundwater, B. consumable water production from surface water and C. consumable water production from riverbank filtration (Moel de *et al.*, 2006)

By improvement of DWTPs, the drinking water quality can be improved. This measure can be applied relatively easily, because due to aging of the system, most DWTPs must be upgraded anyway after a certain period of time. Drawback of this measure is that the new or improved treatment steps are expensive, because they have to be implemented at a large scale. This measure, compared to the previous measure, only improves the drinking water quality, since the OMPs have entered the water cycle already.

To improve the drinking water treatment plants activated carbon, advanced oxidation processes (Ozone and UV, preferably in combination with H_2O_2), nanofiltration and reverse osmosis seem to be the most effective techniques (RIVM, 2008b). Other described techniques, that are suitable for drinking water treatment are coagulation/flocculation, microfiltration, ultrafiltration, ion exchange, chlorination and ozone and UV disinfection. Appendix 5-2 provides detailed information about these treatment techniques (principles, combined with wastewater treatment techniques). Appendix 5-3 summarises the removal efficiencies of those techniques. Appendix 5-4 provides information on promising new techniques. As described in the previous section about WWTPs and effluent treatment, the treatment techniques used in wastewater treatment and drinking water treatment partly overlap. However, the performances and (pre)conditions of the techniques are relevantly different for water production (from surface water or groundwater) compared to effluent treatment.

5.2 Cost estimation and financing

Cost estimation

In order to determine which strategy is most cost-efficient to apply, the average costs per strategy must be known. This section is concerned with cost estimation and financing. Strategies 5-9 (separate/decentralised collection of urine/wastewater and improvement of WWTP/DWTP) include application of certain treatment facilities and are therefore relatively simple to express in costs. The other strategies ('1. green pharmacy', '2. awareness', '3. legislation and policy' and '4. green agriculture') are harder to express in costs. Within the scope of this project it is not possible to determine realistic cost estimation for these strategies.

From literature cost indications are found for different treatment techniques. Those are summarised in table 5-1. To make a comparison, a conventional biological WWTP is estimated to cost about 1.00 €/m^3 (which is about 46 €/i.e./y) and additional treatment with ozone and activated carbon is about 0.50 €/m^3 (23 €/i.e./y) (Grontmij, 2011; STOWA, 2009a). The costs of the different treatment technologies depend highly on the size of the installation and the composition of the influent water. The estimated costs in the table are achieved by doing some assumptions. Costs of treatment techniques applied in a WWTP are based on a model WWTP with 200,000 i.e., 136 g TSS/d, dry weather flow of 12.5 l/i.e.h. in the Netherlands and, unless mentioned otherwise, the cost estimation includes investment costs and operational costs (STOWA, 2005). The total drinking water consumption is 120 L/p/d, the total production of wastewater is 200 L/i.e./d and the total production of urine is 0.5 L/i.e./h (including flushing) (STOWA, 2010a; 2011a). The third column of the table represents the costs for drinking water production in €/p/y, which are derived from the "kostencalculator" and the assumptions mentioned previously (Kostencalculator, 2013). The "kostencalculator" is an online design tool to roughly calculate total cost (€/m^3). In these calculations investment costs and exploitation costs are combined. The costs for drinking water have an inaccuracy of approximately 30% (DHV Water BV, 2009).

Table 5-1 Estimated costs per strategy (investment and operational costs, unless mentioned otherwise)

Method		
Strategies not possible to express in costs		
1. green pharmacy	-	-
2. awareness	-	-
3. legislation and policy	-	-
4. green agriculture and cattle breeding	-	-
Strategies to be expressed in costs	Costs wastewater treatment	Costs drinking water production
5a. decentralised collection and treatment of urine	1340 €/i.e./y [1]	-
5b. centralised collection and treatment of urine	440 €/i.e./y [1]	-
6. decentralised collection and treatment of total wastewater in residential areas	90 €/i.e./y [8] (excl. investment)	-
7. decentralised collection and treatment of total hospital wastewater	600 €/bed/y [2,3]	-
8+9. improvement WWTP and DWTP plant	4-80 €/i.e./y	<1-10 €/p/y
• Conventional treatment plant and additional treatment	46 €/i.e./y [3]	65 €/p/y [7]
• Ozone + activated carbon at all WWTPs in NL (effluent)	35 €/i.e./y [4]	-
• activated carbon at all WWTPs in NL (effluent)	25 €/i.e./y [4]	-
• Upgrading only large WWTPs (>100,000 i.e.)	4 €/i.e./y [4]	-
• Membrane bioreactor	80 €/i.e./y [5]	-
• MF/UF	28 €/i.e./y [5]	7 €/p/y [9]
• NF/RO	21 €/i.e./y [5]	10 €/p/y [9]
• PAC/GAC	18 €/i.e./y [5]	5 €/p/y [9]
• IEX	14 €/i.e./y [5]	3 €/p/y [10]
• Ozone disinfection (WWTP: effluent)	5 €/i.e./y [3,6]	<1 €/p/y [9]
• UV disinfection (effluent)	20 €/i.e./y [3,5]	<1 €/p/y [9]
• UV/H_2O_2 oxidation (effluent)	32 €/i.e./y [6]	2 €/p/y [11]
• Ozone oxidation (effluent)	15 €/i.e./y [6]	*

[1] *(STOWA, 2010a; 2011a)*
[2] *(STOWA, 2010a; 2011a)*
[3] *(Grontmij, 2011; STOWA, 2011a)*
[4] *(STOWA, 2013)*
[5] *(STOWA, 2005)*
[6] *(STOWA, 2009b)*
[7] *(Vewin, 2013a)*
[8] *(STOWA, 2010b)*
[9] *(Kostencalculator, 2013)*
[10] *(Hillegers, 2013)*
[11] *(Smit, 2013)*
** Data not found*

From the table it can be seen that the costs of decentralised and centralised collection and treatment of urine and decentralised collection and treatment of hospital wastewater (strategies 5a, 5b and 7) are one to two orders of magnitude higher than costs for various treatment techniques in strategies 8 and 9. Strategy 6 results in yearly costs of about 90 €/i.e. (STOWA, 2010b). In this reference project no investment costs are included. The total yearly costs will be higher. Upgrading of an existing treatment plant costs about 4-80 €/i.e./y for a WWTP or <1-10 €/p/y for a DWTP, depending on the type of treatment technology applied. It must be noted that for with strategies 8 and 9 the total wastewater is treated (including rainwater runoff), where for strategies 5, 6 and 7 only a part of the total wastewater is treated. Strategies 8 and 9 remove more types of OMPs, but are not necessarily better in qualitative removal of OMPs.

Financing

Within the scope of this project no research is done on the financing of the possible strategies. The goal of the Water Framework Directive is to apply the *polluter pays principle*, where the person who is responsible for the emission of OMPs has to pay (European Union, 2000). However, implementation of this principle is not always possible (RIVM, 2004b; Vewin, 2008).

6 Multi Criteria Analysis

In the previous chapter nine strategies are composed. The strategies are tested with a Multi Criteria Analysis in the first two paragraphs of this chapter. Finally, a sensitivity analysis is performed to see the influence of the weighting factors. The best strategies will be applied on the two case studies (Bethunepolder and Andijk) to see the influence of the strategies on the water quality.

6.1 Multi Criteria Analysis

A Multi Criteria Analysis (MCA) is a tool to find the best solution from a set of options and consists of criteria, weighting factors, a scope and a target group. The possible options are prepared during the synthesis and those are judged based on several criteria. By applying weighting factors for the criteria it is possible to count for some criteria more than for others. To execute the MCA it is important to make the scope of the MCA clear.

Strategies

In chapter 5 the possible strategies are composed and explained in detail. Below an overview of the possible strategies is provided, on which the MCA is performed.

1. Green pharmacy
2. Awareness in use and prescription
3. Legislation and policy
4. Green agriculture, greenhouse farming and cattle breeding
5a. Decentralised collection/treatment of urine
5b. Centralised collection/ treatment of urine
6. Decentralised wastewater collection/treatment on residential scale
7. Decentralised collection/ treatment of hospital wastewater
8. Improvement WWTP
9. Improvement DWTP

Criteria

The criteria on which the MCA is performed are scored by an expert panel (appendix 6-1). Based on the research questions the criteria are divided into cost-efficiency, sustainability and applicability (table 6-1). The criteria are not expressed in exact values. The score is determined by the estimated value in relation to other strategies. This is done by an expert judgement made by the expert panel based on their expertise and experience in the field of water treatment and water quality.

Table 6-1 Criteria

Cost-efficiency	
Life Cycle Costs (hereafter called 'costs')	 Figure 6-1 Life cycle The cost-efficiency is expressed in life cycle costs, in which the following method is applied. The total investment costs, maintenance costs (including energy and water) and disposal costs are summed (figure 6-1). In this way different options and strategies can be compared based on total costs. This method is more accurate than a frequent applied method in which the maintenance costs are determined using a percentage of the investment costs. In that case a project with high investment costs has automatically also high maintenance costs, which is not necessarily true. In the determination of the life cycle costs no inflation needs to be accounted for (Ghimire *et al.*, 2012).
Sustainability	
Energy consumption	The energy consumption is a measure of expressing the impact of the strategy on the climate.
Raw materials	This criterion includes the use of raw materials and chemicals, such as the materials needed for activated carbon or H_2O_2.

Flexibility	The flexibility expresses the ability to be adapted when the future situation changes with respect to the design situation. The flexibility also refers to the ability to be applied on other cases than the two proposed in this project and also on a large scale, like the Netherlands or Europe.
Robustness	The robustness of the strategy can be explained by the extent to which the strategy is performing during its life time. This can be expressed by the question whether this strategy is applicable as a long-term solution.
Applicability	
Complexity (implementation)	Complexity expresses the degree of complexity during the realisation of the strategy. The place of intervention in the water cycle is important in this criterion (upgrading of a WWTP is less complex than changing consumers behaviour).
Ease of operation (management)	Besides the implementation the ease of operation is also important. This includes whether it is hard or less hard to manage the strategy during the operational phase.
Technical risk	This criterion describes the possible technical risks of the strategy. An example of this is bromate formation during ozonation.
Risk in implementation	Risk in implementation expresses the risk during the implementation of the strategy. Aspects that are included in this criterion are the result of the strategy or the sensitivity to changes in the strategy compared to the design (will the result of the strategy be different from the expected result? what happens if there is a power cut? is it likely that the strategy will result in the expected outcome?).
Effectiveness	This criterion focuses on the performances of the strategy: does the strategy really lead to a reduction of the concentration of the selected micro pollutants in surface water and drinking water? Another aspect on this criterion is the dependency on countries upstream of the Netherlands.
Social acceptance	The theoretical acceptance by the experts or decision makers can differ from the acceptance of the consumers. This is expressed as social acceptance.
Transition period	The transition period represents the time it takes till the strategy is fully implemented and the assumed impact can be expected.
Innovation	This criterion describes the innovative character of the strategy. More innovation is better. It contributes to improvement of the performances of a company and increases the employment and prosperity of a region.

Value and weighting factor

All strategies need to be judged on all criteria. For this the following method is applied. Each criterion is scored for each strategy, with a score of very good (2), good (1), does not distinguish (0), moderate (-1) and bad (-2). Each of the criteria is linked with a certain weighting factor, which represents the relative importance of the criterion compared to the others (sum equals one).

Scope and target group

The scope of this MCA is to determine the most sustainable, applicable and cost efficient strategy to reduce concentrations of selected organic micro pollutants in surface water and drinking water in the Netherlands. The focus is on an integral approach in the water cycle, where all aspects are included: wastewater, drinking water, water management, ecology and human interaction. The MCA is executed from a human point of view and thus the target group consist of the consumers of drinking water.

Limitations and assumptions

Within the scope of the project it is tried to make the MCA as complete as possible, but there are always some limitations. The first and very important limitation is the cost estimation. For the different treatment techniques and treatment strategies it is possible to find reference projects and costs, but for the more abstract measures like ‘green pharmacy’ cost estimation is far more uncertain. For some strategies no costs at all were found. This is the same for some other criteria, where the criterion cannot be expressed in numbers or not enough information is available. In this case an estimation is made compared to the other strategies, which is based on an expert judgement of the expert panel.

6.2 Results of MCA

The expert panel has scored the MCA for this project independently of one another for both the weighting factor per criterion and the values for each strategy. The results are averaged, which forms the final weighted result of the MCA (table 6-2). From this table it is concluded that strategies with a good score are ‘green pharmacy’, ‘awareness in use and prescription’, ‘legislation and policy’ and ‘green agriculture and cattle breeding’. Strategies with a moderate score are ‘improvement of wastewater treatment plants and drinking water treatment plants’. The strategies concerning separate and both centralised or decentralised treatment of either only urine or all wastewater score poor on this MCA. From the results of the MCA it is concluded that ‘legislation and policy’ is judged as the best strategy. However, implementation of this strategy requires the need for the implementation of other strategies as well. Reduction of the emission of certain substances requires improvement of treatment facilities or a decrease in use of products from which those certain substances originate from (also section 5.1.1 ‘legislation and policy’). For this reason also the second best strategy is selected to elaborate on, which is ‘green pharmacy’. This second best strategy is also not a stand-alone solution to the problem of OMPs, because it only reduces the emission of (veterinary) pharmaceuticals. This will be further discussed in chapter 9.

6.3 Sensitivity analysis

To determine the sensitivity and thus the robustness of the MCA a sensitivity analysis is carried out. In this analysis the weighting factors of some parameters are changed to see the impact of these parameters and the strong and weak points of each strategy. The following changes are made to the weighting factors of the parameters:

- Weighting factors of all criteria are equal (un-weighted)
- Weighting factors of costs, sustainability and applicability; each time one of those equals zero
- Weighting factors of costs, sustainability and applicability; each time two of those equal zero
- Weighting factor of effectiveness is doubled

In all cases the remaining weighting factors of the parameters are changed in a way that the sum of all weighting factors still is one, but the ratio between the them remains unchanged (Have ten *et al.*, 2009). The sensitivity analysis is performed in this way to show the influence of the different criteria. The criterion that is most influential is the costs (highest weighting factor). Since the costs are difficult to determine for some strategies and estimates are only roughly done, the influence of the costs is an important aspect of the sensitivity analysis.

Results

In table 6-3 an overview is presented, which gives an indication of the strategies that score good, moderate or poor on the sensitivity analysis (see also appendix 6-1 for detailed results). The division between good, moderate and poor is not based on fixed values, but on values that are close together. The table shows in the first column the strategies. The second column represents the normal situation (identical to table 6-2). The columns 3-10 show the situations in which the weighting factors of the MCA are adjusted to zero for all criteria, only costs is zero, all sustainability criteria are zero, all applicability criteria are zero, all costs and sustainability criteria are zero, etc. In the top three of each of these sensitivity analyses the strategies ‘1. green pharmacy’, ‘2. awareness’, ‘3. legislation’, and ‘8/9. improvement of WWTP/DWTP’ are present. ‘3. Legislation’ has shown to be the best in most of the analyses. The most poorly performing strategies are ‘5a/5b. (de)centralised urine treatment’ and ‘6. wastewater treatment on residential scale’. Strategies ‘4. green agriculture’ and ‘7. hospital wastewater treatment’ are mostly scoring moderate.

Table 6-2 Results of the Multi Criteria Analysis

Criteria	Weighting factor	1. Green pharmacy	2. Awareness in use and prescription	3. Legislation and policy	4. Green agriculture and cattle breeding	5a. Decentralised collection and treatment of urine	5b. Centralised collection and treatment of urine	6. Decentralised collection and treatment of wastewater on residential scale	7. Decentralised collection and treatment of hospital wastewater	8. Improve-ment of WWTP	9. Improve-ment of DWTP
Cost-efficiency	0.26										
Life Cycle Costs	0.26	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.26										
Energy consumption	0.09	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.05	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.05	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.07	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.48										
Complexity	0.05	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.05	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.04	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.05	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.15	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.07	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.04	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.03	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
TOTAL	1.00	5.0	2.6	7.8	4.8	-7.6	-4.4	-8.0	0.4	6.4	7.0
Weighted score		**0.68**	**0.61**	**1.01**	**0.46**	**-0.72**	**-0.57**	**-0.55**	**-0.11**	**0.31**	**0.30**

Now comparing the different analyses (situations) to see the influence of the different criteria on the results.

- In the un-weighted situation and the situation where costs are zero it can be seen that ‘3. legislation’ still performs the best, but now followed by the strategies ‘8/9. improvement of WWTP/DWTP’.
- This outcome is similar to the situation where costs and sustainability are zero (applicability important), where also strategies 8 and 9 perform very well, in this case even better than strategy 3. The applicability incorporates the effectiveness, which shows that if effectiveness of the measure is more important than in the normal situation, the strategies in which the WWTP or DWTP are upgraded perform best.
- In the situations where sustainability or applicability or both are zero the results are very similar to the weighted situation. This is mostly caused by the relatively high importance of the costs in the MCA (weighting factor of 0.26, compared to 0.03-0.15 for other criteria).
- When looking only at sustainability (where costs and applicability are zero) we again see a very similar result as in the weighted situation.
- The last situation is when the weighting factor of the effectiveness is doubled. A small change compared to the weighted situation is the result.

From this analysis it appears that a relatively high importance of applicability compared to costs and sustainability results in a different ranking of the strategies compared to the weighted situation. In other words, as the effectiveness becomes more important, strategies ‘8/9. improvement of WWTP/DWTP’ perform better than in the normally weighted situation. From the general similarity of the ranking of the different strategies in the sensitivity analyses it is concluded that this MCA is only little sensitive to changes in weighting factors. ‘3. Legislation and policy’ and ‘1. green pharmacy’ are the best scoring strategies and will be applied to the case studies. More on the discussion of the MCA and sensitivity analysis can be found in chapter 9.

Table 6-3 Result of the sensitivity analysis

	Weighted score	Un-weighted	costs = 0	Sustainability = 0	Applicability = 0	costs/sustainability = 0	costs/applicability = 0	Sustainability/ applicability = 0	Effectiveness doubled
1. Green pharmacy	0.68	5.00	0.36	0.59	1.26	0.05	0.93	1.60	1.00
2. Awareness in use and prescription	0.61	2.60	0.12	0.54	1.40	-0.26	0.81	2.00	0.47
3. Legislation and policy	1.01	7.80	0.72	1.06	1.32	0.66	0.84	1.80	1.07
4. Green agriculture, greenhouse farming and cattle breeding	0.46	4.80	0.33	0.42	0.68	0.21	0.57	0.80	0.38
5a. Decentralised collection and treatment of urine	-0.72	-7.60	-0.40	-0.82	-1.01	-0.39	-0.42	-1.60	-0.52
5b. Centralised collection and treatment of urine	-0.57	-4.40	-0.20	-0.61	-1.01	-0.07	-0.43	-1.60	-0.40
6. Separate and decentralised collection and treatment of wastewater on residential scale	-0.55	-8.00	-0.47	-0.60	-0.61	-0.49	-0.42	-0.80	-0.35
7. Separate collection and treatment of hospital wastewater	-0.11	0.40	0.13	-0.04	-0.56	0.37	-0.32	-0.80	0.01
8. Improvement of WWTP	0.31	6.40	0.71	0.49	-0.49	1.20	-0.18	-0.80	0.57
9. Improvement of DWTP	0.30	7.00	0.69	0.45	-0.44	1.13	-0.09	-0.80	0.49

Green: good score, orange: moderate score, red: poor score

7 Case study I: Bethunepolder

The theoretical information discussed in the previous chapters is applied on two cases, which are the groundwater extraction area Bethunepolder and the surface water extraction area Andijk. For both cases a water and mass balance is composed, to provide an insight into the sources of the organic micro pollutants. The future scenarios for emission of OMPs and the best two strategies, which resulted from the MCA, are applied on the balances to see the influence of the trends and strategies. This chapter is concerned with the case study Bethunepolder, which is a groundwater system that depends on the seepage water in the polder.

7.1 Bethunepolder

The Bethunepolder is a polder near Utrecht, bordering the Loosdrechtse Plassen in the north and surrounding polders the south, east and west (figure 7-1). This polder is chosen as case study, because it fulfils different roles: agriculture, living, nature and drinking water extraction area. The polder is managed by Waternet and is situated within the River Basin District Rijn West. The Bethunepolder covers an area of 537 ha, of which about 382 ha is reserved for nature and 155 ha is used for agriculture and living. Since 1887 the polder is a land reclamation where the ground level is about 3 meters lower than of the surrounding polders and the water table of these polders. This results in an upward movement of the water in the Bethunepolder (seepage, figure 7-2). Because of the low resistance of the ground, the seepage is locally more than 20 mm/d (RIVM, 2008a). Figure 7-3 shows the seepage from the surrounding polders to the Bethunepolder. At the borders of the polder the seepage water is coming from the polders close by, seepage water at the middle of the polder is coming from deeper groundwater, which originates from further away. More about the origin of the seepage water can be found in section 7.4.1. Surface water from the polder is pumped by the pumping station Bethune. With a capacity of two times 100 m^3/min it discharges on the Waterleidingkanaal, which transports the water to the drinking water production area. About 90% of the pumped water is seepage, the rest is rain water. There are no other sources of water. From the 31 M m^3 water that is discharged onto the Waterleidingkanaal yearly, 25 M m^3 is used for the production of drinking water. The surplus water discharges at an overflow to the Loosdrechtse Plassen (western part of polder Muyeveld, figure 7-1). The subsurface below the Bethunepolder consists mainly of peat. In the south eastern corner almost all peat is removed due to human use of peat as fuel. In this region sand is the most upper layer (RIVM, 2008a).

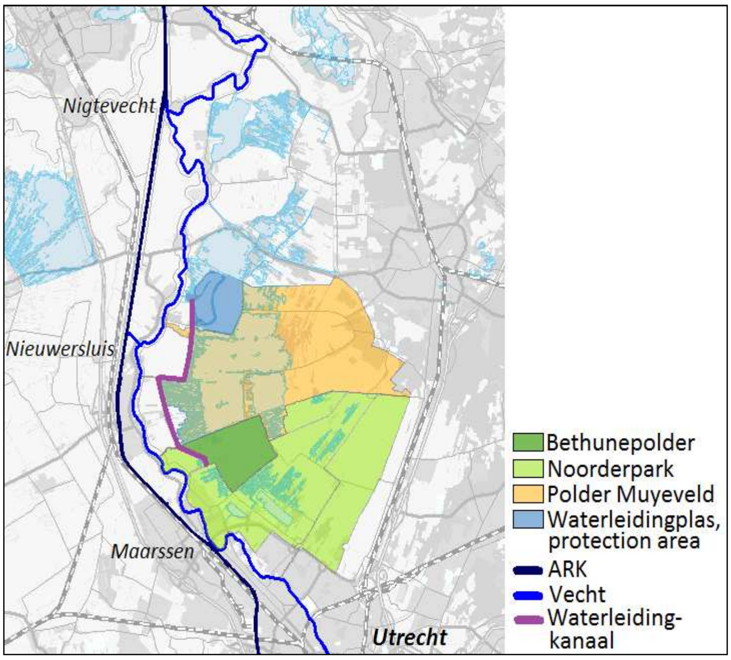


Figure 7-1 Overview of Bethunepolder and surrounding polders and surface waters

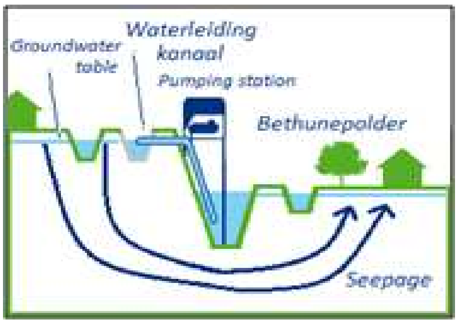


Figure 7-2 Cross section of Bethunepolder

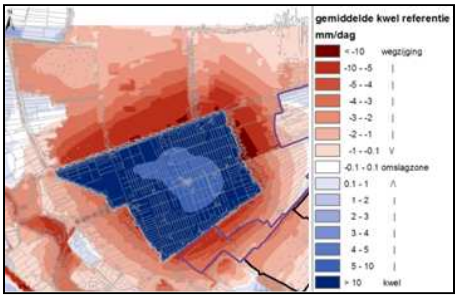


Figure 7-3 Infiltration and seepage (Witteveen+Bos, 2011)

In the Bethunepolder the functions agriculture, living, nature and drinking water extraction are combined. One of the main functions, drinking water extraction, will be discussed in the next paragraph. Only two farmers are still active in the polder, who have to meet the strict rules regarding the use of pesticides. No pesticides are allowed, except the use of glyphosate by local residents under certain conditions. The municipality Stichtse Vecht use only non-chemical weeding methods on pave areas (Provincie Utrecht, 2011).

7.2 Drinking water extraction

The water that is infiltrated in surrounding polders travels to the Bethunepolder, enters the polder as seepage water and is subsequently pumped into the Waterleidingkanaal. This channel transports the water from the Bethunepolder to the Waterleidingplas, a part of the Loosdrechtse Plassen about 6 kilometers north of the Bethunepolder (figure 7-1). Once it reaches the Waterleidingplas it is transported to the drinking water production plant Weesperkarspel. In very dry periods water from the Amsterdam Rijnkanaal (ARK) is let in, with a maximum of 5% of the total amount of water, because this water has a poorer quality (Provincie Utrecht, 2011).

The water transported to the Waterleidingplas is first injected with ferric chloride ($FeCl_3$), where after it coagulates and flows into the Waterleidingplas. There it stays for 100 days while bacteria, ammonium and organic compounds are degraded. To decrease the pH hydrogen chloride (HCl) is dosed. The last step in the treatment at the Waterleidingplas is rapid sand filtration. From here the water is transported to Weesperkarspel where advanced post-treatment takes place. Ozone (O_3) is dosed followed by softening with caustic soda (NaOH). To regulate the pH HCl is dosed after the softening. The following treatment step is activated carbon filtration. Again NaOH is dosed in combination with oxygen (O_2) and the water is transported to the slow sand filtration (figure 7-4) (Grefte, 2013).

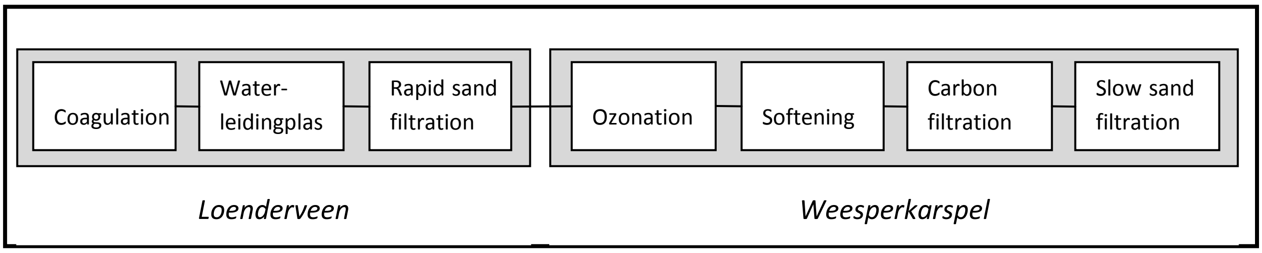


Figure 7-4 Treatment scheme

7.3 Water quality and composition

7.3.1 Composition of the water

The surface water quality in the Bethunepolder is influenced by the seepage water. It has a low concentration sulphate, chloride and oxygen, but it has a high concentration of nutrients, calcium and magnesium. The water is turbid due to seepage and short residence time of the surface water in the polder. These low concentrations of sulphate make the water less aggressive towards peat and organic compounds and this results in less intern eutrophication than water from the Rhine (RIVM, 2008a). Waternet carried out two studies to determine which OMPs are present in and around the Bethunepolder, in what concentrations and where they are coming from. More information on the measurement locations and detected compounds can be found in appendix 7-1. Each group of OMPs is discussed below.

Pharmaceuticals and X-ray agents

For pharmaceuticals there are no regulations in the Drinking Water Decree. These type of OMPs are not detected in the Waterleidingplas. Concentrations of pharmaceuticals above the precautionary limits of RIWA (section 3.1) are found in ARK, Vecht and incidentally in the groundwater and surrounding polders.

Domestic tracers

Artificial sweeteners and caffeine are used as tracer compounds, because they only originate from human activity. Only acesulfame-K and caffeine are measured above RIWA limits and only in the groundwater and in the ARK, Vecht and in the surrounding polders. On other locations these measurements are not carried out.

Industrial chemicals

The problem of presence of chelating agents in surface water is that they release heavy metals from sludge and increase their mobility. Chelating agents are used as replacement for phosphates in detergents. In the ARK, Vecht, groundwater and after the pumping station concentrations of chelating agents are measured higher than recommended by RIWA. Plasticizers are exceeding the precautionary limits of RIWA after the pumping station and in the Waterleidingplas. The only OMPs, other than chelating agents and plasticizers that are found in the groundwater of the Bethunepolder, are components of oil.

Pesticides and antifouling

In the groundwater of the Bethunepolder concentrations of bentazone and MCPP above the limits of the Drinking Water Decree are found. At the measurement point after the pumping station these concentrations are no longer exceeding the limit. In ARK water only AMPA is incidentally found.

7.3.2 Limits for drinking water and surface water

In section 4.2 the (precautionary) limits and standards by law, Benchmark Quotient and PNEC are described. Table 7-1 shows a summary of these limits. From the BQ calculations it results that carbamazepine, iopromide, metformin and MTBE form a potential risk for the production of drinking water. For those compounds the additional limit of 1.0 µg/L in drinking water applies (MTBE has already a limit of 1.0 µg/L (Dutch Government, 2009b). For surface water intended for the production of drinking water only limits are set by law for pesticides (each individual pesticide 0.1 µg/L and all pesticides combined 0.5 µg/L).

Table 7-1 Benchmark Quotient calculations for the selected compounds at the Bethunepolder system in the current situation and in future scenarios REST and STEAM

				Current	Rest	Steam	Limits sw for production of dw[1]	Target values sw for production of dw[2]	Target values sw (PNEC)[3]
	TDI [µg/kg/day]	pGLV [µg/L]	$c_{max, BP}$ [µg/L]	BQ_{BP} [-]	BQ_{BP} [-]	BQ_{BP} [-]	[µg/L]	[µg/L]	[µg/L]
ACEK	25000	87500	5.10	5.83E-05	6.41E-05	6.70E-05	-	1.0	-
AMPA	300	1050	1.00	9.52E-04	9.76E-04	1.01E-03	0.1	0.1	-
BENT	100	350	0.23	6.57E-04	6.74E-04	6.97E-04	0.1	0.1	-
CAFF	300	1050	0.51	4.86E-04	7.14E-04	7.63E-04	-	1.0	182
CARB	0.34	1.19	0.51	**0.43**	**0.61**	**0.65**	1.0[4]	0.1	0.42
GLYF	300	1050	0.59	5.62E-04	5.76E-04	5.96E-04	0.1	0.1	-
IOPR	21	73.5	1.10	**0.015**	**0.016**	**0.016**	1.0[4]	1.0	256
METF	79	277.9	3.20	**0.012**	**0.016**	**0.018**	1.0[4]	0.1	511
MTBE	300	1050	62.00	**0.059**	**0.059**	**0.065**	1.0	1.0	2600
NDMS	-	-	-	-	-	-	0.1	0.1	140
SULF	130	455	1.00	2.20E-03	2.96E-03	3.08E-03	-	0.1	0.118
Pesticides combined							0.5	-	-

[1] (Dutch Government, 2009b), [2] (IAWR, 2008), [3] section 4.2, [4] based on BQ value (section 4.2)

To test the models on water quality regarding OMPs target values for the remaining substances are used. These are target values determined by the DMR Memorandum (IAWR, 2008). The target value for water intended for the production of drinking water is 1.0 µg/L for acesulfame-K, caffeine, iopromide and MTBE. The target value for all other compounds is 0.1 µg/L. To test the risk for aquatic life the PNEC values are used as target values in surface water. Target values in surface water with no predicted negative effects on aquatic life are found for caffeine, carbamazepine, iopromide, metformin, MTBE, N,N-DMS and sulfamethoxazole. The concentrations vary between 0.118 and 2600 µg/L. This is only done for water bodies intended for the production of drinking water. Finally, for each compound the lowest limit applies.

7.4 Sources of OMPs

Since the Bethunepolder is a groundwater driven system the most important source of pollution with OMPs is transport through groundwater. These OMPs have entered the groundwater through point sources, diffuse sources or line sources on the surrounding land (appendix 7-1). Surface water is an indirect source since the water first has to infiltrate to the groundwater before entering the Bethunepolder as seepage water.

7.4.1 Groundwater

Seepage water entering the Bethunepolder originates from infiltrated water of other polders, which has travelled through the groundwater to the Bethunepolder. An existing groundwater model of Waternet is used for the calculations of the origin of the seepage water of the Bethunepolder. The main contributors to groundwater seepage in the Bethunepolder are the Loosdrechtse Plassen, Kivietsbuurt, Vecht and Tienhovense Plassen (appendix 7-2). It is remarkable that water is not originating from the Utrechtse Heuvelrug, since this is a higher area east from the Bethunepolder. The impact of a source and the contribution to the total amount of seepage depends on the seepage intensity. For each source of origin the intensity is determined. Within the Bethunepolder it varies from 2.5 to 25 mm/d, where the highest intensity occurs at the borders of the polder. Another important aspect is the age of the water seeping to the Bethunepolder. Areas with water with a residence time shorter than 50 years are vulnerable, because mobile pollutants like pesticides have too little time to degrade. Locations with a residence time longer than 50 years are less vulnerable for mobile substances (Provincie Utrecht, 2011). Relatively new substances (like ETBE) are not present at the locations with seepage water with a long residence time, because these substances are recently introduced in the environment.

7.4.2 Surface water

Around the Bethunepolder three large water bodies are situated. These are the Vecht, ARK and Loosdrechtse Plassen. The Bethunepolder itself is only fed by seepage and rain water, where the seepage water is originating from groundwater around the Bethunepolder.

The Vecht is a river flowing from Utrecht to the IJmeer. It is the most important channel used for discharging excess water from the polder (figure 7-1). The Vecht is fed by water from the city of Utrecht in the south and in dry periods by water from the IJmeer in the north, where the flow direction from Utrecht till Nigtevecht is northward and between Nigtevecht and the IJmeer is southward (brackish water). The excess water coming from the IJmeer is discharged on the ARK at Nigtevecht and is not intruding more southward. The sewage treatment plants of Utrecht and Maarssen are discharging effluent on the Vecht, which negatively influences the water quality (table 7-2 and appendix 7-1).

The ARK flows from south to north through the area of AGV, from Tiel through Utrecht to Amsterdam. When water supply from the Waterleidingkanaal to the Waterleidingplas is insufficient, water from the ARK is let in into the Waterleidingplas. This inlet is at Nieuwersluis (figure 7-1). Maarssen, Breukelen and Nigtevecht are the locations where the ARK is in open connection with the Vecht, whereby the water bodies influence each other's water quality. The sewage treatment plants of Breukelen, Maarssenbroek, Leidsche Rijn, Houten, Wijk bij Duurstede and De Meern are discharging effluent on to the ARK. The influence on the water quality is relatively small because the discharges are small compared to the total discharge of the ARK (table 7-2). The influence of the ARK on the Bethunepolder is also small, because there is no direct connection from the ARK to the Bethunepolder, but only by groundwater flow. Both ARK and Vecht originate from the river Rhine, which enters the Netherlands at Lobith. Within the scope of this project, the area that is considered to be influencing the water quality of the Bethunepolder consists of ARK, Vecht, polder Muyeveld and Noorderpark (shaded area figure 7-1).

Table 7-2 WWTP data 2008 (2007 for Leidsche Rijn) of WWTPs with potential influence on water quality (Waternet, 2010)

WWTP	Cap. p.e. 136 gr BOD	Owner	Discharging on	Discharge [m^3/d]
Maarssen	25,000	Waternet	Vecht	3,543
Utrecht	530,000	HDSR	Vecht	69,189
Breukelen	35,000	HDSR	ARK	4,647
Maarssenbroek	60,000	HDSR	ARK	6,558
Leidsche Rijn	92,600	HDSR	ARK	6,300
Houten	91,000	HDSR	ARK	11,914
Wijk bij Duurstede	33,500	HDSR	ARK	*
De Meern	53,000	HDSR	ARK	*
Bunnik	42,000	HDSR	Kromme Rijn	*
ARK	Measured discharge		[m^3/d]	2,907,690
Vecht	Weerdsluis/Rode Brug		[m^3/d]	370,559

** Data unknown*

The third large water body is the Loosdrechtse Plassen. It is part of polder Muyeveld, which is situated north of the Bethunepolder and besides the lake, it also covers an area of land (figure 7-1). Water shortage in the Loosdrechtse Plassen is compensated with supplementation water from the ARK at Nieuwersluis, from which phosphorus is removed, and water from the Bethunepolder when more water is pumped than needed at the Waterleidingplas for the production of drinking water. It is assumed that this water body is not as heavily polluted as the ARK and the Vecht, since no WWTPs are discharging on it. A flexible water table management reduces the amount of inlet water from the ARK.

The area south of the Bethunepolder is the Noorderpark and consists of the polders Oostelijke Binnenpolder van Tienhoven, Polder Achttienhoven, Polder Maarssenveen-Westbroek and Gansenhoef (appendix 7-2). Because the surface water in this area is not in connection with the Bethunepolder and the lakes are small compared to those of polder Muyeveld, this area is not considered as surface water of influence. Nevertheless, the infiltrated groundwater from this area is taken into account to make the balance as correct as possible.

7.5 Models

The groundwater model described previously is incorporated in the newly composed water and mass balance. In this paragraph the composed models are discussed. A balance is based on a model, which is a simplified view of the actual situation. Three sub-models are combined to form one integrated model that describes the behaviour of the water and substances between Lobith and the seepage water in the Bethunepolder. These sub-models are:

- Within the surface water balance all incoming and outgoing discharges between Lobith and Nieuwersluis are modelled. This sub-model results in certain discharges at the ARK and Vecht at Nieuwersluis. These discharges are compared to measured discharges and with that the validity of the model is determined.
- In the mass balance of OMPs the incoming discharges of the water balance are combined with the measured concentrations at these points. This sub-model results in calculated concentrations of OMPs

at all other points in the mass balance. To check the validity of this sub-model the calculated concentrations are compared to the actual measured concentrations at the specific points.

- In the groundwater balance the sources of the seepage water in the Bethunepolder are determined.

Finally, the calculated concentrations from the mass balance are multiplied by the seepage water and the total load of each OMP in the Bethunepolder is determined. This is the integrated model.

7.5.1 Surface water balance

The water balance is composed in Excel and consists of all incoming and outgoing rivers, branches and other fluxes in the target area. The target area starts at Lobith, where the river Rhine enters the Netherlands. Branches to the rivers Waal and IJssel are not part of the model. From Lobith the water flows to Wijk bij Duurstede, where an incoming branch (ARK) is mixed with the three outgoing branches (ARK, Lek and Kromme Rijn). The Lek flows to the border of the target area, Nieuwegein, where the branches Lekkanaal and Vaartsche Rijn are part of the model (no connection to ARK) (figure 7-5). The WWTP of Bunnik discharges its effluent on the Kromme Rijn, whereafter the river is combined with the Vaartsche Rijn, which is a small flow from an old canal between the Lek and the city of Utrecht. Two other connections between the Kromme Rijn and the ARK are situated in the city of Utrecht at Oog in Al and Merwedekanaal. Of these three small streams hardly any data are available and for this reason they are combined to one surplus stream that discharges from the Kromme Rijn into the ARK. After the location of this discharge, the Kromme Rijn receives the effluent of the WWTP of Utrecht and flows to Amsterdam as the river Vecht. The ARK flows along Utrecht, where the only connection with the Kromme Rijn and Lek is at the point where the surplus water of the city of Utrecht (Kromme Rijn) flows to the ARK (Hoogheemraadschap De Stichtse Rijnlanden). A second modelled connection between the Vecht and the ARK is located at Maarssen, where the WWTP of Maarssen is discharging on the Vecht. At this location a sluice is open almost all the time (Stichting Recreatietoervaart Nederland, 2008). Here 60% of the water from the Vecht flows into the ARK and 40% remains as Vecht. At Nieuwersluis there is also a connection between the ARK and the Vecht, but this connection is only open in very dry periods. Water can be let in the Loosdrechtse Plassen or in very exceptional cases into the Waterleidingkanaal. This has not happened the past years, so this is neglected in the model. Between Utrecht and Nieuwersluis the WWTPs of Leidsche Rijn, De Meern, Breukelen and Maarssenbroek are discharging effluent on the ARK. In the model these effluents are combined with the effluent of WWTPs of Wijk bij Duurstede and Houten to one discharge.

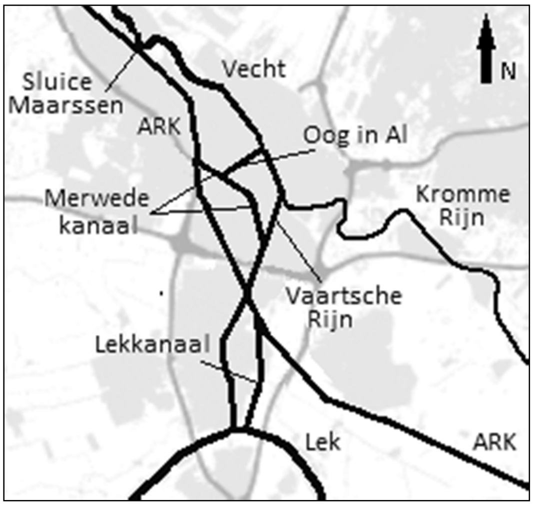


Figure 7-5 Overview of Utrecht

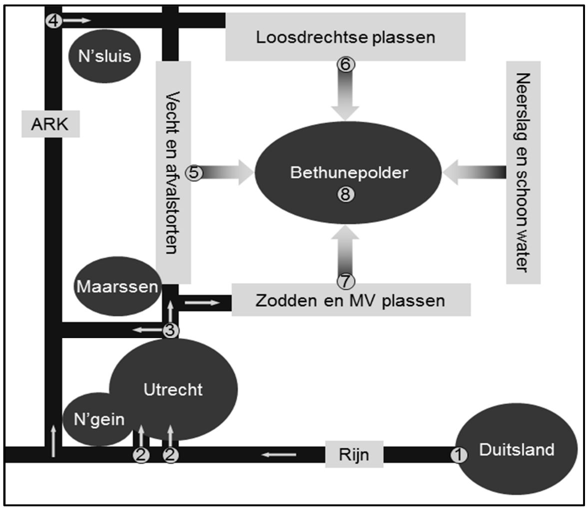


Figure 7-6 Water balance (Waternet, 2013)

A part of the water from the Vecht is discharged into the polder areas Zodden and Maarsseveense Plassen and a part of the ARK is mixed with the Vecht and discharged into the Loosdrechtse Plassen at Nieuwersluis, which are both situated close to the Bethunepolder. The last incoming flow is considered to be precipitation and runoff of the Utrechtse Heuvelrug, which is a moraine area remaining from the second last ice age. Figure 7-6 shows an overview of the whole water balance and figure 7-7 shows the schematisation of the model.

The water balance is modelled over the period 2003-2012, where the distinction is made between the wet season (October-March) and the dry season (April-September). Once the balance is applied the calculated discharges can be compared to the measured values at the ARK and Vecht at Nieuwersluis and the balance can be adjusted if needed. The balance can be used to test composed future scenarios and strategies to reduce the amount of OMPs in the environment.

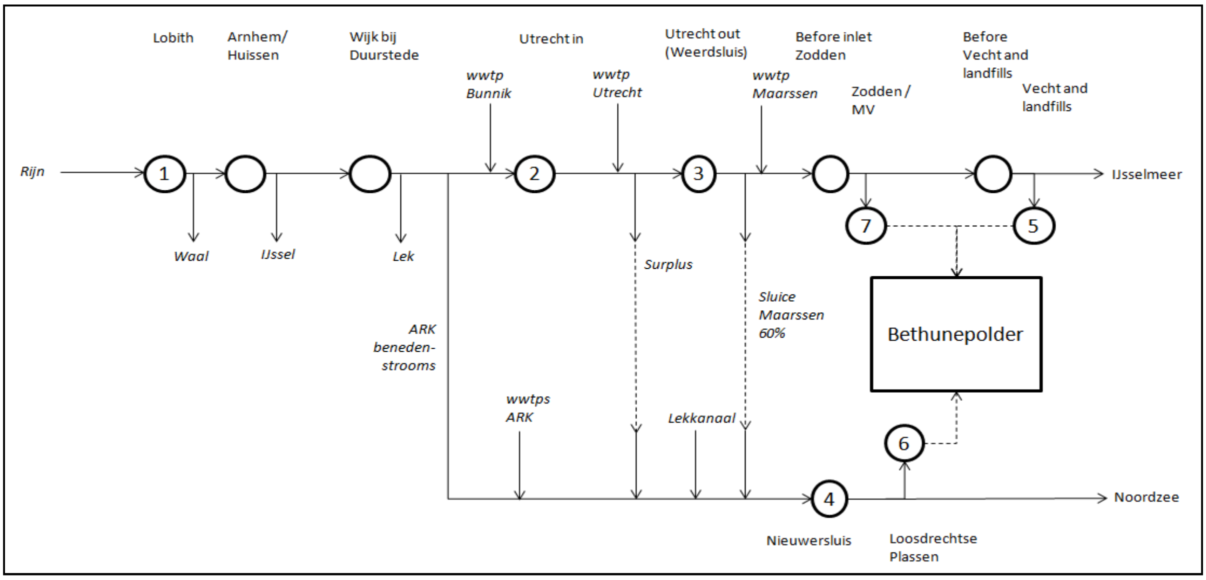


Figure 7-7 Schematisation of the model

7.5.2 Groundwater model

The influences of the different groundwater flows on the water quality within the Bethunepolder are simulated with the groundwater model. The input of the model is the total seepage within the Bethunepolder. This results from an analysis of data from a groundwater model composed by Waternet. The output of this model is a map of seepage intensity [m/d] of the Bethunepolder (fluctuating from 0.0225 m/d at the border of the polder to 0.0025 m/d at the centre) and a map of sources of the seepage water [m^2]. These maps are combined to determine the total seepage per source [m^3/d] (table 7-3 and appendix 7-2 for details about this procedure). Some sources are merged together to create six global sources (figure 7-8). These sources are comparable with the sources from the surface water model in figure 7-6. Precipitation is the average yearly precipitation expressed in [m^3/s] at De Bilt over 2010-2012, which is the intensity [m/s] multiplied by the surface area [m^2]. In the groundwater model no distinction is made between the wet and the dry season, but a yearly average seepage and yearly average concentrations are used. This is done as a result of the long residence time of the groundwater.

Table 7-3 Total seepage per source

	Seepage [m^3/s]		Seepage [m^3/s]
Loosdrechtse Plassen	0.200	Vecht	0.058
Precipitation	0.161	Molenpolder (nature)	0.043
Taartpunt (nature)	0.136	Residential area of Maarssen	0.018
Maarsseveense Plassen and Zodden	0.059		

To determine the load of OMPs of each specific source the seepage intensity [m/s] needs to be multiplied by the surface area [m^2] and the corresponding concentration [mg/L or mg/m^3] of this source to get the total load [mg/s]. Concentrations of OMPs at Loosdrechtse Plassen, Maarssenveense Plassen and Zodden, Vecht and residential area of Maarssen are determined by the mass balance of OMPs. Precipitation, Taartpunt (nature) and Molenpolder (nature) are considered not to be contaminated with OMPs.

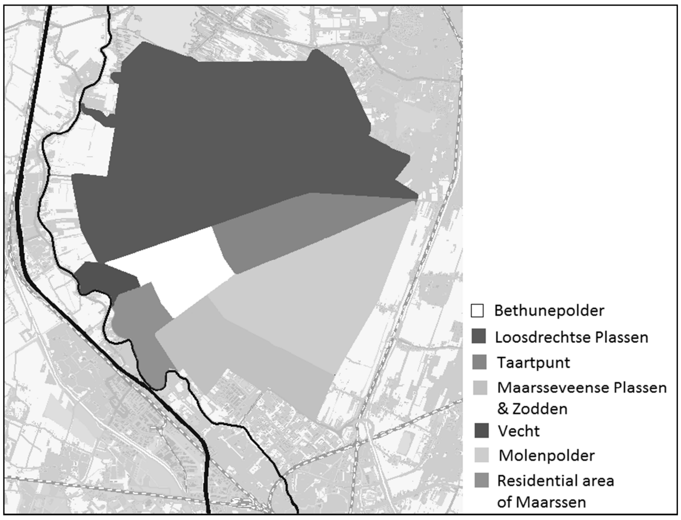


Figure 7-8 Sources of groundwater

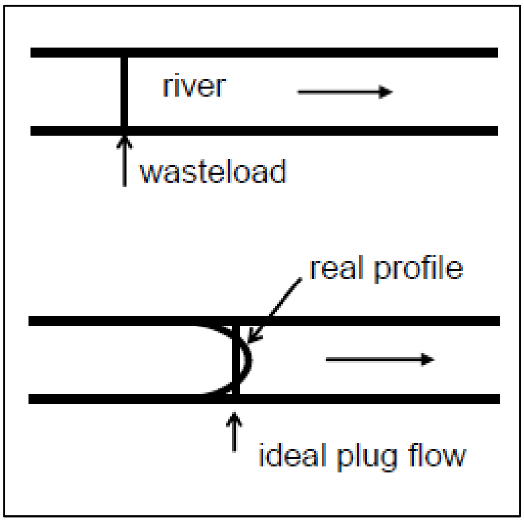


Figure 7-9 Schematic representation of 1-D plug flow (Baptist, 2006)

7.5.3 Mass balance of OMPs

The mass balance of OMPs is very similar to the surface water balance. The concentrations of OMPs at Lobith are combined to the surface water balance to calculate the concentration at downstream locations. Concentrations at all other incoming streams must be known or estimated to complete the model. This is done by using measurements, reference values or the concentration of a comparable location. In figure 7-6 the locations at which the concentrations of OMPs are calculated are presented with a green circle. The calculated concentrations can be compared to the measured values to determine the validity of the mass balance.

In water quality modelling the decay rate of a certain type of pollutant is very important. In this section two types of modelling mechanisms with and without the influence of degradation are compared to see the influence. This is done to determine whether the assumptions made in the models are valid (paragraph 7.5.5).

One-dimensional plug flow

The plug flow model is based on the assumption that a discharged substance mixes instantaneously over the cross-section, but will not mix in the longitudinal direction (figure 7-9). This method is applied to rivers or river segments. The method can be applied with or without decay.

Without decay

Persistent micro pollutants can be seen as conservative substances. The concentration of conservative, or non-degradable and non-adsorbable, substances is determined by dilution only. The concentration downstream of a waste load can be estimated using the following equation:

$$C_p = C_i + \frac{\sum W}{Q_p} \qquad (7.1)$$

Where:
C = concentration [ML^{-3}]
Q = flow [$L^{3}T$]
W = waste load [MT^{-1}]
(Baptist, 2006)

With decay

The formula that describes first-order decay in a simple system is:

$$C_p = C_0 * e^{-k*\tau} \tag{7.2}$$

Where:
k = first-order loss rate constant [T^{-1}]
τ = travel time [T]
(Baptist, 2006)

The concentration at the end of a given plug-flow river segment can be estimated by using the following equation:

$$C_P = \frac{(M_0 * e^{-k*\tau_R}) + \sum(M_i * e^{-k*\tau_i})}{Q} \tag{7.3}$$

Where:
M_0 = mass loading from prior segment [MT^{-1}]
M_i =mass loading from spill [MT^{-1}]
(Anderson *et al.*, 2004)

The first-order loss rate constant, k, as used in equation (7.2 and 7.3) is a composite rate that is calculated as the sum of all relevant first-order loss rate constants as might be associated with biodegradation, hydrolysis, photolysis, evaporation, sedimentation, and so forth.

The calculations with decay are only performed on four OMPs, since no other decay data were found. Table 7-4 shows the decay rate of caffeine, carbamazepine, metformin and MTBE. For this reason in the final integral model for all compounds no decay is assumed, although it is not clear yet what method fits better to the measurements: with or without decay. The 1-D plug flow model (eq. 7.1 and 7.3) is applied on the surface water balance of the Bethunepolder, because this is a river model. In the groundwater system a comparison is made between the situation with and without decay, by applying eq. 7.2.

Table 7-4 Decay rate of OMPs

	Decay rate [day^{-1}]
Caffeine	0.005[1]
Carbamazepine	0.0088[2]
Metformin	0.0001[1]
MTBE	0.001[3]

[1] (Anderson et al., 2004), [2] (Cunningham et al., 2010), [3] (Prince, 2000)

7.5.4 Integrated model

In the integrated model the three previously described models are combined. From the groundwater model the sources of origin of the seepage water are determined and they are interacting with the surface water balance and the mass balance (figure 7-10).

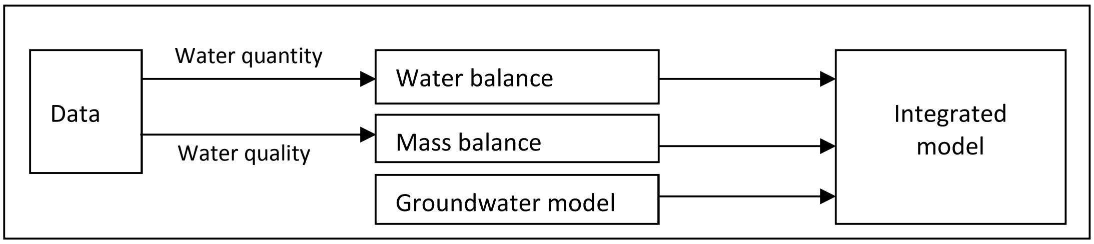


Figure 7-10 Relation balances and models to integrated model

7.5.5 Assumptions

In the integrated model some assumptions are made to simplify the real situation. These assumptions are:

1. There is no degradation and adsorption. This means that the compounds present in the water behave like infinite persistence.
2. It is a well-mixed system (plug flow). The measured concentrations are representative for the whole part of the water body. Discharges from a source are mixed instantaneously.
3. Only the discussed discharges are taken into account. Other discharges or intakes by farmers or factories, pumping stations or small water bodies are disregarded, due to missing data.
4. Measured concentrations are representative. This means that the concentrations measured in surface water bodies are equal to the concentrations of these sources in the groundwater and in the seepage water of the Bethunepolder. For this assumption 1 is also important. This is assumed in order to combine the groundwater balance with measured concentrations from the corresponding sources, since the Bethunepolder is being fed by groundwater. This assumption is not correct, but within the scope of the project it is not possible to determine the behaviour of the 11 OMPs during groundwater transport over a long period (1-100 years). For this reason it is expected that the calculated concentrations of the seepage water of the Bethunepolder are higher than the actual measured concentrations in the groundwater of the Bethunepolder and thus in the Waterleidingkanaal.
5. The modelled years are representative. No extreme dry or wet years occur, except an extremely dry spring and an extremely wet summer in 2011 (KNMI, 2013). It is assumed that this has no significant influences since it levels out. This is also the case for the used measurement data.

7.5.6 Water quality data

Water quality measurements are available from different institutions. In this case data from Rijkswaterstaat (RWS) and Waterbase, Association of River Water Supply Companies (RIWA), measurement and monitoring network Waternet, Het Waterlaboratorium (HWL) commissioned by Waternet and Hoogheemraadschap De Stichtse Rijnlanden (HDSR) are used (Rijkswaterstaat, 2013; RIWA, 2013; Waterbase, 2013). From all water quality data collected average concentrations are determined. Yearly averages are calculated for the period 2008-2012, where only 2011 had an extremely dry spring and an extremely wet summer (KNMI, 2013). It is assumed that this has no significant influences since it levels out.

Data

Figure 7-11 shows the measured concentrations of bentazone, caffeine, iopromide and N,N-DMS. Although bentazone is not permitted in the Bethunepolder, this pesticide is still found in the groundwater and seepage water. When looking at the graph of caffeine, it is remarkable that the concentration at Utrecht IN is much higher than at Utrecht OUT, and that the concentration at the Vecht is higher than at Utrecht OUT. This can be explained by the fact that of both Utrecht OUT and Vecht only one measurement is available, which is measured during the summer. From caffeine measurements at other locations it can be seen that the concentrations in summer are much lower than in winter. The iopromide measurements at Utrecht OUT and Vecht are also performed only once, which could cause the contradictory results at these locations. From these graphs it can be seen that the measured concentrations per compound of the incoming streams are of the same order of magnitude. The only compound for which the difference between the concentrations of all incoming streams is more than one order of magnitude, is N,N-DMS at the Loosdrechtse Plassen. This high value can be explained by the presence of water recreation in that area. The results from the models (next paragraph) should also be in the same order of magnitude as these measured concentrations, otherwise the model would not be correct. Graphs of other compounds can be found in appendix 7-3B.

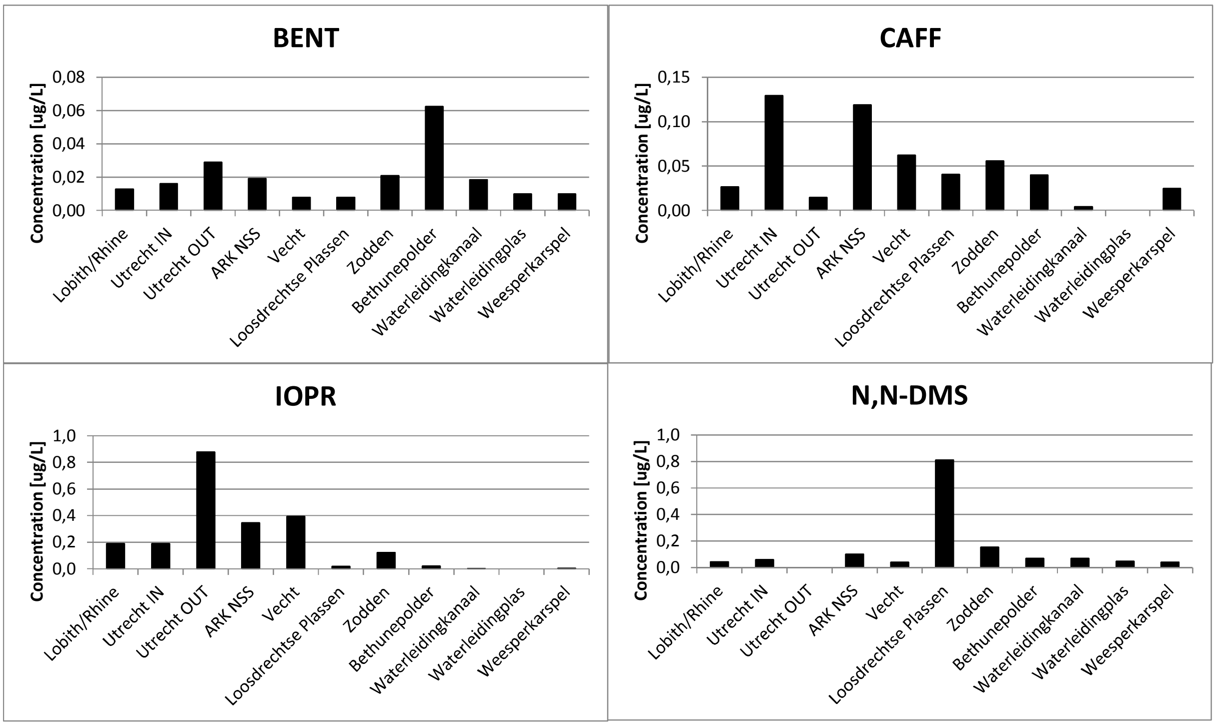


Figure 7-11 Measured concentrations of bentazone, caffeine, iopromide and N,N-DMS

Data processing

Of all available measurement series seasonal averages of the wet (October-March) and the dry (April-September) season are calculated. Since a static model is used there is only one value for the wet and one value for the dry season derived. Data measured below the detection limit are assumed to represent a value half of the detection limit. In table 7-5 the water quality data are given (also appendix 7-3A). In this table values are marked when more than 1/3 of all values on a measurement point are below the detection limit, or when only one measurement value is available. This gives an indication of the reliability of the data. Almost all values of the table are reliable.

Table 7-5 Water quality data [µg/L]

	ACEK	AMPA	BENT	CAFF	CARB	GLYF	IOPR	METF	MTBE	NDMS	SULF
1. Lobith	1.890	0.349	0.013	0.027	0.070	0.036	0.190	0.874	0.135	0.045	0.038
2. Utrecht IN	1.190	0.408	0.016	0.130	0.070	0.048	0.189	0.650	0.158	0.060	0.068
3. Utrecht OUT	2.575	0.348	0.029	0.015	0.103	0.084	0.878	0.965	0.065	0.000	0.027
4. ARK Nieuwersluis	3.300	0.464	0.019	0.119	0.063	0.052	0.346	0.573	0.086	0.102	0.029
5. Vecht and landfills	10.050	0.202	0.008	0.062	0.080	0.079	0.394	1.700	0.120	0.040	0.076
6. Loosdrechtse Plassen	1.375	0.124	0.008	0.041	0.018	0.012	0.019	0.065	0.473	0.810	0.000
7. Zodden	1.700	0.048	0.021	0.056	0.040	0.080	0.123	0.080	0.057	0.155	0.002
8. Bethunepolder	0.410	<0.100	0.063	0.040	0.043	0.022	0.022	<0.05	0.030	0.070	<0.01
100. Waterleidingkanaal	0.440	0.000	0.019	0.004	0.003	0.000	0.001	0.014	0.048	0.070	0.005
110. Waterleidingplas	▨	0.050	0.010	▨	▨	0.025	▨	▨	0.050	0.050	▨
120. Weesperkarspel	▨	0.050	0.010	0.025	0.025	0.025	0.005	▨	0.040	0.040	0.005

□	*reliable value*	▒	*more than 1/3 of data is below detection limit*
░	*only 1 measurement available*	▨	*missing value*

Missing values

Not all substances are measured at all locations. Missing values are replaced by the averages of other locations as close as possible to the missing value. Of the WWTPs discharging on the ARK, Kromme Rijn or Vecht no effluent measurements are available. The missing measurement data are replaced by indicators of other WWTPs. Table 7-6 gives an overview of data from all found WWTPs (international), data from a STOWA project on pharmaceuticals in the environment, data from a study on the drinking water extraction area of Utrecht and data of all WWTPs in the Netherlands. These values are used as reference values. The last column shows the average concentration per compound in the effluent of a WWTP with these reference values, assuming a daily use of 150-180 L/p (Lenntech, 2013).

Table 7-6 Indicators WWTP effluent

	All [1]			STOWA [2]	Gebiedsstudie Utrecht [3]	All in NL [4]	WWTP effluent
	average [g/p/y]	min [g/p/y]	max [g/p/y]	average [g/p/y]	average [g/p/y]	average [g/p/y]	average [µg/L]
Acesulfame-K	1.507	0.602	2.519				25.525
AMPA	0.186	0.081	0.279			0.186	3.397
Bentazone							
Caffeine *	0.035	0.002	0.293		0.021	0.021	0.384
Carbamazepine	0.037	0.003	0.074	0.050	0.043	0.042	0.767
Glyphosate	0.272	0.189	0.460			0.272	4.968
Iopromide	0.670	0.443	0.896			0.896	16.365
Metformin	0.459	0.145	0.999	0.525	0.446	0.459	8.384
MTBE	0.134	0.001	0.347				2.447
N,N-DMS							
Sulfamethoxazole	0.012	0.009	0.016	0.010	0.012	0.012	0.219

** Caffeine measurements in the Netherlands are below the detection limit; half of the detection limit is considered to give an acceptable assumption*

[1] *(Buerge et al., 2009; Buerge et al., 2003; Grontmij, 2009; Kumar et al., 2010; Rosell et al., 2006; Scheurer et al., 2010; STOWA, 2011a; b; Ternes et al., 2000)*

[2] *(Kumar et al., 2010)*

[3] *(STOWA, 2011a)*

[4] *(Grontmij, 2009; 2010; Kumar et al., 2010; STOWA, 2011a; b)*

Only Bentazone and N,N-DMS result in no effluent values. This can be explained by the fact that these compounds are in general not discharged by the sewer system. All pharmaceuticals give representative values. The values for iopromide, glyphosate and AMPA measured in the Netherlands are comparable with measurements at other places. The measurement data for caffeine differ significantly (order of magnitude 10 or more) between all measurements. This can be explained by the fact that caffeine measurements are really sensitive to the analytical procedure. Finally, acesulfame-K and MTBE are not measured in the Netherlands at all. A reason for this could be that acesulfame-K is a relatively new substance and is assumed to be harmless to the environment and human health. MTBE is a compound that is mainly transported into the WWTP by rainwater discharge. To calculate the WWTP effluent discharge in the water balance, the values of ‘all in NL’ are used. The missing values are replaced by the average values of ‘all’.

7.6 Results and discussion

The results of the models are discussed based on the sub-models. Paragraph 7.6.3 contains the results of the integral model.

7.6.1 Results surface water and groundwater balances

Surface water balance

First the surface water balance is validated. The balance has two checks, where the calculated flow can be compared with the measured flow. These checks are at the Vecht and the ARK at Nigtevecht. Appendix 7-4A provides a table of the calculated concentrations in the dry and wet season compared to the measured concentrations. At the check at the Vecht the calculated discharges are somewhat higher than the measured discharges for both seasons. This exceedance is less than 2.5%. For the check at the ARK this difference is somewhat larger. In summer the measured discharge is about 3% lower than calculated and in winter the measured discharge is about 15% higher than the calculated discharge. From these both checks it can be concluded that the water balance fits very well (figure 7-12).

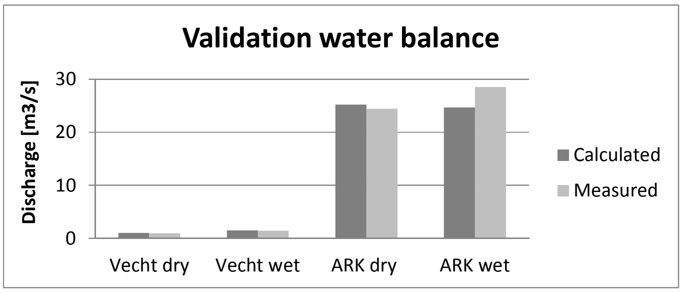


Figure 7-12 Validation water balance

Figure 7-13 shows the distribution of the discharge over the different origin sources. The first graph (A) shows that at the point where the Kromme Rijn enters the city of Utrecht almost 100% of the discharge originates from water from Lobith. At the point where the water leaves the city in the north at the Weerdsluis the WWTP of Utrecht contributes for more than 25% to the total amount of water (B). After the sluice at Maarssen, where a part of the Vecht water is transported to the ARK, the distribution is almost similar, only a relatively small amount of water originates from the WWTP Maarssen (C). The ARK after Utrecht consists mainly of water originating from Lobith, the Lekkanaal and the surplus water from the city of Utrecht (D). The last graph shows the situation where for the surplus water and the sluice in Maarssen it is determined which amount originates from Lobith, or the WWTPs Bunnik and Utrecht (E). For both the Vecht and ARK after Utrecht about 60-75% of the water originates from Lobith and thus from upstream of the Netherlands.

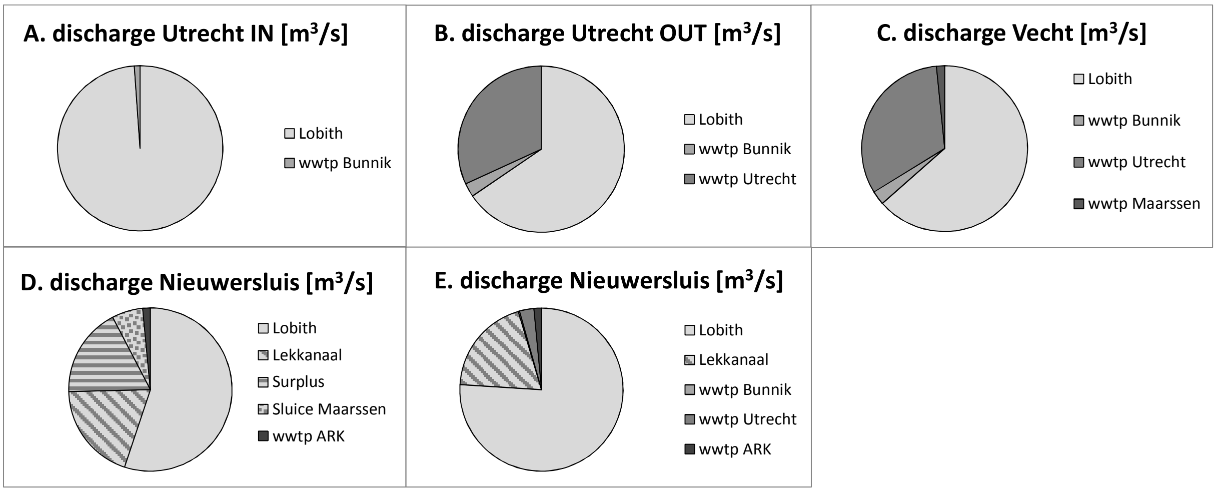


Figure 7-13 Distribution graphs of discharge in current situation of the Vecht (A, B and C) and the ARK (D and E)

Groundwater balance

From the groundwater balance the origin sources and the amount of seepage is determined. From figure 7-14 it can be seen that the main source of origin of discharge to the seepage water in the Bethunepolder is the Loosdrechtse Plassen, second is precipitation and third is the Taartpunt (nature). A smaller contribution is made by the Maarsseveense Plassen and Zodden, the Vecht and the Molenpolder (nature). The residential area of Maarssen contributes the least. See figure 7-8 for the location of these sources. Precipitation, the Taartpunt and the Molenpolder are considered to be clean contributors, because those are nature areas with water more or less free of OMPs.

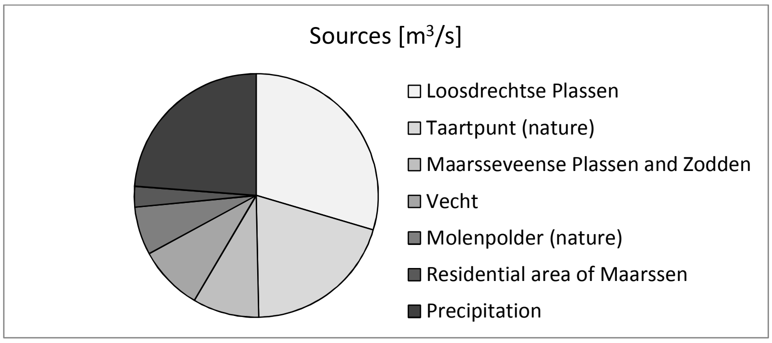


Figure 7-14 Distribution of the sources of water in the Bethunepolder

7.6.2 Results mass balance of OMPs

One-dimensional plug flow

The situation with and the situation without decay are applied to four substances (caffeine, carbamazepine, metformin and MTBE). These are the only substances of which a decay factor in water and soil was found (table 7-4). First the concentrations in the surface water system (Lobith till the Vecht after Utrecht) are calculated with eq. 7.1 (without decay) and eq. 7.3 (with decay). Thereafter the concentrations in the groundwater system at the Bethunepolder are calculated with eq. 7.2. The calculated concentrations are compared to the measured concentrations.

The river section from Lobith till the Vecht at Breukelen (in model called 'before inlet Zodden') is divided in five segments, based on the water balance. Each new segment starts where in the water balance a node is assumed. Of each segment the discharge and travel time is determined, where the travel time is calculated with a minimum flow velocity of 0.5 m/s. At the starting point at Lobith the measured concentrations are used. Besides this starting point the only incoming sources are the effluents of WWTPs Bunnik, Utrecht and Maarssen. Equations (7.1) and (7.3) are applied on the model.

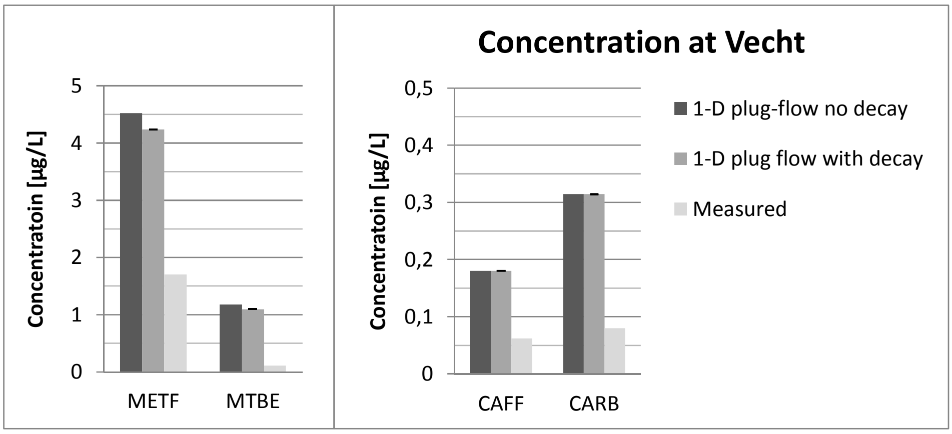


Figure 7-15 Comparison between calculated concentrations at Vecht with and without decay and measured concentrations (other compounds can be found in figure 7-17)

From the results in figure 7-15 it can be seen that the calculations of 1-D plug flow with and without decay are in the same order of magnitude for each of the four compounds. Carbamazepine has the largest difference of the four modelled OMPs, because it has the highest decay rate. Error bars (black lines) are shown in the figure to see the influence of the decay factor k, by using 0.5*k and 2*k. The influence of the decay factor is negligible, which is caused by the relatively short travel time (approximately 2 days).

Figure 7-16 shows the calculations of the decay in the groundwater system of the Bethunepolder. Equation 7.2 is used, with different travel times (τ=1 years, τ=10 years and τ=50 years). For metformin, carbamazepine and MTBE the calculated concentration without decay is higher than the measured concentration. For caffeine the measured concentration is higher. This could be caused by the difficulty in analysing caffeine samples (also see chapter 9). The figure also shows that the longer the travel time, the lower the calculated concentration. For metformin a travel time of 50 years approaches the measured concentration, where for carbamazepine and MTBE a travel time of 50 years results in too low concentrations. Similar to the previous calculations of the Vecht, the influence of the height of the decay rate is determined by applying decay rates of 0.5*k and 2*k. This is shows by the error bar. Contrary to the Vecht the height of the value k is important. A small difference in k results in noticeable changes in calculated concentrations. From this figure it can be concluded that the situation with decay in groundwater is more accurate than the situation without decay. Nevertheless, only of four substances a decay rate is found and in the further modelling no decay is assumed. See appendix 7-4B and appendix 7-4C for more detailed data.

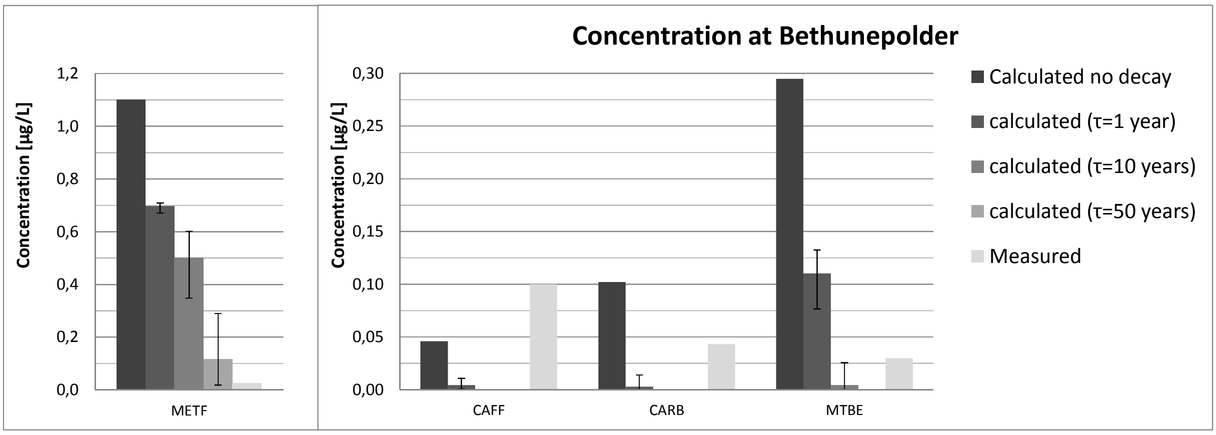


Figure 7-16 Comparison between calculated concentrations at Bethunepolder with and without decay and measured concentrations (other compounds can be found in figure 7-17)

Mass balance

The mass balance of OMPs is performed with the assumptions in paragraph 7.5.5 (1-D plug flow without decay). The mass balance has six checks, where the measured and the calculated concentrations can be compared: Utrecht in, Utrecht out, inlet Maarsseveense Plassen and Zodden, Vecht, inlet Loosdrechtse Plassen and Nieuwersluis. Table 7-7 provides the output of the balance in the dry season (also see appendix 7-4B). The calculated concentrations are compared to the measured concentrations. At almost all checks the calculated values are in the same order of magnitude as the measured data, which indicates that the model gives a good presentation of the real situation. It must be taken into account that all measurements are instantaneous and there still is an uncertainty in the (smaller) unknown inlets. With instantaneous measurements it is possible that they do not provide representative values due to incomplete mixing, the time and day of the measurement or because only a limited amount of measurements is available.

Table 7-7 Results mass balance in the dry season [μg/L]

	Utrecht in	*CHECK Utrecht in*	Utrecht out	*CHECK Utrecht out*	Inlet Zodden	*CHECK Inlet Zodden*	Vecht	*CHECK Vecht*	NSS	*CHECK NSS*	Inlet LDP	*CHECK Inlet LDP*
ACEK	2.509	1.190	12.978	0.000	14.163	1.200	14.163	15.000	3.620	0.000	3.620	1.900
AMPA	0.451	0.472	1.743	0.095	1.889	0.048	1.889	0.202	0.597	0.564	0.597	0.124
BENT	0.018	0.016	0.018	0.043	0.018	0.012	0.018	0.008	0.020	0.022	0.020	0.008
CAFF	0.031	0.088	0.177	0.015	0.194	0.022	0.194	0.062	0.046	0.075	0.046	0.011
CARB	0.084	0.066	0.375	0.103	0.408	0.020	0.408	0.080	0.115	0.067	0.115	0.012
GLYF	0.105	0.057	1.994	0.069	2.208	0.000	2.208	0.080	0.284	0.062	0.284	0.000
IOPR	0.373	0.164	6.597	0.878	7.301	0.085	7.301	0.394	0.964	0.289	0.964	0.014
METF	0.975	0.465	4.164	0.965	4.525	0.080	4.525	1.700	1.327	0.439	1.327	0.049
MTBE	0.144	0.195	1.074	0.065	1.180	0.091	1.180	0.112	0.237	0.119	0.237	0.309
NDMS	0.049	0.060	0.049	0.000	0.049	0.155	0.049	0.040	0.052	0.090	0.052	0.415
SULF	0.065	0.108	0.148	0.027	0.157	0.002	0.157	0.076	0.076	0.030	0.076	0.000

7.6.3 Integrated model

The validation of the integrated model is done by calculating for each origin source the corresponding total seepage and the corresponding load. This is used to calculate the average concentration, which can be compared with the measured concentration in the groundwater of the Bethunepolder measured with monitoring wells and in the Waterleidingkanaal just after the pumping station of the Bethunepolder. Table 7-8 provides the validation of the integrated model (also see appendix 7-4D). Most of the calculated values are higher than the measured values. A reason for this could be that in the subsurface degradation takes place (due to long residence time) and the subsurface partly acts as a sand filter (adsorption of compounds) (Waternet, 2010). However, the assumptions in section 7.5.5 are still applied on the models. For the comparison with the concentrations measured in the monitoring wells three out of 11 substances are in the same order of magnitude as the calculated values (bentazone, caffeine and N,N-DMS). The remaining substances have a difference between measured and calculated in a range of one or more orders of magnitude. For the comparison of the calculated values with the measured values in the Waterleidingkanaal two substances are in the same order of magnitude. All other measured substances are two to four orders of magnitude lower than the calculated values.

Table 7-8 Validation of groundwater model

	calculated concentration [μg/L]	Measured groundwater [μg/L]	Validation same order of magnitude [Y/N]	Measured Waterleidingkanaal [μg/L]	Validation same order of magnitude [Y/N]
ACEK	38.0998	0.410	N	0.4250	N
AMPA	5.1746	<0.100	N	0.0020	N
BENT	0.0527	0.040	Y	0.0186	Y
CAFF	0.5286	0.063	Y	0.0043	N
CARB	1.1313	0.043	N	0.0030	N
GLYF	5.6315	0.022	N	0.0010	N
IOPR	18.8495	0.022	N	0.0005	N
METF	12.8236	<0.05	N	0.0226	N
MTBE	3.2538	0.030	N	0.0526	N
N,N-DMS	0.1833	0.080	Y	0.0700	Y
SULF	0.3981	<0.01	N	0.0050	N

Combining the total seepage in the Bethunepolder with the concentrations of the sources from the model, it results in a total concentration of each compound in the seepage water of the Bethunepolder (figure 7-17). The difference between this approach and the previously discussed approach is that here the precipitation is included. In this integrated model the distinction between a dry and a wet period is no longer used, because once entered the groundwater the residence time is more than a half year and the seasonal variation disappears. In the figure also the limits and target values for water used for the production of drinking water are shown (respectively red and orange line). It can be seen that for the measured concentrations none of the compounds exceeds these limits. Bentazone and N,N-DMS are very close to the limit. These compounds could cause problems in the future. For the calculated concentrations it can be seen that AMPA, glyphosate and total pesticides exceed the limits. Target values for water intended for the production of drinking water are exceeded by acesulfame-K, iopromide and metformin for the calculated concentrations only. The target values for the effect of compounds on aquatic life in surface waters (PNEC) are found for caffeine, carbamazepine, iopromide, metformin, MTBE, N,N-DMS and sulfamethoxazole (table 7-1). These target values are not exceeded by any of the substances.

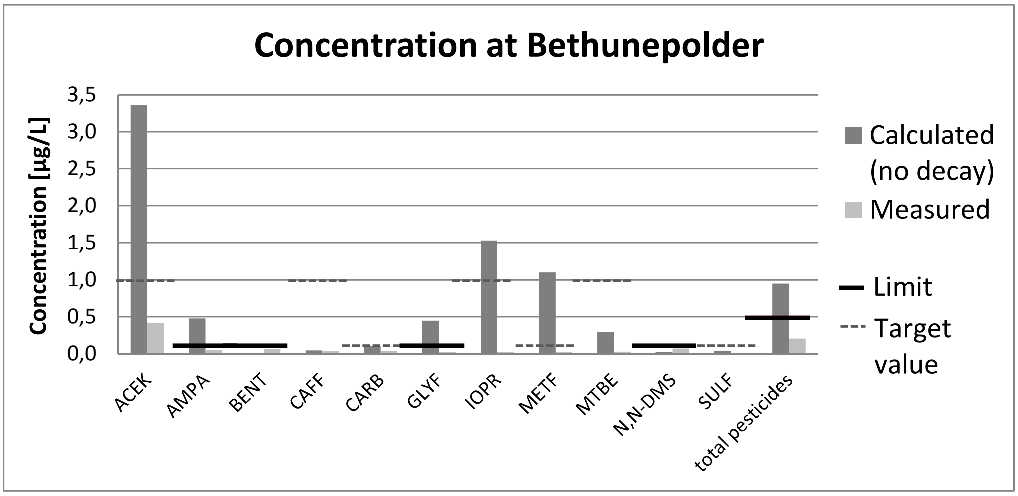


Figure 7-17 Concentrations of compounds in seepage water Bethunepolder with limits and target values (including precipitation)

The load per origin source can tell something about the impact of a discharge. The distribution of the sources is given in figure 7-18. This figure represents the distribution of acesulfame-K over the sources. It can be seen that about 30% of the total load of acesulfame-K in the Bethunepolder originates from the Vecht, another 30% comes from the Loosdrechtse Plassen and also about 30% originates from the residential area of Maarssen. The second graph shows that within the Vecht a major part of the total acesulfame-K load originates from the WWTP of Utrecht and only a small part from the Rhine at Lobith. Contrary to what was expected from the discharge distribution (figure 7-13C) the major part of the load of acesulfame-K in the Vecht originates from the WWTP of Utrecht.

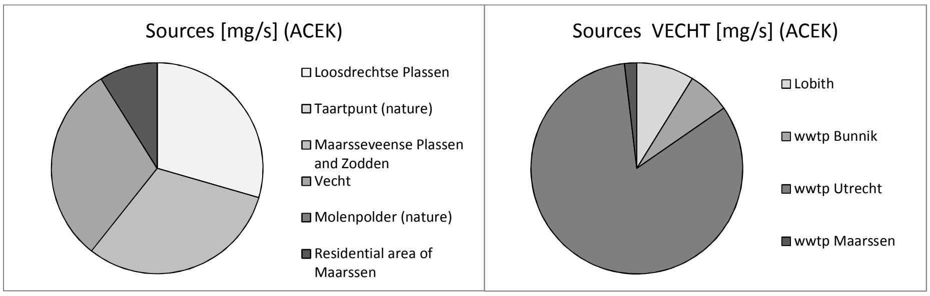


Figure 7-18 Distribution of load of acesulfame-K in current situation

In appendix 7-5A the graphs of all other substances can be found. About the same distribution can be found for AMPA, caffeine, carbamazepine, metformin and MTBE. For bentazone, N,N-DMS and sulfamethoxazole the Loosdrechtse Plassen is the main contributor. For iopromide and glyphosate the Vecht and residential area of Maarssen contribute for more than 30% each. The graphs representing the distribution of the Vecht differ less.

Only bentazone and N,N-DMS do not originate from any WWTP. All other substances originate for more than 75% from the effluent of the WWTP of Utrecht. Measures to reduce the amount of those compounds in the water should focus on WWTP effluent. Influences of river discharge originating from upstream of the Netherlands are relatively small.

7.7 Results and discussion future scenarios

The same model and procedure as described previously is applied to the two future scenarios REST and STEAM. For the future scenarios the balances are not validated again. In these scenarios the concentrations of compounds in the different origin sources change as well as the river discharge of the Rhine and the precipitation according to section 3.3. Below the results of the integrated model are shown.

Integrated model

The distribution graphs are composed for the loads in both future scenarios (figure 7-19, appendix 7-5B and 7-5C). The differences in distribution between the current situation, scenario REST and scenario STEAM are very small. The Loosdrechtse Plassen, Maarsseveense Plassen and Vecht are contributing about equally. This distribution is the same for almost all other compounds in the two future scenarios. Bentazone and N,N-DMS originate for more than 50% from the Loosdrechtse Plassen. For glyphosate and iopromide the Loosdrechtse Plassen is contributing less than the Maarsseveense Plassen and Vecht, where for sulfamethoxazole the contribution of the Loosdrechtse Plassen is larger than for the Maarsseveense Plassen and Vecht.

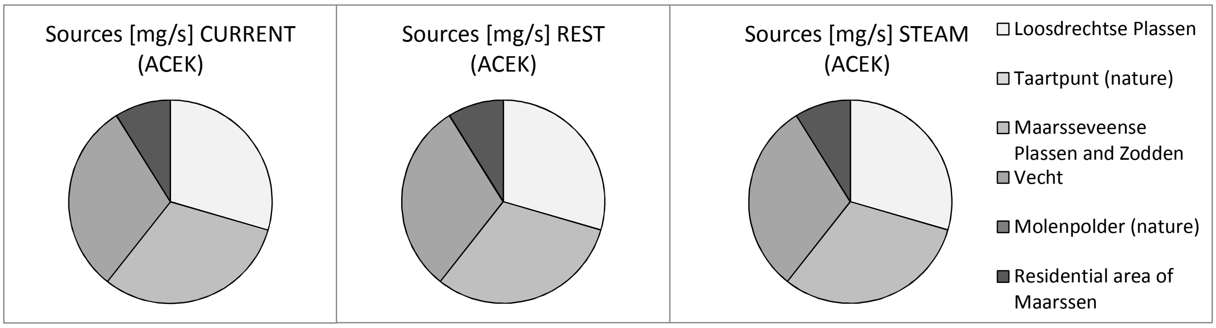


Figure 7-19 Distribution graph of acesulfame-K load in future scenarios REST and STEAM

The future scenarios are modelled as a change in fixed percentages in emission of OMPs by, Rhine discharge and precipitation (section 3.3 and appendix 3-3). This is calculated by dividing the total load of all sources by the pumping discharge in the polder. In figure 7-20 the limits and target values for water used for the production of drinking water are shown by a line. AMPA, glyphosate and total pesticides exceed the limits given in section 7.3.2. The target values for water intended for the production of drinking water are exceeded for acesulfame-K, iopromide and metformin. It must be taken into account that in the modelling of the concentrations in the seepage water the assumptions in section 7.5.5 are applied. The target values for the effect of compounds on aquatic life in surface waters (PNEC) (after seeping into the Bethunepolder) are relatively high and none of the values are exceeded by the calculated concentrations in the seepage water in the Bethunepolder.

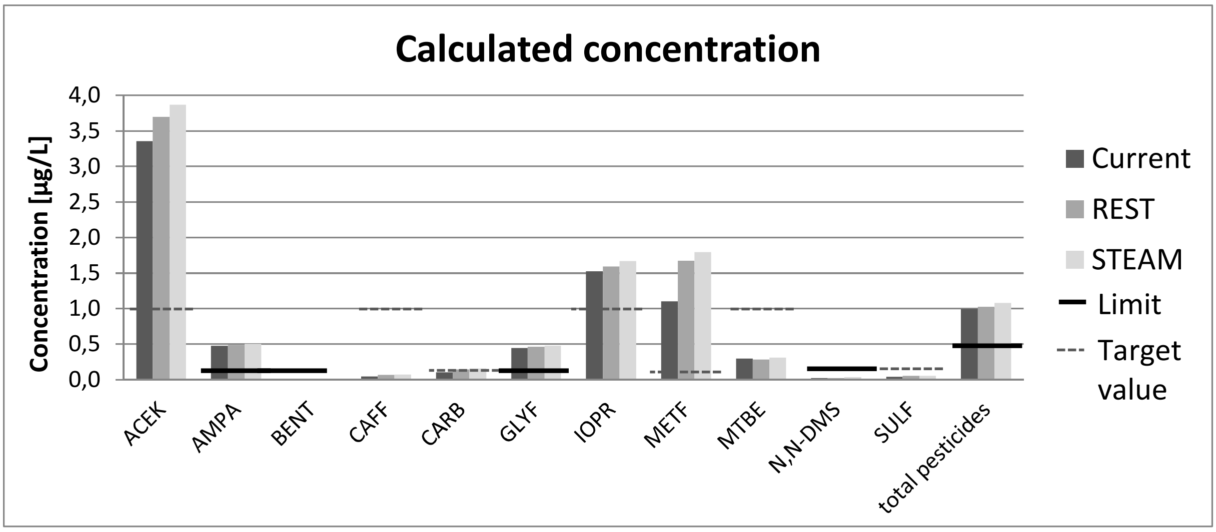


Figure 7-20 Concentration of compounds in seepage water Bethunepolder with limits

Although the future scenarios cause a change in calculated concentrations, the (non) exceedance of the limits does not change. Except for acesulfame-K, iopromide and metformin the change is only very small in the future scenarios. The differences in concentration increase or decrease for the selected compounds in the two future scenarios are discussed below.

- Pharmaceuticals and X-ray agent. It can be seen that for the pharmaceuticals the concentrations in scenario STEAM are higher than in scenario REST. This is consistent with the increase of concentrations of all compounds in the Rhine at Lobith. The trend in emission at other location is in scenario REST decreasing and in scenario STEAM increasing. This is not visible in the graph and for that reason it is concluded that the change in concentrations caused by the trend in emission is subordinate to the increase at Lobith.
- Domestic tracers. Both the trend in future consumption and the increase in concentrations of all compounds in the Rhine at Lobith are in both scenarios increasing. This results in increasing concentrations for both scenarios for acesulfame-K and caffeine.
- Industrial chemicals. For MTBE the concentration in the Rhine at Lobith is increasing in both scenarios. The trend of emission of MTBE in the scenario REST is decreasing and in the scenario STEAM it is increasing. This can be seen in the graph. The influence of the trend in emission is superior to the change in concentration at Lobith.
- Pesticides. For all pesticides the concentrations in the Rhine at Lobith are increasing for the scenario STEAM compared to the current situation. Emission of N,N-DMS decreases in scenario REST and increases in scenario STEAM, for the other compounds both scenarios show an increase compared to the current situation. For AMPA, bentazone and glyphosate the influence of the trend is subordinate to the influence of the changing concentrations at Lobith. For N,N-DMS the influence of the trend is superior.

The fixed percentages result in unchanged distribution graphs of the total load of OMPs over the sources within the Bethunepolder compared to the results of the current situation (appendix 7-5ABC). Explanation of the graphs can be found the previous section. It must be taken into account that all graphs are produced with the model and that the actual measured data are one to four orders of magnitude smaller (also see section 7.6.3 and chapter 9).

7.8 Results and discussion strategies

In order to test the influence of the strategies, the best two strategies following from the MCA are applied on the Bethunepolder balance. The strategy ‘legislation and policy’ is modelled as a reduction in concentration of all substances in surface water of 50%. The strategy ‘green pharmacy’ is modelled as a reduction in concentration of all pharmaceuticals in surface water by 50% and of caffeine by 20%. The concentration of caffeine is decreasing less, because only a part of the caffeine entering the water cycle is used as a pharmaceutical additive. The given percentages in decrease are an estimation to give the relative changes in concentration of all compounds in the current situation and in both future scenarios. For each strategy the focus is on the compounds appearing in the highest load and the compounds which exceed the limits set in section 4.2. Three graphs are produced: no strategy applied, ‘legislation and policy’ applied and ‘green pharmacy’ applied. For each graph the current situation is given as well as the situation in the scenarios REST and STEAM.

Results

Figure 7-21 shows the total concentration per OMP in the seepage water in the Bethunepolder for the current situation, the future scenario REST and the future scenario STEAM if no strategies are applied (identical to figure 7-20). Figure 7-22 and figure 7-23 show the situation if either strategy ‘legislation and policy’ or ‘green pharmacy’ is applied. In the future scenarios changes in emission of OMPs are taking into account as well as changes in river discharge and precipitation. The influence of applying the strategies is discussed below.

- Pharmaceuticals and X-ray agent. This group of compounds benefits from both strategies, ‘legislation and policy’ and ‘green pharmacy’. By applying one of both strategies the concentration of carbamazepine will decrease below the limit. The concentration of metformin still exceeds the limits, for both strategies and both future scenarios. The concentration of sulfamethoxazole was already below the limit concentration in the situation with no strategy applied. The concentration of iopromide only decreases far enough to be below the limit for the strategy ‘legislation and policy’.
- Domestic tracers. For the domestic tracers acesulfame-K only the strategy ‘legislation and policy’ causes a change in concentration. However, this decrease is not enough to result in a concentration below the limit. For caffeine both strategies decrease the concentration. The concentration in the situation when no strategy is applied already below the limit.
- Industrial chemicals. The concentration of MTBE is already below the limit. For this compound only the strategy ‘legislation and policy’ results in a decrease.
- Pesticides. For this group of compounds only the strategy ‘legislation and policy’ results in a decrease in concentration. The decrease in concentration of AMPA and glyphosate is not enough to decrease below the limit. Bentazone and N,N-DMS concentrations are already below the limit.

As expected the strategy ‘legislation and policy’ results in an overall decrease in concentration, where ‘green pharmacy’ only reduces the concentrations of pharmaceuticals. This result is trivial, because the strategies are modelled as a decrease in all compounds or only in pharmaceuticals, respectively for ‘legislation and policy’ and ‘green pharmacy’. For this reason the decrease in concentration between ‘no strategy’ and one of both applied strategies is always 0%, 20% or 50%. From figures 7-21, 7-22, 7-23 it can be seen that in the case of the Bethunepolder ‘green pharmacy’ does not decrease the concentration of substances appearing in the highest concentrations (acesulfame-K and iopromide), but it does decrease the concentration of carbamazepine, which forms a potential risk for drinking water. The concentrations of iopromide and metformin (also potentially risky) remain exceeding the limit, while MTBE was already far below the limits. For the Bethunepolder ‘legislation and policy’ is more effective, based on this model and corresponding assumptions. It must be taken into account that these graphs are produced with the model and that the actual measured data are one to four orders of magnitude smaller (also see section 7.6.3 and chapter 9).

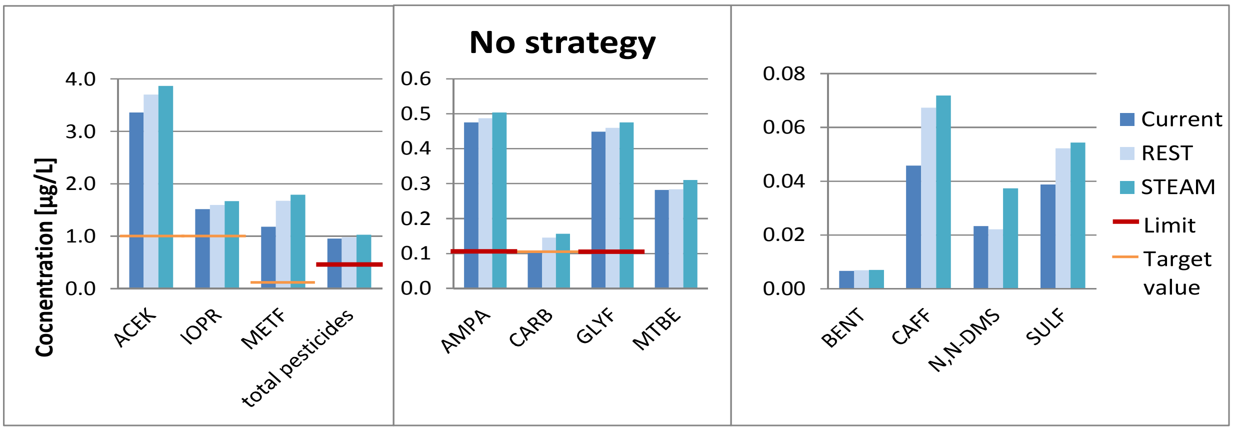


Figure 7-21 Concentration in current situation, scenario REST and scenario STEAM if no strategy is applied with limits

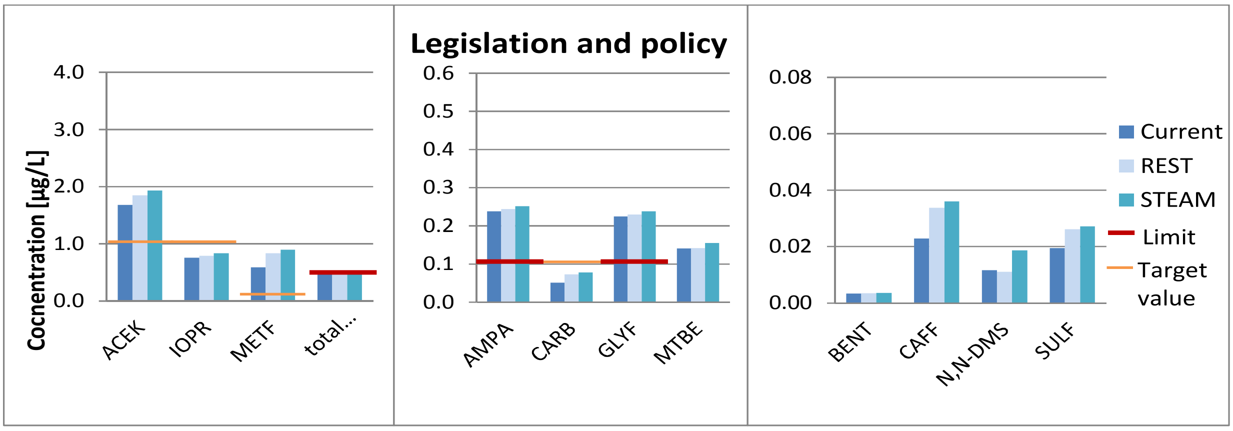


Figure 7-22 Concentration in current situation, scenario REST and scenario STEAM if the strategy 'legislation and policy' is applied with limits

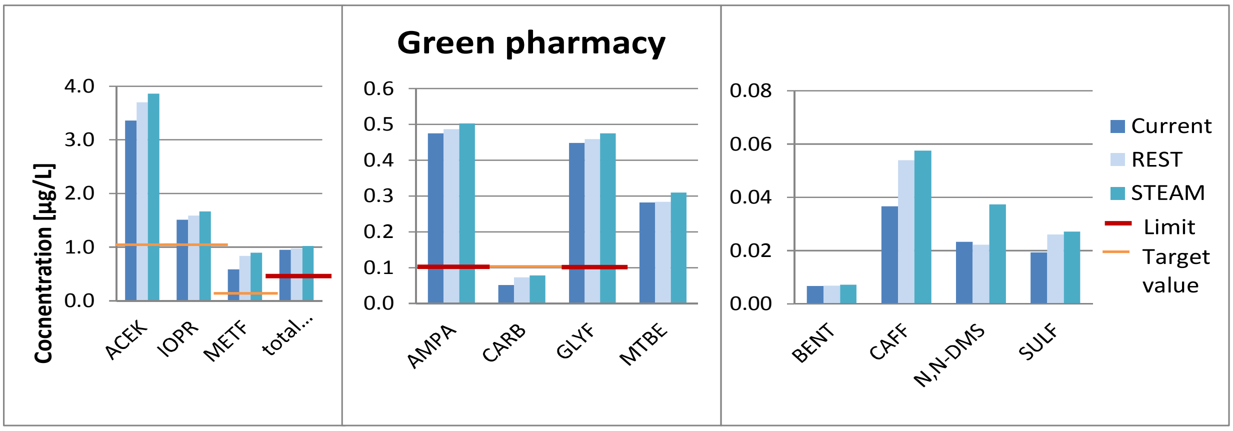


Figure 7-23 Concentration in current situation, scenario REST and scenario STEAM if the strategy 'green pharmacy' is applied with limits

Solutions for Bethunepolder

In the Bethunepolder the compounds which exceed the limits for water intended for the production of drinking water are mainly pesticides. Other compounds that exceed the target values are acesulfame-K, carbamazepine, iopromide and metformin. From the previously described figures it is determined that 'legislation and policy' is more effective in the Bethunepolder than 'green pharmacy'. However, none of both strategies result in such a decrease that no limits and target values are exceeded anymore. AMPA and glyphosate even exceed the limits when applying 'legislation and policy'.

From the discharge distribution graph in figure 7-24 it can be seen that the Loosdrechtse Plassen is the main contributor to the total load, followed by Maarsseveense Plassen and the river Vecht. Figure 7-25 shows that the concentration of AMPA in the Rhine at Lobith already is high. This suggests that transboundary solutions might be necessary to decrease the concentration of AMPA. For other compounds this is similar (appendix 7-3B and 7-5A).

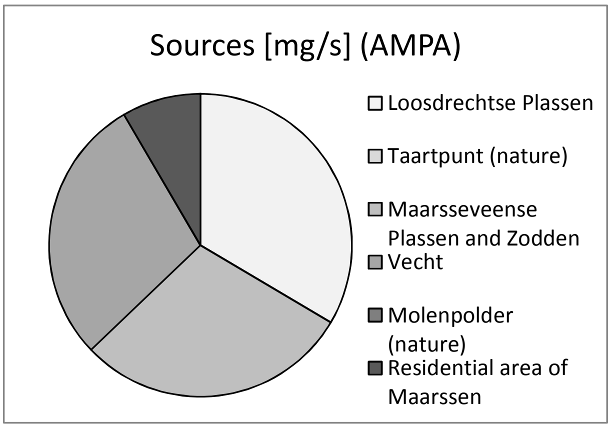


Figure 7-24 Distribution graph of AMPA load in current situation

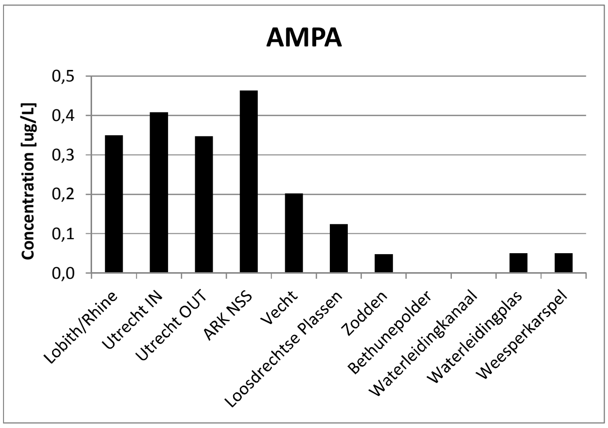


Figure 7-25 Measured concentrations of AMPA

Since AMPA is a degradation product of glyphosate, the focus of a solution for the high concentrations of these compounds should be on the reduction of glyphosate in the water cycle. Currently only one farmer in the Bethunepolder uses glyphosate (section 7.1). Possibly, the use of this pesticide on paved areas (mainly municipal weeding) results in high concentrations of glyphosate in the river Vecht. A potential measure is to restrict the use of glyphosate in and around the polder and as a pesticide on paved areas. With a reduction of glyphosate, the concentrations of AMPA and finally also total pesticides will reduce.

Current developments show that this measure is going to be implemented. The professional use of herbicides (e.g. glyphosate) except in agricultural use, will be forbidden on paved areas from November 2015. For private use (e.g. gardening) this prohibition applies to all types of areas (paved/unpaved). From November 2017 the professional use of herbicides will be prohibited on all types of areas (paved/unpaved), agricultural use excluded (Dutch Government, 2013; Ministerie van Infrastructuur en Milieu, 2013). These measures are taken to achieve the goals of the WFD by improving the water quality, and to protect employees and residents, secure food safety and increase the biodiversity.

For compounds other than pesticides other measures are possibly effective. From figure 7-18 the distribution of the total load of acesulfame-K shows that about 30% of the total load in the seepage water of the Bethunepolder originates from the river Vecht. The distribution graph of the river Vecht shows that more than 75% of the total load in the Vecht originates from the WWTP of Utrecht (also appendix 7-5A). For compounds that are used to be discharge into the water cycle via the WWTP, this is an interesting graph. For those compounds the largest effect could be achieved by measures at the WWTP of Utrecht.

8 Case study II: Andijk IJsselmeer

This case concerns the surface water extraction for the production of drinking water at Andijk. The extraction side is managed by the drinking water company PWN, which provides the largest part of the province of North-Holland with drinking water. The pumping stations at Andijk extract water from the IJsselmeer, which is fed for the major part with water from the river IJssel, originating from the Rhine. The choice for this case is based on three aspects. In the first place the extraction area is situated in the same RBD as the Bethunepolder. Secondly, it is a totally different system than the Bethunepolder, namely a surface water system. And thirdly, the choice is based on cooperation of the concerned drinking water company and availability of measurement data. In this chapter the water and mass balances of the IJsselmeer are composed. The balances provide an insight into the sources of the OMPs. The future scenarios for emission of OMPs and the two best strategies, which resulted from the MCA, are applied on the balances to see the changes in the future situation.

8.1 IJsselmeer area

The IJsselmeer is the biggest fresh water lake in the Netherlands. It has a surface of about 1,100 km^2 and an average depth of 4.5 m. The lake is fed with water from the river IJssel, which originates from the river Rhine, for 70%, the river Overijsselse Vecht for 12%, other smaller rivers, brooks, pumping stations and sluices for more than 10% and precipitation for about 5%. The IJsselmeer discharges water on the Wadden Sea by two sluices in the Afsluitdijk, which discharge about 88% of the water by gravity. This means that the ability to discharge depends on the tide on the Wadden Sea and the impoundment by the wind. The last 12% disappears by open water evaporation. The residence time of the water in the lake is 3 to 6 months. The direction of the flow, which influences the mixing in the lake, is determined by the wind (Ministerie van Verkeer en Waterstaat, 2006). The management area of the IJsselmeer exists of three compartments. The first compartment is the IJsselmeer itself, the Ketelmeer and the Zwarte Meer (figure 8-1). It receives water directly from the river IJssel and Overijsselse Vecht. The sluice complexes Stevinsluizen (61%) and the Lorentzsluizens (39%) discharge water into the Wadden Sea. The use of the Stevinsluizen is preferred, because this reduces the salt intrusion from locking and therefore increases the water quality at Andijk.

Figure 8-1 Overview of the IJsselmeer area (Ministerie van Verkeer en Waterstaat, 2006)

Compartment 2 and 3 consists of several smaller lakes, which are not part of this case study. Compartment 2 (Markermeer) and 3 (Veluwerandmeren) are separated by a dike. The third compartment is discharging by a sluice in the north to compartment 1 and by another sluice in the south to compartment 2. The drinking water extraction at Andijk extracts water directly from the Ijsselmeer and is indirectly influenced by the river Rhine, the Markermeer, the Veluwerandmeren and several other (smaller) rivers, brooks and drainage canals. The total catchment area of the IJsselmeer, from which the drainage by several drainage canals and sluices originates, is about 20,000 km^2 (Ministerie van Verkeer en Waterstaat, 2006). In the IJsselmeer area the functions surface water management, professional use and recreational use are combined. Surface water management consists of drainage of the surrounding areas (polders). By drainage canals and sluices the surplus water is discharged directly or indirectly on the IJsselmeer in wet periods. In dry periods water is extracted from the lake to supply the surrounding land with water. On the IJsselmeer, Markermeer and Veluwerandmeren several types of commercial activities take place, such as commercial shipping, sand mining, aviation, agriculture and horticulture. Recreational use of the IJsselmeer area can be fulfilled by nature, recreational shipping and swimming and water recreation. These are all potential sources of pollution. See appendix 8-1 for more detailed information.

8.2 Drinking water extraction

The extraction at Andijk consists of two intake points. The pumping station Andijk (PSA) pumps the water in the western basin and the water intake station Prinses Juliana (WPJ) delivers water to the eastern basin (figure 8-2). There is a physical border between the two basins. The water from PSA is purified to drinking water and the water from WPJ is pre-treated for dune infiltration, the membrane factory at Heemskerk and Tata Steel at IJmuiden. The water from WPJ can also be used for drinking water treatment and therefore the water quality in both basins must be sufficient for drinking water production. The total production of water at Andijk is 75-90 M m^3/year. Operating under full capacity the basins offer storage of water for four days, in case of an intake stop. The past years this situation occurred only three times (Rijkswaterstaat, 2012b).

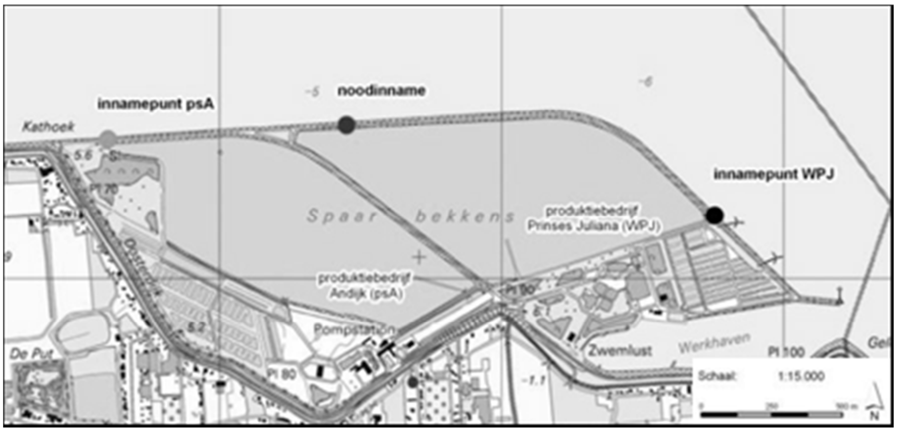


Figure 8-2 Overview of the extraction area at Andijk (Rijkswaterstaat, 2012b)

PSA

PSA is in operation since 1967. It has a production capacity of 30 M m^3/year and an average yearly intake from the IJsselmeer of 25-30 M m^3. Figure 8-3 shows the treatment scheme of PSA. From this scheme it can be seen that also feed water from WPJ is possible and filtrate from the sand filtration from WPJ can be introduced in the process of drinking water purification at PSA. The function of the basin is to soften the water and damp the differences in water quality in the IJsselmeer. Flocculation and rapid sand filtration remove suspended solids. The next step is disinfection and oxidation by hydrogen peroxide and UV. Activated carbon filters neutralise the hydrogen peroxide and adsorb organic material. The pure water micro sieves remove the carbon particles (Rijkswaterstaat, 2012b).

WPJ

WPJ is in operation since 1980. It has a production capacity of 110 M m^3/year. The intake of WPJ on yearly basis is 50-60 m^3, which that only a part of the production capacity is used. Figure 8-3 shows the treatment scheme of WPJ. The drum screens remove coarse material from the water. Coagulation and sedimentation remove the finer material. Rapid sand filters remove the remaining particles. The function of the activated carbon filters is to remove compounds like organic micro pollutants (Rijkswaterstaat, 2012b).

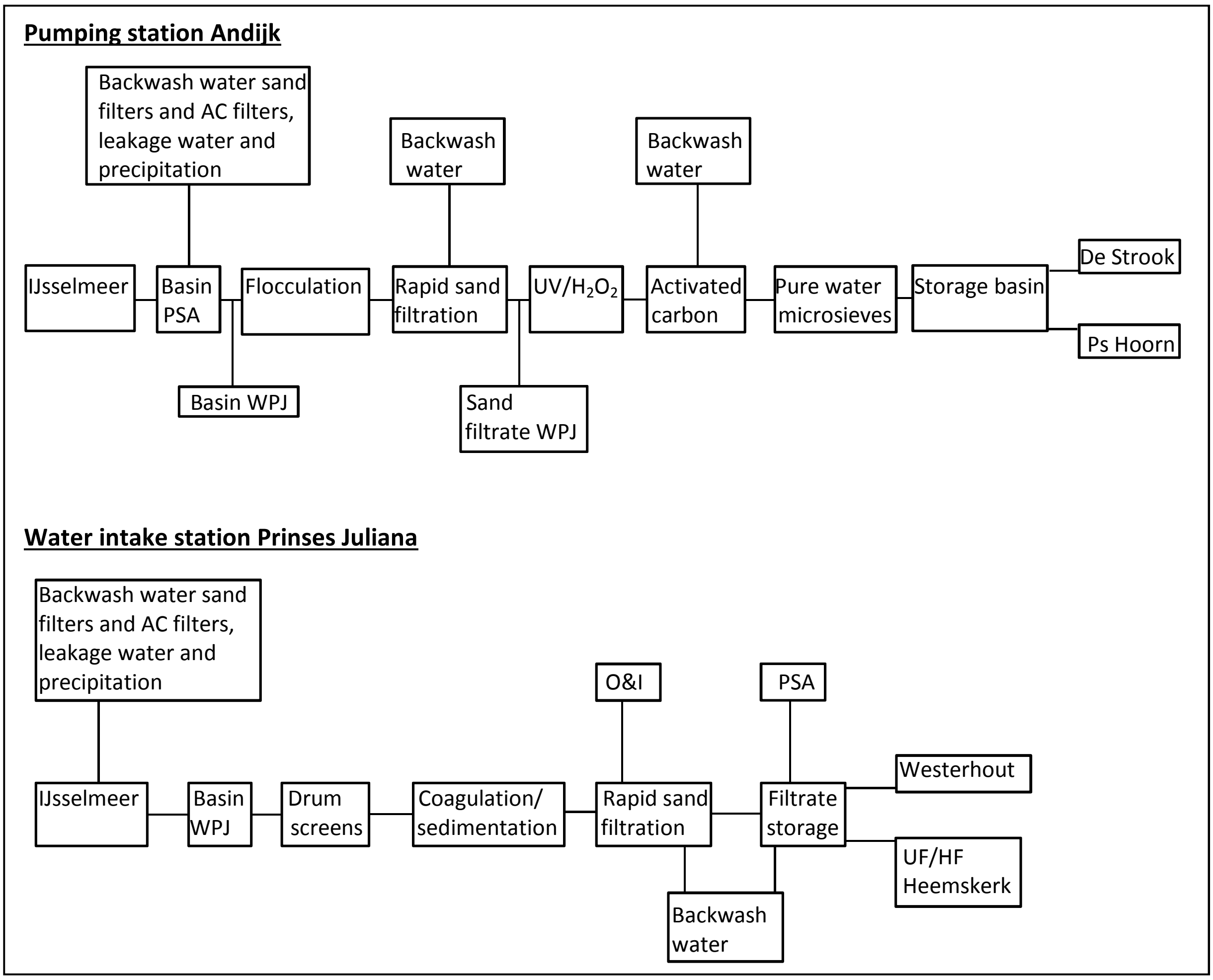


Figure 8-3 Treatment schemes PSA and WJP

8.3 Water quality and composition

8.3.1 Composition of the water

The extracted water at Andijk is surface water from the IJsselmeer. It is influenced by several sources described in the next section. More information on the measurement locations and the results of these measurements can be found in appendix 8-1 and 8-2A. Each group of OMPs is discussed below.

Pharmaceuticals and X-ray agents

For pharmaceuticals there are no limits provided in the Drinking Water Decree. Of the pharmaceuticals compounds only caffeine and carbamazepine exceed the quality limit of the DMR (section 4.2). Apart from caffeine and carbamazepine, no exceedance of limits of signalling parameters or quality limits of DMR and the Drinking Water Regulation by pharmaceuticals occurred. Sulfamethoxazole did not exceed any limits, but shows an increasing trend over the past years. Concentrations of X-ray agents show an increasing trend, but still the concentrations measured at Andijk are lower than that at Lobith (Rijkswaterstaat, 2012b).

Domestic tracers

Artificial sweeteners and caffeine are used as tracer compounds, because they only originate from human activity. Acesulfame-K exceeds the limits of DMR and the Drinking Water Regulation for both Andijk and Lobith. No further information was found within the scope of the project (Rijkswaterstaat, 2012b).

Industrial chemicals

The DMR limits are exceeded for DTPA, EDTA and NTA, which are chelating agents. Concentrations in Lobith are comparable with those in Andijk. MTBE only exceeds the limits of DMR and the Drinking Water Regulation at Lobith (Rijkswaterstaat, 2012b).

Pesticides and antifouling

Glyphosate only exceeds the limits of DMR and the Drinking Water Regulation at Lobith, Amsterdam and the rivers IJssel and Overijsselse Vecht. Its metabolite AMPA exceeds the limit of DMR and the Drinking Water Regulation at these locations and additionally at Andijk. Bentazone is only found in concentrations far below the limits. N,N-DMS is only measured at Lobith, and in concentrations below the limits (Rijkswaterstaat, 2012b).

8.3.2 Limits for drinking water and surface water

In section 4.2 the (precautionary) limits and standards by law, Benchmark Quotient and PNEC are described. Table 8-1 shows a summary of these limits. From the BQ calculations it results that only carbamazepine forms a potential risk for the production of drinking water. For those compounds the additional limit of 1.0 µg/L in drinking water applies. For all pesticides the standard for drinking water is 0.1 µg/L and for all pesticides combined the standard is 0.5 µg/L. For surface water intended for the production of drinking water only limits are set by law for pesticides (each individual pesticide 0.1 µg/L and all pesticides combined 0.5 µg/L).

Table 8-1 Benchmark Quotient calculations for the selected compounds at the Andijk system in the current situation and in future scenarios REST and STEAM

				Current	Rest	Steam	Limits sw for production of dw[1]	Target values sw for production of dw[2]	Target values sw (PNEC)[3]
	TDI [µg/kg/day]	pGLV [µg/L]	$c_{max, BP}$ [µg/L]	BQ_{BP} [-]	BQ_{BP} [-]	BQ_{BP} [-]	[µg/L]	[µg/L]	[µg/L]
ACEK	25000	87500	2.30	2.63E-05	2.89E-05	3.02E-05	-	1.0	-
AMPA	300	1050	0.83	7.90E-04	8.10E-04	8.38E-04	0.1	0.1	-
BENT	100	350	0.02	5.71E-05	5.86E-05	6.06E-05	0.1	0.1	-
CAFF	300	1050	0.23	2.19E-04	3.22E-04	3.44E-04	-	1.0	182
CARB	0.34	1.19	0.14	**0.12**	**0.11**	**0.18**	1.0[4]	0.1	0.42
GLYF	300	1050	0.09	8.57E-05	8.79E-05	9.09E-05	0.1	0.1	-
IOPR	21	73.5	0.22	2.99E-03	3.14E-03	3.29E-03	-	1.0	256
METF	79	277.9	0.99	3.56E-03	5.06E-03	5.41E-03	-	0.1	511
MTBE	300	1050	<0.05	4.76E-05	4.79E-05	5.24E-05	1.0	1.0	2600
NDMS	-	-	-	-	-	-	0.1	0.1	140
SULF	130	455	0.03	6.59E-05	8.88E-05	9.23E-05	-	0.1	0.118
Pesticides combined							0.5	-	-

[1] (Dutch Government, 2009b), [2] (IAWR, 2008), [3] section 4.2, [4] based on BQ value (section 4.2)

To test the models on water quality regarding OMPs target values for the remaining substances are used. These are target values determined by the DMR Memorandum (IAWR, 2008). The target value for water intended for the production of drinking water is 1.0 µg/L for acesulfame-K, caffeine, iopromide and MTBE. The target value for all other compounds is 0.1 µg/L. To test the risk for aquatic life the PNEC values are used as target values in surface water. Target values in surface water with no predicted negative effects on aquatic life are found for caffeine, carbamazepine, iopromide, metformin, MTBE and sulfamethoxazole. The concentrations vary between 0.118 and 2600 µg/L. This is only done for water bodies intended for the production of drinking water. Finally, for each compound the lowest limit applies.

8.4 Sources of OMPs

In chapter 4 the different types of sources are already explained. The rivers IJssel, Overijsselse Vecht and precipitation are main contributors (>85%) to the total water discharge onto the lake. The river IJssel originates from the Rhine, which rises in the Swiss Alps and flows to the Netherlands. At Lobith the river splits in the Waal and the Pannerdensch Kanaal and only a few kilometres downstream the Pannerdensch Kanaal splits in the Nederrijn and the IJssel. The IJssel flows with about 300 m^3/s to Kampen where it discharges into the Ketelmeer. The Overijsselse Vecht rises in the Munsterland in Germany. The rivers Regge and Dinkel flow into the river in the Dutch part of the river. From the eastern part of the country the Overijsselse Vecht flows towards Genemuiden, where it discharges just a few kilometres apart from the IJssel into the Zwarte Meer. The surface water quality of these rivers is determined by influences upstream of the Netherlands, discharges of WWTPs and discharges of other companies and industries. The remaining water in the IJsselmeer comes from small rivers, pumping stations of the surrounding land and from the surrounding water bodies (Markermeer and Veluwerandmeren) (figure 8-1). Appendix 8-1 gives an overview of the sources.

8.5 Models

In this chapter the models are discussed. There are two models used: a (surface) water balance and a mass balance of OMPs. The water balance is composed using a scheme of the target area and define all incoming and outgoing streams. The mass balance is composed by multiplying the water balance by the measured concentrations. In paragraph 8.6 the results of the models will be discussed.

8.5.1 Surface water balance

The water balance for the Andijk case is composed in Excel as the water balance of the IJsselmeer. It is a simplification of the water balance of the IJsselmeer proposed in (Ministerie van Verkeer en Waterstaat, 2006).

The IJsselmeer is simulated as a basin with a retention time of 6 months. The IJssel flows in northern direction to Kampen where it discharges into the Ketelmeer and eventually into the IJsselmeer (figures 8-1 and 8-4). Between Lobith and Kampen no other large discharge enters the IJssel. The load of OMPs at Kampen originates almost completely from Lobith and thus upstream of the Netherlands. Another stream discharging here is the Overijsselse Vecht at Genemuiden, which is in the balance called the Zwarte Meer. The Zwarte Meer is the part between the Overijsselse Vecht and the Ketelmeer. The rivers IJssel and Overijsselse Vecht contribute for about 85% of the total incoming water in the IJsselmeer. A third stream that enters the IJsselmeer via this route is water from the Veluwerandmeren. The water from the Markermeer entering the IJsselmeer is discharged by two sluices. Water flows in both directions, depending on the season and water quality of the Markermeer and surrounding areas (city of Amsterdam and polders between Utrecht and Amsterdam). A small amount of water (about 7%) is discharged by the many pumping stations situated around the lake. These pumping stations are modelled as one source in the balance. Saline water from the Wadden Sea enters the IJsselmeer as sluicing losses. The last source in the model is the precipitation on the lake, which contributes for about 5%. Water leaves the IJsselmeer mainly by sluicing at the Lorentzsluizen and the Stevinsluizen to the Wadden Sea (about 92%). Around 4% of the water evaporates in open water evaporation. The last 4% are divided by the intake of PWN, inlets into the surrounding areas and flows to the Markermeer and the Veluwerandmeren by sluices. Water quantity data are collected for the period 2002-2004, because data were only available on this period(Ministerie van Verkeer en Waterstaat, 2006). No distinction is made between the wet season (October-March) and the dry season (April-September), because the residence time of the water in the IJsselmeer is up to 6 months. The water balance is composed based on an existing water balance from (Ministerie van Verkeer en Waterstaat, 2006) and it is assumed that this balance is correct. No further validation is done. The balance can be used to test composed future scenarios and strategies to reduce the amount of OMPs in the environment and drinking water.

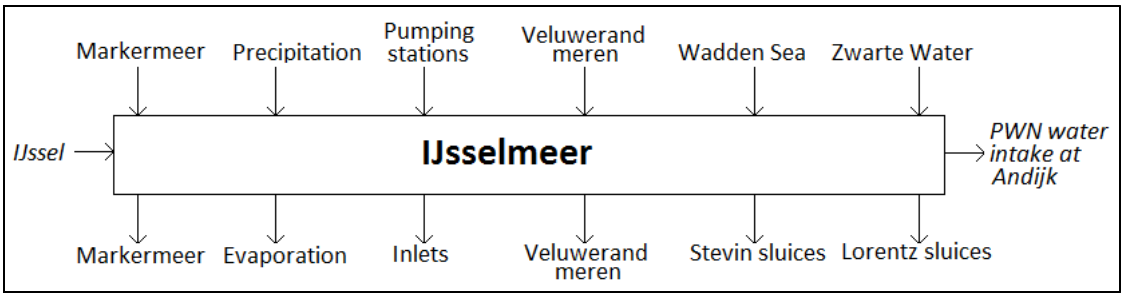


Figure 8-4 Model of IJsselmeer

8.5.2 Mass balance of OMPs

The mass balance of OMPs is very similar to the water balance of the IJsselmeer. The concentrations at all incoming streams are combined with the discharges of these streams. This is the same method as used in chapter 7. The total concentration of each of the selected micro pollutants is calculated at Andijk and compared to the measured concentrations at Andijk to determine the validity of the model. In water quality modelling the decay rate of a certain type of pollutant is very important. This is done by modelling two situations to see the influence of degradation: a completely mixed tank without decay and a series of completely mixed tanks with decay. This is done to determine whether the assumptions made in the models are valid (paragraph 8.5.3). As explained in the previous chapter, the final model will be performed by a completely mixed tank without decay, because decay rates of only four substances are found (table 7-4). Figure 8-4 shows all incoming streams, in which it is assumed that precipitation is a clean discharge where the concentration of all selected OMPs is zero.

Completely mixed reservoir without decay

The least complicated option to model the concentration of the selected OMPs in the IJsselmeer at Andijk is to assume a completely mixed system without decay. In this system it is assumed that incoming loads are mixed instantaneously with the loads of the receiving water body and that no type of degradation of the OMPs will occur. The concentration of OMPs at Andijk can be calculated with the following formula:

$$C_{Andijk} = \frac{\sum Q_i * C_i}{\sum Q_i} \qquad (8.1)$$

Where:
C = concentration [ML^{-3}]
Q = flow [L^3T]

Series of completely mixed tanks with decay

Where in a river segment system plug flow is a good assumption, in a reservoir system the mixing process may be significant and needs explicit consideration. A reservoir is represented as a series of well-mixed tanks where advective flow moves mass from one tank to the next (figure 8-5).

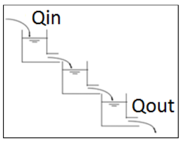


Figure 8-5 Series of completely mixed tanks (Baptist, 2006)

The concentration of reservoir outflow can be estimated with the following equation:

$$C_{out} = \left(\frac{Q}{Q+kV}\right)^n * C_{in} + \sum_{j=1}^{n}\left[\left(\frac{Q}{Q+kV}\right)^{n-1} * \frac{W_j}{Q+kV}\right] \tag{8.2}$$

Where:
k = first-order loss rate constant [T^{-1}]
V = volume of an individual tank [L^3]
n = number of tanks [-]
W = waste load [MT^{-1}]

The number of tanks can be calculated with:

$$n = 1 + INT\left(\frac{L*U}{2*E}\right) \tag{8.3}$$

$$E = 3.2 * 10^{-4} * L_c^{1.1} \tag{8.4}$$

Where:
INT = integer function
L = reservoir length [m]
U = longitudinal advective velocity [m/s]
E = longitudinal turbulent diffusion/dispersion coefficient [m^2/s]
L_c = reservoir characteristic length (sum of reservoir mean width and length divided by 2) [m]
(Anderson *et al.*, 2004)

8.5.3 Assumptions

In the model some assumptions are made to simplify the real situation. These assumptions are:

1. There is no degradation and adsorption. This means that the compounds present in the water behave like infinite persistence.
2. It is a well-mixed system, which consists of one completely mixing tank. The measured concentrations are representative for the whole part of the water body. Discharges from a source are mixed instantaneously. Where this assumption for a river model could be plausible, it is questionable whether this is true for a lake system. Within the scope of this project no time is available to work out a lake based balance and therefore this assumption is made.
3. Only the discussed discharges are taken into account. Other discharges (contribution <5% of total), such as intakes by farmers or factories, pumping stations or small water bodies are disregarded, due to missing quality and quantity data. This assumption includes the fact that effluent discharges of WWTPs and other direct or point sources from the land into the IJsselmeer are combined in the source ‘pumping stations’.
4. Groundwater flows are not contributing to this system.
5. It is assumed that the concentration of OMPs at the Wadden Sea and in precipitation are zero. For the Wadden Sea only concentrations of bentazone are found and it is a diluted stream.
6. From all water quality data only the data in the dry season are used, since no distinction is made between the dry and the wet season (long residence time).
7. In the balance with future scenarios the increase in IJssel discharge isderived from the relative increase in Rhine discharge from the future scenarios REST and STEAM. The increase or decrease in discharge of other streams is derived from the percentage increase or decrease in precipitation from the scenarios REST and STEAM.
8. The modelled years are representative. No extreme dry or wet years occur, except an extremely dry spring and an extremely wet summer in 2011 (KNMI, 2013). It is assumed that this has no significant influences since it levels out. This is also the case for the used measurement data.

8.5.4 Water quality data

Water quality measurements are available from different institutions. In this case data from Rijkswaterstaat (RWS) and Waterbase and Association of River Water Supply Companies (RIWA) are used (Rijkswaterstaat, 2013; RIWA, 2013; Waterbase, 2013). From all water quality data collected average concentrations are determined. Yearly averages are calculated for the period 2008-2012.

Data

Except for the river IJssel the streams entering the IJsselmeer are relatively small (below 10% of total discharge), which makes it very cost inefficient to perform water quality measurements on a regularly basis. Appendix 8-1 shows the locations where water quality measurements are performed. From the data it can be concluded that the concentrations of almost all compounds are highest in Lobith, except for the pesticides, which are highest at Kampen and Genemuiden (appendix 8-2AB). A reason for this could be that agriculture has a large influence on the receiving water bodies. The measurements in Amsterdam give for most substances higher concentrations than all other points. At Andijk most concentrations are lowest, which could be explained by the fact that the water is most diluted there. Another notable concentration is that of MTBE, where it is in Amsterdam a factor 2 higher than the second highest measured value. MTBE is a gasoline additive and the densely populated area of Amsterdam is most likely to be the reason for this. N,N-DMS is only measured at Lobith.

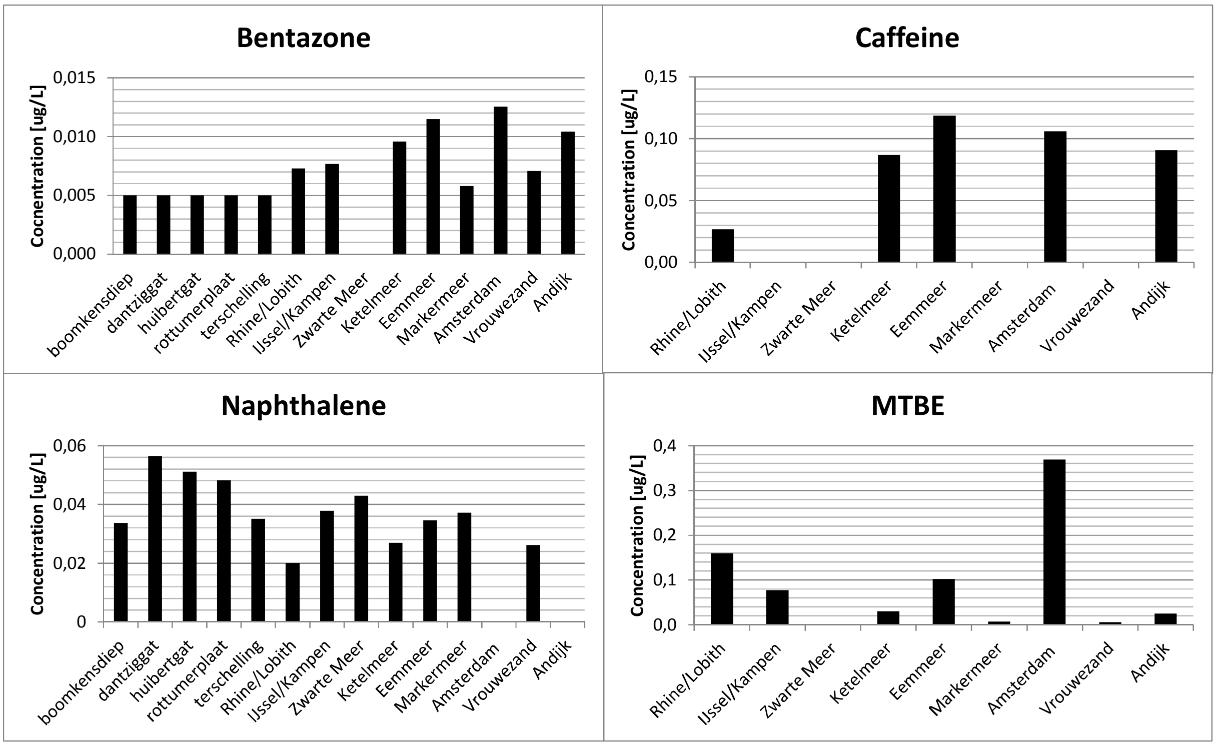


Figure 8-6 Measured concentrations of bentazone, caffeine, naphthalene and MTBE

Figure 8-6 shows the measured concentrations of bentazone, caffeine, naphthalene and MTBE. Bentazone was the only selected OMP for which water quality data of Wadden Sea are found. Naphthalene is shown to give an idea of the relative difference between the measurement locations of another compound than bentazone and which is also measured at the Wadden Sea. Caffeine and MTBE concentrations are measured at most locations, compared with the other selected compound in this study and these compounds had the largest difference in concentrations between the locations. Although the variation in concentrations of bentazone, caffeine and MTBE are expected (bentazone high in rural areas, caffeine increasing after Lobith and MTBE high in urban areas), the difference in caffeine concentrations between the Andijk case and the Bethunepolder case are strange[6]. From these graphs it can be seen that all measured concentrations per compound are of the same order of magnitude. The distribution of bentazone and naphthalene is different, but in both cases the order of magnitude is between the different locations is the same. The results from the models (next paragraph) should also be in the same order of magnitude as these measured concentrations, otherwise the model would not be correct. Graphs of other compounds can be found in appendix 8-2B.

Data processing

Of all available measurement series yearly averages are calculated. Since a static model is used there is only one value for each year derived. Data measured below the detection limit are assumed to represent a value half of the detection limit. In table 8-2 the water quality data are given (appendix 8-2A). In this table values are marked when more than 1/3 of all values on a measurement point are below the detection limit, or when only one measurement value is available. This gives an indication of the reliability of the data. However, a lot of values are missing, almost all present values are reliable.

Missing values

Not all substances are measured at all locations. Missing values are replaced by the averages of other locations as close as possible to the missing value.

Table 8-2 Water quality data [μg/L]

	ACEK	AMPA	BENT	CAFF	CARB	GLYF	IOPR	METF	MTBE	NDMS	SULF
1. Lobith	1.713	0.338	0.007	0.027	0.072	0.033	0.186	0.943	0.159	0.044	0.042
2. Kampen		0.324	0.008			0.060			0.077		
3. Genemuiden		0.491				0.081					
4. Ketelmeer			0.010	0.087	0.045		0.156		0.030		0.024
5. Vrouwezand			0.007		0.019				0.006		
6. Andijk	1.693	0.212	0.010	0.091	0.045	0.031	0.080	0.362	0.025	0.0003	0.017
7. Markermeer			0.006		0.010				0.007		
8. Eemmeer			0.011	0.119					0.102		
9. Amsterdam		0.311	0.013	0.106		0.057			0.369		

☐	*reliable value*	▒	*more than 1/3 of data is below detection limit*
░	*only 1 measurement available*	▓	*missing value*

8.6 Results and discussion

In this section the results from the water balance and the mass balance are discussed.

8.6.1 Results surface water balance

In the surface water balance no actual calculations are made. The water balance composed in (Ministerie van Verkeer en Waterstaat, 2006) is used (appendix 8-3A). The model is based on measurement data, so no validation is necessary. Figure 8-7 shows the distribution graph of the incoming discharges in the IJsselmeer. It shows that the river IJssel contributes for over 75% to the total incoming discharge in the IJsselmeer. Precipitation, Zwarte Meer and pumping stations contribute about equally. The contribution of the Veluwerandmeren and the Wadden Sea is very small. Due to the size of the source ´pumping station´ (about 7% and together with precipitation third largest contributor) the mass balance will be influenced by the missing data of the source 'pumping stations'.

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[6] *The Vecht in the Bethunepolder case consists almost completely of WWTP effluent, from which it is expected that the concentration of caffeine in the Vecht would be very high. From the measurements it is shown that the concentration at Andijk (0.09μg/L) is higher than the concentration at the Vecht (0.06μg/L). This difference can be explained by the fact that both for Utrecht OUT and Vecht only one measurement is available (also see section 7.5.6).*

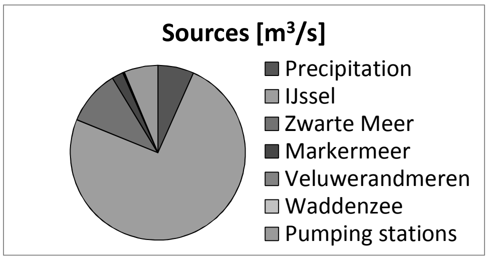

Figure 8-7 Distribution graph of discharge in current situation

8.6.2 Results mass balance of OMPs

Completely mixed tank(s) with and without decay

First of all a situation with and a situation without decay is applied to four substances (caffeine, carbamazepine, metformin and MTBE). These are the only substances of which a decay factor in water and soil was found. For the situation without decay the IJsselmeer is modelled as one completely mixed tank. In the situation with decay equation (8.3) is used, which results in a system with three tanks. For each tank it is determined which streams discharge on the tank in the model. On tank 1 the river IJssel, the Zwarte Meer and the Veluwerandmeren discharge, tank 2 receives water from the Markermeer and precipitation and finally the Wadden Sea and the pumping stations discharge water on tank 3 (figure 8-1). Of all incoming discharges the measured concentrations are used. Equations (8.1) and (8.2) are applied on the water balance. The validation of the two situations of decay (with and without) is based on the difference between measured and calculated concentrations at Andijk. When the measured and calculated concentrations are in the same order of magnitude, the model is valid. From the results in figure 8-8 it can be seen that the calculations of completely mixed tank(s) with and without decay are similar for metformin, carbamazepine and MTBE. Although carbamazepine and not caffeine has the highest decay rate, the calculated concentrations with and without decay differ most for caffeine. Error bars (black lines for METF, CAFF, CARB and MTBE) are shown in the figure to see the influence of the decay factor k, by using 0.5*k and 2*k. There is an influence of the decay factor on the calculated concentration, which is caused by the long residence time.

For all substances the calculated concentrations without decay are higher than the measured concentrations. However, almost all calculated concentrations are in the same order of magnitude as the measured concentrations. Since of only four compounds the decay rate is found, in further modelling no decay is assumed. See appendix 8-3B and appendix 8-3C for more detailed data.

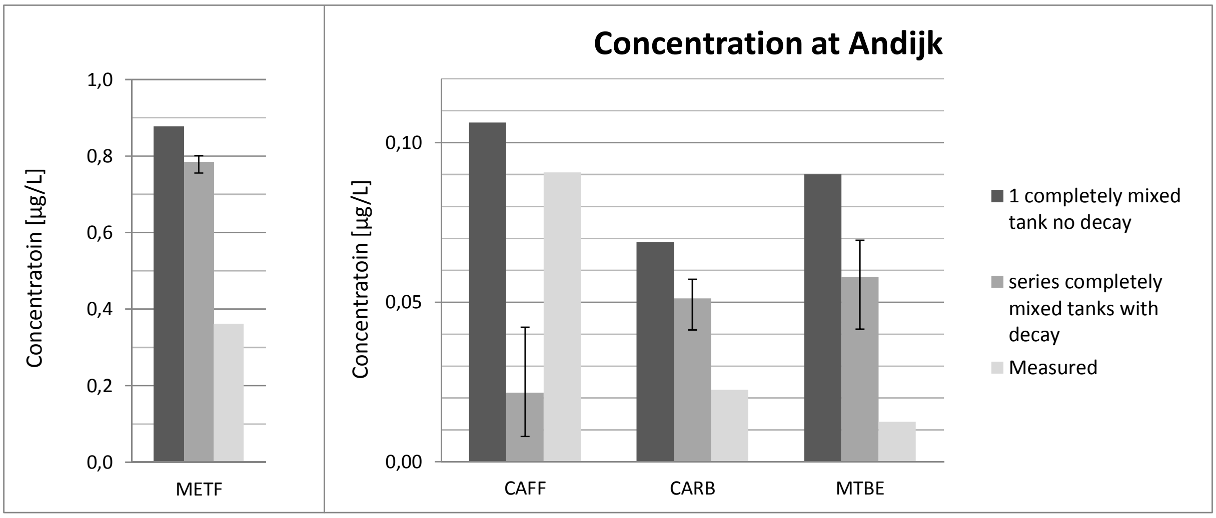

Figure 8-8 Comparison between calculated concentration at Andijk with and without decay and measured concentration (other compounds in figure 8-9)

Mass balance

The mass balance of OMPs is performed with the assumptions in paragraph 8.5.2 (completely mixed tank without decay). The mass balance has only one check at Andijk. Table 8-3 provides the output of the balance in (also see appendix 8-3B). The calculated concentrations are compared to the measured concentrations. For almost all compounds the calculated values are in the same order of magnitude as the measured data, which indicates that the model gives a good presentation of the real situation. It must be taken into account that all measurements are instantaneous and there still is an uncertainty in the (smaller) unknown inlets. With instantaneous measurements it is possible that they do not provide representative values due to incomplete mixing, the time and day of the measurement or because only a limited amount of measurements is available.

Table 8-3 Results mass balance

	concentration Andijk						
	Calculated [µg/L]	Measured [µg/L]	same order of magnitude [Y/N]		Calculated [µg/L]	Measured [µg/L]	same order of magnitude [Y/N]
ACEK	1.9308	1.693	Y	IOPR	0.1768	0.080	Y
AMPA	0.4544	0.212	Y	METF	0.8776	0.362	Y
BENT	0.0079	0.005	Y	MTBE	0.0900	0.013	Y
CAFF	0.1063	0.091	Y	N.N-DMS	0.0491	0.00013	N
CARB	0.0689	0.023	Y	SULF	0.0250	0.017	Y
GLYF	0.0927	0.031	Y				

This table is represented graphically in figure 8-9. In the figure also the limits and target values for water used for the production of drinking water are shown (respectively red and orange line). The measured concentrations are for all compounds (slightly) lower than the calculated concentrations. A reason for this could be that no degradation and instantaneously mixing is assumed. It can be seen that for the measured concentrations only AMPA exceeds this limit. For the calculated concentrations it can be seen that AMPA and total pesticides exceed the limits. Glyphosate is very close to the limit. Target values for water intended for the production of drinking water are exceeded by acesulfame-K, iopromide and metformin. The target values (PNEC) for the effect of compounds on aquatic life in surface waters are found for caffeine, carbamazepine, iopromide, metformin, MTBE and sulfamethoxazole (table 8-1). These target values are not exceeded by any of the substances.

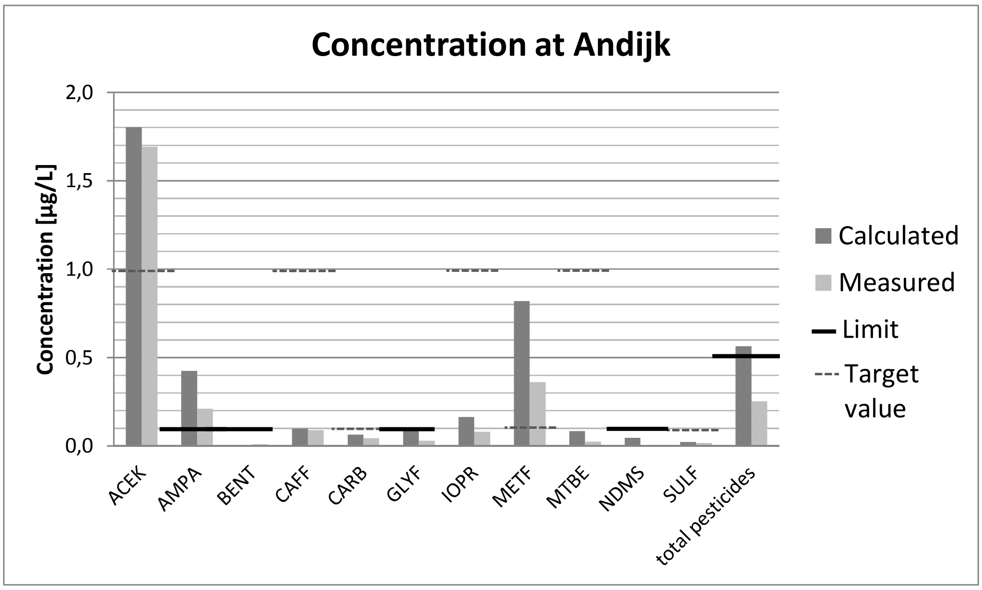

Figure 8-9 Concentrations of compounds in surface water IJsselmeer with limits and target values

The load per origin source can tell something about the impact of a discharge. Figure 8-10 shows the distribution of acesulfame-K over the sources. It can be seen that more than 75% of the total load of acesulfame-K in the IJsselmeer originates from the IJssel. Pumping stations and Zwarte Water contribute more or less equally. In the wet season this distribution changes a bit, where the IJssel becomes a smaller contributor and the contribution of the Zwarte Water increases a bit relatively to the other sources.

In appendix 8-4A the graphs of all other selected OMPs can be found. For most substances the river IJssel contributes for more than 75% of the total load, except for AMPA. For AMPA the Zwarte Water is a more important contributor than for all other substances. The other remarkable thing is that the Markermeer contributes for a small part for all substances, except for carbamazepine and MTBE. For those substances the Markermeer is not a contributor.

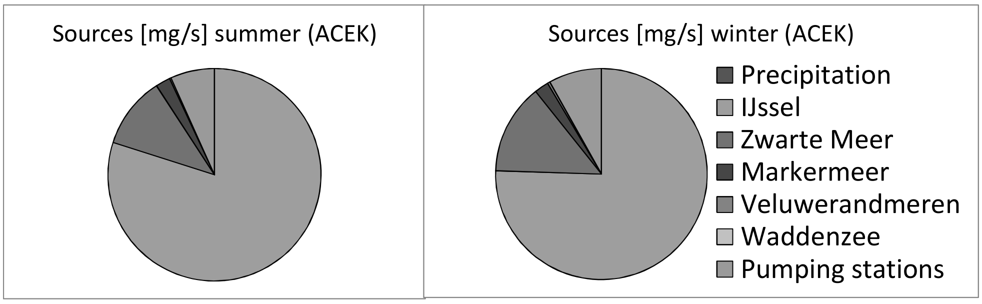

Figure 8-10 Distribution graph of acesulfame-K load in current situation

8.7 Results and discussion future scenarios

The same model and procedure as described previously is applied to the two future scenarios REST and STEAM for the situation of one completely mixed tank without decay. In these scenarios the river discharge of the Rhine and the precipitation changes as well as the concentrations of compounds in the different origin sources according to section 3.3. The future scenarios are modelled as a change (fixed percentages) in emission of OMPs, Rhine discharge and precipitation (section 3.3 and appendix 3-3). For the future scenarios the balances are not validated again.

The distribution graphs are composed for the loads in both future scenarios (figure 8-11, appendix 8-4B and 8-4C). The differences in distribution between REST and STEAM are very small, but compared to the current situation there are differences in distribution. The IJssel is main contributor with more than 75% of the total discharge, except for AMPA and sulfamethoxazole in the scenario REST and AMPA, MTBE and sulfamethoxazole in the scenario STEAM, where the IJssel is the main contributor as well, but with less than 75%. In both scenarios the Markermeer is no contributor for carbamazepine and MTBE, like it is the case in the current situation.

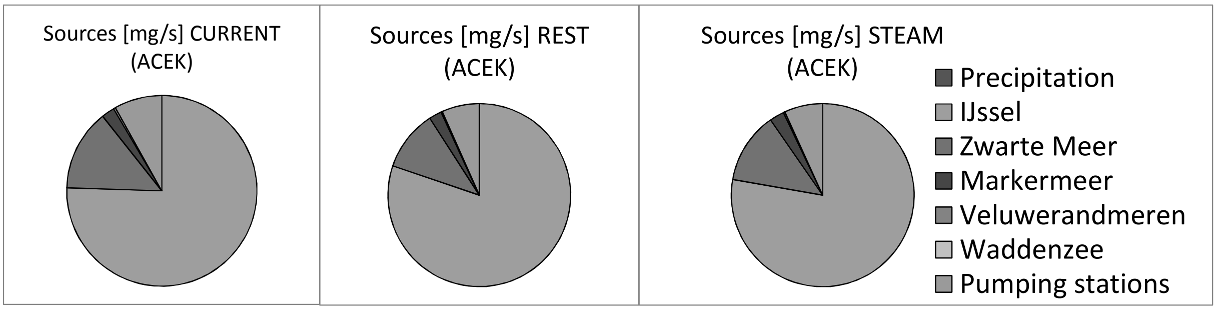

Figure 8-11 Distribution graph of acesulfame-K load in future scenarios REST and STEAM

In figure 8-12 the limits and target values for water used for the production of drinking water are shown by a line. AMPA and total pesticides exceed the limits given in section 8.3.2. Glyphosate and N,N-DMS are just below this limit. The target values for water intended for the production of drinking water are exceeded for acesulfame-K and metformin, carbamazepine is just below this target value. The target values (PNEC) for the effect of compounds on aquatic life in surface waters are relatively high and none of the values are exceeded by the calculated concentrations in the IJsselmeer at Andijk.

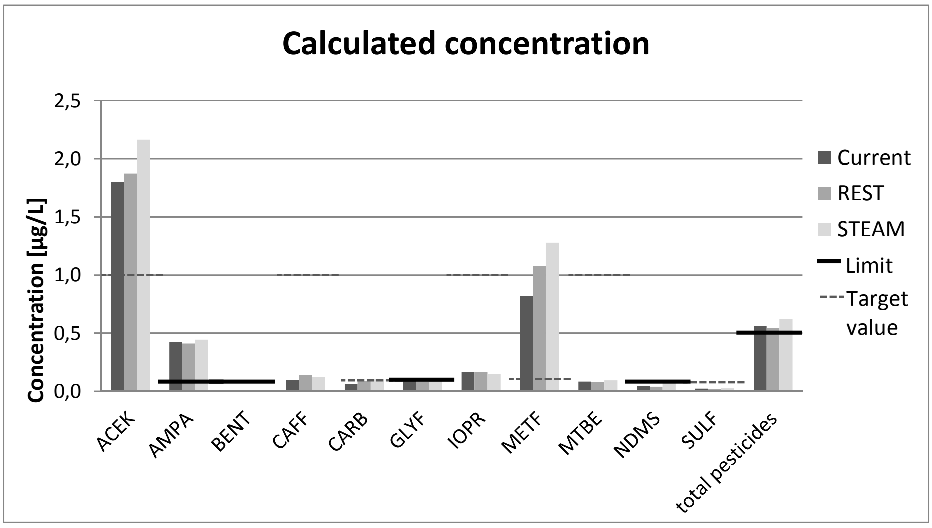

Figure 8-12 Concentrations of compounds in IJsselmeer at Andijk with limits

Although the future scenarios cause a change in calculated concentrations, the (non) exceedance of the limits does not change. Except for acesulfame-K and metformin the change is only very small in the future scenarios. The differences in concentration increase or decrease for the selected compounds in the two future scenarios are discussed below.

- Pharmaceuticals and X-ray agent. It can be seen that for the pharmaceuticals the concentrations in scenario STEAM are higher than in scenario REST. This is consistent with the increase of concentrations of all compounds in the Rhine at Lobith. The trend in emission at other location is in scenario REST decreasing and in scenario STEAM increasing. This is not visible in the graph and for that reason it is concluded that the change in concentrations caused by the trend in emission is subordinate to the increase at Lobith. The concentration of iopromide is only fluctuating a little bit. This can be caused by very small measured concentrations in the sources.
- Domestic tracers. Both the trend in future consumption and the increase in concentrations of all compounds in the Rhine at Lobith are in both scenarios increasing. This results in an increasing concentration acesulfame-K in both scenarios. It is expected that caffeine concentrations in both scenarios would increase to. The figure shows that this is not the case for the scenario STEAM. A cause of this could be that the incoming streams with high concentrations of caffeine have a relatively small increase in discharge, compared to streams with lower concentrations of caffeine. Another possible reason is the fact that for the calculation of figure 8-12 the concentrations and discharges in the dry period are used (section 8.5.3).
- Industrial chemicals. For MTBE the concentration in the Rhine at Lobith is increasing in both scenarios. The trend of emission of MTBE in the scenario REST is decreasing and in the scenario STEAM it is increasing. This can be seen in the graph. The influence of the trend in emission is superior to the change in concentration at Lobith.
- Pesticides. For all pesticides the concentrations in the Rhine at Lobith are increasing for both scenarios. Emission of AMPA, bentazone and glyphosate decrease in both scenario REST and STEAM. The concentrations of AMPA, bentazone and glyphosate decrease in scenario REST and increase in scenario STEAM. A possible reason for this is that in the calculations the dry season is assumed (section 8.5.3). Emission of N,N-DMS decreases in scenario REST and increases in scenario STEAM. This

is also what can be seen for the concentration of N,N-DMS in the future scenarios. For N,N-DMS the influence of the trend is superior to the change in concentration at Lobith.

8.8 Results and discussion strategies

In order to test the influence of the strategies, the best two strategies following from the MCA are applied on the IJsselmeer balance. The strategy 'legislation and policy' is modelled as a reduction in concentration of all substances in surface water of 50%. The strategy 'green pharmacy' is modelled as a reduction in concentration of all pharmaceuticals in surface water by 50% and of caffeine by 20%. The concentration of caffeine is decreasing less, because only a part of the caffeine entering the water cycle is used as a pharmaceutical additive. The given percentages in decrease are an estimation to give the relative changes in concentration of all compounds in the current situation and in both future scenarios. For each strategy the focus is on the compounds appearing in the highest load and the compounds which exceed the limits set in section 4.2. Three graphs are produced: no strategy applied, 'legislation and policy' applied and 'green pharmacy' applied. For each graph the current situation is given as well as the situation in the scenarios REST and STEAM.

Results

Figure 8-13 shows the total concentration per OMP in the IJsselmeer at Andijk for the current situation, the future scenario REST and the future scenario STEAM if no strategies are applied (identical to figure 8-12). Figure 8-14 and figure 8-15 show the situation if either strategy 'legislation and policy' or 'green pharmacy' is applied. In the future scenarios changes in emission of OMPs are taking into account as well as changes in river discharge and precipitation. The influence of applying the strategies is discussed below.

- Pharmaceuticals and X-ray agent. This group of compounds benefits from both strategies, 'legislation and policy' and 'green pharmacy'. The concentration of metformin still exceeds the limits, for both strategies and both future scenarios. The concentrations of carbamazepine, sulfamethoxazole and iopromide are already below the limit concentration in the situation with no strategy applied.
- Domestic tracers. For the domestic tracers acesulfame-K only the strategy 'legislation and policy' causes a change in concentration. For the current situation and the future scenario REST this decrease is sufficient for the concentration to be below the limit. In the scenario STEAM the concentration is just above the limit. For caffeine both strategies decrease the concentration. The concentration in the situation when no strategy is applied already below the limit.
- Industrial chemicals. The concentration of MTBE is already below the limit. For this compound only the strategy 'legislation and policy' results in a decrease.
- Pesticides. For this group of compounds only the strategy 'legislation and policy' results in a decrease in concentration. In the current situation bentazone, glyphosate and N,N-DMS are already below the limit. After applying the strategy 'legislation and policy' the concentration of AMPA is still exceeding the limit. The decrease in concentration of total pesticides results in a concentration below the limit.

As expected the strategy 'legislation and policy' results in an overall decrease in concentration, where 'green pharmacy' only reduces the concentrations of pharmaceuticals. This result is trivial, because the strategies are modelled as a decrease in all compounds or only in pharmaceuticals, respectively for 'legislation and policy' and 'green pharmacy'. For this reason the decrease in concentration between 'no strategy' and one of both applied strategies is always 0%, 20% or 50%. From figures 8-13, 8-14 and 8-15 it can be seen that in the case of the IJsselmeer 'green pharmacy' does not decrease the concentration of the substance appearing in the highest concentrations (acesulfame-K), but it does decrease the concentration of metformin (also very high concentration). The concentration of carbamazepine, which forms a potential risk for drinking water, is decreased by applying this strategy. For the IJsselmeer 'legislation and policy' is more effective, based on this model and corresponding assumptions.

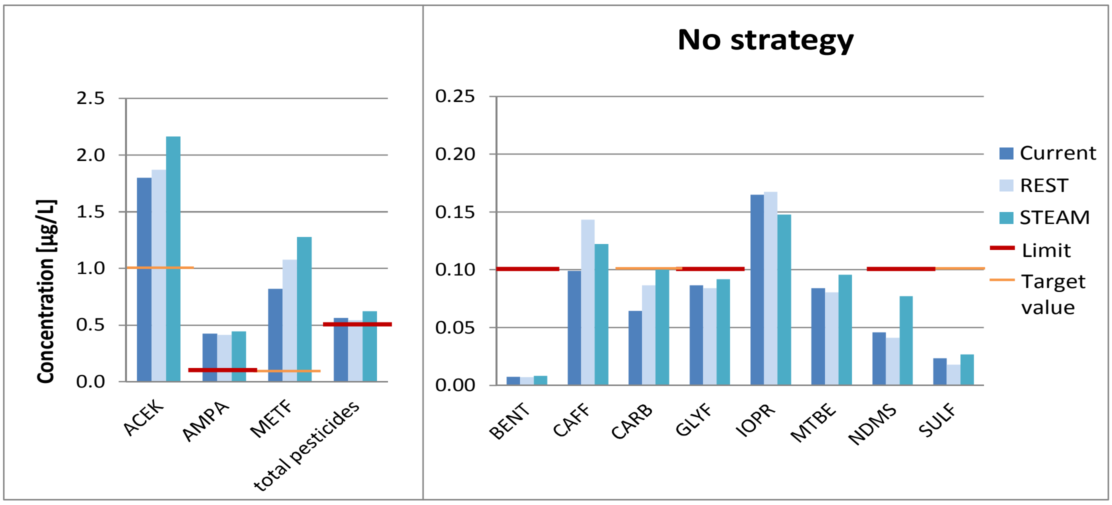

Figure 8-13 Concentrations in current situation, scenario REST and scenario STEAM if no strategy is applied with limits

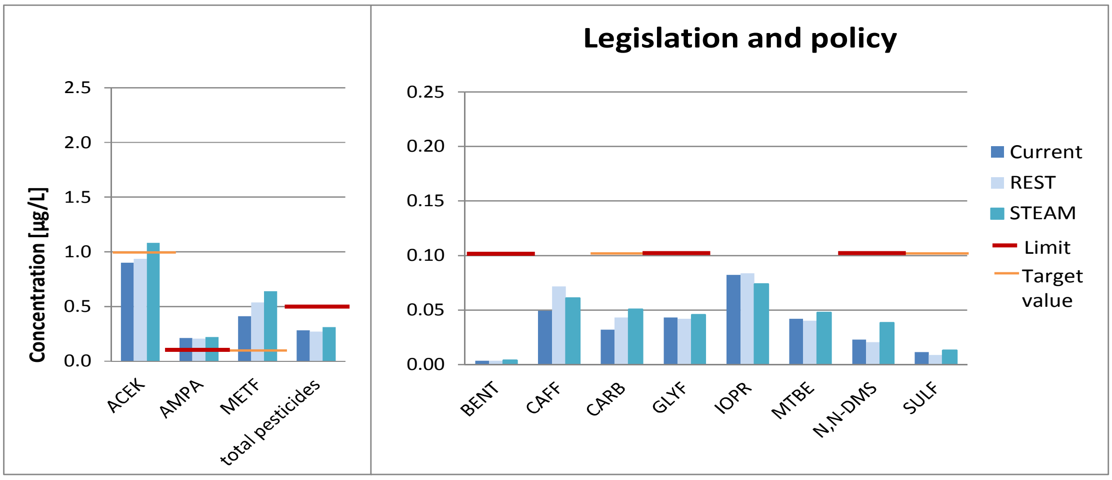

Figure 8-14 Concentrations in current situation, scenario REST and scenario STEAM if the strategy ‘legislation and policy’ is applied with limits

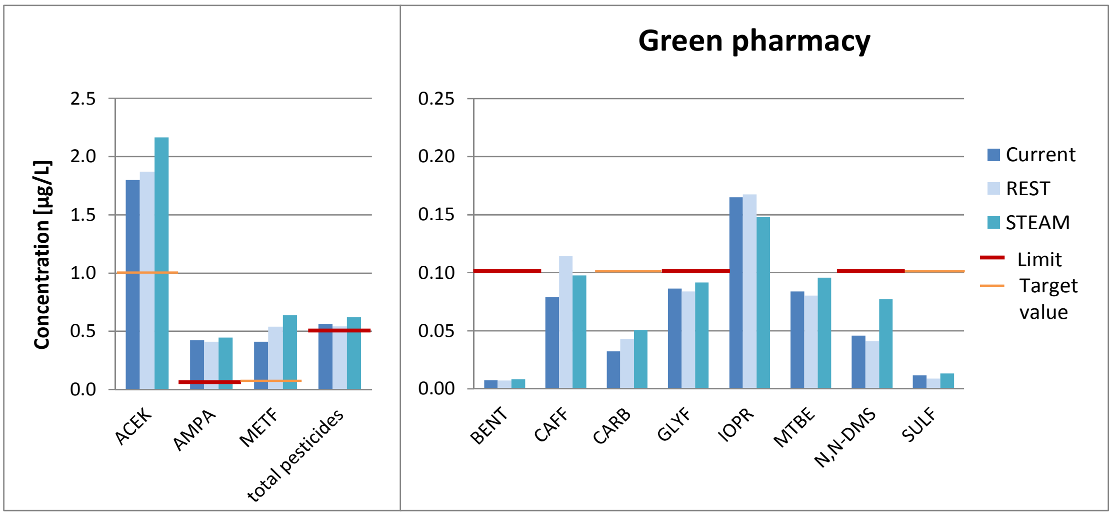

Figure 8-15 Concentrations in current situation, scenario REST and scenario STEAM if the strategy ‘green pharmacy’ is applied with limits

Solutions for Andijk

In the IJsselmeer at Andijk the compounds which exceed the limits for water intended for the production of drinking water are mainly pesticides. Other compounds that exceed the target values are acesulfame-K and metformin. From the previously described figures it is determined that 'legislation and policy' is more effective in the IJsselmeer than 'green pharmacy'. However, none of both strategies result in such a decrease that limits are not exceeded anymore. AMPA, acesulfame-K (only for scenario STEAM) and metformin even exceed the limits when applying 'legislation and policy'.

Since the concentration of total pesticides consists mainly of AMPA, the focus of a solution for the high concentrations of these compounds should be on the reduction of AMPA or glyphosate in the water cycle. From the discharge distribution graph in figure 8-16 it can be seen that the IJssel is the main contributor to the total load of AMPA, followed by Zwarte Meer and pumping stations. Figure 8-17 shows that the concentration of AMPA in the Rhine at Lobith already is high. This suggests that transboundary solutions might be necessary to decrease the concentration of AMPA. For other compounds this is similar (appendix 8-2B and 8-4ABC).

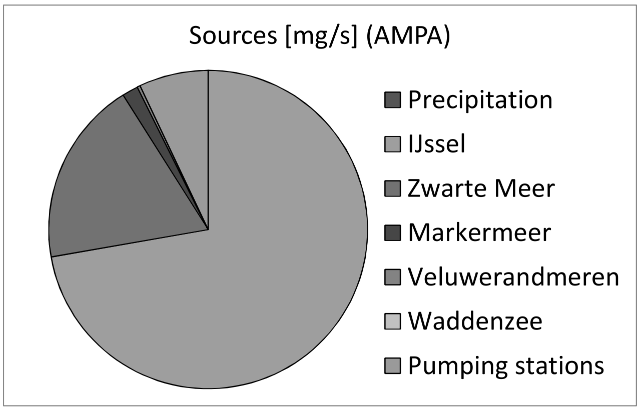

Figure 8-16 Distribution graph of AMPA load in current situation

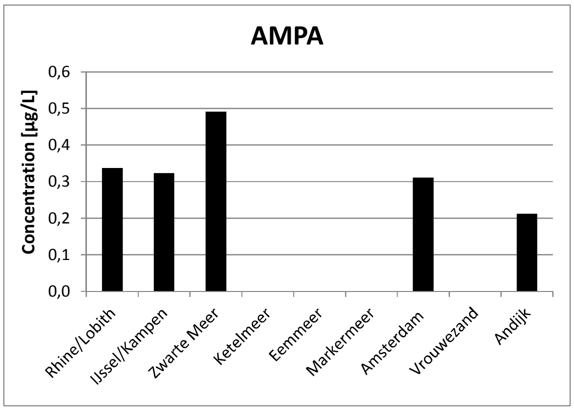

Figure 8-17 Measured concentrations of AMPA

Since AMPA is a degradation product of glyphosate, the focus of a solution for the high concentration of these compounds should be on the reduction of glyphosate in the water cycle. A potential measure in the Netherlands is to restrict the use of glyphosate in and around Andijk. In this way its metabolite AMPA is not discharged by pumping stations close to the extraction area at Andijk. With a reduction of glyphosate in agriculture and for weeding of paved areas (mainly by municipalities), the concentrations of AMPA and finally also total pesticides will reduce. More information on current developments on prohibition of herbicides can be found in section 7.8.

For compounds other than pesticides other measures are possibly effective. From figure 8-11 the distribution of the total load of acesulfame-K shows that about 75% of the total load in the IJsselmeer at Andijk originates from the river IJssel (similar for metformin). Possibly WWTPs discharging on the IJssel contribute to this load. Although beyond the scope of this project, a possible measure could be to equip the WWTPs discharging on the IJssel with additional treatment, specialised in the removal of OMPs.

9 General discussion

This chapter focuses on the general discussion of the research on OMPs in the water cycle. Specific discussion of the results of the water and mass balances is already done in chapters 7 and 8. The results of the Multi Criteria Analysis and the two case studies are discussed below. I acknowledge that the outcome of the study is subject to limitation and error, which are also stated in the section limitations.

9.1 Interpretation of results

In this section the results of the future scenarios, the selection of target compounds, the cost estimation of the strategies, the MCA and sensitivity analysis and the two case studies are discussed.

9.1.1 Future scenarios

The future scenarios are selected from the existing Deltascenarios. The percentages in increase or decrease of concentrations of selected OMPs representing these scenarios are estimated based on literature. Within the scope of the project this is done only roughly.

9.1.2 Target compounds

The selected target compounds are carbamazepine, metformin, sulfamethoxazole (pharmaceuticals), iopromide (X-ray contrast agent), acesulfame-K, caffeine (domestic tracers), MTBE (industrial chemical), AMPA, bentazone, glyphosate and N,N-DMS (pesticides). These compounds cover most of the emission routes to the (aquatic) environment. No substances of the WFD-priority list are selected, because those compounds are especially toxic for aquatic life and in most cases not relevant for drinking water. The WFD has as goal to increase the condition of surface water and groundwater with regard to aquatic life, where the subject of this project is on the reduction of concentrations of compounds in water bodies intended for the production of drinking water.

9.1.3 Strategies

A difficult aspect regarding the strategies is the cost estimation of the various strategies. For most of the treatment technologies costs are estimated based on full-scale operating units. These costs are expressed as [€/i.e./y] for wastewater treatment or [€/p/y] for drinking water, where the assumed daily production of wastewater is 180 L/p and the assumed daily consumption of drinking water is 120 L/p (table 5-1). For the strategies incorporating ‘separate collection and treatment of urine’ and ‘decentralised collection and treatment of wastewater on residential scale and in hospitals’ cost estimates are found. For the remaining strategies (‘green pharmacy’, ‘awareness’, ‘legislation and policy’ and ‘green agriculture’ no costs are found. From the found costs it can be seen that upgrading of a WWTP or DWTP is less expensive than applying one of the strategies with ‘separate urine or total wastewater collection and treatment’. This corresponds with the scoring in the MCA. However, for the strategies 1-4 the scoring of the criterion ‘costs’ is very globally estimated.

9.1.4 Multi Criteria Analysis

Results

The best strategy which results from the MCA is ‘legislation and policy’ (table 6-2 and 6-3). This strategy scores 1.01 in total, with a difference of 0.33 and 0.40 on the strategies ranked in second and third place respectively. However, this strategy is not a stand-alone solution. Implementation requires the need for the implementation of other strategies or measures as well. Reduction of the emission of certain substances requires improvement of treatment facilities or a decrease in use of products from which those certain substances originate (section 5.1.1). The relatively low costs and high sustainability will be affected in negative perspective when other measures are incorporated in this strategy. For this reason also the second best strategy is selected to elaborate on, which is ‘green pharmacy’. This second best strategy is also not a stand-alone solution to the problem of OMPs, because it only reduces the emission of (veterinary) pharmaceuticals. Although the criterion ‘effectiveness’ in the MCA for this strategy scores third worst, it scores second best on the total MCA. This is mainly caused by the weighting factor of the criterion 'effectiveness' (0.15), which results in a weighted value of 0.03 for 'effectiveness', while much lower valued weighting factor of 'energy consumption' (0.09) results in a value of 0.144 for that criterion. The judgement of the expert panel for the strategy 'green pharmacy' is on most other criteria very positive. Even a negative score for 'effectiveness' of -2 (least possible score), would result in an overall ranking in fourth place for this strategy.

Strategies that score very high on 'effectiveness' are 'improvement of WWTP' and 'improvement of DWTP'. In the overall ranking these strategies score moderate. The reasons for this are the high 'costs' and high 'consumption of energy' and 'raw materials'. Of the strategy 'awareness in use and prescription' mainly the score of 'applicability' is the cause of the moderate overall score. In 'green agriculture and cattle breeding' not only one aspect scores low, but all criteria score only moderate. Strategies that incorporate 'separate collection and treatment of urine' and 'decentralised collection and treatment of wastewater on residential scale and in hospitals' result in the lowest overall scores. These strategies have a low score on 'costs' and 'applicability'.

A major drawback of this MCA is that for almost none of the strategies almost none of the criteria could be expressed in exact numbers. Only the costs of the treatment techniques of the strategies 'improvement of WWTP/DWTP' are estimated wit exact numbers. This compensates with the fact that for the criteria 'sustainability' and 'applicability' also no exact numbers are given. The scoring of the strategies in the MCA is based on expert judgement and relies on the expertise of the expert panel. Although, a more reliable outcome would be achieved from the MCA when expressing the criteria 'costs', 'sustainability' and 'applicability' in exact numbers, the functioning of the strategy depends also a lot on the case study and the selected compounds. Incorporating other criteria would influence the MCA as well.

Sensitivity analysis

The sensitivity analysis shows the ranking of the strategies when something in the weighting factors is changed (table 6-3). This analysis results in changed rankings for each time a weighting factor is changed. In most cases the same strategies result in the top three and in almost all cases the strategies with 'separate collection and treatment of urine' and 'decentralised collection and treatment of wastewater on residential scale and in hospitals' result in the lowest ranking. When looking at 'costs' as the most important aspect, with corresponding best strategy 'awareness', than the weighting factors of 'applicability' or 'sustainability and applicability' should be zero. When 'sustainability' is the most important aspect (corresponding best strategy 'green pharmacy') weighting factors of 'costs' and 'applicability' should be zero. A high ranking of the strategies 'improvement of WWTP/DWTP' is reached when effectiveness is the most important aspect. This is the case when weighting factors of 'costs' and 'sustainability' are zero and in the un-weighted situation. The sensitivity analysis shows the situations in which other strategies score better than in the normally weighted MCA. The used criteria are of influence on the outcome of the MCA. This is further elaborated in section 9.2.4.

9.1.5 Case studies

Water quality data

For most compounds the measured concentrations meet the expectations (concentrations at Lobith lower than further downstream, difference in concentrations of certain compounds between Andijk and Bethunepolder). Especially carbamazepine and MTBE show no disturbing concentrations. A remarkable thing is the concentration of caffeine, which is expected to be very high in the Vecht compared to the concentration at Andijk, since the Vecht consists almost completely of WWTP effluent. There are two reasons found: there is only one measurement available at Vecht and Utrecht OUT and this measurement is performed during summer, when concentrations of caffeine are much lower than in winter. In (Ferrari *et al.*, 2003) seasonal variation in presence and concentration of pharmaceuticals in the river Rhine is described. Variation in concentrations might be caused by changes in use, variations in sorption and degradation as a result of environmental factors such as light and temperature, or variations in the flux of water. Contrary to caffeine, the expectations regarding the concentration of acesulfame-K are met. Concentrations of acesulfame-K at the

Vecht are much higher than at Utrecht OUT (just before the WWTP) and are much higher than at Andijk. However, the concentration at the Bethunepolder is much lower than at the Vecht and also lower than at Andijk. It might seem obvious that degradation and adsorption play a role in the groundwater transport of the Bethunepolder. This might also be a reason for the lower iopromide and metformin concentrations in the Bethunepolder, compared to concentrations measured at other locations in the Bethunepolder case. The bentazone concentration is higher in the Bethunepolder than at Andijk, which could be a result of the mostly agricultural function of the area around the Bethunepolder and the long residence time in the groundwater. N,N-DMS is found in the Bethunepolder in higher concentrations than in the IJsselmeer. The Loosdrechtse Plassen are bordering the Bethunepolder, where extensive water recreation takes place. N,N-DMS is used as an anti-fouling agent in water recreation. The Loosdrechtse Plassen is a relatively shallow lake and the density of recreational boats is much higher than in the IJsselmeer. Glyphosate and its metabolite AMPA are found in both case studies, where the concentration of AMPA is much higher than that of glyphosate. This is caused by the degradation of glyphosate into AMPA. Finally, sulfamethoxazole is only found in very low concentrations in both case studies. The substance might be degraded before the water enters the water extraction points.

Models

Water and mass balances are composed for both case studies, in order to test the strategies on and see the influence of these strategies. The water balances of both case studies fit very well. However, missing or incomplete quality data result in differences between the calculated concentrations and the measured concentrations. It is expected that decay of the compounds, which is assumed to be negligible, plays a role in this. To test this the decay rate is applied (see below).

The two best strategies are tested on the cases: ‘legislation and policy’ and ‘green pharmacy’. In both cases the strategy ‘legislation and policy’ results in a decrease of all compounds, where ‘green pharmacy’ only reduces the concentrations of pharmaceuticals. From the results it can be seen that both case studies behave similar after applying one of both strategies (figure 7-21, 7-22, 7-23, 8-13, 8-14 and 8-15), with the exception that the concentrations of acesulfame-K and glyphosate in the Bethunepolder the limits are still exceeded and in Andijk the limits are met (for CURRENT and REST) (figure 9-1). The results in chapter 7 and 8 show that ‘legislation and policy’ is more effective than ‘green pharmacy’.

It must be noted that in the Bethunepolder the assumption of no degradation and adsorption is the weak point, since the water travels through the subsurface and the residence time is very long. This affects the concentrations (figure 7-16 and 8-8). A big difference between the groundwater driven situation and the surface water driven situation is the residence time of the substances in the water before arriving at the extraction location. In the Bethunepolder this residence time varies between 1-100 years, where the residence time in the IJsselmeer is only 3-6 months. Although, from the results it is concluded that the decay factor does influence the calculated concentrations, it is not applied in the models. The reason for this is that of only four substances a decay factor is found in literature. Finally, the models show a certain distinction between the calculated and measured concentrations, but globally the models are considered to be useful in this project.

Table 9-1 Exceedance of limits in the case studies

	Bethunepolder		Andijk	
	No strategy	'Legislation and policy'	No strategy	'Legislation and policy'
Pharmaceuticals and X-ray agent				
• Carbamazepine	✗	✓	✓	✓
• Metformin	✗	✗	✗	✗
• Sulfamethoxazole	✓	✓	✓	✓
• Iopromide	✗	✓	✓	✓
Domestic tracers				
• Acesulfame-K	✗	✗	✗	✓ (CURRENT & REST), ✗ (STEAM)
• Caffeine	✓	✓	✓	✓
Industrial chemicals				
• MTBE	✓	✓	✓	✓
Pesticides				
• AMPA	✗	✗	✗	✗
• Bentazone	✓	✓	✓	✓
• Glyphosate	✗	✗	✓	✓
• N,N-DMS	✓	✓	✓	✓

9.2 Limitations

In this section the limitations of the project are discussed. This is done based on the different aspects of the project.

9.2.1 Future scenarios

The applied future scenarios are based on the scenarios of the Deltaprogramma and are assumed to be realistic. However, the impact of the scenarios on the emission of OMPs and the concentration of OMPs in the water is more uncertain. Although the percentages of increase and decrease are estimated based on literature they still are estimates of which the reliability is questionable (section 3.3). Within the scope of this project it is not possible to investigate this further.

9.2.2 Target compounds

In this project 11 substances are selected as target compounds, which are used in the modelling in the case studies. Of some of the compounds and some of the measurement locations no measurements are available. In that case a value of another location is used. Another aspect is the frequency of measurements. Some measurements are performed monthly or even more frequently, but other measurements are performed only once. This results in an error in the results. Especially the measurements of caffeine are less reliable, because the analysis of caffeine in samples is very sensitive to disturbance.

9.2.3 Strategies

The strategies are modelled as a reduction of all compounds by 50% ('legislation and policy') and a reduction of carbamazepine, metformin and sulfamethoxazole by 50% and caffeine by 20% ('green pharmacy'). Within the scope of this project these percentages are only estimated roughly.

9.2.4 Multi Criteria Analysis

The strategies composed in this project are focussing only on the Netherlands, but more effective strategies should also focus on countries upstream of the Netherlands. In addition to the composed criteria, some other criteria could be important. Additional benefits results in a higher total score for strategies that score worse on aspects such as costs or sustainability, but have a positive influence on aspects that are not (drinking) water related. Another example is 'ease of control', in which the verifiability is expressed. Transboundary solutions are harder to verify. The criteria of the MCA are scored based on an expert judgement of the expert panel. The uncertainty in scoring can be found in the fact that none of the criteria can be expressed in actual values. Other aspects influencing the outcome of the MCA are the size of the panel (only five members) and the interpretation of the criteria by the panel.

9.2.5 Case studies

As explained before, models are a schematic representation of the real situation, where simplification and assumptions are necessary. For the models quantitative and qualitative data is used. Enough data of the major rivers is available. However, data of smaller rivers and streams is not available. The composed models are static models, where only one value per parameter is used and no distinction is made between the wet and the dry season, because of the long residence times in the subsurface or lake. A yearly average value is used, but this levels out the extremes that occurred and potentially are of importance. Water quality data is often scarce and often only from a relatively short period within the past 20 years. This results in measurements of compounds at different periods, which makes comparison of these compounds less reliable due to changing conditions in time. Another aspect is the rapid change in concentration on a measurement point. In the modelling it is assumed that no degradation or adsorption will occur. Calculations with decay rate suggest that there is degradation in the system. No literature is found on adsorption. Also the mixing of the system plays a role in uncertainties in measurement data. In the model it is assumed that the system is well-mixed and that incoming discharges mix instantaneously with the receiving water. In reality this is not correct. Besides the reliability of the data also another aspect is important. The models are validated based on the criteria whether or not the results of the models are in the same order of magnitude as the measured concentrations. From the quality data it can be seen that almost all concentrations per compound are in the same order of magnitude on different locations. The consequence of this is that the calculated concentrations in the same order of magnitude as the measured concentrations do not necessarily mean that the model is correct. Missing data is also a cause for uncertainties. When no quality data are available of a source the data of the closest source are used.

10 Conclusions and recommendations

10.1 General conclusions

The purpose of this report is to determine the most sustainable, applicable and cost-efficient strategy to reduce the concentrations of organic micro pollutants (OMPs) in surface water and drinking water in the Netherlands. The research is conducted by determining what target compounds need to be reduced, where these pollutants originate from, which treatment technologies are available, what strategies are possible to reduce the concentration of OMPs and how this relates to the costs of these strategies. In order to do so two case studies are used of which a water and mass balance of OMPs is composed. These balances are used to test the strategies on and determine whether they reach the desired decrease in concentration of the target compounds or not. Due to the long-term character of the strategies, future scenarios regarding the emission of OMPs and precipitation and river discharge are composed and also applied on the water and mass balances. Finally, the conclusions are drawn on these mass balances and the research questions are answered.

10.1.1 Research questions

The research question and sub-questions of this project are:

What is the most sustainable, applicable and cost-efficient strategy to reduce concentrations of selected micro pollutants in surface water and drinking water in the Netherlands?

1. What are the target compounds, what is their impact on aquatic life and human health and what concentrations are accepted?
2. What are the sources of origin of the pollution?
3. Which treatment techniques are available and what is known about the removal of organic micro pollutants by these techniques?
4. Which strategies are possible to reduce the amount of organic compounds in the surface and drinking water?

Answers to these sub-questions can be found in section 10.1.3, 10.1.5 and 10.1.6 (sub-question 3 and 4) respectively. From the previously described methods and results it can be concluded that the most sustainable, applicable and cost-efficient strategy to reduce concentrations of selected micro pollutants in surface water and drinking water in the Netherlands is ‘legislation and policy’, in which governmental regulations regarding the emission of OMPs into the water cycle are improved.

10.1.2 Issues on OMPS

The current problems of OMPs in the water cycle are not that the concentrations present in the water cycle are too high to guarantee the safety of drinking water, but the long-term effects of these concentrations, the increase in concentrations (due to changing circumstances) and the unknown effect of OMPs in mixtures with other OMPs.

10.1.3 Sources (sub-question 2)

Wastewater treatment plants are the main contributors for compounds with regards to domestic use (such as pharmaceuticals and personal care products). Although the effluent of a hospital is much more concentrated regarding pharmaceuticals and other hospital specific OMPs, the total load of these compounds originating from residential areas is much higher. Pesticides are mainly applied in agriculture and in removal of weeds on paved areas. They end up in the water cycle by infiltration and runoff. Industrial chemicals (MTBE) are used as gasoline additives or other industrial purposes and are mainly discharged into the water cycle by runoff from paved areas.

10.1.4 Future scenarios on emission of OMPs

In order to respond to changes in demographic aspects, usage patterns and climate, it is important to take the future situation into account in new designs. Demographic trends and the assumed climate change are combined with existing future scenarios, which can be used to test strategies on and to see the influence of the strategies in the future situation. In this study two Deltascenarios are used: REST and STEAM (figure 10-1) (Deltaprogramma, 2011). REST is a scenario of economic stagnation with moderate climate change. In STEAM both the economic situation and climate change increase.

10.1.5 Emerging compounds (sub-question 1)

In this study 11 target compounds are selected to serve as indicator compounds in the mass balances. The selection is based on various criteria. The most important criterion is the relevance of the chemicals for drinking water quality (criterion 1). These are substances that are persistent and mobile in groundwater (polar). Furthermore, the potential effect of the substances on human health and aquatic life is important (criterion 2). This is determined by the presence on a list of priority substances or on a watch list of Waternet, Riwa-Rijn, WFD-priority substances, STOWA, GWCR or the list of Rhine substances of ICBR. Finally, compounds are selected of which measurement data are available at different locations within the River Basin District Rhine West, at locations significant for the case studies and in the drinking water (criterion 3). The selected target compounds in this study are carbamazepine, metformin and sulfamethoxazole (pharmaceuticals), iopromide (X-ray contrast agent), acesulfame-K, caffeine (domestic tracer compounds), MTBE (industrial chemical), AMPA, bentazone, glyphosate and N,N-DMS (pesticides) (figure 10-2).

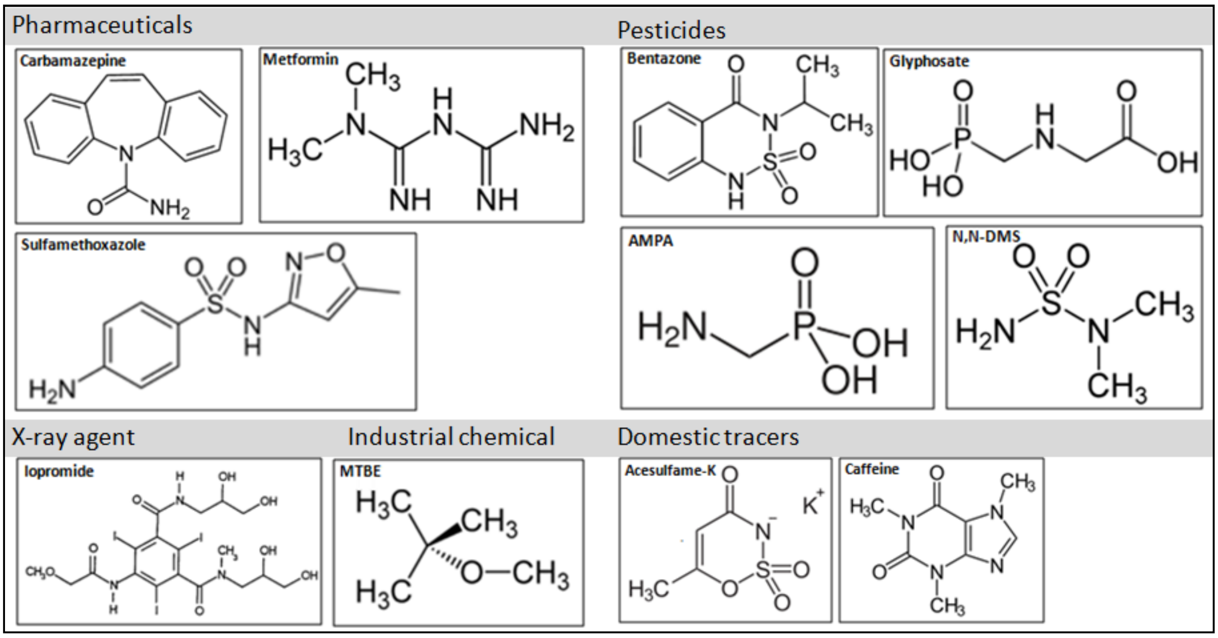

Figure 10-1 Selected compounds and their structural formulas

None of the selected compounds are present on the Water Framework Directive priority substances list, because compounds present on this list are especially relevant for aquatic life and in most cases not relevant for drinking water. Limits and target values of the selected compounds are based on Dutch law and regulations and the Danube, Meuse and Rhine Memorandum. Additional to this the Benchmark Quotient (BQ) is used to represent the risk of a certain compound to drinking water and is calculated based on the maximum measured concentration in a water body and the acceptable daily intake for humans of this compound (European Environment Agency, 2011). Using the BQ only carbamazepine, iopromide, metformin and MTBE form a potential risk for drinking water.

10.1.6 Strategies (sub-questions 3 and 4)

The aim of this project is to find strategies that reduce the concentration of OMPs in the water cycle. Different strategies that are composed are based on a source approach, a mitigation approach or an end-of-pipe approach. Source approach strategies are focussing on decreasing the *use* of chemical compounds, where mitigation approach strategies are focussing on decreasing the *emission* of chemical compounds and end-of-pipe approach strategies are focussing on improving the quality of *drinking water*.

- Source approach
    1. 'Green pharmacy' is based on both the sustainable production of pharmaceuticals and the production of sustainable pharmaceuticals.
    2. 'Awareness in use and emission' focuses on the behaviour of users of chemical compounds.
    3. 'Legislation and policy' is concerned with governmental regulations regarding the emission of OMPs into the water cycle. This strategy is inextricably connected with other strategies. When effluent discharges of a WWTP must contain lower concentrations either the emission from the sewer system on the WWTP must decrease (less use of pharmaceuticals and other chemicals) or the WWTP must be improved with more advanced technologies. Legislation and policy has to be applied on all scales: regional, national and international.
    4. 'Green agriculture, greenhouse farming and cattle breeding' is a strategy in which the amount of OMPs that are discharged into the water cycle directly by runoff and leaching is decreased.
- Mitigation approach
    5. 'Separate collection of urine in residential areas and hospitals' is based on the fact that about 80% of the pharmaceuticals applied on humans are excreted via urine, which is the more concentrated stream of wastewater.
    6. 'Separate and decentralised collection of total wastewater in residential areas' is a concept in which all wastewater streams are collected separately and treated in the area itself.
    7. 'Separate and decentralised collection of total wastewater in hospitals' is in principle the same as described in the previous strategy, but with the difference that hospital wastewater contains higher concentrations of pharmaceuticals.
    8. 'Improvement of wastewater treatment plants and effluent treatment' can lead to an improved effluent quality.
- End-of-pipe approach
    9. 'Improvement of drinking water treatment plants' may be more effective than improving an WWTP, because the amount of water to be treated is smaller and pollution other than OMPs is for the major part already removed.

Strategies that incorporate separate collection and treatment of urine and decentralised collection and treatment of total wastewater (strategies 5, 6 and 7) cost about 90-1310 €/i.e./y. The techniques used in advanced wastewater and drinking water treatment partly overlap (strategy 8 and 9). Techniques that are well-accepted in the field of water treatment and that are suitable for the removal of OMPs are activated carbon, nanofiltration, reverse osmosis, advanced oxidation processes and ozone and UV disinfection. Removal efficiencies depend highly on the exact type of OMP and the type of water. Since there are thousands of registered chemicals in the European Union alone, not of all selected compounds removal efficiencies are found. Each separate treatment technique costs about 4-80 €/i.e./y for wastewater treatment and <1-10 €/p/y for drinking water treatment. The costs of other strategies are not possible to determine within the scope of this project.

10.1.7 Multi Criteria Analysis

As mentioned previously the most sustainable, applicable and cost-efficient strategy to reduce the concentrations of organic micro pollutants in surface water and drinking water in the Netherlands has to be determined. This is done by applying a Multi Criteria Analysis (MCA) on the composed strategies. The criteria used in the MCA are:

Cost-efficiency

- Life Cycle Costs

Sustainability

- Energy consumption
- Raw materials
- Flexibility
- Robustness

Applicability

- Complexity (implementation)
- Ease of operation
- Technical risk
- Risk in implementation
- Effectiveness
- Social acceptance
- Transition period
- Innovation

The MCA is scored based on an expert judgement by an expert panel, from which it can be concluded that 'legislation and policy' is the best strategy (table 10-1). From this table it can be seen that 'legislation and policy' is by far the best strategy (first column). However, this strategy only holds when incorporating other measures to reduce the emission of OMPs into the water cycle. For this reason also a second best strategy is determined. Strategies 1, 2, 4, 8 and 9 are in the same range and score moderately, where strategies 1 and 2 score higher than the remaining three strategies. Although without a big difference, the second best strategy is 'green pharmacy'. All strategies with '(de)centralised collection and treatment of urine or total wastewater' score poor, due to a poor score on all three aspects: sustainability, applicability and cost-efficiency. A sensitivity analysis is performed, in which consecutive all criteria are un-weighted, criterion 'costs' weighted as zero, criterion 'sustainability' is weighted as zero, criterion 'applicability' is weighted as zero, criteria 'costs' and 'sustainability' are weighted as zero, criteria 'costs' and 'applicability' are weighted as zero, criteria 'sustainability' and 'applicability' are weighted as zero and criterion 'effectiveness' is weighted double. It is concluded that the MCA is only moderately sensitive, because the best and second best strategies (3 and 1) score in the top three in almost all cases, while the scores vary throughout the sensitivity analysis.

Table 10-1 Results of the Multi Criteria Analysis

	Weighted score	Un-weighted	costs = 0	Sustainability = 0	Applicability = 0	costs/sustainability = 0	costs/applicability = 0	Sustainability/ applicability = 0	Effectiveness doubled
Weighting factor									
1. Green pharmacy	0.68	5.00	0.36	0.59	1.26	0.05	0.93	1.60	1.00
2. Awareness in use and prescription	0.61	2.60	0.12	0.54	1.40	-0.26	0.81	2.00	0.47
3. Legislation and policy	1.01	7.80	0.72	1.06	1.32	0.66	0.84	1.80	1.07
4. Green agriculture, greenhouse farming and cattle breeding	0.46	4.80	0.33	0.42	0.68	0.21	0.57	0.80	0.38
5a. Decentralised collection and treatment of urine	-0.72	-7.60	-0.40	-0.82	-1.01	-0.39	-0.42	-1.60	-0.52
5b. Centralised collection and treatment of urine	-0.57	-4.40	-0.20	-0.61	-1.01	-0.07	-0.43	-1.60	-0.40
6. Decentralised collection and treatment of wastewater on residential scale	-0.55	-8.00	-0.47	-0.60	-0.61	-0.49	-0.42	-0.80	-0.35
7. Separate collection and treatment of hospital wastewater	-0.11	0.40	0.13	-0.04	-0.56	0.37	-0.32	-0.80	0.01
8. Improvement of WWTP	0.31	6.40	0.71	0.49	-0.49	1.20	-0.18	-0.80	0.57
9. Improvement of DWTP	0.30	7.00	0.69	0.45	-0.44	1.13	-0.09	-0.80	0.49

Green: good score, orange: moderate score, red: poor score

10.1.8 Case studies

To determine the impact of the strategies two case studies are investigated: Bethunepolder and Andijk. Both case studies are drinking water extraction areas. The Bethunepolder is a deep polder in which all the surface water originates from seepage and rainfall; no external sources of water are present. Andijk is the water extraction location where the water is extracted from the IJsselmeer. Both water systems are partly fed by the river Rhine, either by groundwater infiltration or by surface water (figure 10-3). For both cases limits and target values are determined (table 10-2). Water and mass balances on these case studies are composed and validated. This is done by comparing the calculated discharge and concentrations with the measured discharge and concentrations. In the case studies it is assumed that the water is completely and instantaneously mixed with incoming discharges and no degradation or decay takes place, both in surface water and in groundwater. In order to check the assumption of no decay, calculations on decay are done. The decay rate was only found for four substances. From calculations with and without decay of one-dimensional plug flow of the surface water, first-order decay calculations of the groundwater and a series of completely mixed tanks it is concluded that the calculations with decay result in lower concentrations than without decay, but in most cases still higher concentrations than measured. However, one-dimensional plug flow with decay results in a concentration closer to the measured concentration than calculations without decay, but since only for four substances a decay factor is found, the calculations in the models are performed without decay. In the modelling a normal situation regarding pollution is assumed. In case of an accidental spill, the models would react differently.

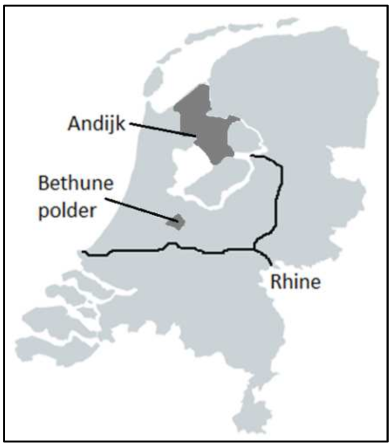

Figure 10-2 Map of the Netherlands with Bethunepolder and Andijk (IJsselmeer)

	Target values sw (PNEC)	Limits sw intended for dw		Target values sw (PNEC)	Limits sw intended for dw
	[µg/L]	[µg/L]		[µg/L]	[µg/L]
ACEK	-	1.0*	IOPR	256	1.0*
AMPA	-	0.1	METF	511	0.1*
BENT	-	0.1	MTBE	2600	1.0*
CAFF	182	1.0*	NDMS	140	0.1
CARB	0.42	0.1*	SULF	0.118	0.1*
GLYF	-	0.1	Pesticides combined	-	0.5

** Precautionary target values*

Table 10-2 Target values for surface water (Predicted No Effect Concentration, PNEC) and limits for surface water intended for the production of drinking water

Comparison of the two case studies

Although, the two case studies are both partly fed with water originating from the river Rhine (via the groundwater and via the river IJssel), the measured concentrations and exceedance of limits and target values are not the same. In the Bethunepolder the calculated concentrations exceed the limits for six compounds, while none of the measured concentrations exceed the limits. In the Andijk case the concentrations of three compounds exceed the limits, for both the measured and the calculated concentrations. After applying the strategies on the models in the Bethunepolder case concentrations of most compounds decrease to below the limits, where this decrease is in the Andijk case not enough to go below the limits. For both case studies the results show that the best strategy is ‘legislation and policy’, because concentrations of all compounds are reduced, but when only looking at the selected compounds with a higher risk (carbamazepine (both BP and AN), iopromide, metformin and MTBE (only BP)) ‘green pharmacy’ results in a decrease to below the limits only at the Andijk case.

The most important difference between the groundwater driven system and the surface water driven system is the residence time of the substances in the water before arriving at the water extraction point. In the Bethunepolder this residence time varies between 1-100 years, where the residence time in the IJsselmeer is only 3-6 months. The difference between the calculations with and without decay show the importance of decay in situations with a long residence time. In this project no decay is assumed and thus this difference is neglected. In general it can be concluded that in a groundwater driven system the influence of OMPs seems to be less acute than in a surface water system. However, in the groundwater system the effects of the presence of OMPs will be noticeable after a longer period, which make this system more unpredictable and it takes more time till measures are resulting in a decrease in concentration.

10.2 Recommendations

General recommendations

As concluded from this project implementation of the strategy 'legislation and policy' reduces the concentrations of selected OMPs. However, the mass balances of the case studies showed that the modelled decrease in concentrations and emission of all selected compounds by an assumed reduction of all compounds by 50% is not sufficient to decrease all concentrations of selected compounds to below the limits. This emphasizes the need for an integral approach with international cooperation in which measures are combined and all member state within a river basin are participating. Control by the European Union is necessary. It is recommended to follow the approach of the Water Framework Directive and expand this to surveillance of the drinking water quality by protecting drinking water extraction areas from emerging compounds. The Priority Substances list should be expanded as well. On shorter-term national legislation and policy should be adapted to reduce the use and emission of OMPs as much as possible. Below some recommendations are made regarding specific aspects of this project.

Emerging compounds

The variety of compounds selected in this project is good, compounds of various sources are selected. However, more measurement data are needed. It is also important to gain more knowledge on the toxicology of the compounds and their behaviour in combination with each other.

Strategies

Although, the focus of this project is on two case studies in the Netherlands, there should also be strategies that are transboundary, on river basin or European scale.

Multi Criteria Analysis

Regarding the reliability of the MCA it is important to find reference costs of all strategies, where it could be more likely to use a cost-benefit analysis or even a social cost-benefit analysis instead of just reference costs. Also more criteria should be included in the MCA, such as 'additional benefits' and 'ease of control'. The panel needs to be expanded with members of other disciplines to get a well-balanced MCA.

Case studies

To increase the reliability and accuracy of the models some improvements can be made. First of all there is a need for more detail in the models; unknown and small streams, smaller time scale, dynamic instead of static model, groundwater model integrating with surface water model, mixing processes in large water bodies, behaviour of substances in groundwater and accounting for degradation and adsorption of compounds in water. Also more measurement data is required (mostly on water quality) to get more representative concentrations and discharges. The focus of strategies must be on larger scale (catchment) to include all sources and all possible measures to the target area. Also other strategies should be tested on the case studies to make a good comparison of the influence of the strategies on the concentration of OMPs.

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Appendices

Appendix 3-1 Trends and legislation indirectly related to the emission of OMPs

Dutch legislation and policy

Water Law (Waterwet)

The Water Law is in operation since 2009 and is concerned with everything that has a relation to water: water resources, flood protection, groundwater, surface water pollution, seawater pollution, polder embankment and land reclamation and waterworks. Integrated water management is the cornerstone of this law. All discharges of wastewater, contaminated with harmful substances on surface waters are only legal with a licence. The Water Law contains standards for emissions of substances in the water cycle, including OMPs. The Water Law is consistent with the WFD (Dutch Government, 2009c).

Water board

The Water Management Plan (Waterbeheerplan) is a plan for the water systems under the management of a water board. The water boards are aiming on a better cooperation with the municipalities regarding wastewater collection and treatment to increase the awareness of the water cycle as a whole (RIVM, 2008b). The Water Area Plan (Watergebiedsplan) is a plan on a subarea within the management area of the water board. The focus is only on rural areas. It contains information about the (desired) water levels, supply and drainage of (ground) water, sewerage, water quality and flora and fauna (RIVM, 2008a).

Trends

Social and environmental awareness

During the 1960s and 70s the environmental movement began and became very strong. Many environmental laws were passed and there was much public support. In the 1980s and 90s various environmental organisations were established. Since then the support of the public decreased a little. All in all the Dutch population has a positive mind-set with regards to the environment and nature life and has the conviction that an increased water quality is important (Larsson *et al.*, 2002). However, the willingness to pay for improved (surface) water quality and reliability of drinking water is generally low. In general people are more involved and interested if they are involved in the decision making process, as required under the WFD. To respond to this interest in involvement companies and government will have to invest more in consumer relations and education initiatives in the future (Cleuvers, 2003). It is preferred that these aspects are to be reflected in the composed strategies.

Management and economy

Economic growth has decreased the past years and is still decreasing, which is directly affecting Europe, the US, India, China and Japan. A new management idea is supposed to counteract this trend: New Public Management (NPM). NPM stands for a shifting focus of governmental policy towards market-based management (KWR, 2011). The present economic crisis may create an opportunity for breaking away from current trends and thoughts. Development of a 'green economy' could create a range of economic opportunities (Vuuren van *et al.*, 2009). The green economy is an economy in which policies and innovations enable society to make efficiently use of resources and enhance human well-being, while maintaining the natural systems. Another trend related to economy is the change the transition from linear to circular economy, in which the recycling of all biodegradable wastes of industrial and human activity (Greyson, 2007). These are solutions to both the economic crisis as the decreasing stock of non-renewable resources (European Environment Agency, 2012b). In certain strategies for the reduction of OMPs from the water cycle this circular economy can be an addition, which compensates for higher costs or higher impact on consumers for these strategies. An example of this is the reuse of by-products from a WWTP, like biogas and bio-plastics (European Environment Agency, 2012a).

Ecology

The growing world population and increasing use of raw materials leads to a high rate of decrease of natural capital. To reduce the negative effects production processes need to be more efficient, where a global approach is inevitable. National governments play a key role in upgrading sustainability on a long-term base by integrating governmental organizations and the private sector. The more fortunate countries, which use more of the global stock of raw materials, are morally obligated to take more responsibility for the decrease in raw materials and the decline in biodiversity. Within Europe one of the measures that is currently being undertaken is the WFD, which regulates the groundwater and surface water. Measures to improve the surface water quality consist of subsidies for use of renewable energy sources and more investment should be made in Research and Development to introduce new technologies that are socially accepted (Vuuren van *et al.*, 2009).

The influence of agriculture on the ecological status is enormous. A measure to decrease the pressure of agriculture on the loss of biodiversity in spatial respect is to intensify the agriculture, which on the other hand creates more locally concentrated problems, e.g. local loss of biodiversity and more water pollution (KWR, 2011; Vuuren van *et al.*, 2009). This is only one example to illustrate the complexity of the problem.

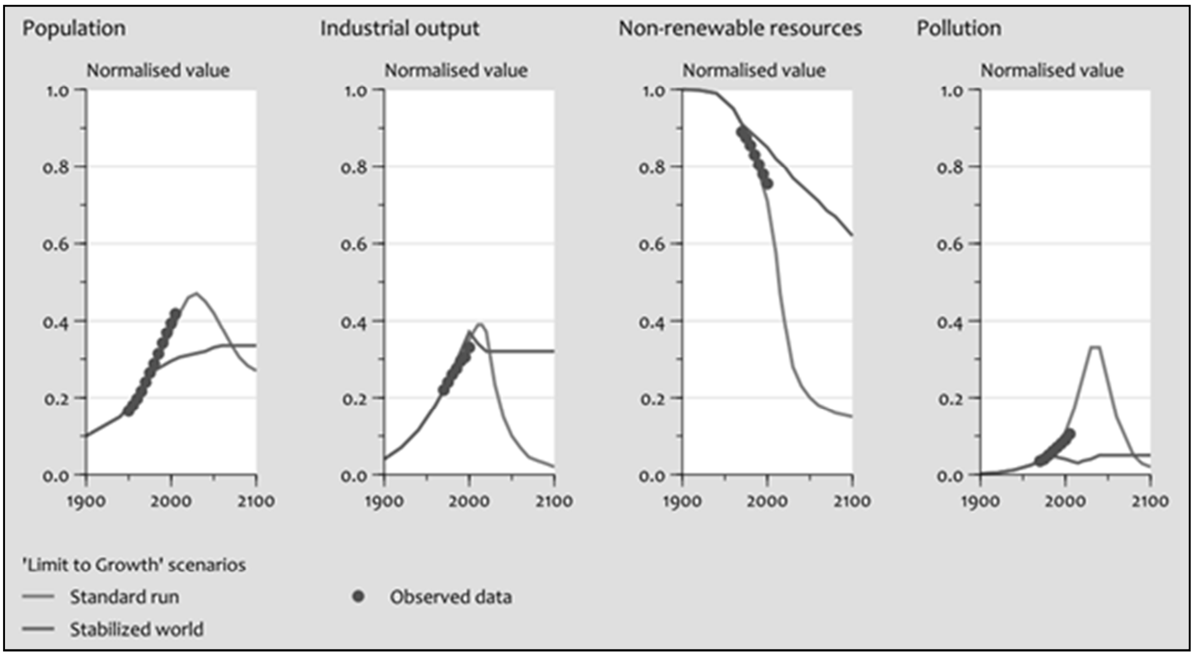
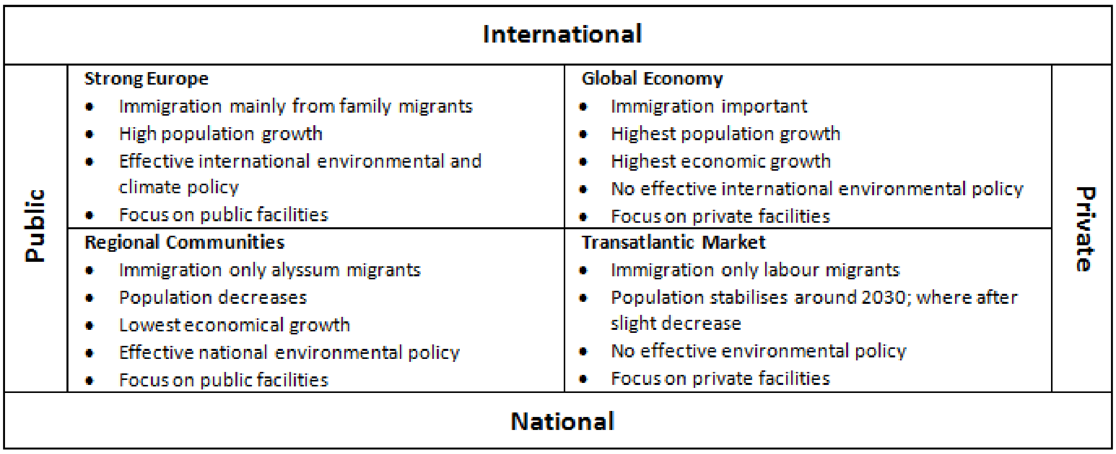


Figure C Comparing 'Limits to growth' scenarios to observed global data (Vuuren van *et al.*, 2009)

In 1972 the report 'The limits to growth: a global challenge' was presented, about economic and population growth with finite resource supplies. The authors drew three scenarios of which 'standard run' represents values of growth consistent with those of the period 1900-1970 and 'stabilized world' represents a state in which both technological solutions and deliberate social policies are implemented to achieve equilibrium states for key factors including population, material wealth and food per capita (Turner, 2008). Figure A shows the results of the two mentioned scenarios compared to actual observed global data. It shows that for most parameters the observations tend to follow the scenario 'standard run', which is not a positive prospect for the sustainability of the planet.

Appendix 3-2 Existing future scenarios



Strong Europe

- Immigration mainly from family migrants
- High population growth
- Effective international environmental and climate policy
- Focus on public facilities

Global Economy

- Immigration important
- Highest population growth
- Highest economic growth
- No effective international environmental policy
- Focus on private facilities

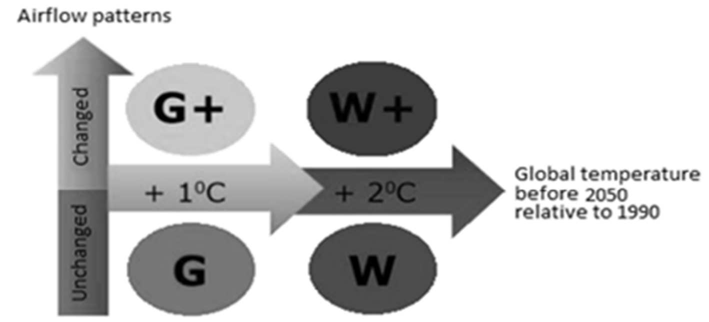
Regional Communities

- Immigration only alyssum migrants
- Population decreases
- Lowest economical growth
- Effective national environmental policy
- Focus on public facilities

Transatlantic Market

- Immigration only labour migrants
- Population stabilises around 2030; where after slight decrease
- No effective environmental policy
- Focus on private facilities

Figure D WLO-scenarios with short description (RIVM, 2011)



Scenario	Global temperature increase in 2050 relative to 1990	Dutch temperature increase in 2050 relative to 1990	Circulation in atmosphere	Average precipitation in winter	Average precipitation in summer	Sea level rise
G	+ 1 ºC	+ 0.9 ºC	No change	+ 4 %	+ 3 %	15-25 cm
G+	+ 1 ºC	+ 1.2 ºC	Winter: more west wind Summer: more east wind	+ 7 %	- 10 %	15-25 cm
W	+ 2 ºC	+ 1.8 ºC	No change	+ 7 %	+ 6 %	20-35 cm
W+	+ 2 ºC	+ 2.6 ºC	Winter: more west wind Summer: more east wind	+ 14 %	- 19 %	20-35 cm

Figure E Climate change scenarios (KNMI) (RIVM, 2011)

Table III Deltascenarios REST and STEAM (Bruggeman *et al.*, 2011)

Climate Change		**Reference**	**REST**	**STEAM**
		2000	2050	2050
Av discharge Rhine in feb	[m^3/s]	2,900	3,100	3,400
Av discharge Rhine in sept	[m^3/s]	1,800	2,000	1,300
Sea level rise	[cm]	-	15	35
Extreme high discharge Rhine 1/100 year	[m^3/s]	12,000	13,000	14,000
Extreme low discharge Rhine 1/10 year	[m^3/s]	630	650	520
Av precipitation winter		-	+4%	+14%
Av precipitation summer		-	+3%	-19%
Socio economic development		**Reference**	**REST**	**STEAM**
		2000	2050	2050
Inhabitants NL	x million	16	15	20
Economic growth	(%/year)		0.7	2.6
Urbanisation	(% area)	16	17	20
Agriculture	(% area)	67	62	59
Nature	(% area)	17	21	21
Rapid climate change (W+)				
Moderate climate change (G)				
Global Economy				
Regional Communities				

Appendix 3-3 Description of scenarios REST and STEAM and impact on the water balance

REST	Influence on water balance	Influence on strategy
International issues		
➢ Only limited international trading and no changes in international agreements concerning environmental issues	Increase in concentrations at Lobith by 5% (1)	Solution only focussed on the Netherlands
Migration		
➢ Moderate or no immigration, which means no additional increase in water consumption and use of OMPs	Decrease in water consumption by 6.25% (2) Decrease in concentration of pharmaceuticals by 37% (3) Increase in concentration of caffeine by 5% (4) Increase in concentration of acesulfame-K by 5% (4)	
Production		
➢ Production will be on a small scale and the country will be regional independent		Small scale solution
Urbanisation		
➢ Decrease in urbanisation	No additional change, only relative to population growth (5)	Decentralised solution possible
➢ More people move to the eastern, southern and northern part of the Netherlands		Decentralised solution possible
Agriculture and nature		
➢ Decrease in agriculture	Decrease in concentration of pesticides by 2.5% (6) Decrease in concentration of sulfamethoxazole by 7.3% (7)	
➢ Intensification of greenhouse farming, but very water efficient	-	
➢ Increase in nature area and Ecological Main Structure	-	Solution with high nature perspective
Transport		
➢ Decrease in cargo by road and water	Decrease in concentrations of MTBE by 4.4% and N,N-DMS by 10% (8)	
Climate		
➢ Moderate or no climate change (precipitation and sea	BP&AN increase in river discharge at Lobith in winter to 3100 m^3/s, in summer to	

level)	2000 m^3/s AN change in precipitation at Ijsselmeer in winter by +4%, in summer by +3% AN change in evaporation at Ijsselmeer in winter by 1%, in summer by 3% (11) Concentrations change relative to changing river discharge; loads remain equal	
STEAM	**Influence on water balance**	**Influence on strategy**
International issues		
➢ A growing (inter)national economy, but no international agreements concerning environmental issues	Increase in concentration of all compounds at all locations by 5% (1) Additional increase in concentration of pharmaceuticals by 5% (9)	
Migration		
➢ Many economic immigrants, which means increase in water consumption and use of OMPs	Increase in water consumption by 30.5% (2) Increase in concentration of pharmaceuticals by 37% (3) Increase in concentration of caffeine by 5% (4) Increase in concentration of acesulfame-K by 5% (4)	
Production		
➢ Production is based on good national and international trading, later it will be a ‘biobased’ economy due to scarcity of resources	-	Solution based on good trading and ‘biobased’ economy
Urbanisation		
➢ Increase in urbanisation	BP increase in water demand (urban area) by 25% (5) AN decrease in water demand (rural area) by 5% (5)	Centralisation solution possible
➢ More people live in nature areas or close to water bodies	Increase in concentration of all compounds at Lobith by 5% (1)	(Partly) decentralised solution possible
Agriculture and nature		
➢ Decrease in agriculture	Decrease in concentration of pesticides by 4% (6) Decrease in concentration of sulfamethoxazole 12% (10)	
➢ Increase in agriculture in greenhouses	-	Special attention to greenhouses
➢ Increase in nature area, but also in recreation and living in nature; nature areas will be subject to good management	-	Special attention to combination nature and recreation/Living
Transport		

➢ Increase in cargo by water (inland and maritime)	Increase in concentration of N,N-DMS by 50% (8)	
Climate		
➢ Exteme climate change, resulting in dry summers, extreme river discharges and salination by sea water intrusion (groundwater and surface water)	BP&AN change in river discharge at Lobith in winter to 3400 m^3/s, in summer to 1300 m^3/s AN change in precipitation at Ijsselmeer in winter by +14%, in summer by -19% AN change in evaporation at Ijsselmeer in winter by 1%, in summer by 15% (11) Concentrations change relative to changing river discharge; loads remain equal	Special attention to drinking water facilities (flooding and bacteria growth) and saline water intrusion
➢ Discharge of surplus water becomes harder due to a rising sea level		Special attention to discharging surplus water (Andijk)

(1) No international agreements concerning water quality result in an increase in concentration of all compounds of 5% at Lobith. This is an estimation, since no data were found.

(2) Water consumption is relative to population numbers (see scenarios). In one of the scenarios there is an increase in immigrants from 25% in 2010 to 50% in 2050. Immigrants use 23% more water. (RIVM, 2011; Vewin, 2011)

(3) As an effect of aging the pharmaceutical consumption will increase, except for sulfamethoxazole. It is both used for veterinary practise and human practise. The ratio between the two is calculated from sale data and WWTP effluent data. For more information see (7). Human sulfamethoxazole is only 3% of the total amount, so this increase can be neglected. (Nationaal Kompas Volksgezondheid, 2013; RIVM, 2011)

(4) From three websites similar trends are found, about 5% increase in caffeine concentration. Since no data were found on acesulfame-K, it is assumed that the increase in acesulfame is similar to caffeine (5%). (Bloomberg, 2013; National Coffee Association USA, 2013; Nederlandse Vereniging Frisdranken, 2011)

(5) Water demand is relative to population numbers (see scenarios). Increasing urbanisation leads to an increase in inhabitants in urban areas (Bethunepolder) and a decrease in rural areas (Andijk). (Bruggeman *et al.*, 2011)

(6) Decrease in pesticides is relative to decrease in agricultural area. From the load of pesticides measured in the downstream part of the target area, 2/3 is originating from countries upstream of Lobith. (RIVM, 2011)

(7) Sulfamethoxazole (SULF) used as veterinary pharmaceutical has a consumption of 65 tonnes in 2010 (from sales data). Another approach is to multiply the used amount [g/animal year] by total amount of animals [number animal/year] and by the ratio trimethoprim:sulphonamides (1:5) used in veterinary antibiotics. This gives a total amount of 45 tonnes in 2010. From this it is assumed that 50 tonnes SULF per year are used in veterinary practise. Human practise of SULF is determined by an average value of effluent concentration of WWTPs [0,02 g/p/y]. With 16 million inhabitants this gives a ratio of SULF practise 97% veterinary and 3% human. The decrease of SULF veterinary is relative to the decrease in agricultural area (see scenarios). The given value in the table is accounted for the change in veterinary practise and no change in human practise. (College voor zorgverzekeringen, 2013; Duijkeren van *et al.*, 1994; Laak ter *et al.*, 2010)

(8) There is no additional change in biocide concentration apart from the relative change due to increasing or decreasing shipping. Since no data were found on ratio N,N-dimethylsulfamide originating from antifouling or one of the metabolites, it is assumed that the concentration DMS is origination for 50% from antifouling and 50% from pesticide metabolites. The ratio between passenger cars and cargo traffic on Dutch roads is 78% passenger cars and 22% cargo traffic. Since no data were

found on decreasing road and water cargo (scenario REST), it is assumed that the decrease is 20% on both water and roads. In scenario STEAM the cargo by water and road is doubled. (CBS, 2009; RIVM, 2011)

(9) The scenario Global Economy yields an additional increase in consumption of pharmaceuticals, because it is possible to buy them on the market without a prescription. Since no data were found, it is assumed that this will yield an increase in pharmaceutical concentration. (RIVM, 2011)

(10) As discussed under (7) sulfamethoxazole is divided in a part originating from veterinary use and a part originating from human use. Decreasing agricultural area yields only an decrease in the veterinary part of the total sulfamethoxazole. Also see (6).

(11) The increase in evaporation in summer directly follows from the KNMI climate change scenarios. A value for winter evaporation is not given, but a yearly value is. From the summer evaporation and yearly evaporation the winter evaporation is calculated.

Appendix 4-1 Additional information on selected compounds

Pharmaceuticals

Carbamazepine

Various studies showed kidney damage in carp and accelerated aging processes and more offspring in daphnia due to stress (Gibson *et al.*, 2012; Ogunseitan, 1996). Death of the algae is also mentioned as a result of increasing concentrations of carbamazepine in surface water in Germany (Huschek *et al.*, 2004). It is expected that the majority of the prescribed amount of carbamazepine is ingested and only a small part is discharged directly into the waste (water) since it is prescribed to cure chronic diseases (Dutch Government, 2009b).

Sulfamethoxazole

The amount of veterinary pharmaceuticals that enter the water cycle by runoff from grasslands is minimal. The major part is discharged after the treatment of the manure directly discharged on the surface water. The reason for this is that the capacity of the press sewers is too low to discharge on them. Some water boards have reached an agreement with the farmers to apply a reverse osmosis (RO) installation between the manure treatment facility and the discharge on the surface water. Most compounds present in the manure have molecules large enough to be removed by RO (Alterra, 2011; RIVM, 2007b). Besides the negative effects on the environment there is a possible radical effect for public health. By discharging antibiotics into the environment bacteria can become resistant to antibiotics (Botta *et al.*, 2009; Hoek van der *et al.*, 2013; Kowal *et al.*, 2009; KWR, 2009). Figure E shows the total percentage of veterinary antibiotics in daily dose per animal year. Due to stricter monitoring and more awareness of farmers and consumers of meat, the use of veterinary antibiotics is decreasing.

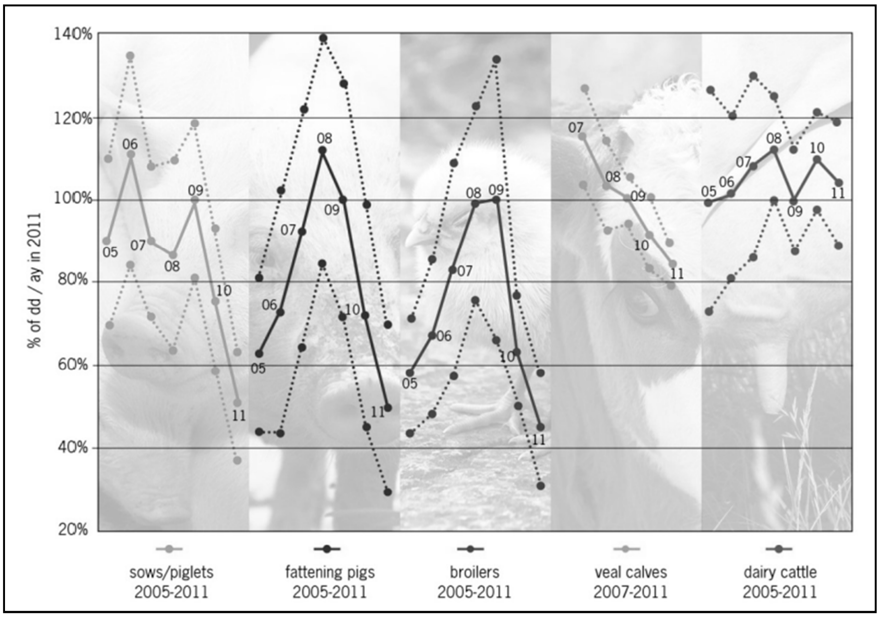


Figure F Trends in antibiotic use 2005-2011 in the Netherlands (Bondt *et al.*, 2012; Compendium voor de Leefomgeving, 2013a; b)

X-ray agents

Iopromide

No adverse effects on human health are proven. Eco-toxicity results in inhibition of light emission, growth inhibition, immobilization and reproduction and mortality (Ghimire *et al.*, 2012; STOWA, 2009b). The removal efficiency in conventional WWTPs differs between 0% and 73%. A reason for this variation in removal cannot be detected (Satyavani *et al.*, 2011; Thomaidis *et al.*, 2012; Wezel van *et al.*, 2009). No information was found on removal efficiencies in DWTP.

Domestic tracers

Acesulfame-K

Because the insulin level of the human body is not affected by the consumption of acesulfame-K (and other sweeteners), it is suitable for diabetics. Studies about eco-toxicity of artificial sweeteners are scarce and mostly on sucralose. In general, no harmful effects to the environment are found, which could also be caused by the fact that studies on the environmental effects of sweeteners are relatively recent (Cunningham *et al.*, 2010; Huerta-Fontela *et al.*, 2008; Waternet, 2013). The ADI ranges from 5-50 mg/kg bw/day, which is three to four orders of magnitude above the maximum possible daily human intake by drinking water (Waternet, 2013). A correlation is found between the concentrations of acesulfame-K and carbamazepine. The predicted pathway of exposure of acesulfame-K to the environment can therefore be used to predict the pathway of carbamazepine *(Richardson, 2012)*.

Industrial chemicals

Methyl tertiary-butyl ether (MTBE)

Unchanged excretion takes place for 50-80% in rats (Benson *et al.*, 2003). Although, very little information is available, it is assumed that the toxicity is low (RIVM, 2004a). It is likely that the negative effects on water taste (>15 µg/L) and odour (>7 µg/L) appear sooner than the toxic limit is reached (Rijkswaterstaat, 2012b).

Pesticides

Bentazone

Bentazone and N,N-dimethylsulfamide are among the most detected pesticides in European rivers exceeding the concentration limit for surface water intended for drinking water production of 0.1 µg/L (Carlsson *et al.*, 2006). Information about ecotoxicology and removal efficiency in WWTPs and DWTPs is very limited.

Glyphosate

Glyphosate enters the aquatic environment by the processes of runoff and leaching for terrestrial applications. Glyphosate only has a low acute toxicity towards animals. However, in the last decades various studies have shown possible toxicological effects linked to its use. Some of these effects are reduction in fertility, decrease in larval population and endocrine effects on mammals after long exposure (Sanchís *et al.*, 2012). Because of its considered low toxicity, the health-based value for glyphosate is orders of magnitude higher than concentrations normally found in drinking water (WHO, 2011a). Recently, the emission of glyphosate from runoff of paved areas has increased, which results in the fact that emission from urban runoff contributes more to the total emission than runoff from agricultural land (RIVM, 2006). Also the contribution from countries upstream of the Netherlands is an important source of glyphosate (Dutch Government, 2009b). Since 1 January 2008 professional application of glyphosate is only permitted under certain restrictions. The application for individuals is not permitted. Measurements in the river Meuse and in WWTPs in 2008 showed that there is an increase in concentration of glyphosate, which shows that the regulations for glyphosate do not have a positive effect yet.

Appendix 5-1 Current research on OMPs

In Europe several programs are currently initiated. These programs are not discussed in detail, but they give an idea of current developments.

1. **Interreg TAPES** (Transnational Action Program on Emerging Substances) on gaining knowledge and sharing information on international scale of how to deal with emerging substances.
2. **Endetech** (ENzymatic Decontamination TECHnology) on development of a technology which aims at eliminating persistent pharmaceutical pollutants in wastewaters originating from pharmaceutical drug manufacturing sites, households, hospitals and animal farms.
   (http://www.endetech.eu)
3. **DEMEAU** (Demonstration of promising technologies to address emerging pollutants in water and wastewater) on promising technologies that tackle emerging pollutants in water and wastewater.
   (http://demeau-fp7.eu)
4. **REACH** (Registration, Evaluation, Authorisation and Restriction of Chemical substances) is a law on regulation of chemicals and their safe use
   (http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm)
5. **PILLS project and follow-up project noPILLS** (Pharmaceutical Input and Elimination from Local Sources) on gaining knowledge about treatment technologies on removing pharmaceuticals from wastewater and to increase awareness for this problem in Europe (http://www.pills-project.eu/)
6. **Neptune** on new sustainable concepts and processes for optimisation and upgrading municipal wastewater and sludge treatment
   (http://www.eu-neptune.org/index_EN)
7. **TECHNEAU** (Technology Enabled Universal Access to Safe Water) on gaining and providing access to capabilities of technologies and management practices of the water supply chain. This is not particularly on OMPs.
   (http://www.techneau.org)
8. **POSE^{2}IDON** (Power optimised ship for environment with electric innovative designs onboard) on providing a working guide on how to improve efficiency and reduce the environmental impact of the combined European commercial shipping fleet and to enhance the electric ship concept so that it can be applied to a wider range of vessels than is currently the case.
   (http://www.poseidon-ip.eu/)

Appendix 5-2 Discussed treatment techniques

	PRECIPITATION, COAGULATION / FLOCCULATION Fact sheet nr. 07 WASTEWATER & DRINKING WATER
Unit operation	Precipitation, coagulation / flocculation
Treatment principle	Chemical bonding
Applicable for	Advanced effluent treatment, drinking water treatment
Stage of development	full-scale
Process	
function:	removal of ions (heavy metals and nutrients) and suspended solids
feed:	WWTP effluent
Keywords:	precipitation, coagulation, flocculation

Background

Precipitation is a method of causing ionic contaminants to settle out of solution as a solid precipitate by the addition of chemicals. Coagulation and flocculation are terms given to the irreversible agglomeration of fine particles into large particles, caused by the use of coagulants such as ferric chloride and aluminium sulphate. In general it is believed that a coagulant neutralises the electrical charges of the fine particles, causing destabilisation of the particles and consequent coagulation. Coagulation and flocculation can be used to remove undissolved particles and colloidal particles. The particle size-increase of the formed flocs caused by coagulation can be accelerated using polymers. The formed flocs and precipitates can be filtered, settled, or otherwise separated from the WWTP effluent. Different forms of coagulation/flocculation techniques include: in-line coagulation, flocculant filtration, flocculation filtration, “Actiflo” and pellet reactors. Coagulation/flocculation can be applied in wastewater treatment, drinking water treatment and as an dephosphatation step for inlet water at a nature reserve or other water body with specific requirements according water quality.

Description and working principle

In the treatment water precipitation is generally applied for the purpose of precipitating phosphate using iron or aluminium salts. The iron or aluminium ions in solution will react with phosphate to produce insoluble metal phosphates. The degree of insolubility for these compounds is pH-dependent. Theoretically, the minimum solubility of aluminium phosphate occurs at about pH 6.3, and that of iron phosphate at pH 5.3. However, practical applications have yielded efficient phosphorus removal at around pH 7.0, which is compatible with most biological treatment processes. Hydroxides or sulphides of heavy metals can also be precipitated, however for the formation of these precipitates pH corrections are necessary, which for the treatment of WWTP-effluent are not realistic due to the buffering capacity of the effluent. Since iron and aluminium salts also act as a coagulant, precipitation and coagulation cannot be considered separately. The addition of iron and aluminium ions for phosphate precipitation destabilizes fine particles in the water, thereby forming flocs. The types of iron and aluminium salts most commonly used are:

- $FeCl_3$
- $Al_2(SO_4)_3.14H_2O$
- PAC (polyaluminiumchloride)

- **required pre-treatment**

No pre-treatment is required.

- **waste products**

Inorganic sludge is produced, the quantity depending on the level of chemical dosage.

treatment performance

The water containing the formed precipitates and flocs should be treated to remove the precipitates. This treatment generally consists of a filtration step. In table 1 efficiencies of a flocculation filtration process are presented. When sedimentation is used the efficiencies given in table 2 can be obtained (STOWA, 2001).

Table 1 Treatment efficiency of flocculation filtration process for WWTP effluent

parameter	influent concentration range [mg/L]	removal efficiency Fe [%]	removal efficiency Al [%]
COD	30 – 75	10 – 25	~ 35
TSS	5.1 – 7.4	~ 60	55 – 65
P_{tot}	0.1 – 0.83	30 – 70	10 – 99

Table 2 Treatment efficiency of coagulation, flocculation followed by sedimentation

parameter	removal efficiency [%]
COD	40 - 60
TSS	60 - 80
Ammonia	0 - 20
Phosphate	80 – 100
Copper	80 – 100
Zinc	60 – 80
E. Coli	40 - 60
DOC	0 - 40
PCB	60 – 80

Table 3 Removal efficiency coagulation/flocculation

Compound	**Removal rate coagulation/flocculation [%]**
Acesulfame-K	Poor
Bentazone	30
Carbamazepine	0-60
Metformin	Poor
Sulfamethoxazole	33

- **energy consumption**

Mixing energy is required in the range of 2 – 40 kW/m^3 (Metcalf&Eddy, 2003).

- **chemical demand**

The quantity of chemicals needed depends on the concentrations to be precipitated in the incoming stream. The exact application rate is determined by onsite testing and varies with the characteristics of the water and the desired removal. For precipitation, a molar ratio Me / P of 2 is normally used. For a phosphate concentration of 1 mg/L phosphate, 3.6 mg/L Fe should be dosed or 1.7 mg/L Al. Coagulation dosages are in the order of 2 – 5 mg Al/L, or 5 – 10 mg Fe/L.

Design guidelines / Technical data

For precipitation and coagulation, a chemical addition step and a mixing step are required. The mixing step can be performed in a mixed tank or by creating turbulence in the stream of effluent. The flocculation is performed in a zone with less turbulence then the zone for precipitation and coagulation. The design parameters for coagulation and flocculation are determined using the G-value, the residence time and the dissipated power (for mixing). For mechanically stirred tanks this relation is as follows:

$$G = \sqrt{\frac{P}{V \cdot \mu}}$$

with:

G	mean velocity gradient, s^{-1}
P	power requirement, W
V	volume, m^3
μ	dynamic viscosity, Ns/m^2

For coagulation, a zone is required with $G > 1000\ s^{-1}$ and a residence time of 10 – 60 s. For flocculation, a zone is required in which the G-value is in the order of 10 – 200 s^{-1} and the total residence time is in the order of 15 – 45 min.

Operational stability and maintenance

The stability of the process depends on the quality of the feed water. If the quality of the feed changes in the sense that the interference of other components with the added chemicals is increased, the treatment efficiencies might be less than expected. No specific maintenance is necessary.

Reference installations, Suppliers / Patents

For the treatment of WWTP effluent, coagulation/flocculation is almost always followed by filtration to remove the formed aggregates. A large scale application in use until 2004 is the Water Factory 21, Orange County. Also the water reuse plant at Windhoek, Namibia, applies coagulation preceding flotation and dual media filtration. The tertiary treatment of San Diego wastewater treatment plant (California Code of Regulations 1978) consists of coagulation with lime followed by clarification in a center-fed upflow sludge bed clarifier.

Literature references

- Metcalf & Eddy (2003). Wastewater engineering; treatment and reuse (4th international edition). McGraw-Hill, New York
- Stowa (2001), Compendium rwzi-effluent als bron voor "ander water", 2001-14
- www.epa.gov/owm/mtb – Wastewater Technology Fact Sheet, Chemical Precipitation (2005)

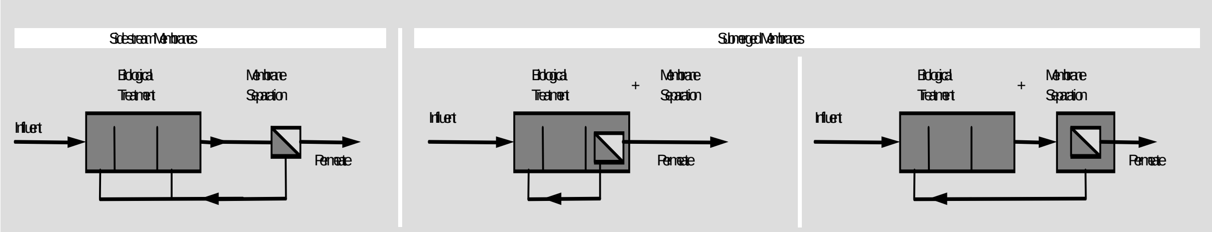
MEMBRANE BIOREACTOR
Fact sheet nr. 01
WASTEWATER

Unit operation	Activated sludge system and membrane filtration
Treatment principle	Biological system and separation
Applicable for	Integrated treatment
Stage of development	full scale
Process	
function:	degradation and conversion of COD, BOD, nitrogen and phosphorus containing substances, removal of suspended solids, pathogenic organisms, bacteria
feed:	WWTP effluent
Keywords:	activated sludge, membrane filtration

Background

The membrane bioreactor combines the activated sludge process with a membrane filtration step. The filtration can be in side stream configuration with pressurised membranes or with submerged membranes, either in the aeration tank or in a separate membrane tank (Figure 1). The applied membranes can be microfiltration membranes with pore sizes of 0.1 to 1 µm, or ultrafiltration membranes with pore sizes of 0.001 – 0.1 µm. Compared to the conventional activated sludge process the biological treatment can be operated with higher MLSS concentrations, leading to smaller tank volumes. A further reduction in footprint is caused by the absence of sedimentation tanks. The effluent quality is higher because the membrane forms an absolute barrier for microorganisms and particles. Operation and maintenance costs are high compared to conventional activated sludge treatment, mainly caused by the intensive pre-treatment and the aeration needed for membrane air scouring. The higher MLSS concentration leads to lower oxygen transfer coefficients (α-values) of about 0.5 (-) at 15 g/L.

Figure 1 MBR with different membrane configurations



Description and working principle

There are several options for the membrane choice in MBR.

- <u>Submerged membranes</u> (outside-in filtration):
    - hollow fibre membranes, vertically mounted
    - hollow fibre membranes, horizontally mounted
    - plate and frame membranes
- <u>Side stream membranes</u> (inside-out filtration):
    - Tubular membranes

The membrane material is commonly a hydrophilised or hydrophilic organic polymer. For a more detailed description of the types of membranes available refer to Fact Sheet 10 Microfiltration/Ultrafiltration.

- **required pre-treatment**

Special attention should be paid to remove fats and hairs, to avoid clogging of membrane modules. Especially with submerged hollow fibre system there is a risk of sludging of the membrane modules; the characteristic size of the screen should be <1 mm for these systems. For plate and frame modules the pre-treatment can be somewhat less extensive up to characteristic sizes of 3 mm.

- **membrane separation step**

The membrane filtration step of the MBR can be regarded as the bottle-neck of the process: all water has to pass through the membrane, which has a restricted pore size. The maximum achievable membrane permeate flux depends on the type of membrane and ranges from 20 to 60 $l/m^2.h$. This will have implications for systems where storm weather flow has to be treated. A good option for this is the hybrid configuration where several alternatives exist. The hybrid configuration consists of a conventional activated sludge system with a secondary clarifier and a MBR in parallel or in series with this installation. In the hybrid configuration the capacity of the MBR is designed to treat dry weather flow and during storm weather events the surplus inflow is treated in the conventional lane.

- **waste products**

Primary sludge (screenings) and secondary (waste) sludge.

- **treatment performance**

Because of the membrane step the effluent is disinfected and particle free. Depending on the type of wastewater the achievable effluent quality may vary. Some general values are listed in Table 1.

Table 2 Treatment efficiency of MBR process

Compound	**Removal rate [%]**
Caffeine	>85
Carbamazepine	20
Iopromide	20-30
Sulfamethoxazole	20-43

- **energy consumption**

The specific energy consumption of an MBR system is dependent on many factors, like system design, operational philosophy and plant size. Therefore a rather wide range of energy consumption figures is reported in literature. With a design flux of 20 – 30 l/m^2h the hollow fibre MBR requires a total amount of energy of 0.6 - 1.2 kWh/m^3 (Lesjean *et al.*, 2004).

- **chemical demand**

Periodic chemical cleaning is required depending on the type of membrane and wastewater. Commonly applied chemicals include: NaOCl, H_2O_2, citric acid.

Design guidelines / Technical data

design loads
hydraulically: membrane step: 10 – 30 l/m^2h, depending on design temperature and required effluent quality
kinetically: 0.03 – 0.07 kg BOD / kg active biomass day

Operational stability and maintenance

The operation of the biological part of the membrane bioreactor is essentially the same as a conventional activated sludge system. If the system is designed to treat sewage from a mixed sewer system, special attention should be paid to cope with hydraulic peaks. Current practice is to keep a stable membrane permeability throughout dry weather periods by means of frequent low-dosage chemical cleaning with hollow fibre systems (once every two weeks/once per month), relaxation time (e.g. 2 minutes in 8 minutes production) and/or backwashing. For plate and frame systems the frequency of chemical cleaning is considerably lower, generally once or twice a year.

Reference installations, Suppliers / Patents

Table 3 Reference installations for municipal MBRs

city, country	year	membrane system[1]	capacity	mean flow	max flow	flux mean/ max
			p.e.	m^3/hr	m^3/hr	l/m^2·hr
Varsseveld, NL	2005	HF, Zenon	23,150	275	755	12 / 50
Nordkanal, D	2004	HF, Zenon	80,000	1,000	1,880	15 / 30
Cardigan, UK	2004	PF, Kubota		-	360	-/-
Schilde, B [2]	2004	HF, Zenon	20,000	300	350	- / 45
Brescia, IT[2]	2002	HF, Zenon	46,000	530	-	-/-
Lowestoft, UK	2002	HF, Zenon	46,000	300	590	26 / 31
Knautnaundorf, D	2001	RD, Huber	900	-	-	-/-
Swanage, UK	2000	PF, Kubota	23,000	1,580	-	-/-
Rödingen, D	1999	HF, Zenon	3,000	-	100	- / 25.5
Porlock, UK	1998	PF, Kubota	3,800	80	-	16 / 31

[1] HF Hollow Fibre; RD Rotating Disk; PF Plate and Frame

[2] Parallel with conventional system

Membrane Suppliers

Submerged hollow fibre membranes - Zenon, Puron, Mitsubishi

Plate and frame modules – Kubota, Toray

Rotating disk – Huber/VRM

Side stream

Tubular membrane – X-Flow (vertically mounted), Koch, Nadir, Berghof

Literature references

- Lesjean, B.; S. Rosenberger and J.-C. Schrotter (2004) Membrane aided biological wastewater treatment – overview an applied systems and their fields of application. Membrane Technology, August 2004.
- T. Stephenson, S. Judd, B. Jefferson and K. Brindle (2000) Membrane Bioreactors for Wastewater Treatment. IWA Publishing, London, UK.
- Ellis, T.G. C. G. Schmit, K. Jahan, E. Debik and B. Elioso (2004). WER Review: Activated sludge and other aerobic suspended culture processes. Water Environment Research, Volume 76, Number 6
- STOWA (2002). MBR for municipal wastewater treatment – pilot plant research at Beverwijk WWTP. STOWA 2002-11A, Utrecht, the Netherlands
- STOWA (2004). Comparative investigation of MBR and sandfiltration at Maasbommel WWTP (in Dutch). STOWA 2004-28, Utrecht, the Netherlands

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- Membrane Academia Industry Network http://www.main.wizzy.co.uk/
- MBR WWTP Varsseveld www.mbrvarsseveld.nl
- Zenon references http://www.zenon.com/MBR/case_studies.shtml
- Kubota references in UK http://www.copa.co.uk/products/mbr choose -sewage-
- Koch/Puron: www.puron.de
- Huber/VRM: www.huber.de choose: - solutions – Membrane Technology
- Toray: www.segherskeppel.com
- X-Flow: www.X-Flow.com

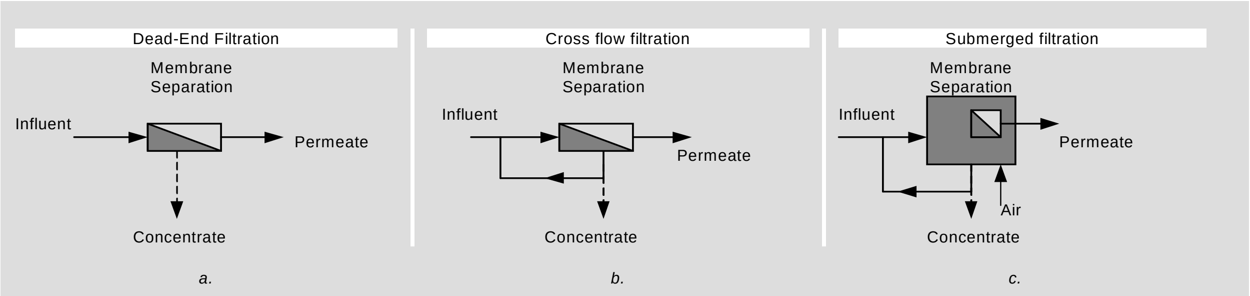
MICROFILTRATION / ULTRAFILTRATION
Fact sheet nr.01
WASTEWATER & DRINKING WATER

Unit operation	Membrane filtration
Treatment principle	Separation
Applicable for	Drinking water, advanced effluent treatment or integrated treatment in MBR
Stage of development	full scale
Process	
function:	concentration and removal of suspended solids, bacteria
feed:	WWTP effluent
Keywords:	membrane, filtration, suspended solids, bacteria

Background

Membrane filtration processes can be classified according to the pore size of the membrane. Microfiltration is a membrane filtration process designed to retain particles in the ‘micron’ range (0.10 µm – 5 µm). Microfiltration is used mainly as a clarification technique, separating suspended particles from dissolved substances, provided the particles meet the size requirements for microfiltration membranes (Cheryan, 1998). Ultrafiltration (UF) membranes have a pore size in the range 0.005 – 0.1 µm. Due to the smaller pore size, UF can retain macromolecules, viruses and bacteria in addition to suspended solids.

Figure 2 Membrane filtration with different configurations



Description and working principle

In microfiltration and ultrafiltration the separation mechanism is sieving, i.e. particles bigger than the pore size are retained by the membrane. Smaller particles pass the membrane. The membrane filtration process can be designed as a dead end system with periodic discharge of concentrate (Figure 1a). Alternatively, cross flow filtration can be used, where the concentrate is (partially) recycled back to the influent stream (Figure 1b). Because of the relatively low concentration of suspended solids in the influent water, dead-end filtration is commonly applied for treatment with membranes (Crittenden *et al.*, 2005; Moel de *et al.*, 2006).

- **membranes**

For the application in drinking water and tertiary wastewater treatment, several membrane types are available:
Hollow fibre, inside-out. The membranes are configured as hollow fibres, potted in pressure vessels. The feed flow enters the inside of the fibres and effluent permeates through the fibre wall.
Hollow fibres, outside-in. The membranes are submerged (Figure 1c) in the feed and effluent is forced to the inside of the fibres by a suction pressure. Usually, the membrane modules also have a coarse bubble aeration to provide turbulence around the membrane for fouling control.

- **required pretreatment**

A fine screen is optional to remove coarse material. For an optimal operation of dead end membrane filtration of WWTP effluent, inline coagulation can be useful. Coagulants increase the filterability of the water. As coagulants iron or aluminium salts can be used in concentrations of 0.5 – 2 mg/L.

- **waste products**

Concentrate is produced in the filtration step, containing suspended solids and microbes.

treatment performance

The membrane-treated effluent is disinfected and particle free. The removal of nutrients occurs by removal of nutrients within the suspended solids.

Table 4 Treatment efficiency of microfiltration and ultrafiltration process

Compound	**Removal rate MF [%]**	**Removal rate UF [%]**
Caffeine	4	7
Carbamazepine	8	16
Iopromide		<1
Sulfamethoxazole	2	5

- **chemical demand**

Periodical chemical cleaning is required depending on the type of membrane and feed water quality.

Design guidelines / Technical data

membrane technology	typical pore size nm	operating pressure kPa	permeate flux rate $l/m^2 \cdot hr$	energy consumption kWh/m^3
microflitration	100-5000	7 – 150	15 – 80	0.05 – 0.15
ultrafiltration	5-100	7 – 150	15 – 80	0.05 – 0.15

(Karabelas *et al.*, 2011)

Operational stability and maintenance

Filtration performance is dependent on feed water characteristics and operational conditions. Because of the separation process, suspended matter and macromolecules will accumulate at the membrane surface. This process leads to an increase in required trans membrane pressure, commonly described by the term ‘fouling’. The amount and type of fouling that occurs is dependent on the feed flow characteristics and operation of the membrane system. Fouling can be controlled by several measures, such as cleaning (back flush, forward flush, soaking in chemical solution), depending on the type of membrane system and the type of fouling.

Reference installations, Suppliers

Table 5 Reference installations for micro / ultrafiltration of WWTP-effluent

city, country	year	membrane system[1]	pore size	max flow	flux min/ max
			µm	m^3/hr	$l/m^2 \cdot hr$
Tilburg, NL	2004	HF, Zenon	0.020		
Torreele, B[2]	2002	HF, Zenon	0.045	400	
Windhoek, Namibia	2002	HF, X-flow		1000	
Flag Fen, UK[2]	2003	HF, Pall	0.1	65	24 / 37

[1] HF Hollow Fibre

[2] Pretreatment for Reverse Osmosis

Membrane Suppliers

- Zenon, Pall, Memcor, X-Flow (see also Fact Sheet 01 Membrane Bioreactor)

Literature references

- Cheryan. M (1998) Ultrafiltration and Microfiltration Handbook. Technomic Publishing AG, Basel, Switzerland
- Mulder, MN. (1996) Basic Principles of Membrane Technology. Kluwer Academic Publishers, Dordrecht, The Netherlands

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- Membrane Academia Industry Network http://www.main.wizzy.co.uk/
- Zenon references http://www.zenon.com/resources/case_studies/wastewater/IWVA.shtml
- X-Flow: www.X-Flow.com
- Pall: www.pall.com

NANOFILTRATION / REVERSE OSMOSIS
Fact sheet nr. 11
WASTEWATER & DRINKING WATER

Unit operation	Membrane filtration
Treatment principle	Separation
Applicable for	Advanced effluent treatment, drinking water treatment
Stage of development	full scale in drinking water treatment; pilot-scale development for WWTP effluent treatment
Process	
function:	concentration and removal of suspended solids, bacteria, bi-valent ions partially (hardness)
feed:	WWTP effluent
Keywords:	membrane, filtration, suspended solids, bi-valent ions, hardness

Background

Nanofiltration (NF) is used when low molecular weight solutes such as inorganic salts or small organic molecules such as glucose, have to be separated from a solvent. Compared to MF/UF, nanofiltration membranes are denser with a much higher hydrodynamic resistance. The separation principle is solution-diffusion and the driving force is a hydraulic trans-membrane pressure.

Description and working principle

The retention for bivalent ions is high in nanofiltration. In addition the retention is high for micropollutants such as herbicides, insecticides and pesticides and for other low molecular components such as dyes and sugars.

- **membranes**

Several membrane configurations exist in nanofiltration:
spiral wound membranes
tubular or capillary membranes

The major practical difference between these two is the pretreatment that is needed. Spiral wound membranes need a thorough pretreatment to remove suspended matter to a high extent, which is less important for the other types. Also chemical and hydraulic cleaning is more difficult, energy consuming for spiral wound membranes. For both systems a cross flow stream is required to ensure retention capacity; in practice moderate values of about 0.5 m/s are a good compromise between retention capacity and energy consumption.

- **required pre-treatment**

For proper operation suspended solids must be removed before NF, which is normally accomplished by a microflitration step.

- **waste products**

The concentrated feed flow, the brine, contains high concentrations of bivalent ions and macromolecules. Therefore, special measures have to be taken to cope with this stream. Important design parameter in this respect is the recovery of the process, i.e. the ratio between permeate and influent flow. This ratio is usually ≈ 0.80.

- **treatment performance**

Because of the membrane step the effluent is disinfected and particle free and may be used for indirect potable reuse. Table 1 and 2 provide an overview of the removal efficiency of NF and RO

- **energy consumption**

See Design/Guidelines/Technical data.

chemical demand

Periodical chemical cleaning depending of type of membrane and feed water quality.

Table 6 Retention characteristics of nanofiltration process (Mulder 1996, Metcalf&Eddy 2003, Duin, *et al. 2000*)

Parameter	removal efficiency [%]
mono valent ions (Na, K, Cl, NO_3)	< 50
bivalent ions (Ca, Mg, SO_4, CO_3)	> 90
bacteria and viruses	< 99
microsolutes (MW > 100)	>50
microsolutes (MW<100	0 – 50
EC	25
Zinc	75 – 80
Copper	70 – 75
Diuron	±25

Table 2. Removal of organic compounds with NF and RO

Compound	**Removal rate NF [%]**	**Removal rate RO [%]**
Bentazone	100	100
Caffeine	50-80	>99
Carbamazepine	50-80	>90
Iopromide	>80	>99
Metformin	40	40
MTBE	60-99	60-99
N,N-DMS	30-95	30-95
Sulfamethoxazole	50-80	>99

* Depending on the amount of PAC used; lower rate is for 5 mg/L, higher rate is for 35 mg/L

Design guidelines / Technical data

membrane technology	operating pressure kPa	permeate flux rate $l/m^2 \cdot hr$	energy consumption kWh/m^3
microfiltration	7 – 250	15 – 120	0.05 – 0.15
ultrafiltration	7 – 250	15 – 80	0.05 – 0.15
nanofiltration	500 – 1000	5 – 40	0.20 – 0.40

Operational stability and maintenance

Filtration performance is dependent on feed water characteristics and operational conditions. Bacause of the separation process, suspended matter, macromolecules and salts will accumulate at the membrane surface. This process leads to an increase in required trans membrane pressure, commonly described by the term ‘fouling’. Fouling can be controled by periodic cleanings (backflushing with permeate and/or air, forward flushing, soaking of the membrane in a chemical solution) depending on the type of membrane and the occurring fouling. A specific fouling problem is ‘biofouling’ which is the growth of micro organisms at the feed side of the membrane. Once this occurs it is only difficulty removable. Therefore, an anti-biofouling strategy should aim at avoiding biofouling. This can be achieved by removing nutrients from the feed stream, which requires special attention in the case of WWTP effluent.

Reference installations, Suppliers

For nanofiltration there are only pilot scale references, see

Table 3.

Table 3 Reference installations for nanofiltration of WWTP effluent

city, country	year	membrane system	pore size	max flow	flux
			nm	m^3/hr	L/m^2·hr
Ede[1], NL	1999	Stork	0.5 – 2.0	-	25

[1] Pilot plant trial

Membrane Suppliers

- Capillary membranes – Norit
- Spiral wound membranes – Hydranautics, TriSep, Koch Membrane systems, Osmonics

Literature references

- Ultrafiltration and Microfiltration Handbook (1998) M. Cheryan.Technomic Publishing AG, Basel, Switzerland
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- Pall: www.pall.com

	ACTIVATED CARBON Fact sheet nr.08 WASTEWATER & DRINKING WATER
Unit operation	Adsorption
Treatment principle	Physical bonding
Applicable for	Advanced effluent treatment
Stage of development	full scale in drinking water treatment; effluent: only pilot scale
Process	
function:	removal of organic micro pollutants, pesticides, endocrine disruptors and medicinal substances
feed:	WWTP effluent
Keywords:	adsorption, activated carbon, pesticides, nutrients, medicine residue

Background

Activated carbon has a broad spectrum of adsorptive activity, as most organic molecules are retained on its surface. The adsorption of substances onto activated carbon can be predicted according to their K_{ow} coefficient, which is the octanol/water partition coefficient. Substances with a log $K_{ow} < 0$ are not retained by activated carbon. Activated carbon can be applied in several ways, such as in a granular activated carbon (GAC) filter, by in-line addition of powder activated carbon (PAC), in a membrane assisted affinity separator (MAAS) or a continuous moving bed adsorption system (MBA).

Description and working principle

Treatment with a Granular Activated Carbon (GAC) filter involves passing the water through a bed of activated carbon. A typical filter is represented in Fig. 1. The GAC particles have a diameter of 0.25 – 3 mm. When the column is fully loaded with a certain organic compound this compound will not be adsorbed anymore and will break through the filter. At that moment, the GAC needs to be regenerated and reactivated. The moment of breakthrough differs per organic compound and depends (among others) on the polarity of the compound.

- **Required pre-treatment**

Special attention should be paid to remove suspended solids and easily removable organic compounds from the influent of the GAC-filter. Suspended solids can cause the filter bed to clog. Easily removable organic compounds will block the adsorption sites on the activated carbon, on which organic micro pollutants are to be adsorbed.

- **Waste products**

Loaded carbon in a granular filter can be regenerated and reactivated by intensive heat treatment. Powdered activated carbon is injected as a slurry (1% w/w) and cannot be regenerated. The powdered carbon is separated from the effluent stream as sludge.

- **Energy consumption**

Considering filters of the same size, the pumping costs for activated carbon filters are similar to the cost for depth filters. Regeneration of the activated carbon is an energy intensive process, consuming between 1 – 3 kWh/m^3 for the reactivation process alone.

- **Treatment performance**

The removal rate of organic compounds differ per compound. Table 1 provides an overview of the removal rate of the selected OMPs.

Design guidelines / Technical data

The design values for a GAC filter are listed in table 2.

Figure G. Typical activated carbon filter in a pressure vessel (Metcalf& Eddy, 2003)

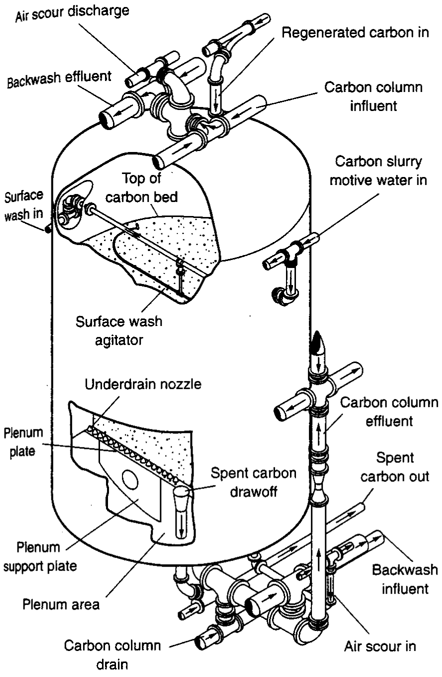

Table 1. Removal of organic compounds

Compound	**Removal rate GAC [%]**	**Removal rate PAC [%]**
Acesulfame-K	60	60
Bentazone	100	100
Caffeine	59	16
Carbamazepine	>70	>70
Iopromide	31	31
Metformin	90	90
Sulfamethoxazole	43	43

Table 2. Typical design values for GAC contactors (Metcalf & Eddy, 2003)

Parameter	Unit	Value
Volumetric flow rate	m^3/h	50 – 400
Bed volume	m^3	10 – 50
Cross-section area	m^2	5 – 30
Length	m	1.8 – 4
Void fraction	m^3/m^3	0.38 – 0.42
GAC density	kg/m^3	350 – 550
Approach velocity	m/h	5 – 15
Effective contact time	min	2 – 10
Empty bed contact time	min	5 – 30
Operation time	d	100 – 600
Throughput volume	m^3	10 – 100
Specific throughput	m^3/kg	50 – 200
Bed Volumes	m^3/m^3	2,000 – 20,000

Operational stability and maintenance

Loaded activated carbon requires regular regeneration. Upon regeneration and reactivation activated carbon is lost. After each life-cycle activated carbon has to be added to compensate this loss.

Reference installations, Suppliers

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ADVANCED OXIDATION PROCESSES
O_3/H_2O_2, UV/O_3 and UV/H_2O_2
Fact sheet nr. 04
WASTEWATER & DRINKING WATER

Unit operation	Advanced oxidation
Treatment principle	Oxidation
Applicable for	Advanced effluent treatment
Stage of development	Full-scale development for drinking water production, not yet applied at full-scale for WWTP effluent treatment, techniques researched since 1970
Process	
function:	Disinfection, oxidation of inorganic compounds, organic micro-pollutant oxidation (taste and colour removal, phenolic pollutants, pesticides), organic macro-pollutant oxidation, improvement of biological degradability of water.
feed:	WWTP effluent
Keywords:	advanced oxidation, UV, hydrogen peroxide, ozone

Background

Advanced oxidation processes (AOP) are used to oxidise complex organic constituents that are difficult to degrade biologically into simpler end products. An AOP is a highly accelerated oxidation reaction that typically involves the use of the hydroxyl free radical ($OH^{\cdot}$) as a strong oxidant to destroy compounds that cannot be oxidised by conventional oxidants such as oxygen, ozone and chlorine. Free radicals can be produced from ozone (O_3) or hydrogen peroxide (H_2O_2) by means of direct reaction with each other (Eq 1) or by reaction with UV light (photolysis) (Eqs 2 – 3). The most commonly applied methods in water treatment until now are UV/O_3, O_3/H_2O_2 and UV/H_2O_2, although the techniques have not yet to applied widely to WWTP effluent. The free radicals react with pollutants to initiate a series of oxidative degradation reactions. When UV light is used a large fraction of organic breakdown occurs due to photolysis of organics. Until now AOPs have been mostly applied to drinking water and specific industrial (e.g. textile) wastewater. Their main treatment purpose is for removal of substances such as SOCs (Synthetic Organic Chemicals), pesticides, and odour-causing compounds. The complexity of the chemistry of AOPs is high due to the large number of reactions that are possible. This makes it difficult to predict the products of an AOP. Disadvantages of AOPs are that the toxicity of the byproducts is not always better than the original compounds (e.g. bromate formation is a problem with O_3/H_2O_2 treatment), and the chemical consumption can be high due to the non-specificity of the technique. Other disadvantages are high cost, complex maintenance and the reduced effectiveness in presence of radical scavenging compounds. An important advantage of AOPs is that complete oxidation to CO_2 and water is possible and no sludge or concentrate is produced.

Production of $OH^{\cdot}$ from ozone and peroxide:

$$2O_3 + H_2O_2 \rightarrow 2\,{\cdot}OH + 3\,O_2 \qquad \text{(Eq 1)}$$

Production of $OH^{\cdot}$ by photolysis of ozone and peroxide:

$$H_2O_2 + hv \rightarrow 2\,OH^{\cdot} \qquad \text{(Eq 2)}$$

$$O_3 + hv + H_2O \rightarrow O_2 + O(^1D) + H_2O \rightarrow 2\,OH^{\cdot} \rightarrow H_2O_2 \qquad \text{(Eq 3)}$$

where $O(^1D)$ = excited oxygen atom.

The rate of oxidation in an AOP depends on the radical concentration generated, the oxygen concentration and pollutant concentration. Many factors can affect the radical concentration such as pH, temperature, the presence of ions, the type of pollutant and the presence of radical scavengers such as bicarbonate ions.

Description and working principle

The efficiency of AOPs requires precise design and operation of the process. In general it is important to emphasize that pilot testing is always recommended because of the specificity of each wastewater.

UV/H_2O_2: There is growing interest in UV-based AOPs to degrade trace organic contaminants in drinking water, however the applicability to wastewater is limited by the suspended solids concentration (UV-transmittance). UV/H_2O_2 is the most commonly used AOP for industrial water treatment and has been applied for the removal of N-Nitrosodimethylamine (NDMA), sex and steroidal hormones, human prescription/nonprescription drugs, antibiotics and personal care products. At the very low (usual) concentrations tested (µg/L) their oxidation appears to follow first order kinetics (Parsons, 2004). H_2O_2 absorbs UV light in the range 200 – 280 nm. In some cases this process is not feasible because H_2O_2 has a low molar extinction coefficient, requiring high concentrations of H_2O_2 (> 10 mg/L) and inefficient UV energy use. The extent of removal of impurities is determined by a number of factors: the UV- and H_2O_2- dosage, the transmission of the wastewater, the design of the UV reactor, and the choice of UV lamps. Understanding the processes requires knowledge of fundamental photochemistry and it consequences in the design of efficient UV reactors.

UV/O_3: As shown in equation 3 the photolysis of ozone in water leads to the formation of hydrogen peroxide, which is subsequently photolysed to form hydroxyl radicals. Essentially, the UV/O_3 process is an expensive way of producing H_2O_2, which makes the use of ozone in this application generally not cost-effective. The ozone/UV process is more effective when the compounds of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with the hydroxyl radicals. Some industrial applications (e.g. treatment of TNT) require the UV/O_3 process. A major disadvantage with the UV/O_3 technique is the formation of the toxic bromate ion.

O_3/H_2O_2: For removal of compounds that do not absorb UV, this AOP may be more effective. Organic micro pollutants such as trichloroethylene (TCE) and perchloroethylene (PCE) have been reduced significantly with this technique. The H_2O_2 is added to the influent before it comes into contact with the ozone (Fig 3). The performance is greatly dependent on the H_2O_2/O_3 ratio applied. The optimal ratio is around 0.3.

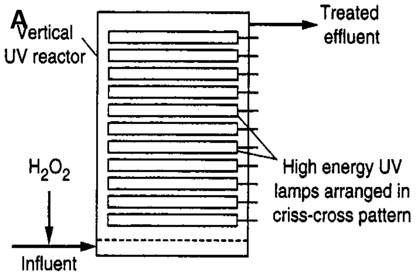

Figure 1. Schematic representation of AOP involving peroxide and UV radiation.

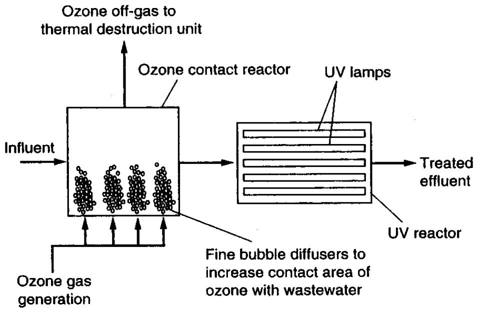

Figure 2. Schematic representation of AOP involving UV/O_3 (Metcalf & Eddy 2003).

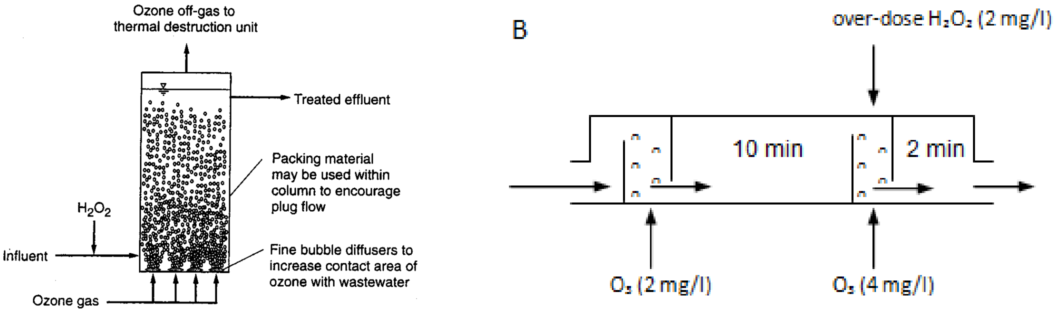

Figure 3. Schematic representation of AOP involving ozone and peroxide in a column diffuser (A) or in a plug-flow contactor (B).

- **required pre-treatment**

Advanced oxidation (especially in combination with UV) is sensitive to the suspended solids concentration due to the reduced UV transmittance of the water. It is not economical for (waste)water with high levels of suspended solids (SS), biochemical/chemical oxygen demand (> 1 g/L COD) or total organic carbon and requires pre-treatment. A typical pre-treatment process for suspended solids removal is (multi) media filtration and/or activated carbon.

- **waste products**

In AOPs involving ozone the oxidation reaction with bromide ion produces hypobromous acid and bromate ion and precludes their usage with waters containing high concentrations of bromide ion (> 0,10 mg/L). AOPs in general produce no waste products as such, as compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated there is no need to dispose of or regenerate materials. However the nature of the oxidation products is difficult to predict and may include toxic products or intermediates.

- **treatment performance**

Available data for removal efficiencies of various compounds vary largely in the literature. It is very difficult to predict the efficiency of pollutant removal since results vary significantly with the specific oxidant in question and the characteristics of the treated wastewater (pH, temperature etc). Moreover, the cited processes can be very effective with some compounds and almost pointless with others, especially in the case of refractory organic substances. The best approach is therefore to rely on previous experiences with wastewater similar to the one being treated and/or to conduct lab-scale and pilot tests. During UV/H_2O_2 treatment of drinking water at the Andijk DWTP > 80% conversion of 11 selected priority pollutants could be achieved at 0.6 kWh/m^3 (540 mJ/cm^2) and 6 mg/L H_2O_2. Table 1 provides an overview of the removal efficiencies of the different techniques.

Table 1. Removal of organic compounds by AOP

Compound	Removal rate AOP general [%]
Acesulfame-K	
AMPA	poor
Bentazone	
Caffeine	89
Carbamazepine	88
Glyphosate	100
Iopromide	91
Metformin	34
Sulfamethoxazole	>99

- **energy consumption**

In AOPs involving UV radiation electrical energy is the principal factor in the operating costs. The electrical energy required for the oxidation of organic compounds is expressed in EE/O units, defined as the electrical energy input per unit volume per log order of pollutant reduction. EE/O values for various pollutants such as NDMA, chlorinated alkene, 1,4-dioxane, atrazine and MTBE vary between 0,15 – 5 kWh/order/m^3 and 2 – 10 kWh/order/m^3 for benzene and its derivatives. For the new UV/H_2O_2 drinking water plant at Andijk the energy consumption is 0,6 kWh/m^3. Variations in the literature are very large and energy requirements must be established in pilot tests. Energy consumption in the H_2O_2/O_3 process is relatively much lower than UV based AOPs.

- **chemical demand**

The principle chemical demand in AOPs is due to H_2O_2 and O_3 consumption. Ozone is typically dosed at a concentration of 4 g/m^3, resulting in a consumption of 6 ton/year for small-scale plants (4,000 m^3/d) and 30 ton ozone/year for large-scale plants (20,000 m^3/d). Hydrogen peroxide is typically dosed at a concentration of 1 –

2 g/m^3, resulting in a consumption in the order of 2 ton/year for a small-scale plant and 9 ton/year for large-scale plants.

Design guidelines / Technical data

Table 2 Some important published design parameters for AOPs

Design parameter	unit	value
H_2O_2/O_3		
Ozone concentration	g O_3/m^3	2 – 4
H_2O_2/O_3	g H_2O_2/g O_3	0.3
O_3/DOC (dissolved organic carbon)	g O_3/g DOC	1 – 3
UV/O_3 and UV/H_2O_2		
CCT (concentration x contact time)	mg/L * min	> 10
UV dosage	mJ/cm^2	500 – 1,000
UV-lamp output	nm	200 – 280
UV power output	kWh/m^3	0.3 – 2
H_2O_2 dosage	mg/L	5 – 25

Operational stability and maintenance

Ozone and H_2O_2 delivery systems are complex using highly technical instruments, however the processes are highly automated and reliable, requiring only a modest degree of operator skill and time to operate them. Maintenance of ozone generators and UV systems requires skilled technicians and regular maintenance.

Reference installations, Suppliers

Reference installations:

- H_2O_2/O_3: Neuilly sur Marne drinking water production plant, France, 6.300 m^3/h, 5 mg/L ozone, 1,5 mg/L H_2O_2.
- UV/H_2O_2: Andijk drinking water production plant (4.000 m^3/h).
- Widely applied in textile industry for colour removal.

Commercial-scale AOP systems:

- Calgon Carbon Corboration Peropure^{TM} and Rayox^{TM} UV/H_2O_2 systems, Magnum Water Technology Inc. CAV-OX$^{®}$ UV/H_2O_2 system, Trojan and Wedeco UV/H_2O_2 and UV/O_3 systems and US Filter/Zimpro Inc UV/H_2O_2/O_3 system.

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ION EXCHANGE
Fact sheet nr.12
WASTEWATER & DRINKING WATER

Unit operation	Adsorption
Treatment principle	Bonding
Applicable for	Advanced effluent treatment, drinking water treatment
Stage of development	full scale
Process	
function:	removal of dissolved solids and/or organics or heavy metals
feed:	pre-treated WWTP effluent
Keywords:	advanced treatment WWTP effluent, ion-exchange., selective removal of heavy metals, cadmium, nickel, copper, sink , selective chelating ion exchange resins

Background

In this unit process the exchangeable given species attached to an insoluble material (resin) are displaced by ions of a different species present in the solution. The displacement is mainly ruled by electromagnetic forces and/or adsorption. The ion-exchange resins can be either of natural origin or manufactured. Natural materials are better known as Zeolites, which are complex aluminosilicates with sodium as a mobile ion. Manufactured materials can also be synthetic aluminosilicates, in which case they are still called Zeolites, but more often they are resins (styrene and divinylbenzene copolymerised) or phenolic polymers. Five types of synthetic ion-exchange resins are in use: (1) strong-acid cation, (2) weak-acid cation, (3) strong-base anion, (4) weak-base anion, and (5) heavy metal selective chelating resins. Besides, resins can be of macro-porous structure for adsorption of organic material. The relevant properties of ion-exchange resins are the following:

Exchange capacity [eq/L] or [eq/kg]: quantity of exchangeable ions that the resin can take up. The "ideal" value is much higher than the actual operating capacity, which is influenced by competing ions, flow rates, temperature and regeneration level. For removal of organics, the exchange capacity is (normally) expressed in [$KMnO_4$/L].

Particle size: important towards the hydraulics and the kinetics of the ion-exchange;

Stability: chemical-physical resistance in the long term.

Selectivity: the ion-exchange process is basically a chemical equilibrium where the taking up capacity of the resin towards a certain ion is specific, depending upon the nature and the valence of the ion, as well as from the operating conditions (such as saturation of the resin, ions concentrations, pH, presence of concurrent ions). The selectivity coefficient is basically the constant of the equilibrium of the ion exchange; therefore it is valid only for the conditions under which it was measured. On the basis of selectivity, a "series" of the affinity towards different ions is created for each resin. For strong acid cation exchange resins the selectivity in order of decreasing preference is: $Ba^{2+} > Pb^{2+} > Hg^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+}$. Furthermore, especially for drinking water production, in the past years selective chelating ion exchange resins have been developed for the efficient removal of heavy metals with a high removal efficiency on a ppb level (Stetter, D., 2002). Commercially viable ion exchange processes are often confined to dilute solution of lower than 40 eq/m^3 due to cost reasons (Harland C.E, 1994). For organics removal, the process is merely used for TOC/DOC containing waters in order to protect downstream anion resins becoming (irreversibly) fouled. Macroporous resins are also used for (high) colour containing waters at drinking water production. Use of cation exchange resins is also used for heavy metals removal, e.g. in the metal plating and surface finishing industry where, in some cases, recovery of valuable metals is aimed at. There is less experience with this process for effluent treatment aiming at heavy metal polishing in the ppb range.

Description and working principle and picture/scheme

The process can be operated either in batch or continuous mode. In batch mode, the resin and the water to be treated are stirred together in a reactor. When the reaction is complete the spent resin is separated by settlement, regenerated and reused. The continuous mode is usually run in down-flow packed-bed columns; therefore the wastewater flows from the top to the bottom of the column, through the resin bed. The exhausted resins are regenerated through backwash operation (see Figure 1).

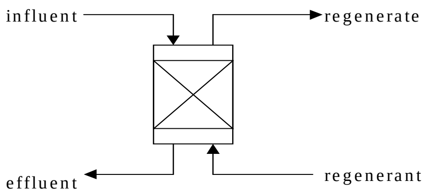

Figure 1 Ion exchange process

Aiming at heavy metals removal the following reactions can be given as an example:

$2\ (R\text{-}SO_3H) + NiSO_4 = (R\text{-}SO_3)2Ni + H_2SO_4$ (production cycle)

$(R\text{-}SO_3)2Ni + H_2SO_4 = 2(R\text{-}SO_3H) + NiSO_4$ (regeneration cycle with acid)

- **required pre-treatment**

The ion exchange process is susceptible for suspended solids (max. 2-3 mg/L, Harland, 1994) and organics and requires adequate pre-treatment. A typical pre-treatment process for removal of suspended solids is (multi) media filtration, and in case of presence of organics either polishing by macroporous resins is applied or activated carbon.

- **waste products**

The waste product of the ion exchange process is a regeneration stream containing salts. Typical regeneration compounds are: $Ca(Cl)_2$, $Ca(OH)_2$, NaCl, NaOH. In general, regeneration with sodium salts is found to be more economic thanks to a greater throughput per cycle (de la Torre, 1999). For heavy metals removal regeneration with a strong acid (H_2SO_4 or HCl) is required and produces regeneration liquids comprising metal complexes next to metal salts.

- **effluent**

Applying ion exchange processes, the removal efficiency of a resin depends upon the characteristics of the feed water (concentrations and ions concurrency) and the applied process parameters (flow, regenerative level, etc.). As a consequence it is usual to design the whole process on the basis of the desired concentration value in the effluent. For heavy metals removal and/or recovery, experiences show effluent concentrations in the order of <0.1 ppm. Lower concentrations are not yet experienced and need to be pilot tested.

Design guidelines and technical data

design loads

hydraulically: 20-30 BedVolume/h; regeneration and rinsing load: 90 g HCl per liter resin;

kinetically: exchange capacity between 0.2 and 0.7 meq/L

energy consumption; the energy consumption of ion exchange process is general less than 0.3 – 0.4 kWh/m^3.

chemical demand; regeneration chemicals (acid and base chemicals, salts like lime or NaCl) are required at intervals. Consumption figures are much dependent on feed water composition, regeneration frequency and load. General figures cannot be given. Treatment performance; See table 2.

Operational stability and maintenance

The ion exchange process is a well-known and robust process used merely in the industry. The process can be operated fully automatic. Filter vessels are generally installed in parallel for continuous filtration of the wastewater. Maintenance is mainly required for chemical dosing facilities (especially lime) and during resin exchange after exceeding its lifetime.

Table 2 Treatment performance

Compound	Removal rate IEX [%]
AMPA	93
Caffeine	<20
Carbamazepine	<20
Glyphosate	95
Iopromide	<20
Sulfamethoxazole	20-50

Reference installations, Suppliers

The ion exchange process is in general a well-known and robust process and is applied worldwide, mostly for the production of demineralised water in the industry, but also for treatment and/or recovery of (heavy) metals at e.g. the galvano industry. Worldwide, numerous installations are installed at industries, from small size (several m^3/h) upto large size (>1000 m^3/h) units. For effluent polishing, reducing organics and/or trace (heavy) metals, the process is relatively new. Suppliers of (synthetic) ion exchange resin are (a.o.): Rohm&Haas, Purolite, ResinTech, Dow Chemical, Bayer. Natural ion exchange material (Zeolite) can be extracted at several places (mountain and vulcanic areas).

Alternative processes

Alternative processes for removal of soluble organic substances and/or suspended solids are: denitrifying (sand) filters, activated carbon filtration, membrane filtration and coagulation/flocculation processes. An alternative resin to remove heavy metal ions is the AlgaSORB® technology being a biological sorption process. This system functions as an biological ion exchange resin to bind metallic cations. The product is composed of a non-living algal biomass immobilised in a silica polymer. A second alternative process for removal of heavy metals achieving metal effluent concentrations at ppb level would be the MAAS technology. This technology is developed by TNO-MEP specifically for the removal of heavy metals and combines the high selectivity of ion exchange resins with the continuous membrane filtration process. The MAAS technology has been tested on pilot scale level.

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CHLORINE AND CHLORINDE DIOXIDE DISINFECTION
Fact sheet nr.08
WASTEWATER & DRINKING WATER

Unit operation	Disinfection
Treatment principle	Oxidation by chlorine or ClO_2
Applicable for	Advanced wastewater treatment, drinking water treatment
Stage of development	full scale
Process	
function:	destruction of pathogens
feed:	WWTP effluent,
Keywords:	Chlorine, disinfection

Background

The primary use of chlorine is disinfection. Chlorine is an effective disinfectant for inactivating bacteria and is a highly effective viricide, however it is less effective against certain parasites such as Giardia cysts and Crypotosporidium oocysts. Chlorine is typically used in one of three forms: gaseous form (Cl_2), liquid form (e.g. NaOCl) or solid form (e.g. $Ca(OCl)_2$). Each compound reacts in water to produce the disinfectants HOCl (hypochlorous acid) and OCl^- (hypochlorite ion), which is the effective disinfecting agent (Eqs 1 – 3).

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \qquad \text{(eq 1)}$$
$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^- \qquad \text{(eq 2)}$$
$$Ca(OCl)_2 + 2\,H_2O \rightarrow 2\,HOCl + Ca^{2+} + 2\,OH^- \qquad \text{(eq 3)}$$

The disadvantage of chlorine for disinfection is the formation of toxic chlorinated organic compounds (trihalomethanes or THMs). This led in recent years to a quest for replacement of chlorine. An effective replacement for chlorine can be the use of chlorine dioxide (ClO_2).

ClO_2: ClO_2 is less reactive than ozone or chlorine yet the compound reacts more selectively with organics, which allows lower dosages to achieve a more stable residual than either chlorine or ozone. The most important advantage is that THM precursors are not produced. Other advantages of ClO_2 in comparison to ozone or chlorine are:

the germicidal efficiency is unaffected in the pH range 4 – 10,
ClO_2 is more efficient in destruction of bacteria, spores and viruses on an equal residual base,
the required contact time is lower and the solubility in water is higher,
there is no corrosion associated with higher concentrations which reduces maintenance costs.

ClO_2 can be generated on-site or it can be ordered in stabilised form (SCD), which can be activated on-site when required. Safety and cost issues have until now however restricted the wide use of chlorine dioxide as a viable replacement.

Chlorine gas: Gaseous chlorine is relatively inexpensive and has the lowest production and operating costs for large continuous disinfection operations. It is a stable compound that may be stored for an extended period of time, but only as a liquefied gas under high pressure. Chlorine gas is extremely toxic and corrosive and reacts with almost any organic material in wastewater. Organics, ammonia and phenolic compounds will often react with chlorine before it has a chance to react with pathogens. The use of chlorine gas should be closely monitored to ensure its effectiveness as a disinfectant. Chlorination using Cl_2 is preferred at lower pH (<7.5).

Sodium hypochlorite: NaOCl can be manufactured on site or purchased in liquid containing 3 – 15 % available chlorine. Decay of the original product will occur as a result of exposure to light, increase n temperature or because of concentration of the compound. NaOCl solution is the most expensive of the three forms. It is safer to handle than Cl_2 and can be generated and stored on site. The addition of NaOCl to water yields a hydroxyl ion that increases the pH of the water (eq 2).

Calcium hypochlorite: Granular calcium hypochlorite is typically available commercially containing 65 % available chlorine. It is a strong oxidant and extremely hazardous. Calcium hypochlorite can crystallise and clog pumps, pipes, valves. The addition of calcium $Ca(OCl)_2$ increases the pH of the

Description and working principle

When the physical parameters controlling the chlorination process are held constant, the germicidal effects of chlorine, as measured by bacterial survival, depend primarily on dosage (and form) and contact time (equation 4). Increasing either the dosage or contact time, while simultaneously decreasing the other, can achieve approximately the same degree of disinfection. The point at which the formation of residual chlorine compounds occurs is known as the “breakpoint”. Thus, the term “breakpoint chlorination” refers to the process in which sufficient chlorine is added to obtain a free chlorine residual. When breakpoint chlorination is praticed properly the bactericidal effect is considered good and the viricidal effect moderate. For optimal performance a chlorine disinfection system should display plug flow and be highly turbulent for complete initial mixing in less than one second.

- **required pre-treatment**

Bacteria embedded in particulate matter can be shielded from the disinfectant. Water with a high suspended solids concentration should therefore be pre-treated for removal of suspended solids to ensure effective disinfection.

- **waste products**

When added to water, free chlorine reacts with organic matter and bromide to form byproducts, primarily trihalomethanes (THMs), some haloacetic acids and others. The pH of water being chlorinated has an impact on the formation of halogenated byproducts. THM formation increases with increasing pH. Trichloroacetic acid, dichloroacetonitrile and trichloropropanone formation decrease with increasing pH. Overall TOX formation decreases with increasing pH. To limit the amount of DBP formation chlorination should be carried out as downstream as possible when organic concentrations are reduced.

- **treatment performance**

Some compounds are known to affect the effectiveness of chlorine disinfection. These substances are shown in table 2.

Table 1: wastewater characteristics affecting chlorination performance

Wastewater characteristic	Effects on chlorine disinfection
Ammonia	Forms chloramines when combined with chlorine
Biochemical oxygen demand (BOD)	The degree of interference depends on their functional groups and chemical structures
Hardness, iron, nitrate	minor effect, if any
Nitrite	Reduces effectiveness of chlorine and results in THMs
pH	Affects distribution between hypochlorous acid and hypochlorite ions among the various chloroamine species
Total suspended solids	Shields embedded bacteria and increases chlorine demand

- **energy consumption**
- **chemical demand**

Design guidelines / Technical data

Disinfection performance is often assessed through changes in concentrations of indicator organisms (primarily faecal and total coliform) over time. For example, the Collins model predicts the reduction in bacterial concentration as a function of the chlorine residual concentrations and system contact time:

$$Y_t = Y_o\,(1 + 0{,}23 \cdot C_R \cdot T)^{-3} \qquad \text{(eq 4)}$$

where Y_t is the bacterial concentration after time T (MPN/100 ml), Y_o is the starting bacterial concentration, C_R is the chlorine residual concentration after time T (mg/L) and T is the contact time (min). Other factors such as the chlorine dosage, contact time, flow characteristics and mixing intensity also influence the effectiveness of chlorine disinfection. Reactors should be designed for as close to ideal plug flow as possible and include effective mixing of the chlorine solution. Strong initial mixing is critical in high rate disinfection where contact times are short. The factor $C_R \cdot T$ (Eq.4) is the most important design parameter for chlorine disinfection. Depending on the required removal efficiency and a minimum contact time, the chlorine dosage can be calculated according to eq. 4.

Table 2. Typical chlorine dosages at water treatment plants

Chlorine compound	Range of dose	Contact time
Chlorine dioxide	0,1 – 1,5 mg/L	1 – 6 min
Chlorine gas	0,5 – 5 mg/L	1 – 6 min
Calcium hypochlorite	0,2 – 2 mg/L	1 – 6 min
Sodium hypochlorite	1 – 16 mg/L	1 – 6 min

Table 3 Treatment performance

Compound	**Removal rate IEX [%]**
Acesulfame-K	Poor
Caffeine	<20
Carbamazepine	20
Metformin	100
Sulfamethoxazole	100

Operational stability and maintenance

Chlorine is relatively simple to apply and control. It is introduced into the wastewater by solution feeders or gas injectors. Chlorine gas is normally stored in steel containers (150-pound or 1-ton cylinders) and transported in railroad cars and tanker trucks. Sodium hypochlorite solution must be stored in rubber-lined steel or fiberglass storage tanks. Calcium hypochlorite is shipped in drums or tanker trucks and stored with great care. Because chlorine is hazardous, safety precautions must be

exercised during all phases of shipment, storage, handling, and use. Regular operation and maintenance involves disassembling and cleaning the various components, such as meters and floats, once every 6 months.

Reference installations, Suppliers

East Bay WWTP, Oakland, California, 1.000.000 m^3/d, chlorination and dechlorination.
Marsh Creek WWTP Geneva, New York, 50.000 m^3/d, chlorination and dechlorination.

Literature references

- United States Environmental Protection Agency (EPA), Alternative disinfectants and oxidants guidance manual, Office of Water 4607, EPA 815-R-99-014, April 1999.
- AWWA (American Water Works Association), Water Quality and Treatment, edited by Pontius FW, McGraw-Hill, New York, 1990.
- Black BD, Harrington GW and Singer PC (1996) Reducing cancer risks by improving organic carbon removal, Journal of the American Water Works Association, 88 (6): 40.

Websites:

- The chlorine dioxide water treatment resource centre: www.clo2.com
- Lenntech: www.lenntech.com/chlorine_dioxide.htm
- Severn Trent: www.severntrentservices.com/water_purification/disinfection_products/disinfection_chlorine.jsp

OZONE DISINFECTION
Fact sheet nr.06
WASTEWATER & DRINKING WATER

Unit operation	Disinfection
Treatment principle	Oxidation
Applicable for	Advanced effluent treatment, drinking water treatment
Stage of development	full scale
Process	
function:	degradation of pathogenic organisms, decolouring, oxidation of metal ions, destruction of metal complexes, partial or complete removal of micro-pollutants (PACs, pesticides, chlorinated hydrocarbons)
feed:	WWTP effluent
Keywords:	oxidation, disinfection, ozone

Background

Ozone is a powerful oxidant, second only to the hydroxyl free radical among the chemicals used in water treatment. It is able to achieve disinfection with less contact time and concentration than all weaker disinfectants such as chlorine, chlorine dioxide and monochloramine.

Description and working principle

Ozone is an effective agent for at least the partial oxidation of simple ions and species containing multiple bonds. In acidic or neutral solutions ozone is unstable and decomposes via a series of chain reactions to oxygen. In alkaline solutions however, ozone may decompose into hydroxyl radicals through the following steps:

$$O_2 + OH^- \rightarrow O_2^{-\cdot} + O_2$$

$$O_3 + H_2O \rightarrow 2OH^{\cdot} + O_2$$

The formation of free radicals at high pH is the reason why alkaline oxidation rates by ozone are several orders of magnitude higher than those in acidic media. In water with high alkalinity the rate of oxidation may however decrease as the pH increases because of the formation of carbonate ions, which are more effective scavengers of hydroxyradicals than bicarbonate ions. The direct oxidation pathway with aqueous ozone is relatively slow but the concentration of aqueous ozone is relatively high. On the other hand, the hydroxyl radical reaction is fast but the concentration of radicals under normal ozonation conditions is relatively low.

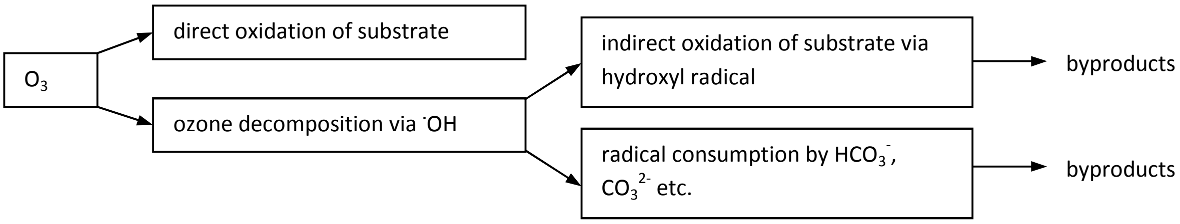

Figure 1. Possible mechanisms during ozone oxidation

- **required pre-treatment**

Ozonation is not economical for water with high levels of suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand or total organic carbon. These levels should be reduced before treatment. If O_3 oxidation is combined with UV treatment, pre-treatment is necessary to remove precipitated products as UV treatment is also sensitive to the solids concentration.

- **waste products**

An important advantage of chemical oxidation is that no sludge or concentrate is produced. The off-gases from the contact chamber must be treated to destroy any remaining ozone before being released into the atmosphere. The ozone off-gases that are not used are sent to the ozone destruction unit or are recycled.

- **treatment performance**

Table 1 provides an overview of the removal efficiency during ozone disinfection.

- **energy consumption**

Ozone generation uses a significant amount of electrical power. Thus constant attention must be given to the system to ensure that power is optimised for controlled disinfection performance. Energy consumption for ozone generation is in the order of 0,02 – 0,058 kWh/m^3.

Table 1. Removal efficiencies during ozone disinfection process

Parameter	removal efficiency [%]
COD	80 – 100
E. Coli	95 – 100
AOC	60 – 80
PCB	60 – 80

Table 2. Removal of organic compounds ozone

Compound	**Removal rate ozone [%]**
Acesulfame-K	30-50
AMPA	100
Bentazone	68
Caffeine	>80
Carbamazepine	>95
Glyphosate	100
Iopromide	20-50
Metformin	
Sulfamethoxazole	>95

Design guidelines / Technical data

The effectiveness of disinfection using ozone depends on the contact time, the ozone concentration in the feed gas mixture, the temperature and the susceptibility of the target organisms. The components of an ozone disinfection system include feed-gas preparation, ozone generation, ozone contacting and ozone destruction. On-site production of ozone is necessary as ozone decomposes to oxygen within minutes.

Ozone generation

Ozone generators are generally classified by 1) the control mechanism (voltage or frequency unit), 2) the cooling mechanism (water, air, or water plus oil) or 3) the physical arrangement of the dielectrics (either vertical or horizontal), 4) the name of the inventor. Low frequency (50 or 60 Hz) and medium frequency (60 – 1000 Hz) generators are the most common found in the water industry, however some high frequency generators are available. Medium frequency generators are efficient and can produce ozone economically at high concentrations, but they generate more heat than low frequency generators and require a more complicated power supply to step up the frequency supplied by utility power.

Ozone contacting

The main purpose of the contactor is to transfer ozone from the gas bubble into the bulk liquid while providing sufficient contact time for disinfection. Ozone not transferred into the process water during contacting is released from the contactor as off-gas. Transfer efficiencies of greater than 80 % are typically required for efficient ozone disinfection. Common ozone dissolution methods include:

- Bubble diffuser contactors (co-current and counter-current);
- Injectors (positive pressure injection and negative pressure injection (Venturi));
- Mechanically agitated (e.g. turbine mixers), and;
- Packed tower.

Because ozone is consumed quickly, it must be contacted uniformly in a near plug flow contactor. The key process control parameters for ozone disinfection are the dosage, mixing and contact time. An ozone disinfection system strives for maximum solubility of ozone in wastewater, as disinfection depends on the transfer of ozone to the wastewater. The amount of ozone that will dissolve in wastewater at a constant temperature is a function of the partial pressure of the gaseous ozone above the water or in the gas feed stream. The solubility of ozone in water is also affected by the temperature and pH. The solubility of ozone in water is indirectly proportional to the temperature. The required dosage varies depending on the compound being treated. Ozone concentrations of between 3 – 8 mg/L are required for the destruction of most pesticides.

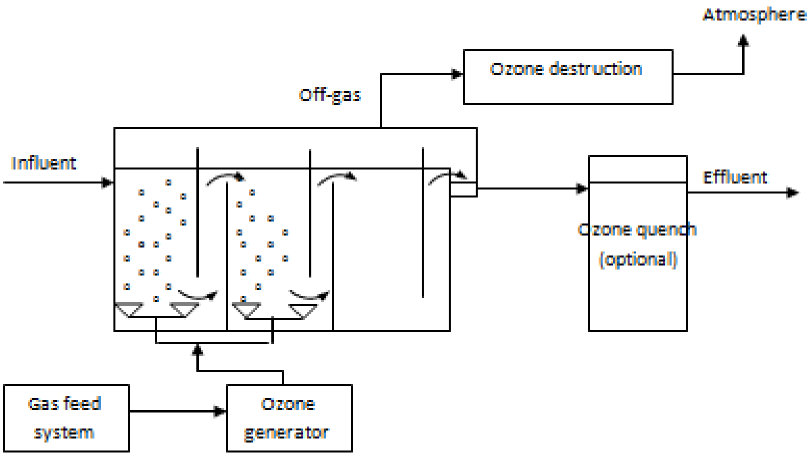

Figure 1. Simplified counter current contacting ozone system schematic

It is critical that all ozone disinfection systems be pilot tested and calibrated prior to installation to ensure they meet discharge permit requirements for their particular sites.

residence time

Depending on the components to be oxidised and the oxidant to be used, the residence time varies between 0.5 – 4.0 hours. The optimal residence time can be relatively easily determined in pilot/Lab tests.

Typical design parameters for ozone oxidation

parameter	unity	value/range
Dosage requirements		
Iron oxidation	mg O_3/mg Fe	0.43
Manganese oxidation	mg O_3/mg Mn	0.88
Taste and odour oxidation	mg O_3/L	2.5 – 2.7
3 – 20 % reduction trihalomethanes	mg O_3/mg C	0.2 – 1.6
Contact time		
Taste and odour oxidation	min	10
Ozone contacting		
Dosage (O_3 mg/L) x contact time (HRT min)	mg/L * min	> 4.0
Required dosage for pesticide destruction	mg/L	3 – 8
Height/diameter ratio of bubble columns	-	> 7.6
Energy requirement		
Electrical input	kWh/kg O_3	4 – 7

Operational stability and maintenance

Although ozone systems are complex using highly technical instruments, the process is highly automated and reliable, requiring only a modest degree of operator skill and time to operate an ozone system. Maintenance on generators requires skilled technicians and must be carried out with high frequency. Ozone is not flammable but can react explosively upon reaction with other compounds. Ozone irritates the eyes and lungs. Rooms containing ozone equipment must be properly ventilated and fitted with an “ozone alarm”.

Summary of advantages and disadvantages of disinfection with ozone

advantages	disadvantages
more effective than chlorine in destroying viruses and bacteria	chances of formation of the toxic bromate ion
a short contact time (approximately 10 – 30 minutes)	low dosage may not effectively inactivate some viruses, spores and cysts
no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly	more complex technology than chlorine or UV disinfection
no regrowth of microorganisms after ozonation, except for those protected by particulates	ozone is very reactive and corrosive thus requiring corrosion-resistant material such as stainless steel
ozone is generated onsite and thus there are fewer safety problems associated with shipping and handling	not economical for (waste)water with high levels of TSS, BOD, COD or TOC
the increase in DO can eliminate the need for reaeration also raise the DO concentration in the receiving stream (WWTP)	ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed
	the cost of treatment can be relatively high in capital and power intensiveness

Reference installations, Suppliers

- O_3/H_2O_2 Paris water production plant, France, 200,000 m^3/d (constructed early 1990´s)

Literature references

- Alternative Disinfectants and Oxidants Guidance Manual (1999) U.S. Environmental Protection Agency. EPA 815-R-99-014
- Parsons, S. (ed.)(2004) Advanced Oxidation Processes for Water and Wastewater Treatment. IWA Publishing, London, UK.

websites

- http://www.epa.gov/owm/mtb/ozon.pdf
- http://www.gewater.com/Library/tp/index.jsp
- http://www.lenntech.com/faqozone.htm

UV DISINFECTION
Fact sheet nr.05
WASTEWATER & DRINKING WATER

Unit operation	Disinfection
Treatment principle	UV radiation
Applicable for	Advanced wastewater treatment, drinking water treatment
Stage of development	full scale
Process	
function:	degradation of pathogenic organisms, photolysis of organic material, decolouring, destruction of metal complexes, partial or complete destruction of micro-pollutants (PACs, pesticides, chlorinated hydrocarbons)
feed:	WWTP effluent,
Keywords:	UV, disinfection

Background

Ultra violet (UV) light is the range of the electromagnetic spectrum with a wavelength between 100 – 400 nm. The range between 200 – 280 nm (UV C) has a germicidal effect. The germicidal properties of UV radiation have been used in a wide variety of applications since its use was pioneered in the early 1900s. With the proper dosage, ultraviolet radiation has proven to be an effective germicide and virucide for wastewater and drinking water, without the formation of toxic by-products. The efficiency of UV radiation depends on the UV-absorbancy of the compound to be destroyed. Nucleic acids and proteins are effective absorbers of UV radiation, which is the reason UV is an effective (physical) disinfection method. UV radiation of micro-organisms causes irreversible photo-biochemical alterations in the DNA structure, causing the inability of microbes and viruses to reproduce.

Description and working principle

The extent of disinfection achieved with UV radiation is expressed in log units and is directly related to the UV dose[7] (Eq 1). The UV dose required for effective inactivation is determined by site-specific data relating to the water quality and log removal required. The effectiveness of the UV radiation is strongly affected by the UV transmittance of the water to be treated. The efficiency decreases with increasing turbidity. For this reason, UV disinfection is not feasible for water with a high suspended solids concentration. The presence of some dissolved or suspended matter may shield microbes from the UV radiation. Iron, sulphites, nitrites and phenols all absorb UV light. Accordingly, the absorbance coefficient of the water is an indication of this demand and is unique for each water. The UV-dose can be calculated as the specific intensity per unit surface (mW/cm^2) multiplied by the exposure (or contact) time (s) (Eq 1):

$$\text{Dose} = \text{UV Intensity} * \text{Exposure Time (mJ/cm}^2\text{)} \qquad \text{(Eq 1)}$$

Specific "design" parameters vary for individual waters and should be determined empirically for each application. The UV demand of water can be measured simply in a spectrophotometer set at a wavelength of 254 nm using a 1 cm thick water layer.

<u>UV lamps</u>

Almost all UV lamps are mercury arc discharge lamps in which an electric current is sent through mercury vapour, causing mercury atoms to become excited and emit light at UV wavelengths. The mercury "arc" is inherently unstable and requires specific current conditions. A ballast is used to control the current. There are 3

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[7] Reduction by 99% is a factor 10^2 reduction and is equal to log 2 inactivation. Reduction by 99.9% is equal to log 3 units and so on.

main types of lamps, 1) Low pressure (LP), 2) Low pressure/high output (LPHO) and 3) Medium pressure (MP). Low-pressure lamps are generally more energy efficient, while medium pressure lamps emit up to 10 times more energy but are more expensive. The output of a UV lamp decreases during its lifetime (12 – 20 months, depending on type of lamp) and lamps need to be replaced when the output is reduced to 70%. For disinfection purposes low pressure lamps are preferred due to the specific wavelength that can be produced and the lower energy consumption. For AOP purposes medium pressure lamps are preferred due to the more intensive oxidation reactions they can produce. The broad emission spectrum and the higher intensity of medium pressure lamps is used to produce free radicals ($OH^{\cdot}$) from hydrogen peroxide and ozone, as well as disinfection.

ballasts

Ballasts are transformers that control the power to the UV lamps. They generally generate enough heat to supply cooling fans or air conditioning. Ballasts should be compatible with the UV lamps and must be in a waterproof remote location.

UV reactor design

The design of a UV reactor has a large influence on the efficiency of the process. The following factors need to be taken into account, 1) Hydraulics: direction and flow rate of the water flow through the reactor; 2) Positioning of the lamps; 3) Radiation intensity of the lamps in relation to the water flow; 4) Configuration of the reactors in series; 5) Use of space due to the lamp dimensions, and 6) Energy consumption due to the water flow. Most conventional UV reactors are available in two types: closed channel and open channel. Closed channel systems are generally applied in drinking water production plants, however they are becoming increasingly popular for WWTP effluent. Open channels are commonly used in WWTP effluent disinfection, however they are more susceptible to fouling.

- **required pre-treatment**

The efficiency of UV treatment is sensitive to the dissolved organics concentration and solids concentration in the water. UV radiation is generally not effective for effluent with TSS > 30 mg/L. Since disinfection in a drinking water treatment is usually at the end of the treatment train, the water is sufficiently treated and no extra pre-treatment is required. An overview of some interfering substances to UV radiation is shown in table 1.

- **treatment performance**

Since UV radiation is energy in the form of electromagnetic waves, its effectiveness is not limited by chemical water properties. It appears that pH, temperature, alkalinity and total inorganic carbon do not impact the overall effectiveness. The addition of oxidants (H_2O_2 or ozone) enhances the effectiveness. The quality of the treated water is however dependent on the extent of fouling of the lamps, the UV transmittance of the water (UVT) and the turbidity, which make this technique ineffective for water with a high suspended solids concentration (> 30 mg TSS/L). UVT is the most important performance parameter. As a rule of thumb, for every 5% decrease in UVT, 50% less UV is available for disinfection. Table 2 shows the removal efficiency for the target compounds.

- **energy consumption**

Energy consumption for disinfection purposes (UV intensity 40 – 125 mJ/cm^2) is in the range 0.1 – 0.2 kWh/m^3. For the use of UV in advanced oxidation processes (UV intensity 600 – 1,000 mJ/cm^2) the energy consumption is much higher (0.2 – 0.6 kWh/m^3).

chemical demand

Chemical addition is not required in UV disinfection, which is a major advantage of this technique.

Table 1. Disturbing substances for UV disinfection (Metcalf & Eddy 2003)

Constituent	Effect
BOD, COD, TOC	No, or minor effect
Humic material	Strong adsorbers of UV radiation
Oil and grease	Can accumulate on quartz sleeves of UV lamps, can absorb UV radiation
	Absorption of UV radiation, can shield embedded bacteria

Constituent	Effect
TSS	Can impact scaling potential
pH, Alkalinity, Hardness	

Table 2. Removal of organic compounds UV disinfection

Compound	Removal rate UV [%]
Acesulfame-K	
AMPA	100
Bentazone	
Caffeine	10-40
Carbamazepine	60
Glyphosate	60
Iopromide	99
Metformin	6
Sulfamethoxazole	>99

Design guidelines / Technical data

design loads

hydraulically: UV installations have been designed for systems as small as 90 m^3/d to large-scale systems (1.600.000 m^3/d). Installation of enough hydraulic capacity is generally a question of installing more units and elements. Single UV units can treat flow rates of up to 200 m^3/h.

kinetically: For adequate disinfection of most viruses and micro-organisms a UV dosage of 40 – 125 mJ/cm^2 is required.

residence time: UV disinfection has a shorter contact time when compared with other disinfectants (approximately 20 to 30 seconds with low pressure lamps).

Operational stability and maintenance

UV lamps have a limited life (1 – 2 years LP lamps, 0.5 – 1 year MP lamps), meaning lamps need to be replaced regularly. A major disadvantage is the development of biofilm (fouling) on the exposed surfaces of the UV reactor. Especially open channel systems that are exposed to daylight may encounter fouling. Closed UV systems, however, can also experience fouling. Fouling occurs essentially when treating any water. Removal of biomass growth must be conducted on an as-need basis either with a mechanical wipe or by a chemical (acid) clean. In addition, UV sensors can drift over time and need to be recalibrated periodically. UV installations do not require any storage of hazardous material, neither proportioning nor handling of chemical substances is involved. Installation is relatively simple.

Reference installations, Suppliers

reference installations

city, country	year	supplier	Pretreatment	system	capacity, max	number of lamps
					m3/h	#
Manukau, N-Z	2001	wedeco	anthracite filtration	open channel, tangential,	57	7,700
Bad Tölz, D	2003		sand filtration-TSS=5 mg/L	open channel, low pressure	2	144
Fairfield, Ohio, USA	2003	Aquionics		medium-pressure	56	

suppliers

- Berson, Neunen, the Netherlands, http://www.bersonuv.com
- Trojan, Ontario, Canada, http://www.trojanuv.com
- Wedeco, Herford, Germany, http://www.wedecouv.de
- Calgon Carbon Corporation, http://www.calgoncarbon.com
- Magnum Water Technology, http://www.magnumwater.com

Literature references

- König, R. (2001) UV wastewater disinfection: the key to the future, Water21, April 2001
- Metcalf & Eddy (2003). Wastewater engineering; treatment and reuse (4th international edition). McGraw-Hill, New York
- Parsons, S. (ed.)(2004) Advanced Oxidation Processes for Water and Wastewater Treatment. IWA Publishing, London, UK.

websites

- International Ultraviolet Association (IUVA): www.iuva.org
- ANSI/NSF: www.nsf.org/water.html
- Austrian Standards (ONORM): www.onorm.at
- NWRI/AWWA Guidelines: www.awwa.org.bookstore

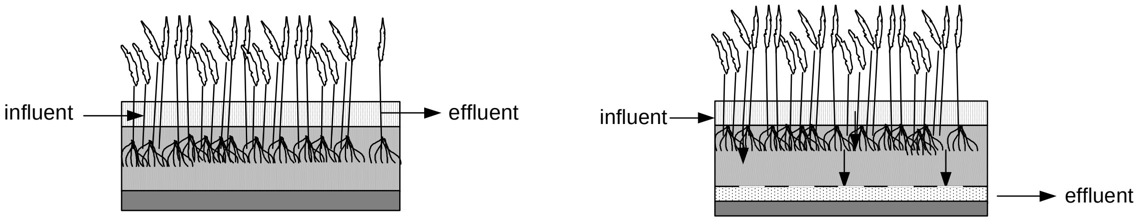
CONSTRUCTED WETLANDS
Fact sheet nr.02
WASTEWATER

Unit operation	Biological degradation
Treatment principle	Sedimentation and biological degradation
Applicable for	Post treatment of effluent
Stage of development	full scale application
Process	
function:	removal of suspended solids, N_{tot}, P_{tot}, COD and pathogens
feed:	WWTP effluent
Keywords:	Reed bed, pond system, biological degradation

Background

Constructed wetlands can remove suspended solids (SS), organic matter, nutrients, microorganisms, and even heavy metals from a wide variety of wastewaters (Hammer, 1989). But unlike traditional biological treatment systems, no specific guidelines yet exist for designing a constructed wetland system to treat wastewater. The main difficulty in creating general design guidelines is that many factors can affect their behaviour: climate, type of vegetation, effects of the local environment, operating strategies, etc. Among these factors, only the type of macrophytes and loading rate can be controlled by the designer. Constructed wetlands use the sedimentation and degradation capacity of reed beds, open ditches and ponds to remove suspended solids, nutrients and organic material from WWTP effluent or inlet water for a nature reserve. In this way the quality of the effluent produced can be significantly improved. The technique is however not capable of removing nutrients or pollutants to the level required in the Water Framework Directive (WFD) as a stand-alone technique. The conversions take place by plants, micro-organisms, higher organisms and sunlight.

Description and working principle



horizontal filter

vertical filter

Figure 1. Two types of reed beds

In constructed wetlands microbial and biological processes are stimulated for sedimentation and natural breakdown of polluting compounds. There are several forms of constructed wetlands (Figure 1):

Horizontal flow:

The water flows over a fixed surface in which reed is planted.

The water flows horizontally through the root zone of reed plants

Vertical flow. The water flows downwards through the root zone of reed plants

In both systems this can be combined with open surface flow through ditches or ponds.

- **required pre-treatment**

No special pre-treatment is required.

- **waste products**

In the case of reed beds, the reed must be harvested (once per year, in winter) and can be composted. A large fraction of the pollutants accumulate in the sediment of the ponds/reed beds, which has to be removed and treated.

- **treatment performance**

The following conversions can take place:

- sedimentation
- microbiological denitrification
- physical: filtration through the soil or the root zone reducing the suspended solids. Disinfection by UV-radiation.
- biological: uptake of nutrients by plant roots.

For removal efficiencies of several substances, see table 1. The treatment performance is generally lower during periods of high flow and lower temperature, which cannot be controlled in wetland systems.

- **energy consumption**

The constructed wetlands can be operated under gravitational flow, i.e. with minimum extra pumping devices.

chemical demand

No chemicals are used.

Table 7 Removal efficiency of constructed wetland (Stowa, 2004) (horizontal flow reed bed, 220-270 mm/day)

Parameter	removal efficiency %
N_{tot}	10-30
P_{tot}	8-40
COD	5-20
SS	0-80[1]
E.coli	>99[2]

[1] the composition of the suspended solids in the effluent of the reed bed is generally significantly different from the suspended solids in WWTP effluent

[2] the removal of pathogens is dependent on the season. In the Netherlands, in summer time a residence time of 3 days seems to be enough to reach bathing water quality with respect to E.coli.

Table 2. Removal of organic compounds constructed wetlands

Compound	Removal rate constructed wetland [%]
Carbamazepine	13-40
Sulfamethoxazole	15

Design guidelines / Technical data

The applied hydraulic loading rate of reed beds and wetlands (in horizontal or vertical flow configuration) varies largely and ranges from 150 – 1000 mm/d. The residence time applied generally ranges between 3 to 6 days.

Operational stability and maintenance

Excessive growth of surface covering water plants must be removed. Once per year the reed has to be harvested.

Reference installations, Suppliers

In the Netherlands there has been a three-year full-scale trial at the Land van Cuijk WWTP, as well as long term research at the Everstekoog WWTP, however these systems were not aimed at achieving water of Water Framework Directive quality.

Literature references

- STOWA 2004/45 (2004). Praktijkonderzoek moerassysteem rwzi Land van Cuijk
- Toet, S. (2003) A treatment wetland used for polishing tertiary effluent from a sewage treatment plant: performance and processes, PhD-thesis, Utrecht, the Netherlands
- Hammer, D.A. (ed.) 1989. Constructed wetlands for wastewater treatment—Municipal, industrial and agriculture. Lewis Publ., Chelsea, MI, United States.

websites

- www.waterharmonica.nl
- research, consulting and information on the treatment of wastewater with reed beds (in Dutch) Onderzoek, advies en informatie over de zuivering van afvalwater m.b.v. helofytenfilters http://www.compris.nl/eco/
- International Ecological Engineering Society http://www.iees.ch/
- Constructed Wetlands: Using Human Ingenuity, Natural Processes to Treat Water, Build Habitat http://ag.arizona.edu/AZWATER/arroyo/094wet.html
- Natural Resources Fact Sheet Index http://ohioline.osu.edu/a-fact/
- http://www.ecofyt.nl/ (commercial)

Appendix 5-3 Summary of treatment techniques, removal efficiencies and estimated costs (WWTP)

	Acesulfame-K	AMPA	Bentazone	Caffeine	Carbamazepine	Glyphosate	Iopromide	Metformin	MTBE	N,N-DMS	Sulfamethoxazole	Costs based on WWTP
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[€/m^3]
CAS nr.	55589-62-3	1066-51-9	25057-89-0	58-08-2	298-46-4	1071-83-6	73334-07-3	657-24-9	1634-04-4	3984-14-3	723-46-6	
Log K_{ow}	-1.33	0.76	2.5 to 3.8	-0.07	2.45	-4.6 to -1.6	-2.05	-2.64	0.94	-0.2	0.89	
Physical treatment												
Coagulation/ flocculation	Poor[1]		30[4]		0-60[10]			Poor[113]			33[10]	
Biological treatment												
MBR				>85[9]	20[9]		20-30[9]				20-43[9]	80 €/i.e./y[19]
Filtration techniques												
Sand filtration				7[10]	75[10]							
Micro/ultra fitration				MF: 4[9] UF: 7[9]	MF: 89 UF: 16[9]		UF: <1[9]				MF: 2[9] UF: 5[9]	28 €/i.e./y[19]
Nanofiltration/ reverse osmosis			100[5]	NF: 50-80[9] RO: >99[9]	NF: 50-80[9] RO: >90[9]		NF: >80[9] RO: >99[9]	40[14]	60-99[14]	30-95[14]	NF: 50-80[9] RO: >99[9]	21 €/i.e./y[19]
Advanced treatment												
Activated Carbon (GAC+PAC)	60[1]		100[6,7]	GAC: 59[9] PAC: 16[9]	>70[9,10]		31[9]	90[13]			43[9]	18 €/i.e./y[19]
Advanced Oxidation Processes		poor[1]		89	88[9]	100[2]	91[9]	34[15]			>99[9]	31 €/i.e./y[19,20]
Ion Exchange		93[2]		<20[9]	<20[9]	95[3]	<20[9]				20-50[9]	14 €/i.e./y[19]

Disinfection												
Chlorination	poor[1]			<20[9]	20[10]			100[13]			100[10]	
Ozonation	30-50[1]	100[2]	68[8]	>80[9]	>95[9,10]	100[2]	20-50[9]				>95[9]	35 €/i.e./y [21] (ozone+activated carbon) 5 €/i.e./y [22] (effluent)
UV-disinfection		100[2]		10-40[9]	60[9]	60[2,12]	99[9]	6[15]			>99[9]	20 €/i.e./y [22] (effluent)
Effluent treatment												
Constructed wetlands					13-40[11,18]						15[18]	
OTHER												
Conventional activated sludge				>95[9,16]	10-20[9,16,17]		72[9]				60-85[9,16]	
Riverbank infiltration	poor[1]			97[9]	13[9]		93[9]					

[1] *(Scheurer et al., 2010)*
[2] *(Assalin et al., 2010)*
[3] *(Royer et al., 2000)*
[4] *(Thuy et al., 2008)*
[5] *(Karabelas et al., 2011)*
[6] *(Heijman et al., 1999)*
[7] *(Rashed, 2013)*
[8] *(Bonne et al., 2000)*
[9] *(U.S. Department of the Interior Bureau of Reclamation, 2009)*
[10] *(Kumar et al., 2010)*
[11] *(Matamorosa et al., 2008)*
[12] *(Sillanpää et al., 2011)*
[13] *(Scheurer et al., 2012)*
[14] *(Lipp et al., 2010)*
[15] *(Cruz de la et al., 2012)*
[16] *(Oppenheimer et al., 2011)*
[17] *(Gagnon et al., 2012)*
[18] *(Breitholtz et al., 2012)*
[19] *(STOWA, 2005)*
[20] *(STOWA, 2009b)*
[21] *(STOWA, 2013)*
[22] *(Grontmij, 2011)*

Appendix 5-4 Promising techniques

Currently, some new techniques are in development. Because of the little information found on these and some other techniques, they are not included in this project. But to give an idea of the newest developments, a list is given. These are both drinking water and wastewater treatment techniques.

1. **Managed Aquifer Recharge** (MAR)
   Managed aquifer recharge (MAR) is stipulated by the EU Water Framework Directive to be a supplementary measure to reach good quantitative and good qualitative water status by regulating the water cycle on the basin scale within an integrated water resource management. The EU Groundwater Directive, on the other hand, prohibits any actions that may deteriorate groundwater quality – a demand which needs to be evaluated on a site-by-site basis. Within this context, emerging pollutants *are of special concern, since some have shown to be poorly degradable or may only be removed under specific redox conditions.*
   (from: http://demeau-fp7.eu/technology-description/managed-aquifer-recharge)
2. **Hybrid Ceramic Membrane Filtration** (HCMF)
   Polymeric membranes are widely used in water treatment to remove pathogens, particles and organics from surface, ground, process and filter backwash water. However, ceramic membranes are currently only used for these purposes in Japan. Because ceramic membranes are much more resilient under extreme conditions (e.g. temperature, pH and chemicals), they facilitate a more rigorous cleaning, resulting in a better overall filtration performance than that of polymeric membranes. DEMEAU will stimulate the application of ceramic membranes by addressing the following aspects. (from: http://demeau-fp7.eu/technology-description/hcmf)
3. **Hybrid Advanced Oxidation** (HAO)
   UV-based and chemical oxidation processes are preferred treatment technologies for the elimination of emerging pollutants *in drinking water and wastewater because of their flexibility, long-term stability, low costs, and controllability.* (from: http://demeau-fp7.eu/technology/hao)
4. **1-STEP filter**
   This is a treatment techniques invented for the treatment of WWTP effluent. The filter is filled with activated carbon and several processes take place in it. By coagulation, flocculation and filtration phosphate is removed (figure F). Denitrification takes place to remove nitrogen. Filtration removes turbidity. The activated carbon stimulates removal of priority substances by adsorption. Heavy metals are removed by binding to organisms and filtration.
5. **Optimix**
   Removal of priority substances by sedimentation with organic flocculants. The current outcome of this research is that the priority substances do not bind to the colloidal fraction, which results in bad removal performance. However, the technique shows higher biogas production, less $FeCl_2$ addition for phosphorus removal and increased sludge dewatering performances (Kreuk de, 2013).
6. **Priomf** (Priority organic micro pollutants filter)
   This filter is designed for the treatment of wastewater to remove a wide range of micro pollutants. In the filter adsorption to activated carbon is combined with biodegradation. The technique makes use of a fluidised bed in a conical column (figure G).
7. **Molecularly imprinted membranes**
   MIP are prepared from cross-linked polymers containing cavities specific to an analyte. These cavities are created by copolymerization of cross-linking monomers and functional monomers along with an imprinting molecule or template. Following polymerization, the template is removed, leaving a cavity specific to the analyte. The MIP then selectively re-binds to the analyte compound. Although MIP are designed with one template molecule, similar molecules are also capable of binding into the specific cavity, and the template experiences some competition fromthese similar compounds. (from: (Murray *et al.*, 2012))

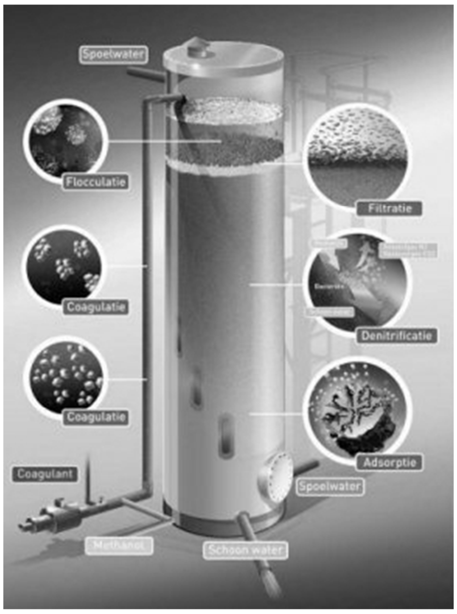


Figure H 1-STEP filter (Witteveen+Bos, 2013)

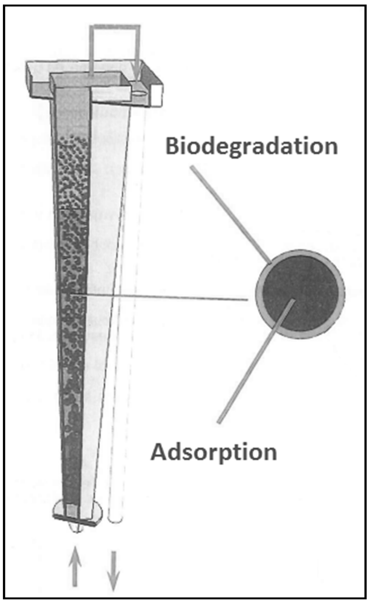


Figure I Priomf (Ridder de, 2013)

8. **Nereda**

   Nereda® is an innovative and advanced biological wastewater treatment technology that purifies water using the unique features of 'aerobic granular biomass'. Contrary to conventional processes, the purifying bacteria concentrate naturally in compact granules, with superb settling properties. As a result of the large variety of biological processes that simultaneously take place in the granular biomass, Nereda® is capable of producing excellent effluent quality. Even when not particularly targeted, extensive biological phosphorus and nitrogen reduction is an intrinsic attribute of this technology, resulting generally in chemical-free operation. These unique process features translate into compact, energy saving and easy to operate Nereda® installations for both industrial and municipal wastewater treatment. Nereda® presents attractive new solutions for green field installations and retrofitting or extending conventional activated sludge plants. The technology is also highly recommended for performance and capacity upgrades of existing SBR-facilities.

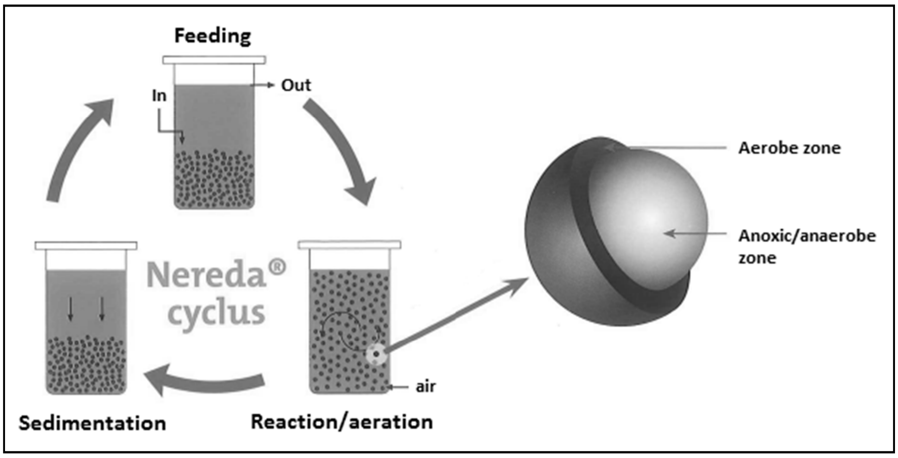


Figure J Principle of Nereda
(from: http://www.nereda.net)

9. **SOURCE** (Simultaneous Removal of Human and Veterinary Pharmaceuticals and Nutrients)

   The concept is based on separate collection of human urine and veterinary manure. The aim is to recover phosphorus and remove pharmaceuticals (SOURCE, 2013).

Appendix 6-1 MCA and sensitivity analysis

A. Expert panel

Prof. dr. ir. J.P. van der Hoek	TU Delft Drinking water
Ir. R.T. van der Velde	Witteveen+Bos Drinking water
Dr. ir. A.F. van Nieuwenhuijzen	Witteveen+Bos Wastewater
Ir. A. Fischer	Phd researcher Watermanagement TU Delft
J. van Tol	Student Watermanagement TU Delft

B. Sensitivity analysis

	Weighting factor	1 Green pharmacy	2 Awareness	3 Legislation and policy	4 Green agriculture	5a Decentralised urine coll/ treatment	5b Centralised urine coll/ treatment	6 Wastewater residential scale	7 Hospital wastewater	8 Improve-ment WWTP	9 Improve-ment DWTP
Weigted / unweighted											
Costs	0.26										
Life Cycle Costs	0.26	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.26										
Energy consumption	0.09	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.05	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.05	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.07	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.48										
Complexicity	0.05	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.05	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.04	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.05	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.15	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.07	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.04	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8

Innovation	0.03	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
TOTAL	1.00	5.0	2.6	7.8	4.8	-7.6	-4.4	-8.0	0.4	6.4	7.0
Weighted score	1.00	14.20	17.80	13.32	9.52	-7.24	-9.04	-5.60	-6.72	-9.32	-9.80
Costs zero											
Costs	0.00										
Life Cycle Costs	0.00	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.35										
Energy consumption	0.12	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.07	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.07	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.09	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.64										
Complexicity	0.07	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.06	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.05	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.06	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.21	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.09	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.06	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.04	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	14.20	17.80	13.32	9.52	-7.24	-9.04	-5.60	-6.72	-9.32	-9.80
Sustainability zero											
Costs	0.35										
Life Cycle Costs	0.35	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.00										
Energy consumption	0.00	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.00	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.00	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.00	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6

Applicability	0.65										
Complexicity	0.07	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.06	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.06	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.06	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.21	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.09	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.06	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.04	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	0.59	0.54	1.06	0.42	-0.82	-0.61	-0.60	-0.04	0.49	0.45
Applicability zero											
Costs	0.50										
Life Cycle Costs	0.50	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.50										
Energy consumption	0.16	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.10	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.10	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.13	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.00										
Complexicity	0.00	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.00	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.00	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.00	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.00	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.00	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.00	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.00	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	1.26	1.40	1.32	0.68	-1.01	-1.01	-0.61	-0.56	-0.49	-0.44
Costs and sustainability zero											

Costs	0.00										
Life Cycle Costs	0.00	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.00										
Energy consumption	0.00	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.00	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.00	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.00	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	1.00										
Complexicity	0.11	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.10	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.09	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.10	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.32	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.14	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.09	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.06	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	0.05	-0.26	0.66	0.21	-0.39	-0.07	-0.49	0.37	1.20	1.13
Costs and applicability zero											
Costs	0.00										
Life Cycle Costs	0.00	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	1.00										
Energy consumption	0.33	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.20	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.21	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.27	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.00										
Complexicity	0.00	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.00	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.00	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2

Risk in implementation	0.00	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.00	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.00	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.00	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.00	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	0.93	0.81	0.84	0.57	-0.42	-0.43	-0.42	-0.32	-0.18	-0.09
Sustainability and applicability zero											
Costs	1.00										
Life Cycle Costs	1.00	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.00										
Energy consumption	0.00	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2
Raw materials	0.00	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.00	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.00	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.00										
Complexicity	0.00	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.00	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.00	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.00	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.00	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.00	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.00	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.00	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	1.60	2.00	1.80	0.80	-1.60	-1.60	-0.80	-0.80	-0.80	-0.80
Effectiveness double											
Costs	0.22										
Life Cycle Costs	0.22	1.6	2.0	1.8	0.8	-1.6	-1.6	-0.8	-0.8	-0.8	-0.8
Sustainability	0.22										
Energy consumption	0.07	1.6	1.8	1.6	1.2	-1.0	-1.6	-1.2	-1.0	-1.2	-1.2

Raw materials	0.04	2.0	2.0	2.0	1.4	-1.4	-1.0	-1.4	-1.0	-1.2	-1.0
Flexibility	0.04	0.0	0.4	-0.4	0.0	0.4	0.4	0.2	0.0	0.4	0.4
Robustness	0.06	0.0	-1.0	0.0	-0.4	0.4	0.8	0.8	0.8	1.4	1.6
Applicability	0.57										
Complexicity	0.04	-0.8	-1.2	-0.6	0.0	-0.6	-0.2	-1.6	0.0	0.4	0.6
Ease of operation	0.04	-1.0	-0.8	0.2	-0.8	-1.2	-0.4	-1.6	-0.2	0.8	1.0
Technical risk	0.03	0.8	1.0	1.0	1.0	-1.0	-0.8	-1.2	-0.2	0.2	0.2
Risk in implementation	0.04	0.0	0.2	0.2	0.2	-1.0	-0.4	-1.0	-0.2	0.8	1.0
Effectiveness	0.30	0.2	-0.2	1.4	0.0	0.4	0.4	0.6	0.6	1.8	1.4
Social acceptance	0.06	1.2	0.4	1.6	1.4	-0.8	-0.2	-1.0	1.2	2.0	1.8
Transition period	0.03	-1.6	-1.2	-0.6	-0.8	-1.4	-0.8	-1.4	-0.4	0.4	0.8
Innovation	0.03	1.0	-0.8	-0.4	0.8	1.2	1.0	1.6	1.6	1.4	1.2
Weighted score	1.00	0.60	0.47	1.07	0.38	-0.52	-0.40	-0.35	0.01	0.57	0.49

Appendix 7-1 Measurement locations and sources

Details about the measurement locations

Figure I and J and table V show the transformation of all used measurement locations into the combined water quality points.

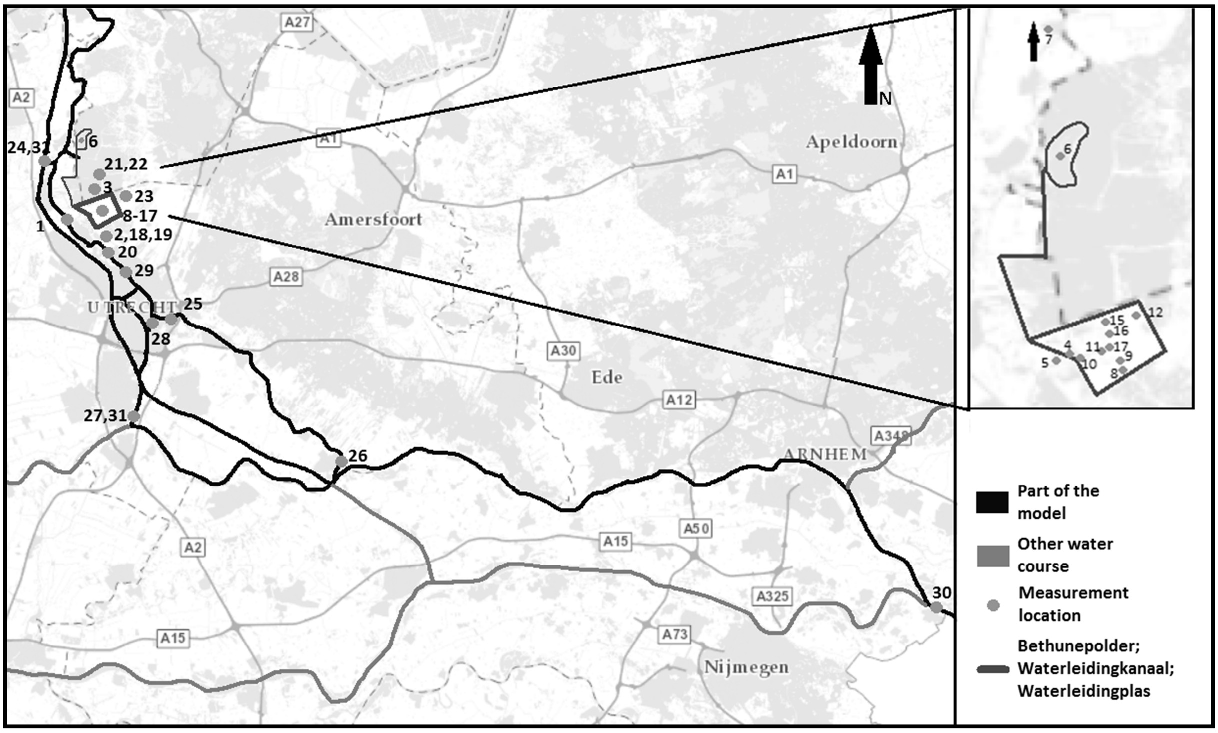


Figure K Model with all measurement locations

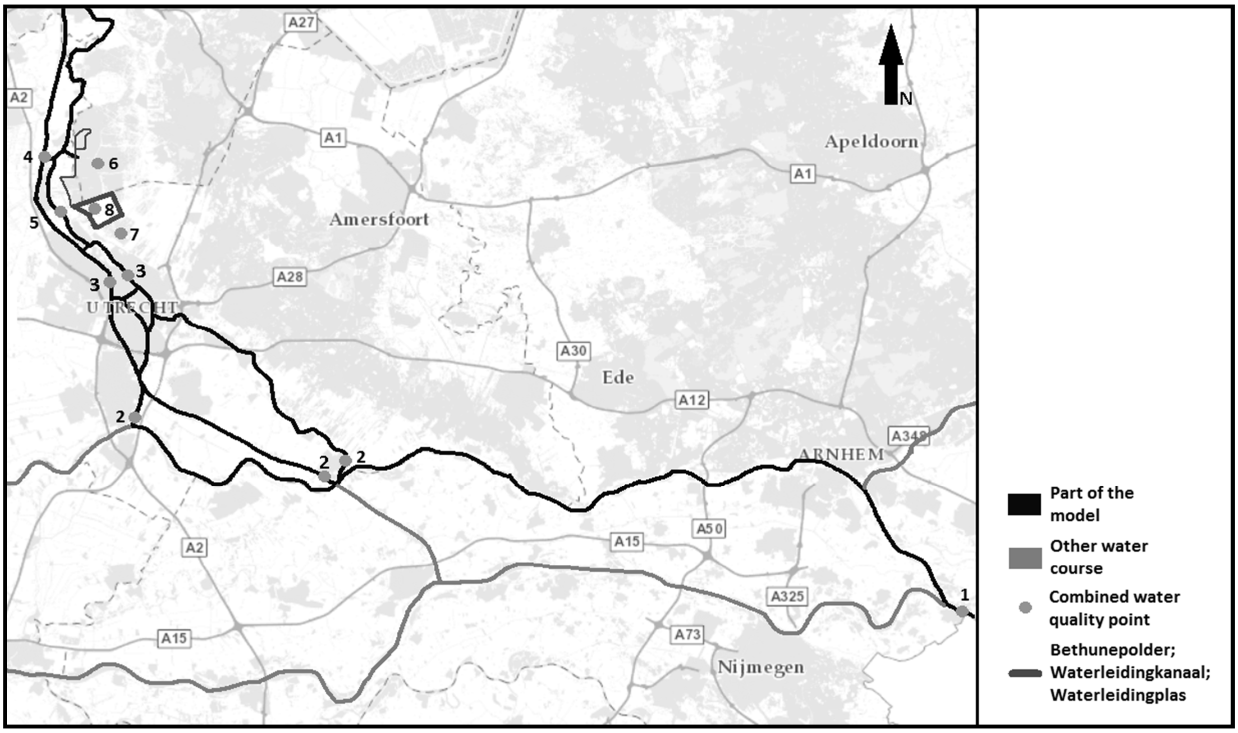


Figure L Model with combined water quality points

Table IV Measurement locations and water quality points (all surface water unless noted)

All measurement locations			
No.	Name	No.	Name
1	Vecht na Maarssen	22	Polder Muyeveld
2	Zodden	23	Tienhovense Plas
3	De Strook	24	Amsterdam Rijnkanaal
4	Inlaat Waterleidingkanaal	25	Kromme Rijn Utrecht
5	Na inlaat WLK	26	Kromme Rijn Wijk bij Duurstede
6	Waterleidingplas	27	Inlaat Vreeswijk
7	Weesperkarspel	28	Vaartsche Rijn
8-17	pijlbuizen BP (GW)	29	Vecht voor RWZI Utrecht
18	Kleine Maarsseveense Plassen	30	Lobith
19	Wilgenplas	31	Nieuwegein
20	Vecht voor Maarssen	32	Nieuwersluis
21	Vijfde Plas/ Loosdrechtse Plassen	33	Andijk

Combined water quality points		
No.	Name	Consist of
1	Lobith	30
2	Utrecht in	25-28, 31
3	Utrecht out	20, 29
4	ARK Nieuwersluis	24, 32
5	Vecht and landfills	1
6	Loosdrechtse Plassen	3, 21, 22, 23
7	Zodden	2, 18, 19
8	Bethunepolder	8-17
90	Andijk	33
100	Waterleidingkanaal	4, 5
110	Waterleidingplas	6
120	Weesperkarspel (DW)	7

Sources

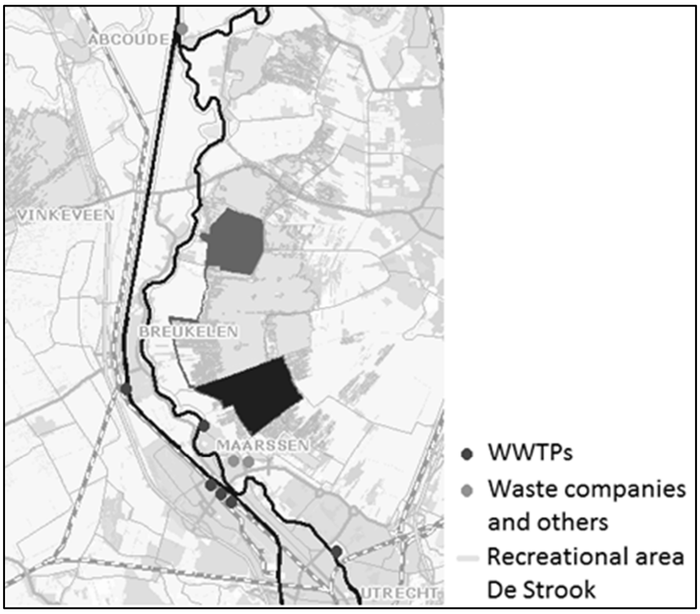


Figure M Sources of contamination

Point sources

Point sources of pollution around the Bethunepolder are sewer overflows, discharges of waste management companies, landfill Maarssen, and former yacht club Maarssen, of which the last three already have been remediated (Provincie Utrecht, 2011; Rijkswaterstaat, 2012a). No information was found about the sewer overflows and therefore it has been chosen to not include these (Waternet, 2010). One point source must be taken into account and that is the supplementation of ARK water to the Waterleidingplas in a dry period. Water is let in into the Waterleidingkanaal where it is mixed with the seepage water from the Bethunepolder, with a maximum of 5% of the yearly production due to health reasons. In recent years this has not occurred (Provincie Utrecht, 2011). Water from the ARK is also let in into the Nieuwe Polderplas, a part of the Loosdrechtse

Plassen, in dry periods. Before it discharges on the Nieuwe Polderplas phosphorus is removed. This water can influence the Bethunepolder by infiltrating into the groundwater.

Diffuse sources

The Bethunepolder, the Waterleidingkanaal and the Waterleidingplas are classified as water extraction areas. Around the Bethunepolder is an area with a higher level of protection against (water) pollution to protect the seepage water in the polder. The land use of this area is mainly agricultural. This means a higher risk for leaching of pesticides, fertiliser and veterinary pharmaceuticals. In the Bethunepolder itself only the pesticide glyphosate is permitted but with the obligation to report the use of it. Another large part of this area consists of water, with a recreational function and some yacht clubs. This results in pollution with antifouling from ships and discharge of untreated wastewater from recreational boats. Although the Loenderveense Plas, the lake bordering the Waterleidingplas, is not open to the public, there is a risk of pollution of the water in the Waterleidingplas by the same substances by groundwater transport. The ARK, Vecht and the polders surrounding the Bethunepolder (Muyeveld and Noorderpark) can be designated as diffuse sources, because the water infiltrated in the ground can transport OMPs to the Bethunepolder. Since wastewater treatment plants and industrial factories discharge their effluent on the ARK and Vecht and the rivers function as excess channels for polder water, they contain low concentrations of pharmaceuticals and other chemicals from human and industrial usage, pesticides and antifouling from shipping (Provincie Utrecht, 2011; Waternet, 2010).

Line sources

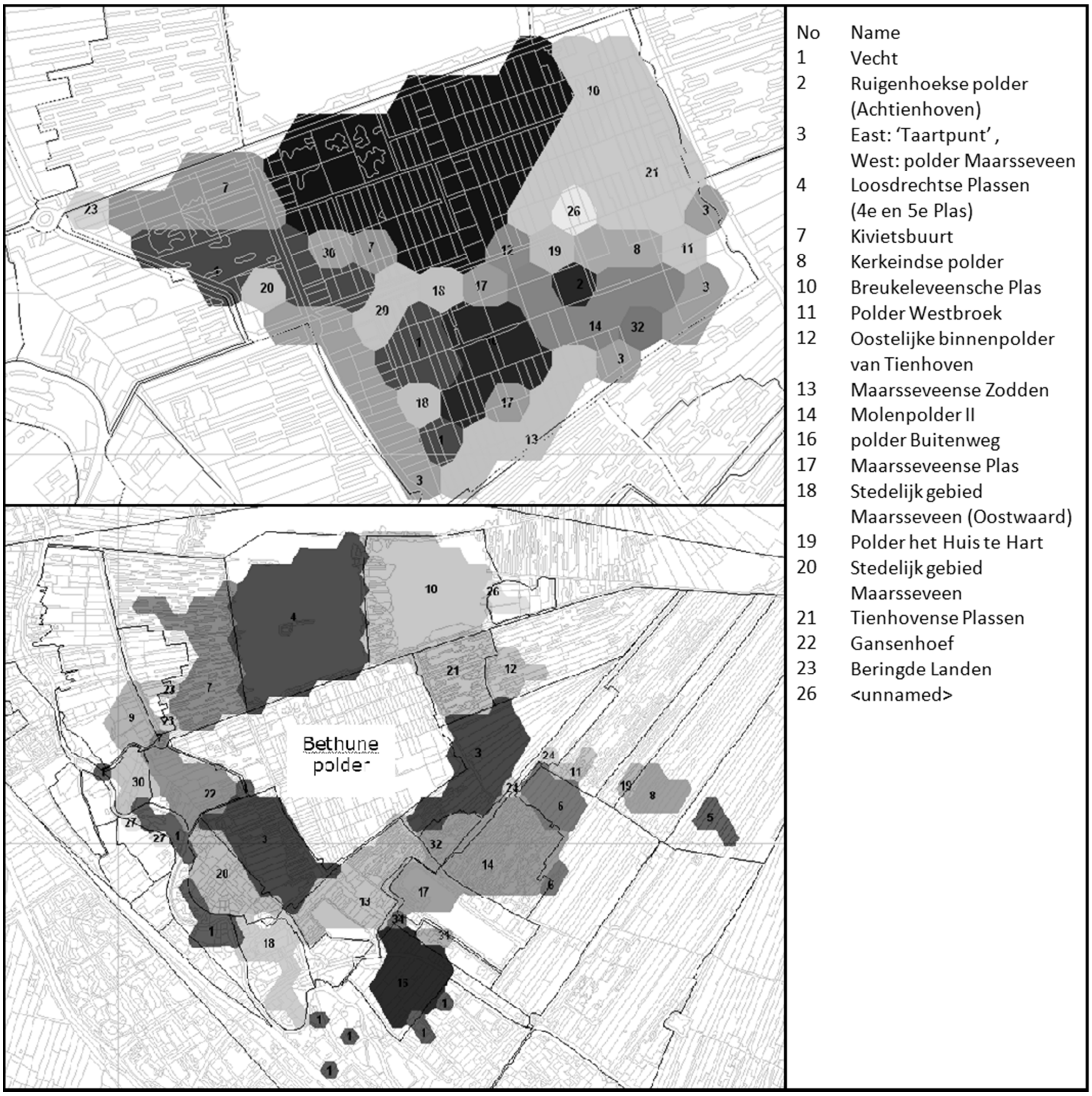
Influence of line sources in the water extraction and protection area are important in case of calamities with cargo traffic on provincial and regional roads, railway and on the ARK and Vecht. At Nigtevecht there is an oil company, which is supplied by shipping on the ARK (Provincie Utrecht, 2011). The northern border of the Bethunepolder is situated next to the recreational area De Strook, which is growing and the increasing (cargo) traffic could influence the water quality of the polder. Although it is questionable whether it is point or line source, the underground sewerage system will be assumed to be a line source. Underground sewerage can break and this causes pollution with untreated sewage (Provincie Utrecht, 2011).

ARK

The ARK flows from south to north through the area of AGV, where it is connected in Amsterdam with in the east the IJmeer and in the west the North Sea canal. Both water bodies are salt or brackish, whereby the ARK comes in contact with brackish water. At the western end of the North Sea canal the water is sluiced into the North Sea at IJmuiden. Only at ebb sluicing is possible and for that reason the water from the North Sea canal, and thus ARK, is stopped flowing twice a day. This results in a backwater curve, where the flow direction of the water in the ARK is suddenly from north to south and brackish and otherwise polluted water flows in the direction of the Bethunepolder. When water supply from the Waterleidingkanaal to the Waterleidingplas is insufficient, water from the ARK is let in into the Waterleidingplas. This inlet is at Nieuwersluis. In this case brackish or otherwise polluted water from Amsterdam can enter the Waterleidingplas. Rijkswaterstaat (government concerning national water bodies, sluices, dikes etc.) aims to minimize the amount of water flowing in southern direction by keeping the average flow at a minimum of 10 m^3/s in northern direction. Calculations of Waternet show that by this minimum average flow influences of discharges on the ARK further north than 1 km from Nieuwersluis are negligible (Provincie Utrecht, 2011).

Appendix 7-2 Groundwater modelling

Figure L shows the origin of the seepage water calculated by backward tracing. The calculation by forward tracing results in the catchment from where the seepage water in the Bethunepolder is coming from. At the northwest corner polder Gansenhoef (22) is also contributing to the seepage water, but this is smaller than the water from the Vecht contributing and therefore neglected.



No	Name
1	Vecht
2	Ruigenhoekse polder (Achtienhoven)
3	East: 'Taartpunt', West: polder Maarsseveen
4	Loosdrechtse Plassen (4e en 5e Plas)
7	Kivietsbuurt
8	Kerkeindse polder
10	Breukeleveensche Plas
11	Polder Westbroek
12	Oostelijke binnenpolder van Tienhoven
13	Maarsseveense Zodden
14	Molenpolder II
16	polder Buitenweg
17	Maarsseveense Plas
18	Stedelijk gebied Maarsseveen (Oostwaard)
19	Polder het Huis te Hart
20	Stedelijk gebied Maarsseveen
21	Tienhovense Plassen
22	Gansenhoef
23	Beringde Landen
26	<unnamed>

Figure N Origin of seepage water Bethunepolder (Ministerie van Infrastructuur en Milieu, 2013)

The seepage intensity is given in figure M. A smaller contribution area at the border of the polder can have a bigger total flux than a larger contribution area in the centre of the polder. Sources of origin at the borders of the polder are mainly polders closely surrounding the Bethunepolder: Kievitsbuurt, Loosdrechtse Plassen, Tienhovense Plassen, polder Maarsseveen-oost, Maarsseveense Zodden, polder Maarsseveen-west and Vecht/Gansehoefsche polder. The age of the seepage water in the Bethunepolder is given in figure N. The Bethunepolder is reclaimed in 1870 (about 51,000 days ago). This means that no water older than 51,000 d has entered the polder. Figure O shows the translation of figures L and M into a total seepage per area of origin.

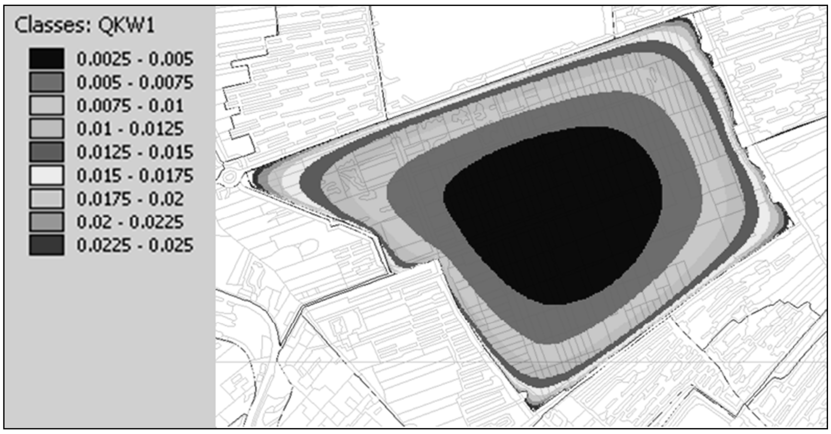


Figure O Seepage intensity in Bethunepolder [m/d] (Ministerie van Infrastructuur en Milieu, 2013)

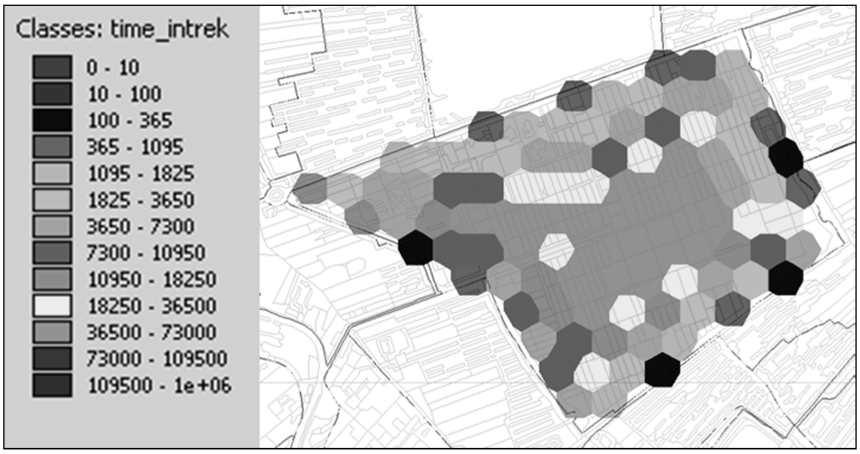


Figure P Residence time of seepage water Bethunepolder [d] (Ministerie van Infrastructuur en Milieu, 2013)

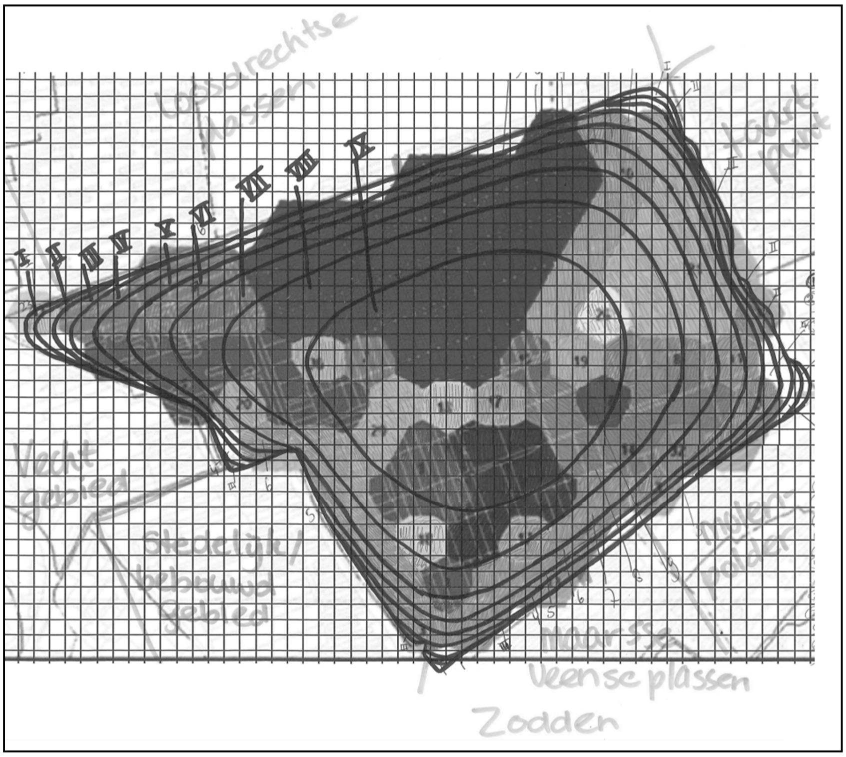


Figure Q Translation from seepage intensity and area of origin into total seepage per area of origin

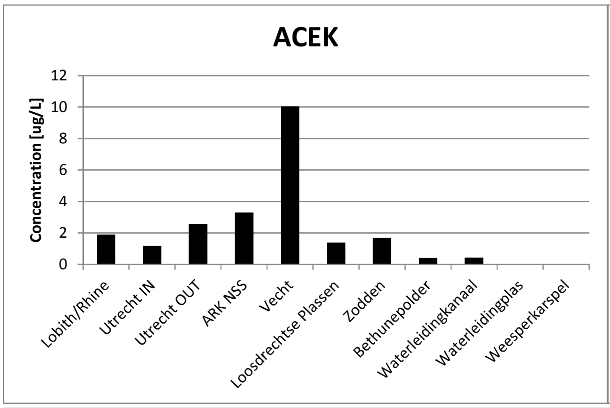
Appendix 7-3 Water quality data

A. Measurement data [µg/L]

	ACEK		AMPA		BENT		CAFF		CARB		GLYF		IOPR		METF		MTBE		NDMS		SULF	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
1. Lobith	**1.588**	**2.192**	**0.287**	**0.412**	**0.008**	**0.018**	▓	**0.027**	**0.065**	**0.075**	**0.024**	**0.047**	**0.197**	**0.184**	**0.870**	**0.879**	**0.155**	**0.115**	**0.041**	**0.049**	**0.015**	**0.062**
yearly average	**1.890**		**0.349**		**0.013**		**0.027**		**0.070**		**0.036**		**0.190**		**0.874**		**0.135**		**0.045**		**0.038**	
2. Utrecht IN	**1.190**	▓	**0.344**	**0.472**	**0.016**	**0.016**	**0.171**	**0.088**	**0.074**	**0.066**	**0.040**	**0.057**	**0.214**	**0.164**	**0.835**	**0.465**	**0.120**	**0.195**	**0.060**	▓	**0.028**	**0.108**
yearly average	**1.190**		**0.408**		**0.016**		**0.130**		**0.070**		**0.048**		**0.189**		**0.650**		**0.158**		**0.060**		**0.068**	
3. Utrecht OUT	**2.575**	▓	▓	**0.095**	**0.015**	**0.043**	▓	**0.015**	▓	**0.103**	▓	**0.069**	▓	**0.878**	▓	**0.965**	▓	**0.065**	▓	**0.000**	▓	**0.027**
yearly average	**2.575**		**0.348**		**0.029**		**0.015**		**0.103**		**0.084**		**0.878**		**0.965**		**0.065**		**0.000**		**0.027**	
4. ARK Nieuwersluis	**3.300**	▓	**0.363**	**0.564**	**0.016**	**0.022**	**0.164**	**0.075**	**0.059**	**0.067**	**0.042**	**0.062**	**0.402**	**0.289**	**0.708**	**0.439**	**0.053**	**0.119**	▓	**0.090**	**0.027**	**0.030**
yearly average	**3.300**		**0.464**		**0.019**		**0.119**		**0.063**		**0.052**		**0.346**		**0.573**		**0.086**		**0.102**		**0.029**	
5. Vecht and landfills	**5.100**	**15.000**	▓	**0.202**	▓	**0.008**	▓	**0.062**		**0.080**		**0.079**	▓	▓	▓	▓	▓	**0.112**	▓	**0.040**	▓	**0.076**
yearly average	**10.050**		**0.202**		**0.008**		**0.062**		**0.080**		**0.079**		**0.394**		**1.700**		**0.120**		**0.040**		**0.076**	
6. Loosdrechtse Plassen	**0.850**	**1.900**	▓	**0.124**	▓	**0.008**	▓	**0.011**	▓	**0.012**	▓	**0.000**	▓	**0.014**	▓	**0.049**		**0.309**		**0.415**		**0.000**
yearly average	**1.375**		0.124		**0.008**		**0.041**		**0.018**		**0.012**		**0.019**		**0.065**		**0.473**		**0.810**		**0.000**	
7. Zodden	**2.200**	**1.200**	▓	**0.048**	▓	**0.012**	▓	**0.022**	▓	**0.020**	▓	**0.000**	▓	**0.085**	▓	**0.080**	▓	**0.091**	▓	**0.155**	▓	**0.002**
yearly average	**1.700**		0.048		**0.021**		**0.056**		**0.040**		**0.080**		**0.123**		**0.080**		**0.057**		**0.155**		**0.002**	
8. Bethunepolder																				0.080		▓
yearly average	**0.410**		**<0.100**		**0.063**		**0.100**		**0.043**		**0.022**		**0.022**		**<0.05**		**0.030**		**0.070**		**<0.01**	
90. Andijk	**1.500**	**2.200**	**0.214**	**0.180**	**0.020**	**0.020**	**0.102**	**0.080**	**0.060**	**0.090**	**0.060**	**0.050**	**0.114**	**0.079**	**0.312**	**0.387**	**0.050**	**0.050**	▓	▓	**0.011**	**0.014**
yearly average	**1.850**		**0.197**		**0.020**		**0.091**		**0.075**		**0.055**		**0.097**		**0.349**		**0.050**		▓		**0.014**	
100. Waterleidingkanaal	**0.440**	▓	▓	▓	▓	**0.016**	▓	**0.009**	▓	**0.004**	▓	▓	▓	▓	▓	0.013	▓	**0.080**	▓	**0.080**	▓	▓
yearly average	**0.440**		**0.000**		**0.019**		**0.004**		**0.003**		**0.000**		**0.001**		**0.014**		**0.048**		**0.070**		**0.005**	
110. Waterleidingplas	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
yearly average	▓		**0.050**		**0.010**		▓		▓		**0.025**		▓		▓		**0.050**		**0.050**		▓	
120. Weesperkarspel	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
yearly average	▓		**0.050**		**0.010**		**0.025**		**0.025**		**0.025**		**0.005**		▓		**0.040**		**0.040**		**0.005**	

□	reliable value
░	only 1 measurement available
▒	more than 1/3 of data is below detection limit
▓	Missing value

B. Measured concentrations at measurement locations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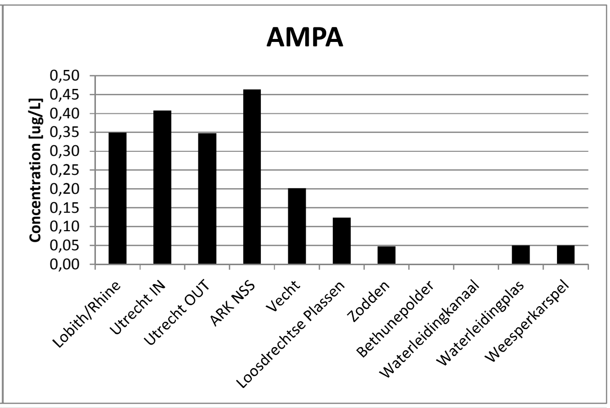
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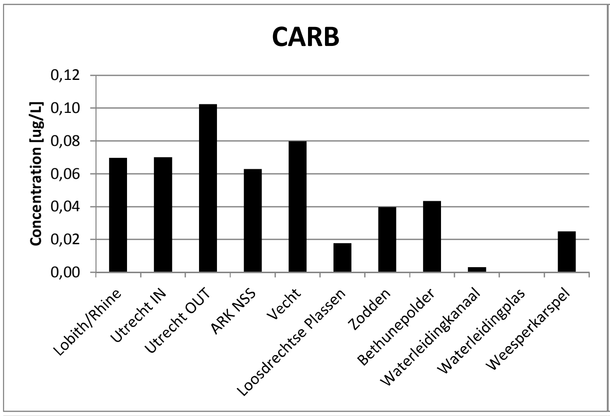
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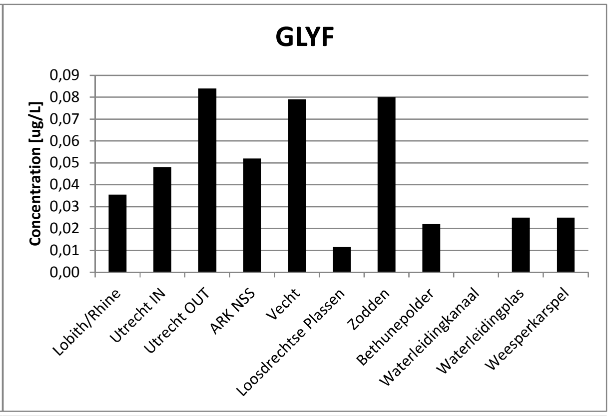
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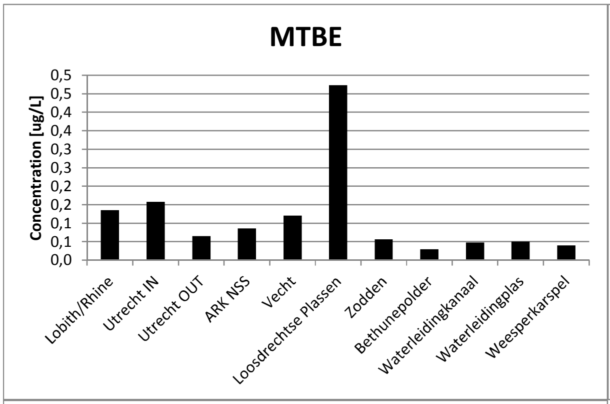
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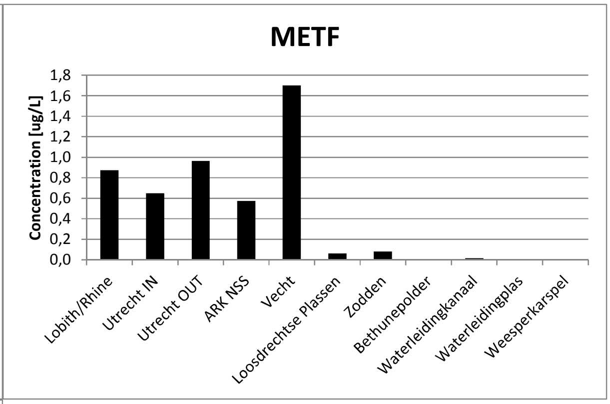
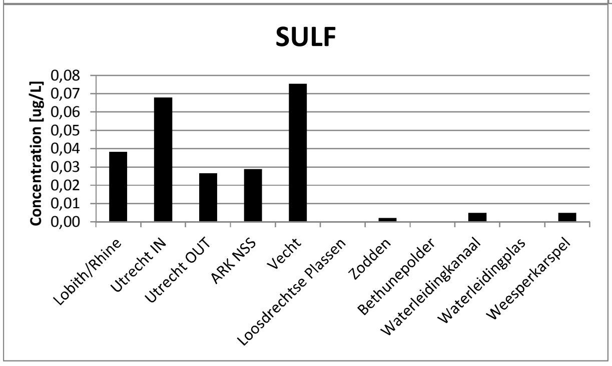

METF


SULF

Appendix 7-4 Validation of surface water balance, mass balance of OMPs and groundwater model

A. Validation of surface water balance

$[m^3/s]$	Lobith	Huissen	WbD	Utrecht in	Utrecht uit	voor inlaat	Inlaat Zodden	Vecht afval	Vecht Nigtevecht	Nieuwer-sluis	Inlaat LDP	ARK na inlaat	ARK Nigtevecht
dry	1910	527	201	6.331	2.629	1.051	0.0288	1.023	1.000	25.69	0.47	25.23	24.42
wet	2257	658	294	6.858	3.798	1.519	0.0015	1.518	1.500	24.69	0.00	24.69	28.51

B. One-dimensional plug flow without decay

		Lobith	Huissen	WbD	Utrecht in	*CHECK UTRECHT IN*	Utrecht uit	*CHECK UTRECHT UIT*	rwzi utrecht	voor inlaat	Inlaat zodden	*CHECK INLAAT ZODDEN*	Vecht afval	*CHECK VECHT AFVAL*	IJssel meer	CHECK IJSSELMEER	NSS	*CHECK NSS*	rwzi's ARK	Inlaat LDP	*CHECK INLAAT LDP*	North Sea	*CHECK NORTH SEA*
		[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
ACEK	dry	2.192	2.192	2.192	2.509	1.190	12.978	0.000	30.004	14.163	14.163	1.200	14.163	15.000	14.163	15.000	3.620	0.000	27.525	3.620	1.900	3.620	0.000
	wet	1.588	1.588	1.588	1.881	1.190	8.869	2.575	28.821	9.660	9.660	1.700	9.660	10.050	9.660	10.050	3.088	3.300	27.525	3.088	1.375	3.088	3.300
AMPA	dry	0.412	0.412	0.412	0.451	0.472	1.743	0.095	3.703	1.889	1.889	0.048	1.889	0.202	1.889	0.202	0.597	0.564	3.397	0.597	0.124	0.597	0.564
	wet	0.287	0.287	0.287	0.323	0.344	1.185	0.348	3.557	1.283	1.283	0.048	1.283	0.202	1.283	0.202	0.480	0.363	3.397	0.480	0.124	0.480	0.363
BENT	dry	0.018	0.018	0.018	0.018	0.016	0.018	0.043	0.000	0.018	0.018	0.012	0.018	0.008	0.018	0.008	0.020	0.022	0.000	0.020	0.008	0.020	0.022
	wet	0.008	0.008	0.008	0.008	0.016	0.008	0.015	0.000	0.008	0.008	0.012	0.008	0.008	0.008	0.008	0.008	0.016	0.000	0.008	0.008	0.008	0.016
CAFF	dry	0.027	0.027	0.027	0.031	0.088	0.177	0.015	0.418	0.194	0.194	0.022	0.194	0.062	0.194	0.062	0.046	0.075	0.384	0.046	0.011	0.046	0.075
	wet	0.027	0.027	0.027	0.031	0.171	0.128	0.015	0.402	0.139	0.139	0.022	0.139	0.062	0.139	0.062	0.039	0.031	0.384	0.039	0.011	0.039	0.164
CARB	dry	0.075	0.075	0.075	0.084	0.066	0.375	0.103	0.836	0.408	0.408	0.020	0.408	0.080	0.408	0.080	0.115	0.067	0.767	0.115	0.012	0.115	0.067
	wet	0.065	0.065	0.065	0.073	0.074	0.268	0.103	0.803	0.290	0.290	0.020	0.290	0.080	0.290	0.080	0.108	0.059	0.767	0.108	0.012	0.108	0.059
GLYF	dry	0.047	0.047	0.047	0.105	0.057	1.994	0.069	5.415	2.208	2.208	0.000	2.208	0.080	2.208	0.079	0.284	0.062	4.968	0.284	0.000	0.284	0.062
	wet	0.024	0.024	0.024	0.077	0.040	1.338	0.069	5.202	1.480	1.480	0.080	1.480	0.080	1.480	0.079	0.270	0.042	4.968	0.270	0.000	0.270	0.042
IOPR	dry	0.184	0.184	0.184	0.373	0.164	6.597	0.878	17.839	7.301	7.301	0.085	7.301	0.394	7.301	0.394	0.964	0.289	16.365	0.964	0.014	0.964	0.289
	wet	0.197	0.197	0.197	0.371	0.214	4.525	0.878	17.136	4.996	4.996	0.123	4.996	0.394	4.996	0.394	1.019	0.402	16.365	1.019	0.019	1.019	0.402
METF	dry	0.879	0.879	0.879	0.975	0.465	4.164	0.965	9.139	4.525	4.525	0.080	4.525	1.700	4.525	1.700	1.327	0.439	8.384	1.327	0.049	1.327	0.439
	wet	0.870	0.870	0.870	0.959	0.835	3.088	0.965	8.778	3.328	3.328	0.080	3.328	1.700	3.328	1.700	1.363	0.708	8.384	1.363	0.065	1.363	0.708
MTBE	dry	0.115	0.115	0.115	0.144	0.195	1.074	0.065	2.668	1.180	1.180	0.091	1.180	0.112	1.180	0.112	0.237	0.119	2.447	0.237	0.309	0.237	0.119
	wet	0.155	0.155	0.155	0.181	0.120	0.802	0.065	2.563	0.872	0.872	0.057	0.872	0.120	0.872	0.120	0.289	0.053	2.447	0.289	0.473	0.289	0.053
NDMS	dry	0.049	0.049	0.049	0.049	0.060	0.049	0.000	0.000	0.049	0.049	0.155	0.049	0.040	0.049	0.040	0.052	0.090	0.000	0.052	0.415	0.052	0.090
	wet	0.041	0.041	0.041	0.041	0.060	0.041	0.000	0.000	0.041	0.041	0.155	0.041	0.040	0.041	0.040	0.045	0.090	0.000	0.045	0.810	0.045	0.090
SULF	dry	0.062	0.062	0.062	0.065	0.108	0.148	0.027	0.239	0.157	0.157	0.002	0.157	0.076	0.157	0.076	0.076	0.030	0.219	0.076	0.000	0.076	0.030
	wet	0.015	0.015	0.015	0.017	0.028	0.073	0.027	0.229	0.079	0.079	0.002	0.079	0.076	0.079	0.076	0.027	0.027	0.219	0.027	0.000	0.027	0.027

C. One-dimensional plug flow with decay

	HUISSEN						WBD					UT IN				
	M lob g/d	Mi g/d	k 1/d	travel time d	Q m3/d	c out mg/L	M huissen g/d	Mi g/d	travel time d	Q m3/d	c out mg/L	M WBD g/d	Mi B g/d	travel time d	Q m3/d	c out mg/L
caff	466	0	0.005	0.46	17366400	2.67634E-05	465	0	0.81	17366400	2.66552E-05	15	2.4	0.35	544320	3.10453E-05
carb	129	0	0.0088	0.46	17366400	7.42348E-06	129	0	0.81	17366400	7.37075E-06	4	4.8	0.35	544320	1.62096E-05
metf	9973	0	0.0001	0.46	17366400	0.000574259	9973	0	0.81	17366400	0.000574213	313	52.8	0.35	544320	0.000671173
mtbe	2553	0	0.001	0.46	17366400	0.000146921	2551	0	0.81	17366400	0.000146802	80	15.4	0.35	544320	0.000174995

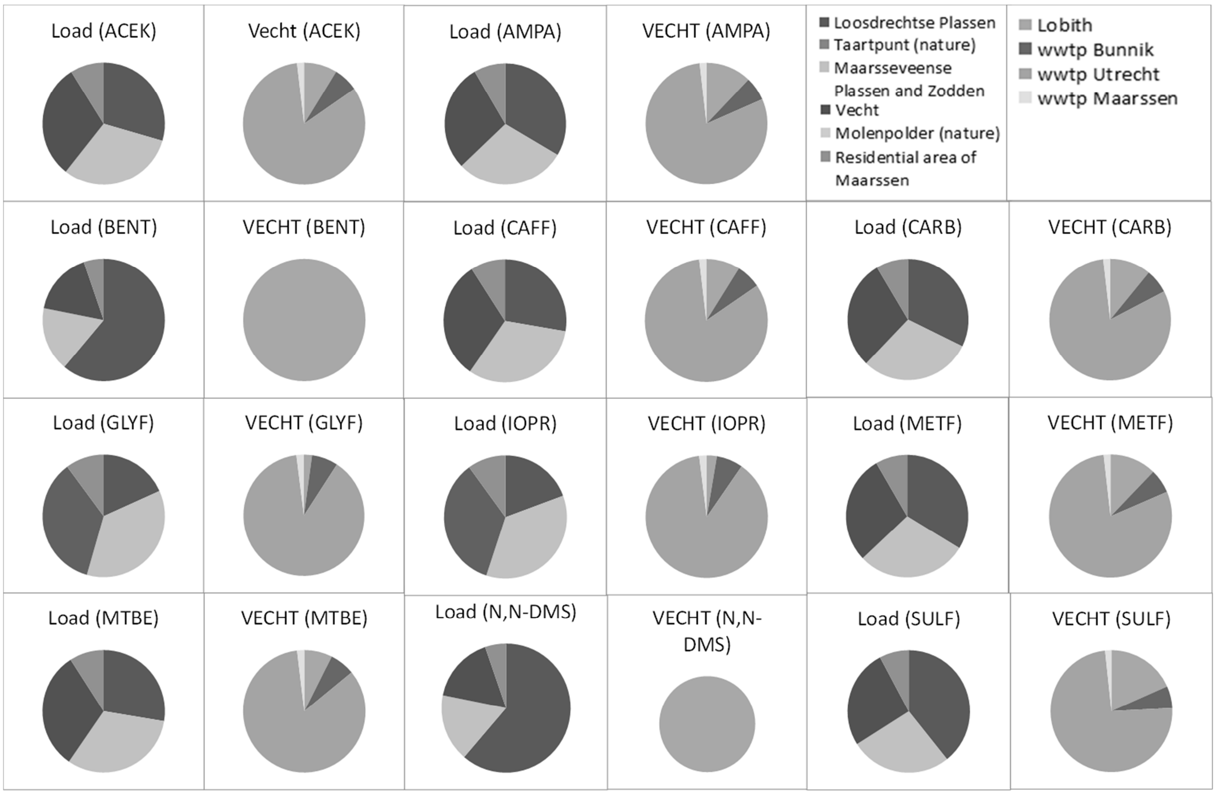
	UT UIT						Vecht					calculated without decay	measured
	M UT IN g/d	Mi ut g/d	k 1/d	travel time d	Q m3/d	c out mg/L	M Ut UIT g/d	Mi M 1/d	travel time d	Q m3/d	c out **µg/L**		
caff	7	30	0.005	0.16	227232	0.000165134	15	1.4	0.16	90806	0.18021301	0.194	0.062
carb	4	61	0.0088	0.16	227232	0.00028425	26	2.8	0.16	90806	0.314254607	0.408	0.08
metf	153	666	0.0001	0.16	227232	0.003604196	327	30.2	0.16	90806	3.936197321	4.525	1.7
mtbe	40	195	0.001	0.16	227232	0.001031104	94	8.8	0.16	90806	1.127973541	1.211	0.112

D. Validation of groundwater model

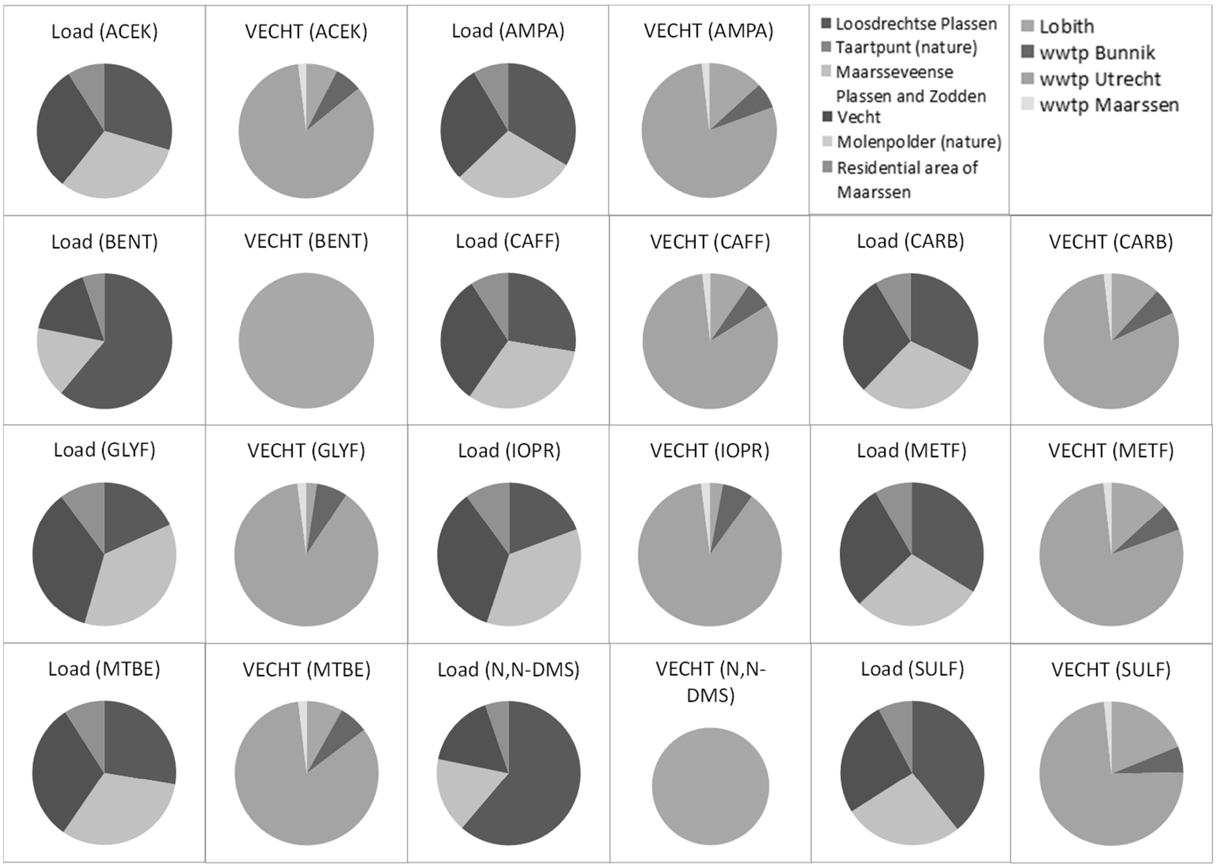
	load					seepage					calculated concentration	measured concentration groundwater	validation same order of magnitude	measured concentration Waterleidingkanaal	validation same order of magnitude
	LPD [mg/s]	MVP [mg/s]	Vecht [mg/s]	Maarssen [mg/s]	prec. [mg/s]	LPD [m^3/s]	MVP [m^3/s]	Vecht [m^3/s]	Maarssen [mg/s]	prec. [mg/s]	[µg/L]	[µg/L]		[µg/L]	
ACEK	0.671	0.708	0.693	0.202	0	0.200	0.059	0.058	0.018	0.161	38.0998	0.410	N	0.4250	N
AMPA	0.108	0.094	0.092	0.027	0	0.200	0.059	0.058	0.018	0.161	5.1746	<0.100	N	0.0020	N
BENT	0.003	0.001	0.001	0.000	0	0.200	0.059	0.058	0.018	0.161	0.0527	0.063	Y	0.0186	Y
CAFF	0.009	0.010	0.010	0.003	0	0.200	0.059	0.058	0.018	0.161	0.5286	0.063	Y	0.0043	N
CARB	0.022	0.021	0.020	0.006	0	0.200	0.059	0.058	0.018	0.161	1.1313	0.043	N	0.0030	N
GLYF	0.055	0.110	0.107	0.031	0	0.200	0.059	0.058	0.018	0.161	5.6315	0.022	N	0.0010	N
IOPR	0.198	0.365	0.358	0.103	0	0.200	0.059	0.058	0.018	0.161	18.8495	0.022	N	0.0005	N
METF	0.269	0.233	0.228	0.067	0	0.200	0.059	0.058	0.018	0.161	12.8236	<0.05	N	0.0226	N
MTBE	0.053	0.061	0.060	0.017	0	0.200	0.059	0.058	0.018	0.161	3.2538	0.030	N	0.0526	N
N,N-DMS	0.010	0.003	0.003	0.001	0	0.200	0.059	0.058	0.018	0.161	0.1833	0.080	Y	0.0700	Y
SULF	0.010	0.007	0.007	0.002	0	0.200	0.059	0.058	0.018	0.161	0.3981	<0.01	N	0.0050	N

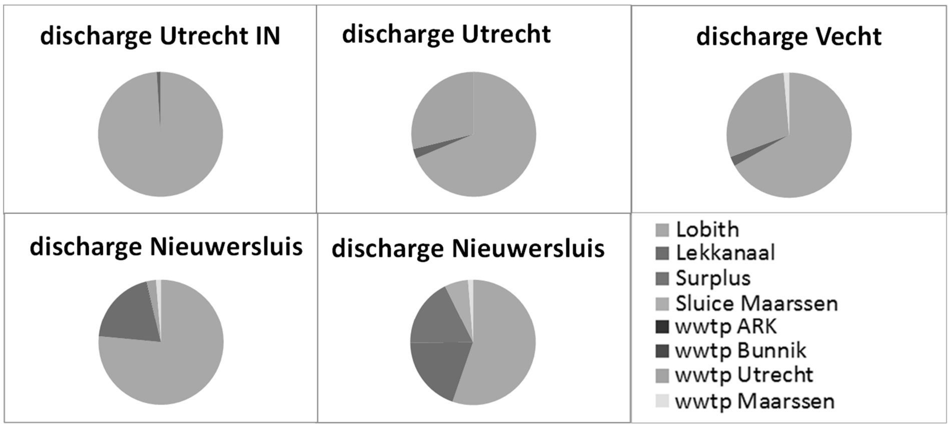
Appendix 7-5 Results distribution graphs

A. Current situation

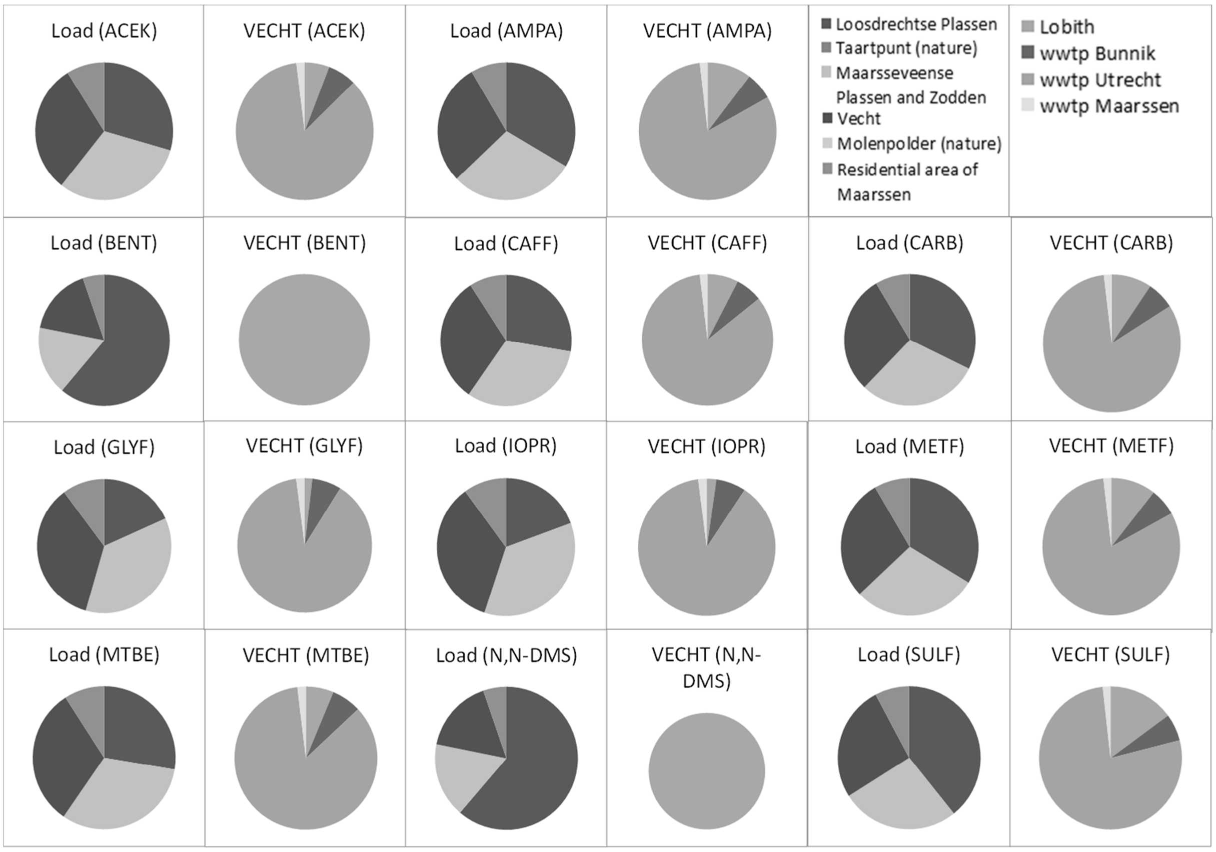


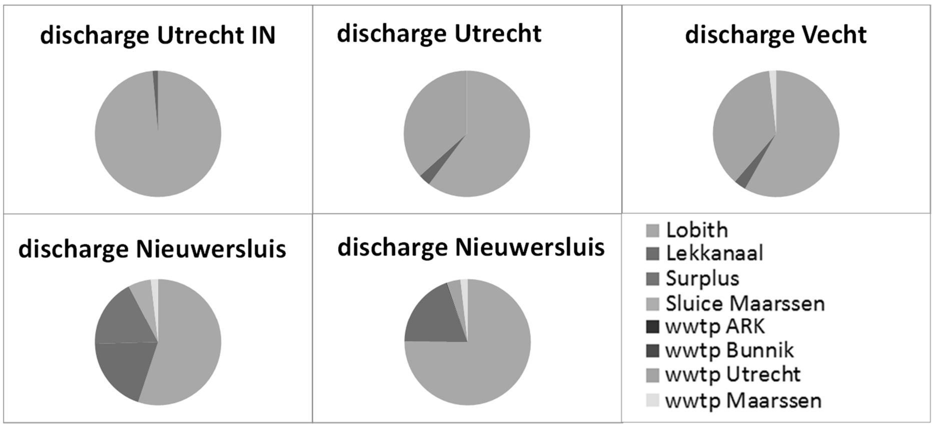
B. Scenario REST





C. Scenario STEAM





Appendix 8-1 Measurement locations and sources

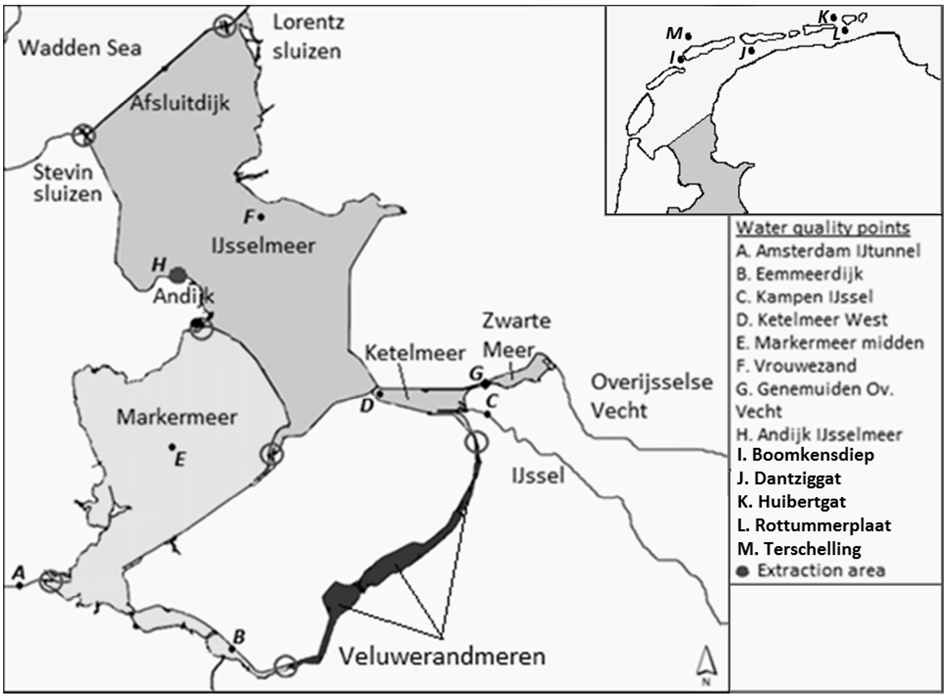


Figure R Measurement locations

Missing measurement data

Since the water quality data are not complete, missing data must be replaced. This is done by using data from measurement locations upstream and as close as possible to the location of the missing data, to use the most representative data. For the compounds iopromide and sulfamethoxazole only a few measurements were available and almost all missing data are replaced by data from the Ketelmeer, which gives a distorted picture of the sources. Missing values for incoming streams are only replaced by values originating from other incoming source (location Vrouwezand is not used).

Point sources

The effluent of WWTP Wervershoof (Enkhuizen) discharges directly on the IJsselmeer, which makes this a point source. There are also some companies nearby Andijk which handle hazardous substances and in case of an emergency these substances can enter the Andijk extraction point. Point sources are also the discharges of the river mouths of the IJssel, Overijsselse Vecht, Utrechtse Vecht, Eem and other smaller rivers and brooks that discharge directly on the IJsselmeer area (Rijkswaterstaat, 2012b).

Diffuse sources

Diffuse sources in the IJsselmeer area are pumping stations discharging the surplus surface water of residential areas, agricultural land and small industries. These discharges are schematised as diffuse sources, because they do not directly discharge on the IJsselmeer. From the discharges of the pumping stations it cannot be determined where the possible pollution originates from. Shipping, either commercial or recreational, is a diffuse source, since leakage of wastewater, cargo or anti-fouling can influence the water quality (Rijkswaterstaat, 2012b).

Line sources

Along the IJsselmeer two highways are situated. The A6 crosses Flevoland and is connected with the eastern part of the Netherlands by a bridge. The A7 is the highway which is situated nearby Andijk and leads over the Afsluitdijk. On both highways transport of hazardous substances takes place (Rijkswaterstaat, 2012b).

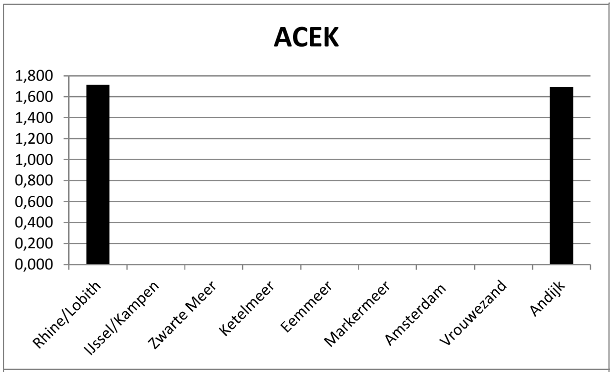
Appendix 8-2 Water quality data

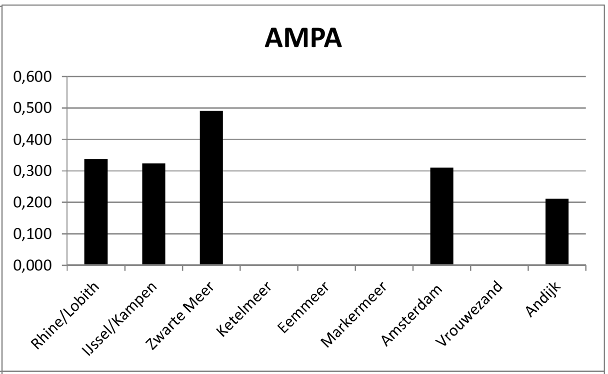
A. Measurement data [µg/L]

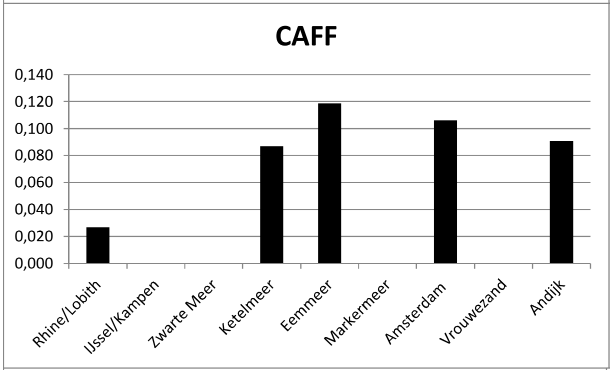
	ACEK		AMPA		BENT		CAFF		CARB		GLYF		IOPR		MET F		MTBE		NDMS		SULF	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
1. Lobith							*	*			*	*					*	*	*	*	*	*
average	1.493	1.933	0.297	0.378	0.007	0.007	■	0.027	0.071	0.073	0.067	0.088	0.185	0.186	1.007	0.879	0.149	0.153	0.040	0.049	0.056	0.04
yearly average	1.713		0.338		0.007		0.027		0.072		0.033		0.186		0.943		0.159		0.044		0.042	
2. Kampen	■	■	0.236	0.411	0.008	0.008	■	■	■	■	0.031	0.089	■	■	■	■	0.068	0.086	■	■	■	■
yearly average	■		0.324		0.008		■		■		0.060		■		■		0.077		■		■	
3. Genemuiden	■	■	0.199	0.784	■	■	■	■	■	■	0.036	0.125	■	■	■	■	■	■	■	■	■	■
yearly average	■		0.491		■		■		■		0.081		■		■		■		■		■	
4. Ketelmeer																						
average	■	■	■	■	0.010	0.009	0.062	0.112	0.040	0.051	■	■	0.135	0.176	■	■	0.027	0.033	■	■	0.025	0.024
yearly average	■		■		0.010		0.087		0.045		■		0.156		■		0.030		■		0.024	
5. Vrouwezand																						
average	■	■	■	■	0.008	0.006	■	■	0.017	0.020	■	■	■	■	■	■	0.007	0.005	■	■	■	■
yearly average	■		■		0.007		■		0.019		■		■		■		0.006		■		■	
6. Andijk																						
average	1.467	1.920	0.226	0.197	0.010	0.011	0.106	0.076	0.049	0.041	0.034	0.029	0.088	0.073	0.334	0.390	0.025	0.025	0.0003	0.0003	0.017	0.018
yearly average	1.693		0.212		0.010		0.091		0.045		0.031		0.080		0.362		0.025		0.0003		0.017	
7. Markermeer																						
average	■	■	■	■	0.006	0.006	■	■	0.010	0.009	■	■	■	■	■	■	0.009	0.005	■	■	■	■
yearly average	■		■		0.006		■		0.010		■		■		■		0.007		■		■	
8. Eemmeer																						
average	■	■	■	■	0.012	0.011	0.146	0.091	■	■	■	■	■	■	■	■	0.090	0.115	■	■	■	■
yearly average	■		■		0.011		0.119		■		■		■		■		0.102		■		■	
9. Amsterdam																						
average	■	■	0.290	0.332	0.014	0.012	0.162	0.050	■	■	0.050	0.064	■	■	■	■	0.423	0.316	■	■	■	■
yearly average	■		0.311		0.013		0.106		■		0.057		■		■		0.369		■		■	

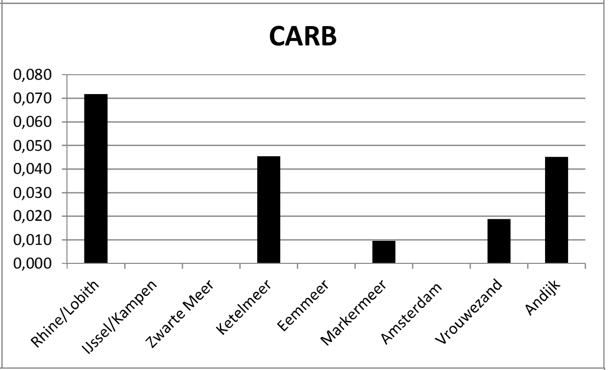
☐	reliable value	▒	more than 1/3 of data is below detection limit	* copied from MEETREEKSEN DEF (Bethunepolder measurements)
░	only 1 measurement available	■	missing value	

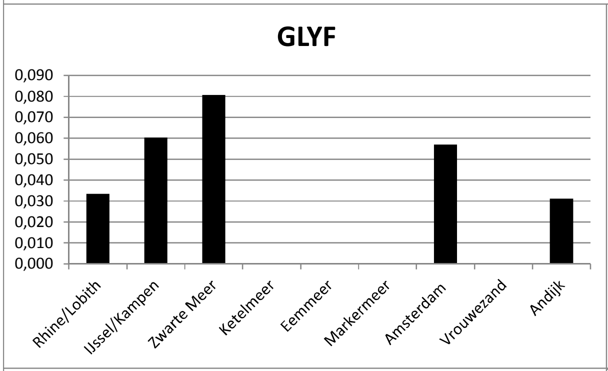
B. Measured compounds

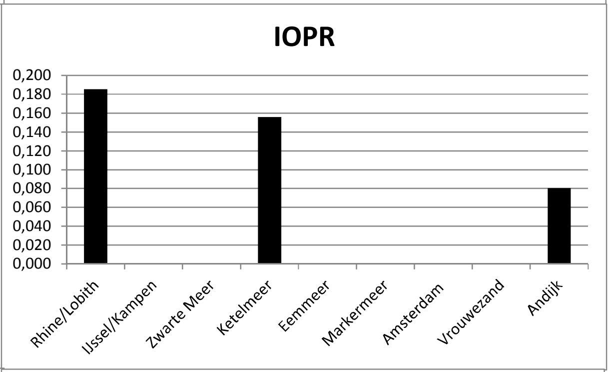


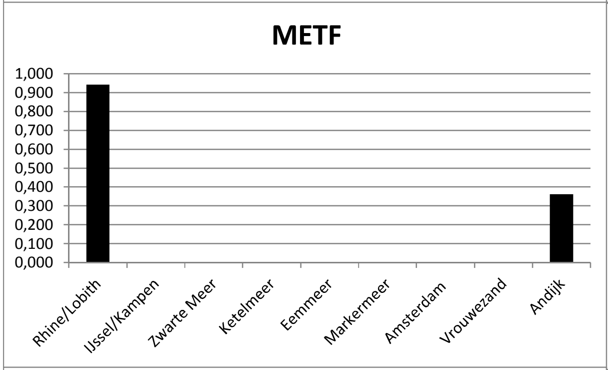


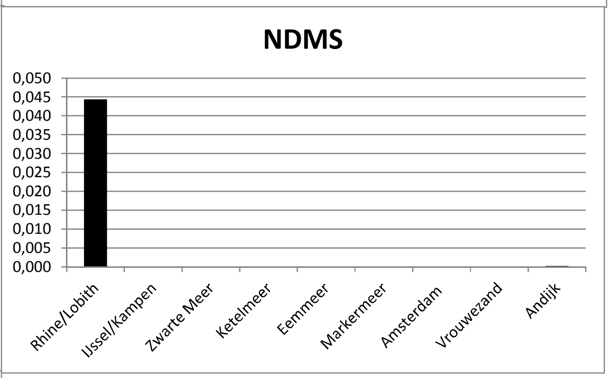


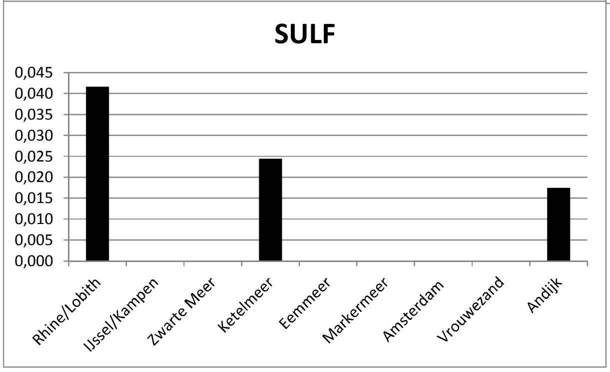












Appendix 8-3 Validation of surface water model

A. Surface water balance of IJsselmeer

SUMMER	Incoming [m^3/s]							Outgoing [m^3/s]							
	Precipitation	IJssel	Zwarte Water	Marker-meer	Veluwe randmeren	Wadden zee	Pumping stations	Evaporation	Stevin sluizen	Lorentz sluizen	PWN	Marker-meer	Veluwe randmeren	Inlets	SLUITFOUT
2002	32	375	43	12	1	0	27	43	243	150	2	29	0	26	-3
2003	20	262	28	7	0	0	20	43	116	88	2	35	0	50	4
2004	35	332	61	9	1	0	35	43	194	165	2	26	0	33	9
average	29	323	44	9	1	0	27	43	184	134	2	30	0	36	3
WINTER	Incoming [m^3/s]							Outgoing [m^3/s]							
	Precipitation	IJssel	Zwarte Water	Marker-meer	Veluwe randmeren	Wadden zee	Pumping stations	Evaporation	Stevin sluizen	Lorentz sluizen	PWN	Marker-meer	Veluwe randmeren	Inlets	SLUITFOUT
2002	36	602	91	41	3	0	71	8	500	371	2	1	0	2	-39
2003	25	400	73	0	2	0	32	8	353	239	2	6	0	4	-80
2004	29	393	92	0	2	0	48	8	373	281	2	5	0	1	-106
average	30	465	85	14	2	0	50	8	409	297	2	4	0	2	-75

B. Completely mixed tank without decay

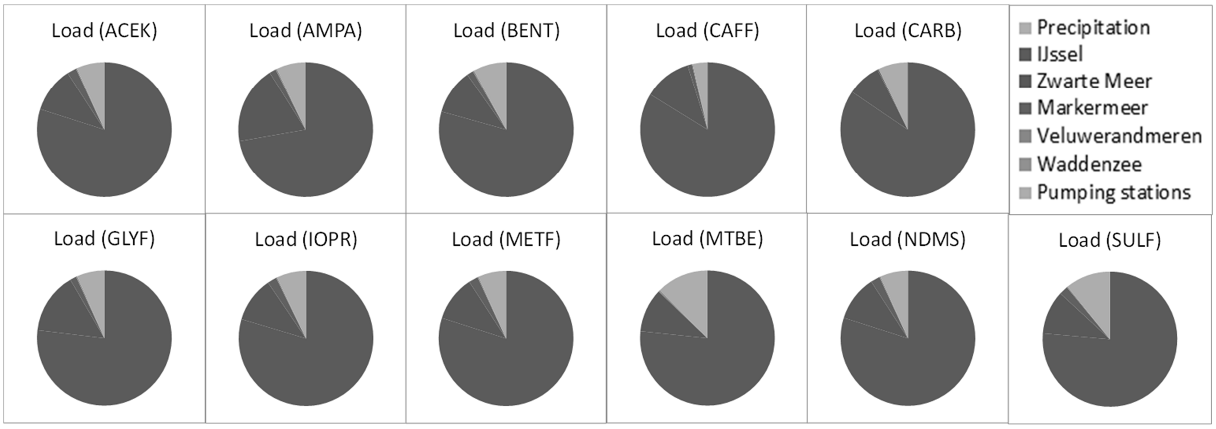
SUMMER	load							discharge							concentration Andijk		
	Prec.	IJssel	Zwarte Water	Marker-meer	Veluwe-randmeren	Wadden Sea	Pumping stations	Prec.	IJssel	Zwarte Water	Marker-meer	Veluwe-randmeren	Wadden Sea	Pumping stations	Calculated	Measured	same order of magnitude
	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[µg/L]	[µg/L]	[Y/N]
ACEK	0.0	624.5	85.2	17.5	1.8	0.0	52.3	29.0	323.0	44.1	9.1	0.954	0.445	27.1	1.9308	1.693	Y
AMPA	0.0	132.8	34.5	3.0	0.6	0.0	12.9	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.4544	0.212	Y
BENT	0.0	2.5	0.3	0.0	0.0	0.0	0.3	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0079	0.005	Y
CAFF	0.0	36.1	4.9	0.5	0.1	0.0	1.5	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.1063	0.091	Y
CARB	0.0	23.6	2.3	0.1	0.0	0.0	2.0	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0689	0.023	Y
GLYF	0.0	28.8	5.5	0.6	0.1	0.0	2.5	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0927	0.031	Y
IOPR	0.0	57.0	7.8	1.6	0.2	0.0	5.1	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.1768	0.080	Y
METF	0.0	283.8	38.7	8.0	0.8	0.0	23.8	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.8776	0.362	Y
MTBE	0.0	27.9	3.8	0.0	0.1	0.0	4.5	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0900	0.013	Y
N.N-DMS	0.0	15.9	2.2	0.4	0.0	0.0	1.3	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0491	0.00013	N
SULF	0.0	7.7	1.1	0.2	0.0	0.0	1.1	29.0	323.0	44.1	9.1	0.954	0.445	27.1	0.0250	0.017	Y

C. Series of completely mixed tanks with decay

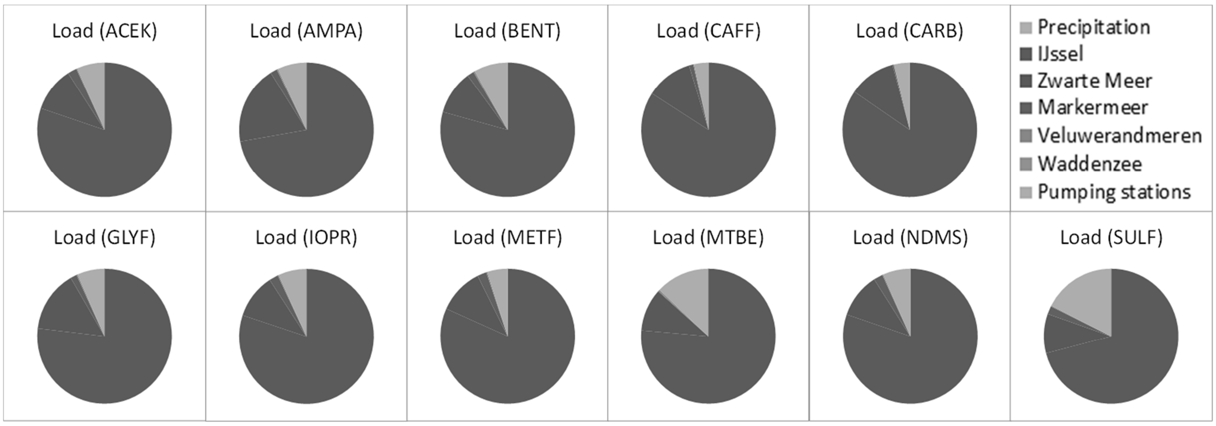
SUMMER			load							discharge							concentration			
	k	V	IJssel	Zwarte Water	Veluwerand-meren	Markermeer	Precipitation	Wadden Sea	Pumping stations	IJssel	Zwarte Water	Veluwerand-meren	Markermeer	Precipitation	Wadden Sea	Pumping stations	Cin	Cout	measured	same order of magnitude
	[1/s]	[m^3]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[mg/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[m^3/s]	[µg/L]	[µg/L]	[µg/L]	[Y/N]
CAFF	5.79E-08	4.95E+09	36.1	4.9	0.1	0.5	0.0	0.0	1.5	323.0	44.1	0.954	9.1	29.0	0.445	27.1	0	0.0217	0.106	Y
CARB	6.94E-09	4.95E+09	23.6	2.3	0.0	0.1	0.0	0.0	2.0	323.0	44.1	0.954	9.1	29.0	0.445	27.1	0	0.0511	0.049	Y
METF	1.16E-09	4.95E+09	283.8	38.7	0.0	8.0	0.0	0.0	23.8	323.0	44.1	0.954	9.1	29.0	0.445	27.1	0	0.7855	0.334	Y
MTBE	1.16E-08	4.95E+09	27.9	3.8	0.1	0.0	0.0	0.0	4.5	323.0	44.1	0.954	9.1	29.0	0.445	27.1	0	0.0579	0.025	Y

Appendix 8-4 Results distribution graphs

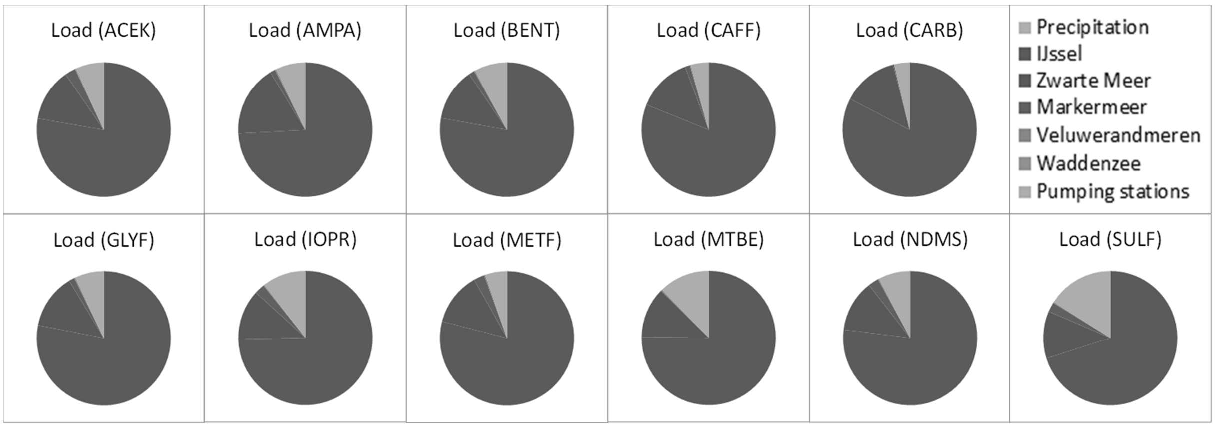
A. Current situation



B. Scenario REST



C. Scenario STEAM



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