





Aspects of Sustainable Wastewater Treatment

A Case Study of AkzoNobel PPC Conducting MFA of Nitrogen

Master's thesis in Industrial Ecology

VICTORIA KARLSSON

Department of Energy and Environment Division of Physical Resource Theory CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2017

REPORT NO. 2017:05

Aspects of Sustainable Wastewater Treatment

A Case Study of AkzoNobel PPC Conducting MFA of Nitrogen

VICTORIA KARLSSON

SUPERVISORS

Johanna Grundsell and Evalotta Stolt of AkzoNobel Pulp and Performance Chemicals

EXAMINER

Ulrika Lundqvist of the Division of Physical Resource Theory at Chalmers University of Technology

Department of Energy and Environment

Division of Physical Resource Theory

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2017

Aspects of Sustainable Wastewater Treatment

Master's Thesis within the Industrial Ecology Program

VICTORIA KARLSSON

© VICTORIA KARLSSON, 2017

REPORT NO. 2017:05 Department of Energy and Environment Division of Physical Resource Theory Chalmers University of Technology SE-412 96 Gothenburg Sweden Telephone: +46 (0)31-772 1000

Cover: Top two images of Göta Älv and AkzoNobel PPC Bohus from Wikipedia Commons, reuse and modification allowed. Bottom image of the Bohus site central wastewater plant, Centrala Reningsverk, photographed by the author.

Chalmers Reproservice

Gothenburg, Sweden 2017

Master's Thesis within the Industrial Ecology program VICTORIA KARLSSON Department of Energy and Environment Division of Physical Resource Theory Chalmers University of Technology

ABSTRACT

Water is a building block of life as well as being a valuable energy source. Ensuring that water bodies are not harmed by human actions is essential. Laws and policies govern water management including the general framework of wastewater treatment. Wastewater from industrial processes can contain toxic pollutants and nutrients which cause eutrophication and must therefore be properly treated. In this study AkzoNobel Pulp and Performance Chemicals in Bohus, Sweden, and its' central wastewater treatment plant, Centrala Reningsverket (CRV), are used as case examples. In the CRV there has been an issue of growth of biological matter which has a possible correlation with the trend of the increasing suspended solids concentration. To assess if the growth was dependent on the nutrient nitrogen, two different types of studies were conducted. Firstly, a growth identification was attempted which resulted in the conclusion that it consists of different species of bacteria, algae and uni-cellular organisms. Secondly, two Material Flow Analysis (MFA) studies were conducted where the stocks and flows of nitrogen were mapped. One MFA was conducted over the entire Bohus site and one was conducted over the CRV to see if there existed any correlations with the growth. Large stocks and flows of nitrogen do exist at the Bohus site. The results for the MFA of the CRV were statistically uncertain, however, they did hint towards a correlation with the growth. This indicates that the hypothesis regarding the growth being dependent on nitrogen as a nutrient is most likely correct. For removal of biological growth, disinfectants such as Chloride compounds are the most common approach, however these are highly toxic to higher life forms and microorganisms. To hinder further growth, wastewater flows with higher nitrogen concentrations should be rerouted away from the CRV when possible. It is necessary to treat wastewater so as to not pollute water bodies or poison human, animal and plant life. However, the treatment methods should be of a sustainable nature to ensure no adverse effects occur elsewhere. Wastewater treatment is a very energy intensive process whereas both facilities and technologies used should be energy efficient.

ACKNOWLEDGEMENTS

I would like to thank Johanna Grundsell for her expertise and support and for all the laughs and memories gained during my master thesis project work at AkzoNobel Pulp and Performance Chemicals (PPC) in Bohus, Sweden. I would also like to thank Evalotta Stolt for her help and expertise and quick responses to questions and emails. In general, I would like to thank the entire staff of the Silica Sol factory for making my time at their facilities an enjoyable learning experience and for making me feel welcomed. You are a lovely lot, and will be missed. I would also like to extend a thank you to the staff of the Analysis Lab for their time and expertise.

I would like to thank my examiner, Ulrika Lundqvist, for her guidance and support during my thesis work. Many question marks were untangled thanks to her.

I would also like to thank Joshua Mayers at the Division of Industrial Biotechnology for his time and help during the growth experiment stages of the thesis work.

Lastly, I would like to thank my colleague and friend Stina Månsson for the constant support, day and night, during the entire thesis work, as well as being part of my creative think tank and my 'solutions consultant'.

Without each and every one of the people mentioned above this work could not have been completed. Thank you, and best wishes to you all.

ABBREVIATIONS

BAT	Best Available Technology
CRV	Central Wastewater Treatment Plant – Centrala Reningsverket
ClO ₂	Chlorine Dioxide
ClO ₂ ⁻	Chlorite
ClO	Hypochlorite
H_2O_2	Hydrogen Peroxide
IE	Industrial Ecology
MFA	Material Flow Analysis
Ν	Nitrogen
N_2	Nitrogen Gas
NH ₃	Ammonia
NO ₂ ⁻	Nitrite
NO ₃ ⁻	Nitrate
NO _x	Nitrous Oxides
NaClO	Sodium Hypochlorite
OH	Hydroxide
PPC	Pulp and Performance Chemicals

Table of Contents

1. Introduction	1
1.2 Aim and Research Questions	3
1.3 Delimitations	3
2. Background	5
2.1 Wastewater Treatment Methods	5
2.2 Suspended Solids	5
2.3 Biological Matter – Bacteria and Biofilms	6
2.3.1 Nitrifying Bacteria	6
2.3.2 Biofilms	7
2.3.3 Methods for Removal of Biofilms	8
2.4 Sustainable Wastewater Treatment	8
2.4.1 The IE Perspective, Swedish Generational Goal and the Environment	al Quality
Objectives	9
2.4.2 Aspects of Wastewater Treatment Affecting Sustainability	11
3. AkzoNobel Pulp & Performance Chemicals - Site Bohus	15
3.1 Centrala Reningsverket - CRV	15
3.1.1 CRV and Suspended Solids	17
3.1.2 The Biological Matter Found in the CRV	19
3.2 Site Bohus and Nitrogen	20
4. Methodology	23
4.1 Material Flow Analysis	23
4.2 Method	24
4.2.1 Identifying Type of Growth	24
4.2.2 Conducting MFA on Nitrogen over the Site	25
4.2.3 Tracking N over CRV	25
5. Results and Analysis - Growth Identification	27
5.1 Results of the Growth Identification	27
5.2 Analysis of the Results for the Growth Identification	29
6. Results and Analysis of the MFA of Nitrogen	30
6.1 Results of MFA over AkzoNobel PPC Bohus Site	30
6.2 Analysis of the Results for the MFA of the AkzoNobel PPC Bohus Site	
6.3 Results of MFA over AkzoNobel PPC Bohus Site CRV	33
6.4 Analysis of the Results for the MFA of the CRV	35
7. Discussion	
7.1 Discussion of Method and Results	

7.2 Suggested Improvements for a Modern and Environmentally Friendly Wastewater Treatment Plant	r . 39
7.3 Future Studies	41
Conclusions	43
References	44
ppendix A	49
A.1 Calculations for Silica Sol	49
A.2 Calculations for Separation Products	51
A.3 Calculations for CRV	52
A.4 Calculations for Hydrogen Peroxide	53
ppendix B	56

1. Introduction

Water is an essential component for all life on earth. It is one of the corner stones needed for humans and ecosystems. Besides a building block for life, water is also used as an energy source through e.g. hydropower and used in industrial processes, both as a cooling agent and as a component of commercial products. Water is both a renewable and a non-renewable resource depending on if it comes from rainfall or from deep aquifers, a.k.a. groundwater.(WWF, 2017) While water resource management is important when it comes to quantity to ensure sustainable use of non-renewable water sources, it is also of great importance to manage the quality of all water since the two are interconnected. Polluted water cannot sustain the human population or the earth's ecosystems. If water bodies become polluted, renewable or non-renewable, this means that the quantity of usable water is diminished. Therefore it is important to manage both quality and quantity of water through policy and technology.(WWAP, 2012)

There are several existing policies from the European Commission regarding protecting water quality. One of those is the Drinking Water Directive (Council Directive 1998/83/EC) which aims at protecting water quality for human consumption by stating that Member States of the EU must ensure that water for consumption is *"wholesome and clean"*. As previously mentioned, water is not only used for consumption but also in industrial processes which is related to the Directive on Industrial Emissions (Council Directive 2010/75/EU). This directive states that industry of Member States should have the required permits, use the best available technology and conduct business with a precautionary approach. Both of these objectives aim, in different manners, to ensure that water quality is protected.

As a Member State of the EU, Sweden must comply with all of the directives including those related to water and environment. Sweden has one over-arching environmental objective, the Generational Goal (Generationsmålet). This goal states that all environmental politics and policies should aim at handing down to the next generation a society where the major environmental issues have been solved without causing adverse effects outside of Sweden's borders.(Swedish EPA, 2016) To be able to achieve this goal sixteen environmental quality objectives have been derived to guide national environmental politics. Four of the objectives directly relate to water and aim to ensure that water quality is maintained.(Environmental Objectives, 2016)

All of Swedish environmental law is focused towards protecting human and ecosystem health with the Generational Goal encompassing future generations. This means that besides having the right to use natural resources, such as water, the human population has an obligation to care for and manage those resources as well. This responsibility lies both with private persons but also with industrial organizations. All aspects related to this are covered in and governed by the Swedish Environmental Code (SFS 1998:808).

This legally established responsibility placed on industrial organizations also affects the Swedish branches of AkzoNobel, a global paints and coatings company with headquarters in the Netherlands. This means that AkzoNobel must ensure that the industrial processes they conduct comply with, and preferably reach beyond, existing regulation, both on the EU and Swedish level. It is also a prioritized interest within AkzoNobel to work proactively towards producing sustainable products by minimizing resource use and reducing industrial emissions (AkzoNobel, 2017). This proactive outlook is proven by the four year streak (2012 - 2015) ranking number one on the Dow Jones Sustainability Index (AkzoNobel, 2015).

In Bohus, Sweden, AkzoNobel Pulp and Performance Chemicals (PPC) is located with site activity dating back to 1924 (AkzoNobel, 2017a). The business unit is focused towards Specialty Chemicals with customers worldwide. On-site there is production of hydrogen peroxide (Hydrogen Peroxide factory), chemically pure alkali (Fine Chemicals factory), silica sols (Silica Sol factory) and separation products (Separation Products factory). There are R&D facilities, chemical analysis laboratories and facilities for administrative staff. The site has its own wastewater treatment plant, Centrala Reningsverket (CRV), which chemically treats water used in the industrial processes. The treated water is then transported to Ryaverket, the municipal wastewater treatment facility in Gothenburg.(AkzoNobel, 2016) Because of this it is of outmost importance that the water treatment at the CRV is fully functional at all times and that all threshold values decided by the Swedish Land and Environment Court are kept. In recent years a trend of increase of the concentration of suspended solids, colloidal particles commonly found in water bodies, has been seen and also of growth of biological matter in the CRV. The two are thought to be correlated; however, the cause of the increases is not fully understood.(AkzoNobel, 2016)

1.2 Aim and Research Questions

The aim of the master thesis work is to study what makes a wastewater treatment process sustainable from the perspective of Industrial Ecology (IE) and from a lawbased perspective. This was done by conducting different experiments and studies using the AkzoNobel Pulp and Performance Chemicals (PPC) Bohus site as a case study. Two different Material Flow Analyses (MFA) are performed over the site and the central wastewater treatment plant, Centrala Reningsverket (CRV) where nitrogen (N) flows and changes in stocks are mapped. Nitrogen is chosen as the tracked nutrient due to the effects it has on the environment via eutrophication, and also since it is knows that larger quantities of N-containing products are used at the Bohus site. In the case study a simple experiment is also performed to analyze and attempt identification of the biological growth which is found in the Bohus site CRV, to assess possible correlations with the N flows and changes in stocks. AkzoNobel PPC is chosen as the case study organization due to their vision of maintaining a modern and environmentally friendly central wastewater treatment plant.

To reach the aim the following objectives are addressed:

- What type of biological matter is found at the central wastewater treatment plant, Centrala Reningsverket (CRV), and what substances likely facilitate its growth?
- What are the changes in stocks and flows of nitrogen over the AkzoNobel Bohus site and are they connected to the growth of biological matter found in the CRV?
- What sustainable methods can be used to decrease/remove the growth found in the CRV and/or nitrogen concentrations of the Bohus site?
- What aspects are important and relevant for a sustainable wastewater treatment?

1.3 Delimitations

The delimitations of this study are described below:

- Gaseous forms of nitrogen are excluded from this study. This is due to gaseous nitrogen not entering the CRV.

- The Fine Chemicals factory is not included in the MFA over the AkzoNobel PPC Bohus site. This is because all nitrogen related to the factory is gaseous, and therefore there are no emissions relevant to the CRV.
- Process cooling water and municipal wastewater used at the site are not included in this study due to them not being connected to the CRV system.
- Storm water runoff that is not collected in the CRV is also excluded from the study.
- Wastewater inlets to the CRV which are no longer in use are excluded from this study.
- Rainwater that enters the CRV from the atmosphere is excluded from this study.
- General characteristics of the biological matter were assumed to be valid and relevant to the organism/s identified in this study.

2. Background

To properly know how to preserve and manage water quality and quantity it is important to understand how treatment processes work and the challenges connected to this. This chapter aims at giving a brief presentation of different treatment methods and the role suspended solids and biological matter (bacteria and biofilms) play in this.

2.1 Wastewater Treatment Methods

There are three commonly used types of methods to treat wastewater. These are mechanical, chemical and biological treatment methods. The chosen method depends on the type of wastewater and the recipient of the treated water. The methods can also be combined e.g. biological-chemical treatment.

During mechanical treatment larger debris and particles are caught via screens or filters so as to not clog pumps or interfere with consequent steps of treatment. In the following pre-sedimentation step particles not large enough to be caught in the filters are removed by sedimentation and scraping. This mechanical treatment step is very common and is most often used as a pre-treatment step before chemical and/or biological wastewater treatment.

During chemical treatment, a chemical compound is added which allows flocculation (particles forming larger masses) to occur. This method removes particles by forming 'heavier' particles which sink to the bottom (sediment) forming sludge which allows it to be removed by e.g. scraping and transferred to separate sludge storage basins.

Biological treatment uses microorganisms that remove nutrients, such as nitrogen (N), from the organic wastes found in the wastewater and form sludge which can be removed by sedimentation and scraping.(Swedish EPA, 2009)

2.2 Suspended Solids

Suspended solids are defined as colloidal and particulate matter (e.g. sand or clay) and finely divided organic material (e.g. algae) that floats on or is suspended in water (Park and Allaby, 2013). They are also defined as particles adhering to a filter with a pore size of 1 μ m (Bydén et al., 2003). Other substances can attach to suspended solids and examples of such are organic pollutants (e.g. bacteria, protozoa etc.), metals, nutrients and pesticides. While dissolved nutrients, such as nitrogen, do not directly affect the suspended solids concentration they fuel the growth of organic

matter. This in turn may increase the suspended solids concentration.(Fondriest Environmental Inc., 2014)

Water salinity can also contribute to the suspended solids concentration. This is due to the salt ions creating aggregates and the increased weight allows the particles to sediment more easily. More importantly however is the flow rate of water regarding sedimentation of suspended solids. Higher water flow rates allow larger particles to sediment and smaller to remain suspended. This means that a slower water flow rate allows for suspended solids to sediment.(Fondriest Environmental Inc., 2014) The correlation between higher water flow rate and increased concentrations of suspended solids is corroborated by the findings of the study conducted by Rivetti et al. (2015).

2.3 Biological Matter – Bacteria and Biofilms

Bacteria are fascinating organisms particularly since they are the oldest life forms on earth. There are several different types of bacteria which can use different compounds in their metabolism.(Rogers and Kadner, 2017) Bacteria can be for example autotrophic (derive energy from carbon), heterotrophic (obtain energy from absorbing other organisms), chemolithotrophic (derive energy from inorganic compounds) or phototrophic (obtain energy from light) or a combination of some of these e.g. photoautotrophic (ability to conduct photosynthesis). There are several more classifications and mixtures of classifications.(Madigan et al., 2012) Bacteria can be found in deep ocean trenches, frozen high mountaintops or in hot springs. They can also be found on surfaces and in liquids as well as both on and in the human body.(Microbeworld, 2014)

2.3.1 Nitrifying Bacteria

Some bacteria live in symbiosis with other organisms for example nitrifying bacteria inhabiting plant root soil that convert ammonia (NH₃) stepwise to nitrates (NO₃⁻) for plant uptake in aerobic environments. Through the conversion reaction the nitrifying bacteria gain energy for their metabolism (called respiration) and plants gain nutrients for their growth. The nitrifying reaction is conducted in two steps by different types of bacteria, ammonia-oxidizing bacteria and nitrite-oxidizing bacteria. The chemical reactions can be seen below where the ammonia-oxidizing reaction is displayed in equation 1 and the nitrite-oxidizing reaction is seen in equation 2.(Madigan et al., 2012)

$$NH_3 + 1\frac{1}{2}O_2 \to NO_2^- + H_2O + H^+$$
 (Equation 1)

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$
 (Equation 2)

Nitrifying bacteria are present in high numbers where there is an abundance of NH_3 e.g. sewage treatment facilities and lakes and streams which receive a high input of NH_3 .(Madigan et al., 2012)

N in the form of NO_3^- is used in plants via plant uptake. In other, specifically anaerobic, environments NO_3^- is instead converted into gaseous N. These pathways are conducted by other types of heterotrophic bacteria which use energy from this process in their metabolism. The heterotrophic bacteria need both oxygen and organic compounds, e.g. other organisms, to gain energy. In environments where there is no 'free', available oxygen, called anoxic environments, the bacteria must use bound oxygen atoms in their respiration. What this means is that the bacteria use the oxygen bound in NO_3^- combined with organic matter in a process known as denitrification.(Daily Paulsen, 2016) This chemical pathway is presented in equation 3.

$$Organic \ Compounds + \ NO_3^- \rightarrow \ N_2 + OH^- + Energy \qquad (Equation 3)$$

The nitrogen gas (N_2) that is produced floats to the surface and is released into the atmosphere (Daily Paulson, 2016). Denitrification can also be done by autotrophic bacteria, meaning the bacteria do not need organic compounds for their respiration but can use other inorganic compounds such as sulphur or ferrous compounds (Neshat et al., 2017).

2.3.2 Biofilms

Bacteria have, besides being able to adapt to extreme environments, evolved the ability to form biofilms. Biofilms are defined by Merriam-Webster (2017) as "*a thin, usually resistant, layer of microorganisms (as bacteria) that form on and coat various surfaces*". This means that biofilms are comprised of both live, and dead, bacteria as well as other types of microorganisms such as uni-cellular organisms, algae etc.. The bacteria can adhere to surfaces and begin colonizing. Depending on the environment other types of microorganisms begin colonization as well and an 'ecosystem' forms. The types and composition of species are dependent on environmental conditions e.g. temperature and pH. It is beneficial to bacteria to construct these biofilms as this can

strengthen resistance against antimicrobials and uptake of other organisms such as protozoans (uni-cellular organisms).(López et al., 2010)

2.3.3 Methods for Removal of Biofilms

Due to this strengthened resistance, biofilms are difficult to remove and to keep from forming on surfaces. Chlorine dioxide (ClO₂) and hypochlorite ions (ClO⁻) are two chemicals used in treating wastewater, where chlorine dioxide has been seen to have a stronger ability to remove biofilms in water systems (Lenntech, 2017). A study conducted by Gagnon et al. (2005) corroborated this, showing that ClO₂ proved more efficient in removing heterotrophic biofilms in water systems than hypochlorite ions (ClO⁻). Another study conducted by Simon et al. (2014) showed that in seawater sodium hypochlorite (NaClO) did have a slightly better disinfectant ability than ClO₂. However, the concentration of potentially hazardous disinfectant by-products was higher with usage of NaClO than with ClO₂.

It is also possible to use UV-radiation to inhibit biofilm formation and growth. This allows for the water to be treated without the use of chemical cleaning agents.(Lenntech, 2017a) Ozone can also be used to disinfect water and inhibit biofilm growth and formation (Lenntech, 2017b). A study conducted by Murray et al. (2015) found that while both UV-radiation and ozone were viable options for inhibiting biofilm growth and formation, ozone had a slightly higher effect. The study also investigated whether hydrogen peroxide (H_2O_2) could be used as a disinfectant with positive results. According to the results, H_2O_2 was most effective compared to UV-radiation and ozone treatment.

2.4 Sustainable Wastewater Treatment

When discussing sustainable wastewater treatment methods the first step is to define what 'sustainable' means. There are many different definitions and associations to the terms sustainable and sustainability and in this chapter they are defined on the basis of the Industrial Ecology (IE) perspective and the Swedish Generational Goal (Generationsmålet). They are also based partly on the Environmental Quality Objectives connected to the Generational Goal. The IE perspective gives a holistic approach to the term sustainable, while the Generational Goal and the Environmental Quality Objectives encompass the Swedish political view on sustainability. Together these form the basis of what sustainable means in this study. The chapter aims, besides giving an explanation to the term sustainable, at presenting different aspects of sustainable wastewater treatment.

2.4.1 The IE Perspective, Swedish Generational Goal and the Environmental Quality Objectives

The industrial ecology perspective means that a system of processes, usually an industrial type system, is seen not as isolated from its surrounding world, but integrated in it (Kapur and Graedel, 2004). The surrounding world affects the system, and the system affects the surrounding world. This means that the system processes must be in symbiosis with the processes of the surrounding world. Besides being integrated, the processes must also resemble those of the surrounding world. Imagine an industrial system where the surrounding world is an ecologic system of nature. In nature all processes are cyclic; no waste is produced, which means that the industrial system must mimic this to be able to properly integrate itself with the surrounding world. In the industrial system all processes should be circular meaning any waste that is produced is used as a raw material in another process and/or system, as is done in nature.

The Swedish Generational Goal (Generationsmålet) states that all policies and politics related to environment should aim at handing down a society where the major environmental issues have been solved to the next generation, and to do so without causing adverse effects outside of Sweden's borders (Swedish EPA, 2016). The Swedish Environmental Code (SFS 1998:808) covers and governs the environmental aspects and describes that the human population has an obligation to care for and manage natural resources. These together are key aspects in strategizing towards a sustainable society. To aid in the work towards achieving the Generational Goal, sixteen environmental quality objectives have been derived which should be met by 2020. Four of those are directly related to water, and one is directly related to eutrophication.(Environmental Objectives, 2016) These goals are listed and shortly described in table 1 below.

Table 1. The table lists and gives a description of the four environmental objectives directly related to water, and for the one directly related to eutrophication (Environmental Objectives, 2016)

Zero Eutrophication	Eutrophication is caused by excessive	Goal will not be
(Swedish EPA,	levels of phosphorous and nitrogen in	met by 2020
2016a)	water and in soil. Goal states that "nutrient	based on decided

	levels in soil and water must not be such	or planned policy
	that they adversely affect human health,	instruments.
	the conditions for biological diversity or	
	the possibility of varied use of land and	
	water".	
Flourishing Lakes	Lakes and watercourses are important for	Goal will not be
& Streams	both ecosystems and humans. These are	met by 2020
(Swedish EPA,	used for e.g. drinking water, animal	based on decided
2016b)	habitats and fishing. Goal states that	or planned policy
	"lakes and watercourses must be	instruments.
	ecologically sustainable and their variety	
	of habitats must be preserved. Natural	
	productive capacity, biological diversity,	
	cultural heritage assets and the ecological	
	and water-conserving function of the	
	landscape must be preserved, at the same	
	time as recreational assets are	
	safeguarded".	
Good-Quality	Groundwater is important as a drinking	Goal will not be
Groundwater	water source and affects animals and	met by 2020
(Swedish EPA,	plants. Water which seeps from the	based on decided
2016c)	surface through soil and rock forms	or planned policy
	groundwater. Goal states that	instruments.
	"groundwater must provide a safe and	
	sustainable supply of drinking water and	
	contribute to viable habitats for flora and	
	fauna in lakes and watercourses".	
A Balanced Marine	The marine environment is affected by	Goal will not be
Environment,	e.g. fishing and emissions of nutrients	met by 2020
Flourishing Coastal	which cause eutrophication. Goal states	based on decided
Areas and	that "the north sea and the Baltic Sea must	or planned policy
Archipelagos	have a sustainable productive capacity,	instruments.
	and high aging linersity must be	

2016d)	preserved. Coasts and archipelagos must		
	be characterized by a high degree of		
	biological diversity and a wealth of		
	recreational, natural and cultural assets.		
	Industry, recreation and other utilization		
	of the seas, coasts and archipelagos must		
	be compatible with the promotion of		
	sustainable development. Particularly		
	valuable areas must be protected against		
	encroachment and other disturbance".		
Thriving Wetlands	Wetlands have the ability to capture	Goal will not be	
(Swedish EPA,	carbon and clean water. Animal and plant	met by 2020	
2016e)	life are also dependent on different types	based on decided	
	of wetlands. Goal states that "the	or planned policy	
	ecological and water-conserving function	instruments.	
	of wetlands in the landscape must be		
	maintained and valuable wetlands		
	preserved for the future".		

For wastewater treatment this means that water bodies which come in contact with treated wastewater from treatment facilities must be protected from contamination. This is to ensure that those water bodies can continue to meet the water demand of current and future generations and for the continued health of animal and plant life. Water bodies must also be protected to ensure healthy habitats for animal and plant life. Resources that are used during wastewater treatment should not be used in a dissipative fashion while they should still aim at ensuring a cyclic use of water. What can also be noted is that further development of policy instruments is needed, for example policies which can guide and facilitate technology evolution and implementation.

2.4.2 Aspects of Wastewater Treatment Affecting Sustainability

Wastewater treatment is necessary for water reuse to be able to meet human demands and to make sure that water flowing back into nature is not highly polluted. Since most wastewater treatment facilities are centralized this means that massive amounts of water are moved via sewer systems for treatment. An interesting, and not often thought of, negative aspect of this is that water and nutrient fluxes become imbalanced which can affect ecological and hydrological systems. While the treated water may contain very low concentrations of chemical components, a large discharge can allow for a high input of those components into a water body which in turn affects the water quality.(Muga and Mihelcic, 2007)

Different disinfectants are used in treating wastewater to remove pollutants such as for example bacteria (UN, 2013). Some of these disinfectants have already been mentioned previously in this report in chapter 2.3.3, and they are ClO₂, NaClO, UVradiation, Ozone and H_2O_2 . In table 2 below these are listed with relevant characteristics to this study. The characteristics are form, toxicity to microorganisms and to higher forms of life respectively as well as availability/cost. These are deemed relevant as they are the factors most interesting to the case study of the central wastewater treatment plant, Centrala Reningsverket (CRV), at the AkzoNobel PPC Bohus site.

Disinfectant	Form	Toxicity to	Toxicity to Higher	Availability/Cost	
		Microorganisms	Forms of Life	v	
Chlorine dioxide	Gas	High	Toxic	Moderately Low	
(ClO ₂)	Gas	Ingn	TOXIC	Cost	
Sodium hypochlorite	Solution	High	Toxic	Moderately Low	
(NaClO)	Solution	Ingn	TUXIC	Cost	
Ozone	Gas	High	Toxic	Moderately High	
Ozone	Gas	Ingn	TUXIC	Cost	
UV-radiation	N/A	High	Toxic	Moderately High	
	1 1/2 1	Ingn	TOALE	Cost	
Hydrogen Peroxide*					
(H_2O_2)	N/A	N/A	N/A	N/A	
*Not included in table 8 of					
UN report (2013)					

Table 2. Table with an overview of relevant characteristics based on table 8 in the report by the United Nations (UN, 2013). The compounds listed in this table are 4 of the 7 common disinfectants mentioned in the UN report.

Properly functioning disinfectants are highly important to assure the removal of pollutants so as to not degrade water quality. However, using the wrong type or amount of disinfectant can lead to the disinfectant itself becoming a pollutant and degrading the water quality and/or poisoning human, animal and plant life. Care and

consideration must be taken when deciding on what type of disinfectant to use in wastewater treatment as well as consideration of the economic costs. This is covered in chapter 2 of the Swedish Environmental code (SFS 1998:808) which states that when possible alternative chemicals with a lesser environmental load can be used they should be.

In most wastewater treatment some type of flocculation is used to allow for removal of certain substances, and to create flocs some type of flocculation compound is used, usually a polymer. The polymer and flocculated substances are removed from the treatment process as sludge, and the sludge is most often incinerated or landfilled. This means that the use of polymer is dissipative since the polymer cannot be reused. New research conducted by Shen et al. (2016) has shown that emerging technologies may, after sludge removal, be able to recycle the used polymer without deteriorating the treatment performance. These technologies can then allow for reuse of polymer which may decrease costs and decrease resource use.

Water and energy are closely linked in several areas, both regarding energy usage to acquire potable water but also in regards to using water to gain electrical energy from for example hydro dams. For a sustainable use of water the water quality and quantity must be preserved, however the energy intensive technologies related to water treatment must also become more efficient to decrease the environmental load born from the energy sector (the definition of efficient wastewater treatment technologies is not further implored in this thesis). Both municipal and industrial wastewater treatment technologies are energy intensive and in that carry a certain environmental load. Connected to the energy use is also the correlated cost of said energy.(Hernández-Sancho et al., 2011) While energy costs have decreased in the past couple years for both industry and households the economic factor is a continuously interesting aspect (Eurostat, 2017). Cost saving strategies allow for resources to be allocated and invested in other areas which may be of higher interest e.g. new innovations. The usage of more energy efficient technologies can thus decrease energy demand both in municipal and industrial wastewater treatment which decreases the environmental load from the energy sector (e.g. decease of carbon emissions) and decreases costs for relevant parties.

13

Wastewater treatment is necessary so as to not pollute water bodies or poison human, animal and plant life, as previously mentioned. The treatment processes need to be conducted in an environmentally conscious manner and certain aspects need to be addressed such as energy and chemicals usage, technology efficiency and economic costs. With more efficient technologies the energy usage can be decreased as can the costs associated with energy use. However, investment costs to install and implement more efficient technologies must be considered as well. Depending on the type of wastewater treatment method used the types of chemicals used may differ, and the chemicals with the lesser environmental load and health risk should be used.

3. AkzoNobel Pulp & Performance Chemicals - Site Bohus

AkzoNobel Pulp & Performance Chemicals (AkzoNobel PPC) in Bohus, Sweden, is a chemical company comprised of four different factories sharing the same site space. These factories produce hydrogen peroxide, chemically pure alkali, silica sols and separation products (e.g. products made for high performance chromatography usage). Besides the production facilities there are also extensive R&D facilities as well as analytical laboratories and facilities for administrative staff.(AkzoNobel, 2016)

Water used in the industrial processes in Bohus is collected from Göta Ålv as is water used for cooling. The cooling water is treated separately from water used in the industrial processes and is therefore not connected to the on-site central wastewater treatment plant, Centrala Reningsverket (CRV). The wastewater from the different processes of the factories as well as the laboratories is collected at the CRV where it is chemically treated and sent via the Ale community sewer system to Ryaverket in Gothenburg. Dependent on the type of industrial process, the wastewater may go through prior treatment before being transferred to the CRV. For example, process water used in the hydrogen peroxide factory is first treated with a carbon filter before being sent for further treatment at the CRV.(AkzoNobel, 2016)

3.1 Centrala Reningsverket - CRV

The central wastewater treatment plant, Centrala Reningsverket (CRV), consists of collector basins, flocculation and sedimentation units, a sludge treatment unit and drainage equipment and a unit for pH adjustment. A graphical representation can be seen in figure 1. The majority of the wastewater treated in the CRV derives from the Silica Sol plant and is thus responsible for its operation.(AkzoNobel, 2016)



Figure 1. A graphical representation of the central wastewater treatment plant, Centrala Reningsverket (CRV). Process water is first collected from the Silica Sol factory and the pH adjusted to about 7. In the next step a polymer is added and the formed flocks sediment and are scraped to a sludge storage basin. After this process wastewater from other on-site activities is mixed with the treated Silica Sol process water and the pH adjusted again to about 7. The water is transferred to a lamella separator where sedimentation occurs before the water is further transferred and sampled before final storage in the buffer basin. Treated and sampled water is then sent to Ryaverket via the municipal wastewater system.

Process water from the Silica Sol factory is collected in the first step where it is adjusted to a pH of about 7 (basin ID 7507). When the pH has been adjusted the water is pumped into sedimentation basins where flocculation occurs with the aid of a polymer and allowed to settle (basin ID 7516). The separated sludge is pumped into a sludge storage basin. The treated water is transferred to another basin and mixed with the process water from the remaining factories (basin ID 7502). The pH is again adjusted to about 7. After pH adjustment the water is transferred to the lamella sedimentation basin. Sludge is separated and transferred to the sludge storage basin and the treated water transferred to another basin where water sampling occurs (basin ID 7503). Before being sent to Ryaverket via the municipal system the treated process water is stored in a buffer basin (basin ID 7524). If necessary the water in the buffer

basin is again pH adjusted to be in the interval pH 6,5-11, as required by Ryaverket.(AkzoNobel, 2015a)

3.1.1 CRV and Suspended Solids

In the CRV at the Bohus site there is an issue with controlling the threshold values of suspended solids in the wastewater. This threshold is decided by the Swedish Land and Environment Court. The court decision from Vänersborgs Tingsrätt case nr M 269-99 stated 2014-03-14 that the outlet process water threshold of suspended solids should:

- Not exceed 80 mg/L (calculated as a yearly average)
- Not exceed 60 mg/L calculated as a monthly average during 9 months out of 12 per calendar year.

The decision also states that:

"CRV processes and other pollution control measures shall be conducted with the best available treatment effect in regards to suspended solids, organic pollutants and heavy metals".

This means that the CRV processes, among others, should be conducted in compliance with the Industrial Emissions Directive (Council Directive 2010/75/EU). The directive states that the permissions granted, with e.g. threshold values, should be decided on the basis of Best Available Technology (BAT). The BAT Reference Document for the Chemical Industry (European Commission, 2016) says that all measuring and monitoring should be done according to standards over all key processes, e.g. the monitoring of total suspended solids should be conducted daily and according to the EN 872 standard (Water quality standard for determination of total suspended solids by the method of filtration through glass fiber filters). The BAT also states that:

"In order to reduce the usage of water and the generation of wastewater, BAT is to reduce the volume and/or pollutant load of wastewater streams, to enhance the reuse of wastewater within the production process and to recover and reuse raw materials".

It also states that:

"In order to prevent the contamination of uncontaminated water and to reduce emissions to water, BAT is to segregate uncontaminated wastewater streams from wastewater streams that require treatment".

However, when considering the applicability of the above statement, it also states that:

"The interim storage of contaminated rainwater requires segregation, which may not be applicable in the case of existing wastewater collection systems".

The reason behind the decision from Vänersborgs Tingsrätt is to decrease the burden on the water treatment process at Ryaverket. Figure 2 shows a graph of the monthly average concentrations of suspended solids of the treated process water leaving the CRV during the years 2014, 2015 and 2016 (AkzoNobel, 2016a). As can be seen the concentration increases with each passing year, with some of the monthly averages breaching the threshold value of 60 mg/L. The breaches can be seen in April and for July for the year 2016, and in December for year 2015. However, these breaches did not mean that AkzoNobel violated the court decision from Vänersborgs Tingsrätt during any of the mentioned years.



Figure 2. Graph showing the suspended solids concentrations as a monthly average over a 3 year period. The dashed red line shows the threshold value decided by the Swedish Land and Environment Court.

The suspended solids may also contribute to the toxicity of the process water (AkzoNobel, 2016). This hypothesis is strengthened by the findings of the study conducted by Rivetti et al. (2015). The study showed that there was a strong correlation between toxic effects on the studied test subject and the concentration of suspended solids.

3.1.2 The Biological Matter Found in the CRV

There is, as has been previously mentioned, an issue of growth of biological matter in the basins and on the separation equipment. This growth is believed to contribute to the increase in the amount of suspended solids. The growth can be found at the inlet pipe from the pump pit at the CRV, on the sides of the basins and pipes and on the lamella separation equipment. In figure 3 the growth at the pipe inlet from the pump pit can be seen.



Figure 3. The growth found at the pipe inlet from the pump pit at the CRV. The growth has both an orange and a greenish tint and has been marked with red squares. The picture is taken from above.

This growth also affects the treatment capacity of the lamella as sedimentation cannot properly occur. An image of the growth found on the separation equipment can be seen in figure 4.



Figure 4. The growth found on the panels of the lamella separator of the CRV.

The on-site lab in Bohus tested a sample of the growth found on the lamella separator using mass spectrometry. The results showed that the growth was indeed biological and contained indoles, ergosterol and fatty acids. Indoles are a chemical synthesis byproduct of bacteria's metabolism, meaning the presence of indoles in the sample suggests that the biological growth contains bacteria (Pubchem, 2017). Ergosterol is a steroid which can be found in fungi, meaning that the growth sample also contains some type of fungi (Pubchem, 2017a). Fatty acids are also markers of biological organisms such as algae and microalgae and therefore the growth sample results suggest that besides containing bacteria and fungi, the sample most likely also contained some type of algae (Kharlamenko et al., 1995).

3.2 Site Bohus and Nitrogen

Nitrogen (N) is a critical component in the environmental discussion. It is one of the key aspects of nutrient pollution leading to eutrophication causing e.g. algal blooms which may have toxic effects on humans and wild life (Havs- och Vattenmyndigheten, 2014). Activities related to N production and usage are therefore important to keep record of.

N is present in different forms in the processes found at the site, both as a component in manufactured products and in the process water from Göta Älv (AkzoNobel, 2016). Since N is a crucial aspect of environmental issues it is of interest to AkzoNobel PPC to keep records of activities related to usage of and emissions containing N. Related to this, AkzoNobel have, as with suspended solids, certain thresholds which must be kept. The threshold level values are:

- For total N found in the process water leaving the separation products factory
 25 kg per 24 hours as a target value and a monthly average, stated 2001-06-28
 in the court decision from Vänersborgs Tingsrätt case nr M 170-00
- For N emissions to the process wastewater from catalyst production (Hydrogen Peroxide factory) 5000 kg per year, stated 2003-10-10 in the permit granted by the County Administrative Board of Västra Götaland reference nr 555-48606-2003.

In figure 5 below, the total amount of N from catalyst production can be seen from year 2012 to year 2016. Numbers were gathered from the 2016 environmental report for the AkzoNobel PPC Bohus site (AkzoNobel, 2017b). As can be noted the threshold value set by the permit granted by the County Administrative Board of Västra Götaland has not been breached.



Figure 5. Total nitrogen (in kg) from catalyst production of the Hydrogen Peroxide factory from 2012 to 2016. The red dashed line shows the threshold value decided by the County Administrative Board of Västra Götaland. Numbers were gathered from the 2016 environmental report (AkzoNobel, 2017b).

In figure 6 the total amount of N of the P3 basin for the year 2016 is presented in a graph using monthly averages from the weekly samples taken throughout the year (AkzoNobel, 2016a). The samples were taken at the P3 basin of the CRV, meaning after treatment. As one can see there are variations throughout the year which most likely are due to the fluxuations of production.



Figure 6. The monthly averages of total nitrogen of the P3 basin of the CRV, based on the weekly samples taken throughout the year 2016 from the CRV at the AkzoNobel PPC Bohus site (AkzoNobel, 2016a).

4. Methodology

The following chapter aims at describing the Material Flow Analysis (MFA) methodology and how it was used during the thesis work. The chapter also describes how the thesis work was conducted throughout the different steps.

4.1 Material Flow Analysis

Brunner and Rechberger (2004) describe Material Flow Analysis (MFA) as "a systematic assessment of the flows and stocks of materials within a system defined in space and time". Using MFA can allow for a thorough description of a specified material (meaning material goods or a substance) in a system, as well as imports and exports. Using the theory of conservation of matter (input equals output) and conducting simple mass balance calculations hidden flows and stocks can be identified. Specific terminology is used when conducting an MFA. A short description of this terminology can be seen below in table 3.

Table 3. Definitions of the terminology used in the MFA method based on the Practical Handbook of Material Flow Analysis by Brunner and Rechberger (2004).

Process	The transport, transformation or storage of materials. These			
	processes can be natural or man-made. E.g. flow of water in			
	pipeline.			
Stocks	Material reservoirs found in the system e.g. resource reservoirs. It is			
	the part of the process which comprises the mass that is stored			
	within the process. The physical unit is kilograms.			
Flows	Pathway that links processes and is measured in mass per time.			
Fluxes	Pathway that links processes and is measured in mass per time and			
	cross section.			
Imports/exports	Flows and fluxes which cross the system boundaries.			
Inputs/outputs	Flows and fluxes which enter or exit a process.			
System	The joint term for the set of material flows, stocks and processes in			
	a defined boundary. The defined boundary means the system			
	boundary is defined in space and time. E.g. a factory or a			
	geographical area.			

MFA can therefore be used as a tool to map e.g. nitrogen over a geographical area during a defined time period. The results of an MFA can be used to understand where critical flows and stocks are and if any hidden flows or processes exist.

A common way to present the results of an MFA is through the use of Sankey diagrams. In a Sankey diagram, the flows are depicted most commonly by arrows, with the width of the arrow being proportionate to the size of the flow (Stenum GmbH, 2011). This allows for a simple graphical representation of an investigated system which in an intuitive way relays the results to an audience.

4.2 Method

The thesis work was conducted in a series of steps. The first step was to attempt to identify the type of growth present on the lamella panels of the CRV using microscope and cultivation of samples. The next step was to map out the flows and changes in stocks of N over the Bohus site using MFA to find possible correlations with the growth of biological matter. Two MFAs were conducted, one over the entire site and one over the CRV. These were done by calculating and tracking the flows and changes in stocks of N for the year 2016. The results have also been gathered and presented in Sankey diagrams.

4.2.1 Identifying Type of Growth

Samples of the growth were taken from the lamella of the CRV on the 26th of January for the growth experiment. The samples were stored in sterilized bottles to avoid unnecessary contamination for 6 days with cotton wool to allow airflow. One sample was stored in a refrigerator in an attempt to 'freeze' the growth rate of the biological matter to allow for a more accurate representation of the water of the lamella at the future microscope analysis. The other sample was stored on a windowsill in room temperature. Both sample bottles were shook a few times daily to allow circulation of oxygen and nutrients. The samples were analyzed February 1st by microscope at Chalmers University of Technology to be able to find and identify organisms present in the sample. Pictures were taken of the results.

After microscope analysis samples were stored for 5 more days under the same previous mentioned conditions. The samples were then split into new sterilized bottles for further cultivation on February 6th. Boiled tap water and tomato feed (Nelson Garden Tomatnäring NPK 7-1-5) were used as growth medium. Both split samples were stored in room temperature in cultivation bottles and periodically

shaken. Samples were stored until April 6^{th} , a total of 2 months, and the results of the growth experiment documented with photographs. Pictures of the cultivation bottles were taken both on the start of (February 6^{th}) and at the end of (April 6^{th}) cultivation.

4.2.2 Conducting MFA on Nitrogen over the Site

The MFA on N was done over the Bohus site. The system boundaries were those of the site beginning with the import of e.g. raw materials production and ending with the export of e.g. finished products. Data sources for the MFA were internal reports and analysis data but also the different internal databases containing e.g. sales data, raw material data etc. All data was based on the year 2016, except for those data points which were based on the samples taken during the thesis work since data for the year 2016 could not be obtained. Reference products used were the different raw material compounds, e.g. ammonia (19%) containing products, used in production at the factories of the site. For each compound the weights consumed during the year 2016 were used as the input flow data. If consumed data could not be obtained the purchased amount data for the year 2016 was used and all amounts purchased were assumed to be used in production. Unless stated otherwise, all compounds were assumed to be 100 % pure. To calculate the amount of nitrogen for each compound the molar masses were obtained with the aid of the periodic table and then the percentages of nitrogen were calculated. For the export flows the same procedure was used. Some compounds which were consumed in production are exported outside of the system boundaries due since they comprise the finished products. The consumed amount of compound in those cases was then the basis for the calculation of the output to export flows. Changes in stocks were calculated by using mass balance. For further details regarding all calculations of flows and stocks, please see Appendix A. The results were gathered and presented in a table and in a Sankey diagram with flows and changes of stocks in the unit kg/year.

4.2.3 Tracking N over CRV

The CRV was zoomed in upon and N tracked using MFA throughout the system of pipe inlets, basins and processes. Data was collected via sampling of wastewater which was analyzed at the on-site lab in Bohus and from internal documents (AkzoNobel, 2016a). Thirty water samples from the CRV and the Silica Sol factory were taken using 1 L plastic bottles. Two samples were taken for each sample area meaning fifteen samples were analyzed for total N and fifteen were analyzed for

suspended solids. The samples were taken at three separate occasions during a one week period. Samples 1-5 were taken on 6^{th} of March 2017. Samples 6-10 were taken on 8^{th} of March 2017. Samples 11-13 were taken on 10^{th} of March 2017. This was due to the capacity of the on-site laboratory to preserve sample freshness until lab analysis. The results from the analysis and from the calculations based on the data from internal documents were gathered and presented in a Sankey diagram with flows (and stocks) in the unit mg/L. All calculations for the MFA can be seen in Appendix B.

5. Results and Analysis - Growth Identification

In this chapter the results of identifying the growth matter are displayed. This is related to the following objective:

"What type of biological matter is found at the central wastewater treatment plant, Centrala Reningsverket (CRV), and what substances likely facilitate its growth?".

This chapter concludes with a analysis of the gained results.

5.1 Results of the Growth Identification

The microscope analysis showed that there was a presence of some type of algae, bacteria and also protozoa, a uni-cellular organism. The protozoan was identified as most likely being some type of *Colpidium*. A picture of what could be seen on the microscope slide is shown in figure 7. The surrounding 'dots' are most likely algae and/or bacterial mats, biofilms of congealed bacteria which are most likely dead. The algae and bacterial species could not be identified in this study.



Figure 7. A picture taken of the growth sample slide as seen through the microscope lens using a mobile phone camera. The results showed that some type of algae and/or congealed bacteria could be seen, as well as some type of protozoa which was identified as being some type of Colpidium One of the protozoa has been circle in red.

A difference between the two samples could also be seen with the naked eye. The sample which has been refrigerated had the same beige hue as the day of sampling.

The sample which had been stored on a window sill in room temperature had turned a darker green. A picture of the two samples can be seen in figure 8.



Figure 8. The two samples taken from the lamella panels. The left sample had been stored in a refrigerator while the right had been stored in room temperature and direct daylight. As can be seen the left sample has a beige hue, similar to that of the day of sampling. The right sample had turned a darker green.

Figure 9 shows the before and after of the growth experiment conducted on the samples taken from the lamella separator of the CRV. The left image shows the samples on the start date of the experiment, February 6th, while the right image shows the samples on the end date, April 6th.



Figure 9. The left image shows the two split cultivation samples on February 6th where the previously refrigerated sample is marked with a red F. The right image shows the cultivated samples on April 6th, with the previously refrigerated sample marked with a red F.

The results show that the previously refrigerated sample, marked with a red F, had a higher amount of white dots. Consultation with contacts at Chalmers University of

Technology stated that the white dots may be either growing bacteria or spores. However, no conclusive results on the type of organisms were gained, meaning no conclusive results on what the nutrients are which are needed for its growth.

5.2 Analysis of the Results for the Growth Identification

The biological growth could not be identified further than stating that it comprised of bacteria, algae and uni-cellular organisms, where the uni-cellular organism may likely be a type of *Colpidium*. Since the wastewater of the CRV will have fluctuating composition due to differences in production the environment changes slightly. These small changes may favor different organisms, meaning that depending on when sampling of organisms occur different type of organisms may have a stronger ecological advantage giving a non-accurate representation of the eco-system. Therefore the results can give an idea of the types of different organisms which may occur; however identifying the exact type of organism may not be favorable since this may likely differ depending on the time of sampling. Considering this, for the sake of this study it is sufficient to conclude that these are the different types of organisms most likely found in the CRV, keeping in mind that the exact species may change dependent on the changing environment.

6. Results and Analysis of the MFA of Nitrogen

In this chapter the results from the data collection and the MFA over both the AkzoNobel PPC Bohus site and the CRV are presented in tables and in Sankey diagrams. For each of the two MFA an analysis of the results is performed and follows each MFA result.

6.1 Results of MFA over AkzoNobel PPC Bohus Site

The collected and calculated data for the MFA and the tracking of N flows and changes in stocks of the Bohus site are presented here in table 4 and in the form of a Sankey diagram, see figure 10. The data was collected from reports, databases and from water sampling. All calculations are presented in Appendix A.

Flow Number	Flow Type	Flow Magnitude (kg/year)	Data Source
А	Input Silica Sol	904	Internal database
В	Output to Export Silica Sol	485	Internal documents
С	Output to CRV Silica Sol	800	Internal documents Sampling
D	Output to Separation Products Silica Sol	N/A	Contact person of factory
-	Change in Stock Silica Sol	-381	
Е	Input Separation Products	2840	Contact person of factory
F	Output to CRV Separation Products	2431	(AkzoNobel, 2016b)
-	Change in Stock Separation Products	409	Contact person of factory (AkzoNobel, 2016b)
G	Input Hydrogen Peroxide	4856	Contact person of factory
Н	Output to CRV Hydrogen Peroxide	3824	Contact person of factory Environmental report (AkzoNobel, 2017b)
Ι	Output to Export Hydrogen Peroxide	1423	Contact person of factory
-	Change in Stock Hydrogen Peroxide	-391	Contact person of factory
J	Output to Export CRV	4100	Environmental report (AkzoNobel, 2017b)
K	Output to Export (filter cake) CRV	140	Environmental report (AkzoNobel, 2017b) Analysis results from table 3 chapter 6.1.2
L	Total Output to Export CRV	4240	
_	Change in Stock CRV	2815	

Table 4. Flow number, type and magnitude for the MFA of nitrogen (N) conducted over the AkzoNobel Bohus site. Data was collected mainly from the 2016 environmental report (AkzoNobel, 2017b), contact persons of each factory and from internal databases. Conducted calculations can be found in Appendix A.

In figure 10 the results from the MFA conducted over the AkzoNobel PPC Bohus site can be seen represented in a Sankey diagram. Data for the results are found in table 4. The input flows to the factory are based on nitrogen found in raw materials, while the output flows from factory to export are based nitrogen found in finished products. The flows from factory to CRV and from CRV to export are water based nitrogen flows. All gaseous forms of nitrogen are represented by orange, dashed arrows in figure 10.



Flows: kg/year Stocks: kg/year

Figure 10. Sankey diagram of the results gained from the MFA of nitrogen over the AkzoNobel PPC Bohus site. The Fine Chemicals factory was excluded from the MFA due to nitrogen being in gaseous form. All flows of nitrogen in gaseous form have been represented with orange, dashed arrows.

6.2 Analysis of the Results for the MFA of the AkzoNobel PPC Bohus Site

About 70 % of the nitrogen entering the Bohus site in the form of raw materials exits the site in the form of wastewater, finished products and filter cake waste. This means there are some amounts of nitrogen found over the site, most likely in the form of stored raw materials, products and wastes. An aspect which might affect the mass balance is the possibility of missed products during data collection in this study.

For the Silica Sol factory it can be seen that the input and output (flow A and flow B, table 4) do not comply with the mass balance criteria. The difference between them leads to a negative change of stock. One reason for the negative change is due to the output flow to the CRV (flow C, table 4) being based on the sampling conducted during the thesis work. Since different products and volumes are produced at a non-fixed frequency the water of the CRV inlets will have different compositions both in

time and in space. This may therefore be the reason for the 30 % difference in the input and output over the Silica Sol factory.

About 86 % of the nitrogen input (flow E, table 4) to the Separation Products factory is transported via wastewater to the CRV (flow F, table 4). Between the Silica Sol factory and the Separation Products factory there is a flow (flow D, table 4) with an unknown amount of nitrogen. This flow may affect the output flow (flow F, table 4) to a certain degree, which may affect the nitrogen change in stock in the CRV.

Comparing the input (flow G, table 4) and output (flows H and I, table 4) of nitrogen over the Hydrogen Peroxide factory shows that about 10 % of nitrogen is missing, leading to a negative change in stock.

About 60 % of the nitrogen entering the CRV via wastewater is exported. It should also be noted that the amount of nitrogen exported from the CRV (flow L) is based partly on numbers gained from the sampling conducted during the thesis work.

6.3 Results of MFA over AkzoNobel PPC Bohus Site CRV

The collected data and the results for the MFA conducted over the AkzoNobel PPC Bohus site are presented here in table 5 and in a Sankey diagram, see figure 11. Data is based on sampling conducted during the thesis work. For concentrations lower than 2 mg/L results could not be obtained. Calculations can be seen in Appendix B. Note that the unit is mg/L, meaning a concentration. Because of this the mass balance criteria cannot be used, and consideration must be taken to this when looking at these results.

	Origin/Responsible		~	Total Nitrogen
Flow Number	Actor	Flow Type	Sample Date	(mg/L)
Z1	Silica Sol	Alkaliska gropen (7510)	2017-03-06	3.5
Z2	Silica Sol	Surt avlopp (7610)	2017-03-06	2.8
Z3	Site/CRV	P2 Pumpgrop (7548)	2017-03-06	19
Z4	Hydrogen Peroxide	Elpanna Lok Ångcentral	2017-03-06	4.4
Z5	Silica Sol (Separate process/building)	РАА	2017-03-06	<2
Z6	Hydrogen Peroxide Separation Products	VP Kromasil	2017-03-08	<2
Z7	Fine Chemicals	Kokeri Pump 7510	2017-03-08	<2
Z8	Separation Products	Gamla Kromasil	2017-03-08	<2
Z9	Separation Products	Pamp Lab	2017-03-08	<2
Z10	Silica Sol	7515	2017-03-08	<2
Z11	R&D	TK Byggnad 301	2017-03-10	<2
Z12	Site/CRV	Förlaget lamellen	2017-03-10	41
Z13	Site/CRV	Efter lamellen	2017-03-10	26
Z14	Site/CRV	Filterkaka	2017-03-23	125 mg/L
Z15	Site/CRV	P3	2016	1.83

Table 5. Results from the water sampling conducted by the author and the on-site lab during the master thesis work Due to the analysis method results with concentrations less than 2 mg/L could not be obtained. Flow 15 was calculated using data from previously conducted water sampling for the year 2016.

In figure 11 the results from the MFA conducted over the CRV can be seen represented in a Sankey diagram. Data for the results are found in table 5.



Figure 11. The Sankey diagram presenting the results from the MFA conducted over the CRV. The processes are depicted as brown boxes, the stocks as orange with dashed outlines and the flows as red arrows. The red arrows with dashed outlines are flows where data could not be found. The unit for the flows(and the stocks) is mg/L. The green, dashed arrows represent the rainwater which enters the CRV from the atmosphere.

6.4 Analysis of the Results for the MFA of the CRV

When conducting a mass balance over the CRV it can be seen that about 70 % of imported nitrogen is missing if the mass balance criteria is to be applied (input=output). However, since the flows are concentrations the mass balance criteria cannot actually be used. It can only be noted that the concentration entering the CRV is lower than the concentration exiting.

An interesting aspect is the significantly larger flow of nitrogen going into the pHadjustment basin (7502) of 19 mg/L. In comparison, it is 4-5 times larger than the other input flows. This sample is taken from the input flow sourced from one of the site pump pits which is pumped directly into the CRV (see also figure 3 chapter 3.1.2), where biological growth has been spotted. Taking into consideration the changing environment's effect on species composition, this shows that there may still be some type of correlation between nitrogen and the biological growth. Another interesting aspect to note regarding the results gained is that about 63 % of the nitrogen which passes through the lamella separator goes into the P3 basin. This means that nitrogen is most likely removed via sludge removal in the lamella separator, but it may also be in part due to uptake by the biological growth found on the separator equipment.

Some of the flows depicted in the Sankey diagram have been noted with a question mark. This is because the flows were not/could not be analyzed in this study. The flows are known and therefore they have been included in the Sankey diagram. This also affects the overall results since the magnitude of these flows affects the change in stocks e.g. the change in stock of pH-adjustment basin (basin ID 7502).

7. Discussion

In this chapter the results and method are discussed, and suggested improvements and suggested future studies are given.

7.1 Discussion of Method and Results

The method for the growth identification could have been improved. For example, instead of shaking the cultivation bottles manually daily, a shaker could have been used or the samples could have been aerated using an air pump. Tomato feed was used, and instead it may have been more appropriate to use a standardized growth medium specifically created for these types of experiments. However, since the growth identification step was conducted to be able to state the types of organisms this method was deemed sufficient. If any future studies regarding identifying the growth found in the CRV are of interest, a proper scientific method for cultivating the growth should be used with the aid of proper tools and instruments and the experiment conducted over a longer time period. However, due to the changing environmental conditions there will always be a difficulty regarding identification of all organisms of the CRV.

The growth has been concluded to be some type of organic, biological material composed of bacteria, algae and uni-cellular organisms. About 63 % of the nitrogen entering the lamella separator goes into the P3 basin (chapter 6.3). Since nitrogen is a common nutrient for growth, it is not an unlikely possibility that part of the nitrogen is removed via these organisms. This combined with the fact that the lamella separator has a continuous issue of being covered in biological matter shows that there may likely be this correlation between nitrogen and biological growth. Besides nitrogen being removed via sludge or taken up by organisms, there is also a possibility that some of it is removed in gaseous form to the atmosphere.

Parts of this study were conducted based on assumptions and delimitations which greatly affected the results, for example assuming that a one-time spot-check sampling would be sufficient for the MFA over the CRV. The composition of the water is dependent on production at the different factories on-site, and since production changes at non-set frequencies (related to customer demands, orders, and production stops etc.) this composition is highly likely to change over time and space (space meaning different areas of the CRV). This means that depending on when sampling, using this 'spot-check method', occurs different results may be obtained. In

this study it has been assumed that the one time sampling should be representative for the year of 2016, while in reality this is not so. This assumption gives a simplified picture of reality, and to be able to gain a more accurate one continuous sampling over a long time period should be done. It should be noted that while this may ensure a higher statistical certainty, it will still only model reality and not give a 100 % accurate representation of it since the water composition will still fluctuate over space and time. These results can give a hint of what may be occurring in the CRV, however further studies are necessary to gain conclusive conclusions. Sensitivity analyses were not conducted since these would have not given any relevant or reliable information to complement the gained results. While a future study may have to rely on excessive sampling it is worth noting that the MFA methodology may not be suitable for these types of studies. The amount of sampling which would be required would be both time consuming and expensive. If it is to be used, two aspects need to be considered. Firstly, a well-thought out sampling plan should be derived that identifies the key areas which should be sampled during the longer time period e.g. key inlets to the CRV and the input and output of the lamella separator basin. Secondly, the flows cannot be represented using concentrations if the mass balance criterion is to be applied. Therefore, the water flow magnitudes must be known as well to be able to calculate the masses based on the concentrations, as such the flow magnitudes need to be measured as well.

An example of a delimitation which affected the results for both MFA results is not including gaseous nitrogen. Gaseous nitrogen originated in part from used raw material containing nitrogen, which may have led to a skewing of the changes in stocks identified in the different processes (for example the stock in the Separation Products factory process). For a more accurate mapping of nitrogen over both the AkzoNobel PPC Bohus site and the site CRV, gaseous nitrogen should have been included.

The two MFA Sankey diagrams are represented using different units, so a direct comparison between both is not really possible. It is possible, however, to spot trends between them. When looking at the flow magnitudes it is seen there are some discrepancies. For example, the flows originating from the Silica Sol factory (flow 1, 2 and 10 in table 5) are larger than those of the other factories. Comparing this trend to the MFA done over the Bohus site it can be seen that the flows from the other

factories are larger than those of Silica Sol, despite the output of nitrogen from Silica Sol to the CRV being based on the spot-check sampling and its accuracy being slightly uncertain. The difference in magnitude is still large enough to warrant question.

Comparing the output flows from the CRV between the two MFA studies conducted it should be noted that they do not have the nearly same value. For the MFA conducted over the Bohus site the flow is 4240 kg and has been based on the environmental report and on calculations based on sampling (see Appendix A). For the MFA conducted over the CRV the flow is 624 kg (see calculations for flow Z15, Appendix B) and was calculated using average values based on the weekly sampling allowing it to be presented in mass. This may be a reason why the numbers do not add up.

One of the compounds of the input flow to the Hydrogen Peroxide factory of the MFA for the entire Bohus site is known to be fractioned into different endpoints; some enters the atmosphere in gaseous form, some is exported off-site via products and some enters the CRV. However, the fraction magnitudes are unknown and could not be properly assumed for this study. This would mean that the change in stock is more negative than has been calculated. This also means that the output flows (flow H and I, table 4, figure 10) and the change in stock of the CRV are affected as well.

It is also important to note that the sampling has been conducted in the year 2017, while the other data is from the year 2016. This may have affected the overall results, with an example being the difference in mass balance over the Silica Sol factory. A second important note to make is that there is the possibility of not all types and amounts of raw materials and products being accounted for. This also affects the results, and is therefore a threat to the validity of them.

7.2 Suggested Improvements for a Modern and Environmentally Friendly Wastewater Treatment Plant

The wastewater treatment done at the AkzoNobel PPC Bohus site is done 'by the book'. Consideration is taken to ensure that the industrial process water is treated before being sent to further treatment at Ryaverket, and weekly samples are done to ensure that the threshold values set by the Land and Environment Court are held. When looking at the wastewater treatment system used at the AkzoNobel PPC Bohus

site it is noted that while all laws and permits are met, there are certain things which could be improved. One example of this is methods to decrease the amount of suspended solids. Decreasing the amount of suspended solids means decreasing the risk of spreading toxins to water bodies. One way to do this is making sure that the water flow rate is adapted to allow optimal sedimentation at the lamella separator, while still allowing for efficient use of the CRV capacity. The correlation between the biological growth matter and the suspended solids has not been proven, however based on the literature research the growth does affect the concentration of suspended solids. Removing and decreasing the growth by using disinfectants is one possible way. In this study, examples of common disinfectants, e.g. Chloride compounds, have been given, with a majority of them having a toxic effect on higher life forms and on microorganisms (chapter 2). Toxicity to microorganisms is desired since the growth should be stopped, however residues from the disinfectant shouldn't be let out with the output of wastewater to Ryaverket since this will very likely disturb their treatment processes. Therefore an optimal amount of disinfectant should be used, which is also beneficial from an economical perspective. Due to the parts of the growth most likely being bacteria and biofilms it may be of interest to sanitize the entire CRV system and remove all the growth. The practicality and benefits of this have not been investigated. A continuous input of disinfectant may be enough to remove and hinder growth, keeping in mind that dead and decaying matter debris may affect the suspended solids concentration until the biological matter has been removed from the system.

A more drastic way of meeting the vision of a modern and environmentally friendly wastewater treatment plant is building new facilities to replace the old ones. The basic facility infrastructure is, while still functioning properly, quite old. Much has happened in recent years regarding technological development and in the field of sustainability which affects what being 'modern' and 'environmentally friendly' means. Old infrastructure, both in industry and in private households, has in general not been adapted to guarantee e.g. energy efficiency. Wastewater treatment is an energy intensive process, and in building new infrastructure special care can be taken to ensure that maximum energy efficiency is guaranteed. Since production at the site is not the same as in the 1920s or even going back 20-30 years, the new facilities can be built and optimized capacity wise according to today's and the future's production

volumes and processes. The facilities can also be built to reroute water which does not need to undergo the same treatment as the industrial process water and which is currently pumped into the CRV e.g. water from site pump pits containing rainwater and storm water runoff. It may also be interesting to investigate if roofing should be added to remove falling rainwater since this can affect the capacity of the CRV, depending on the amount of downpour. Both of these types of streams affect the capacity of the CRV, but they also transfer nutrients such as nitrogen to the CRV. Since there is a likely possibility that the biological growth is favored by nutrients such as nitrogen, it might be worth removing such water inlets from the CRV. It should be noted that rerouting and removing these types of water inlets can be achieved without building new infrastructure by remodeling the existing facilities. The BAT reference document by the European Commission does say that wastewater streams should be separated from other water streams, but does also take into consideration that current systems may not allow for this and thus does not demand for it to happen. A question does arise for how long consideration will be taken to this, and if in the long run it will be a question of not 'if' but 'when' an investment into building new infrastructure or remodeling the existing one will need to be made. This becomes especially interesting considering how none of the listed Swedish environmental objectives will be met by 2020, and that after 2020 new goals will be set along with the possibility of new, and most likely stricter, laws and policies. In short, it may be worth noting that while today it may seem a drastic measure to build new or remodel old facilities, it may become necessary in the not so distant future.

7.3 Future Studies

There are certain areas of this thesis work which may be interesting to study further. One of those is continuing to map nitrogen over the CRV by deriving a sampling plan for key areas of the CRV to gain a higher statistical certainty. Nitrogen is one of the major nutrients which cause eutrophication, and since there are large quantities of nitrogen found at the AkzoNobel PPC Bohus site it may be of interest to map the flows and stocks over a longer time. Besides this, nitrogen may be one of the causes for the growth of biological matter and continuing to study the nitrogen flows and stocks of the CRV can identify with a higher statistical certainty the sources of nitrogen. However, this sampling will need to be done while measuring the water flow magnitude, as has been mentioned in chapter 6.1. While nitrogen was mapped in this study, it may also be of interest to map phosphor, another key nutrient which causes eutrophication and is needed for the metabolic processes of organisms. This would be interesting since if it can be concluded that there are considerably higher amounts of both nitrogen and phosphor in areas of the CRV which correlate with the growth of biological matter, it can be possible to remove and manage the growth more effectively by removing the key sources of the nutrients.

It may also be interesting to conduct experiments to further identify the different organism compositions found in the CRV. Based on this, studies using different disinfectants can be conducted to identify the type of disinfectant which is most effective in removing and stopping organism growth. This is interesting from both an environmental and an economical perspective. A decreased amount of disinfectants will decrease the environmental load associated with wastewater treatment. It will also lead to cost savings since fewer resources are used, as well as decreasing the environmental load associated with raw material acquisition.

Another way to decrease costs and the environmental load of raw material acquisition is investigating further the possibility of reusing polymer. This was not an aspect which was assessed in depth in this thesis, and the studies and technologies behind being able to reuse polymer are very new. It may however still be an interesting lead to follow in the future and to keep up to date in that research field.

8. Conclusions

The biological matter found in the central wastewater treatment plant, Centrala Reningsverket (CRV), could not be identified. However, it could be concluded that it most likely consists of bacteria, algae and uni-cellular organisms. After conducting two MFA studies, one over the Bohus site and one over the CRV, there may be possible correlations between higher nitrogen concentrations and areas where growth are found. However, this cannot be stated without doubt since not all other possibilities could be rejected. Removal of the growth can be done by using e.g. Chloride compounds, but further studies should be conducted to assess which method is most efficient and sustainable.

Since wastewater treatment in general is a very energy intensive process consideration should be taken to ensure that the facilities and technologies used are as energy efficient as possible. Treatment should be conducted to ensure that water bodies are not polluted, neither because of insufficient treatment nor due to overusage of disinfectants. Wastewater treatment is necessary to both insure the continued use of water and to make sure no pollution or poisoning of human, animal or plant life occurs. It should, however, be conducted in a sustainable way to avoid adverse effects elsewhere.

9. References

AkzoNobel (2015) *AkzoNobel Ranked Top of DJSI for Fourth Year In a Row* [Online] Available at: <u>https://www.akzonobel.com/for-media/media-releases-and-features/akzonobel-ranked-top-djsi-fourth-year-row</u> [2017-03-02]

AkzoNobel (2015a) CRV Driftinstruktion [Internal Documents]

AkzoNobel (2016) Miljörapport 2015 [Internal Documents]

AkzoNobel (2016a) CRV 2016 Data [Internal Documents]

AkzoNobel (2016b) Bilaga 6 Q4 Separation Products [Internal Documents]

AkzoNobel (2017) *Planet Possible - Hur vi skapar mer värde med mindre resurser* [Online] Available at: <u>https://www.akzonobel.com/se/hallbar_utv/planet_possible/</u> [2017-03-02]

AkzoNobel (2017a) *History – Eka From the 1890s to Today* [Online] Available at: https://www.akzonobel.com/eka/aboutus/history/ [2017-03-02]

AkzoNobel (2017b) Miljörapport 2016 [Internal Documents]

Brunner, P. and Rechberger, H. (2004) *Practical Handbook of Material Flow Analysis*, USA: CRC Press LLC. ISBN 978-1-56670-604-9

Bydén, S., Larsson, A-M. and Olsson, M. (2003) *Mäta vatten – Undersökningar av sött och salt vatten*, Sweden: Institutionen för miljövetenskap och kulturvård Göteborgs universitet.

Council Directive 1998/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption.

Council Directive 2010/75/EU of 24 November 2010 on Industrial Emissions (Integrated Pollution Prevention and Control).

Daily Paulson, L. (2016) *What is Denitrification?* [Online] Available at: <u>https://www.rwlwater.com/what-is-denitrification/</u> [2017-03-16]

Environmental Objectives (2016) *Environmental Objectives* [Online] Available at: <u>http://www.miljomal.se/sv/Environmental-Objectives-Portal/Undre-meny/About-the-</u> <u>Environmental-Objectives/</u> [2017-03-01]

European Commission (2016) COMMISSION IMPLEMENTING DECISION (EU) 2016/902 of 30 May 2016 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for common waste water and waste gas treatment/ management systems in the chemical sector [Online] Available at:

http://eippcb.jrc.ec.europa.eu/reference/BREF/BATC_CWW.pdf [2017-05-12]

Eurostat (2017) *Energy Price Statistics* [Online] Available at: <u>http://ec.europa.eu/eurostat/statistics-explained/index.php/Energy_price_statistics</u> [2017-05-12]

Fondriest Environmental, Inc. (2014) *Turbidity, Total Suspended Solids and Water Clarity - Fundamentals of Environmental Measurements*, [Online] Available at: <u>http://www.fondriest.com/environmental-measurements/parameters/water-</u> <u>quality/turbidity-total-suspended-solids-water-clarity/</u> [2017-02-14]

Gagnon, G. A., Rand, J. L., O'Leary, K. C., Rygel, A. C., Chauret, C. and Andrews R. C. (2005) *Disinfectant Efficacy of Chlorite and Chlorine Dioxide in Drinking Water Biofilms*, Water Research [Electronic] vol. 29, pp. 1809-1817 Available at: http://dx.doi.org.proxy.lib.chalmers.se/10.1016/j.watres.2005.02.004 [2017-03-03]

Havs- och Vattenmyndigheten (2014) *Övergödning* [Online] Available at: <u>https://www.havochvatten.se/hav/fiske--fritid/miljopaverkan/overgodning.html</u> [2017-03-14]

Hernández-Sancho, F., Molinos-Senante, M. and Sala-Garrido, R. (2011) *Energy Efficiency in Spanish Wastewater Treatment Plants: A Non-Radial DEA Approach,* Science of the Total Environment [Electronic] vol. 409, pp. 2693-2699 Available at: <u>http://www.sciencedirect.com.proxy.lib.chalmers.se/science/article/pii/S00489697110</u> 03755 [2017-05-12]

Kapur, A. and Graedel, T. E. (2004) *Industrial Ecology*, Encyclopedia of Energy [Electronic] vol. 3 pp. 373-382 Available at: <u>http://user.iiasa.ac.at/~gruebler/Lectures/Leoben00-01/IEArticle_Leoben.pdf</u> [2017-04-24]

Kharlamenko, V. I., Zhukova, N. V., Khotimchenko, S. V., Svetashev, V. I. and Kamenev, G. M. (1995) *Fatty Acids as Markers of Food Sources in a Shallow-water Hydrothermal Ecosystem (Kraternaya Bight, Yankich Island, Kurile Islands),* Marine Ecology Progress Series [Electronic] vol. 120 pp. 231-241 Available at: <u>http://www.int-res.com/articles/meps/120/m120p231.pdf</u> [2017-03-08]

Lenntech (2017) *Biofilm Removal and Control* [Online] Available at: <u>http://www.lenntech.com/biofilm_removal.htm</u> [2017-03-03]

Lenntech (2017a) *UV Disinfection Systems* [Online] Available at: http://www.lenntech.com/systems/uv/uv_disinfection.htm [2017-03-06]

Lenntech (2017b) Ozone from an Ozone Generator [Online] Available at: <u>http://www.lenntech.com/ozone.htm</u> [2017-03-06]

López, D., Vlamakis, H. and Kolter R. (2010) *Biofilms*, Cold Spring Harbor Perspectives in Biology [Electronic] vol. 2 Available at: <u>https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2890205/</u> [2017-03-03] Madigan, M. T., Martinko, J. M., Stahl, D. A. and Clark, D. P. (2012) *Brock Biology* of *Microorganisms*, 13th edition, USA: Pearson Education Inc. ISBN 978-0-321-73551-5

Merriam-Webster (2017) *Biofilm* [Online] Available at: <u>https://www.merriam-webster.com/dictionary/biofilm</u> [2017-03-03]

Microbeworld (2014) *Bacteria* [Online] Available at: http://www.microbeworld.org/types-of-microbes/bacteria [2017-03-03]

Muga, H. E. and Mihelcic, J. R. (2007) *Sustainability of Wastewater Treatment Technologies*, Journal of Environmental Management [Electronic] vol. 88, pp. 437-447 Available at:

http://www.sciencedirect.com.proxy.lib.chalmers.se/science/article/pii/S03014797070 01028 [2017-05-03]

Murray, K. E., Manitou-Alvarez, E. I., Inniss, E. C., Healy F. G., and Bodour, A. A. (2015) *Assessment of Oxidative and UV-C Treatments for Inactivating Bacterial Biofilms from Groundwater Wells*, Frontiers of Environmental Science and Engineering [Electronic] vol. 9, pp. 39-49 Available at: <u>http://link.springer.com.proxy.lib.chalmers.se/article/10.1007%2Fs11783-014-0699-0</u> [2017-03-06]

Neshat, A. A., Rashidi Merhrabadi, A., Alighardashi, A. and Tajrobehkar O. (2017) *Nitrate Removal from Waters Containing Sulfate Using Autotrophic Denitrification with Sulfide Return*, Water, Air and Soil Pollution [Electronic] 228:39 Available at: <u>http://link.springer.com.proxy.lib.chalmers.se/article/10.1007%2Fs11270-016-3218-z</u> [2017-03-16]

Park, C. and Allaby, M. (2013) *A Dictionary of Environment and Conservation*, 2nd edition, UK: Oxford University Press. eISBN: 9780191744471

Pubchem – Open Chemistry Database (2017) *Indole* [Online] Available at: <u>https://pubchem.ncbi.nlm.nih.gov/compound/indole#section=Top</u> [2017-06-08]

Pubchem – Open Chemistry Database (2017a) *Ergosterol* [Online] Available at: <u>https://pubchem.ncbi.nlm.nih.gov/compound/ergosterol#section=Top</u> [2017-06-08]

Rivetti, C., Gómez-Canela, C., Lacorte, S., Díez, S., Lázaro, W. L. and Barata, C. (2015) *Identification of compounds bound to suspended solids causing sub-lethal toxic effects in Daphnia magna. A field study on re-suspended particles during river floods in Ebro River*, Aquatic Toxicology [Electronic] vol. 16, pp. 41-50 Available at: http://dx.doi.org.proxy.lib.chalmers.se/10.1016/j.aquatox.2015.01.021 [2017-03-01]

Rogers, K. and Kadner R. J. (2017) *Bacteria* [Online] Available at: <u>https://global.britannica.com/science/bacteria</u> [2017-03-03]

Shen, L-C., Hankins, P. N. and Singh, R. (2016) *Surfactant and Polymer-Based Technologies for Water Treatment*, Emerging Membrane Technology for Sustainable Water Treatment [Electronic] pp. 249-276 Available at:

http://www.sciencedirect.com/science/article/pii/B9780444633125000103 [2017-05-12]

SFS 1998:808 Miljöbalken, Stockholm: Miljö- och energidepartementet

Simon F. X., Berdalet, E., Gracia, F. A., España F. and Llorens, J. (2014) *Seawater Disinfection with Chlorine Dioxide and Sodium Hypochlorite – A Comparison of Biofilm Formation*, Water, Air and Soil Pollution [Electronic] 225:1921 Available at: <u>http://link.springer.com.proxy.lib.chalmers.se/article/10.1007%2Fs11270-014-1921-1</u> [2017-03-06]

Stenum GmbH (2011) *What is a Sankey Diagram?* [Online] Available at: <u>http://www.stenum.at/en/?id=software/sankey/sankey-glossar</u> [2017-04-10]

Swedish Environmental Protection Agency (2009) *WasteWater Treatment in Sweden* [Electronic] Available at:

http://www.naturvardsverket.se/Documents/publikationer/978-91-620-8416-5.pdf?pid=4098 [2017-03-27] ISBN 978-91-620-8416-5

Swedish Environmental Protection Agency (2016) *Generationsmålet* [Online] Available at: <u>http://www.naturvardsverket.se/Miljoarbete-i-samhallet/Sveriges-miljomal/Generationsmalet/</u> [2017-03-01]

Swedish Environmental Protection Agency (2016a) *Zero Eutrophication* [Online] Available at: <u>http://www.swedishepa.se/Environmental-objectives-and-</u> <u>cooperation/Swedens-environmental-objectives/The-national-environmental-</u> <u>objectives/Zero-Eutrophication/</u> [2017-05-03]

Swedish Environmental Protection Agency (2016b) *Flourishing Lakes and Streams* [Online] Available at: <u>http://www.swedishepa.se/Environmental-objectives-and-cooperation/Swedens-environmental-objectives/The-national-environmental-objectives/Flourishing-Lakes-and-Streams/</u> [2017-05-03]

Swedish Environmental Protection Agency (2016c) *Good-Quality Groundwater* [Online] Available at: <u>http://www.swedishepa.se/Environmental-objectives-and-cooperation/Swedens-environmental-objectives/The-national-environmental-objectives/Good-Quality-Groundwater/</u>[2017-05-03]

Swedish Environmental Protection Agency (2016d) *A Balanced Marine Environment, Flourishing Coastal Areas and Archipelagos* [Online] Available at: <u>http://www.swedishepa.se/Environmental-objectives-and-cooperation/Swedens-</u> <u>environmental-objectives/The-national-environmental-objectives/A-Balanced-</u> <u>Marine-Environment-Flourishing-Coastal-Areas-and-Archipelagos/</u> [2017-05-03]

Swedish Environmental Protection Agency (2016e) *Thriving Wetlands* [Online] Available at: <u>http://www.swedishepa.se/Environmental-objectives-and-</u> <u>cooperation/Swedens-environmental-objectives/The-national-environmental-objectives/Thriving-Wetlands/</u> [2017-05-03] WWAP, World Water Assessment Programme (2012) *The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk*, Paris: UNESCO. ISBN 978-92-3-104235-5

WWF, World Wildlife Fund (2017) *Water as a Natural Resource* [Online] Available at: <u>http://wwf.panda.org/about_our_earth/teacher_resources/webfieldtrips/water/</u>[2017-03-02]

Appendix A

For each of the flows of the MFA the calculations can be found under each respective section. The flows are grouped according to factory unit.

PLEASE NOTE THAT CALCULATIONS HAVE BEEN EDITED DUE TO SECRECY/CONFIDENTIALITY REASONS

A.1 Calculations for Silica Sol

Calculations for the flows connected to the Silica Sol factory are presented below. The data used in the following calculations has been collected from internal databases and documents, sales data for the Silica Sol factory and the periodic table.

Silica Sol Flow A

The amount of ammonia (19%) product consumed during production in the year 2016 was 5802 kg. The molar mass of ammonia is 17.031 g/mol, and the molar mass of nitrogen is 14.007 g/mol. This means the percentage of nitrogen in ammonia is;

$$\frac{14.007}{17.031} = 0.8224 \dots \approx 82\%$$

The ammonia content is 19%, therefore the amounts of consumed ammonia and consumed nitrogen are;

 $0.19 * 5802 \approx 1102 \ kg \ consumed \ ammonia$

 $0.82 * 1102 \approx 904 \ kg \ consumed \ nitrogen$

Flow A is thus 904 kg.

Silica Sol Flow B

Flow B is based on the amount of produced product to customer during the year 2016. Two different products containing nitrogen in the form of ammonia were produced during that time period, hereon denoted Product 1 and 2 respectively. Ammonia (19 %) containing product was used in both types of products produced at the Silica Sol factory.

Product 1 produced during the year 2016 required in total 499 kg of ammonia (19 %) containing product. This means that the amount of consumed ammonia for Product 1 in the year 2016 was;

$499 * 0.19 = 94.81 \approx 95 \ kg \ ammonia$

As has been calculated previously in flow A, the percentage, or fraction, of nitrogen found in ammonia is about 82 %. Therefore, the amount of nitrogen consumed for Product 1 in the year 2016 was about 78 kg, see calculation below.

 $95 * 0.82 = 77.9 \approx 78 \ kg \ nitrogen$

Product 2 produced during the year 2016 required in total 2609 kg of ammonia (19%) containing product. The amount of consumed ammonia for Product 2 in the year 2016 was;

 $2609 * 0.19 = 495.71 \approx 496 \ kg \ ammonia$

The amount of nitrogen consumed for Product 2 in the year 2016 was about kg, see calculation below.

 $496 * 0.82 = 406.72 \approx 407 \ kg \ nitrogen$

The total amount of nitrogen consumed for Product 1 and 2 was;

 $78 + 407 = 485 \ kg \ nitrogen \ in \ total$

Flow B is therefore 485 kg.

Silica Sol Flow C

The total amount of water from the Silica Sol factory to the CRV was under 2016 288 654 m³. The amount of nitrogen released is based on the sampling conducted during the thesis work (table 5, chapter 6.2.1). The flows which are relevant are flow 1, flow 2 and flow 10. The average concentration of nitrogen from these flows is about 2.77 mg/L, see calculation below. Note that the maximum value of flow 10 is 2 mg/L, therefore it is the value used in this calculation.

$$\frac{(3.5+2.8+2)}{3} \approx 2.77 \ \frac{mg}{L} = 2.77 \ \frac{mg}{dm^3}$$

Since 288 654 m³ is equal to 288 654 000 dm³, the total amount of nitrogen going from the Silica Sol factory to the CRV was;

 $2.77 * 288\ 654\ 000 = 799\ 571\ 580\ mg = 799\ 571.5..g \approx 800\ kg$

Flow C is thus 800 kg.

A.2 Calculations for Separation Products

Calculations for the flows connected to the Separation Products factory are presented below. The data used in the following calculations has been collected from the contact person of the Separation Product factory, the periodic table and the environmental report for the year 2016 (AkzoNobel, 2017b)

Separation Products Flow E

The input of raw materials is divided into three parts due to the production processes. The calculations are done over the three parts and the results of these give the total raw material input. The total input is thus the total raw material input plus the process water input. The calculations are based on data received by the contact person at the Separation Products factory, the environmental report for the year 2016 and the periodic table.

In the first part two different types and amounts of nitrogen-containing products are used for one batch, 35 kg of Product A and 175 kg of Product B. Both of these products are assumed to be pure. The percentage of nitrogen in Product A is 18 %.

The nitrogen content of Product A is thus;

35 * 0.18 = 6.3 kg nitrogen

The batch was produced 19 times in the year 2016; therefore the total amount of nitrogen is;

 $6.3 * 19 \approx 120 \ kg \ total \ nitrogen$

The percentage of nitrogen in Product B is about 40 %. The amount of nitrogen in Product B is thus;

 $0.4 * 175 = 70 \ kg \ nitrogen$

The total amount of nitrogen in the first part is therefore 120 + 70 = 190 kg nitrogen.

In the second and third part of the process Product C and Product Y are used. Product C has a nitrogen content of about 22 %. Product Y has a nitrogen content of about 82 %.

In the second step the amounts used were 65.2 kg Product C (65.3% solution) and 53 kg Product Y. This means that the amount of nitrogen in each product is;

 $65.2 * 0.653 * 0.22 \approx 9 \ kg \ nitrogen \ in \ Product \ C \ (65.3\%)$

 $53 * 0.19 * 0.82 \approx 8,2 \ kg \ Product \ Y$

This type of batch was run 91 times in the year 2016. The total amounts of nitrogen used in the second step for the year of 2016 are, respectively;

 $9 * 91 = 819 \ kg \ nitrogen$

 $8.2 * 91 \approx 746 \ kg \ nitrogen$

The total amount of nitrogen used in the second part is thus 819 + 746 = 1565 kg nitrogen.

In the third, and final, part of the process 85.3 kg of Product C (65.3%) and 62.2 kg of Product Y. The amounts of nitrogen in both are, based partly on the previous calculations for the second step, respectively;

 $85.3 * 0.653 * 0.22 \approx 12 \text{ kg nitrogen in Product C (65.3\%)}$

 $62.2 * 0.19 * 0.82 \approx 9.7 \text{ kg nitrogen in Product Y}$

The batch was run 50 times in the year 2016. The total amounts of nitrogen used in the third step for the year of 2016 are, respectively;

 $12 * 50 \approx 600 \ kg \ nitrogen$

 $9.7 * 50 \approx 485 \ kg \ nitrogen$

The total amount of nitrogen used in the third part is thus 600 + 485 = 1085 kg nitrogen. The overall total for the input of raw material to the Separation Products factory was thus 190 + 1565 + 1085 = 2840 kg. This means that flow E is equal to 2840 kg.

Separation Products Flow F

The flow magnitude was based on the numbers found in the internal document Bilaga 6 Q4 Separation Products (AkzoNobel, 2016b). Flow F is equal to 2431 kg.

A.3 Calculations for CRV

Calculations for the flows connected to the CRV factory are presented below. The data used in the following calculations has been collected from sampling and

analysis, the periodic table and the environmental report for the year 2016 (AkzoNobel, 2017b)

CRV Flow J

Flow J was based on the numbers presented in the environmental report for 2016 (AkzoNobel, 2017b). The flow is 4100 kg.

CRV Flow K

The environmental report for 2016 (AkzoNobel, 2017b) stated that 1507 tons of filter cake was produced in the year 2016. This means that 1 507 000 kg of filter cake was produced. According to the filter cake sample analysis the concentration of nitrogen is 93 mg/kg. This means that the total amount of nitrogen found in the filter cake (flow M) was;

 $93 * 1507000 = 140151000 mg = 140151 g \approx 140 kg nitrogen$

Flow K is therefore 140 kg.

CRV Flow L

Flow L is the total output to export from the CRV and is comprised of flow J and flow K. Flow L is thus 4240 kg, see calculation below.

 $4100 + 140 = 4240 \ kg \ nitrogen$

A.4 Calculations for Hydrogen Peroxide

Calculations for the flows connected to the Hydrogen Peroxide factory are presented below. The data used in the following calculations has been collected from the contact person of the Hydrogen Peroxide factory, the periodic table and the environmental report for the year 2016 (AkzoNobel, 2017b)

Hydrogen Peroxide Flow G

Flow G, the input to the Hydrogen Peroxide factory, comprises of four different compounds. The compounds are listed below with calculations for nitrogen contents.

Ammonia containing products are purchased and used in production both in weight and volume. Both types have an ammonia content of 19%. The amount of ammonia used in weight-based form was about 846 kg. The amount of ammonia used in volume-based form was about 1.64 kg. The total amount of ammonia from ammonia (19%) containing products is thus;

$1.64 + 846 \approx 848 \ kg \ ammonia$

The molar mass of ammonia is 17.031 g/mol, and the molar mass of nitrogen is 14.007 g/mol. This means the percentage of nitrogen in ammonia is;

 $\frac{14.007}{17.031} = 0.8224 \dots \approx 82\%$

The amount of nitrogen found in the ammonia (19%) based products is thus about 695 kg nitrogen, see calculation below.

 $848 * 0.82 \approx 695 \ kg \ nitrogen$

The second product of the input flow, flow G, is based on is Product D. In the year 2016 12 000 kg of Product D was purchased, and about 8895 kg was used in production. The input is based on the amount purchased, which is therefore 12 000 kg. Product D is assumed to be 100% pure. The percentage of nitrogen found in Product D is about 16 %. The amount of nitrogen purchased in the year 2016 is thus;

 $12000 * 0.16 = 1920 \ kg \ nitrogen$

The third product of flow G is Product Q which is assumed to be 100% pure. The amount of Product Q used in production in the year 2016 was 4320 kg. The percentage of nitrogen found in Product Q is about 26 %. The amount of nitrogen used in production in the year 2016 is therefore about;

 $4320 * 0.26 \approx 691 \, kg \, nitrogen$

The fourth and final compound of flow G is Product X. The amount of Product X used in production in the year 2016 was 31 000 kg and the product is assumed to be 100 % pure. The percentage of nitrogen found in Product X is about 5 %, see calculation below. The amount of nitrogen found in Product X is thus;

 $31000 * 0.05 = 1550 \ kg \ nitrogen$

The total amount of nitrogen comprising flow G, which is based on the four compounds mentioned above, is 4856 kg, see calculation below.

695 + 1920 + 691 + 1550 = 4856 kg total nitrogen

This means that flow G is 4856 kg.

Hydrogen Peroxide Flow H

The data for the amount of nitrogen comprising the output flow to the CRV is based on the environmental report for the year 2016 (AkzoNobel, 2017b), which was 3 824 kg. Flow H is therefore 3 824 kg.

Hydrogen Peroxide Flow I

Based on information gained from the contact person at the Hydrogen Peroxide factory the amount of Product D used in production also leaves the site entirely in the finished product sold to customer. Therefore the amount of Product D which is used in production is the same as is exported to customer and therefore comprises flow I. The amount of Product D used in production for the year 2016 was 8895 kg and is assumed to be 100 % pure. The percentage of nitrogen found in Product D is about 16 %, which has been stated in the calculations for flow G. The amount of nitrogen found in Product D of flow I is therefore;

 $8895 * 0.16 \approx 1423 \ kg \ nitrogen$

Flow I is thus 1423 kg.

Appendix B

Calculations for the MFA on Nitrogen over the CRV at the AkzoNobel PPC Bohus site can be found below.

Flow Z14

Flow Z14 was based on the sampling conducted during the thesis work with the analysis results given in the unit mg/kg. To be able to compare this data point with the others, calculations were performed to convert it to mg/L using the density of the filter cake which was 1.34 kg/L according to internal documents. The calculation pathway is presented below.

93
$$\frac{mg}{kg} * 1.34 \frac{kg}{l} = 124.62 \frac{mg}{L} \approx 125 mg/L$$

Flow Z15

Flow Z15 was calculated using the data for previously conducted water sampling for the year 2016 (AkzoNobel, 2016a). The total sum amount of nitrogen was calculated by multiplying the average amount of nitrogen (12 kg) based on the weekly sampling with 52, the amount of weeks during 2016, see calculation below.

$12 * 52 = 624 \ kg \ nitrogen$

The total water flow was 341 771 m3. This means that the concentration of nitrogen in the water leaving the final basin, P3, of the CRV for the year 2016 was 1.83 mg/L, see calculation below.

$$\frac{624}{341771000} \left(\frac{kg}{dm^3}\right) = 1.8257..* \ 10^{-6} \ \frac{kg}{L} \approx 1.83 \ \frac{mg}{L}$$