Summary

The growing number of people, their increasing longevity and expanding treatment of ailments and illnesses result in a worldwide increase, in the use of pharmaceutical compounds. After these compounds are being excreted from the body, they end up in wastewater treatment plants. Detectable concentrations of pharmaceutical compounds found in surface waters prove that current wastewater treatment plants are not sufficient in removing the pharmaceutical compounds present in the wastewater. Upgrading existing treatment plants with advanced technologies (system A) and source separation, where black and grey water are treated separately (system B), are two of the approaches, that have potential to improve removal efficiencies of pharmaceuticals. In this study, the advantages and disadvantages of these approaches were evaluated using life cycle assessment. Both systems were analyzed and they were compared according to their potential impacts on eutrophication, recovery of nutrients, emission loads of representative pharmaceutical compounds and their energy consumption. Carbamazepine, diclofenac, ibuprofen and metoprolol were selected as representative pharmaceutical compounds. Different wastewater treatment processes were investigated according to their pharmaceutical removal efficiencies, nutrient recovery and energy consumption. The treatment configurations were determined for both upgraded conventional and the source separated wastewater treatment systems. Each selected treatment processes for both systems A and B were designed and emission loads of organic compounds, nutrients and representative pharmaceutical compounds were calculated. As a conclusion system B had a significantly smaller eutrophication potential compared to system A. System B was found to be a promising option, considering the nutrient recovery. System A was a better option in removing carbamazepine, ibuprofen and metoprolol whereas system B was a better option in removing diclofenac. System B was found to consume much less energy than system A.

Key words: Conventional sanitation system, source separated sanitation system, carbamazepine, diclofenac, ibuprofen, metoprolol, nutrient recovery, energy consumption

OUTLINE

1 Introduction

1.1 Occurrence, Fate and Impacts of Pharmaceutical Compounds

In order to cure or treat diseases, people use pharmaceuticals. In Europe approximately 3000 different pharmaceuticals including painkillers, antibiotics, antidiabetics, beta blockers, contraceptives, lipid regulators, antidepressants, impotence drugs and cytostatic agents are used (Ternes and Joss, 2006).

The pharmaceutical compounds enter the human body through alimentary track (oral application), intramuscular tissues (tissue application), skin or lungs (Debska et al., 2004). After the pharmaceuticals enter the body, most of them are bio-transformed into more hydrophilic metabolites. Although these metabolites are generally inactive, there are many common used drugs (e.g. paracetamol (analgesics) or phenacetin (analgesics), whose metabolites still show pharmacological activity (Hinson et al., 1994). A small part of the parent compounds are not absorbed in the alimentary track and have low solubility in body fluids. These compounds do not change their form in the body. After all the transformation processes take place in the human body, the pharmaceutical compounds and their metabolites are excreted via mainly the kidneys with urine, liver with bile, intestines with faeces, lungs (volatile compounds) or skin with perspiration (Debska et al., 2004).

Pharmaceutical compounds removed from the body via kidneys with urine and via intestines with faeces end in the domestic wastewater. The wastewater is usually treated by wastewater treatment plants (WWTP). Also outdated pharmaceuticals are sometimes flushed down toilets and reach WWTPs. Although the exact fate of pharmaceutical compounds in WWTP is not well understood, there are a lot of studies showing that many compounds are only partially removed and some are not removed at all (Castiglioni et al., 2006;Clara et al., 2005;Joss, 2005;Khan and Ongerth, 2004;Ternes, 1998). There are different reasons of poor removal of pharmaceuticals in WWTP. One of them is that some of the compounds are highly persistent and can not be removed by degradation processes. Another reason states that the hydrophilic character of most compounds allows them to be easily swept away from the system. Besides these, the compounds may be toxic to the microroganisms that play a role in purification processes in WWTPs. Some of the metabolites, which become inactive in the body, are retransformed into their parent compounds and regain their activity with the help of microorganisms found in the treatment processes (Dray et al., 1972).

Large numbers of 200-300 pharmaceutical compounds were detected in WWTP effluents, surface waters and even in ground waters. Limited available methods used for the detection of pharmaceutical compounds do not allow us to measure all of the pharmaceutical compounds, which are found in the receiving water bodies (Martine Hammer, personal communication). A part of the compounds

can be mineralized by microorganisms during biological treatment. Another part is trapped in the sludge. The other compounds that are neither trapped nor degraded in WWTP are easily transported to receiving water bodies (Debska et al., 2004). Wastewater sludge application on land and the usage of WWTP effluents as irrigation water result in the transfer of the pharmaceutical compounds to the soil and then to the groundwater (Boxall, 2004). Pharmaceutical compounds can be taken up by plants and then enter the food chain. The possible paths of pharmaceutical compounds in environment after being consumed by humans are shown in Figure 1.1.

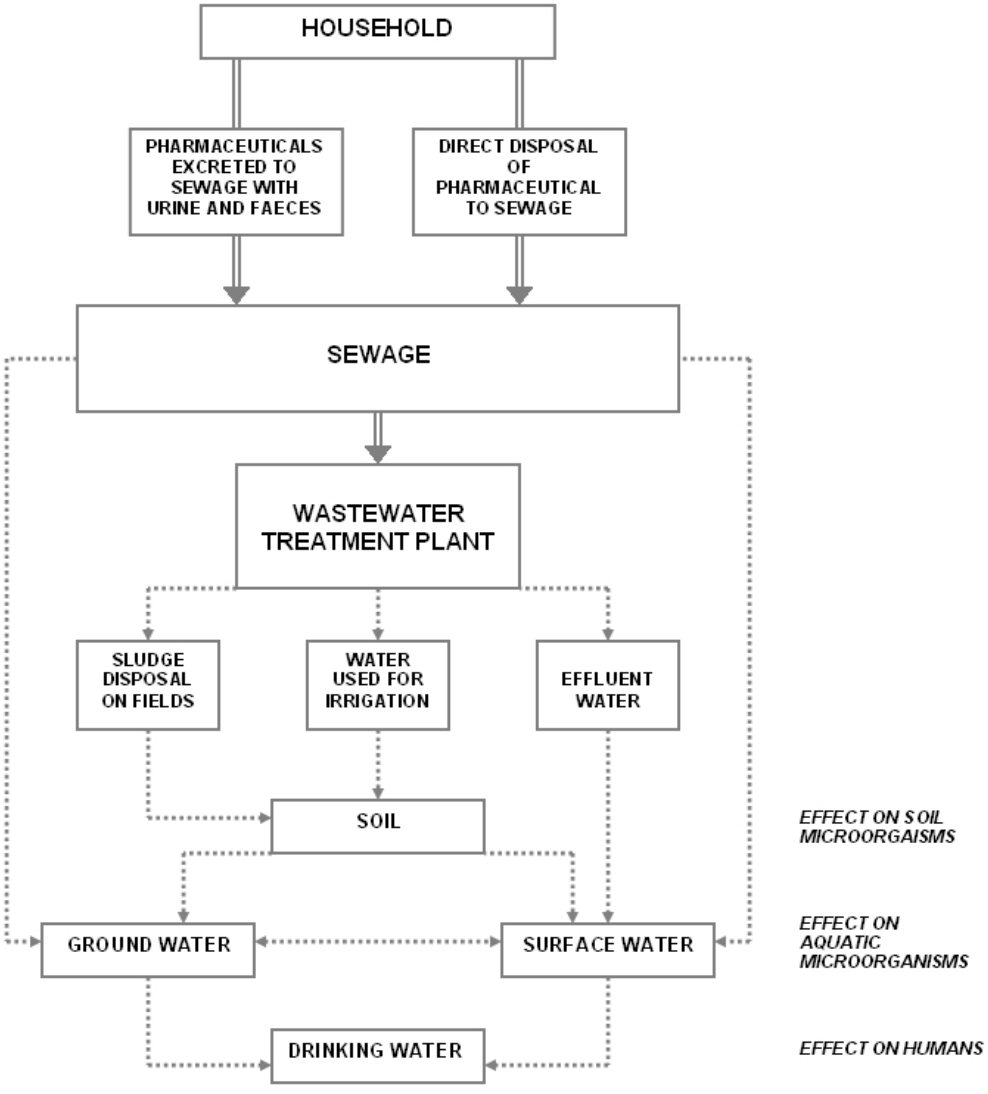


Figure 1.1 Paths of human pharmaceuticals in the environment (Alder et al., 2006;Daughton and Ternes, 1999;Debska et al., 2004;Jorgensen and Halling-Sorensen, 2000)

Since the pharmaceutical compounds are highly active and interact with the receptors of organisms, many groups of aquatic and terrestrial organisms may be affected by these compounds or their metabolites released to environment. These organisms, which are affected by the toxicity of the pharmaceutical compounds, often have a crucial role in functioning of ecosystems (Fent et al., 2006;Lürling et al., 2006;Pomati et al., 2004).

Although synergic effects and most of the potential impacts of pharmaceutical compounds on environment are not determined yet, there are evidences showing that micropollutants including pharmaceuticals have negative effects on living organisms. For example, a 50% decline of catching fish in many rivers and streams in Switzerland has been observed in the past 5 years and there was evidence that organic micropollutants contributed to this effect (Burkhardt-Holm et al., 2000;Jobling et al., 1998;Routledge et al., 1998). According to (Elvers and Wright, 1995), ibuprofen, which is a pain killer, caused inhibition of growth of some bacteria species. (Harrass et al., 1985) indicated that growth of six blue-green algae species is inhibited by streptomycin (antibacterial) at concentrations of 0.09 to 0.86 mg L^{-1}. (Richards et al., 2003) stated that organisms were affected by a mixture of pharmaceuticals applied to an artificial aquatic environment. Different effects such as fish mortality, macrophyte mortality, increased abundance, reduced diversity, and community-level effects among plankton populations were observed in their study.

In conventional WWTPs, the main aim is to remove bulk substances, such as primarily organic compounds and nutrients, nitrogen (N) and phosphorous (P). These substances occur in large quantities in the influent wastewater whereas pharmaceutical concentrations are in between ng L^{-1} and µg L^{-1}. To remove pharmaceutical compounds with the existing conventional wastewater treatment systems is not easy, since pharmaceuticals have individual behaviors and they form only a small part of the organic load in wastewater. Therefore significant removal of all pharmaceutical compounds in conventional WWTPs has not been demonstrated yet (Heberer, 2002;Larsen et al., 2004). Scientists are searching for various options to minimize the emissions of pharmaceutical substances to environment. There are different approaches to reduce the release of pharmaceuticals into the environment. One of these approaches is to upgrade the conventional WWTPs by adding additional units, which increases the removal efficiency of the pharmaceutical compounds in the system (system A). The other approach is the separation of wastewater at the source into black (urine and feces) and grey water (water coming from the kitchen and the showers) and efficient treatment of these streams (system B) (Daughton, 2003a;Daughton, 2003b;Ternes et al., 2004;Ternes et al., 2002). By the separation of black water, more target treatment of pharmaceuticals can be applied since the black water is the only stream which includes pharmaceutical compounds.

1.2 Combined and Source Separated Sanitation System

A number of different wastewater streams are produced in households as a consequence of various human activities (Figure 1.2). In the existing combined

sanitation system, all the streams originating from the households are collected with the same piping system and end up to the conventional WWTPs.

Wastewater streams can be separated based on their composition and concentrations (STOWA, 2005). Black water originating from the toilets is one of the most concentrated streams and consists of faeces, urine and flush water (Kujawa-Roeleveld and Zeeman, 2006;Otterpohl et al., 1999). Grey water is the combination of the sub-streams originating from shower, bath, laundry and kitchen and is relatively diluted (Kujawa-Roeleveld and Zeeman, 2006). Black water contains high organic contents as well as the major fraction of the nutrients in domestic wastewater. Besides, most of the pathogens and mico pollutants (pharmaceuticals, hormones etc.) are also present in this stream which has a small volume. Separating the black stream from the others provides us to concentrate the risks in a very small volume. This gives an opportunity to have a better control, enabling the recovery of nutrients and energy and limit the negative environmental effects (Kujawa-Roeleveld and Zeeman, 2006).

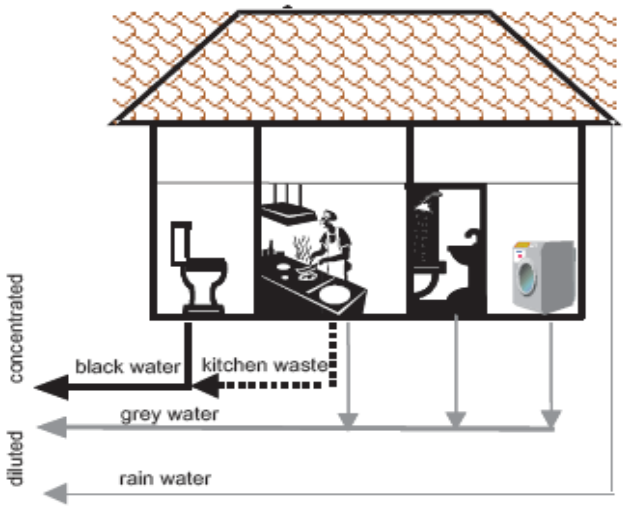


Figure 1.2 Wastewater streams produced in households (STOWA, 2005).

Water usage differs according to the type of activity in the household. This is why each wastewater stream is generated in different volumes and has a different composition (Figure 1.3). The largest fraction of the wastewater is grey water which forms 72% of the total domestic wastewater volume (91.4 L person^{-1}.day^{-1}) (NIPO/VEWIN, 2002). It is difficult to reduce this volume since people demand a certain amount of water for their personal care. On the other hand, amount of black water generated can be strongly reduced with the application of low flush or water free (compost) toilets. An example of low flush toilets is a vacuum toilet, which is used in households, especially in source separated sanitation systems. They operate with a pump generating vacuum which ensures that the waste is transported and provides consumption of small volumes of water to flush. Vacuum (STOWA, 2005).

In the Netherlands the black water generation was 34.8 L.person^{-1} day^{-1} in 2001 which forms 28% of total drinking water usage (NIPO/VEWIN, 2002;STOWA, 2005). By using vacuum toilet, this amount can be reduced with 70-80%.

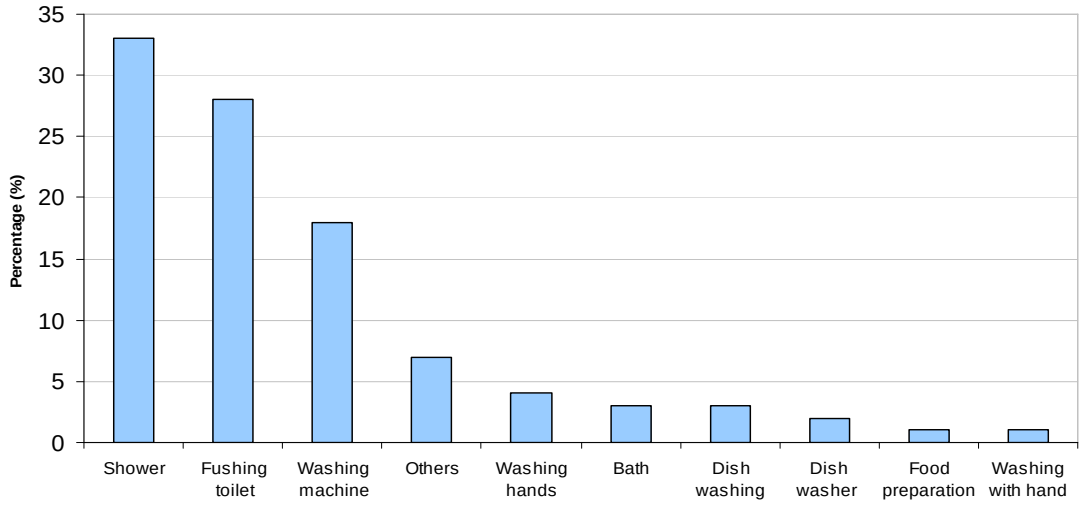


Figure 1.3 Water usages per household activity in Netherlands (NIPO/VEWIN, 2002).

1.3 Importance of Nutrient and Energy Recovery

The main aim of conventional WWTP is to prevent plant nutrients from getting into the receiving waters (Larsen et al., 2004). This is done by elimination of nitrogen and phosphorus during biological processes. Separate treatment of black water has some advantage regarding nutrient recovery. Although black water represents small portion of the total wastewater volume, the majority of nutrients (80% N, 55% P in total wastewater) is present in this stream. This provides an opportunity to recover and recycle the nutrients and close the nutrient cycle (Larsen et al., 2004). Recycling nutrients especially phosphorus, is one of the key issues for sustainable development. There is a depletion of quality and quantity of phosphate rocks where the phosphorus is gained from (USGS, 2002).

The recovered nutrients could be used as fertilizers for the agriculture (Maurer et al., 2003). Therefore, recovery of nutrients is essential for preventing the source depletion of phosphorus as well as reducing the energy consumption for the fertilizer production.

Another important aspect during the treatment processes is energy consumption and recovery in the system. Energy recovery strongly benefits the environment since it leads to less usage of fossil fuels, which causes global climate change (Palme et al., 2003).

1.4 Problem Definition

The growing number of people, their increasing longevity combined with expanding treatment of ailments and illnesses result in a worldwide increase in

the use of pharmaceutical compounds. This increase results in emissions of different of pharmaceutical compounds into the environment. These sources include residential areas, industries and hospitals. The most significant and diffuse sources are residential areas. After their application and excretion, the compounds and their metabolites mix with the wastewater and go to the municipal WWTPs to be treated. The conventional wastewater treatment systems are not effective in removing all pharmaceuticals since there are compounds which are highly persistent.

Because there are thousands of different pharmaceutical compounds, it is impossible to investigate all of the compounds and their fate during the treatment processes in the scope of this study. This is why four representative pharmaceutical compounds were selected: carbamazepine (anti-epileptic), diclofenac (anti-inflammatory), ibuprofen (pain killer and anti-inflammatory) and metoprolol (beta-blocker for hart patients). The selection of these compounds was based on consumption, physical-chemical properties, their behavior on WWTP, effects on aquatic organisms and abundance in surface waters.

As more and more research is done, the impacts of pharmaceutical compounds on environment and health are better understood. Although few studies are available on the precise effects of the pharmaceutical compounds at environmental concentrations, there is evidence that, these compounds and their metabolites may have negative effects on both aquatic and terrestrial living organisms.

New approaches are being investigated to treat the pharmaceutical compounds more efficiently. Upgrading existing treatment plants with advanced technologies and source separation, where black and grey water are treated separately, are two of the approaches that have potential to improve removal efficiencies of pharmaceuticals and other micropollutants. It is important to evaluate the two approaches to provide better understanding of the advantage and disadvantage of the both systems.

There are different treatment processes that enable to remove the pharmaceuticals from the wastewater. The most efficient configuration for source separated wastewater treatment system and the upgrading technologies for the existing conventional (combined) wastewater systems are not known. In order to improve removal efficiencies, the configurations of treatment processes with highest removal capacities of pharmaceuticals should be determined for both combined and source separated wastewater treatment systems.

Beside pharmaceuticals, there are other important aspects that are essential in a design of a WWTP. To allow for an objective comparison between two approaches to remove the pharmaceuticals, other aspects should also be taken into account to meet the criteria of sustainable sanitation. In this study, energy and nutrient recovery are the main additional research issues next to the pharmaceuticals. Energy recovery plays an important role in reduction of fossil fuel usage which causes climate change. Recovering nutrients also improves the

sustainable solutions (especially for phosphorus) because it provides a possibility to close the nutrient cycle.

Analysis and the evaluation of the upgraded conventional and the source separated wastewater treatment systems based on the removal efficiency of the pharmaceutical compounds, nutrient and energy recovery is a research challenge. This evaluation could help to find out the advantage and disadvantage of both systems.

1.5 Objective and Research Questions

The objective of this study is:

- To determine the configurations of treatment processes that have the highest pharmaceutical removal capacity for combined (System A) and source separated (System B) wastewater treatment systems.
- To evaluate the systems A and B with respect to the treatment efficiency of pharmaceutical compounds in combination with nutrient and energy recovery.

In order to achieve the objective, the following research questions are set to be answered:

1. What are the removal mechanisms and the removal potentials of the selected representative pharmaceutical compounds, carbamazepine, diclofenac, ibuprofen, metoprolol, in conventional wastewater treatment plants?
2. What are the removal efficiencies of subsequent treatment processes for the selected representative pharmaceutical compounds?
3. What is the configuration of treatment processes in order to remove pharmaceutical compounds with the highest removal efficiency of pharmaceuticals, after removing the macro pollutants, for combined wastewater treatment system?
4. What is the configuration of treatment processes in order to remove pharmaceutical compounds with the highest removal efficiency of pharmaceuticals, after removing the macro pollutants, for source separated wastewater treatment systems?
5. What is the overall evaluation (comparison) of the combined and source separated wastewater treatment systems, considering the removal efficiency of pharmaceutical compounds, nutrient and energy recovery?

1.6 Outline of the thesis

The next chapter describes the methods used, in order to achieve the objective and answer the research questions. Chapter 3 addresses the reasoning of the selection of the representative pharmaceutical compounds as well as the characteristics of each representative compound. In the first part of Chapter 4, the mechanisms responsible for the removal of the organic pollutants are explained and they are related to the removal potentials of the representative pharmaceutical compounds. Chapter 4.2 gives an overview of the removal

efficiencies of the representative compounds in the conventional WWTPs. Different wastewater treatment processes are investigated according to their removal efficiencies of macro and micro pollutants in Chapter 4.3. This investigation was done considering two different systems which are combined and separated wastewater treatment systems (System A and B, respectively). With the results of Chapter 4, the configurations of treatment processes for systems A and B were determined. These determinations were done by comparing the removal efficiencies of treatment processes. The influents were characterized for both systems A and B in Chapter 5.1 which is followed by Chapter 5.2 where both systems were designed. Chapter 6 gives the results of the effluent loads of the pollutants, nutrient recovery capacities and energy consumptions of both systems. These results are used to compare the two systems. Chapter 7 gives the conclusions of the study while discussing the results and the study itself where as in Chapter 8, the recommendations are summarized.

2 Methodology

The methods which were used to answer the research questions are summarized in Table 2.1

Table 2.1 Methods to answer the research questions

Research Questions	***Methods***
Determination of treatment processes and configuration **(Q-1,2,3)**	Literature Review
Analysis and evaluation of source separated and combined wastewater treatment systems **(Q- 4,5)**	Life Cycle Assessment

2.1 Literature review

This research is mainly based on literature review. The data related to the macro and micro pollutant removal efficiencies, the recovery of nutrients and the energy consumption were gathered from the literature to determine the configuration of treatment processes and to design the two wastewater treatment systems. The determination of the configurations was based on the following criteria:

- sufficient removal of organics, solids and nutrients (according to the Dutch standards)
- high nutrient recovery
- low energy consumption (high recovery)
- high pharmaceutical removal capacity

2.2 Life Cycle Assessment

Life cycle assessment is a technique used for analyzing the environmental aspects and potential impacts of products and services. The analysis is done by bringing together an inventory of relevant inputs and outputs of a system, evaluating the potential impacts associated with those inputs and outputs and relating the results of the inventory analysis and impact assessment phases to the objectives of the study. By comparing the alternatives and studying the technical systems, function of the products or services as well as the impacts on the natural environment is assessed (Baumann and Tillman, 2004). The comparison may provide improvements in existing products or services and may help in the design of new products or services (Berg et al., 1995). Life cycle assessment provides us to describe the natural resource use and pollutant emissions in quantitative terms (Baumann and Tillman, 2004).

Whole procedure of life cycle analysis and the phases, which were used in this study, are shown in Figure 2.1.

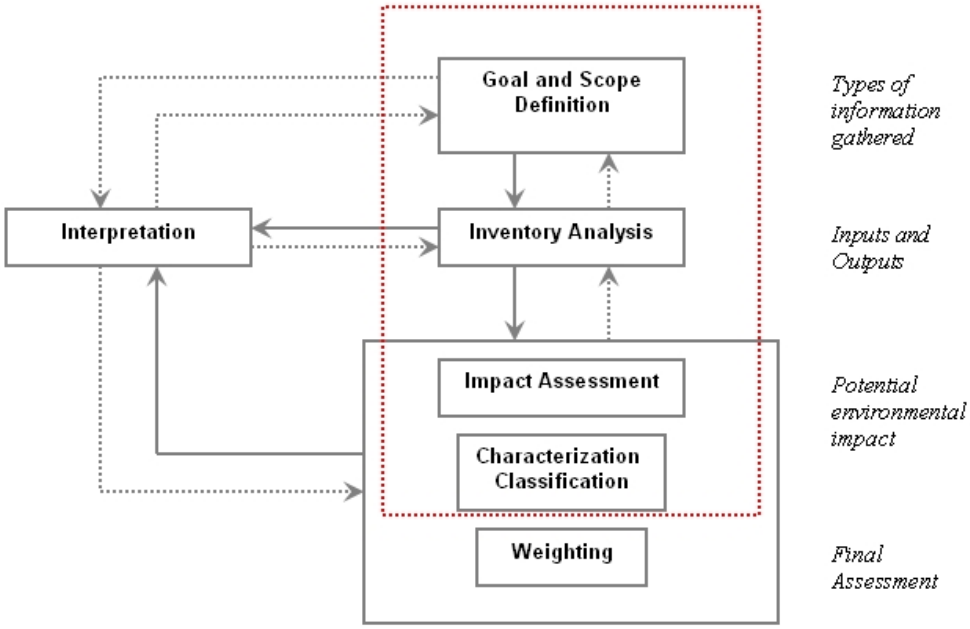


Figure 2.1 The procedure of Life Cycle Analysis (Baumann and Tillman, 2004).

2.2.1 Goal and Scope Definition

The purpose of this study and the systems which were analyzed are specified in the goal and scope definition. The main aim of conducting life cycle assessment is to analyze and compare combined (system A) and source separated (system B) wastewater treatment systems. The criteria which were determined for the comparison of the systems are:

- the eutrophication potential based on the emissions of Chemical Oxygen Demand (COD), total nitrogen and total phosphorus
- emission loads of carbamazepine, diclofenac, ibuprofen and metoprolol
- the amount of nitrogen and phosphorus recovered
- net energy consumption

2.2.1.1 System Definition

As it was explained in the introduction part, two wastewater treatment systems were analyzed. These systems are combined and source separated wastewater treatment systems. Under the scope of this research both of the systems consist of wastewater and sludge treatment units. The determination of the wastewater and sludge treatment processes of the systems was one of the objectives of this study. This is why, specific description for the processes and the systems were done in Chapter 4 and 5. For the configuration of the system A and B, different treatment processes were investigated according to their efficiencies of macro and micro pollutants in Chapter 4.

The studied systems were based on WWTPs in the Netherlands. As there are thousands of pharmaceutical compounds and it is not reasonable to investigate all of them in the systems, four pharmaceutical compounds were chosen representing a large part of the compounds. These four compounds are carbamazepine, diclofenac, ibuprofen and metoprolol. The motivations for the selection are discussed in detail in Chapter 3.

Functional unit

As a starting point for the comparison, a reference flow is needed which can be related by all the other flows of the system. This flow which should be quantitative is known as functional unit in life cycle assessment. The functional unit of this analysis will be *treatment of one yearly person equivalent of sewage (pe.year).* The WWTP will be designed for *100,000 population equivalents (p.e.)* in the Netherlands.

2.2.1.2 System boundaries:

The whole system and the system boundaries for system A and system B are shown in Figure 2.2 and 2.3. Although there are a lot of processes which could be investigated in the systems, the time for this research is limited to include all of them. This is why the flow of substances was limited in a system boundary including wastewater treatment and the sludge treatment. The production of chemicals being added during the treatment of wastewater, collection of the wastewater, fertilizer production and the transportation and disposal of sludge were excluded from the system boundaries. According to (Lundin et al., 2000), it is not appropriate to exclude fertilizer production and agricultural practice while assessing the environmental consequences of conventional and source separated wastewater systems. However, considering the available time for this research, the system had to be limited by the treatment of wastewater and sludge.

Considering the outflows of the system, only the emissions to the water was included in the system. Sludge, which is being disposed into soil through landfills or the gasses being emitted during the treatment processes were not included in the inventory analysis. Energy and nutrients were the used resources which were investigated during the assessment. The comparison of the systems was mainly done considering the effluent loads of the systems coming out of the system. Only the potential impact of eutrophication, related to certain emissions (COD, BOD, total N and total P), was chosen to be considered. The impacts imposed during the construction of the processes in treatment processes, were also not included in the system boundary of the life cycle assessment.

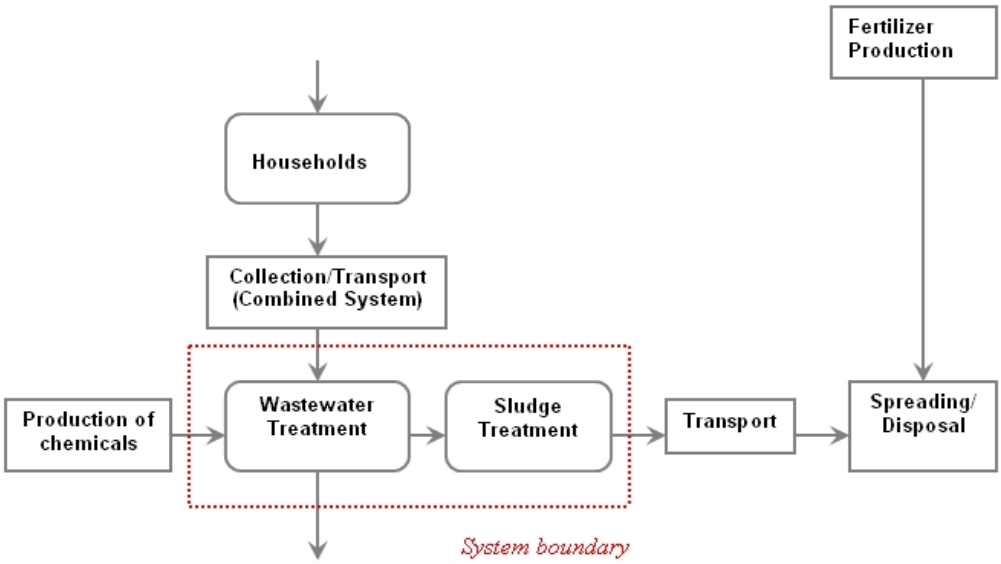


Figure 2.2 System diagram and system boundary for combined wastewater sanitation system (Lundin et al., 2000).

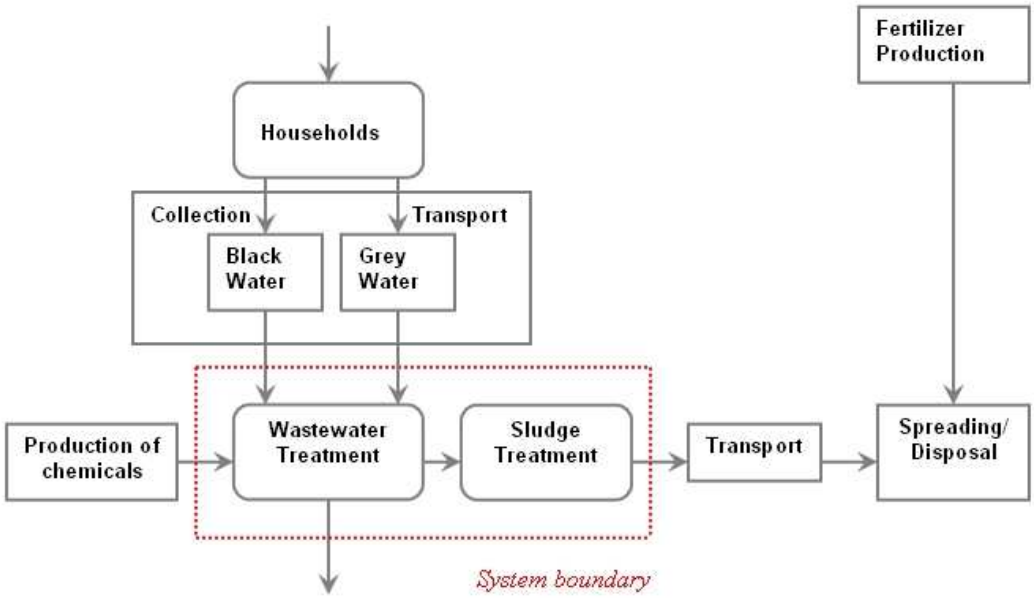


Figure 2.3 System diagram and system boundary for source separated wastewater sanitation system (Lundin et al., 2000).

2.2.2 Inventory Analysis

Construction of the life cycle model, calculations of the resources used and the emissions produced were carried out in the inventory analysis. In the first step of inventory analysis the flow models of conventional and source separated wastewater treatment systems (Systems A and B) were constructed. The models consist of flowcharts of the systems with different wastewater and sludge treatment unit processes. While the model was being constructed, only the unit processes of wastewater and sludge treatment were included considering the system boundaries. The unit processes for both systems were determined in Chapter 4 after the investigation of single processes considering their efficiencies of pharmaceutical removal, nutrient recovery and energy recovery.

2.2.2.1 Process Flowchart

The flow charts of the unit processes for both systems A and B were determined after the investigations of specific treatment processes. The flow charts for systems A and B are given in Figure 4.16 and 4.17 in Chapter 4.3 and 4.4, respectively.

2.2.2.2 Data Collection and Processing

Organic macro pollutants, pharmaceuticals, energy and nutrients are the four issues, which were analyzed during the assessment. Following the data gathering and investigating the flow of organic macro pollutants, pharmaceuticals, energy and nutrient between the environment and the technical systems, the amount of energy use and pollutant emissions were calculated based on the functional unit. All the calculations were based data found in the literature and are detailed in Chapter 5 including the formulas. The results of the calculations and the data used from the literature were demonstrated in Annex A.5. For the comparison of the effluents, pollutant loads in the influents are taken the same for system A and B. System influents are explained and quantified in details in Chapter 5.1 and 5.2 during the characterization of the influent streams for both systems.

2.2.3 Impact Assessment

In the impact assessment phase of the life cycle assessment, the emissions of COD, BOD, total N and total P were expressed in as potential impact on eutrophication through the act of classification and characterization. Impact assessment was only done for eutrophication in this study. The calculations related to the potential impact on eutrophication are given in Chapter 6.2.

3 Selection and Characterization of the representative pharmaceutical compounds

The wastewater reaching the wastewater treatment plants may contain hundreds of different pharmaceutical compounds. Since there is not a complete picture about the fate of these chemical compounds in the WWTPs and the impacts of the compounds on environment are largely unknown, it is difficult to conclude, which specific compounds represent the majority of the pharmaceutical compounds.

For the purpose of this study four pharmaceutical compounds were chosen. These compounds are (1) carbamazepine from anti-epileptic group, (2) diclofenac from anti-inflammatory group, (3) ibuprofen from pain killer and anti-inflammatory group and (4) metoprolol from beta-blocker group. Selection of the compounds was mainly based on the consumption amounts and abundance in the environment. Besides, some motivations related to the persistency and effects of the selected representative compounds on living organisms are given in the following chapters.

3.1 Consumption of the Selected Pharmaceutical Compounds

The consumption of pharmaceutical compounds differs from one to another country. The global consumption of human pharmaceuticals is predicted to be 100,000 (metric) tons per year. This number corresponds to a worldwide average pro capita consumption of 15 g $p^{-1}.y^{-1}$ for human pharmaceuticals (Alder et al., 2006;Kummerer, 2004). In Table 3.1, all groups of pharmaceutical compounds and their consumption in number of users in the Netherlands are given for the recent years. Highlighted groups are the first four which have the largest number of users, excluding the pharmaceutical groups used for dermatology and inhalation.

Among the pharmaceutical compounds used for cardiovascular system, metoprolol, furosemide and simvastatine are the first three compounds respectively which are used by the largest number of people in Netherlands according to the data given by GIP/CVZ (2006). The number of users does not indicate what the loads of the considered compounds are. Daily Defined Doses (DDD) is a dimensionless unit defining the assumed average maintenance dose for a pharmaceutical compound used for its main indication in adults (WHO, 2006). A DDD for each specific compound corresponds to a weight of that specific compound in grams per person per day. Considering the DDD, the consumption of a given compound is calculated in tones.$year^{-1}$ using equation 3.1.

Table 3.1 Groups of pharmaceutical compounds and number of users per each group in the Netherlands (GIP/CVZ, 2006)

	Year				
Therapeutic group	**2001**	**2002**	**2003**	**2004**	**2005**
A Alimentary tract and metabolism	2 831	2 899	3 002	2 767	3032
B Blood and blood forming organs	1 641	1 655	1 663	1 667	1 720
C Cardiovascular system	***2 606***	***2 684***	***2 759***	***2 910***	***3 080***
D Dermatologicals	3 412	3 421	3 465	3 192	3 200
G Genito urinary system and sex hormones	2 824	2 784	2 703	1 418	1 437
H Systematic hormonal preparations	787	828	854	890	947
J Antiinfectives for systematic use	***3 884***	***3 840***	***3 826***	***3 775***	***3 978***
L Antineoplastic and immunomodulating agents	134	145	157	169	184
M Musculo-skeletal system	***3 442***	***3 403***	***3 423***	***3 322***	***3 182***
N Nervous system	***3 590***	***3 605***	***3 597***	***3 344***	***3 385***
P Antiparasitic agents, insecticides, repellents	137	144	148	160	163
R Respiratory system	3 094	3 158	3 064	3 033	3 155
S Sensory organs	1 777	1 786	1 802	1 759	1 787
V Various	33	34	36	40	43

$$Yearly\ \ Amount = \frac{DDD}{year} \cdot \frac{g}{DDD} \cdot \frac{year}{365\ \ day} \cdot \frac{kg}{1000\ \ g} \cdot \frac{tonne}{1000\ \ kg} \quad \text{Eqn 3.1}$$

Yearly Amount: Amount of pharmaceutical compound consumed (tones/year)

In Figure 3.1, the calculated consumption amounts for metoprolol, furosemide and simvastatine are given. It was determined that metoprolol is consumed in the highest amount, as having the highest DDD year^{-1} as well as administered by the largest number of users in the recent years (Annex A3, Table A3.1).

In the pharmaceuticals group of musculo-skeletal system, diclofenac, ibuprofen and naproxen are the first three compounds respectively, which have the highest DDDs used per year and which are used by the largest number of people in Netherlands (GIP/CVZ, 2006). In Figure 3.2, calculated consumptions, in tonnes per year, using equation 3.1 are shown for these three compounds (Annex A3, Table A3.2). It is clear that the amount of ibuprofen consumed is the highest in the recent years while naproxen is the second and diclofenac is the third.

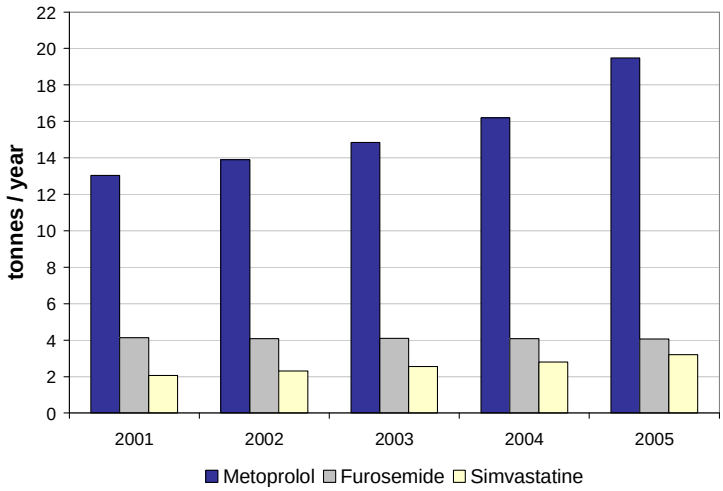


Figure 3.1 Consumption of pharmaceutical compounds for cardiovascular system in the years 2001-2005 (GIP/CVZ, 17/06/07).

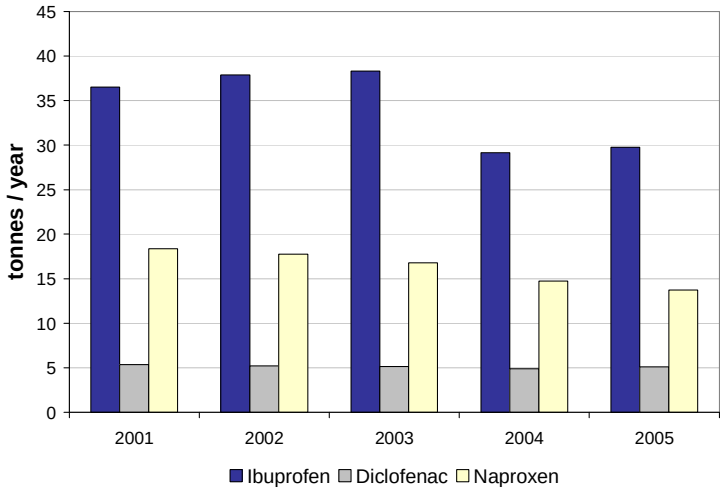


Figure 3.2 Consumption of pharmaceutical compounds for musculo-skeletal system in the years 2001-2005 (GIP/CVZ, 17/06/07).

For the pharmaceuticals used for nervous system oxazepam, paracetamol in combination and temazepam are the first three compounds respectively, which are consumed by the largest amount of people (GIP/CVZ, 2006). On the other hand, when the consumption loads are calculated with eqn 3.1 for the compounds which have DDD year^{-1} values above 10 million, it was found out that paracetamol-sinaspril (other analgesics and antipyretics), valproinezuur (anti-epileptics) and carbamazepine are the first three compounds respectively which are consumed in the highest amounts (Figure 3.3, Annex A3; Table A3.3). The calculated consumption amounts are given in Figure 3.3 for paracetamol-sinaspril, valproinezuur and carbamazepine.

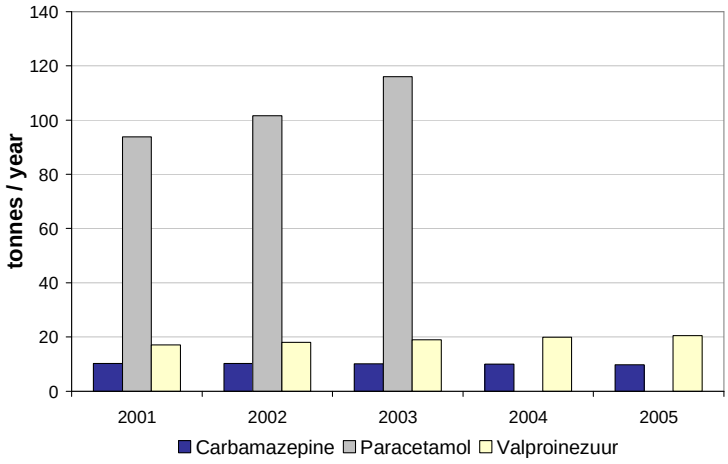


Figure 3.3 Consumption of pharmaceutical compounds for nervous system in the years 2001-2005 (GIP/CVZ, 17/06/07)

Consumption of pharmaceuticals varies over different countries and over time (example shown in Figure 3.4). In the figure it is shown that ibuprofen is generally consumed as a first choice to kill the pain in Finland, Spain and Sweden. In Germany, the consumption of some compounds such as metoprolol, carbamazepine, diclofenac, iomeprol (contrast media) and ciprofloxacin (anti-infective agents) has been increasing between 1996 and 2001 (Figure 3.4).

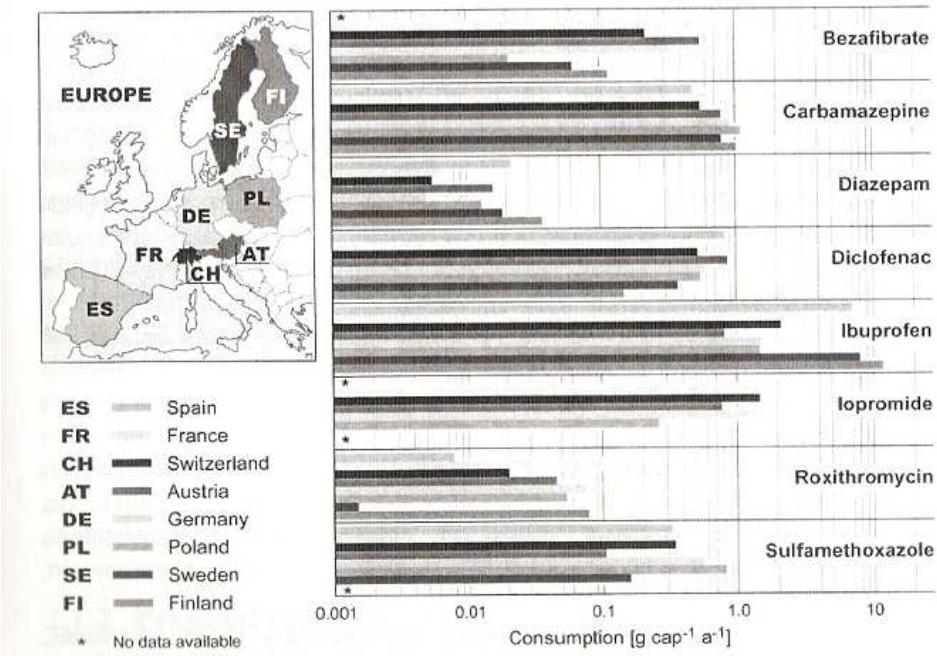


Figure 3.4 Annual prescribed consumption rates of the pharmaceuticals (Ternes and Joss, 2006)

It is expected that concentrations of these compounds in wastewater will increase more in the following years as their consumption increases. While some compounds are being used more compared to the recent years there are some

compounds which loose their popularity such as gemfibrozil (antihyperlipidemic), naproxen and erythromycin (antibacterial). The consumption of other compounds (eg. Iopromide (contrast media), sulphamethoxazole (anti-infective agent) has not been relatively changed.

3.2 Abundance of Pharmaceutical Compounds in Environment

After the pharmaceuticals were taken in, they are metabolized and excreted through mainly kidneys and intestines as active substance or their metabolites. An example of 40 pharmaceutical compounds excreted in urine and faeces are shown in Figure 3.5 (Moffat et al., 2004). In the figure the share of pharmaceutical compounds and the percentage of the presence of each compound in urine and faeces are included. It can be stated that 30% of the compounds are excreted in faeces and 70% are excreted in the urine (J. Lienert, congress in Aachen, 2007).

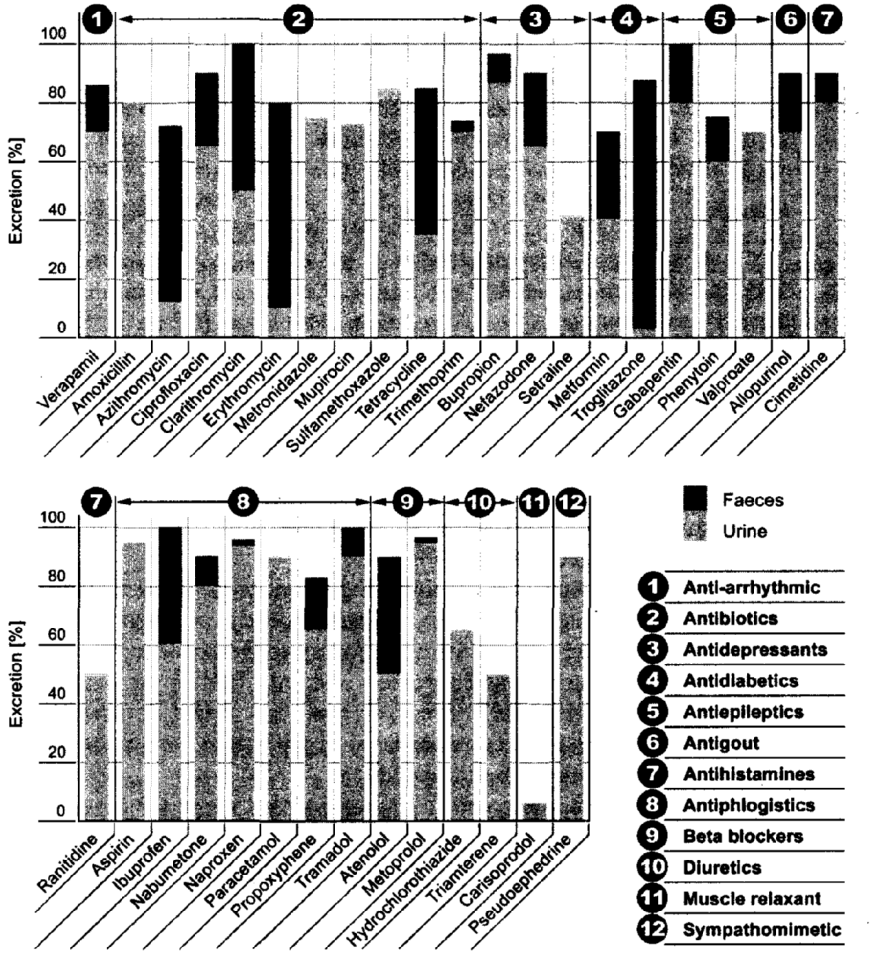


Figure 3.5 Fraction of excreted pharmaceuticals (including metabolites) in urine and faeces for 40 selected compounds (Moffat et al., 2004).

A lot of investigations are being done to determine the concentrations of different pharmaceutical compounds found in the surface water to be able to predict their negative effects on the living organisms. In Table 3.2, the maximum concentrations of human pharmaceuticals found in surface water are given in ng/l (Boxall, 2004).

Table 3.2 Pharmaceuticals detected in surface water monitoring studies (Boxall, 2004;Boxall et al., 2004a;Daughton and Ternes, 1999;Kolpin et al., 2002).

MEDICINE CLASS	SUBSTANCES DETECTED	MAX. CONCENTRATION (ng/l)
Antibiotics	Chloramphenicol	355
	Chlortetracycline	690
	Ciprofloxacin	30
	Lincomycin	730
	Norfloxacin	120
	Oxytetracycline	340
	Roxithromycin	180
	Sulphadimethoxine	60
	Sulphamethazine	220
	Sulphamethizole	130
	Sulphamethoxazole	1,900
	Tetracycline	110
	Trimethoprim	710
	Tylosin	280
Analgesic	Codeine	1,000
	Acetylsalicylic acid	340
	Carbamazepine	**1,100**
	Diclofenac	**1,200**
	Aminopyrine	340
	Indomethacine	200
	Ketoprofen	120
	Naproxen	390
	Phenazone	950
Antianginal	Dehydronifedipine	30
Antihypertensive	Diltiazem	49
Antidepressant	Fluoxetine	12
Antihyperlipidemic	Gemfibrozil	790
Antidiabetic	Metformin	150
Antipyretic	Acetaminophen (Paracetamol)	10,000
Anti-inflammatory	**Ibuprofen**	**3,400**
Beta blockers	Betaxolol	28
	Bisoprolol	2,900
	Carazolol	110
	Metoprolol	**2,200**
	Propanolol	590
	Timolol	10
Bronchodilator	Clenbuterol	50
	Fenoterol	61
	Salbutamol	35
Contraceptive	17a-Ethinylestradiol	4.3
Lipid regulator	Bezafibrate	3,100
	Clofibrate	40
	Gemfibrozil	510
X-ray contrast media	Diatrizoate	100,000

Figure 3.6 based on the data from Table 3.2, demonstrates the pharmaceutical compounds, which are found in the surface water in the highest concentrations. Paracetamol is normally the most easily biodegradable compound in a biological WWTP (Ternes and Joss, 2006). Diatrizoate is an X-ray contrast media given to the patients to enhance contrast in computed tomography, to image the kidneys and related structures, and to image blood vessels (Wikipedia, 2006). Although diatrizoate is detected in the highest concentrations in surface water, it was assumed not to cause any eco-toxicological effects since there is no documented toxicological effect of X-ray contrast media (Ternes and Joss, 2006).

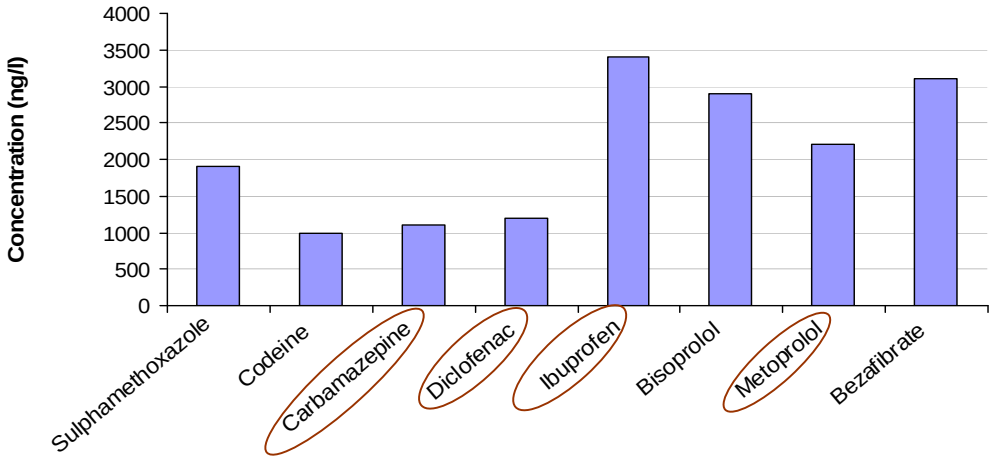


Figure 3.6 Maximum concentrations in ng/l of pharmaceuticals found in surface water. The highest concentrations are chosen from Table 3.2.

Carbamazepine was detected and measured in 44 rivers of the USA, in Canadian surface waters, Korean WWTPs effluents, in many surface waters in Europe and in North Sea (Fent et al., 2006;Han et al., 2006;Jones et al., 2001). The highest measured concentration of carbamazepine was 1075 ng/L, in the surface water samples in Berlin (Heberer, 2002). Considering the studies of (Ternes, 1998) and (Kim et al., 2007), ibuprofen was detected among the compounds of highest occurrence frequency (>80%) in rivers and streams found in Germany and Korea.

According to several literatures, diclofenac is one of the most frequently detected pharmaceuticals in water bodies (Buser et al., 1998;Buser et al., 1999;Perez-Estrada et al., 2005;Stumpf et al., 1999;Ternes, 1998). In the studies performed with sampled rivers and streams in Germany, it was found out that metoprolol was one of the frequent contaminants (Ternes, 1998). Besides Germany, Metoprolol was detected in the wastewater effluent samples in United States up to 1200 ng/L (Huggett et al., 2003).

Considering Figure 3.6 and the information given above it can be stated that the representative pharmaceutical compounds are not sufficiently being removed during the wastewater treatment plants and they end up in the surface waters. Overflows during the heavy rain or the lack of wastewater treatment plants could

be the other reasons for the presence of high concentrations of pharmaceutical compounds in the surface waters.

3.3 Environmental Risks of the Selected Pharmaceutical Compounds

According to the literature, very little is known about the long term effects of the pharmaceutical compounds and their metabolites on the aquatic organisms (Fent et al., 2006). The data accessed on the ecotoxicological effects of the selected compounds at the given concentrations are summarized in Table 3.3.

Table 3.3 Toxicity effects of carbamazepine, diclofenac, ibuprofen and metoprolol on living organisms at low environmental concentrations

Pharmaceutical	Concentration	Effect	Reference
Carbamazepine	1 µg/l	Slightly earlier maturation and reproduction of Daphnia and higher production of offspring	(Lürling et al., 2006)
Diclofenac	1 µg/l	Subtle sub cellular effects in fish	(Fent et al., 2006)
	5 µg/l	Renal lesions and alteration of gills in fish	(Fent et al., 2006)
Ibuprofen	1 and 10 ng/L	Significant decrease in activity of crustacean G. pulex	(De Lange et al., 2006)
	10 µg/l	Toxic effects to microbial communities	(Dorne et al., 2007)
	1, 10, 100 and 1000 µg/l	Growth inhibition of duckweed L. minor, up to 25%	(Pomati et al., 2004)
Metoprolol	No data	Accelerates the heart beat rate in D. magna, toxic on algae and daphins	(Cleuvers, 2005;Villegas-Navarro et al., 2003)

According to the results of the studies done, all of the representative pharmaceutical compounds showed toxicological effect on the organisms at environmental concentrations. These effects increase the necessity of the better removal of pharmaceutical compounds during the WWTPs.

3.4 Motivation of the Selection of the Representative Pharmaceutical Compounds

Carbamazepine is used in third highest quantity of 9.7 tonnes year^{-1} within nervous system therapeutic group in the Netherlands. According to the literature, it has the minimum removal efficiency in the WWTPs compared to the other pharmaceuticals studied. It is found in surface water above 1000 ng L^{-1}.

In the recent years, diclofenac is consumed by the largest number of users and in the third highest quantity of 5.1 tonnes year^{-1} within musculo-skeletal therapeutic group in the Netherlands. Although naproxen is used in the second highest amount in tonnes/year; according to literature naproxen is becoming demanded less while the demand for diclofenac is increasing.

Ibuprofen is consumed in the highest amount of 29.7 tonnes year^{-1} in musculo-skeletal therapeutic group. Although ibuprofen is stated as an easily

biodegradable compound in WWTPs, it is detected in surface water in the highest concentration (above 3200 ng L^{-1}).

Metoprolol is used in the highest amount (19.5 tonnes $year^{-1}$) among the cardiovascular therapeutic group as well as it is one of the compounds which are detected in surface water with high concentrations (above 2000 ng L^{-1}).

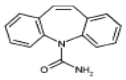
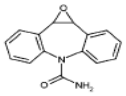
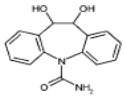
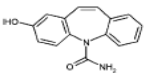
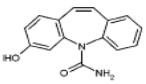
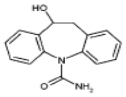
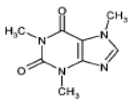
All of the representative compounds have toxicological effects on the living organisms the surface waters in which these compounds are being discharged with the wastewater.

3.5 Therapeutic, Physical and Chemical Characteristics of the Selected Compounds

3.5.1 Carbamazepine (anti-epileptic)

Carbamazepine is a pharmaceutical compound which is used for the control of grand mal and psychomotor epilepsy. It is a neutral compound also effective in the treatment of trigeminal neuralgia and is used in bipolar depression. Predominant elimination phase of this compound takes place in liver after the intake into the body. In the liver it is metabolized into carbamazepine 10,11-epoxide, which is pharmacologically active and other derivatives (Clara and Strenn, 2004;Rooyen et al., 2002). In a study done by (Frey and Janz, 1985), it is stated that 1-2% of the given dose is excreted in unchanged form via urine whereas in another publication, it is stated as 31% (Khan and Ongerth, 2004;Pharmacopeia, 2000). The chemical characteristics of carbamazepine and its metabolites are given in Table 3.4.

Table 3.4 Molecular structures and chemical characteristics of carbamazepine and its metabolites (Miao et al., 2005).

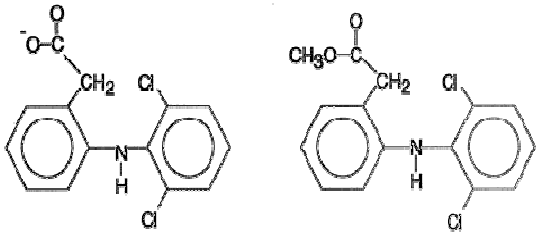
Structure	Analyte	Abbreviation [CASRN[a]]	Formula and MW[b]	Log K_{ow}
	Carbamazepine	CBZ [298-46-4]	$C_{15}H_{12}N_2O$ 236.10[a]	2.25[c], 2.67 ± 0.38[d]
	10,11-dihydro-10,11-epoxycarbamazepine	CBZ-EP [36507-30-9]	$C_{15}H_{12}N_2O_2$ 252.09	1.26 ± 0.54[d]
	10,11-dihydro-10,11-dihydroxycarbamazepine	CBZ-DiOH [35079-97-1]	$C_{15}H_{14}N_2O_3$ 270.10	0.13 ± 0.41[d]
	2-hydroxycarbamazepine	CBZ-2OH [68011-66-5]	$C_{15}H_{12}N_2O_2$ 252.09	2.25 ± 0.65[d]
	3-hydroxycarbamazepine	CBZ-3OH [68011-67-6]	$C_{15}H_{12}N_2O_2$ 252.09	2.41 ± 0.73[d]
	10,11-dihydro-10-hydroxycarbamazepine	CBZ-10OH [29331-92-8]	$C_{15}H_{14}N_2O_2$ 254.10	0.93 ± 0.33[d]
	1,3,7-trimethylxanthine	Caffeine [58-08-2]	$C_8H_{10}N_4O_2$ 194.08	-0.07[e]

[a] Chemical Abstracts Service registry number, [b] Molecular weight (MW) was calculated for the lowest isotopomer, [c] (Jones et al., 2002), [e] (Weigel et al., 2002)

3.5.2 Diclofenac (anti-inflammatory)

Diclofenac is an acidic, non-steroidal anti-inflammatory drug which is used for musculoskeletal complaints. It reduces inflammation and an analgesic lessening the pain in conditions such as damages in joints or acute injury (Wikipedia, 2006). It is readily metabolized after oral use (Buser et al., 1998). Structure of diclofenac and its metabolite diclofenac methyl ester are given in Figure 3.7.

Different excretion rates for the unchanged form of diclofenac are given in different studies. A 15% excretions rate was given in the study of Landsdrorp et al. (1990) whereas 2% was stated in another study (Khan and Ongerth, 2004;Pharmacopeia, 2000).



.**Figure 3.7** Molecular structure of diclofenac and diclofenac methyl ester (Buser et al., 1998),

3.5.3 Ibuprofen (pain killer and anti-inflammatory)

Ibuprofen is a non-prescription pharmaceutical compound which is used in the treatment of pain and fever. It is an acidic, anti-inflammatory, analgesic and antipyretic pharmaceutical compound. After the compound ibuprofen is taken into the body they are excreted to a degree of 1-10% in an unchanged form (Khan and Ongerth, 2004;Pharmacopeia, 2000;Ternes, 2000).

The moleclular structure of ibuprofen and its metabolites, hydroxyibuprofen (OH-Ibu), carboxyibuprofen (CA-Ibu) and carboxyhydratropic acid (CA-HA) are given in Figure 3.8 (Buser et al., 1999;Zwiener, 2002). In the study of (Buser et al., 1999), it was shown that besides the parent compound of Ibuprofen, its metabolites are also detected at the WWTPs.

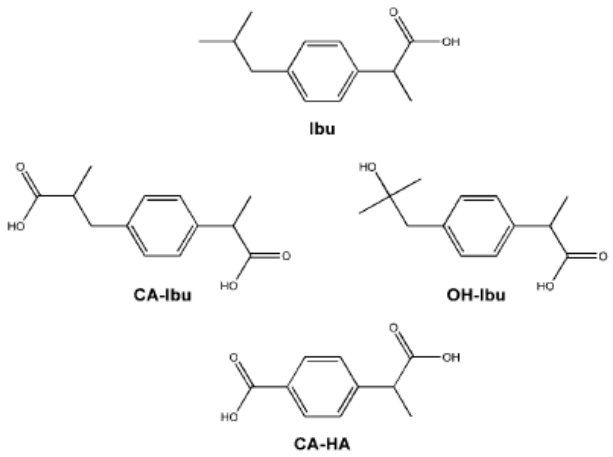


Figure 3.8 The molecular structure of ibuprofen and its metabolites (Zwiener, 2002)

3.5.4 Metoprolol (beta-blocker for hart patients)

Metorprolol is pharmaceutical belonging to beta-blockers group. Betablockers are used in order to treat angina and hypertension. Metoprolol is largely metabolized in the body and 3-10% of the taken dose can be excreted from the body in an unchanged form via urine (Khan and Ongerth, 2004;Pharmacopeia, 2000;Ternes, 2000;Ternes and Joss, 2006). The molecular structure of metoprolol is given in Figure 3.9.

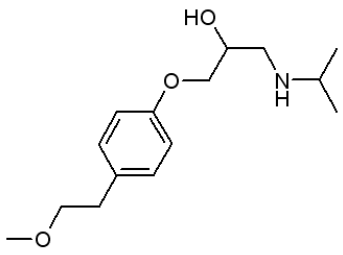


Figure 3.9 The molecular structure of Metoprolol (Wikipedia, 2006)

The metabolites of the metoprolol are stated as metoprolol-glucoronide, O-desmethylmetoprolol, 4-(2-hydroxyl-3-isopropylamino-pro-poxy)-phenylacetic acid, α-hydroxymetoprolol, 2-hydroxyl-3[4-(2-methoxyethyl)phenoxy] propionic acid in the study of Escher (2006).

3.5.5 Remarks on metabolites

A fraction of the pharmaceutical compounds, which are hardly soluble in body fluid and un-metabolized fraction are excreted in a non-changed form. The other pharmaceutical compounds are excreted from the body in the form of metabolites after the biotransformation process. Metabolites are generally inactive form of the parent compounds. However there are some metabolites, which still show pharmacological activity (Debska et al., 2004). Several researchers stated in their studies that big fraction of the compounds are excreted as metabolites and both parent compounds and their metabolites are found in the influent of the WWTPs (Buser et al., 1999;Khan and Ongerth, 2004;Pharmacopeia, 2000;Ternes, 2000;Ternes and Joss, 2006). Low excretion values of carbamazepine, diclofenac, ibuprofen and metoprolol in unchanged form are 1-31%, 2-15%, 1-10% and 3-10% respectively. However, it was not possible to conduct this study considering the high concentrations of metabolites present in the wastewater because of the limited data available on the removal of each specific metabolite in the treatment processes of WWTPs. On the other hand, it was not easy to predict the real amount of parent compound and metabolites found in the wastewater because of limited and contradictory data as well as the possibility of retransformation of the metabolites into their parent compounds.

In this research 100% excretion rate values are used, considering that pharmaceutical compounds are being released in 100% unchanged form to the sewage system. This percentage was used for the simplification of the calculations, simulating the worse case scenario. The same percentage was used in the environmental risk assessments assuming that almost all of the compounds are excreted as parent compound and metabolites which can be retransformed to parent compounds in a sewer or/and in the treatment system (Huschek et al., 2004).

4 Removal Mechanisms of Pharmaceuticals and Their Removal Efficiencies in Treatment Processes in Wastewater Treatment Systems

In this chapter, studies described in literature were reviewed in order to analyze specific wastewater treatment units in relation to pharmaceutical removal. Each treatment unit was studied for its capacity of organic pollutant removal, pharmaceutical removal, nutrient and energy recovery. As a conclusion of this chapter, the configurations of treatment processes were determined for combined and source separated systems separately, system A and B respectively. These configurations form the flow charts of both systems, which were compared using life cycle assessment

In the first part of this chapter, mechanisms for removing the pollutants from wastewater were studied in order to get a better understanding on the treatment processes. The information on removal mechanisms were used especially in the assumption of some removal efficiencies, which could not be found in the literature during the design phase in Chapter 5.

4.1 Mechanisms Relevant For Removing the Pollutants in Wastewater

There are different mechanisms playing role in the removal of organic pollutants in the treatment processes. These mechanisms are explained below including the applicability for the representative pharmaceuticals.

4.1.1 Biological Degradation

Biological degradation is one of the most relevant mechanisms for the removal of organic compounds including the pharmaceuticals occurring in the treatment processes. Biological degradation rates show big differences from one to another compound. These differences seem not to be dependent only on the molecular or quantitative structure. This is why degradation rate of each compound should be determined by experiments. The degradation rate of pharmaceutical compounds can be identified by pseudo first order degradation given in Equation 4.1 according to batch experiments (Ternes et al., 2005).

$$\frac{dC_i}{dt} = k_{i,biol} \cdot SS \cdot C_i \qquad \text{(Eqn 4.1)}$$

C_i soluble substance concentration of the compound i inside the reactor [µg/L]

$k_{i,biol}$ kinetic constant for pseudo first order degradation [L/gSS.d]

SS suspended solids concentration [gSS/L]

According to the aerobic batch reactor experiments, relation between removal capacity and kinetic degradation constant, $k_{i,biol}$, of the pharmaceuticals was attempted to be determined. For typical reactor configuration, the following relation was derived (Ternes et al., 2005):

- $k_{i,biol}$ < 0.1 [L gSS^{-1} d^{-1}]: no substantial removal due to biological degradation;
- 0.1 < $k_{i,biol}$ < 10: degree of removal is strongly dependent on reactor configuration; and
- $k_{i,biol}$ > 10: more than 95% removal by biological degradation.

In Figure 4.1, degradation constants, $k_{i,biol}$, for some pharmaceutical compounds are shown. According to the results of the experiments done with activated sludge process, it was found out that the pharmaceutical compounds, which have degradation constant values below a minimum $k_{i,boil}$, show no significant degradation in WWTPs. The thick horizontal line emphasizes the minimum $k_{i,biol}$ value, which is 0.1 L/gSS.d, required for degradation to occur. It can be stated that ibuprofen is the only one among the selected pharmaceutical compounds, which can be degraded significantly in WWTPs, since its $k_{i,biol}$ is much higher than 0.1 L/gSS.d.

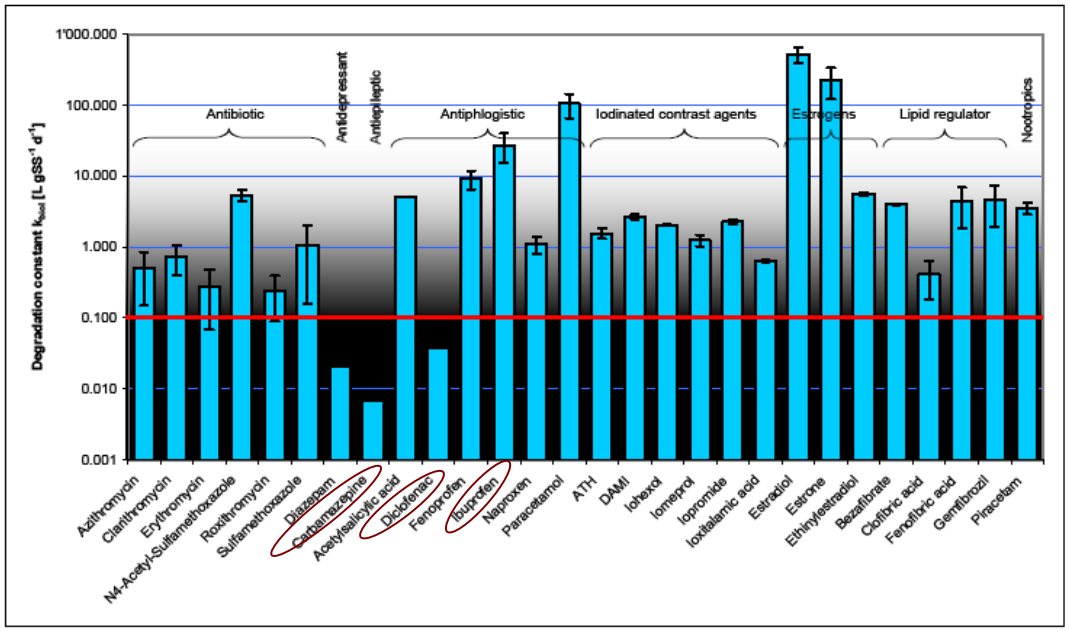


Figure 4.1 Biological pseudo first order degradation rate constants k_{biol} for carbamazepine, diclofenac and ibuprofen (in aerobic batch experiments with activated sludge, SRT≥8d). Thick horizontal line shows the limit below, which there is no significant degradation expected in WWTPs (Ternes et al., 2005).

Sludge retention time which is an important design parameter for biological wastewater treatment, has thought to be one of the influencing factors for pharmaceutical degradation (Equation 4.2). However, there are still researches being done to determine the effects of the SRT on the removal of specific pharmaceutical compounds (Ternes et al., 2005).

$$\frac{C_{i,out}}{C_{i,in}} = e^{-k_{i,biol} \cdot SS \cdot HRT} = e^{-k_{i,biol} \cdot SP \cdot SRT} \qquad \text{(Eqn 4.2)}$$

$C_{i,\,in}$: influent substance concentration of the compound *i* [µg L^{-1}];

$C_{i,\,out}$: final substance concentration of the compound *i* [µg L^{-1}];

HRT: hydraulic retention time of the whole reactor or duration of the batch [d];

SP: specific sludge production per amount of wastewater treated [gSS m^{-3} wastewater];

SRT: sludge age [d]

The behaviors of representative compounds in full scale WWTP were investigated, considering the relation between the removal capacity and their $k_{i,biol}$ in Table 4.1 (Maurer et al., 2007;Ternes et al., 2005).

Table 4.1 Biological pseudo first order degradation rate constants for selected pharmaceutical compounds and their removal potential in full scale WWTPs

Pharmaceutical	$k_{i,biol}$	Unit	Fate	Reference
Carbamazepine	< 0.1	L gSS-1 d-1	no significant removal	(Ternes et al., 2005)
Diclofenac	0.25±0.2	L gSS-1 d-	15-40% removal, mainly in aerated compartment, at ≥ 2 days SRT.	(Ternes et al., 2005)
Ibuprofen	23±10	L gSS-1 d-1	>90% biological removal, mainly in aerobic reactor at ≥ 5 days SRT	(Ternes et al., 2005)
Metoprolol	0.58±0.05	L d-1g-1COD	44% elimination in WWTPs, sludge concentrations of 4 gCODL-1, at HRT of 6h.	(Maurer et al., 2007)

It can be concluded that Ibuprofen is expected to be degraded with the highest efficiency under aerobic conditions, whereas degradation of diclofenac and metoprolol possibly will be less efficient, considering the kinetic degradation constants of the representative compounds. It can be also stated that for the removal of ibuprofen and diclofenac minimum 2 days of sludge age is required based on the study mentioned above (Ternes et al., 2005). No significant degradation of carbamazepine is expected in aerobic reactors.

4.1.2 Sorption onto Sludge

Sorption onto particulate matter is an important removal mechanism, when the tendency of organic compounds to partition onto the primary or secondary sludge is high (Ternes et al., 2005). There are two mechanisms on which the sorption of the organic compounds on the sludge depends; absorption and adsorption.

Absorption is the hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms and with the lipid fraction of the sludge. Adsorption is the electrostatic interactions of positively charged groups of the chemicals with the negatively charged surfaces of the biomass (Figure 4.2) (Larsen et al., 2004;Schwarzenbach et al., 2003).

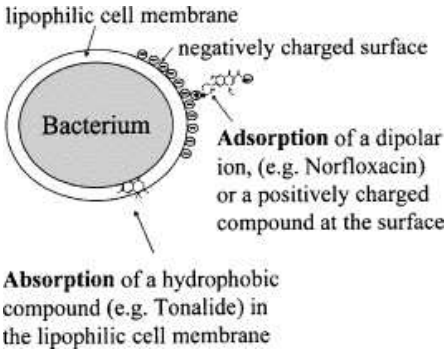


Figure 4.2 Absorption and adsorption mechanisms of the pharmaceuticals on the sludge (Golet et al., 2002). (tonalide; personal care products, norfloxacin; antibacterial)

In sorption mechanism, sorption coefficient constant, K_d, describes the solid liquid partitioning characteristics of a compound. Only the substances, which have sorption coefficient, K_d, values higher than 500 L.kgSS^{-1} are sorbed significantly onto the sludge (Ternes et al., 2005). Available data show that only hydrophobic compounds and positively charged ionic substances have high K_d values enough to be sorbed onto the sludge (Ternes et al., 2005).

The Equation 4.3 shows that the concentration of a compound sorbed onto the sludge is assumed to be proportional to the concentration of the same compound in the solution (Ternes et al., 2005):

$$C_{i,sorbed} = K_{d,i} \cdot SS \cdot C_{i,so\,\mathrm{lub}\,le} \qquad \text{(Eqn 4.3)}$$

$C_{i,sorbed}$ the particulate concentration of the micropollutant *i* [µg.L^{-1}];

$K_{d,i}$ the sorption constant of the pharmaceutical *i* [L.kg^{-1}];

SS suspended solids concentration in raw wastewater or production of suspended solids in primary or secondary treatment, per L of treated wastewater [kg.L$^{-1}_{wastewater}$];

S_i the soluble concentration of the pharmaceutical *i* [µg.L^{-1}]

In Table 4.2, the K_d values of the compounds are given for primary and secondary sludge. It can be stated that very low K_d values for carbamazepine ibuprofen and metoprolol show that sorption plays no significant role for removal of these compounds in WWTPs. Diclofenac has a K_d value of ~500 L.kgSS^{-1} in primary sludge. The sorption potential of diclofenac is significantly higher than the carbamazepine, ibuprofen and metoprolol (Maurer et al., 2007;Ternes et al., 2004a).

Table 4.2 Kd, solid-water distribution coefficient of the selected compounds

Compounds	Unit	Kd (Primary Sludge)	Kd (Secondary Sludge)
Carbamazepine	(L/kg)	-(<20) [a]	1.2±0.5 [a]
Diclofenac	(L/kg)	459±32 [a]	16±3 [a]
Ibuprofen	(L/kg)	-(<20) [a]	7.1±2.0 [a]
Metoprolol	(L/g_{COD}.d)	No data	0±0.023 [b]

[a] (Ternes et al., 2004a)
[b] (Maurer et al., 2007)

Regarding mainly hydrophobic interactions, the octanol-water partition coefficient, K_{ow}, or the partitioning coefficient to particulate organic matter, K_{oc} can be used to estimate the sorption constant K_d (Ternes et al., 2005).

High K_{ow} values (i.e. log K_{ow} > 4.0) show that compounds can sorb to the sludge where low values (i.e. log K_{ow} < 2.5) indicate that the compounds generally will stay in the aqueous phase (Jones et al., 2005;Rogers, 1996). However there are ongoing studies to prove the relation between K_{ow} and K_d for the pharmaceutical compounds (Tolls, 2001). The relation between the log K_{ow} value of the representative compounds and their sorption potentials are given in Table 4.3.

Table 4.3 Log K_{ow} values of the representative compounds and their sorption potential

Pharmaceutical	Log K_{ow} value	Sorption potential
Carbamazepine	2.45 [a]	Low
Diclofenac	0.70 [a], 4.6 [b]	Low, High
Ibuprofen	3.97 [a]	Medium
Metoprolol	1.88	Low

[a] (Yoon et al., 2006)
[b] (Hansch *et al.,* 1995)

Conflicting K_{ow} values of diclofenac were found in different studies in literature. Considering the high K_d value and high K_{ow} values from some of the literature, it can be concluded that diclofenac is considered as a hydrophobic and positively charged compound and has the highest ability to be sorped onto suspended solids among the other selected compounds. Regarding the K_d and K_{ow} values, the sorption mechanism is not relevant for carbamazepine. For ibuprofen K_d and K_{ow} values are conflicting with each other. K_d value shows that ibuprofen is not a compound, which has sorption potential whereas K_{ow} value indicates a moderate sorption potential onto sludge. Both, K_d and K_{ow} values for metoprolol show that sorption is not a removal mechanism for this compound.

4.1.3 Stripping

Stripping is the transferring of a compound from the water phase into the gas phase during the aeration process (Ternes and Joss, 2006). Stripping process occurs in the aerobic part of the treatment plant, where there is an intensive aeration of the mixed liquor. Equation 4.4 shows that aeration intensity, liquid-gas partitioning coefficient and Henry coefficient ($K_{i,H}$) of the organic compounds are the most important parameters on which stripping process depends (Ternes et al., 2005;Ternes and Joss, 2006).

$$K_{i,H} = \frac{p_i}{C_{i,so\,\mathrm{lub}\,le} \cdot R \cdot T} \qquad \text{(Eqn 4.4)}$$

$K_{i,H}$: Henry or air water partitioning coefficient of the compound *i* [-];

P_i: Partial pressure in the gas phase [Pa];

R: Universal gas constant; 8.314 [J /Mol.K];

T: Temperature [K];

$C_{i,\ soluble}$: Soluble concentration of the compound i [µg/L]

When $K_{i,H}$> 0.003, it is enough to observe a significant amount of stripping in a bioreactor with fine bubble aeration (Ternes and Joss, 2006). Pharmaceutical compounds generally have high molecular masses (above 250 $g.mol^{-1}$) and very small Henry coefficients (below 0.005) (Larsen et al., 2004;Schwarzenbach et al., 2003). In Table 4.4, the Henry coefficients for the selected pharmaceutical compounds are introduced.

Table 4.4 Henry coefficients of the representative compounds and their stripping (volatilisation) potential (http://chem.sis.nlm.nih.gov/chemidplus/)

Pharmaceutical	Henry Coefficient ($K_{i,H}$)	Stripping potential
Carbamazepine	1.08E-10	no
Diclofenac	4.73E-12	no
Ibuprofen	1.5E-07	no
Metoprolol	1.4E-13	no

Very low Henry coefficients of pharmaceutical compounds (Table 4.4) show that stripping process is not relevant at all for their removal from the wastewater (Larsen et al., 2004).

4.1.4 Chemical Oxidation

Chemical oxidation seems to be very efficient mechanism to remove pharmaceuticals from the biologically treated wastewater. Ozonation and AOPs (Advanced Oxidation Processes) are two of the promising techniques (Huber et al., 2003;Ternes et al., 2005;Ternes et al., 2002;Ternes et al., 2003;Zwiener et al., 2000). Second order rate constants (k_{O3}) of the ozonation process for representative pharmaceutical compounds were determined in bench-scale experiments. The k_{O3} values above $5x10^4$ $M^{-1}s^{-1}$ indicate that the respective compound can be transformed during the ozonation process very efficiently. Next to the reaction with ozone, reaction with hydroxyl radicals (OH) also plays a role in oxidation of micropollutants. This is why second order rate constants (K_{OH}) for the reaction of OH radicals with the representative pharmaceuticals were assessed as well (Huber et al., 2003;Ternes et al., 2004;Zwiener et al., 2000). The k_{O3} and k_{OH} values are given in Table 4.5 for the selected representative compounds.

Table 4.5 Second order rate constants for the reaction of ozone, hydroxyl radicals and chlorine dioxide (Huber et al., 2003;Ternes et al., 2004).

Compound	k_{O3} (T=20°C) ($M^{-1}s^{-1}$)	Reactive Species	OH Generation	k_{OH} (10^9 $M^{-1}s^{-1}$)	k_{ClO2} ($M^{-1}s^{-1}$)
Carbamazepine	$3E10^5$	Neutral	UV/H_2O_2	8.8±1.2	<0.015
Diclofenac	$1E10^6$	Dissociated	γ - radiolysis	7.5±1.5	$1.05E10^4$
Ibuprofen	9.6±1	Dissociated	UV/H_2O_2	7.4±1.2	<0.01
Beta Blockers (Metoprolol)	$1\text{-}10E10^3$ [a]	No data	No data	No data	No data

[a] estimated value

Chlorination with chloride dioxide is an alternative chemical oxidation method for pharmaceutical compounds. To be able to predict the ability of the pharmaceutical compounds to be oxidized, second order rate constants for the reaction of chlorine dioxide (k_{ClO2}) were determined in bench-scale experiments. K_{ClO2} are given in Table 4.5.

Considering the k_{O3} values of the representative compounds, it can be concluded that carbamazepine and diclofenac can be easily chemically oxidized by the reaction of both ozone and hydroxyl radicals whereas ibuprofen can be oxidized mainly by the reaction of hydroxyl radicals. According to the estimated k_{O3} value, which is $<5x10^4$ $M^{-1}s^{-1}$ for metoprolol, it is not a compound, which is oxidized efficiently during the process.

4.1.5 Concluding Remarks

In Table 4.6 the degradation, sorption, stripping and chemical oxidation potentials were summarized for each representative pharmaceutical compound.

Table 4.6 Summary of removal mechanism potentials for representative compounds

	Potential			
	Degradation	**Sorption**	**Stripping**	**Chemical Oxidation**
Carbamazepine	Low	Low	Very Low	High
Diclofenac	Medium	High	Very Low	High
Ibuprofen	High	Low-Medium	Very Low	High
Metoprolol	Medium	Low	Very Low	Low *

* Limited available literature

According to the Table 4.6 stripping is not an appropriate removal mechanism option at all for any of the compounds. Diclofenac, metoprolol and especially ibuprofen can be removed by the degradation to a certain extent. Sorption is an appropriate removal mechanism for diclofenac and to an extent for ibuprofen whereas it has no effect on carbamazepine and metoprolol. Chemical oxidation

seems to be a promising mechanism for carbamazepine, diclofenac and ibuprofen. According to very limited available data on literature, chemical oxidation is not a successful mechanism for removing metoprolol. It can be also concluded that the selected pharmaceutical compounds show different persistency to different removal mechanisms because of their different chemical and physical characteristics. Having compounds of different characteristics, it can be assumed that the selected pharmaceutical compounds represent a large part of the all pharmaceutical compounds used.

4.2 Fate of Representative Pharmaceuticals in Conventional WWTPs

The fate and behaviour of the pharmaceutical compounds in WWTPs are being investigated since the last decade. In this part of the study, the removal efficiencies of the representative pharmaceuticals were searched through the available literature. Their fate in different treatment configurations in conventional WWTPs together with their removal rates is summarized below.

In a WWTP near Frankfurt/Main in Germany, the elimination of different pharmaceuticals was investigated during the passage through a municipal wastewater treatment plant. The municipal WWTP consists of three main common units; primary sedimentation, aeration tank with addition of Fe(2)chloride for phosphate removal and secondary sedimentation. Sorption behaviour of the pharmaceuticals was not investigated during the research. This is why, the removal mechanisms could not be differentiated whether the pharmaceutical compounds were removed by sorption or biodegradation mechanism. The results are given in the Figure 4.3. The removal efficiencies of ibuprofen, diclofenac and metoprolol were 90, 69 and 83%, respectively whereas carbamazepine was removed only 7% (Ternes, 1998).

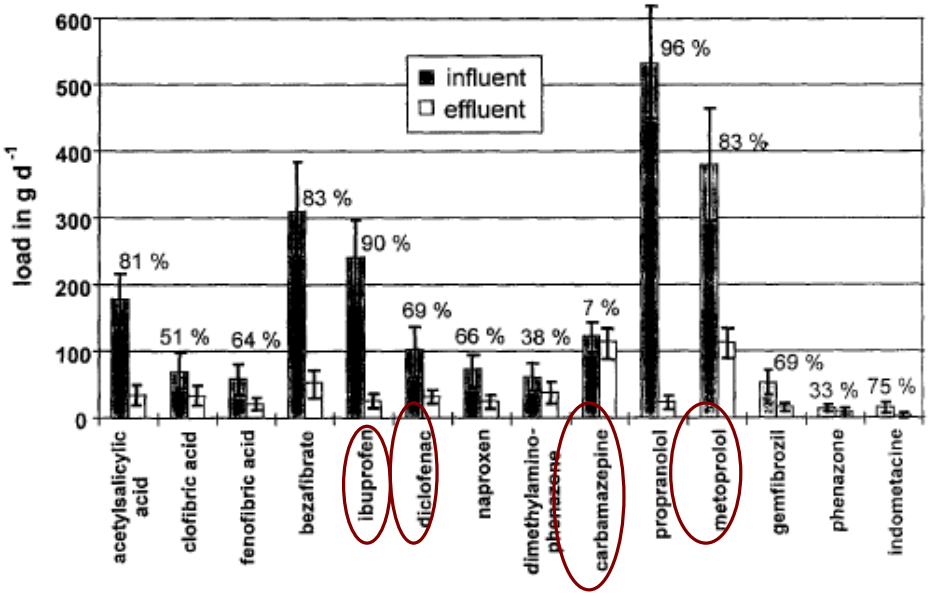


Figure 4.3 Elimination of different pharmaceuticals during a municipal WWTP in Frankfurt/Main including primary sedimentation, aeration tank and final sedimentation (Ternes, 1998).

In another research done by (Miao et al., 2005), the removal efficiencies of carbamazepine and its metabolites over different treatment units of the conventional wastewater treatment plant (consisting of AS system with secondary clarifier) in Canada, were investigated. Overall removal efficiency of the carbamazepine was 29%. However, no significant removal was detected for its metabolites (Miao et al., 2005).

In Italy, removal efficiencies of different pharmaceuticals in six different WWTPs, consisting of primary sedimentation and activated sludge process, were investigated. According to the results no significant removal of carbamazepine was detected in all WWTPs. Ibuprofen showed different removal rates in different WWTPs. Average removal efficiency of ibuprofen (for all WWTPs) was measured as 38% in winter whereas in summer it was 93% (Castiglioni et al., 2006).

In the full scale research done for six different WWTPs from different countries, average 87% removal efficiency for metoprolol was obtained. All treatment plants investigated consisted of activated sludge process, followed by chlorination. The hydraulic retention time (HRT) was changing in a range of 24-48 days (Huggett et al., 2003).

Studies were made on the influence of sludge retention time (SRT) on the removal capacity of full scale WWTPs and no influence was observed during the research. Different plant configurations with primary treatment, activated sludge, anaerobic sludge digestion and trickling filter were operated. According to the results no influence was reported due to the different plant configurations (Clara et al., 2004). In the study of (Clara et al., 2005) differently configured full scale wastewater treatment plants were operated and the removal rates of different pharmaceuticals were investigated together with the influence of SRT on the

removal rates (Table 4.7). Only the results for the representative compounds are given in this section.

Table 4.7 Different WWTP configurations and their characteristics (Clara et al., 2005).

	Plant characterization		$SRT_{10\,℃}$ (d)
○ **WWTP 1**	PS, AS	C, P	2
▲ **WWTP 2**	AS+AS, AD	C, P, N, DN	19
Δ **WWTP 3**	PS, AS, AD	C, P, N, DN	48
■ **WWTP 4**	AS, SSS	C, P, N, DN	>100/42
□ **WWTP 5**	MBR	C, N, DN	22/82/40

(PS—primary settling, AS—activated sludge system, MBR—membrane bioreactor (ultrafiltration), AD—anaerobic sludge digestion, SSS—simultaneous sludge stabilization, C—carbon removal, N—nitrification, DN—denitrification, P—phosphorus precipitation, $SRT_{10\,℃}$–SRT related to 10 ℃)

Carbamazepine was stated as an unaffected compound by SRT during the treatment, since no significant removal for carbamazepine was observed in none of the treatment configurations. For diclofenac SRT was an important factor influencing the removal rate as it is shown in Figure 4.4. In the treatment facilities, for diclofenac different removal rate results were obtained at different SRT values. In some of the facilities high removal efficiencies were achieved whereas in some of them no considerable removal was observed. Since no clear correlation was detected between the removal efficiency and the SRT values no critical SRT value was identified for diclofenac.

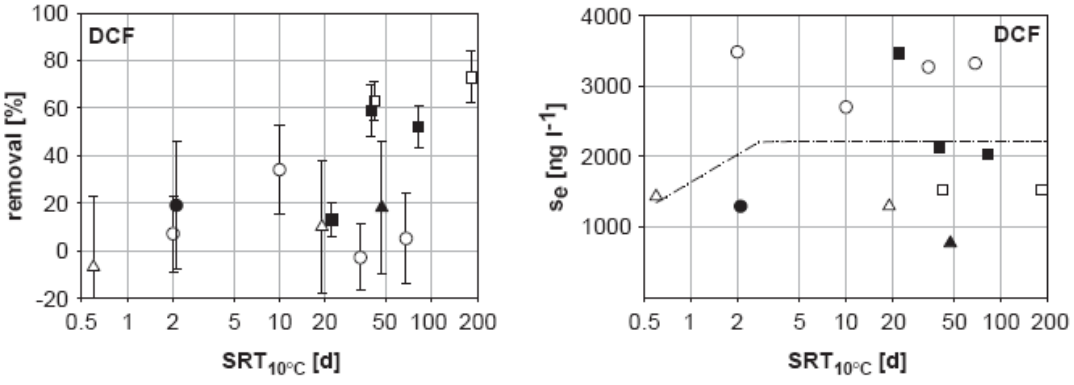
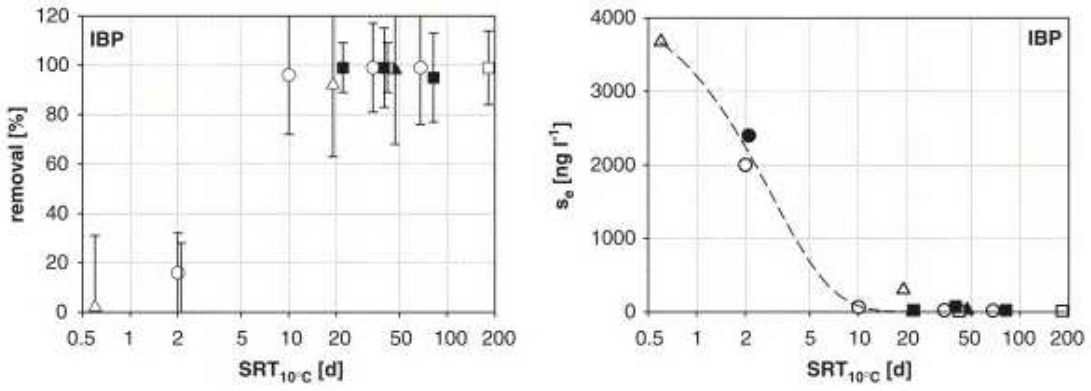


Figure 4.4 (A) Removal efficiencies for diclofenac (DCF) in different plant configurations with different SRT values. (B) The changes in effluent concentration of diclofenac according to the different SRT values (Clara et al., 2005) (● LP1-LP4; LP: lab-scale experiments, ○ WWTP 1, ▲ WWTP 2, Δ WWTP 3, ■ WWTP 4, □ WWTP 5, Table 4.5)

According to the results of the study by (Clara et al., 2005), ibuprofen was removed to a large extent (95%) in wastewater treatment facilities as it is shown in Figure 4.5. Critical SRT value for ibuprofen was stated as 5 days. For

ibuprofen, no significant differences between the removal performances of conventional activated sludge and membrane bioreactor systems were observed.



A B

Figure 4.5 (A) Removal efficiencies for ibuprofen (IBP) in different plant configurations with different SRT values. (B) The changes in effluent concentration of ibuprofen according to the different SRT values (Clara et al., 2005)(● LP1-LP4; LP: lab-scale experiments, ○ WWTP 1, ▲ WWTP 2, Δ WWTP 3, ■ WWTP 4, □ WWTP 5, Table 4.5)

Conventional activated sludge (CAS), membrane bioreactor (MBR) and fixed-bed reactor (FB) were compared according to their removal efficiencies for some selected compounds (Joss, 2005). As it is shown in the graphs in Figure 4.6, similar performances were obtained for carbamazepine, diclofenac and ibuprofen in all three different treatment systems (AS, MBR and FB). Similar to the results of (Castiglioni et al., 2006;Clara et al., 2005;Ternes, 1998) no significant removal for carbamazepine was observed in different SRT and temperature values in all three different treatment systems (Joss, 2005).

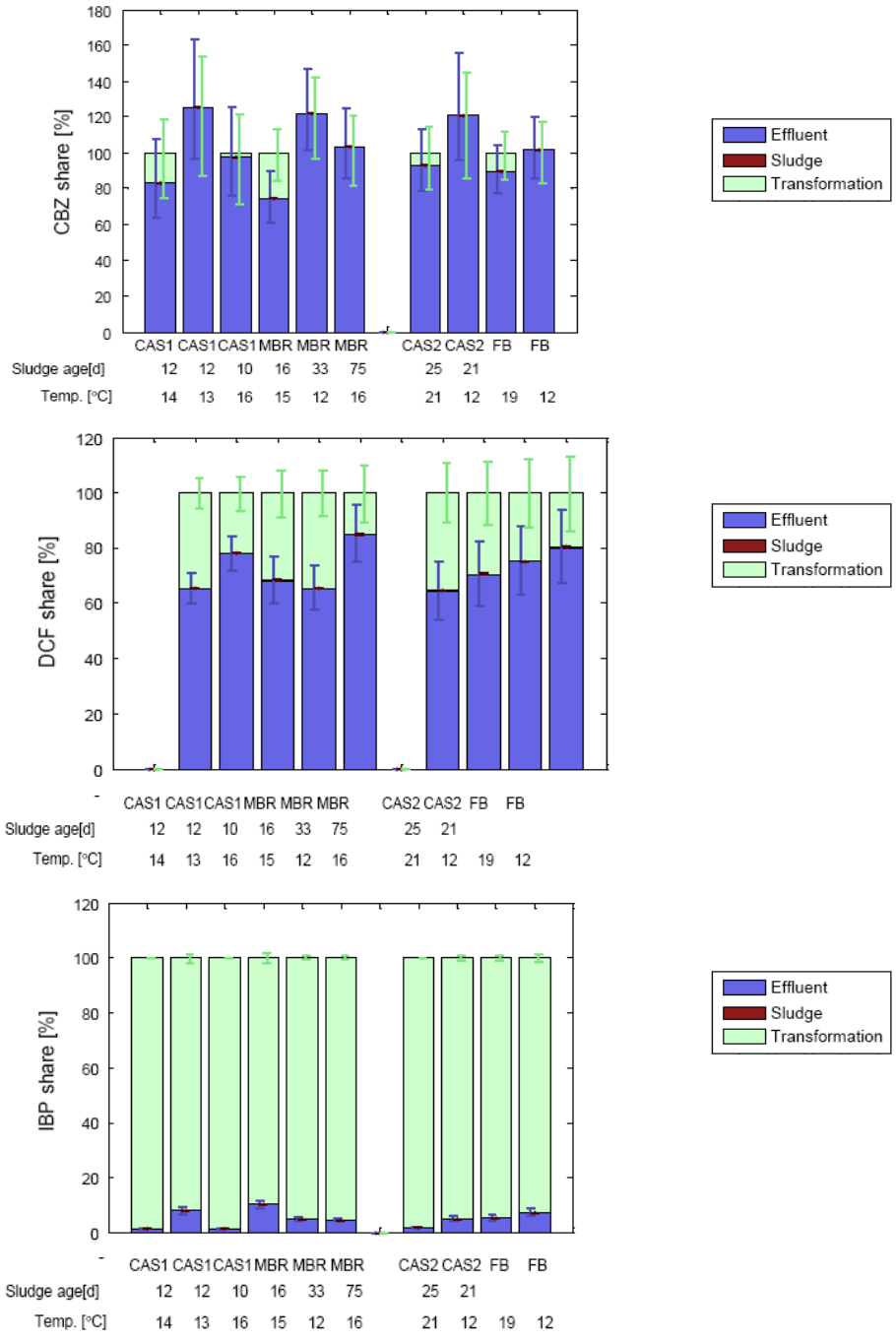


Figure 4.6 Removal of carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBP) in full scale CAS, MBR and FB reactor systems (Joss, 2005).

For diclofenac, 20-40% removal capacity was detected without significant differences dependent on SRT and temperature values. Ibuprofen was removed for more than 95%. Differences in SRT values and different treatment systems did not cause significant differences in removal rates of carbamazepine, diclofenac and ibuprofen (Joss, 2005). As it is seen in the figures, the removal of the pharmaceuticals in all systems was caused mainly by transformation

process. The sorption of the compounds into the sludge was not significant, which is represented by the lines with the darkest color. The calculations for transformation and sorption capacity were done with mass balance equations (Joss, 2005).

In the same research, it was sometimes observed that the amount of the pharmaceutical compounds in the effluent of the treatment processes is higher than the amount in the influent for carbamazepine. Although the reasons for this are not completely known, reconjugation of the metabolites into the original compounds during the treatment can be one of them (Joss, 2005).

A conceptual model for Australian sewage was developed by (Khan and Ongerth, 2004) to be able to predict the removal efficiencies of pharmaceuticals in different stages of a WWTP. 50 pharmaceuticals including the representative compounds are put in the model and the results are given in Table 4.8 Ratios for removal mechanisms (sorption and biodegradation) are also shown in the table. According to the predictions, it was found out that there is no significant removal of the representative compounds either in primary or secondary sedimentation. Aeration tank is the treatment unit where the removal rates are the highest (Mohle et al., 1999).

Table 4.8 Predicted concentrations and removal rates for some pharmaceuticals in a WWTP model.

Name	Influent (µg/l)	Primary Effluent (µg/l)	Aeration tank Effluent (µg/l)	Clarifier effluent (µg/l)	Removal to sludge (%)	Bio Degradation (%)	Total removal (%)
Carbamazepine	2	2	1	1	6	33	39
Diclofenac	0.4	0.4	0.3	0.3	7	24	30
Ibuprofen	1	1	0.6	0.6	4	49	52
Metoprolol	0.09	0.09	0.06	0.05	4	39	42

When the theoretical data from the Table 4.6 and the practical data gathered from the previous studies are compared, it was found out that the practical biodegradation rates of the representative compounds in real WWTPs are much different than the ones, which are predicted. Unreliable results from the conceptual model can be explained by the limited available data gathered from the batch scale studies (Mohle et al., 1999).

4.2.1 Concluding remarks

All the information gathered from the literature on the removal efficiencies of selected pharmaceutical compounds in the conventional WWTPs are given in Table 4.9.

Table 4.9 Summary of the removal efficiencies for each pharmaceutical compound according to the treatment process configurations

		Removal Efficiency (%)			
Reference	**Configuration ***	**Carbamazepine**	**Diclofenac**	**Ibuprofen**	**Metoprolol**
(Ternes, 1998)	PS+AS	7	69	90	83
(Miao et al., 2005)	PS+AS+UV	29			
(Castiglioni et al., 2006)	PS+AS	not significant		65 **	
(Huggett et al., 2003)	PS+AS+CL				87
(Clara et al., 2005)	PS+AS+AD	not significant	not significant	95	
(Joss, 2005)	AS	not significant	20-40	95	

* (PS—primary settling, AS—activated sludge system, AD—anaerobic sludge digestion, UV-Ultra violation, CL-Chlorination)

** Average removal per year (38% winter, 93% summer)

Primary sedimentation and activated sludge are the processes, which are used the most for the conventional systems (Figure 4.7). The general scheme of the conventional WWTPs is given in Figure 4.7.

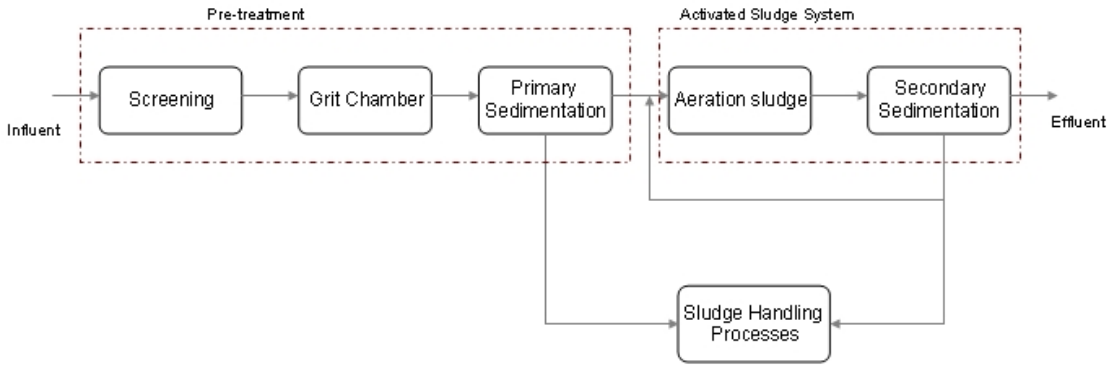


Figure 4.7 The scheme of the conventional wastewater treatment system

According to the studies, no relation was found between the SRT and the removal efficiencies of the pharmaceutical compounds. In one of the studies 5 days was stated as a minimum SRT value for the high removal rates of ibuprofen. Summarizing all the information given in this subchapter (Table 4.9), the conventional WWTPs (Figure 4.7) are not sufficient in removing all pharmaceutical compounds from the wastewater. Only ibuprofen can be removed efficiently until a certain level. Diclofenac and metoprolol are partially removed in full scale systems, whereas no significant removal of carbamazepine

shows that this compound is highly persistent. Different behaviors of the compounds in conventional WWTPs affirm that the selected compounds represent different groups of pharmaceuticals. Further treatment steps are necessary for better removal of the pharmaceuticals to be able to minimize the potential environmental impacts.

4.3 Fate of the Pharmaceuticals in Subsequent Treatment Processes

In this section the behavior of pharmaceutical compounds in each single treatment process was analyzed by studying the published researches.

4.3.1 Pre-treatment:

Screening

Screening is generally the first unit operation placed in the wastewater treatment plants. A screen is a device, which can have different size of openings, used to retain solid particles found in the influent wastewater (Metcalf&Eddy et al., 2003).

In a study of (Carballa et al., 2004) in a WWTP in Spain, no significant reduction on ibuprofen was detected during screening process. Although reported information could not be found for the other representative compounds, it is not expected any representative compounds to be retained during the screening process.

Grit Removal

Grit chambers are generally placed between screening and primary sedimentation. The function of these chambers is to remove heavy mineral solids such as sand, gravel, cinders (Metcalf&Eddy et al., 2003). No significant reduction of ibuprofen was detected during grit removal process in a WWTP in Spain (Carballa et al., 2004). None of the representative compounds are expected to be removed by grit removal process.

Primary Sedimentation

Primary sedimentation unit is a preliminary step, designed to remove readily settleable solids and floating materials. The removal of these materials reduces the suspended solids content of the wastewater (Metcalf&Eddy et al., 2003). Settleable solids accumulating at the bottom of the sedimentation tanks are removed regularly, as sludge. The biological oxygen demands (BOD) can be removed from 25 to 40% and suspended solids from 50 to 70% in an efficiently designed and operated primary sedimentation tanks (Metcalf&Eddy et al., 2003). Literature data for the removal efficiencies obtained in primary sedimentation process are summarized in Table 4.10.

Table 4.10 Removal efficiencies of macro-pollutants in primary sedimentation (Mels, 2001)

	Pre-settling
TSS	30-40%
COD	20-30%
BOD	20-30%
N-Kj	5-10%
Total P	10-20%

No significant reduction of ibuprofen was detected during primary sedimentation process in a WWTP in Spain (Carballa et al., 2004).

Changes in concentration of carbamazepine and its metabolites after different treatment units are shown in Figure 4.8. After the primary treatment an unexpected decrease in the concentration of carbamazepine and its main metabolite, CBZ-DiOH, is presented in the figure (from A to B). Although the removal efficiency of the primary treatment is stated as 46% (Miao et al., 2005), this result is contradictory with the other studies and the lab-scale experiments performed on the sorption potential of the carbamazepine as mentioned in Chapter 4.1.

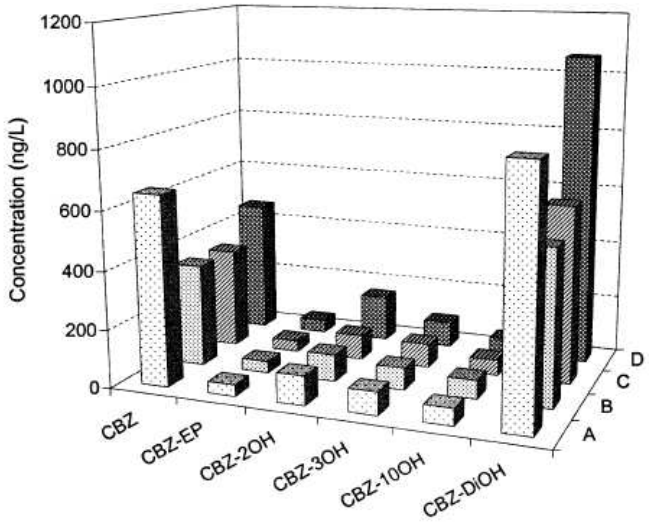


Figure 4.8 Mean concentrations of (ng/L) of CBZ (carbamazepine) and its metabolites in the aqueous phase of wastewater in different sampling sites of Peterborough WWTP. Sampling sites: A; untreated sewage, B; primary sewage, C; after the activated sludge process, D; treated sewage (after UV treatment)(Miao et al., 2005)

According to the K_{ow} value and the sorption potential of the compounds, only diclofenac and ibuprofen are expected to be sorped on the suspended particles. However, there is no literature data, which shows any significant removal of these representative compounds by sorption mechanism in primary sedimentation.

Coagulation- Flocculation

Coagulation-flocculation is a physico-chemical process, which removes the suspended solids and colloidal from the wastewater. To be able to agglomerate the particles mineral salts or organic compounds are added to the process. Agglomeration causes the elimination of these particles by settling or filtration (Carballa et al., 2003)

Addition of coagulation-flocculation and flotation units is a modification possibility as a primary treatment to improve the removal capacity of some pharmaceuticals in the current WWTPs. Usage of additives and the appropriate adjustment of the operational conditions provides better removal efficiencies in coagulation-flocculation process (Carballa et al., 2003).

In a lab research done by (Carballa et al., 2003), it was stated that the behavior of pharmaceuticals were different during the coagulation-flocculation processes for acidic and neutral compounds. It was found out that the higher removal efficiencies (50-70%) of diclofenac occurred with coagulants ferric chloride ($FeCl_3$) and aluminium sulphate (Al (SO_4)) at 25°. It was observed that the removal efficiency was not dependent on the dose of the coagulant. No significant removal of ibuprofen was observed and no effect on carbamazepine was detected in the experiments.

No significant removal of carbamazepine, diclofenac and ibuprofen was observed in lab-scale coagulation-flocculation process experiment (Ternes et al., 2004a). Similar results were obtained in another study with some pilot scale experiments. As a contrary to the study of (Carballa et al., 2003), it was concluded that flocculation with iron (III) chloride is very inefficient for carbamazepine and diclofenac. The high polarity of the compounds causes nonappreciable sorption quantities (Ternes et al., 2002).

Among the studies performed on the removal efficiencies of the representative compounds, there is no clear evidence showing that coagulation-flocculation is an effective process in the elimination of these compounds.

Flotation

The aim of the floatation process is to remove solid or liquid substances by adding fine gas bubbles to the influent water. The bubbles push the solids or emulsified liquid substances to the surface by attaching on them (Mels, 2001).

With flotation process no significant removal of pharmaceutical compounds was obtained in lab scale experiments except 20% removal of carbamazepine (Carballa et al., 2003).

4.3.2 Main Treatment

Conventional Activated Sludge

For the municipal wastewater treatment systems, activated sludge system is one of the most practiced treatment techniques. Degradation of organic material, BOD, in the wastewater is aimed in the activated sludge systems. By using an appropriate configuration of the reactor, nutrient (N, P) can be also removed. Bacterial flocs play a significant role in the removal of the pollutants. These flocs are then removed in the secondary clarifier. One part of the flocs accumulated in the secondary clarifier is returned to the beginning of the plant (return activated sludge) while the other part is disposed as a waste sludge or/and goes to sludge treatment units. Activated sludge systems can be distinguished as high and low loaded. High loaded systems aim to remove organic content. Low loaded systems are designed to remove nitrogen by means of nitrification and denitrification. Removing the phosphorus from the wastewater can be achieved by placing an anaerobic zone in the beginning of the installation. Phosphate accumulating bacteria play role in the removal of phosphorus (Mels, 2001).

The current wastewater treatment plants in the Netherlands are based on activated sludge process (Mels, 2001). According to the Central Bureau Statistics of Netherlands, in 2005 the average removal rates of COD, BOD, Tot N and Tot P were 92%, 98%, 74% and 82% respectively in the treatment plants working with activated sludge process.

In activated sludge systems, biodegradation and sorption are the two mechanisms, which are responsible for the removal of the pharmaceutical compounds from aqueous phase. Biodegradation occurs in the reactor tank, mainly in the aerobic part, where air is provided and sorption takes place in both activated sludge and the secondary clarifier. Several studies, which were done to find out the removal efficiencies of the representative compounds in the activated sludge systems, are mentioned below.

In activated sludge processes in a municipal WWTP, the removal efficiency of metoprolol was reported as high as 83% (Miege et al., 2006;Ternes, 1998). However, according to the results from (Paxeus, 2004), the removal efficiency of metoprolol with activated sludge process was lower than 10%.

According to (Carballa et al., 2004), 60-70% removal efficiency for ibuprofen was obtained. It was stated that suitable SRT and combining the anoxic/aerobic steps could improve the removal efficiencies of pharmaceuticals in activated sludge systems. Many studies were done to determine the effects of SRT, HRT and the reactor configuration on the removal capacity of the pharmaceutical compounds. No significant change was observed in the removal capacity by changing HRT by factors of more than 10 for the compounds, carbamazepine, diclofenac and ibuprofen (Joss, 2005). The same result was observed for different SRT values. Although the sludge age was changed between 10 and 60-80, no significant impact is observed on the transformation efficiency of the compounds, carbamazepine, diclofenac and ibuprofen (Joss, 2005).

Similar results were observed for diclofenac in the research done by (Clara et al., 2005). Although in one of the WWTPs investigated, 70% of removal rate for diclofenac was measured, no removal rate was observed in all of the other WWTPs. In a test done in a pilot sewage plant by (Zwiener and Frimmel, 2003), 60% removal was achieved for ibuprofen. According to this study, 5% of the removal was obtained by sorption to the sludge. Similar to the previous studies, diclofenac was neither degraded in aeration reactor nor sorbed in the settling tank as expected.

As a result of a research where lab scale experiments were performed related to the influence of SRT on carbamazepine removal in activated sludge units, it can be stated that there is no influence of SRT on carbamazepine removal rate (Figure 4.9). No significant removal of carbamazepine either by degradation or by adsorption was observed in the lab analysis (Clara et al., 2005;Clara and Strenn, 2004). In another full scale study carried out in a WWTP in Berlin, a similar result was reported where there was only 8% removal rate, which is not significant (Heberer, 2002).

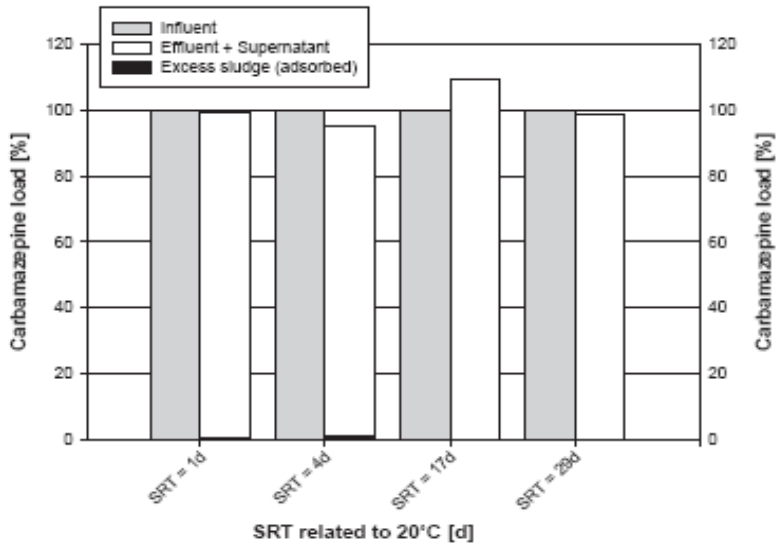


Figure 4.9 Loads of carbamazepine in the influent and effluent in activated sludge with changing SRT (Clara and Strenn, 2004)

In a study perform in Brazil, the removal efficiencies of activated sludge process and biological (trickling) filter for pharmaceutical compounds and their metabolites were compared. It was concluded that activated sludge is more effective process in removing pharmaceuticals and their metabolites than biological filter. A 75% removal efficiency was obtained in activated sludge process for both ibuprofen and diclofenac whereas the efficiency in biological filter was 22% for ibuprofen and 9% for diclofenac Figure 4.10 (Stumpf et al., 1999).

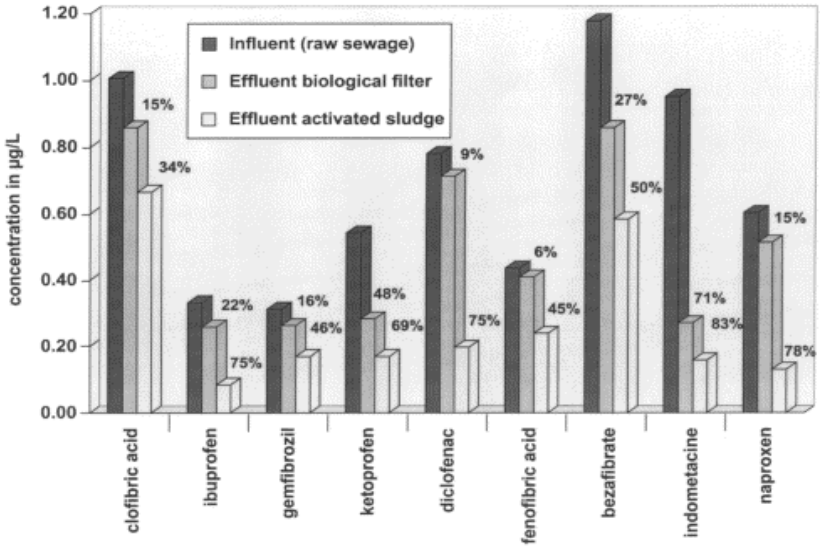


Figure 4.10 Removal efficiencies of biological trickling filter and activated sludge in WWTP (Stumpf et al., 1999).

As a summary of all the information given above, similar results are obtained from the literature review with the expected results considering the biodegradation constants of the representative compounds (Chapter 4.1). It can be concluded that activated sludge system is an efficient unit for ibuprofen, which has a high degradation constant and medium sorption potential. Diclofenac is removed partially in the systems. It can be stated that mainly biodegradation mechanism is responsible for removal of diclofenac, since sorption potential of this compound is low. As expected, because of the low biodegradation constant and low sorption potential, no significant removal of carbamazepine was observed in all of the activated sludge systems studies. Contradictory results were found in the literature review for metoprolol. Considering the sorption and biodegradation coefficients of this compound, to certain extent biodegradation is expected in the activated sludge process whereas no sorption is assumed in the sedimentation phase because of its low sorption coefficient.

Membrane Bioreactor

Membrane bioreactor consists of membrane separation process in combination with biological processes. Almost solid-free permeate is obtained whereas the microorganisms are retained in the bioreactor (Yang et al., 2006).

Not many studies related to the treatment of concentrated water with MBR systems, were found in the literature. In the study of (Machdar et al., 1997), it was reported that 97% removal efficiency was obtained for total solids in an aerated reactor which was used as a post treatment.

MBRs are also used in the treatment of **grey water** as a polishing step. There are some studies carried out to determine the pollutant removal efficiencies of MBRs introduced by grey water. In Table 4.11, the removal rates of pollutants during the aerobic treatment of grey water in MBRs are according to different published studies.

Table 4.11 The removal rates of pollutants of grey water in MBR

MBR	Removal rates (%)					References
	TSS %	COD %	BOD %	Tot N %	Tot P%	
	100	97	98	79		(Cote et al., 1998)
	100	95		53	52	(Lesjean and Gnirss, 2006)
	85	89				(Jefferson et al., 2001a)

In the study where the removal efficiencies of CAS, MBR and fixed bed reactor were compared no significant removal of pharmaceuticals was observed for MBR. Since the molecular size of the compounds are at least 100 times smaller than the pore size of the membranes, it was concluded that micro and ultra filtration membranes can not remove pharmaceutical compounds by sieving (Joss, 2005). No significant change was observed in the removal capacity by changing HRT by factors of more than 10 for the compounds, carbamazepine, diclofenac and ibuprofen (Joss, 2005). Although the sludge age is changed between 10 and 60-80 d, no significant impact is observed on the transformation efficiency of the compounds, carbamazepine, diclofenac and ibuprofen. The overall removal efficiencies was 20-40% for diclofenac and >95% for ibuprofen whereas no significant removal was observed for carbamazepine (Joss, 2005).

A study was carried out on the behavior of ibuprofen during the membrane bioreactor process. During the mineralization of ibuprofen two isomers of hydroxyl-ibuprofen were detected. In the effluent of the membrane bioreactor none of these metabolites was detected, and the removal efficiency of Ibuprofen and its metabolites was stated as approximately 99% (Quintana et al., 2005). Similar result, >90% removal efficiency of Ibuprofen in MBR was achieved in several studies (Buser et al., 1999;Ternes, 1998).

(Clara and Strenn, 2004) searched for the removal efficiencies of carbamazepine in MBR and investigated whether there is any influence of SRT on the removal rates. No significant retention of carbamazepine was detected in MBR even when SRT was changed in a range of 10-100 days, Figure 4.11.

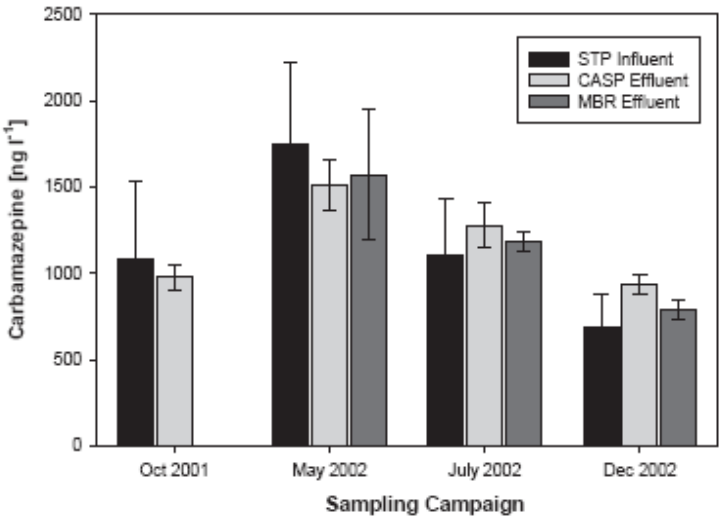


Figure 4.11 Comparison of the concentrations of carbamazepine in the influent and the effluent of the CASP with membrane bioreactor. SRT was increased between May to Dec 2002, from 10 to 100 days (Clara and Strenn, 2004).

No removal of diclofenac was observed in MBR when it was operated with approximately 10 days of SRT. Partial removal of diclofenac was measured only in one of the WWTPs investigated, due to the higher SRT value. However, no explanation could be stated for the increased removal rates (Clara et al., 2005).

It can be stated that according to the available literature, MBR has not more advantage over the conventional systems in removing the pharmaceuticals.

Biofilm Reactor

When a biofilm reactor (BFR) is compared with the activated sludge, it was found out that removal of ibuprofen is more effective in oxic biofilm reactor (70%). In oxic BFR, hydroxyibuprofen was detected as the major metabolite of ibuprofen (Zwiener, 2002) but in the study of (Zwiener and Frimmel, 2003), its concentrations were below 10% of the degraded amount of ibuprofen. In anoxic conditions, no significant removal was obtained for ibuprofen, whereas the removal efficiency of diclofenac was 35%, better than in activated sludge process (Zwiener and Frimmel, 2003).

Anaerobic Digestion

Organic materials from different types of wastewater, solid waste and biomass are converted by the anaerobic digestion process. Biogas is one of the end products of the process. Biogas consists of methane (55-75%) and carbon dioxide (25-45%) (STOWA, 2005). Four major steps occurring during the anaerobic digestion are haydrolysis, acidogenesis, acetogenesis and methanogenesis. There are different types of anaerobic digestion technical configurations. Accumulation system (AC) and upflow anaerobic sludge blanket (UASB) are two of them studied in this research.

Accumulation System (AC)

Accumulation system is the simplest configuration for anaerobic digestion for wastewater. Biological conversion of the wastewater takes place in combination with its storage. The tank is fed continuously until the maximum volume. After reaching the max volume the tank is emptied at once.

According to a study performed, black and brown water collected with vacuum toilets and the solid kitchen waste were introduced into the accumulation system. It was measured that 58% of the organic materials were transformed into biogas at 20℃ in a period of 105 days (Elmitwalli et al., 2006b).

UASB

In the UASB reactors, after the wastewater is introduced to the reactor from the bottom, it moves in an upflow mode through a sludge blanket. UASB reactors have advantage on other anaerobic processes since it allows the use of high volumetric COD loadings (Metcalf&Eddy et al., 2003).

Treatment of grey water in high rate anaerobic systems, such as a UASB reactor is efficient since the grey water has a relatively higher temperature compared to sewage (Elmitwalli et al., 2006a;Eriksson et al., 2002).

UASB Septic Tank

The major difference between a normal UASB tank and a UASB septic tank is that UASB septic tank accumulates and stabilizes the sludge. Besides, UASB septic tank achieves better suspended solids removal and biological conversion (STOWA, 2005). According to (Bogte et al., 1993) and (Lettinga et al., 1993), with higher operational temperatures high removal efficiencies are achieved in UASB septic tanks with total wastewater and concentrated black water (STOWA, 2005).

A UASB septic tank system is the alternative solutions to treat the total wastewater streams with higher removal efficiencies (Lettinga et al., 1993). For the total wastewater treatment with UASB septic tank, it was reported that COD was removed up to 80-90% where 70% average removal efficiency can be obtained at 20℃. Because of low sludge growth rate , withdrawal frequency of the excess sludge is low (once, twice/year) (Seghezzo, 2004).

From the literature the removal efficiencies of the pollutants were found for the UASB septic tank, where concentrated black water collected with vacuum toilets, was treated. These efficiencies are given in Table 4.12. In an ongoing lab experiment, the fraction of BOD_{30}/COD_{tot} was measured in the effluent of an UASB septic tank, which is fed with concentrated black water. It was found out that 50% of the total COD is formed by BOD in the effluent of UASB septic tank (personal communication with de Graaff, Marthe). It was reported that the large amount of the phosphate and nitrogen in the effluent are in soluble form of ammonium and phosphate respectively. Therefore, UASB system is a promising technology for recovery and reuse of the nutrients (Kujawa-Roeleveld et al., 2005).

Table 4.12 Average removal efficiencies obtained by the UASB septic tanks fed with concentrated black water from a vacuum toilet at two temperatures (STOWA, 2005) *(Luostarinen et al., 2007;Luostarinen and Rintala, 2005)

	Removal %	
	T=15 ºC	**T=25 ºC**
TSS	No data	90*
COD total	61	78
COD particulate	88	94
Total N	No data	16
Total P	No data	56

UASB septic tank was reported as an alternative technique for pre-treatment of the grey water in both rural and urban areas (Kujawa-Roeleveld et al., 2006). According to the published studies, COD removal efficiency of UASB septic tank for grey water was reported as 65% (Elmitwalli and Otterpohl, 2007) and 40% (Leal et al., not published). In the study of (Elmitwalli and Otterpohl, 2007), it was reported that with UASB septic tank, total N and total P were removed until 26% and 18% respectively. No solid removal efficiency was found in the literature for the treatment of grey water with UASB septic tank.

Anaerobic degradation of pharmaceuticals

In a research of (Ternes et al., 2005), two conventional anaerobic pilot scale sludge digesters, mesophilic and thermophilic, were operated. Influents containing different pharmaceutical compounds were fed to the reactors to determine their removal efficiencies. Since the data was not accurate, it was not sure if carbamazepine was removed partially or not removed at all. A range for removal was reported as high as 0-60%. Removal of diclofenac could not generally be quantified but in the cases it could be measured, the efficiency was changing between 25 and 75%. For ibuprofen, both reactors gave medium elimination capacity of 20-45% (Ternes et al., 2005).

In the study of (Carballa et al., 2007), some of the representative compounds were removed to some extent whereas no elimination was observed for carbamazepine (Table 4.13).

Table 4.13 Removal of pharmaceuticals in conventional anaerobic digestion of sludge (Carballa et al., 2007)

Compound	**Mesophilic**	**Thermophilic**
Carbamazepine	No removal	No removal
Diclofenac	0-75%	25-75%
Ibuprofen	45±15%	47±10%
Metoprolol	No data	No data

In another study, (Carballa et al., 2006) studied removal efficiency of anaerobic digestion on pharmaceuticals and obtained more certain results. A high removal

rate of diclofenac was obtained after the adaptation of the sludge. The results of that study are shown in Table 4.14.

Table 4.14 Removal of pharmaceuticals in anaerobic digestion of sludge. (Carballa et al., 2006)

Compound	Mesophilic	Thermophilic
Carbamazepine	No removal	No removal
Diclofenac	60±18%	73±9%
Ibuprofen	40±15%	47±10%
Metoprolol	No data	No data

Since there are not many studies done on the removal of pharmaceuticals in anaerobic digestion, no strong conclusion can be made. With the data available, it can be stated that diclofenac and ibuprofen have higher potentials to be removed whereas carbamazepine is not expected to be removed by anaerobic digestion.

Infiltration

A combination of physical, chemical and microbiological processes play role in the purification of the water by infiltration.

A 40% of elimination of diclofenac was measured in unsaturated sand zone whereas carbamazepine showed no removal efficiency. Ibuprofen had similar behavior with diclofenac with approximately 55% removal efficiency (Table 4.15) (Scheytt et al., 2006).

Table 4.15 Comparison of removal efficiencies of pharmaceuticals during sand infiltration (Scheytt et al., 2006)

		Carbamazepine	Diclofenac	Ibuprofen
Sat [a]	Recovery	93-105%	97-106%	9-46%
Unsat [b]	Recovery	102%	63%	46%

[a] Sat = column experiments under water saturated conditions; DOC = 0.2%, pH = 6.7, medium sand (Mersmann et al., 2002;Scheytt et al., 2004)
[b] Unsat = column experiments under unsaturated conditions (this publication).

In another study made by (Ternes et al., 2005;Ternes et al., 2004a), in unsaturated zone the concentration of diclofenac decreased below the limit of detection (LOD) after a flow time of 75 days. On the other hand only 30% removal was achieved for carbamazepine after a flow time of 100 days.

No significant removal of carbamazepine was detected during groundwater infiltration. The concentrations of carbamazepine in the groundwater were lower because of the dilution processes (Clara and Strenn, 2004). The behavior of the carbamazepine was studied by (PreuX et al., 2001) and according to the comparable results poor removal during the soil passage was reported.

4.3.3 Tertiary Treatment

Ozonation, advanced oxidation processes, nanofiltration and activated carbon adsorption were found to be the possible promising techniques for further removal of pharmaceuticals.

Ozonation

Ozone is an oxidant, which is used widely in wastewater and drinking water treatment. It is used for disinfection and oxidation purposes to control taste and odour, decolouration and to remove the micropollutants including pharmaceuticals (Huber et al., 2003;Ternes and Joss, 2006;von Gunten, 2003a). Direct reaction of ozone or OH radicals is required for the ozonation to occur. OH radicals represent the strongest oxidants in water formed during spontaneous ozone decomposition. Electron donating groups such as amines, conjugated double bonds accelerate the reaction rate. On the other hand electron withdrawing groups such as alcohol, aldehydes, ketones, iodine and chloride reduce the reaction rates of ozonation. Chemical oxygen demand of a treated wastewater (generally 15-50 mg COD/L) is another important parameter in ozonation process, since it is significantly higher than the oxidation equivalents required for pharmaceuticals (Ternes and Joss, 2006;von Gunten, 2003b).

According to the study of (Beltrán et al., 1999), with approximately 15 $mg.L^{-1}$ applied ozone does, 11% removal of the COD was reported in a post-ozonation process applied after the activated sludge process whereas no significant change was stated on nutrient removal during the ozonation process.

It is stated that ozonation is a very efficient technique to remove pharmaceuticals in biologically treated wastewater (Huber et al., 2003;Ternes et al., 2002;Ternes et al., 2003;Zwiener et al., 2000). According to (Andreozzi et al., 2002), ozonation is a proper method to eliminate carbamazepine. As a result of a research done in a pilot plant by (Ternes et al., 2003), ozone dose range between 10-15 $mg.L^{-1}$ and 18 minute contact time were necessary to eliminate pharmaceuticals in 90-99%, including carbamazepine, diclofenac, metoprolol and ibuprofen, from the wastewater (Figure 4.12). Higher ozone requirement compared to other researches can be explained by the presence of high bulk organics in the effluent, 30 mg/L COD.

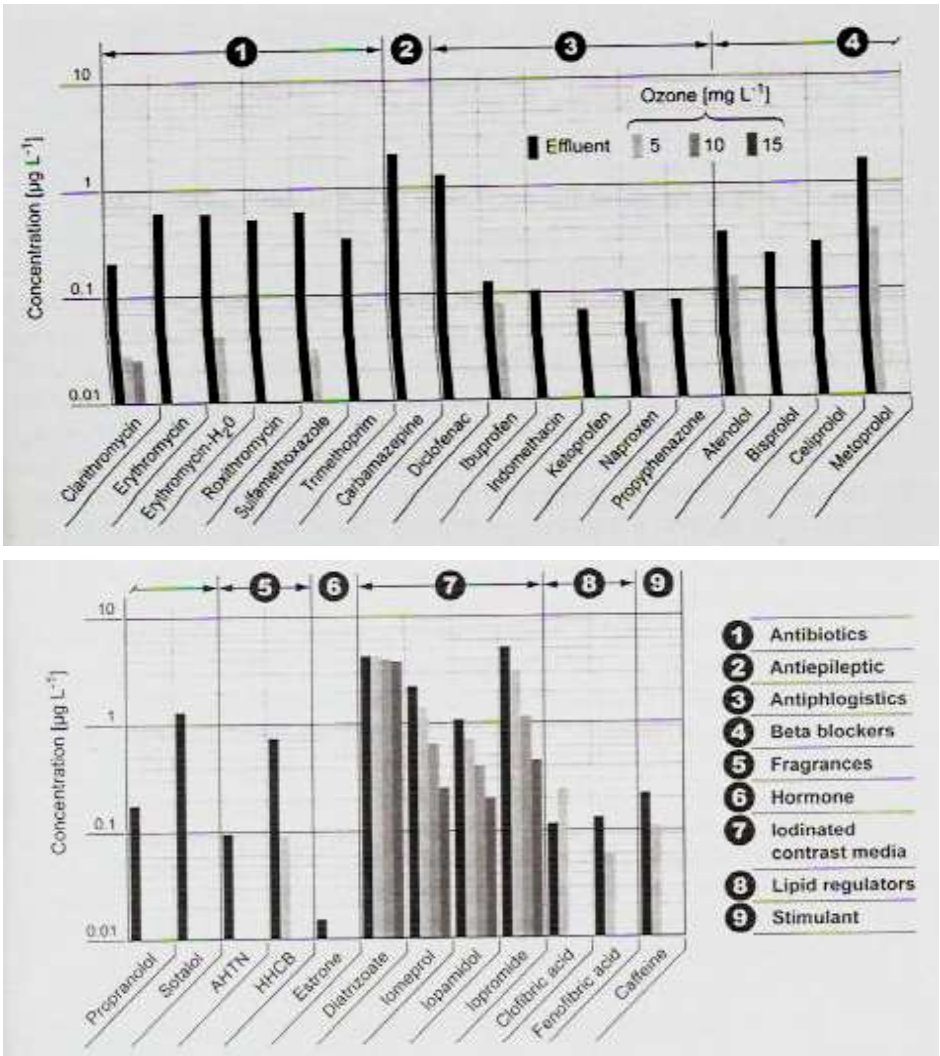


Figure 4.12 Concentrations of pharmaceuticals including carbamazepine, diclofenac, ibuprofen and metoprolol by ozonation in the effluent of a municipal WWTP (Ternes and Joss, 2006;Ternes et al., 2003)

According to (Huber et al., 2003), complete ozonation does not occur after the reaction of the pharmaceutical compounds with ozone. The ozonation may not eliminate all the metabolites and formation of some toxic metabolites can cause further problems. In another research done in experimental conditions, the removal efficiencies of pharmaceutical compounds from urine were investigated in ozonation process. It was found out that 0.6-0.8 g/L ozone dose is enough to decrease propranolol, diclofenac and carbamazepine concentrations below LOD, whereas for ibuprofen, 1.3 g/L ozone dose is required. However it is stated that although all parent compounds disappeared, toxicity of the compounds still appears since the compounds were only transformed and not mineralized (Escher et al., 2006). On the other hand, another study proves that ozonation is an appropriate study to decrease the toxicitiy after 2-3 minutes application of AOPs e to the synthetic aqueous solution (Andreozzi et al., 2004). However full

scale studies should be done to be able to give reliable conclusions about the effect of AOPs on the toxicity of the pharmaceuticals.

Beside ozonation is the most promising treatment process for removing pharmaceuticals from wastewater it is an energy intensive technology. 15-20 kWh/kg ozone is needed for the ozone production and depending on the energy price it costs 0.8-1.6 €/kg (Ternes and Joss, 2006). Approximately 0.1 $kWh.m^{-1}$ is needed for the ozonation process and this cause a 40-50% increase in the energy demand of normal WWTPs (Larsen et al., 2004).

Advanced Oxidation Process (AOP)

AOP is considered as a good choice in order to treat the hazardous nonbiodegradable pollutants including pharmaceuticals. Hydroxyl radicals (OH), which are very reactive and are produced in AOP process, play an important role in the mineralization of the pharmaceutical compounds in the final stage (Perez-Estrada et al., 2005).

There are different AOPs, one of which is photo-fenton treatment. Photo-fenton treatment is the most promising process, which provides complete mineralization of diclofenac among AOPs (Perez-Estrada et al., 2005;Ravina et al., 2002). In photo-fenton treatment, total mineralization of diclofenac (disappearance of DOC) was achieved in 100 minutes, while total degradation required 60 minutes (Perez-Estrada et al., 2005).

With H_2O_2, complete transformation (90-99%) of the parent compounds of carbamazepine and diclofenac is stated in most of the studies done. In some of the studies even better results were obtained with H_2O_2 compared to ozone. However, lack of complete mineralization of the parent compounds and formation of toxic by products during the process provides no reduction in the toxicity effect on the living organisms (Andreozzi et al., 2004).

Membrane Filtration

Membrane filtration is a treatment process where the pollutants and the carrier liquid are separated by forcing the liquid through a permeable or semi permeable membrane. With membrane process, specific pollutants can be removed according to the size of the compounds and the pore size of the membrane. In Table 4.16 removal efficiencies of organic compounds, suspended solids and the nutrients are given.

Table 4.16 Removal efficiencies of direct membrane filtration for the macro pollutants

	Removal Efficiency of Direct Membrane Filtration (%)
TSS	100
COD	69
BOD	No data
P_{tot}	17
N-Kj	36

Nanofiltration and reverse osmosis are the tight membrane filtration processes, which allow the retention of the pharmaceutical compounds by molecular sieving (Ternes and Joss, 2006). Regarding the studies conducted, compound rejection in membrane systems depends on the molecular width, size and the hydrophobicity which describes the charge and the polarity of the compound (Yoon et al., 2006). Less polar, more volatile and more hydrophobic compounds have more ability to be retained by nanofiltration membranes.

According to the results of a study made in a membrane testing unit, carbamazepine, diclofenac and ibuprofen were retained from the surface water in 100% with nanofiltration. The same removal efficiencies were obtained for diclofenac and ibuprofen with ultrafiltration whereas the removal efficiency of the carbamazepine was <80% (Yoon et al., 2006). In general, the results for the selected pharmaceuticals in the study (Yoon et al., 2006) nanofiltration showed better removal efficiencies than ultrafiltration did.

In an experimental research, using nanofiltration for urine, it was found that 74%, 96%, 96% and 59% removal efficiencies were achieved for carbamazepine, diclofenac, ibuprofen and propranolol (beta-blocker, same group with metoprolol), respectively. A nanofilter type of NF270 is used as membrane (Escher et al., 2006). In the same study it was also stated that nanofiltration removed both natural and xenobiotic compounds from the urine. These compounds play an important role in the inhibition of growth and photosynthetic reactions in algae Therefore it can be concluded that by nanofiltration toxicity was reduced 80-90% by nanofiltration (Escher et al., 2006).

(Pronk et al., 2006) found in his laboratory research >92% retention from non-hydrolysed urine at pH=5 was achieved for all micro pollutants investigated including carbamazepine, diclofenac, ibuprofen and propranolol. 92% efficiency was achieved for at pH 5 (Figure 4.13). Again it was demonstrated that NF270 showed the best removal performance among the membranes.

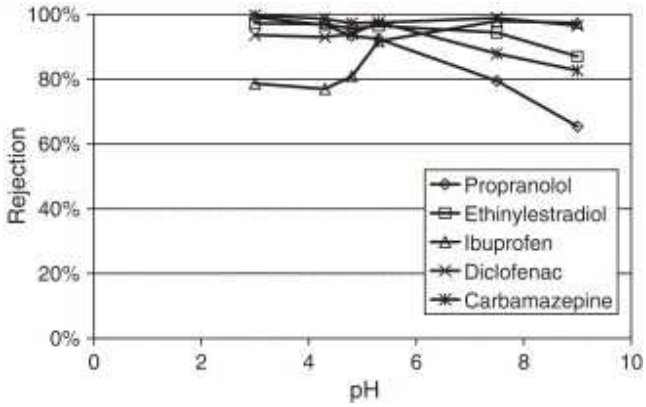


Figure 4.13 Rejection of micropollutants depending on the pH for natural human urine using NF270 nanofiltration membrane (Pronk et al., 2006).

In the same study, recovery of nutrients was also investigated. Separation of nitrogen and phosphorus was done in the nanofiltration process. Figure 4.14 demonstrates the results of the study. Considering the figure, phosphate was

separated from the urine up till 100%, whereas >80% of ammonia passed through the filter.

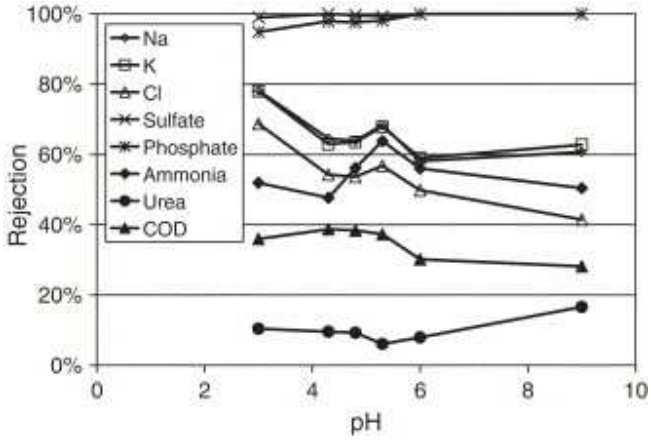


Figure 4.14 Rejection of organic compounds and nutrients depending on pH for natural urine using NF270 nanofiltration membrane (Pronk et al., 2006).

Required energy is changing between 0.5 and 3 $kWh.m^{-3}_{wastewater}$ for nanofiltration process (Joss et al., 2006).

Nanofiltration and reverse osmosis seem to be more promising membrane process types. However since there is not much studies done on the efficiencies of these tight membrane technologies on representative compounds, no conclusion can be made.

Activated Carbon Adsorption

Activated carbon is a common used process used for elimination of micro pollutants including pharmaceuticals (Ternes et al., 2005). In a lab scale experiment the removal efficiencies of pharmaceutical compounds by adsorption on Powdered Activated Carbon (PAC) was investigated. It was found out that 99% removal of carbamazepine can be achieved with < 0.2 $mg.L^{-1}$ PAC dose. As it is shown in Figure 4.15 higher doses of PAC (<1.0 $mg.L^{-1}$) is required to be able to remove ibuprofen (Ternes et al., 2005).

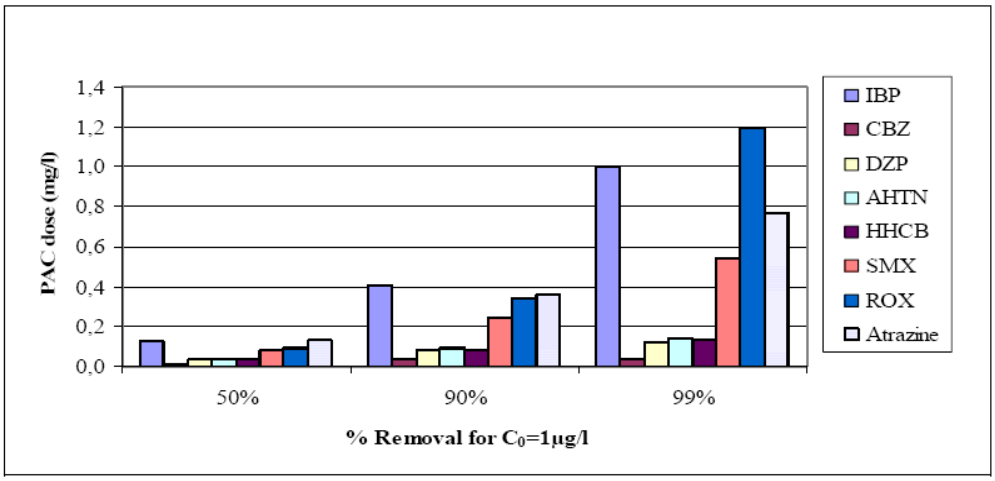


Figure 4.15 PAC doses needed for the removal efficiencies of 50%, 90% and 99% for different pharmaceutical compounds including carbamazepine and ibuprofen.

In one of the studies similar conclusions were derived that activated carbon filtration is efficient for carbamazepine and diclofenac (Ternes et al., 2002).

No information about the removal of metabolites and their toxicity was obtained during the literature review. A <0.05kWh.m$^{-3}_{wastewater}$ energy is required for AC process (Joss et al., 2006).

4.3.4 Treatment Processes for Nutrients Recovery

Stripping

When anaerobic treatment is used as a pre-treatment for the black water, stripping can be an alternative technique for nitrogen recovery (Kujawa-Roeleveld and Zeeman, 2006). At 20°C 95% recovery capacity of ammonia was achieved and 7 kWh.m^{-3} was stated as approximate energy consumption (Maurer et al., 2006).

Struvite ($MgNH_4PO_4$), MAP Precipitation (Phosphorus Recovery)

In the Struvite Precipitation process, Magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) also known as MAP, AMP or struvite is precipitated in the process tank. This precipitate, which is an important product containing two dominant wastewater nutrients (N, P), can be used as a slow release fertilizer (Bridger et al., 1961;Johnston and Richards, 2003;Maurer et al., 2006). According to (Gaterell et al., 2000) a product, 'enhanced struvite', can be produced from struvite, which may have a good market potential.

Application of struvite precipitation process was studied in detail for the recovery of N and P from digester supernatant (Maurer et al., 2006;Wu and Bishop, 2004) and for the treatment of wastewater. Addition of magnesium, in the form of MgO, $Mg(OH)_2$, $MgCl_2$ or bittern (the magnesium-rich brine from table-salt production) is necessary for the precipitation to occur.

In research done with an influent concentration of 110mP/L, which is similar to concentrated black water, is treated with MAP precipitation process and 90% of other phosphate was removed as a result of MAP precipitation (Kujawa-Roeleveld et al., 2006;Ueno and Fujii, 2001).

In an experimental research, removal efficiencies of pharmaceutical compounds from urine by struvite precipitation were investigated. After the filtration process, in filtrate 99% removal efficiency was achieved for carbamazepine, diclofenac, ibuprofen and propranolol (Escher et al., 2006). Similar results to (Escher et al., 2006) were obtained in another study by (Ronteltap and Maurer, 2006).

Ion Exchange (Nitrogen Recovery)

Zeolites (hydrated aluminum-silicate minerals) in synthetic ion exchanger have 87-98% of removal capacity for ammonium ions. These minerals are effective for both concentrated (up to 150gN.m^{-3}) and less concentrated (1000mgN/L) wastewater influents (Kujawa-Roeleveld et al., 2006;Nguyen and Tanner, 1998). In another study, (Lind et al., 2000), shows that 65-80% of the nitrogen was recovered from urine as crystalline or adsorbed ammonium in combination with struvite crystallization. (Ban and Dave, 2004) did laboratory studies on urine and reported that 0.5 mg/l MgO and 15g.L^{-1} zeolite dosages provide 99% and 90% removal efficiencies for P and N, respectively.

4.4 Concluding Remarks

In Table 4.17 the results of the literature review done on the removal efficiencies of the treatment processes for micro pollutants (pharmaceutical compounds, nutrients) and macro pollutants (COD, BOD,etc.) were given. During the design phase of the study (Chapter 5), removal efficiencies of pollutants were assumed within the ranges given for each specific treatment process in the table.

For the conventional system, it can be stated that, according to the previous studies, the removal efficiencies of AS system and MBR are quite similar for carbamazepine, diclofenac and ibuprofen. Since there was no available data for the removal efficiency in MBR for metoprolol, two processes could not be compared. Activated sludge system was used for the configuration of the conventional WWTP since it was the most common used process in the existing WWTPs. It can be concluded that with the available studies, MBR system would not be a more advantageous system from the better removal of pharmaceutical point of view. Concerning the removal mechanisms of the compounds during activated sludge process, it can be concluded the main removal mechanism of the pharmaceutical compounds in activated sludge process is biodegradation. In one of the studies it was stated that sorption was responsible for the 5% of the total pharmaceutical removal in the CAS process (Zwiener and Frimmel, 2003). This percentage was used during the design phase of the conventional WWTP.

Different tertiary treatment processes were investigated for upgrading the conventional WWTPs considering pharmaceutical removal. The main tertiary treatment processes investigated were ozonation, advanced oxidation process, membrane filtration, activated carbon adsorption. As it is shown in Table 4.18,

the removal efficiencies of pharmaceutical compounds for all four options of tertiary treatment were between 80-100%.

Among the anaerobic treatment processes, UASB septic tank was the tank configuration with the best treatment of black and grey water with high efficiencies of macro pollutant removals.

After reviewing the literature available, it was found out that struvite precipitation and ion exchange were the most commonly used phosphorus and nitrogen recovery processes respectively, with high efficiencies.

Table 4.17 The removal efficiencies of treatment processes on BOD, COD, TSS, N, P, Carbamazepine, Diclofenac, Ibuprofen, Metoprolol

	Primary Sedimentation	AS (ENBR)	MBR	(UASB septic)	Struvite Precipitation	Ion Exchange	Ozonation	Advanced Oxidation Process		Membrane Filtration	Activated Carbon Adsorbtion
								Photo-Fenton	H2/O2	Nanofiltration	
BOD removal	(-)	(++)	(++)	(++)							
COD removal		(++)	(++)	(++)						(-)	
TSS removal	(+)	(++)	(++)	(++)							
N removal /**recovery**		(++)				**(++) ***				**(--)**	
P removal /**recovery**		(+)			**(++) ***					**(++)**	
CBZ removal	(--)	(--)	(- -)	(--)	N/A	N/A	(++)	(++)	(++)	(++) **	(++)
DCF removal	(--)	(+ -)	(+ -)	(+)	N/A	N/A	(++)	(++)	(++)	(++) **	(++)
IBP removal	(--)	(++)	(++)	(+ -)	N/A	N/A	(++)	(++)	(++)	(++) **	(++)
MTL removal	(--)	(++)	N/A	N/A	N/A	N/A	(++)	(++)	(++)	(+?) **	N/A

(--) 0-20% removal, (-) 20-40% removal, (+ -) 40-60% removal, (+) 60-80% removal, (++) 80-100 removal, N/A Not available data

* urine, ** urine or surface water

[1] removal, [2] recovery

4.5 Determination of the Configurations of Treatment Processes for Combined Wastewater Treatment System

From the gathered literature data, it was concluded that existing conventional wastewater treatment systems are not sufficient in removing all of the representative pharmaceutical compounds (4.2). Additional treatment processes are necessary for further removal of pharmaceuticals in the existing systems. After the literature survey, ozonation, advanced oxidation process, nanofiltration and activated carbon adsorption were found to be the possible and promising techniques for further removal of pharmaceuticals (Chapter 4.3). It was found out that all four options have 80-100% removal efficiencies of pharmaceutical compounds. This is why the choice of the tertiary treatment process was based on the energy consumption of the processes. In Table 4.18, the removal efficiencies of each option on each pharmaceutical compound were given as well as their energy consumptions.

Table 4.18 The comparison of tertiary treatment options

	Ozonation[1]	**AOP[2]**	**Membrane Filtration[3]**	**Activated Carbon Adsorption[4]**
CBZ removal	90-99	90-99	80-100	90-99
DCF removal	90-99	90-99	90-100	90-99
IBP removal	90-99	90-99	90-100	90-99
MTL removal	90-99	90-99	80-90	N/A
Energy (kWh/m^3)	0.1	>0.1	0.5-3	0.05

[1] (Andreozzi et al., 2004;Escher et al., 2006;Larsen et al., 2004;Ternes et al., 2003)
[2] (Andreozzi et al., 2004;Perez-Estrada et al., 2005)
[3] (Escher et al., 2006;Joss et al., 2006;Pronk et al., 2006;Yoon et al., 2006).
[4] (Joss et al., 2006;Ternes et al., 2005;Ternes et al., 2002)

For activated carbon adsorption (ACA), there was no available data on the removal efficiency of metoprolol. ACA is the best option from the energy consumption point of view but because of the limited available data on the removal efficiencies of representative compounds it was not selected. According to their energy consumptions, ozonation was the option, which required second minimum energy consumption. As a result ozonation was selected for the upgrading the removal efficiency of the conventional WWTP for pharmaceutical elimination. The configuration for the conventional combined wastewater treatment system is given in Figure 4.16.

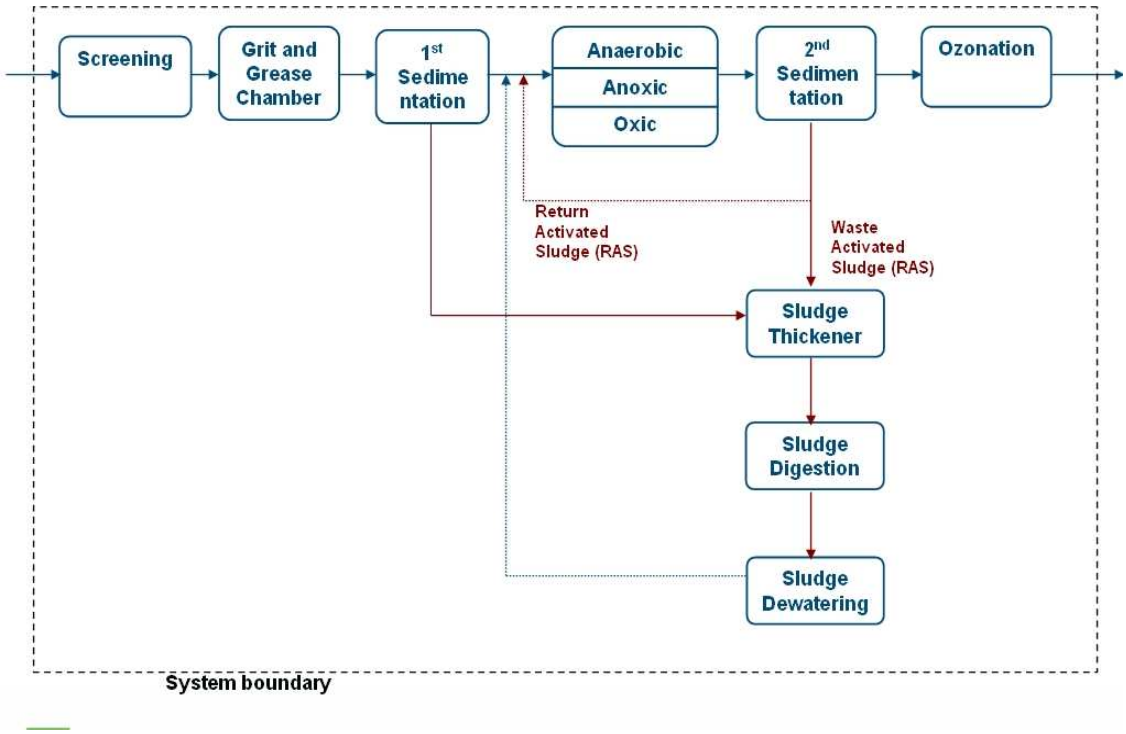


Figure 4.16 Flowchart of Conventional Wastewater Treatment System (System A)

4.6 Determination of the Configurations of Treatment Processes for Source Separated Wastewater Treatment System

Anaerobic pre-treatment is an ideal solution for an optimized treatment of the separated black water. Since the nutrients are concentrated in black water, recovery of them is much more feasible compared to the combined system. Besides the nutrients, energy recovery is also feasible when treating the concentrated streams anaerobically (Kujawa-Roeleveld et al., 2006). Among the anaerobic treatment options, UASB septic tank was selected with 25 C° operational temperature as a first treatment process for the black water.

According to the results of the studies, organic content concentration is high in the effluent of UASB septic tank, since the degradation of organic materials was incomplete because of the very concentrated influet (Kujawa-Roeleveld et al., 2006;Kujawa-Roeleveld and Zeeman, 2006). This is why, a post treatment was needed for the further removal of organic materials. In the literature MBR was found to be the most commonly used post treatment process (Holler and Trosch, 2001;Machdar et al., 1997) It was found out that a low SRT value is an important design parameter required in MBR system. Low SRT values prevent the removal of nitrogen by nitrification process and allow the recovery of nitrogen in the further processes.

Struvite precipitation and ion exchange were chosen to recover the phosphorus and nitrogen from black water. They were commonly used processes in literature for nutrient recovery with high efficiencies.

As a last step, a tertiary treatment process was selected to remove the pharmaceutical compounds while disinfecting the water from pathogenic organisms. For the selection of the tertiary treatment process, the same reasoning was applied as for the conventional WWTP. Ozonation was selected with its high removal efficiency of the selected pharmaceutical compounds and small energy requirement compared to the other options.

For the treatment of grey water, which is less heavily polluted than black water, UASB septic tank was an appropriate pre-treatment technique for most treatment systems (Kujawa-Roeleveld and Zeeman, 2006). As the anaerobic treatment is not a process with complete degradation of organic matter, post treatment was required. A MBR was selected as an appropriate post treatment process. Besides high removal efficiencies of organic materials, according to the literature, there was no E.colibacteria, intestinal enterococus and F-specific bateripphages as an indicator of viruses detected in the effluent of MBR (STOWA, 2007).This is why MBR process was used as disinfection process as well and there was no requirement for further processes. As a result the configurations of the treatment processes for the black and grey water in separated wastewater treatment system are given in Figure 4.17.

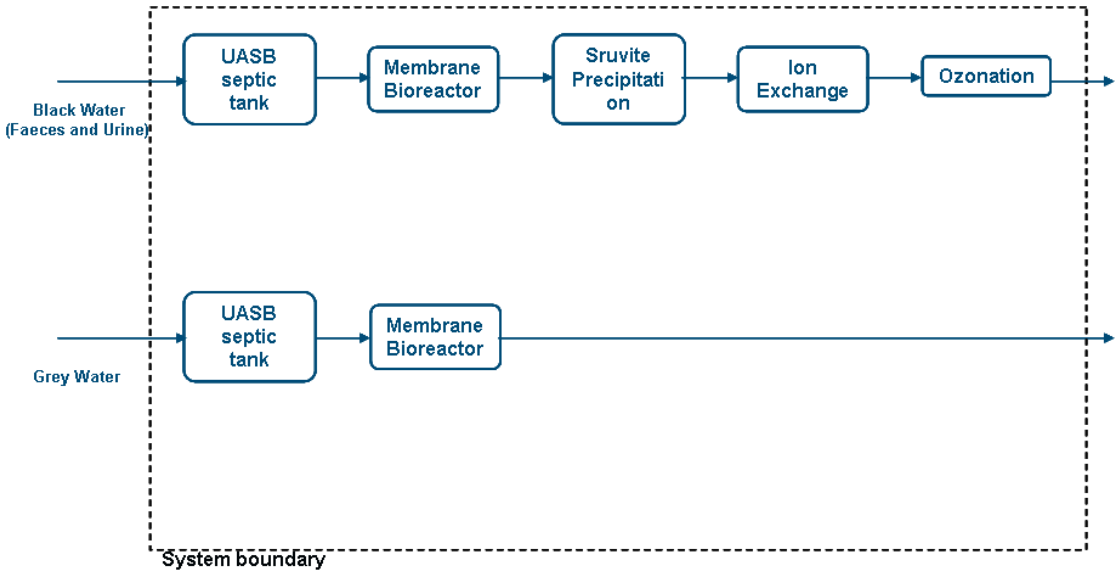


Figure 4.17 Flowchart of Source Separated Wastewater Treatment System (System B)

5 Characterization of the Influent Wastewater and Design for Combined and Source Separated Wastewater Treatment Systems

In the first part of this chapter (Chapter 5.1 and 5.2) the influents of both wastewater treatment systems were characterized and quantified based on the pollutants present in the wastewater streams. Using the same loads of macro and micro pollutants was crucial to have comparable systems in life cycle assessment.

The determined system influents were used in the design phase, in Chapter 5.3 and 5.4. During the design, all input and outputs of the individual processes were studied and calculated considering TSS, COD, BOD, tot N, tot P, carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBF), metoprolol (MTL) and the energy consumption. The amount of nutrients recovered in the systems and the net energy consumption were calculated considering the recovery of energy in the systems. This chapter mainly forms the inventory analysis of the life cycle assessment.

5.1 Characteristics of the Influent Wastewater for the Source-Separated Wastewater Treatment System (System B)

5.1.1 Composition of Black Water

Black water, the combination of flushed urine and faeces, consists of substances, which are extracted from the bloodstream by the kidneys and intestines as well as undigested substances. Undigested substances end up in the faeces. The dry weight of faeces is formed by undigested food, intestinal bacteria and intestine itself. Age of a person, his/her body weight and the amount of food consumed are the parameters affecting the amount of faeces produced (STOWA, 2001;STOWA, 2005). Urine mainly includes water soluble nutrients and water. Gender and fluid intake determine primarily the volume of urine generated (STOWA, 2005).

Pharmaceutical compounds are taken into body and excreted via kidneys and intestines after being metabolized into their metabolites. Urine and faeces contains approximately 70% and 30% respectively of many pharmaceutical compounds and their metabolites excreted from the body (Maurer et al., 2006;Ternes and Joss, 2006). Therefore, the black water is considered as the wastewater stream in households containing the highest amount of pharmaceutical compounds. In addition to the excretion by humans, flushing of outdated pharmaceuticals can contribute to the total amount of pharmaceutical compounds in the black water streams even if the contribution is minimal (Heberer, 2002;Larsen et al., 2004). Besides pharmaceutical compounds high concentrations of hormones and pathogens excreted via urine or faeces are also present in black water (Kujawa-Roeleveld and Zeeman, 2006).

The volume of black water produced is between 1.32 and 1.67 L $p^{-1}d^{-1}$. These values are the summations of the reported minimum and maxiumum, urine and faeces production amounts, 1.25-1.5 kg $p^{-1}d^{-1}$ and 0.07-0.17 kg $p^{-1}d^{-1}$, respectively (Eriksson et al., 2002;Hellstrom and Karrman, 1995;Jonsson et al., 1997;STOWA, 2005;Vinneras, 2002). Total COD amount reported for black water varies between 55.7-66.5 g $p^{-1}d^{-1}$

Food intake (eg. protein) is the important parameter determining the amount of nutrient in the black water. The main fraction of nitrogen (80%), phosphorus (55%) and potassium (60%), in the total domestic wastewater stream originates from urine. On the other hand, urine forms only 1% of volume in the total domestic wastewater stream produced in the household (STOWA, 2005).

In urine, nitrogen is found as urea (80%), ammonia (7%), creatine (6%) and other free amino acids or shorter peptides (Almeida et al., 1999;Fittschen and Hahn, 1998;Guyton, 1992;Johnston and McMillan, 1952;Kirchmann and Pettersson, 1995;Lentner and Wink, 1981) whereas faecal nitrogen contains 20% ammonium, 7% nitrogen in intestinal bacteria and 73% of organic nitrogen included in molecules like uric acid and enzymes. Total nitrogen excretion with black water is 8.5-13 kgN $p^{-1}d^{-1}$ (Eriksson et al., 2002;Hellstrom and Karrman, 1995;Jonsson et al., 1997;STOWA, 2005;Vinneras, 2002). Total amount of phosphorus excreted by urine and faeces is 0.9-1.7 gP $p^{-1}d^{-1}$. In urine more than 95% of phosphorus is found in inorganic form whereas in faeces the main fraction of phosphorus is in the form of undigested calcium phosphate. The amount of other nutrients and metals present in urine, faeces and black water are given in Table 5.1.

During the determination of the concentration of mentioned parameters in the black water, it was assumed that *vacuum toilet systems* were applied in theoretical functional units. The water consumption of each flush in vacuum toilets was taken as high as 1 L and an average number of flushes made by a person per day is assumed to be 6.

Composition of Grey Water

Grey water consists of the wastewater streams originating from the baths, showers, bath sinks, washing machines and kitchen sinks. Each stream has its own composition and characteristics. Grey water is generally considered as a relatively clean if it is compared to black water. It is mainly polluted by different amounts of organic compounds (food residues, personal care products, cleaning agents, detergents, dirt from cleaning, etc.) depending on the location (Jefferson et al., 2001b).

In grey water, nutrients are found in inorganic form but their proportion is small. Usage rate of detergents for cleaning purposes determines the amount of potassium and phosphorus since detergent is the main source of these elements in grey water (STOWA, 2005;Vinneras, 2002). In the report published by (Eriksson et al., 2002) it is stated that 900 different organic chemical materials and compound groups are found in grey water. The way that the food rests are handled in the kitchen is important for the composition of the grey water. Part of

the grey water is made by the food rests in cases where they end in the kitchen sinks.

Greywater can vary significantly in its composition. Wide range of values for macro-pollutants and nutrients has been published in the study of (Eriksson et al., 2002). The range for COD has been reported between 13 and 550 mg L^{-1}, for BOD_5 90-360 mg L^{-1} and for total nitrogen 0.6-74 mg L^{-1}. The total phosphorus content is changing between 4 and 14 mg L^{-1} depending of the use of detergents with or without phosphate.

Composition of domestic black and grey water in terms of volume, pollutants and nutrients are given in Table 5.1.

Table 5.1 The volume and the components of the black and grey Water based on literature survey (STOWA, 2005).

						Average	
LOAD	**Unit**	**Urine**	**Faeces**	**Black Water (Faeces+ Urine+ flush water)**	**Grey Water**	**Black Water (Faeces+ Urine+ flush water)**	**Grey Water**
Volume	L/p.d	1.25-1.5	0.07-0.17	7.32-7.67	91.3	7.5	91.3
Nitrogen	g/p.d	7.0-11.0	1.5-2.0	8.5-13	1.0-1.4	11	1.2
Phosphorus	g/p.d	0.6-1.0	0.3-0.7	0.9-1.7	0.3-0.5	1.3	0.4
Potassium	g/p.d	2.2-3.3	0.8-1.0	3.0-4.3	0.5-1.0	3.65	0.75
Calcium	g/p.d	0.2	0.53	0.73		0.73	
Magnesium	g/p.d	0.2	0.18	0.38		0.38	
BOD	g/p.d	5.0-6.0	14.0-33.5	19.0-39.5	26-28	29	27
COD	g/p.d	10.0-12.0	45.7-54.5	55.7-66.5	52	61	52
Total Solids	g/p.d	20.0-60.0	30	50-90	54.8	70	54.8
Cu	g/p.d	4	400	404	2900	404	2900
Cr	g/p.d	3.7	7.3	11	365	11	365
Ni	g/p.d	2.6	27	29.6	450	29.6	450
Zn	mg/p.y	16.4	3900	3916.4	3650	3916.4	3650
Pb	mg/p.y	0.73	7.3	8.03	365	8.03	365
Cd	mg/p.y	0.25	3.7	3.95	15	3.95	15
Hg	mg/p.y	0.3	3.3	3.6	1.5	3.6	1.5
Bacteria	No/ml	10000					
E.coli	Cfu/g		10E5-10E8				
Fecal Streptococci	Cfu/g		10E5-10E7				

Concentrations of the selected pharmaceutical compounds in the black water are calculated according to the equation 5.1 below and are given in Table 5.2. The basic of the formula is taken from (Ternes and Joss, 2006). A percentage of the users to the whole population in the Netherlands was taken since not all of the people use selected pharmaceutical compounds (giving sewage to the treatment plant.

DDD person^{-1} year^{-1} gives the number of DDDs used per person in a year considering only the people using the pharmaceutical compounds. To calculate the number of DDDs used per person per year including both the users and non users the number is normalized by the factor of users to the whole population in the Netherlands.

Equation 5.1.

$$C_{raw} = \frac{\frac{DDD}{year\ .person} \cdot \frac{users}{total\ \ population} \frac{g}{DDD} \cdot \frac{year}{365\ day} \cdot Excretion\ \ \%}{WWflow}$$

C_{raw} : Concentration of pharmaceutical compound in raw wastewater (g/L)
Excretion rate (%) : Fraction excreted without metabolization in urine and faeces (parent compound)
DDD : Daily defined dose
WWflow : Influent volume of wastewater coming per day per person (L/person.day)

In this research, it is assumed that all the representative pharmaceutical compounds are excreted 100% in unchanged form (as parent compound) because of the limited data on the removal efficiencies of each specific metabolite of each compound (detailed explanation in Chapter 3.5.5).

Table 5.2 Concentrations of selected pharmaceutical compounds in the black water stream for source separated system

Name	2005 usage (DDD/person. year)[1]	number of users [1]	number of users/total population [2]	DDD (g)[3]	Excretion rate (%) unchanged [4]	Flow rate (L/person. d)	Concentration of phar. in ww (mg/L)
Carbamazepine	159	61062	0.0037	1	100	7.5	0.21365
Diclofenac	37	1386000	0.0835	0.1	100	7.5	0.11285
Ibuprofen	29	848610	0.0511	1.2	100	7.5	0.64987
Metoprolol	184	706090	0.0425	0.15	100	7.5	0.42885

[1] http://www.gipdatabank.nl (January/2007)
[2] population of Netherlands (http://statline.cbs.nl/, CBS 26/01/07)
[3] http://www.whocc.no/atcddd
[4] (Huschek et al., 2004)

The pollutant loads and the concentrations, which were used in the design phase of the treatment systems in Chapter 5, are given in Table 5.3 for the two wastewater streams, black and grey water, of the source separated system. Since the pharmaceutical compound concentrations in grey water are negligible it is assumed that there is no pharmaceutical compound in grey water.

Table 5.3 Loads and concentrations of the basic pollutants in the black and grey water as a starting point for design.

	LOAD			CONCENTRATION		
	Unit	**Black Water (Faeces+Urine+flush water)**	**Grey Water**	**Unit**	**Black Water (Faeces+Urine+flush water)**	**Grey Water**
Volume	Kg/p.d	7.5	91.3	L/p.d.	7.5	91.3
Total solids	g/p.d	70	54.8	mg/L	9333.3	600.2
COD	g/p.d	61	52	mg/L	8133.3	569.6
BOD	g/p.d	29	27	mg/L	3866.7	295.7
Tot Nitrogen	g/p.d	11	1.2	g/L	1466.7	13.1
Tot Phosphorus	g/p.d	1.3	0.4	mg/L	173.3	4.4
Magnesium	g/p.d	0.38	0	mg/L	50.7	0.0
Carbamazepine	Mg/p.d	1.6024	0	mg/L	0.2137	0.0
Diclofenac	mg/p.d	0.8464	0	mg/L	0.1129	0.0
Ibuprofen	mg/p.d	4.8740	0	mg/L	0.6499	0.0
Metoprolol	mg/p.d	3.2164	0	mg/L	0.4289	0.0

5.2 Characteristics of the Influent Wastewater for the Combined Wastewater Treatment System (System A)

Characteristics of the influent wastewaters in terms of loads for the both systems should be the same to be able to evaluate have comparable systems This means that the load of the pollutants in the influent wastewater to the combined wastewater treatment system should be equal to the sum of the loads of the pollutants in black and grey water, which are the two streams of the influent wastewater to the source separated system (Table 5.4). For the solids pollutants, all the removal efficiencies are given in terms of total suspended solids for the combined wastewater treatment processes. This is why it was assumed that 50% of the total solids concentration is the concentration of total suspended solids in the influent.

Table 5.4 Loads of the pollutants of the influent wastewater for the combined wastewater treatment system.

	System B			System A
Parameter Load (g/person/day)	**Black Water (Faeces+Urine+flush water)**	**Grey Water**	**Sum (Black+Grey Water)**	**Black Water +Grey Water**
Total Suspended Solids (TSS)	35	27.4	62.4	62.4
COD	61	52	113	113
BOD	29	27	56	56
Tot Nitrogen	11	1.2	12.2	12.2
Tot Phosphorus	1.3	0.4	1.7	1.7
Magnesium	0.38	0	0.38	0.38
Carbamazepine	0.0016	0	0.0016	0.00160
Diclofenac	0.0008	0	0.0008	0.00085
Ibuprofen	0.0049	0	0.0049	0.00487
Metoprolol	0.0032	0	0.0032	0.00322

In Table 5.5, flow rates of the wastewater and the influent concentrations of the pollutants for each year between 2000 and 2004 are given. The calculated values in Table 5.4 are comparable with the average values taken from the statistical website.

Table 5.5 Influent concentration of pollutants in sewage wastewater and the volume of the wastewater in the years 2000-2004 in Netherlands. (http://statline.cbs.nl/, CBS 26/01/07)

		Dutch Wastewater Treatment Plant Influent Water						
	Unit	**2000**	**2001**	**2002**	**2003**	**2004**	**Average**	**Calculated values (Table 5.4)**
Volume	m3/year	1996779	2131929	2047133	1757326	1914946	1969623	
Population	p.e.	25242	25322	25281	25156	25184	25237	
Volume	L/d.person	217	231	222	191	208	214	
TSS	mg/L	214	215	211	253	228	224	292
COD	mg/L	470	461	477	550	506	493	528
BOD	mg/L	180	175	185	213	194	189	262
Total N	mg/L	43	42	44	51	46	45	57
Total P	mg/L	7	7	7	9	8	8	8

Concentrations of the selected pharmaceutical compounds in the wastewater for combined wastewater system are calculated by equation 5.1 and the results are given in Table 5.6. When the concentrations of pharmaceutical compounds in influent wastewater are compared for both systems, low concentrations are found out for the combined system. In combined systems besides the addition of the grey water into the whole system, common usage of the normal flush systems increases the water content of the wastewater while decreasing the concentration of the pharmaceuticals in the influent wastewater.

Table 5.6 Concentrations of selected pharmaceutical compounds in the influent wastewater for combined system

Name	2005 usage (DDD/person.year)[1]	number of users [1]	number of users/total population	DDD (g)[2]	Excretion rate (%) unchanged [3]	Flow rate (L/person.d) [4]	Concentration of phar. in ww (mg/L)
Carbamazepine	159	61062	0.0037	1	100	214	0.00749
Diclofenac	37	1386000	0.0835	0.1	100	214	0.00396
Ibuprofen	29	848610	0.0511	1.2	100	214	0.02278
Metoprolol	184	706090	0.0425	0.15	100	214	0.01503

[1] http://www.gipdatabank.nl (January/2007)
[2] http://www.whocc.no/atcddd
[3] (Huschek et al., 2004),
[4] Table 5.5 (http://statline.cbs.nl/, CBS 26/01/07)

Calculated concentration values of the pharmaceutical compounds for the combined wastewater treatment system are comparable with the literature values (Table 5.7). In the study of (Schrap et al., 2003), the concentration ranges are given for some of the therapeutic groups.

Table 5.7 Comparison of the calculated and literature influent concentrations of the selected pharmaceutical compounds.

Group	Concentration range in the ww for group (residential area) (mg/L) [1]	Name	Calculated Concentrations in ww (mg/L)	Average literature concentrations in ww (mg/L) [2]
Anti-epileptica	<dl - 0.0095	Carbamazepine	0.00749	0.00174
Analgetica	<dl - 0.045	Diclofenac	0.00396	0.00289
Analgetica	<dl - 0.045	Ibuprofen	0.02278	0.00384
ß-blokkers	<dl - 0.0025	Metoprolol	0.01503	0.00700

[1] (EHV, ELB, KRL, BVW). (Schrap et al., 2003)
[2] The average of the concentration values found in the literature (Carballa et al., 2004;Clara et al., 2005;Clara and Strenn, 2004;Joss et al., 2006;Quintana et al., 2005;Ternes et al., 2005;Ternes, 1998)

5.3 Design of the Combined Wastewater Treatment System (System A)

In this research, the configurations and the processes are chosen trying to satisfy the Dutch discharge standards for the wastewater. The standards are given in Table 5.8 below with their references.

Table 5.8 Dutch Discharge Standards as of 2001

Parameter	Unit	Discharge Standard	Reference
TSS	mg/L	<=10	(Mels, 2001)
COD	mg/L	<=50	(Mels, 2001)
BOD	mg/L	<=20	(Dirkzwager, 1997;Mels, 2001)
Tot N	mg/L	<=10	(Dirkzwager, 1997;Mels, 2001)
Tot P	mg/L	<=1	(Dirkzwager, 1997;Mels, 2001)

Pollutant concentrations in the influent wastewater coming from the residential area (domestic) for the conventional wastewater treatment system are given in Table 5.5. The configuration of the combined wastewater treatment system consists of screening, aerated grit and grease chamber, primary sedimentation, activated sludge system and finally ozonation as an additional chosen unit after the investigation done in chapter 4, considering the removal of pharmaceutical compounds, pathogens and energy consumption.

5.3.1 Screening

First step of the treatment plant is screening. A screen is a device, which can have different size of openings and is used to retain coarse solid particles found in the wastewater. These solid particles are removed since they could damage consequent process equipment and reduce overall reliability and effectiveness of the treatment plant. In this study, two types of screens are used in the system A. A coarse screen with 70 mm openings is put to protect pumps, valves and likely apparatus from damage and clogging by large objects. Following the coarse screen, a fine screen with 3 mm openings, is placed as a preliminary treatment. Both screens are mechanically cleaned with the help of scrapers. Conveyor is placed to transport the screened materials to the container (Metcalf&Eddy et al., 2003).

Since none of the micro or macro pollutants are aimed to be removed during the screening process, the process effluent concentrations are the same as the system influent concentrations given in Table 5.5.

Screen and the conveyor are the two apparatus operated by electricity. Energy calculation of the screening process was done considering that one coarse and one fine screen are operated every day. A screen was assumed to consume 0.55 kWh and its conveyor also 0.55 kWh. One screen is assumed to work 4 hours/day in average (Interview with Project Coordinator of Bursa West Wastewater Treatment Plant, Turkey, 7/02/07).

Yearly energy consumption of a coarse screen and fine screen:

2 * (0.55 + 0.55) * 4 h/d * 365 days = **3,212 kWh/year**

5.3.2 Aerated Grit and Grease Chamber

Aerated grit chamber with grease removal is chosen as a second process unit. The function of this unit is to remove heavy solid particles such as sand, gravel, cinders. These particles settle down with the help of a spiral flow pattern perpendicular to the tank created by the air introduced along one side of the tank. The air diffusers are placed less than a meter above the bottom line. There are scrapers, which remove the floating, greasy and settling particles accumulating on the surface and at the bottom of the tank (Metcalf&Eddy et al., 2003).

There is removal of neither macro pollutants nor nutrients and nor pharmaceutical compounds in the grit and grease removal unit. This is why the process effluent concentration values are not different than the ones in Table 5.5.

The main energy consuming parts in the aerated grit chamber are air blowers and scrapers. Total energy needed for the scrapers and the blowers is taken as 15 kWh. Blowers and scrapers are assumed to work 24 hours/day (Interview with Project Coordinator of Bursa West Wastewater Treatment Plant, Turkey, 7/02/07).

The calculated energy requirement of the aerated grit chamber with grease removal:

15kWh* 24 h/d * 365 days = **131,400** kWh/year

5.3.3 Primary Sedimentation

Third unit, Primary sedimentation unit is a preliminary step, designed to remove readily settleable solids and floating materials. The removal of these materials reduces the suspended solids content of the wastewater. Settleable solids accumulating at the bottom of the sedimentation tanks are removed regularly, as sludge (Metcalf&Eddy et al., 2003). Organic content of the sludge is considered as a product. Biogas can be produced by digestion of this product. Besides this, it can be served as a carbon source for denitrification process after being acidified or can be re-used in agriculture as a source of nutrients (Mels, 2001). Haydraulic surface load of 2.5 m h^{-1} was applied and average dry solids concentration of sludge discharged by primary clarifier was taken as 0.75%.

There were no studies found on the removal efficiencies of representative compounds in the primary sedimentation. However, regarding the lab-scale experiments made on the sorbtion potentials of the compounds, 5% removal was assumed only for diclofenac and ibuprofen during primary sedimentation.

The removal efficiencies of TSS, COD, BOD, total N and total P in primary sedimentation were assumed as 40%, 25%, 25%, 7% and 15%. These efficiencies were only used for the sludge calculations. The calculations for the effluent concentrations for primary sedimentation processes were done by using the total average removal efficiencies in existing conventional WWTPs in the

Netherlands. These efficiencies were taken from Statistic Bureau of Nehterlands. It was already stated that existing conventional WWTPs consist of primary sedimentation and activated sludge process. The average removal efficiencies and the effluent concentrations are given in Table 5.9 in the chapter of activated sludge system (Chapter 5.3.4).

The energy requirement of primary sedimentation tank is assumed **35,000 kWh/year** for 100,000 p.e (Mels, 2001).

The sludge produced in primary sedimentation is sent to the sludge digestion to be digested. Not all of the COD reduced in primary sedimentation is converted to biogas anaerobic digestion. It was assumed that 0.5 is the organic fraction, which will be degraded in digestion, of the COD removed (Mels, 2001). The energy that can be produced from the primary sludge in sludge digestion is calculated by the following equation:

$$E_{biogas} = (COD_{removed} \cdot 0.5) \cdot Q \cdot \frac{m^3 biogas}{kgCOD} \cdot \frac{kWhenergy}{m^3 biogas} \cdot E_{electricity}$$

E_{biogas} : Energy generated from the biogas (kWh/year/100000 p.e.)

$COD_{removed}$: Remove COD concentration (g/m^3)

Q : Flowrate (m^3/d)

$E_{electricity}$: Electrical efficiency

0.35 m3 CH4/1 kg COD is assumed to be produced at 273 K during the anaerobic digestion of grey water. Methane has got a combustion heat of 35.8 E10^6 J/m3, at 273 K and p=p0. 1 kWh = 36E10^5 Joule (STOWA, 2005).

$$E_{biogas} = \frac{(528 \cdot 25\%) gCOD}{m^3} \cdot 50\% \cdot \frac{kg}{1000\,g} \cdot \frac{21400\,m^3}{d} \cdot \frac{365\,d}{year} \cdot \frac{0.35 m^3 biogas}{kgCOD} \cdot \frac{kWh}{36E05\,J} \cdot \frac{35.8E06\,J}{m^3 biogas} \cdot 35\%$$

which results in

628,010 kWh.year^{-1} (100.000 p.e)

5.3.4 Activated Sludge with Enhanced Biological Nutrient Removal

In activated sludge systems, degradation of organic material (expressed as COD and BOD) from the wastewater is one of the main aspects. Biological nutrient removal (N&P) is another aspect of the system depending on the reactor configurations. Bacterial flocs play a significant role in the removal of the pollutants. These flocs are then removed in the secondary (final) clarifier. A part of the flocs mass accumulated in the secondary clarifier is returned to the beginning of the plant, whilst the other part goes to sludge treatment units or is disposed as a waste sludge. In order to recirculate the sludge, pumps are placed in the system. Oxic zone of the system is the area where oxidation of organic materials and ammonia take place. For the oxidation process, diffusers, which provide air, are placed in the tank. The amount of air, which is pumped into the tank by the blowers, is directly related to the energy consumption. After the

oxidation of the ammonia into nitrite and then nitrate, nitrate is converted into nitrogen gas in the anoxic zone and is released to the atmosphere. For this study, oxidation ditch was chosen for the tank configuration. In the oxidation ditch impellers are placed in order to move the whole mixture of wastewater and sludge. Considering the configuration of oxic and anoxic zone, anoxic zone is placed before the oxic zone because of the biodegradable COD requirement for the denitrification process. This is why after the biological degradation and nitrification processes the wastewater is internally recirculated back to the anoxic zone by pumps. The pumps, which are used for the circulation of the water and the sludge, are the second main energy consumers besides air blowers. Anaerobic zone is placed in the beginning of the installation aiming to remove the phosphorus from the wastewater. Phosphate accumulating bacteria play a role in the removal of phosphorus. Phosphorus accumulated in the bacteria is removed from the system together with the bacteria via the sludge wasted.

SRT is adjusted according to the biological carbon, nitrogen and phosphorus removal, since no significant influence of SRT on the removal rates of pharmaceutical compounds was stated in the different studies (discussed in Chapter 4.2). The current wastewater treatment plants in the Netherlands are based on primary sedimentation and activated sludge process (Mels, 2001). According to the Central Bureau Statistics of Netherlands, in 2005 the average removal rates of TSS, COD, BOD, Tot N and Tot P were 96%, 92%, 98%, 74% and 82% respectively in the WWTPs in the Netherlands. There removal efficiencies were taken for this study. 20 days of SRT, 16 hr of HRT and 3500 mg/L MLSS were used as the design parameters of the activated sludge process with biological nitrogen and phosphorus removal (Metcalf&Eddy et al., 2003). With these design parameters the assumed effluent concentrations of the pollutants will be as in Table 5.9.

Table 5.9 Removal efficiencies and effluent concentrations of the primary sedimentations, activated sludge process (effluent concentrations, after the secondary sedimentation)

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TSS	292	12	96
COD	528	42	92
BOD	262	5	98
Tot N	57	15	74
Tot P	8	1	82
CBZ	0.00749	0.00689	8
DCF	0.00396	0.00188	52.52*
IBF	0.02278	0.00216	90.52**
MTL	0.01503	0.00225	85

* overall removal; 5% in primary sedimentation, 50% in activated sludge process
**overall removal; 5% in primary sedimentation, 90% in activated sludge process

After the review of the studies performed in the recent years (Chapter 4), it was determined that the average removal efficiencies of carbamazepine, diclofenac, ibuprofen and metoprolol are 8%, 50%, 90% and 85% respectively. A 5% sorption of ibuprofen and diclofenac was assumed to occur in activated sludge system including secondary clarifier considering the results of the study done by

(Zwiener and Frimmel, 2003) and the higher sorption capacities of these compounds with high K_{ow} values (Table 4.2 and 4.3). No sorption of carbamazepine and metoprolol on the sludge was assumed during the activated sludge process, because of the low K_{ow} and K_d values. The effluent concentrations of the selected pharmaceutical compounds are given in Table 5.9. The removal efficiencies of carbamazepine and diclofenac are the overall removal efficiencies of both primary sedimentation and activated sludge process.

There are a lot of energy consuming factors in activated sludge process. The aeration and the recirculation are the two major energy consuming processes. Besides these two, pumps and scrapers in the sedimentation tank, the impellers are the other components increasing the energy consumption. For the total energy consumption in activated process, general electricity used versus flow rate graph from (Metcalf&Eddy et al., 2003) was used. According to the graph, 2000 MJ is the amount of energy required for the treatment of 1000 m^3 wastewater in an activated sludge with nitrification process. The calculation of the total electricity consumption is as below:

$$E_{tot} = \frac{2000\ MJ}{1000\ m^3 ww} \cdot \frac{21400\ m^3}{d} \cdot \frac{365\ d}{year} \cdot \frac{kWh}{3.6\ MJ}$$

Which results in

4,339,444 kWh/year for 100 000 p.e.

A part of the sludge produced in the secondary sedimentation is sent to the beginning of the activated sludge process while the rest is sent to the anaerobic sludge digestion to be digested. Not all of the COD reduced in primary sedimentation is converted to biogas anaerobic digestion. It was assumed that 0.3 is the organic fraction, which will be degraded in digestion, of the COD removed (Mels, 2001). The energy that can be produced from the primary sludge in sludge digestion is calculated by the following equation:

$$E_{biogas} = (COD_{in} - COD_{eff} \cdot 0.3) \cdot Q \cdot \frac{m^3 biogas}{kgCOD} \cdot \frac{kWhenergy}{m^3 biogas} \cdot E_{electricity}$$

E_{biogas} : Energy generated from the biogas (kWh/year/100000 p.e.)

COD_{in}: Influent COD concentration (g/m^3)

COD_{eff}: Effluent COD concentration (g/m^3)

Q : Flowrate (m^3/d)

$E_{electricity}$: Electrical efficiency

0.35 m3 CH4/1 kg COD is assumed to be produced at 273 K during the anaerobic digestion of grey water. Methane has got a combustion heat of 35.8 $E10^6$ J/m3, at 273 K and p=p0. 1 kWh = $36E10^5$ Joule (STOWA, 2005).

$$E_{biogas} = \frac{(396-42\%)\,gCOD}{m^3} \cdot 30\% \cdot \frac{kg}{1000\,g} \cdot \frac{21400\,m^3}{d} \cdot \frac{365\,d}{year} \cdot \frac{0.35 m^3 biogas}{kgCOD} \cdot \frac{kWh}{36E05\,J} \cdot \frac{35.8E06\,J}{m^3 biogas} \cdot 35\%$$

which results in

1,010,527 kWh.year^{-1} (100.000 p.e)

5.3.5 Ozonation

Ozone is an oxidant, which is used widely in wastewater and drinking water treatment. It is used for disinfection and oxidation purposes, providing taste and odour control, decolorization, hygenisation and removal of micropollutants including pharmaceuticals.

COD concentration was assumed to decrease 11% considering the study of (Beltrán et al., 1999).

In literature it was found out that 2-5 mg/L ozone dose is required to remove most pharmaceutical compounds by 90-99% from the biologically treated wastewater containing less than < 8 mg DOC/L (Huber et al., 2005b;Ternes and Joss, 2006;Ternes et al., 2003).

In a study, the relation between chemical oxygen demand (COD) and dissolved oxygen demand (DOC) was analyzed for aerobic, anaerobic and sedimentation ponds where sewage water was introduced. It was assumed that same relations can be predicted in this study. The equations, which were found out, defining the relations, are given in Table 5.10.

Table 5.10 Relation between COD and DOC for different processes (Fadini et al., 2004)

	Formula
Anaerobic effluent	COD = 1.0793DOC + 78.6295
Aerated effluent	COD = 3.5739DOC + 6.2795
Sedimentation effluent	COD = -1.3412DOC + 138.3462
Septic tank effluent	COD = 3.56DOC + 368

For the calculation of DOC concentration in the effluent of activated sludge process the equation for “aerated effluent” was used from Table 5.10. The COD concentration of the effluent of activated sludge process is 42 mg/L. With the equation DOC value is calculated as 9.9 mg/L. Considering that the DOC concentration in the influent of ozonation is slightly larger than 8 mg L^{-1}, ozone dose of 7 mg L^{-1} is used, assuming that 95% of the all selected compounds, carbamazepine, diclofenac, ibuprofen and metoprolol is removed. This removal efficiency was based on the majority of the studies described in the literature (Chapter 4.3.3), showing that that ozonation provides 90-99% removal of many parent pharmaceutical compounds from the treated wastewater. The removal efficiencies of the pharmaceutical compounds and the effluent concentrations after the ozonation process are given in Table 5.11.

Table 5.11 Removal efficiencies and effluent concentrations of ozonation process

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TSS	12	12	0
COD	42	38	11
BOD	5	5	0
Tot N	15	15	0
Tot P	1	1	0
CBZ	0.00689	0.00034	95
DCF	0.00188	0.00009	95
IBF	0.00216	0.00011	95
MTL	0.00225	0.00011	95

In the Table 5.12 energy requirement values are given for air preparation, ozone generation, ozone contacting and all the other uses.

Table 5.12 Energy requirement for ozone application to the treated wastewater (Metcalf&Eddy et al., 2003)(Pg.1289)

Component	kWh/kg ozone (range)	kWh/ kg ozone
Air preparation (compressor and dryers)	4.4-6.6	5
Ozone generation (Air feed)	13.2-19.8	15
Ozone contacting	2.2-6.6	4
All other uses	1.2-2.2	2

The energy required for ozonation of the effluent from the conventional treatment plant (E_o) is calculated as follows:

$$E_O = \frac{7\ gozone}{m^3\ ww} \cdot \frac{21400\ \ m^3\ ww}{d} \cdot \frac{kg}{1000\ \ g} \cdot \frac{(15 + 5 + 4 + 2)kWh}{kgozone} \cdot \frac{365\ d}{year}$$

Which results in:

1,421,602 kWh/year

5.4 Design of the Source Separated Wastewater Treatment System (System B)

During the design of the source separated wastewater treatment system the same discharge standards as given in Table 5.8 were attempted to be reach. Concentrations and loads of pollutants in the separated streams, black and grey water are given in Table 5.3.

For the **treatment of black water**, UASB septic tank, MBR, struvite precipitation, ion exchange and ozonation are the processes, which were selected after the analysis of the treatment processes in Chapter 4. In the following subchapters the calculations for each unit will be given.

5.4.1 UASB Septic Tank

Anaerobic digestion is a technology, which converts organic content of the wastewater with a little energy demand. One of the end products of the process,

biogas, consists of (55-75% volume) methane and (25-25%) carbon dioxide. Biogas is an important renewable energy source. An UASB-septic tank system is one of the technical configurations of the anaerobic treatment processes and it is chosen for concentrated black water treatment in this research. In UASB septic tank system, sludge is accumulated and stabilized. In contrast to a conventional septic tank, an up-flow mode provides improved suspended solid removal and better biological conversion.

The treatment will take place at 25^{o}C and retention time (HRT) of 30 d. Under these conditions, 90% TS, 78% COD, 90% BOD, 16% total N and 56% total P removal were assumed in UASB tank (Kujawa-Roeleveld et al., 2005;Luostarinen et al., 2007;Luostarinen and Rintala, 2005). The effluent concentrations of pollutants are given in Table 5.13.

Table 5.13 Removal efficiencies and effluent concentrations after UASB septic tank

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	9333	933	90
COD	8133	1789	78
BOD	3867	851	90
Tot N	1467	1232	16
Tot P	173	76	56
CBZ	0.21365	0.21365	0
DCF	0.11285	0.04514	60
IBF	0.64987	0.38992	40
MTL	0.42885	0.25731	40

For the pharmaceuticals 0% for carbamazepine, 60% for diclofenac, 40% for ibuprofen are the degradation rates used in UASB septic tank, considering the studies reported by (Carballa et al., 2006;Carballa et al., 2007). Although no data was found for metoprolol, a 40% removal is assumed for this compound. The assumption was based on the fact that the biodegradation and sorption efficiencies of metoprolol show similarities with the ones of diclofenac (Table 4.1, 4.2 and 4.3). The effluent concentrations of selected pharmaceutical compounds are given in Table 5.13.

A considerable amount of energy is recovered by anaerobic digestion of black water in UASB septic tank while energy is required for the heating purposes of the wastewater. Since not all of the COD reduced in UASB septic tank is methanised, it was assumed that 0.7 of influent COD is converted to methane. Energy that can be obtained from the methane is calculated as follows:

$$E_{biogas} = (COD_{in} \cdot 0.7) \cdot Q \cdot \frac{m^3 biogas}{kgCOD} \cdot \frac{kWhenergy}{m^3 biogas} \cdot E_{electricity}$$

E_{biogas} : Energy generated from the biogas (kWh/year/100000 p.e.)

COD_{in}: Influent COD concentration (g/m^3)

COD_{eff}: Effluent COD concentration (g/m^3)

Q : Flowrate (m^3/d)

$E_{electricity}$: Electrical efficiency

0.35 m^3 CH4/1 kg COD is produced at 273 K during the anaerobic digestion of black water (STOWA, 2005). Methane has got a combustion heat of 35.8 $E10^6$ J/m^3, at 273 K and $p=p_0$. 1 kWh = $36E10^5$ Joule (Leeuwen, 2003). Electrical efficiency was assumed to be 35% (Zeeman et al., submitted).

$$E_{biogas} = \frac{(8133 \cdot 0.7)\,gCOD}{m^3 ww} \cdot \frac{750\ m^3 ww}{d} \cdot \frac{kg}{1000\ g} \cdot \frac{0.35\,m^3 CH_4}{kgCOD} \cdot \frac{35.8\,E06\,J}{m^3 biogas} \cdot \frac{kWh}{36\,E05\,J} \cdot \frac{365\,d}{year} \cdot \frac{35}{100}$$

Which results in;

1,898,539 kWh/year (100,000 p.e.)

On the other hand, 50% heat efficiency was assumed to be obtained from the same amount of COD (Reith et al., 2003). Heat energy obtained from the UASB septic tank was calculated as **2,712,310 kWh/year** for 100,000 p.e. which is used to heat up the wastewater to the required operational temperature of the UASB septic tank.

According the law of thermodynamics, a mix of 1.0 litre of flushing water and 0.2 kg of physiological waste of respectively 15 ℃ and 37 ℃ make an influent with a temperature of 20 ℃ (STOWA, 2005). The operation temperature of UASB septic tank is 25 C°. This is why the wastewater requires to be heated up 5 C°. The specific heat capacity is the heat energy required to raise water's temperature one kelvin (equal to one degree Celsius) is approximately 4200 J Kg^{-1} K^{-1} (wikipedia, 2007). Energy needed for heating the wastewater is calculated below:

$$E_{heat} = \Delta T \cdot Q \cdot C$$

E_{heat}: Energy required to heat the wastewater up to 25 C° (KWh/year)

ΔT: Temperature needed to be increased

C: Speicif heat capacity (J Kg^{-1} K^{-1})

$$E_{heat} = (25 - 20)C^o \cdot \frac{750\,m3}{d} \cdot \frac{1000\ L}{m3} \cdot \frac{365\,d}{year} \cdot \frac{4200\ J}{kg \cdot C^o} \cdot \frac{kWh}{3.6\,E06\,J}$$

Which results in:

1,596,875 kWh/year

The energy required for heating the wastewater is covered by the heat energy produced by the methane production during the anaerobic digestion.

5.4.2 Membrane Bioreactor

Although high percentages of the COD, BOD and TS are removed in UASB tank, due to a high strength of the influent, the anaerobic effluent is not sufficient to meet the discharge standards. This is why a membrane bioreactor is used as an aerobic polishing step for further removal of organic and solid content.

Membrane bioreactor system consists of a suspended growth biological reactor integrated with a filtration membrane system. Compared to the conventional activated sludge system, the filtration system replaces the secondary sedimentation. Membranes are generally immersed in an aeration tank, in direct contact with mixed liquor. The membrane modules can be made of different materials and in different sizes. With the help of a pump treated water is vacuumed through the membranes and separated from the suspended biomass. The energy input for mixing of the bioreactor as well as supplying the high flow velocity along the membranes is achieved by a pump (Holler and Trosch, 2001). Cleaning of the membranes is another aspect requiring high energy consumptions (STOWA, 2007).

During the aerobic treatment in the membrane bioreactor, 50% COD removal (personal communication with Marthe de Graaff) and 97% TS removal (Machdar et al., 1997) were assumed.

In the source separated system, recovery of nutrients is aimed instead of removal. Nitrification process requires high SRT to occur. Typical design SRT ranges for nitrification process at different temperatures are 10-20 d at 10 C° and 4-7 d at 20 C° (Metcalf&Eddy et al., 2003). Since the temperature of UASB septic tank effluent will be around 20-25, MBR was designed with 4 days of SRT and 1.5h of HRT (Holler and Trosch, 2001). With this SRT, 20% of nitrogen removal was assumed in the reactor.

SRT parameter for design is too low for high degradation efficiencies of pharmaceuticals except ibuprofen, which requires minimum 5 days of SRT for 95% removal efficiency. With 4 days of SRT, 75% and 20% removal efficiency of ibuprofen and diclofenac were assumed considering the study of (Clara et al., 2005). The same removal efficiency with diclofenac, 20% was assumed for metoprolol because of the similarity between their biodegradation coefficients (Table 4.1). Because of the low SRT values not more than 20% nitrogen removal is expected in the reactor. The removal efficiencies and the concentrations of the pollutants in the effluent of the MBR process are given in Table 5.14.

Table 5.14 Removal efficiencies and effluent concentrations after MBR

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	933	28	97
COD	1789	895	50
BOD	851	425	50
Tot N	1232	986	20
Tot P	76	76	0
CBZ	0.21365	0.21365	0
DCF	0.04514	0.03611	20
IBF	0.38992	0.09748	75
MTL	0.25731	0.20585	20

The energy consumption of the bioreactor is assumed as 0.9 kWh/m^3 treated wastewater (STOWA, 2007). The calculation of the energy requirement for MBR process is given as:

$$E_{MBR} = \frac{kWh_{consumed}}{m^3} \cdot Q \cdot \frac{365\ d}{year}$$ E_{MBR}: Energy consumption by MBR (kWh/year)

$$E_{MBR} = \frac{0.9\ kWh}{m^3} \cdot 750 \cdot \frac{365\ d}{year}$$

E_{MBR} = **246,375 kWh/year** (100,000 p.e)

5.4.3 Struvite Precipitation

In the Struvite Precipitation process, magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$), also called MAP, AMP or struvite is precipitated in the process tank. This precipitate, which is an important product containing two dominant wastewater nutrients (N, P), can be used as a slow release fertilizer. When struvite precipitation is used for wastewater, addition of magnesium, in the form of MgO, $Mg(OH)_2$, $MgCl_2$ or bittern (the magnesium-rich brine from table-salt production) is necessary for the precipitation to occur. According to the literature, >90% phosphate recovery can be achieved in treated wastewater with MAP precipitation process. A portion of ammonium is also recovered in the precipitation next to the phosphate.

According to the information found in the literature in order to obtain 92% removal efficiency of phosphorus with 10% removal of ammonia, 1/1/1 is used as a molar ratio of Mg/N/P. In Table 5.15, the atomic mass of each element is given per mol. Concerning the effluent concentrations of MBR tank; the number of mols of each element was calculated. In order to recover 2.5 mol of phosphorus, 2.5 mol of magnesium and nitrogen were needed. There was enough nitrogen in the influent whereas the amount of magnesium was not enough considering the mol ratios. According to the calculations, 8.4 mg/L wastewater Mg was added externally into the tank, making a yearly requirement of 2291 kg Mg.

Table 5.15 Calculations for struvite precipitation (Meulman, 2006)

	Magnesium	**Phosphorus**	**Nitrogen**
Molar mass (g/mol)	24	31	14
Molar ratio	1	1	1
Influent (mg/L)	50.7	76.3	985.6
Molar ratio/influent	2.111	2.460	70.4
Magnesium added (mg/L)	8.4		
Magnesium added (kg/year)	2299		

$$Mg_{added} = \left((Mol_P - Mol_{Mg}) \cdot Mass_{molar\ (Mg)} \right) \cdot Q \cdot \frac{365\ d}{year}$$

$$Mg_{added} = (2.46 - 2.11) \frac{mol}{m^3} \cdot \frac{24\ g}{mol} \cdot 750\ \frac{m^3}{d} \cdot \frac{365\ d}{year}$$

Mg_{added} = 2299500 g/year = **2299.5 kg/year** (100,000 p.e.)

The recovery efficiencies and the effluent concentrations of pollutants after the struvite precipitation are given in Table 5.16.

Table 5.16 Recovery efficiency of N and P and effluent concentrations after struvite precipitation

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	28	28	0
COD	895	895	0
BOD	425	425	0
Tot N	986	887	10
Tot P	76	6	92
CBZ	0.21365	0.21365	0
DCF	0.03611	0.03611	0
IBF	0.09748	0.09748	0
MTL	0.20585	0.20585	0

16 MJ/kg_P is necessary for P fixation with struvite precipitation (Maurer et al., 2003). This value includes electricity, fuel and chemical consumption but not the energy required for pumps. The energy required for the pumps is assumed **135,000 kWh/year**.

$$E_P = (TotP_{in} - TotP_{eff}) \cdot Q \cdot \frac{kWh \quad required}{kgP}$$

E_P : Energy required for the precipitation of phosphorus (kWh/year.100000 p.e.)

$$E_P = \frac{(76.3-6.1)gP}{m^3 ww} \cdot \frac{750 m^3 ww}{d} \cdot \frac{kg}{1000 g} \cdot \frac{16 MJ}{kgP} \cdot \frac{1E06 J}{MJ} \cdot \frac{kWh}{36E05 J} \cdot \frac{365 d}{year}$$

Which results in

85,368 kWh/year

Total energy required for the struvite precipitation process and the recovery of phosphorus is **220,368 kWh/year** (100 000 p.e.).

5.4.4 Ion Exchange

Ion exchange resins are generally cast as porous beds with considerable external and pore surface where ions can attach. Ion exchange resin is a polymer with electrically charged sites, at which one ion may replace another. Certain minerals called zeolites are found in the resin providing the exchange of the ions. Several researches were done for the ammonium-ion uptake capacity of the zeolites from treated wastewaters and urine. 80-100% recovery ammonia is achievable with zeolite according to the most of the studies (Ban and Dave, 2004;Kujawa-Roeleveld et al., 2006;Lind et al., 2000;Nguyen and Tanner, 1998). A 90% ammonia removal was assumed to occur in the ion exchange process

considering the information from (Nguyen and Tanner, 1998). The effluent concentrations of the pollutants and the recovery efficiency of nitrogen are given in Table 5.17.

Table 5.17 Recovery efficiency of nitrogen and effluent concentrations after ion exchange

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	28	28	0
COD	895	895	0
BOD	425	425	0
Tot N	887	89	90
Tot P	6	6	0
CBZ	0.21365	0.21365	0
DCF	0.03611	0.03611	0
IBF	0.09748	0.09748	0
MTL	0.20585	0.20585	0

Energy needed for the recovery of nitrogen (E_N) is calculated according to:

$$E_N = (TotN_{in} - TotN_{eff}) \cdot Q \cdot \frac{kWh\ \ required}{kgN}$$

No information related to the energy required for the recovery of nitrogen in ion exchange was accessed. It is assumed that the energy requirement in the ion exchange process is same as the one in struvite precipitation since there was no available information in the literature. A 16 MJ is taken as the energy requirement to recover 1 kg of Nitrogen. The energy required for the pumps is assumed **135 000 kWh/year** (Mels, 2001).

$$E_N = \frac{(887-88.7)gN}{m^3ww} \cdot \frac{750m^3ww}{d} \cdot \frac{kg}{1000g} \cdot \frac{16MJ}{kgN} \cdot \frac{1E06J}{MJ} \cdot \frac{kWh}{36E05J} \cdot \frac{365d}{year}$$

Which results in

971,265 kWh/year (100000 p.e.)

Total energy required for the ion exchange process and the recovery of nitrogen is **1,106,265 kWh/year** (100 000 p.e.).

5.4.5 Ozonation

Pharmaceutical removal capacity is assumed to be as high as taken 95% for all four representative compounds considering that most of the studies found in the literature proved that ozonation provides 90-99% removal of parent pharmaceutical compound from the treated wastewater.

COD concentration was assumed to decrease 11% considering the study of (Beltrán et al., 1999).

In literature it was found out that 5-10 mg/L ozone dose is required to remove most pharmaceutical compounds by 90-99% from the biologically treated

wastewater with 23 mg DOC/L (Huber et al., 2005a;Huber et al., 2005b;Ternes et al., 2003). For this research 15 mg/L ozone dose is used assuming that when treating concentrated black water 95% of the all selected compounds, carbamazepine, diclofenac, ibuprofen and metoprolol is removed. This removal efficiency was based on the majority of the studies described in the literature (Chapter 4.3.3), showing that that ozonation provides 90-99% removal of many parent pharmaceutical compounds from the treated wastewater. The removal efficiencies of the pharmaceutical compounds and the effluent concentrations after the ozonation process are given in Table 5.18.

Table 5.18 Removal efficiencies and effluent concentrations after ozonation

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TSS	28	28	0
COD	895	796	11
BOD	425	425	0
Tot N	89	89	0
Tot P	6	6	0
CBZ	0.21365	0.01068	95
DCF	0.03611	0.00181	95
IBF	0.09748	0.00487	95
MTL	0.20585	0.01029	95

The energy needed for the ozone production is changing between 15-20 kWh/kg ozone (Ternes and Joss, 2006). In the Table 5.12 energy requirement values are given for air preparation, ozone generation, ozone contacting and all the other uses. Energy required for ozonation (E_o) was calculated as:

$$E_O = \frac{15\ gozone}{m^3 ww} \cdot \frac{750\ m^3 ww}{d} \cdot \frac{kg}{1000\ g} \cdot \frac{(15 + 5 + 4 + 2)kWh}{kgozone} \cdot \frac{365\ d}{year}$$

Which results in:

106,762 kWh/year

For the **treatment of grey water**, UASB septic tank and MBR were selected after the analysis of the treatment processes in Chapter 4. In the following subchapters the calculations for each unit will be given.

5.4.6 UASB Septic Tank

It is assumed that 90% TS, 45% COD, 60% of BOD, 26% Totl N and 18% Tot P removal occur in UASB septic tank being introduced by the grey water (Elmitwalli and Otterpohl, 2007;Leal et al., not published). Since the influent value for the solids is in total solids and no removal efficiency was found for the total solids 90% removal rates was assumed to be valid for the total solids as well. The removal efficiencies of the macropollutants and the effluent concentrations are given in Table 5.19.

Table 5.19 Removal efficiencies and the effluent concentrations after UASB septic tank (grey water)

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	600	60	90
COD	570	313	45
BOD	296	118	60
Tot N	13	10	26
Tot P	4	3.59	18

Since not all of the COD reduced in UASB septic tank will be methanized, it was assumed 0.7 of COD removed will be converted to methane (STOWA, 2005). Energy that can be obtained from the methane is calculated as follows:

$$E_{biogas} = (COD_{in} - COD_{eff}) \cdot 0.7 \cdot Q \cdot \frac{m^3 biogas}{kgCOD} \cdot \frac{kWhenergy}{m^3 biogas} \cdot E_{electricity}$$

E_{biogas} : Energy generated from the biogas (kWh/year.100000 p.e.)

COD_{in}: Influent COD concentration (g/m^3)

COD_{eff}: Effluent COD concentration (g/m^3)

Q : Flowrate (m^3/d)

$E_{electricity}$: Electrical efficiency

0.35 m3 CH4/1 kg COD is assumed to be produced at 273 K during the anaerobic digestion of grey water. Methane has got a combustion heat of 35.8 E10^6 J/m3, at 273 K and p=p0. 1 kWh = 36E10^5 Joule (STOWA, 2005). 35% efficiency was assumed for the electricity production.

$$E_{biogas} = \frac{(569.5-313.2)\cdot 0.7 gCOD}{m^3 ww} \cdot \frac{9130 m^3 ww}{d} \cdot \frac{kg}{1000 g} \cdot \frac{0.35 m^3 CH_4}{kgCOD} \cdot \frac{35.8E06J}{m^3 biogas} \cdot \frac{kWh}{36E05J} \cdot \frac{365 d}{year} \cdot \frac{35}{100}$$

Which results in:

728,327 kWh/year (100,000 p.e.)

The heat energy produced by the methane production was assumed to be with 50% efficiency which results in **1,040,460 kWh/year** for 100,000 p.e.

The temperature of grey water (18–38 ℃) is relativ ely higher when it is compared to the temperature of domestic wastewater (Eriksson et al., 2002). The grey water has a temperature changing between 18 and 38 ℃ (Eriksson et al., 2002). For this study, an average temperature degree of 28 ℃ is assumed as the temperature of grey water which is sufficient for the operation of UASB septic tank. Since there is no need for energy to heat up the grey water, the heat energy produced by the methane production was not used in the calculations.

5.4.7 Membrane Bioreactor

Although high percentages of the COD, BOD and TS are removed in UASB tank, effluent quality is not sufficient to meet the effluent standards. This is why a membrane bioreactor is used as an aerobic polishing step is placed for further removal of organic and solid content in grey water.

A 95% TS, 93% COD, 93% BOD, 66% total N and 52% total P are the assumed removal efficiencies for the macro pollutants in MBR bioreactor based on the literature (Table 4.13). The removal efficiencies of the macro pollutants and the effluent concentrations are given in Table 5.20.

Table 5.20 Removal efficiencies and the effluent concentrations after MBR (grey water)

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Removal %
TS	60	3	95
COD	313	22	93
BOD	118	8	93
Tot N	10	3	66
Tot P	4	2	52

The energy consumption of the bioreactor is assumed to be 0.9 kWh/m^3 treated wastewater (STOWA, 2007).

$$E_{MBR} = \frac{kWh_{consumed}}{m^3} \cdot Q \cdot \frac{365\ d}{year}$$

E_{MBR}: Energy consumption by MBR (kWh/year)

$$E_{MBR} = \frac{0.9\ kWh}{m^3} \cdot 9130 \cdot \frac{365\ d}{year}$$

Which results in

2 999 205 kWh/year (100,000 p.e)

6 Evaluation of Combined and Source Separated Wastewater Treatment Systems

In the beginning of the study, the comparison of the systems was based on the emissions to the receiving water bodies, nutrient recovery and energy consumption, considering the system boundary. A set of criteria was determined to compare the system A and B. Evaluation of the systems was done by the comparison of these criteria, which were calculated according to 100.000 p.e. and given below:

- The eutrophication potential based on the emissions of COD, BOD, total N, total P (unitless)
- The emission loads of the representative pharmaceutical compounds (carbamazepine, diclofenac, ibuprofen and metoprolol) into receiving water as loads ($kg.year^{-1}$)
- The amount of N and P recovered ($kg.year^{-1}$)
- net energy consumption ($kWh.year^{-1}$)

During the inventory analysis influent and effluent of each treatment process were calculated as concentrations ($mg.L^{-1}$). However, because of the differences between the volumes of the system influents, using concentrations would not have been an appropriate unit, for the comparison of the systems. Less consumption of water in separated system with vacuum toilets, caused to have higher concentrations of pollutants in influent, compared to the combined system. However, the loads of the influents of both systems A and B were the same. This is why the system influent and effluents were calculated and compared as loads ($kg.year^{-1}$). In the following sub-chapters, the results are given in graphs comparing the systems A and B. Dark colored columns represent the combined wastewater treatment system, whereas the combined wastewater treatment system was represented by light colored columns.

6.1 Emissions to Receiving Water

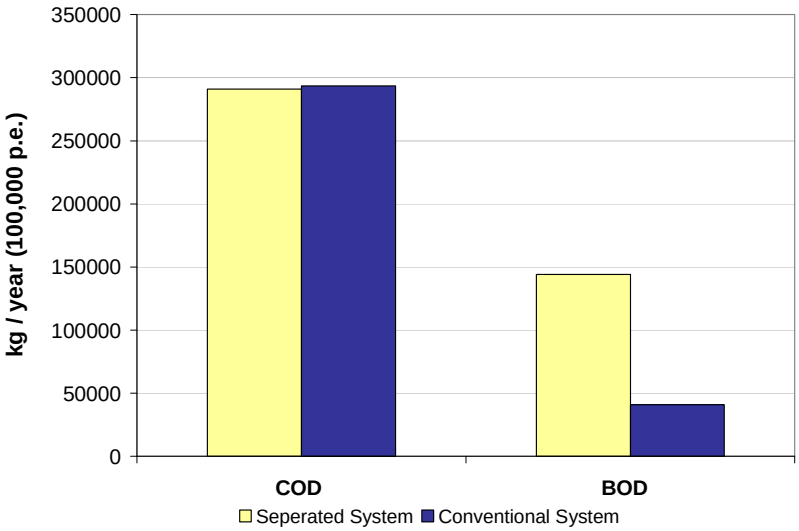


Figure 6.1 The COD and BOD effluent loads discharged to the receiving water (kg/year)

COD and BOD effluent loads of both systems are given in Figure 6.1. There is no significant difference in the effluent loads of two systems considering COD. However, conventional system has an advantage over separated system by eliminating BOD to a larger extent. Therefore, considering the organic loads given to the receiving water bodies, it can be stated that conventional system is a better option compared to separated system.

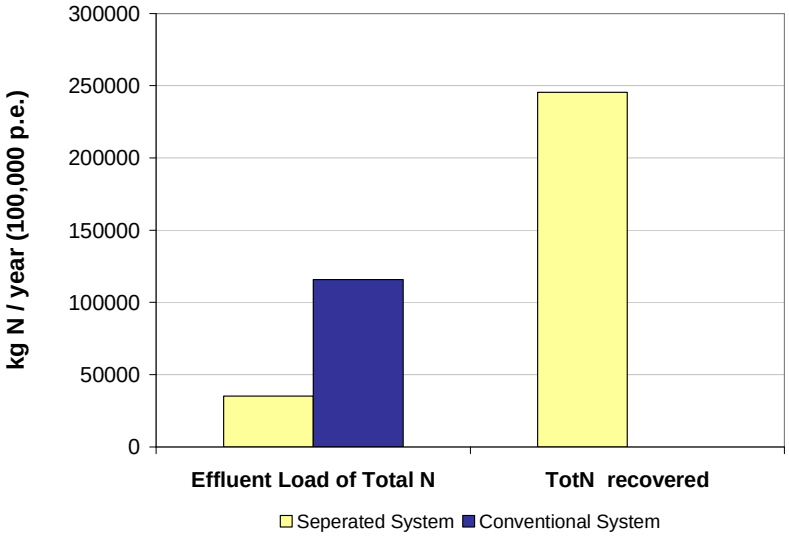


Figure 6.2 The effluent loads of nitrogen discharged to the receiving water and the nitrogen recovered in source separated wastewater treatment system (kg/year)

Recovery of nutrients was one of the aims of the separated system. Light colored column on the right in Figure 6.2 shows the amount of nitrogen recovered, which is approximately 250,000 kg per year. Considering the phosphorus recovery, light colored column on the right in Figure 6.3 demonstrates that the amount of phosphorus recovered by separated system is approximately 20,000 kg per year. Besides the nutrients recovery, lower effluent loads of nitrogen and phosphorus discharged can make us conclude that the separated system is a better option compared to the conventional system.

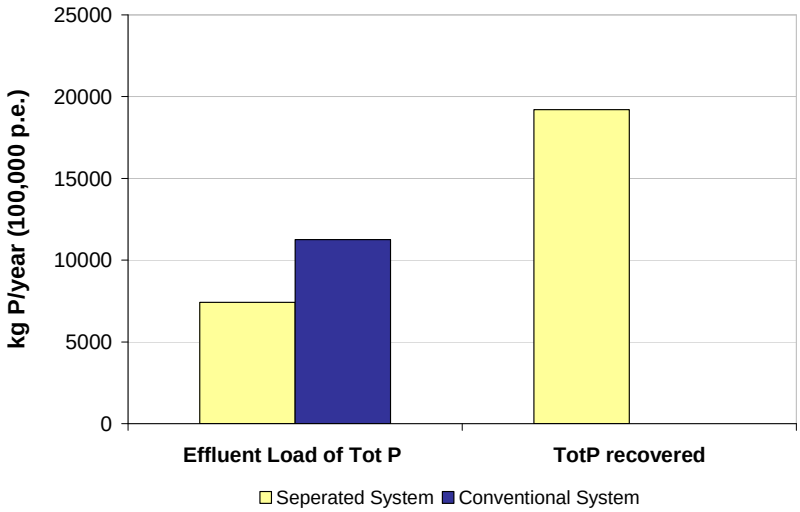


Figure 6.3 The effluent loads of phosphorus discharged to the receiving water and the phosphorus recovered in source separated wastewater treatment system (kg/year)

6.2 Potential Impacts on Eutrophication

The results obtained from inventory analysis, based on COD, total N and total P, were converted into more environmentally relevant information which is eutrophication. This conversion was done by the classification/characterization step of the life cycle assessment. In this study only the impacts of the carbon, nitrogen and phosphorus related environmental loads quantified in the inventory analysis phase was related/classified to the eutrophication category.

In order to convert the emission loads of pollutants into the potential eutrophication effect, some classification factors were used. All the other pollutants such nitrates, COD etc. are expressed in the terms of phosphate equivalent. Characterization factors are given in Table 6.1.

Table 6.1 Related compounds and characterization factors and for europhication (Heijungs, 1992)

Eutrophication	Compounds	Characterization factor	
	1 kg Nox	0.13	PO4 eq
	1 kg NO3	0.1	PO4 eq
	1 kg N	0.42	PO4 eq
	1 kg PO4	1	PO4 eq
	1 kg P	3.06	PO4 eq
	1 kg COD	0.022	PO4 eq

The eutrophication potential is expressed in PO4-3 equivalent in Figure 6.4.

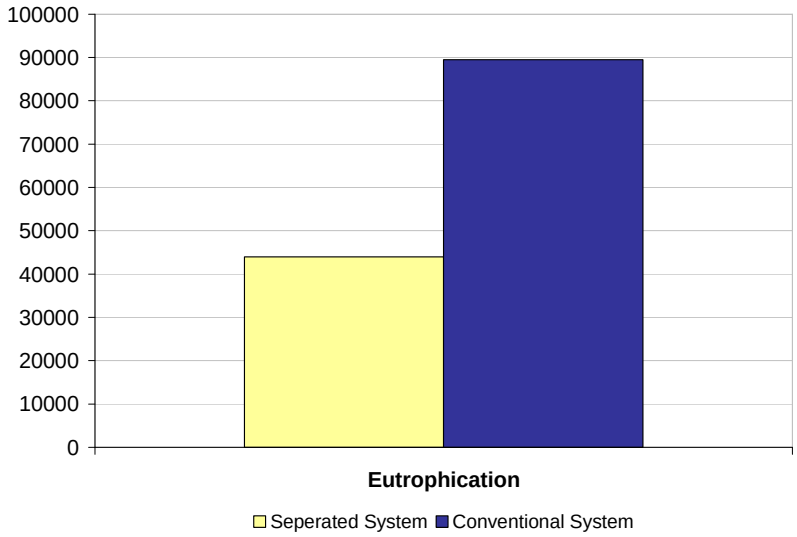


Figure 6.4 The impacts of combined and source separated wastewater treatment systems on eutrophication.

In Figure 6.4, the potential impacts of both systems on eutrophication are given. It can be stated that separated system has much lower potential impact on eutrophication compared to the conventional system.

6.3 Emissions of Representative Pharmaceutical Compounds

In Figure 6.5, the effluent loads of representative pharmaceutical compounds are given. Carbamazepine effluent load of conventional system is slightly lower than the load of the separated system. Compared to the other three compounds, carbamazepine is discharged in the highest effluent loads from the both systems. This shows that carbamazepine is the most persistent compound in WWTPs within the representative pharmaceutical compounds. Separated system gave a slightly lower effluent load for diclofenac compared to the conventional system. The effluent load of ibuprofen from separated system is higher than the load of conventional system. The difference in metoprolol effluent loads is much more significant compared to the other compounds. Conventional system has lower effluent load of metoprolol compared to the separated system.

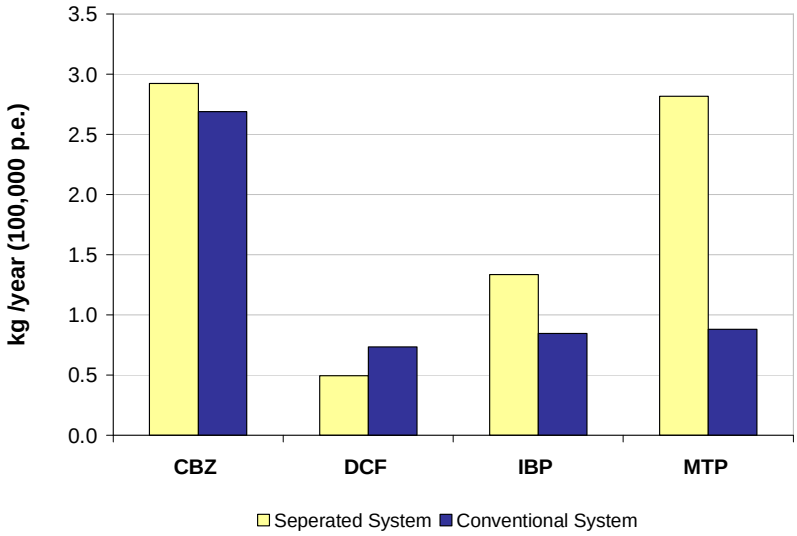


Figure 6.5 The effluent loads of carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBP) and metoprolol (MTP) discharged to the receiving water from combined and source separated wastewater treatment system (kg/year)

In Figure 6.6, the effluent loads of both systems are compared with the effluent load of conventional system without ozonation regarding to representative pharmaceutical compounds. Significant differences in the effluent loads show the high efficiency of ozonation process in removing the pharmaceutical compounds.

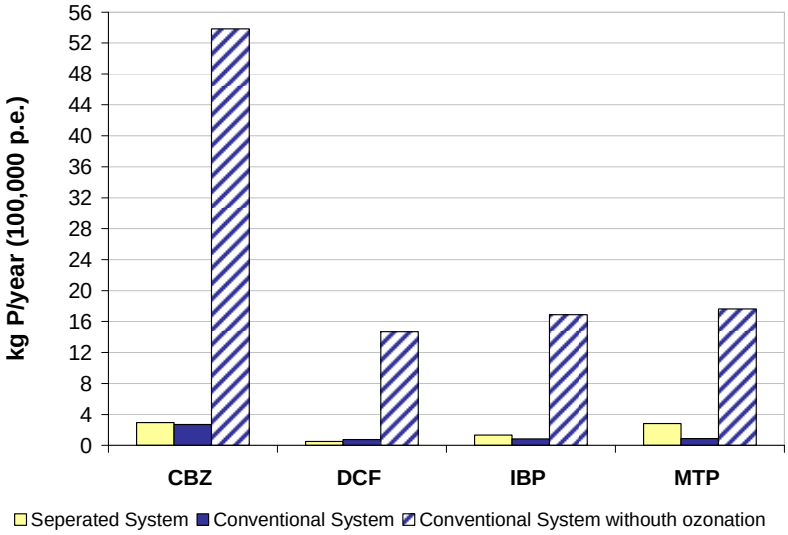


Figure 6.6 The effluent loads of carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBP) and metoprolol (MTP) discharged to the receiving water from conventional and source separated conventional wastewater treatment system and existing conventional wastewater treatment system without ozonation (kg/year)

6.4 Energy Consumption

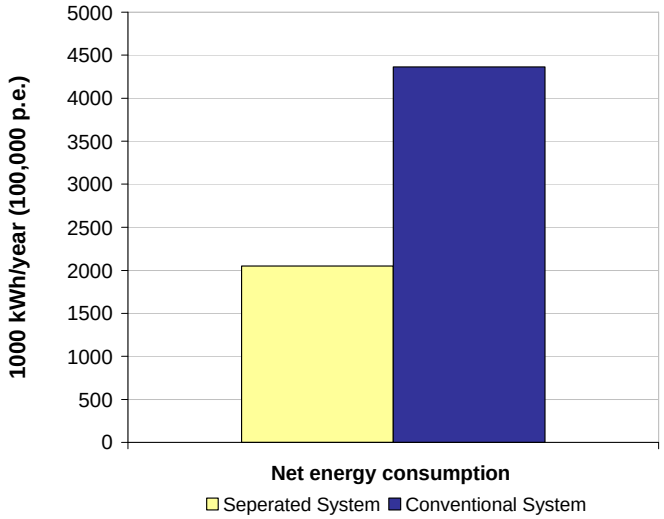


Figure 6.7 The net energy consumption of combined and source separated wastewater treatment systems

The net energy consumptions for both systems are compared in Figure 6.7. Separated system has a considerable advantage over the conventional system considering that it consumes much less energy. The main difference between the amounts of energy utilized by both systems is caused by the energy recovered during the anaerobic degradation process of the black water.

6.5 Overall Evaluation

Considering the results given above, both systems have advantages on different issues. It is not easy to give an overall evaluation of the systems and state which system is better compared to the other one. To be able to do this nutrient recovery, energy consumption and the effluent loads of the representative pharmaceutical compounds should be expressed as environmental impacts as it was done for potential impact of eutrophication. Overall weighting which is the last step of the life cycle assessment would have provided to determine the best option between the two systems.

7 Conclusion and Discussion

Each research question and the related conclusions are given and discussed below.

RQ 1: What are the removal mechanisms and the removal potentials of the selected representative pharmaceutical compounds, carbamazepine, diclofenac, ibuprofen, metoprolol, in conventional wastewater treatment plants?

Biological degradation can be stated as an efficient removal mechanism for ibuprofen. Diclofenac and metoprolol are biodegraded partially whereas biodegradation of carbamazepine is not significant. Diclofenac is expected to be removed to a larger extent by sorption mechanism considering that for the other selected compounds, sorption is not an appropriate mechanism. Chemical oxidation is a promising mechanism in removing all the selected pharmaceutical compounds.

The removal of the selected compounds is not sufficient in existing conventional WWTPs (Chapter 4.2; Table 4.9). The main mechanism, which plays role in the removal of carbamazepine, diclofenac, ibuprofen and metoprolol, is degradation with efficiencies of 8%, 50%, 90% and 85%, respectively. In conventional WWTPs, ibuprofen was found to be removed to a large extent where as diclofenac and metoprolol are partially eliminated confirming lab-scale findings. No significant removal of carbamazepine was concluded in all the analyzed studies. Although in lab-scale experiments, SRT was found to be an influencing factor on the removal efficiency of pharmaceutical compounds, in full scale studies, different SRTs resulted in no difference in the removal efficiencies.

RQ 2: What are the removal efficiencies of subsequent treatment processes for the selected representative pharmaceutical compounds?

The removal efficiencies of COD, BOD, TSS, Total N, Total P, carbamazepine, diclofenac, ibuprofen and metoprolol for each investigated treatment process were given in Table 4.17. Ozonation, advanced oxidation process, nanofiltration and activated carbon adsorption were found to be the most promising techniques for further removal of pharmaceuticals (Chapter 4.3). All these four post-treatment options may result in 80-100% removal of majority of pharmaceutical compounds.

Since this was a literature review study, all the removal efficiencies were gathered from the published studies. Some of the removal rates were taken from the lab-scale studies. However, the results of the lab scale studies are not always in parallel with the results of full scale studies. Besides, some of the removal efficiencies of metoprolol in UASB septic tank by anaerobic digestion were assumed by considering its degradation and sorption coefficients which were taken from lab scale studies. In MBR which was a polishing step for black water treatment, the fate of the selected pharmaceutical compounds was assumed by limited available. All these assumptions and potential errors may cause differences in overall emission loads in the study since the results were very sensitive to the changes in the removal efficiencies.

RQ 3: What is the configuration of treatment processes in order to remove pharmaceutical compounds with the highest removal efficiency, after removing the macro pollutants, for combined wastewater treatment system?

Primary sedimentation followed by activated sludge process is found to be the most commonly used configuration for the conventional WWTPs in the literature. Among the possible tertiary treatment systems, ozonation was chosen as the last step of the combined wastewater treatment system. Ozonation was found to be the less energy consuming tertiary process (0.1 $kWh/m^3_{wastwater}$) with high pharmaceutical removal efficiency (90-99%) and disinfection ability

RQ 4 What is the configuration of treatment processes in order to remove pharmaceutical compounds with the highest removal efficiency, after removing the macro pollutants, for source separated wastewater treatment systems?

UASB septic tank was found to be an appropriate process as a first step of black and grey water treatment. MBR was chosen as a second step for both streams for further removal of organic materials. For the nutrient recovery of phosphorus and nitrogen from the black water, struvite precipitation and ion exchange were chosen with their high efficiencies. Ozonation was chosen as a last step of the black treatment mainly for pharmaceutical compound removal and the disinfection purposes

RQ 5: What is the overall evaluation of (the comparison) of the combined and source separated wastewater treatment systems?

Although the difference in the COD effluent loads of separated and combined system is not significantly different, the effluent BOD load of combined system is less than the separated system. Struvite precipitation process provided almost 20 000 kg of phosphorus and 27 000 kg of nitrogen recovered per year. On the other hand, 223.000 kg of nitrogen was recovered per year. In total 20 000 kg of phosphorus and 250 000 kg of nitrogen were recovered in separated system whereas in combined system a large fraction of the phosphorus and nitrogen were eliminated. Because of the high recovery of nutrients the effluent loads of phosphorus and nitrogen are quite low compared to the combined system.

When the effluent loads of four pharmaceutical compounds are compared it can be concluded that carbamazepine is the most persistent compound among the others. It can be concluded that both systems gave similar loads/emissions of carbamazepine to the receiving water bodies. The reason can be stated as that only the ozonation process, which was placed in both systems, was highly effective in the removal of this compound. Similar effluent loads/emissions were achieved for diclofenac for both systems. Overall elimination of the ibuprofen in separated system is better than the combined system. The effluent load of ibuprofen from combined system is less than the effluent load of separated system. It can be concluded that the effluent load of metoprolol from separated system is more than the load of combined system.

Adjustment of SRT in the MBR process used in the black water treatment as proposed in this study is a critical aspect considering the pharmaceutical compound removal and nitrogen recovery. Low SRT values (<4 days) were

required and used to prevent the removal of nitrogen by nitrification processes. Retained nitrogen in the wastewater was recovered in the ion exchange process. On the other hand, long SRT values (>5 days) was recommended for more effective removal of pharmaceutical compounds, in MBR processes. Besides, longer SRT provides better removal of organic contents. Environmental impact assessment is required to evaluate the impacts of the pharmaceutical compounds, the organic materials and the nitrogen recovery to be able to decide on the SRT value.

In the whole study, removal efficiencies of the parent compounds were considered during the selection of the treatment processes considering the pharmaceutical removal. However, a lot of studies state that a small fraction of the pharmaceutical compounds are excreted as parent compounds while the rest is excreted as metabolites. In this study and it was assumed that the pharmaceuticals are excreted for 100% as parent compounds. This assumption was made because of the limited available data on the removal efficiencies of the metabolites in the wastewater treatment processes. The same percent is used in the environmental risk assessments assuming that almost all of the compounds are excreted as parent compound and metabolites which can be retransformed to parent compounds in a sewer or/and in the treatment system (Huschek et al., 2004). However further researches on the removal efficiencies of the treatment processes should be done for metabolites to have a better understanding of the fate of pharmaceutical compounds during WWTPs.

The impact assessment of both systems was done only for eutrophication in this study. The COD, total nitrogen and total phosphorus effluent loads being discharged to the water were used to calculate the impacts of both systems on eutrophication. According to the results the impact of separated system on eutrophication is approximately 20% less than the impact of combined system. The main reason of this difference can be stated as the lower effluent loads of nutrients from separated system because of the recovery.

The net energy consumption of the combined system is slightly more than the energy consumption of separated system. As it was concluded in the study of (Tillman et al., 1998) source separation is an efficient means of reducing the energy consumption required for the fertilizer production by recovering nutrients. However, considering the time available for this research, fertilizer production was excluded from the system boundaries. If the energy required for the production of fertilizer, which was recovered in the system, would have been included, the results would have been as it is in Figure 7.1. The figure shows the importance of the influence of including the fertilizer production into the system boundaries. The calculations for energy required for the production of fertilizer by recovering nutrients are given in Annex A.4.

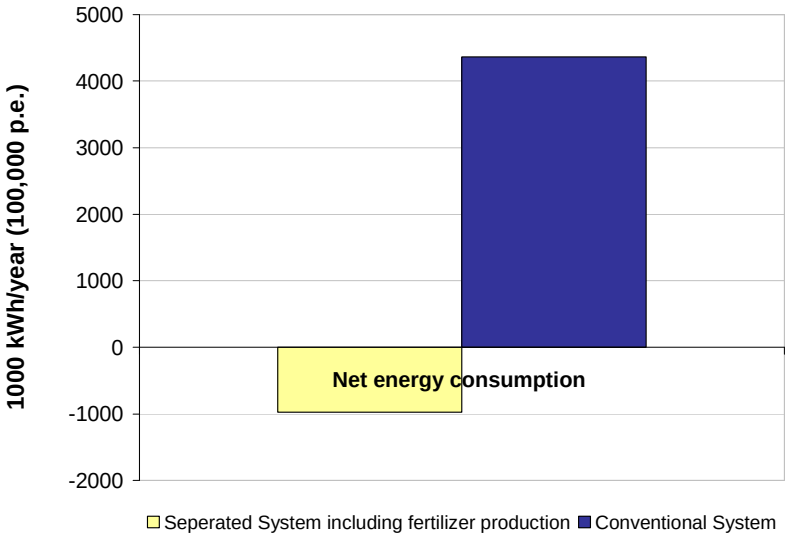


Figure 7.1 The net energy consumption of combined and source separated wastewater treatment systems

Small differences in temperature of wastewater, entering into UASB septic tank, result in large differences in energy consumption for heating up the reactor. For this research average temperature of grey found in the literature was used. Specific temperatures for Netherlands would have given slightly different results in the energy consumption of heating up the wastewater in UASB septic tank.

A large amount of electricity and heat energy is obtained from the biogas in the UASB septic reactor. A large part of the heat energy obtained, is used to heat up the wastewater and the reactor but the rest of the heat energy was not included in the calculations. The rest is an additional amount which could be used for other purposes.

In the energy calculations, besides the fertilizer production, the cost of the wastewater collection systems, the energy consumption for the chemicals being added to the system and the energy consumption of the operational systems were excluded as well. Next to these, the construction phase of the treatment systems was also not considered in energy calculations. In many studies, it was stated that construction phase is of less importance than the operation phases (Lundin et al., 2000;Tillman et al., 1998).

In the study of (Lundin et al., 2000), conventional and separated wastewater treatment systems were compared. In the separated system, black water mixed with kitchen waste was treated with liquid composting (aerobic thermophilic sludge stabilization process) and was used as a fertilizing agent in agriculture. Grey water was treated in a septic tank following by a sand filter. In the results, separated system was found to be having lower emissions to the water, more efficient recycling of nutrients to agriculture which are comparable to the results of this study.

Not all of the environmental aspects were considered in the inventory analysis. The emissions of the treatment processes to air, or the emissions to the soil by

sludge are two important aspects which were excluded during the analysis. Enlarging the system boundaries, may result in differences in the overall picture of the comparison of the systems.

Only two of the options were investigated for better removal of pharmaceuticals from the wastewater in this study. Other methods, such as urine separation, could be included in the comparison.

During this study, only the COD, BOD, total N and total P were expressed as a potential environmental impact which was eutrophication. However, the emissions of the fours representative compounds, the amount of nitrogen and phosphorus recovered and the energy consumption were not expressed as any potential environmental impact. Because of this reason, the best option could not be evaluated but the systems A and B were compared according to each issue separately. For instance, the emission of the pharmaceutical compounds could be expressed as potential toxicity and the energy consumption could be expressed as potential global warming.

As a summary of conclusions:

- Biodegradation is a prevailing mechanism in removing pharmaceutical compounds from wastewater but not for all compounds.
- Ozonation is a promising technology as a tertiary treatment with high percentages of pharmaceutical compounds.
- Separated system has a significantly smaller eutrophication potential compared to the conventional system.
- Separated system is a better option considering the recovery of nitrogen and phosphorus.
- Conventional system is a better option in removing carbamazepine, ibuprofen and metoprolol.
- Separated system is a better option in removing diclofenac and ibuprofen.
- Separated system consumes much less energy than the conventional system.

8 Recommendations

- Environmental impact assessment, as a continuation for the life cycle assessment, is required for the emissions of the representative pharmaceutical compounds, nutrient recovery and the energy consumption for a better overall evaluation of the systems.
- System boundaries can be enlarged including fertilizer production, agriculture practice and wastewater collection for better comparison of the systems.
- Considering the concentration emissions of the separated wastewater treatment systems improvements are required in the treatment processes to be able to give lower emissions complying the Dutch discharge standards.
- Possible further studies on the removal of pharmaceutical compounds, especially metoprolol, would give better understanding of the fate of this compound in conventional WWTPs.
- Further studies on the biodegradation and chemical oxidation potentials of the pharmaceutical compounds could be done, especially investigating the transformation/mineralization of the parent compounds and the formation of toxic intermediates.
- More research can be done on the removal efficiencies of representative pharmaceutical compounds in individual treatment processes.

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Annex

A.1 ABBREVIATIONS USED IN THE CHAPTERS

AC: Accumulated System

BOD: Biological Oxygen Demand

C: Carbon

CASP: Conventional Activated Sludge Plant

CBZ: Carbamazepine, antidepressant and antiepileptic drug

COD: Chemical Oxygen Demand

DCF: Diclofenac

DDD: Defined daily dose; is the assumed average maintenance dose per day for a drug product when used for its major indication in everyday practice

DOC: Dissolved Organic Carbon

HRT: Hydraulic Retention Time

IBF: Ibuprofen

LOD: Limit of detection

MBR: Membrane Biological Reactor

MTP: Metoprolol

N: Nitrogen

N-Kjd: Kjedal Nitrogen

P: Phosphorus

SBR: Sequencing Batch Reactor

SRT: Sludge Retention Time

STP: Sewage Treatment Plant

Tot N: Total Nitrogen

Tot P: Total Phosphorus

TSS: Total Suspended Solids

UASB: Upflow Anaerboic Sludge Blanket

WWTP: Waste Water Treatment Plant

A.2 GLOSSARY

Aliphatic compounds: organic compounds, in which carbon atoms are joined together in straight or branched chains as opposed to aromatic compounds which include a benzene ring

Aromatic compound, an organic chemical compound that contains aromatic rings (arenes) like benzene, pyridine, or indole.

Denitrification: is the process of reducing nitrate and nitrite, highly oxidized forms of nitrogen available for consumption by many groups of organisms, into gaseous nitrogen, which is far less accessible to life forms but makes up the bulk of our atmosphere.

Emulsion: is a mixture of two immiscible (unblendable) substances

Emulsify: also known as an emulgent, is a substance which stabilizes an emulsion, frequently a surfactant

Hydrophilicity: Having a strong affinity for water; tending to dissolve in, mix with, or be wetted by water

Metabolite: Any product formed by biological metabolism (human or microbial)

Micro pollutant: Organic or inorganic pollutant with environmental relevance at concentrations below 0.1 $mg.L^{-1}$. Mostly used as synonymous to trace pollutant

Persistency: designates the compound characteristic of not being readily or inherently degradable

Polishing step: in wastewater and drinking water designates an advanced treatment step for removal of trace contaminant, following in the main treatment steps. In wastewater treatment synonymous to tertiary treatment

Saturated zone: Soil region that has reached the maximum water holding capacity

Sludge: Sludge is a solid, semi-solid or liquid residue, containing micro organisms and their products extracted in sewage treatment processes.

Sludge age/Sludge retention time: in biological wastewater treatment refers to the average retention time of the sludge flocs within a reactor prior to withdrawal as excess sludge.

Steroid: is a terpenoid lipid characterized by a carbon skeleton with four fused rings, generally arranged in a 6-6-6-5 fashion.

Xenobiotics : The body gets rid of xenobiotics by xenobiotic metabolism. This consists of the deactivation and the secretion of xenobiotics, and happens mostly at the liver. Secretion routes are urine, faeces, breath and sweat. Hepatic enzymes are responsible for the metabolism of xenobiotics, by first activating them (oxidation, reduction, hydrolysis and/or hydration of the xenobiotic) and then conjugating the active secondary metabolite with glucuronic or sulphuric acid, or glutathione, followed by excretion in bile or urine.

A.3 CALCULATIONS FOR PHARMACEUTICAL COMPOUNDS CONSUMPTION

Table A3.1 DDD used per year, DDD in grams and the total consumption of the pharmaceutical compounds in theaphetic group C (Cardiovascular System), (GIP/CVZ, 17/06/07).

Therapheutic Compounds		DDD/year					DDD (mg)	tonnes/year				
Cardiovascular system (C)		2001	2002	2003	2004	2005		2001	2002	2003	2004	2005
Enalapril/ enalaprilaat	C09AA02 Enalapril/enalaprilaat (*Renitec* ®)	113,919,100	119,857,600	124,529,500	128,060,400	129,776,500	10	***1.1***	***1.2***	***1.2***	***1.3***	***1.3***
Atorvastatine	C10AA05 Atorvastatine (*Lipitor* ®)	124,804,400	151,115,400	177,199,300	209,270,000	251,456,500	10	***1.2***	***1.5***	***1.8***	***2.1***	***2.5***
Metoprolol	C07AB02 Metoprolol (*Selokeen-zoc* ®)	86,849,600	92,654,400	98,935,200	108,001,000	129,929,300	150	***13.0***	***13.9***	***14.8***	***16.2***	***19.5***
Furosemide	C03CA01 Furosemide (*Lasix* ®)	103,390,300	102,087,900	102,483,400	102,250,400	101,434,400	40	4.1	4.1	4.1	4.1	4.1
Simvastatine	C10AA01 Simvastatine (*Zocor* ®)	137,185,900	153,560,400	169,617,100	187,007,600	213,647,200	15	2.1	2.3	2.5	2.8	3.2

Table A3.2 DDD used per year, DDD in grams and the total consumption of the pharmaceutical compounds in theaphetic group M (Musculo-skeletal System), (GIP/CVZ, 17/06/07).

Therapheutic Compounds		DDD/year					DDD (mg)	tonnes/year				
Musculo-skeletal system (M)		2001	2002	2003	2004	2005		2001	2002	2003	2004	2005
Ibuprofen	M01AE01 Ibuprofen (*Brufen* ®)	30,426,100	31,550,800	31,926,100	24,287,400	24,782,600	1200	36.5	37.9	38.3	29.1	29.7
Diclofenac	M01AB05 Diclofenac (*Cataflam* ®)	53,731,200	52,343,500	51,529,900	48,853,700	51,072,400	100	5.4	5.2	5.2	4.9	5.1
Naproxen	M01AE02 Naproxen (*Naprovite* ®)	36,715,000	35,531,500	33,585,600	29,445,500	27,480,400	500	18.4	17.8	16.8	14.7	13.7

Table A3.3 DDD used per year, DDD in grams and the total consumption of the pharmaceutical compounds in therapeutic group N (Nervous System). The pharmaceutical compounds which have DDD/year values above 10 000 000 (GIP/CVZ, 17/06/07).

Therapeutic Compounds		DDD/year					DDD (mg)	tonnes/year				
Nervous System (N)		2001	2002	2003	2004	2005		2001	2002	2003	2004	2005
Carbamazepine	N03AF01 Carbamazepine (*Tegretol* ®)	10,216,900	10,175,100	10,134,200	10,028,900	9,733,300	1000	***10.2***	***10.2***	***10.1***	***10.0***	***9.7***
Paracetamol	N02BE01 Paracetamol (*Sinaspril* ®)	31,286,800	33,848,900	38,653,200	287	415	3000	***93.9***	***101.5***	***116.0***	***0.0***	***0.0***
Valproinezuur	N03AG01 Valproinezuur (*Depakine-chrono* ®)	11,378,900	12,017,200	12,648,200	13,301,600	13,642,600	1500	***17.1***	***18.0***	***19.0***	***20.0***	***20.5***
Diazepam	N05BA01 Diazepam (*Stesolid* ®)	29,495,600	29,287,200	29,268,100	28,973,500	27,866,400	10	0.3	0.3	0.3	0.3	0.3
Oxazepam	N05BA04 Oxazepam (*Seresta* ®)	39,350,700	38,947,400	39,054,300	38,808,900	37,293,200	50	2.0	1.9	2.0	1.9	1.9
Lorazepam	N05BA06 Lorazepam (*Temesta* ®)	17,237,700	16,820,400	16,556,300	16,502,000	15,996,500	2.5	0.0	0.0	0.0	0.0	0.0
Nitrazepam	N05CD02 Nitrazepam (*Mogadon* ®)	16,422,700	15,551,400	14,822,200	13,931,700	12,753,300	5	0.1	0.1	0.1	0.1	0.1
Lormetazepam	N05CD06 Lormetazepam (*Noctamid* ®)	25,967,100	26,100,300	26,357,200	26,426,700	25,691,800	1	0.0	0.0	0.0	0.0	0.0
Temazepam	N05CD07 Temazepam (*Normison* ®)	49,593,800	49,783,100	50,709,400	50,963,800	49,259,600	20	1.0	1.0	1.0	1.0	1.0
Zopiclon	N05CF01 Zopiclon (*Imovane* ®)	15,494,400	15,953,700	16,503,700	17,452,500	17,391,100	7.5	0.1	0.1	0.1	0.1	0.1
Amitriptyline	N06AA09 Amitriptyline (*Tryptizol* ®)	16,184,500	16,335,300	16,763,800	17,282,700	17,169,600	75	1.2	1.2	1.3	1.3	1.3
Fluoxetine	N06AB03 Fluoxetine (*Prozac* ®)	19,699,500	19,730,700	19,443,600	19,797,000	19,206,200	20	0.4	0.4	0.4	0.4	0.4
Citalopram	N06AB04 Citalopram (*Cipramil* ®)	11,846,600	18,107,900	23,527,300	29,455,300	32,331,400	20	0.2	0.4	0.5	0.6	0.6
Paroxetine	N06AB05 Paroxetine (*Seroxat* ®)	72,656,400	75,136,200	74,276,100	76,438,500	72,292,000	20	1.5	1.5	1.5	1.5	1.4
Fluvoxamine	N06AB08 Fluvoxamine (*Fevarin* ®)	11,178,000	10,781,500	10,470,900	10,292,100	9,608,500	100	1.1	1.1	1.0	1.0	1.0
Mirtazapine	N06AX11 Mirtazapine (*Remeron* ®)	11,420,600	13,155,200	14,786,100	16,626,000	16,907,700	30	0.3	0.4	0.4	0.5	0.5
Venlafaxine	N06AX16 Venlafaxine (*Efexor* ®)	12,464,100	15,321,700	18,668,200	23,155,700	26,178,900	100	1	2	2	2	3
Betahistine	N07CA01 Betahistine (*Betaserc* ®)	23,946,400	25,055,600	25,292,400	25,772,400	24,985,600	24	1	1	1	1	1

A.4 ENERGY CALCULATIONS FOR FERTILIZER PRODUCTION

The amount of energy needed to produce the fertilizers including the same amount of P and N, which is recovered in *struvite precipitation process* is calculated below. The Table A4.1 represents the amount of energy required for the fertilizer production in Europe for each element (N or P).

Table A4.1 Energy requirements for average N- and P-fertiliser production in Europe (Maurer etal, 2003)

Process	Electricity (MJ/kg N or P)	Other (MJ/kg N or P)	Total (MJ/kg N or P)	Total (kWh/kg N or P)
Average N-fertiliser production in Europe	0.8	42	42.8	11.89
Average P-fertiliser production in Europe	4	16	20	5.56

$$E_{N,\,fertlizer} = (TotN_{\,in} - TotN_{\,eff}) \cdot Q \cdot \frac{kWh \quad required}{kgN_{\,fertilizer}}$$

$E_{N,\,fertilizer}$: Energy gained by N recovery as fertilizer (kWh/year.100000 p.e.)

$$E_{N,\,fertlizer} = \frac{(986 - 887)\,gN}{m3ww} \cdot \frac{kg}{1000\ g} \frac{750\ m3ww}{d} \cdot \frac{11.89\,kWh}{kgN_{\,fertilizer}} \cdot \frac{365\,d}{year}$$

$E_{N,\,fertilizer}$ = **320,772** kWh/year.100000 p.e.

$$E_{P,\,fertlizer} = (TotP_{\,in} - TotP_{\,eff}) \cdot Q \cdot \frac{kWh \quad required}{kgP_{\,fertilizer}}$$

$E_{P,\,fertilizer}$: Energy gained by P recovery as fertilizer (kWh/year.100000 p.e.)

$$E_{P,\,fertlizer} = \frac{(76 - 6)\,gP}{m3ww} \cdot \frac{kg}{1000\ g} \frac{750\ m3ww}{d} \cdot \frac{5.56}{kgP_{\,fertilizer}} \cdot \frac{365\,d}{year}$$

$E_{P,\,fertilizer}$ = **106,710** kWh/year.100000 p.e.

$E_{N+P,\,fertilizer}$ = 320772 + 106710 = 427482 kWh/year.100000 p.e.

Total energy required to produce the fertilizer including the same amount of P and N, which is recovered in struvite precipitation process is **427,482 kWh/year** for 100,000 person equivalent.

For the calculation of the energy required to produce the fertilizer including the same amount of nitrogen, which is recovered in *ion exchange process*. The information related to energy consumption during the fertilizer production in Table A4.1 was used.

$$E_{N,\,fertlizer} = (TotN_{\,in} - TotN_{\,eff}) \cdot Q \cdot \frac{kWh \quad required}{kgN_{\,fertilizer}}$$

$E_{N, fertilizer}$: Energy gained by N recovery as fertilizer (kWh/year.100000 p.e.)

$$E_{N,\,fertlizer} = \frac{(887 - 88.7)\,gN}{m3ww} \cdot \frac{kg}{1000\ g} \frac{750\ m3ww}{d} \cdot \frac{11.89\,kWh}{kgN_{\ fertilizer}} \cdot \frac{365\ d}{year}$$

Which results in

2,598,377 kWh/year.100000 p.e.

A.5 INVENTORY ANALYSIS

The inventory analysis including the flow charts and the calculations for both systems is in the CD.