**INTEGRATED MASTER IN ENVIRONMENTAL ENGINEERING**

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# MODELING NUTRIENT LOADS FROM WASTEWATER TREATMENT PLANTS DISCHARGING TO THE BOTHNIAN BAY

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***To my loved ones,***

***Special to my mother***

*“Be a lingering stream*
*Start to wander*
*Beneath the curving skies*
*Be the weakening wind*
*And my bridge to impossible”*

*”Ole viipyvä virta*
*Käy vaeltamaan*
*Alle kaartuvaan taivaan*
*Ole hiipuva tuuli*
*Ja siltani mahdottomaan”*

***Jukka Pekka Leppäluoto***

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## Abstract

In the Baltic Sea the main problem is the eutrophication, which is due to nutrient load e.g. from municipal wastewater treatment plants (WWTPs). Therefore, the main pollutant responsible for this problem is nitrogen, which leads to an excessive growth of organisms and decrease of oxygen concentration instigated an algal bloom. To understand the impact of the nitrogen has on Bothnian bay is necessary to study how it is release as well as the amount that is thrown into the sea. This work focuses on modeling loads of outgoing nitrogen from six WWTPs in the coast line of Bothnian bay. In Finland the implementation of requirements that define the water quality is not yet fully implemented. Although, European Union has set the Directive 91/271/CEE regarding urban wastewater treatment, and together with Finnish legislation, some of the treatment plants have already set the requirements to this problem.

For the six WWTPs studied, the developed models based on historical data, are useful to predict the behaviour of nitrogen loads in the future. Modeling load showed that the implementation of nitrogen removal processes and the nature of wastewater treatment are crucial in the amount of nitrogen that is released to the sea.

Some of the studied WWTPs achieved the basic nitrogen removal of 40% nitrogen as the WWTP of Oulu. The WWTPs in the cities of Kemi, Raahe, Kokkola and Pietarsaari are contributing to the eutrophication problem due to the amount of nitrogen load released. Oulu and Kempele are fulfilling the limit required by the environmental authorities. The best treatment process to accomplish good results in reduce percentage of nitrogen was activated sludge process.



***Keywords:*** *N*itrogen, Baltic Sea, Municipal wastewater, load modeling

# Abstrakti

Itämeren suurin ongelma on rehevöityminen, joka johtuu mereen lasketuista saasteista, joita lasketaan muunmuassa jäteveden puhdistuslaitoksista. Merkittävin rehevöittäjä on typpi, joka edesauttaa orgaanisen materiaalin lisääntymistä, josta seuraava happipitoisuuden lasku lisää leväkukintoja. Ymmärtääksemme typen vaikutukset Perämeren vesistöjen tilaan, on tutkittava, miten reittejä se veteen joutuu ja kuinka paljon sitä mereen lasketaan. Tässä työssä mallinnetaan typpikuormitusta kuudessa Perämeren rannalla olevassajätevedenkäsittelylaitoksessa. Suomessa typen määrän valvonta ei vielä toistaiseksi ole täysin toimeenpantu, vaikkakin Euroopan unionin yhdyskuntajätevesien käsittelyä koskeva direktiivi 91/271/CEE, yhdessä Suomen lainsäädännön kanssa, on aikaansaanut sen, että useat jätevedenpuhdistuslaitokset seuraavat haluttuja vaatimuksia jo nyt.

Kaikille kuudelle tutkitulle jätevedenpuhdistuslaitokselle suunnitellut empiiriseen mittaustietoon perustuvat mallit ovat hyödyllisiä typpikuorman ennustukseen tulevaisuudessa. Mallinnus osoitti, että typinpoistoprosessien käyttöönotolla on merkittävä vaikutus mereen lasketun typpimäärän alentamisessa.

Osa tutkimuksessa mukana olleista jätevedenpuhdistuslaitoksista, kuten Oulun ja Kempeleen jätevedenpuhdistuslaitokset, saavutti tavoitteena olleen 40% typen poiston. Toiset laitokset, kuten Kemin, Raahen, Kokkolan ja Pietarsaaren jätevedenpuhdistuslaitokset eivät saavuttaneet asetettuja rajoja. Parhaiten toimiva typenpoistoprosessi osoittautui olevan aktiivilieteprosessi.

***Avainsanat:*** *Typpi, Itämeri, Yhdyskunnan jätevesi, kuorman mallintaminen*

## Resumo

A eutrofização é o principal problema presente no mar Báltico, o qual deve-se à libertação de fontes de poluição tais como as estações de tratamento de águas residuais (ETARs). Sendo assim, o poluente responsável por este problema é o nitrogénio o qual, em grande quantidade libertada leva ao excessivo crescimento de organismos e à diminuição da concentração de oxigénio originando o desenvolvimento de algas. Para compreender o impacto que este poluente tem no Golfo da Botónia é necessário estudar a forma como se faz a libertação bem como a quantidade que é lançada no mar. Este trabalho centra-se na modelação das cargas de nitrogénio que saem de seis ETARs na linha da costa do Golfo da Botónia. Na Finlândia, a aplicação dos requisitos para controlar os parâmetros que definem a qualidade da água, ainda não está totalmente implementada. Embora, a Diretiva 91/271/CEE da União Europeia, relativa ao tratamento de águas residuais urbanas, juntamente com a legislação finlandesa, já tenha sido implementada em algumas das ETARs existentes.

Para as seis ETARs estudadas, desenvolveram-se modelos matemáticos com base nos registos acumulados, prevendo o comportamento da carga de nitrogénio durante os próximos anos. A modelação veio demostrar que a aplicação de processos de remoção de azoto e o tipo de tratamento das águas residuais são determinantes na carga de nitrogénio à saída para o mar.

Algumas das ETARs estudadas conseguiram atingir o requisito de redução de 40% de nitrogénio tal como a ETAR de Oulu. As ETARs nas cidades de Kemi, Raahe, Kokkola e Pietarsaari estão a contribuir para o problema da eutrofização, devido à quantidade que libertam de carga de nitrogénio. Oulu e Kempele são ETARs que cumprem bem o limite requerido pelas autoridades ambientais. O melhor processo de tratamento para se alcançar bons resultados de redução percentual de nitrogénio é o tratamento com lamas ativadas.

***Palavras chaves****: Nitrogénio, Estações de Tratamento de Águas Residuais; Modelação de Nitrogénio*

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# Abbreviations and symbols list

*Abbreviations*

| | | |
|---|---|---|
| WWTP | Wastewater treatment plant | |
| PAC | Poly Aluminium Chloride | |
| $BOD_7$ | Biochemical oxygen demand, 7 days | |
| N | Nitrogen | kg/d |
| P | Phosphorus | kg/d |
| p.e | Population equivalent | Habitants/$m^2$ |
| DO | Dissolved oxygen | |
| $O_2$ | Oxygen | |
| TSS | Total Suspended solids | |
| ASP | Activated Sludge Process | |
| BOD | Biochemical oxygen demand | |
| EPA | Environmental Protection Act | |
| IWA | International Water Association | |
| WW | Wastewater | |

***Variable and Used Units***

| | |
|---|---|
| $\Theta$ | phase shift |
| $\omega$ | angular frequency of the oscillation |
| m | Curve Declive |
| t | Time |
| W | Load |
| $\bar{W}$ | Mean load |
| $W_a$ | Amplitude of the loading |

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# 1. Introduction

## 1.1 Problems in Baltic Sea and Gulf of Bothnian Bay

Finland has estimated 5.2 million people and average population density of 17 inhabitants per $km^2$ (Lapinlampi et. all , 2002). It is called the “land of thousand lakes” because around 10% of its total surface area is covered by lakes, ponds, rivers and brooks and part of those discharges into the Baltic Sea (Ministry of Agriculture and Foresty, 2009). The Baltic Sea is one of the world’s largest semi-enclosed bodies of salty water and it is located between $53^{0}$N to $66^{0}$N latitude and $20^{0}$E to $26^{0}$E longitude (HELCOM 2010). It is surrounded by nine countries, which are: Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden (Figure 1). In the northern part there is the Gulf of Bothnia, in the northeastern Gulf of Finland, on eastern Gulf of Riga and together they form the Baltic Sea, which has a surface area of approximately 65 000$km^2$ (HELCOM, 2013). Since 1800s, the water quality of the sea has been decreasing, passing from an oligotrophic into an eutrophic environment. This eutrophication problem is defined as an overenrichment of nutrients in water bodies, resulting in the excessive growth of organisms and decrease of oxygen ($O_2$) concentration (J.E., Cloern, 2001). Nutrients are discharged to the sea via rivers, atmospheric deposition and indirect discharges from pollution sources located along the coastline. The discharges are originated from industries such as municipal wastewater plants and from various sources, such as agriculture, scattered dwellings and atmospheric deposition within river basins. Excessive nitrogen (N) and phosphorus (P) loads coming from land based sources are the main cause of the eutrophication of the Baltic Sea. About 75% of the nitrogen load and at least 95% of the phosphorus load enter in the Baltic Sea via rivers

***Figure 1*** *The Baltic Sea and the surrounded countries (HELCOM, 2013).*

or as direct waterborne discharges. About 25% of the nitrogen load comes as atmospheric deposition (HELCOM, 2006). The clarity of seawater integrates many of the concrete effects of eutrophication such as disappearance of plants and algae and intensification of algal blooms (HELCOM, 2006). The decrease of water quality in the Baltic Sea´s littoral communities has awakened to the concern about environment and caused changes in the attitudes of authorities. In 1974, HELCOM convention was held in Helsinki by seven coastal states around the Baltic Sea. The aim of the convention was to consider all sources of pollution in the Baltic Sea and reduce the nutrient loads from atmosphere, river and municipal wastewater sources. To overcome these problems the Baltic Sea Action Plan (BSAP) was launched (HELCOM, 2007) to reach good ecological status by reducing the inputs of P and N into the Baltic Sea for about 43% and 18% respectively (D.Skogen, Morten; Almroth, Elin, 2010).

The HELCOM commission assessed and classified the eutrophication status of 189 'areas' in the Baltic Sea, of which 17 are open areas and 172 are coastal areas. The open waters in the Bothnian Bay and in the Swedish parts of the northeastern Kattegat were classified as 'areas not affected by eutrophication'. The fact that the open parts of the Bothnian Sea are classified as an 'area affected by eutrophication' is related to the increase in chlorophyll concentrations. In the Annex I it is possible to observe which areas are bad, poor, moderate and good (HELCOM, 2009). Bothnian bay is one of the problematic areas of Baltic Sea, which is poor in nutrients and is limited by the amount of P (Wulff & Rahm, 1996). His surface area has 36 260km$^2$ and comprises about 10% of total area of the Baltic Sea (HELCOM 1996). Its position is between the latitudes 63.5°N and 66°N and the Finnish cities Kemi, Oulu, Kokkola and Pietarsaari are on its coast (Figure 2). Since phytoplankton cannot utilize the N totally, its concentrations are higher here than in the more southern basins of the Baltic Sea. In coastal waters within the range of rivers influence, N limits the phytoplankton production during the spring flood (Laine, Anne; Kronholm, Malin , 2005). The floods are related with the strict climate of Finland, which is covered with snow most part of the year and lakes are frozen for five to seven months. Floods are quite common especially in western part of Finland (Ministry of Agriculture and Foresty, 2009). In 2000, approximately 1900 tons of N and 30 tons of P came to the sea through the coastal municipal wastewater treatment plants (WWTP), which combines for 3.5% and 1.2% of the


***Figure 2**- The Bothnian bay approximate locations of the Finnish coastal cities. (HELCOM, 2005).*

total amount of these nutrients respectively (Bothnian Bay Database). In 2001 the environmental authorities, started a project in order to improve the exchange of information between countries, regions, industries and municipalities to develop guidelines for integral management and monitoring and to define targets and priorities towards sustainable development in the area (Laine & Rissanen, 2004). The project name was "Bothnian Bay life" and it was funded by European Union (EU) and several industries, municipalities and other actors of the area, both in Finland and Sweden.

## 1.2 Presenting the project

This thesis was part of the project entitled "Wastewater and nitrogen in the Bothnian Bay coastal waters" and the goal was to find out how wastewater discharge affects Bothnian bay coastal water quality and eutrophication. The thesis is part of the Phase I: Data collection, which includes collecting of existing data from the studied WWTPs and creating a nitrogen model to predict how the loads are coming from the WWTPs.

## 1.3 Thesis objectives and main tasks

The main objective of the thesis was to create a model to predict the nitrogen load that come from the six wastewater treatment plants (WWTPs) in the coastal area of Bothnia Bay. To achieve the goal of the thesis three subtasks were stated (1) to collect nutrient load data from wastewater treatment plants, (2) to use statistical methods to study key parameters effecting on nutrient load, (3) modeling the load from the WWTPs

## 1.4 Structure of thesis

The thesis is organized in 5 chapters, such as Introduction, State of the art, Methodology, Results and Discussions and for last Conclusion

On the Chapter 1 a brief introduction of the problems in Baltic Sea and the history of environmental changes are presented. The deterioration and eutrophication problems are related and mention to the study area of Bothnian bay. Also, are present the project which this thesis is included and the objectives and tasks of it.

Chapter 2 the State of the art, a global view of wastewater treatment in Finland and those treatments processes are described. Description of nitrification and denitrification processes, which are part of biological nitrogen removal. Finally, an overview of water quality modeling evolution and mathematical, empirical and optimization models.

In the chapter 3, it is present the implemented materials and methods. This chapter is divided in two subchapters, first studied WWTPs, where it is made a description of each one and which kind of data was provided. In the second subchapter, the nitrogen modeling processes is described and how it was preceded the study.

Chapter 4, the results of the implemented nitrogen model of the six WWTPs are presented. The results are based on load functions introduced in Matlab and presented in graphical form.

For the conclusion in Chapter 5, all results are compared among all six studied WWTPs and the limitations are envisaged.

# 2. State of the art

## 2.1 Wastewater treatment in Finland

The components of wastewater are depending of the type of collection system used. They can include domestic wastewater (WW) (also called sanitary), industrial WW, infiltration/inflow (waters that enters the collection system through indirect and direct means as like leaking joints, cracks and breaks or porous walls) and also stormwater (runoff resulting from rainfall and snowmelt), which ones can be diluted with storm water, groundwater, and surface water and all together will be discharge into the sea (Metcalf & Eddy, 2003). If there is no WW treatment before the discharge, the results in environmental and human health effects such as the generation of odors, depletion of dissolved oxygen (DO) and the release of nutrients, toxic contaminants and pathogens will be noticed ( Mogens et al., 2008). The treatment of WW is crucial part of water protection and management due the amounts of nutrients, which can accelerate eutrophication of watersheds. From 1970 to 1980's, wastewater treatment objectives were based on aesthetic and environmental concerns. Nowadays, the reduction of biological oxygen demand (BOD), total suspended solids (TSS), and pathogenic organisms continued but with higher standards. Removal of nutrients, such as nitrogen (N) and phosphorus (P) also began to be addressed, particularly in some of the inland streams and lakes, and estuaries and bays (Metcalf & Eddy, 2003).

The most common WW treatment process in Finland lies of activated sludge processes (ASP), with different configurations and basin shapes, where the main objective is to remove the total N, ammonia, organic matter and also P, which is typically carried out by chemical precipitation (E-WAter , 2010). The methods of removal contaminants is brought by physical, chemical or biological processes remains necessary to minimize the potential impacts of the discharge and to favor the production of valuable end-products such as reusable water, nutrients and biosolids. This can be achieved by a combination of units processes known as preliminary, primary, advanced primary, secondary (without or with nutrient removal) and advanced (or tertiary) treatment (Metcalf & Eddy, 2003).The wastewater treatment line in Finland consists of screens, a sand trap, primary clarifiers, activated sludge basins, and secondary clarifiers. Moreover, some of the plants have a tertiary treatment, and an equalization basin or a middle clarifier. Flotation is the most common tertiary treatment unit but it could be use also as a post-filters. The biological treatment process configuration varies in the different plants (E-WAter , 2010). In preliminary treatment, gross solids such as larger objects, gravel and grit are removed for not damage the equipment. In primary treatment, a physical operation, usually sedimentation is used to remove the floating and settleable materials found in wastewater. For advanced primary treatment, chemicals are added to enhance the removal of suspended solids and to a lesser extent, dissolved solids. In secondary treatment, biological and chemical processes are used to remove most of the organic matter. Also, the secondary can have nutrient removal of organic and suspended solids and nutrients such N, P or both. In advanced treatment, additional combinations of unit operations and processes are used to remove residual suspended solids and other constituents that are not reduced significantly by conventional secondary treatment (Metcalf & Eddy, 2003).

WWTPs in Finland have all a common problem, which is the extremely low temperature during winter period. In average the temperature of incoming wastewater is about12°C (E-WAter , 2010). The low temperatures occur usually during snowmelting in springs, but also heavy rains can lower the temperature (E-WAter , 2010). In such situation, the influent flow rate is also high and part of the WW must be bypassed. Environmental Protection Act (EPA) defines bypass as being a process associated with returned of the flows to the sewage treatment and discharging to the environment through the final effluent outfall of the sewage treatment plant. When a bypass occurs, wastewater effluent is deviated past certain treatment processes to safeguard the plant. The bypass is permitted when the inflow of sewage and excess of water exceed the design capacity of the treatment plant. Bypasses that occur during dry conditions are usually caused by technical, maintenance or operational disruptions (Watershed Group, 2009).

A WWTP is characterized by frequent variations in environmental conditions such as flow rate, temperature, and influent concentration of nutrients and concentration peaks of toxic substances that may cause serious problems in a biological wastewater treatment. These variations can affect the process performance significantly, although nowadays there is the application for modeling process to simulate and create control strategies (Haimo et al. , 2009). Development of modeling gives useful information of the plant operations to the people that are responsible to control and find suitable solution for the problems.

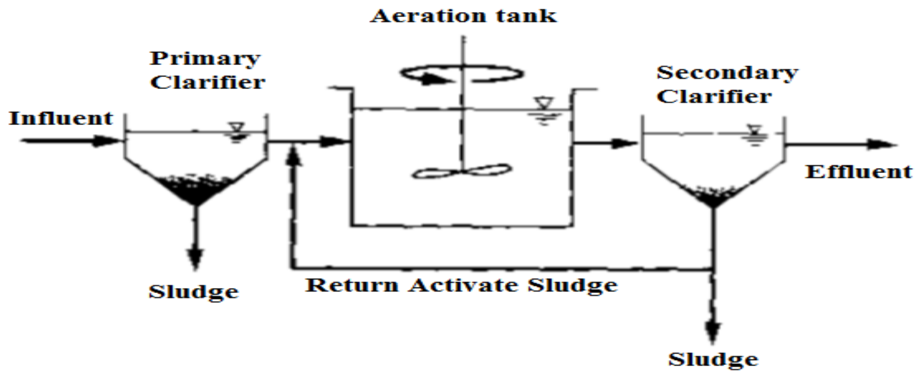



***Figure 3*** *Schematic activated sludge diagram (Metcalf & Eddy, 2003).*

### 2.1.1 Activated Sludge Process

Activated sludge process (ASP) is a bacterial biomass suspension (the activated sludge) which can remove pollutants. Depending on the design and the specific application, an activated sludge can achieve biological N removal and biological P removal, plus the removal of organic carbon substances. Many different ASP configurations have evolved during the years, Jeppsson in 1996 provides an exhaustive review on the historical evolution of the ASP. Nowadays this is a process used routinely for biological treatment of municipal and industrial wastewater and together with chemical treatment (Metcalf & Eddy, 2003). The basic steps of ASPs consist of the following three basic components: (1) a reactor where the microorganisms responsible for treatment are kept in suspension and aerated; (2) liquid solids separation, usually in a sedimentation tank and (3) a recycle system for returning solids removed from the liquid-solids separation unit back to the reactor (Figure 3). An important feature of this treatment is the formation of flocculants which can settle by gravity in sedimentation tanks. In most cases, the ASP is working in conjunction with physical and chemical processes that are used for the preliminary and primary treatment of wastewater and post treatment, including disinfection and possibly filtration (Metcalf & Eddy, 2003).

### 2.1.2. Biological treatment

The overall objectives of the biological treatment are to: transform dissolved and particulate biodegradable constituents into acceptable end products; remove or reduce the concentration of organic and inorganic compounds; capture and incorporate suspended and nonsettleable colloidal solids into a biological floc or biofilm; transform or remove nutrients such as N and P and in some cases remove specific trace organic constituents and compounds. The biological treatment processes may be classified as aerobic and anaerobic suspended growth, attached growth and various combinations (Metcalf & Eddy, 2003). A typical treatment plant comprises three phases of treatment – primary, secondary and tertiary (Figure 4). Primary treatment involves settlement of solids in a clarifier tank. The wastewater then passes to the secondary treatment or aeration tanks. This is the major biological phase of treatment by the activated sludge bacteria. A tertiary phase may be used to further improve the quality of the secondary effluent, by removing nitrogen, phosphates, suspended solids or pathogens as required ( Mogens et al., 2008).

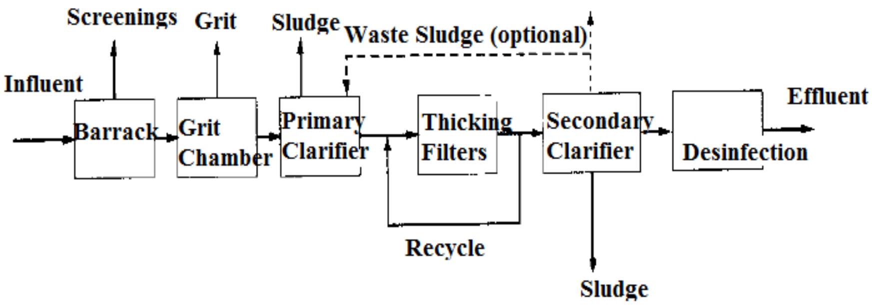



***Figure 4*** *Schematic biological treatment diagram (Metcalf & Eddy, 2003).*

## 2.2 Nitrogen removal

The nitrogen removal is used in wastewater treatment where there are concerns about the good water quality and also: (1) the effect of ammonia on receiving water with respect to dissolve oxygen concentrations and fish toxicity; (2) the need to provide nitrogen removal to control eutrophication, and (3) the need to provide nitrogen control for water-reuse applications including groundwater recharge. Nitrification and denitrification are important processes, which are part of biological nitrogen removal.

### 2.2.1 Nitrification and Denitrification

In wastewater, there are various forms of nitrogen, which combined with organic matter and urea causes the eutrophication of the system. The nitrogen removal processes in wastewater treatment plants are typically two-steps biological processes: nitrification followed by denitrification. Technically, it is a three-step process: ammonification precedes nitrification and denitrification. Nitrification process is described by the oxidation of ammonia ($NH_4^+$) is oxidized to nitrite ($NO_2^-$) and nitrite is oxidized to nitrate ($NO_3^-$). These conversions are in presence of $O_2$ and they were described by Gaudy and Gaudy in 1980. In the first reaction, the bacteria of the genus *Nitrosomonas* convert ammonium ion ($NH_4^+$) to nitrite as shown in equation (1) and in the next step bacteria of the genus *Nitrobacter* convert nitrite to nitrate (equation 2) (Chapra et. all, 1983). Denitrification process is the biological reduction of nitrate to nitrite oxide, and nitrogen gas. The process involves absence of $O_2$; the nitrate reduction reactions involve the steps of equation 3 from nitrate to nitrogen gas. In Annex II it can be seen the generalized nitrogen cycle in the aquatic and soil environment.

***Equation 1***- *Nitrification: conversation of ammonium to nitrite.*

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^-$$

***Equation 2***- *Nitrification: conversion of nitrite to nitrate.*

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

***Equation 3-*** *Denitrification: conversion of nitrate to nitrogen.*

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

## 2.3 Water Quality Modeling

Modeling is defined as a simplified (often mathematical) description of a system that assists in calculations and predications of the condition of that system in a given situation (Baldick, Chris, 1990). The use of models is important to water quality management process. This indicates that water resource managers find significance in the comprehension of a model can provide. Models can be used to answer questions regarding the environmental impact of existing and potential loadings and waste discharges. Use of the computer for simulation water-related processes has made water quality-modeling a relatively inexpensive tool to investigate the impact of alternative development approaches before any irreversible action is taken. Nowadays technology is advancing so fast, it is worthwhile to keep track of the most recent modeling innovations.

### 2.3.1 Mathematical models

Over the past 75 years, engineers have developed water quality models to simulate a wide variety of pollutants in a broad range of receiving waters. Water quality modeling has evolved appreciably since it´s innovation in the early of 20$^{th}$ century. In 1925, two researchers Streeter and Phelps, were studying the oxidation and aeration processes on the Ohio River and developed the first models. This and subsequent investigations provided a means to evaluate dissolve oxygen (DO) levels in streams and estuaries. In addition, bacteria models were also developed by O'Connor in1962 (Chapra et. all, 1983). Due lack of availability of computers, models solutions were closed form meaning that the applications were usually limited to linear kinetics, simple geometries, and steadystate receiving waters. Thus, the scope of the problems that could be addressed was constrained by the available computational tools. Models can be used to answer questions regarding the environmental impact of existing and potential loadings and waste discharges. Models can also help to understand the complex relationships among the biotic and abiotic components of water systems. The extent to which a model can be useful depends on the suitability of the chosen model to the desired application, and the ability of the individuals interpreting the outputs (the individuals need to know the theoretical components on which the model is based in order to understand why certain outputs occur). No model will provide a definitive solution to any problem because there is risk, in form of uncertainty, associated with all methods of prediction. The best models are those that have a solid of theoretical concepts, and have been confirmed by comparing actual measurements to predicted results.

In simple terms, mathematical models are an equation, or a set of equations, that relates input parameters and variables to quantified outputs, based on specific assumptions and simplifications of the real system being modeled (U.S.EPA). Mathematical models can be described by many different criteria. Chapra and Reckhow provide descriptions of the descriptive terms for models in the following topics: physical processes of dispersion and temperature; dissolved oxygen, pH and alkalinity; nutrients; algae; zooplankton; and coliforms (Chapra et. all, 1983). They apply their combined knowledge of modeling, statistics, and environmental engineering in a book with concepts and analytical techniques behind lake management.

In the 1960s, digital computers became widely available. This led to major advances in both the models and the ways in which they could be applied. The first modeling advances involved numerical expressions of the analytical frameworks (Chapra et. all, 1983). Oxygen was still the focus, but the computer allowed analysts to address more complicated system geometries, kinetics and time-variable simulations. In particular, the models were extended to two-dimensional systems such as wide estuaries and bays. The computer brought a more comprehensive approach to water-quality problems. Rather than focusing on local effects of single point sources, one could view the drainage basin as a system. Tools developed originally in the field of operations research were coupled with the models to generate cost-effective treatment alternatives. Although the focus was still on point sources, the computer allowed a more holistic perspective to be adopted. Nowadays the principal water-quality problem addressed during this period is eutrophication. As consequence, modelers broadened their own scope to include more mechanistic representations of biological processes.

### 2.3.2 Empirical and mechanistic models

Empirical models are developed primarily from an analysis of data and they are based more on fitting a set of data and less on theoretical principles. Mechanistic models, on the other hand, are intended to be mathematical descriptions of theoretical principles. It should be emphasized that any good model has both empirical and mechanistic features, but it is possible to classify most models according to a stronger basis in either empiricism or theory (Riecken, Sarah, 1995).Over the past of 25 years a large number of models have been described that arise from the principle of empiricism. These models generally draw some mathematical relationship between two or more quantitative measurements in lakes. The classic example of this is made by Vollenweider in 1968 showing the relationship between phosphorus loading and trophic status of lake. Another early use of empiricism was by Satamoto in 1996 describing the relationship between phosphorus and chlorophyll in lakes. Since Vollenweider's landmark publication the method of using reported results from the literature, and sample results for a wide range of lakes, to derive an understanding of the relationship between the components of a lake ecosystem has been widely used.

### 2.3.3 Optimization and Simulation Software

Simulation models are designed to describe the functioning of system. Optimization models are used to find a solution that is best (minimum or maximum) in some sense (often subject to constraints, such as cost or environmental quality) (Riecken, Sarah, 1995). Those attempts to find analytical solutions enable the prediction of the behaviour of the system from a set parameters and initial conditions. Modeling techniques include statistical methods, computer simulation, system identification and sensitivity analysis. Models applied for prediction aim at providing a precise and fast image of a real system's behaviour under different conditions (Haimo et al. , 2009).

In 1983, the International Water Association (IWA) formed a task group, with the aim to promote development, and facilitate the application of practical models for design and operation of biological wastewater treatment systems. The first goal was to review existing models and the second one was to reach a consensus concerning the simplest mathematical model having the capability of realistically predicting the performance of single-sludge systems carrying out carbon oxidation, nitrification and denitrification. The final result was presented in 1987 as the name of Activated Sludge Model No 1 (ASM1). Nowadays, there are more three models following the first one, which are ASM2, ASM2d, ASM3 models (Haimo et al. , 2009).

Other works were realized using the mathematical representation of the secondary settler and commercial software's. Dynamic simulations based on rigorous and detailed modeling have become a standard tool in many engineering fields. The models are applied for a variety of tasks allowing the exploration of the impact of changing some design configurations. These models can be used to provide tools to explore new ideas and improve the learning process. In the Annex III it is described approaches of software programs, which gives an overview existing in the market concerning dynamical models to estimate measurements of variables and to know parameters. Mostly, the measured parameters are flow rate, nutrient concentrations, turbidity, pH, etc. and essentially they refer to the estimation values of the variables. Thereby, measurement of data often contains errors due the system and the way of doing. To reduce them, it is essential a good methodology of collecting the information. Currently, there are soft sensors, which can provide fault detection and redundancy control. When nutrients analyzers needed measurements and they are not available, they can be estimated a softsensor, which represents a combination of robust hardsensors and a mathematical model defined to reconstruct the time evolution of the unmeasured states (Haimo et al. , 2009). Although, there is not yet a program that can be so sensitive, this can give us measurements without any error.

## 3. Materials and Methods

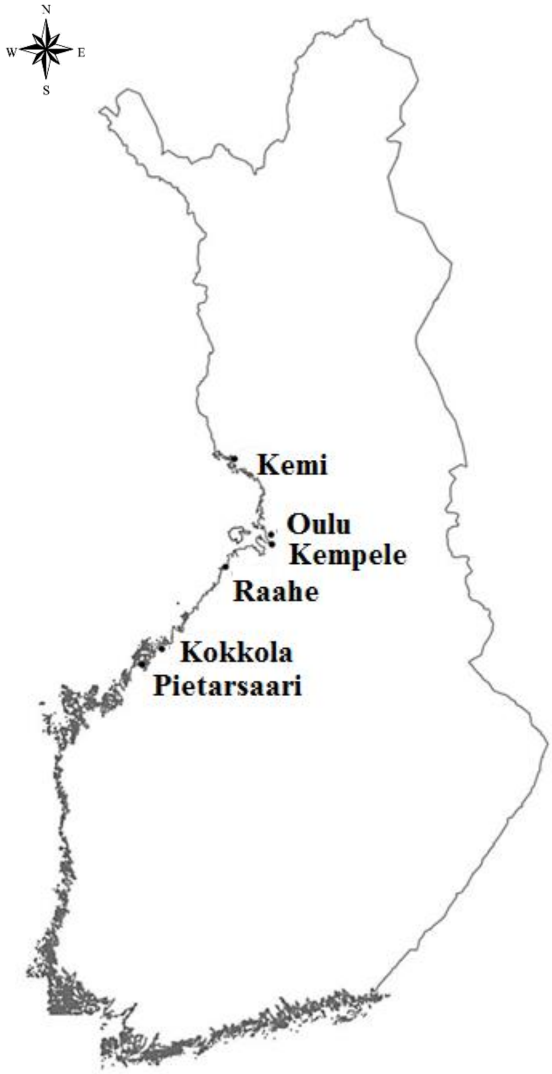



***Figure 5***- *Studied WWTPs in Finland. ArcMap.*

The methodology used was based on collecting information concerning the type of the treatment plant, nitrogen removal requirements, the wastewater temperature, daily discharge and incoming and outgoing concentration of phosphorus, nitrogen, and $BOD_7$. The studied data were for a period of 5 years (2008-2012) until at least 10 years for one of WWTPs (2003-2012). Altogether, there were studied six WWTPs located in the coastal of Bothnian Bay, five of them were medium-sized (30 000 – 100 000 person-equivalent (p.e)) and one large (> 100 000 p.e) in Oulu city (Figure 5). The WWTPs studied have been in operation between 3 to 40 years however all the plants were renovated at least once.

The treatment processes of the plants have consequences for the plant treatment efficiency and performance. The processes used by WWTPs were biological-chemical and activated sludge processes. The WWTP in Kempele have a constructed wetland as a final stage. In Finland the P removal and $BOD_7$ are considered important objectives for the operation. However, since the implementation of the European Directive 91/271/CEE regarding urban wastewater treatment and together with Finnish legislation, it was set in some of the WWTPs (Oulu´s and Kempele´s WWTPs), N removal requirements. Thereby, the set N removal requirements are depending on the sensitivity of the receiving water body in terms of eutrophication (E-WAter, 2010). This European Directive concerns the collection, treatment and discharge of urban wastewater and the treatment and discharge of wastewater from certain industrial sectors. Its aim is to protect the environment from any adverse effects caused by the discharge of such waters. In this thesis, the importance was to evaluate the total nitrogen, which means: the sum of total Kjeldahl-nitrogen (organic N+$NH_3$), nitrate nitrogen ($NO_3^-$) and nitrite nitrogen ($NO_2^-$). The requirements for discharges from municipal wastewater treatment plants to sensitive areas, which are subject to eutrophication and depend the size of the treatment plant: Total nitrogen – 15mg/l N (10 000 - 100 000 p.e); 10mg/l N (more than 100 000 p.e) and 70-80% minimum percentage reduction. The requirements for municipal WWTPs are described more in the Annex IV. The aim of national decree in Finland, which the title is Government Decree on Treating Domestic Wastewater in Areas Outside Sewage Networks (OWSD), is to reduce domestic wastewater discharges. The basic removal requirements are 90% of $BOD_7$, 85% of P and 40% of N must be achieved (Erkki Santala, 2003). The Finnish ministry of environmental, prescribed by law for purified wastewater flowing into the Gulf of Bothnia, that the water samples should be done from external laboratories. All of the treatment process plants have a primary step (mechanical) that removes coarse debris and part of the suspended solids, while a secondary (biological or chemical) treatment step uses aerobic or anaerobic microorganisms to decompose most of the organic matter (up to 90%) and retain some of the nutrients (around 20-30%). Tertiary (advanced) treatment step removes the organic matter even more efficiently (more than 80% of P and 50-90% of N). It generally includes chemical precipitation of P and in some cases extended N removal (HELCOM, 2005).

An overall performance for the following studied plants are given in the Table 1. The data shows that when the annual discharge has been high the load of N, P and $BOD_7$ were considerabel high like in Oulu’s WWTP. Although, in Kempele the discharge had the same amout as Oulu´s but the loads were lower. Among the others, Kempele´s WWTP had the lowest discharge, but also the lowest loads. The type of treatment process and the implementation of N removal have an important influence on the performances. In the following subchapters, a description are presented for each WWTP and the most important happenings during their time line. The created model was based in empirical model. With a help of Excel and Matlab programs and loading functions developed by Chapra, the prediction of N outgoing load was established. First, all the data were provided, introduced into Excel, studied and evaluated the appropriate function and then implement in Matlab. The following steps were: interpolation- finding a function that contains all the data points; model fitting- finding a function that is as close as possible to containing all the data points. That function is called the regression curve and finding the right one the validity of the model was determined by the coefficient denoted by r-square ($R^2$). The empirical model was not derived from assumptions concerning the relationship between variables and also not based on physical principles. The results were the following ones: compared between the same types of wastewater treatments; the impacts of implementing N removal requirements; the best results of N modeling and fitting process; and the behaviour of the WWTPs will have in future.

***Table 1***- *Overall performance of the studied WWTPs for the following parameters: MQin, N, P and $BOD_7$ (outgoing load) and removal efficiency of N, P and $BOD_7$*

| | | | Outgoing load kg/d | | | Removal efficiency % | | |
|---|---|---|---|---|---|---|---|---|
| WWTP | **Data years** | **MQin $m^3/d$** | **N** | **P** | **$BOD_7$** | **N** | **P** | **$BOD_7$** |
| **Kemi** | 2008-2012 | 9 313.5 | 255.5 | 2.4 | 71.9 | 14% | 95% | 92% |
| **Oulu** | 2005-2012 | 42 028.3 | 1 434.6 | 10.4 | 67.7 | 40% | 97% | 97% |
| **Kempele** | 2008-2012 | 4 834.7 | 230.5 | 0.6 | 24.3 | 31% | 99% | 99% |
| **Raahe** | 2008-2012 | 5 052.8 | 199.6 | 1.5 | 36.6 | 21% | 96% | 96% |
| **Kokkola** | 2006-2012 | 8 359.4 | 362.5 | 2.3 | 188.4 | 17% | 96% | 86% |
| **Pietarsaari** | 2003-2012 | 8 741.1 | 303.9 | 3.7 | 95.2 | 31% | 95% | 96% |

## 3.1 Studied WWTP

### 3.1.1 Kemi


***Figure 6***- *Map of Kemi's WWTP (Kemin Vesi Oy, 2011).*

The WWTP of Kemi is located in Peurasaari, one community of Kemi, where the sewage plant was established in 1982 (Figure 6). In 2007, the WWTP was designed to serve of 34 000 person equivalent (p.e). The treatment process of the wastewater is biological-chemical and simultaneous precipitation. The first step of the purification process involves screening to extract the sand, primary clarification, biological aeration and secondary settling basin. The process chart is present in the Annex V. The purified wastewater is discharged into the sea through 400 meters-long discharge pipe. The sludge from the treatment process is dried and dehydrated into centrifuge sludge and transported to Tornio city where the company Perämeren Jätehuolto Oy operates a composting center ( Kemin Vesi Oy, 2013).

The network of Kemi´s WWTP consists in water supply, sewage and storm water drainage as well as the associated pumping plants. For the network work properly it requires maintenance like leak repairs, valve marking and repair of fire hydrants and also the rising the network it is considered. The amount of the leakage in the sewage network is more than 70% in annual average (Hiltula, 2013). The leakage percent is due the mixed rainwater/sewage during the spring time that happening because of the snow melting and is led to bypass.

In 2010, the construction of a network focused on the network-restoration and re-building. The total length of the network in 2011 had 422km, which 199km is of water supply, 161km of sewage and 62km of storm water network (Annex VI). The wastewaters treated at Kemi's are derived from households and industry companies like a slaughterhouse. Wastewaters are conducted to the plant through gravity and pressure sewers. Storm water is collected and piped into watercourses in areas where there is storm water drainage. Stormwater derive from rain and snow melt from the streets, yards, and roofs. While refurbishing the sewage network combined, sewage is normally changed into separate sewerage.

In 2010, the water quality requirements set by the Finnish Environmental Authority was renewed for Kemi to achieve the better water quality of the discharge water. These parameters are quarterly average of the achieved threshold values (Kemin Vesi Oy , 2010), which are the following ones: $BOD_7 \leq 15$ mg/l, Phosphorus $\leq 0.8$mg/l and both parameters with more or equal a 90% of percentage removals. For N removal, there is no removal requirements set until the moment (Kemin Vesi Oy , 2009). In the Table 2, the time line of the WWTP of Kemi is shown.

***Table 2-*** *Time line of Kemi's WWTP.*

| WWTP were built in Peurasaari and started operating | Wastewater treatment Biological-chemical and simultaneous precipitation | Design to serve 34 000 p.e | Qtotal 12 880 $m^3$/d | Renovation of sewage and Implementation of Environmental Permit Authority | Network had a total length of 422km. Sewage 161km, Storm sewer 62km |
|---|---|---|---|---|---|
| **1982** | **1983** | **2007** | **2009** | **2010** | **2011** |

#### *3.1.1.1 Provided Data*

Kemi provided data of the daily discharge from September 2007 to June 2011 and monthly average in the same period for bypass and treated discharge, load and concentration of P, N, and $BOD_7$, temperature of incoming and outgoing water. Further, also bypass and treated concentration of P and N were provided. The water samples were collected once per month for interval 2008-2012 for the following parameters: discharged, incoming and outgoing temperature, concentration of P, N and $BOD_7$.

### 3.1.2 Oulu

***Figure 7****- WWTP view form the top. (Oulun Vesi Oy, 2010).*

Oulun Vesi Oy is the company that takes care of water supply and sewerage in the city of Oulu (Figure 7). The plant was built in 1973 in the district of Taskila and it is used by a total of 150 000 p.e, residential wastewater, and small and medium-sized industrial wastewater, as well as combined sewage storm water areas (Lahdemaki & Lahtinen, 2013). The wastewater comes from the households of three municipalities (Oulu, Muhos and Utajärvi) and from small and medium sized industrial enterprises. The sewage plant started as direct precipitation and in 2004 was introduced as activated sludge treatment plant. Additionally, in 1998 part of the process has become biological filter (Table 3). The present treatment comprises the following steps: screening (sand and grease removal), mixing and flocculation (with polyaluminium chloride), primary settling and reduction of organic matter in a 3 line activated sludge treatment plant and for a secondary settlement it is used a ferric sulphite to remove organic matter and phosphorus and to finalized post-processing bio filter. After the treatment, the purified wastewater is conducted into the Bothnian Bay about 1.6km from the shore (Annex VII).

The plant has also N removal requirements, which were implemented at the time of the construction of new aeration and secondary settling basins in 2008. In the actual process, they use three secondary basins instead of the two previous. Also, it was made the installation of a few aerators and mixers into the two older aeration basins. In order to start N removal in summer months, the sludge retention time was increased and changed the chemical (PAC) dosage in the primary settling. Likewise, it is piped into secondary settling methanol, who acts as carbon source for denitrification (Lahdemaki & Lahtinen, 2013).

The network of WWTP has a leakage in the sewage network in annual average of 35% (Lahdemaki & Lahtinen, 2013). In order to minimizing malfunctions, it is required maintenance of the sewage, which was taken in 2008. In 2010, the water supply and sewer network was about 2 170km (Oulun Vesi Oy, 2010). Environmental permit conditions were implemented in 2008 for the discharge wastewater, which needs to be control before flowing to the Gulf of Bothnia. Overall, the set limits are: $BOD_7$ <15mg$O_2$/l and the purification efficiency of >90%; total phosphorus <0.5mgP/l and the purification efficiency of >90%; Total N≤20mg N/l and the efficiency of purification ≥70% The total N removal is mad just in summertime when the temperature of the wastewater is more than $12^0$C (Oulun Vesi Oy, 2008).

***Table 3*** *Time lime of Oulu´s WWTP*

| Sewer started Operating | Treatment Direct precipitation | Biological filters were built | Sewer from Muhos. | Activated sludge introduced | Length Sewage network 581km | N removal requirement implement Add activated sludge unit and the 2 old modified | Reparation and maintained of the sewer | Municipal sewage treated increase of 1,2 million $m^3$ |
|---|---|---|---|---|---|---|---|---|
| **1902** | **1973** | **1998** | **2002** | **2004** | **2007** | **2008** | **2009** | **2010** |

#### *3.1.2.1 Provided Data*

The operational Oulu laboratories control the analyses, measure water samples of the daily discharge and incoming water temperature. The water samples that were collected correspond to the interval 2008-2012 and it was randomly taken. The parameters N, P and $BOD_7$ were measured twice a month as incoming- and outgoing concentration.

### 3.1.3 Kempele

***Figure 8****- Kempele view from the top (Vesihuolto Oy, 2011).*

The WWTP in Kempele has been running since 1996 (Figure 8). The name of the WWTP is Lakeuden Keskuspuhdistamo and it treats sewage from other five municipalities, which are all located in south of Oulu (Oulunsalo, Liminka, Tyrnävä, Lumijoki and Hailuoto). The plant deals with the sewage of 50 000 p.e (Table 4). The amount of wastewater from Kempele municipality is about 40.9% of the total amount of wastewater treated in that plant (Vesihuolto Oy, 2011). The process in the treatment plant can be divided in two parts. First part the wastewater is treated in ASP and then it ends in a constructed wetland before the discharge point into the sea (Annex VIII). The first part of the process includes screening, primary sedimentation, aeration, intermediate clarification, flocculation, secondary settlement, activated sludge. Treated water is discharged to Peräoja stream from 1 of April to 15 of December and the rest of the year to Kullionoja stream. The trajectory can be seen in Annex IX (Pesala & Roikola, 2013). The old part of the constructed wetland (4.4ha) is used from

December-March and during the rest of the year whole wetland area (total area 17.1ha) is used to polishing the discharged water. The length of sewer network is 179km and in every year about 10.7% of incoming wastewater is leakage water. In 2010, to reduce the losses, it was made replacement of the pipes' system and the maintenance (Vesihuolto Oy, 2011). In table 4, it is possible to observe the works, which have been made in Kempele's WWTP.

The permit conditions for the discharge into the Bothnia Bay are the following ones: $BOD_7 \leq 20mgO_2/l$, phosphorus ≤ 0.5mg /l and the cleaning power of both is at least 95%. Nitrogen set requirements started in 2011 and cannot be more than 20 mg/l and cleaning efficiency at least 70% in June-August (Vesihuolto Oy, 2011).

***Table 4****- Time line of Kempele´s WWTP.*

| WWTP were built Activated sludge Treatment with secondary settling | Add pre-settling | Discharge increased due to sewer from Hailuoto | New post-processing field were introduced. Wetland expansion 4.4ha to 17.1ha | Plant renovation and expansion Biological treatment capacity doubled | Requirements for N removal |
|---|---|---|---|---|---|
| **1996** | **2005** | **2006** | **2009** | **2010** | **2011** |

***3.1.3.1 Provided Data***

The daily discharge was measured frequently during the process and before the discharge wetland point. The N concentration in the wetland was measured once a month in the exact same point of discharge. Quality of the receiving water (Liminganlahti bay) is measured four times a year (in March, June, July, and August). The provided data were the daily discharge from January of 2004 until December 2012. The water samples were collected once a month and analyzed the concentration of the incoming and outgoing P, N, and the temperature of the water.

### 3.1.4 Raahe


***Figure 9*** *Raahen Vesi Oy (Raahen Vesi Oy, 2011).*

In Raahe the WWTP have been introduced in the beginning of 1978 and is located in recent years in Hakotauri (Figure 9). Since 2006, the WWTP has been responsible for 22 500 inhabitants of which only 17 000 are part of the sewage system (Raahen Vesi Oy , 2011). The treatment process is the same since beginning and it is simultaneous biological precipitation. The WWTP is designed for 30 000 p.e and flow rate of 12 500$m^3$/d (Table 5). The processes have screening (sand separation), primary sedimentation, aeration reactor, secondary settling and sludge dryer. (Annex X)

The discharge of treated wastewater is led outside the archipelago of Hakotauri (Figure 9). However, the treatment plant suffer renovations in the sewage as well as screening, sludge drying, aeration and supply pumping stations in 1996-1997. In autumn 2004, a landfill sludge-composting field was built. Summer 2007, the demolition of the old pipe of discharged and replaced with 1 550 meters of a PE pipe sensor ID 800 (Raahen Vesi Oy , 2011). The pipe excavation work led to intermittent water clouding of the site, and in its vicinity. In late of 2007, it was made transmission the sewer from Vihanti to Raahe, which increased the amount of wastewaters about 10-15%. However, since 2009 the wastewater from Vihanti have been piped to Raahe's WWTP and this increased the daily inflow rate about 200-300m$^3$/d. The leakage happens annually in Vihanti area about 70% and in Pattijoki more than 10% of annual wastewater amount (Seppanen, 2013). (Annex XI)

WWTP has set the requirements for the discharge wastewater, which cannot exceed the following limits: $BOD_7$ <15mg$O_2$/l and the purification efficiency >90%; total phosphorus <0.5mgP/l and the purification efficiency >90%. For nitrogen, there are no set limits.

***Table 5****- Time line of Raahe´s WWTP.*

| WWTP were built, Simultaneous biological precipitation | Sewage was renovated | Sludge composting field were built | The decanters chain scraper systems were renewed | WWTP covers 22 500 inhabitants with 30 000p.e. Flow rate 12 5000m$^3$/d | Wastewater from Vihanti piped to Raahe in the end of the year |
|---|---|---|---|---|---|
| **1978** | **1997** | **2004** | **2005** | **2006** | **2007** |

***3.1.4.1. Provided Data***

The provided samples were from the daily discharge from July of 2008 until December of 2012. The incoming and outgoing concentration of phosphorus, nitrogen, $BOD_7$, were provide and analyzed twice per month in the same year period of sampling.

### 3.1.5 Kokkola

Hopeakivenlahti's is the new WWTP in Kokkola, which operated since 2011 and is designed for 30 000 p.e (Figure 10). This new plant has activated sludge process with screening, sand separation, primary settling, aeration, secondary settling and flotation. Next to this new plant, there is a biogas treatment plant, which goes the rejected water and has about 50% of all N load in the plant (Annex XII). The wastewaters, in the old treatment plant were treated as biological-chemical process with


*Figure 10-Wastewater treatment plant in Kokkola. (Jokela, 2013).*

pre settling and aeration in earth basins. All properties connected to the sewage network in Kokkola have septic tanks, which reduce the amount of sludge entered to the plant and can effect on nutrients and C/N ratio of the incoming water (Table 6) (Jokela, 2013).

The discharge will increase 580m$^3$/d when the sewage starts receiving wastewaters from Kälviä and Lohtaja in a near future. All the incoming water comes just from the households of Kokkola. Cleaning requirements in WWTP have come into force in 2012, which are the following ones: $BOD_7$ <10mg$O_2$/l and the purification efficiency of > 95%; total phosphorus < 0.3mgP/l and the purification efficiency of > 95%. For the N removal the target value for the new plant is 70% counted as yearly average and it is a guideline for their process and so processes did not changed (Hopeakivenlahden, 2009).

The process efficiency is also affected by the process temperature, which when is higher than 8°C the N removal can reach 70% in all process and less than 4°C just reach 30%. The leakage of water that happens in the network sewage shows a loss of the flow, which are affected by the low water temperature (minimum 4°C, the annual average of 10°C). This problem affects the ratio of BOD/nitrogen, the biodegradable and inhibiting the biological process.

***Table 6****- Time line of Kokkola´s WWTP.*

| Old plant start operating: Chemical treatment | Biological treatment | Drainage has a total (sewage drains 203 km, rainstorm 113 km). Biological-chemical process with pre settling and aeration in earth basins | Sewage incoming 1250m$^3$ wastewater | New WWTP start (Hopeakivenlahti) Activated sludge process | Implementations of Operating conditions |
|---|---|---|---|---|---|
| **1972** | **1976** | **2001** | **2009** | **2011** | **2012** |

### *3.1.5.1 Provided Data*

In Kokkola's WWTP the discharge and temperature were measured daily and the provided period was 2006-2012. The water samples provided were monthly measures which are made twice a month for incoming and outgoing concentrations of P, N and $BOD_7$.

### 3.1.6 Pietarsaari

***Figure 11** Pietarsaari ´s WWTP coastal view (Pietarsaaren edustan, 2005).*

The first WWTP in Pietarsaari was in Ebba Brahe park in 1936 and it was the first activated sludge treatment plants in Finland. Nowadays, the new plant is in Alheda and has been in operation since 1976 (Figure 11). The new plant was designed for a population equivalent of 36 000 and the process is mechanical, chemical and biological treatment and includes screening, sand separation, aeration, clarification, flocculation and flotation. The sludge is thickened and drying in a centrifuge machine (Annex XIII). The dried sludge is exported for further processing in Kokkola since 2012 where it is used in the biogas plant. The purified wastewater is discharged to the coast of the Gulf of Bothnia. In 1996, the wastewater connection from Uusikaarlepyy started to be piped and the discharge increased 300 000$m^3$/d Annex XIV (Table 7).

The old sewage network wasn't working in good condition and so that the annual average of leakage was about 28% in 2003 (Pietarsaaren edustan, 2005). The problems of mixed sewage with stormwater lead every year a 30-40% of leaking (Kaksonen, 2013). Heavy rains during the snowmelting exceeded the sewer capacity, which in turn lead to basement flooding in certain properties. Also industrial wastewaters are coming to the WWTP from the local food processing industry, a dairy and a couple of factories that produce fodder for fur animals are treated at the plant (Pietarsaaren edustan, 2005). Nowadays the sewage network has a length of 187km.

Implementation of the purification requirements was set in 2005 and it was in concordance of the Environmental Authority. (Pietarsaaren edustan, 2005). The set limits are the following ones: $BOD_7$<10mg$O_2$/l and the purification efficiency of > 95%; total phosphorus < 0.3mgP/l and the purification efficiency of >95%. Starting from 2010 target value of N treatment efficiency is at least 60% counted as annual average. This value is only a guideline for controlling the process and does not have to be reached.

***Table 7****- Time line of Pietarsaari´s WWTP.*

| WWTP in Alheda. Mechanical, chemical and biological treatment | Wastewater from Uusikaarkepyy start been piped Discharge increased 300 000 $m^3$/d | WWTP received annually about 3-4 million $m^3$ | Operating standards According water services act | Sewage renovated Length of sewage network 187km. Received 2,9 million $m^3$ of waste water | Rate 36 000 p.e | Requiremen ts for Operating condition | Length of the sewage network 208 km |
|---|---|---|---|---|---|---|---|
| **1979** | **1996** | **2000** | **2001** | **2003** | **2005** | **2010** | **2011** |

***4.1.5.1. Provided Data***

WWTP provided the daily discharged from January 2003 until the end of 2012 and incoming and outgoing temperature, the same period, of couple of days. The water samples are taken once per month, however some of the days were not provided and therefore it was done an average between the intervals. The water samples that were performed were the following ones: incoming and outgoing phosphorus and nitrogen concentration.

## 3.2 Nitrogen load Modeling

The modeling methodology was made in order to predict the N outgoing load that is discharged from the WWTP to Bothnian bay. To create the model, it was used mathematical equations developed for water quality modeling by Steven C. Chapra. The reaction of the process was considered as continuously stirred tank reactor (CSTR). The modeling techniques included computer simulation and fitting process by Matlab program (Haimo et al. , 2009).

The N load modeling developed was based on collected data of the main parameter, which were discharge and outflow N concentrations of WWTPs. The first step was organizing and compiling all information in Excel and then study the type of load for each WWTP. Following step was the implementation of the files into Matlab and an exhaustive study of the load functions and last fitting process. The types of the loads found were sinusoidal, linear and constant. Subsequent, is present each one of the load functions and in Annex XV are describe all the Matlab codes. Attempts were also made using the Fourier equation, although the square of the correlation between the response values and the predicted response values were always low not reaching a successful fit. So for that, here is not presented the results of the Fourier equation used in the fit process.

### 3.2.1 Load functions

#### *3.2.1.1 Sinusoidal*

The sinusoidal mathematical function developed by *Steve Chapra*, described a pattern in the evolution of the load in function of time. (Chapra , 1997) The function can be represented mathematically as*:*

***Equation 4 -*** *Sinusoidal function.*

$$W(t) = \bar{W} + W_a * \sin(\omega * t - \theta)$$

Where $\bar{W}$ is mean loading, the mean value for the sine wave, $W_a$ amplitude of the loading, how high the oscillation swings vertically, Θ phase shift, how much the function is shifted horizontally relative to the standard sine wave and ω angular frequency of the oscillation, how frequently the sine wave oscillates. In the studied the $\bar{W}$ and $W_a$ are nitrogen load that goes during number of days represent by the letter *t.* (Chapra , 1997).

#### *3.2.1.2 Linear*

A linear function is defined by a polynomial function of degree one in which the relationship between the independent variable x and the dependent variable y is modeled as a first order polynomial and has the form W (t) = m*t + b. In this case, the variable is the time and the value of the function is the load W (t). The graph of a linear function set of all points with coordinates, which form is (t, W (t)) and is a non-vertical line. The slope-intercept form of a linear equation is an equation with two coefficients *m* and *b* (Chapra , 1997).

***Equation 5****- Linear load function.*

$$W(t) = m * t + b$$

In (5) the *m* means the slope of N load and b is a constant where N load slope started.

#### *3.2.1.3 Constant*

A constant function in mathematics language is a function whose values do not vary and thus are constant all over the independent variable *t*. In Eq. 6 the variable *t* means time and the $\bar{W}$ the mean N loading N through time.

***Equation 6*** *-Constant function.*

$$W(t) = \bar{W}$$

### 3.2.2 Fitting process

After the implementation of the load functions, it is need to do a fitting process of the equations. With *Fitting Data* in *Matlab Toolbox Functions,* it was found the statistical parameters to evaluate and described the relationship between predictor and response variables. Goodness of Fit process is given by the following parameters: sum of squares due to error (SSE), r-square ($R^2$), adjusted r-square (Adjusted $R^2$), root mean squared error (RMSE), which each one have different meanings. Good interpretation leads to a right conclusions, in the following are described the meaning of those parameters:

- SSE- measures the total deviation of the response values from the fit to the response values. A value closer to 0 indicates that the model has a smaller random error component, and that the fit will be more useful for prediction (Matlab, 2013).
- $R^2$- measures how successful the fit is in explaining the variation of the data. In another way, $R^2$ is the square of the correlation between the response values and the predicted response values. $R^2$ and can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of variance is accounted by the model (Matlab, 2013).
- Adjusted $R^2$-is generally the best indicator of the fit quality when compare two models that are nested that is, a series of models each of which adds additional coefficients to the previous model. The adjusted $R^2$ can take on any value less than or equal to 1, with a value closer to 1 indicating a better fit. Negative values can occur when the model contains terms that do not help to predict the response (Matlab, 2013).
- RMSE- is known as the fit standard error and the standard error of the regression. It is an estimate of the standard deviation of the random component in the data, and is defined as where MSE is the mean square error or the residual mean square. Just as with SSE, an MSE value closer to 0 indicates a fit that is more useful for prediction (Matlab, 2013).

All the fitting have 95% confidence bounds and the statistical inferences were calculated using algorithm Levenberg-Marquardt with bisquare robusty. Once a regression model has been fitted to the group of data, examination of the residuals allows to investigate the validity of the relationship. Plotting and analyzing residuals is a way to quantify the difference between the values implied by the prediction method and the true values. Residual bars are differences between the one-step-predicted output from the model and the measured output from the validation data set. The residuals from a fitted model are defined as the differences between the response data and the fit to the response data at each predictor value. Mathematically, the residual for a specific predictor value is the difference between the response value y and the predicted response value $\hat{y}$. $r = y - \hat{y}$.

However, the fit model also creates random errors. Therefore, if the residuals appear to behave randomly, it suggests that the model fits the data well. Nonetheless, if the residuals display a systematic pattern, it is a clear sign that the model fits the data poorly (Matlab, 2013).

# 4. Results and Discussion

The models developed were based on collected nitrogen data to predict the outgoing N load in the future. The results are going to be useful to study of the impact of wastewaters in the coastal area of Bothnian Bay in the next phases of the project "Waste water and nitrogen in the Bothnian Bay coastal waters". The results of the modeling process are given to each WWTP and they shall be presented in the following subchapters.

## 4.1 Results

### 4.1.1 Kemi

The WWTP of Kemi, as said before, is a process combining with biological and chemical treatment with simultaneous precipitation. The purified wastewater (WW) is discharged into the sea through a pipe about 400 meters-long. The daily discharge during September 2007 until June 2011 have varied from 4 298m$^3$/d up to 29 001m$^3$/d and had an average of 9 091m$^3$/d (Figure 12). The annual variation of the discharge was similar in the different years, with high peaks during the spring seasons (from March to May) and low in wintertime (from December to February). The variations of the flow are the same in Finland due the weather, in winter it is covered with snow and when spring arrives the snow starts melting and brings a vast volume of water. The runoff waters enter in huge amounts into the pipes systems and the peaks appear in the registers. In the year of 2010, the sewage was renovated and that increased the average annual discharge in 300-500m$^3$/d.

In this study just the N, P, $BOD_7$ load, discharge and incoming temperature were case of discussion. The provided sample period was 2008-2012, having an average discharge of 9 297m$^3$/d, which was not too far from the average quoted interval in 2007-2011 (9 091m$^3$/d). The results for the water sampling in average for 2008-2012 are presented in following percentage removal: 92% $BOD_7$, 95% P, and 14% N for the period of studied and 8°C of incoming temperature.

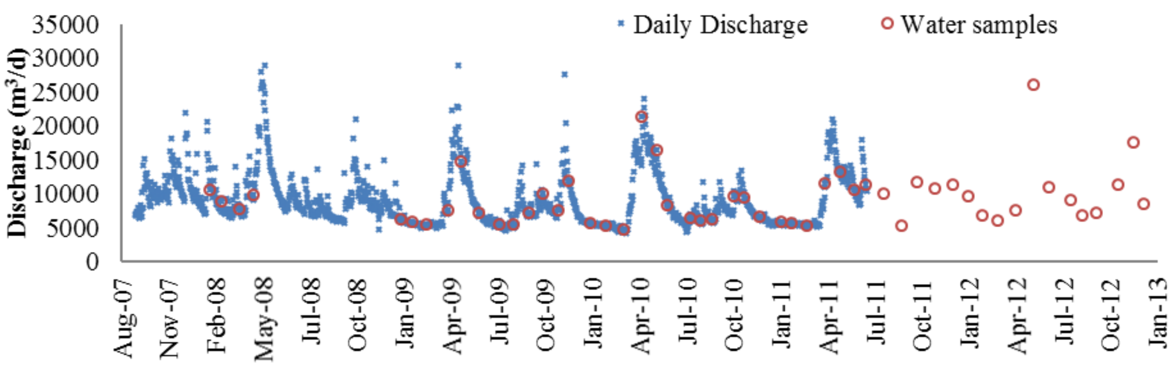



***Figure 12***- *Daily discharge measured continuously in Kemi WWTP during the interval 2007-2011and water sampling days for nutrient analysis during the years 2008-2012.*

***Lucinda Matos***

The bypass and treated discharged are represented in Figure 13 for the years 2000-2010. The amount of bypass varied between 9m$^3$/d and 3 038m$^3$/d and it occurred typically in spring time. Bypass occurs because of the inflow of the sewage and excess water that exceed the design capacity of the treatment plant (Watershed Group, 2009). Therefore, in the spring flood the treatment plant was inundated with extremely high volumes of water from snowmelt or rain. In 2009 there was no register of bypass. Also, the mean N load for treated WW has an average of 252.25kg/d while for the N load for bypassed WW was an average of 1.75kg/d in the years 2000-2010. The N load caused by bypassed WW was small and can be assumed to be negligible when total N load from WWTP are estimated. Generally, the bypasses caused by heavy rain or snow melt causes less risk to the river to which it is discharged, than in dry weather bypasses because the sewage is diluted due to the higher flows (Watersheds Group, 2009).

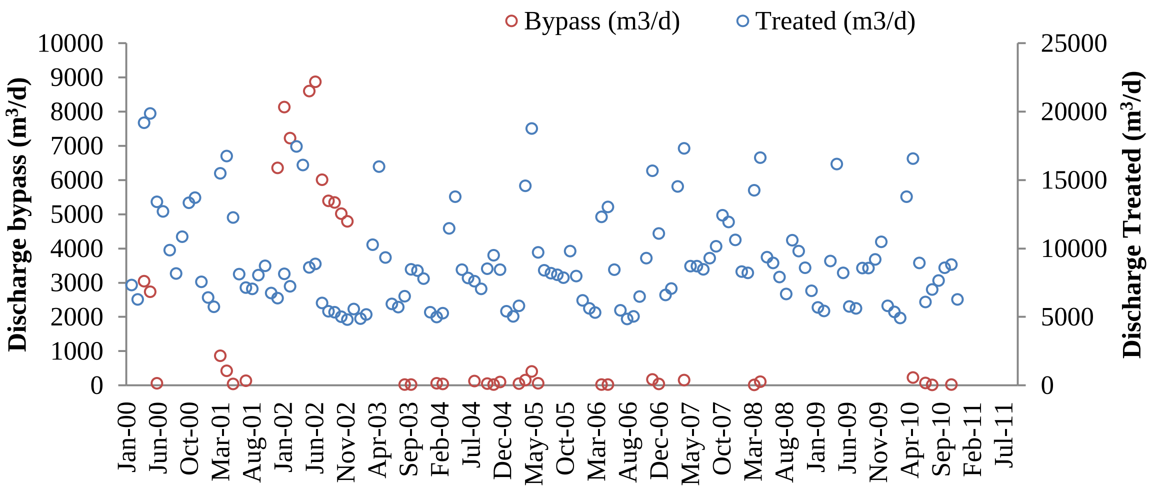



***Figure 13*** *Treated average monthly discharge and bypass for 2000-2010.*

In Figure 14 it can be seen the study of N load for the sample period and it seems to be constant and not having a pattern. However, there are three high peaks with normal discharge and no bypass, which happened in the following dates: November 2008 (423kg/d), April 2010 (407 kg/d), and August 2011 (423kg/d), which could be measurement errors. The percentage of N removal has been increasing for over the years rising from 11% in 2008 to 16% in 2012 and in average 14%. In 2010, it reached the highest percentage (20%), however in 2011 the lowest N removal efficiency (10%) was observed. Explanation can be found because the discharge in 2011 was 11% higher than the previous year, and in both years (2010 and 2011) the N outgoing concentration was the same with 32mg/l.

The N load was usually higher in the months of April/May, when also the discharge was high, and it leads to a lower percentage removal of N. In those three critical peaks, the registered N outgoing concentrations were 27, 19, 42mg/l respectively. Nonetheless, in these days the percentage of N removal was lower than the closest months. In August 2011, percentage removal were negative about (-56%), which indicate to a measurements errors. During the cold months the N removal has the lowest results. Information about the average N bypassed, shows that all over the years, from 2000 to 2010, the N bypassed have been decreasing from 9.21kg/d to 0.614kg/d. In 2009 it was not detected of N bypass and this resulted in a better efficiency of the process. In this WWTP, the behaviour of the N load is continuous and with an average of 256kg/d.

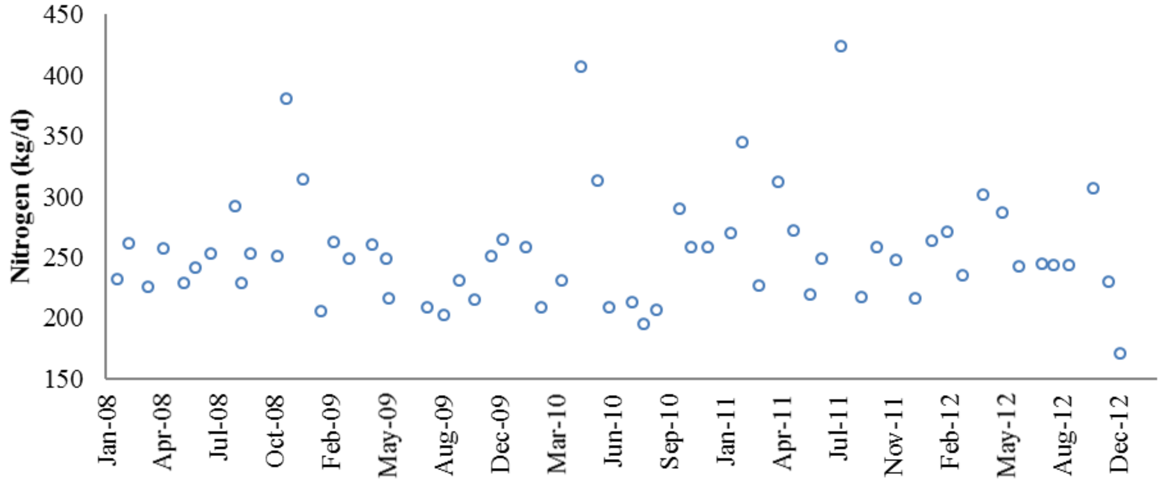



***Figure 14***-- *Nitrogen load from the WWTP of Kemi in 2008-2012.*

Generally, discharge can be used to estimate N load of the wastewaters (Chapra et. all, 1983). However, any relationship was found by regression analysis between Q and N for Kemi WWTP ($R^2$ =0.173). Also, there is no relation between N load and the temperature ($R^2$ =0.0376). (Figure 15) In the cold countries the temperature of the incoming water may change rapidly as a result of rain (E-WAter, 2010).

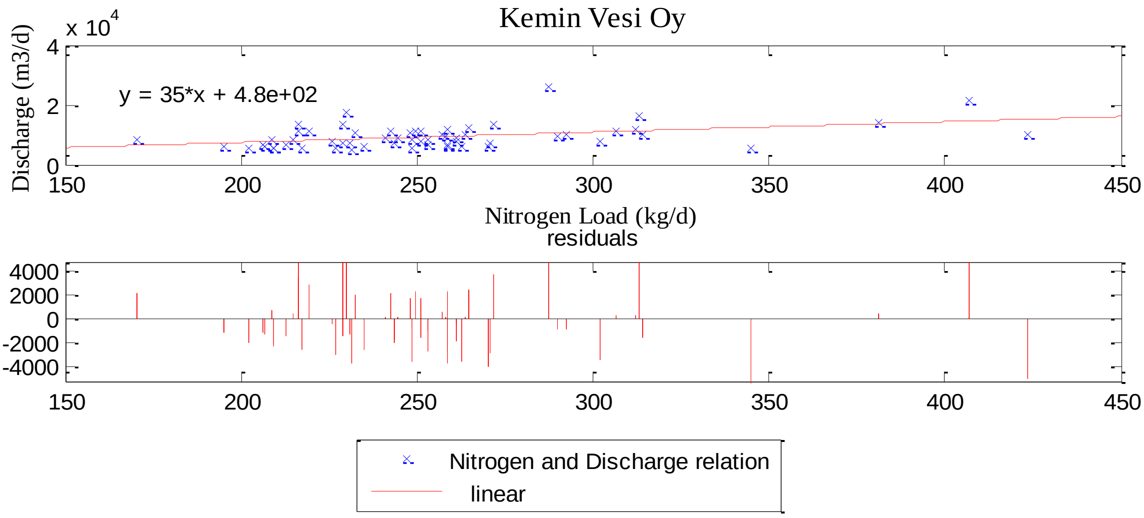



***Figure 15**- Linear regression analysis between discharge and N load of Kemi WWTP. Date from 2008-2012.*

The N removal efficiency over this period of time (2008-2012) had average of 15%, which means a low percentage of N removal. However, this plant does not have any N removal process so this fact comes to confirm, if they might introduce the requirements proposed by Finnish environmental authorities, they could be successful. According to Figure 16 the temperature of the inlet water was lower than 12°C. When the temperature exceed those 12°C the N percentage removal was more efficient. To reduce the N transporting to the coastal areas, an important task is to achieve high N removal during the colder period (Bastviken, 2006). The activity of N transforming processes is slower in cold temperatures, and thus the hydraulic load must be lower during winter to achieve the same percentage N removal as in summer. Nevertheless, studies have shown that on an annual basis the area-specific nitrate removal, expressed as kg/ha.y, is higher at higher loads of nitrate (in kg/ha.y), also in colder climate (Fleischer et al., 1994).

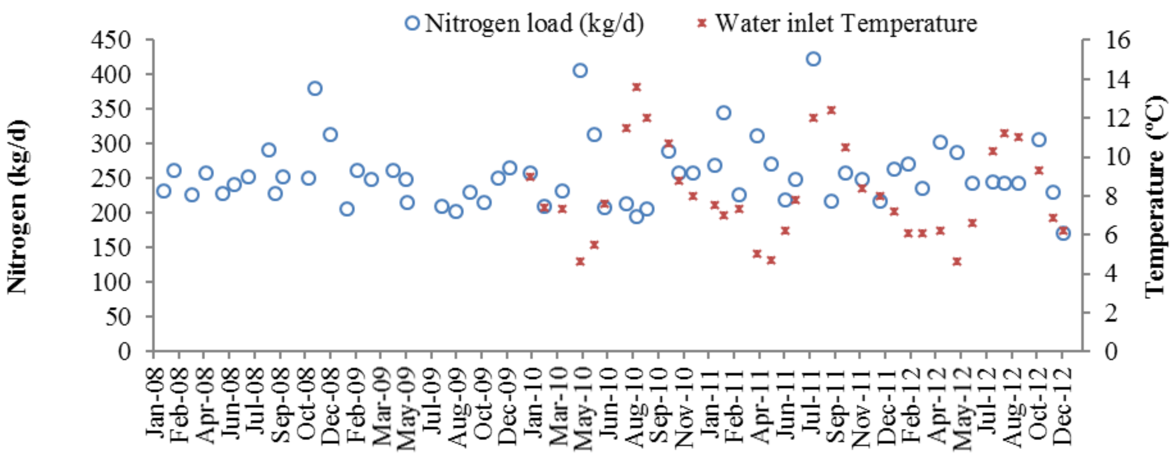



***Figure 16**-Water inlet temperature and N outgoing load in Kemi WWTP in 2008-2012*

### 4.1.2 Oulu

WWTP in Oulu uses direct chemical precipitation, active sludge and post-filtration to treat the water. The plant receives water from the households of Oulu, Muhos, Utajärvi and from small and medium industrial enterprises.(Annex XIV) During the years 2005-2012, the daily discharge varied from 39 000m$^3$/d to 51 052m$^3$/d being 42 028m$^3$/d in average (Figure 17). In 2004, the sewer from Utajärvi was built, which increased temporarily the annual average discharge around 600 000-700 000m$^3$/y in 2005. After the reparation of sewer the annual average discharge decreased slightly because maintenance works in the network. The variation of the flow in all years had the same pattern, the highest flow occurred during snow melt in spring due the amount of the water that come into the sewer and in winter the flow was lower.

For the interval of 2005-2012, the annual average of $BOD_7$ was 67.7kg/d, P 10.4kg/d and N 14 34.6 kg/d. The removal percentages were 97%, 97% and 40% respectively. This results show that the municipal sewage in Oulu is doing effective treatments. The concentration of P outgoing increased a little bit, passing from an average of 6.7mg/l in the previous year to 9.1mg/l in 2011 and being 23mg/l in 2012. This P concentration was higher than 0.5mg/l although, the amount of P that enters to the WWTP was high and so the efficiency was good enough to accomplish the 90%. As noticed, in spring the concentration of P and N were lower than in the rest of the year, which is a good thing to minimize the eutrophication problem. Also, the amount of $BOD_7$ concentration, which represents the water quality, was always in conformity with the requirements, lower than 15mg/l.

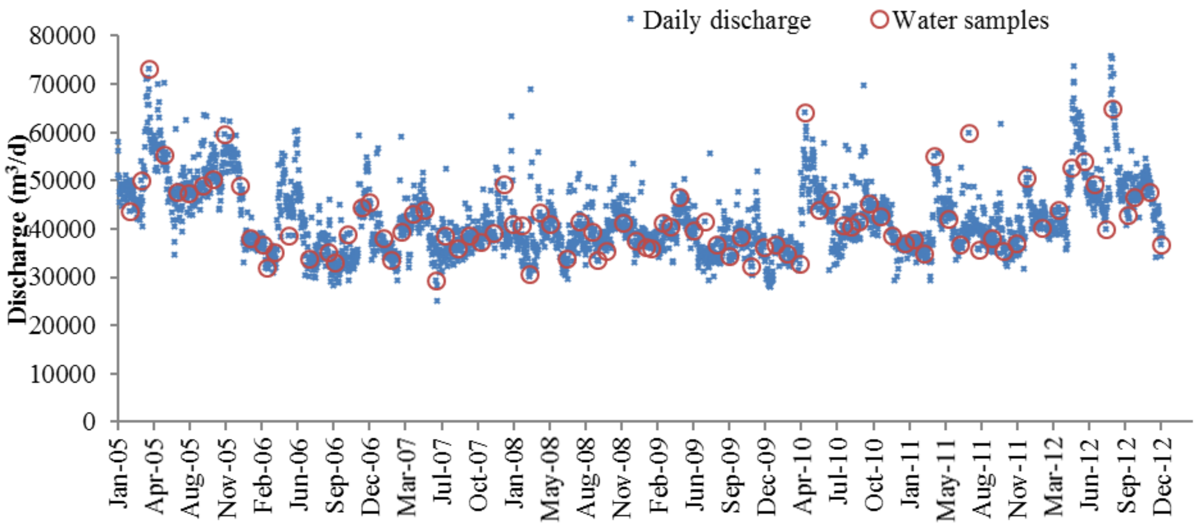



***Figure 17**- Daily discharge in Oulu WWTP during 2005-2012*

As mentioned in Oulu´s WWTP, the N removal implemented by the end of 2008, as consequence the removal of N increased, changing from 27% in 2008 to 31% in 2009. The percentage of N removal is related with the discharge, when the discharge increase the N removal is higher and so the N load is also lower. Before the renovations of the treatment plant in 2008, the N load had a different pattern, changing from constant to sinusoidal as it is possible to understand in the following graphic (Figure 18). To have a clear vision of the behavior of the load it was made a more detailed study, which focuses in the range of 2005-2007 and 2008-2012.

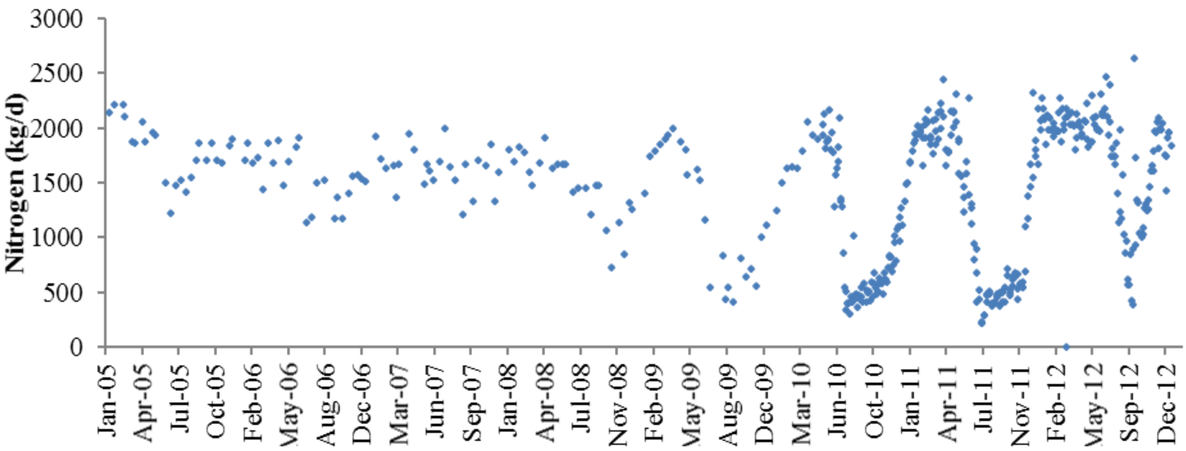



***Figure 18****- Nitrogen load from Oulu WWTP during 2005-2012.*

The constant N load before 2008 ranged from 1 559.6kg/d to 1 799.6kg/d (the average was 1 665kg/d) (Figure 19). The N load was always lower in summer months and higher in spring. This fact was related with the discharge, in spring it is always higher due snow melting and the load that goes to the sea is higher, and in summer is lower (Figure 19). In 2007, the N removal process was not working yet and even then, the percentage of N removal had an average of 28%.

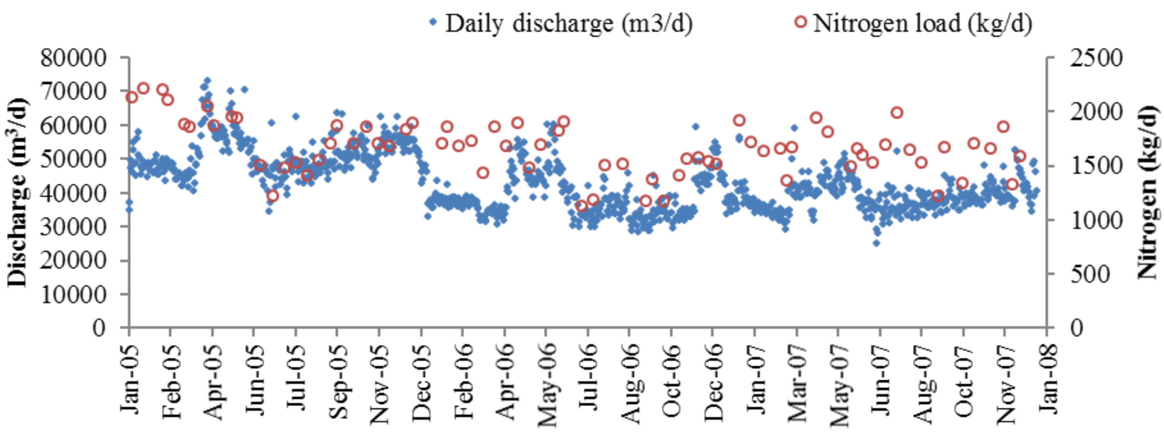



***Figure 19*** *Daily discharge and the Nitrogen load from 2005-2007 in Oulu WWTP.*

The subsequent study of N load showed a different behavior during the interval 2008-2012 as being a sinusoidal pattern (Figure 20). The importance of improvements in the treatment is present in the results of the percentage N removal, which went from 28%, in the previous period 2005-2007, and increase for an annual average of 42% in 2008-2012. This also brought a lower N load into the sea that comes from 1 635kg/d in 2007 to 1 469kg/d in 2008. Nevertheless, in 2008 the discharge was different from the others years, being inconstant and having a range of 29 679m$^3$/d and 69 053m$^3$/d and an average of 39 447m$^3$/d. This year was different, because of the renovation and for that the oscillation of the discharge was an unusual situation. (Figure 20) In the end of 2008, the discharge variation back to normal standard, increasing in spring time due the snow melting and the rain season.

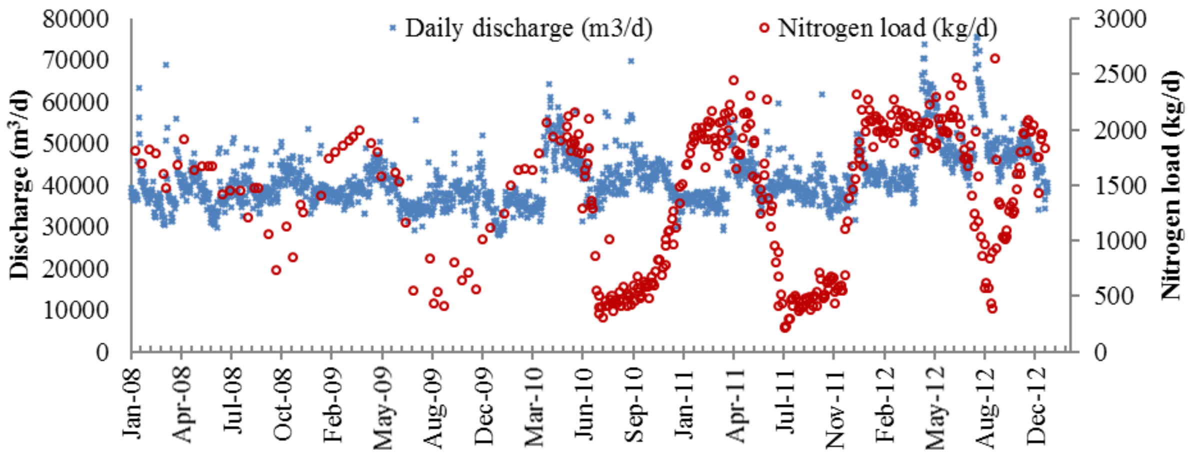
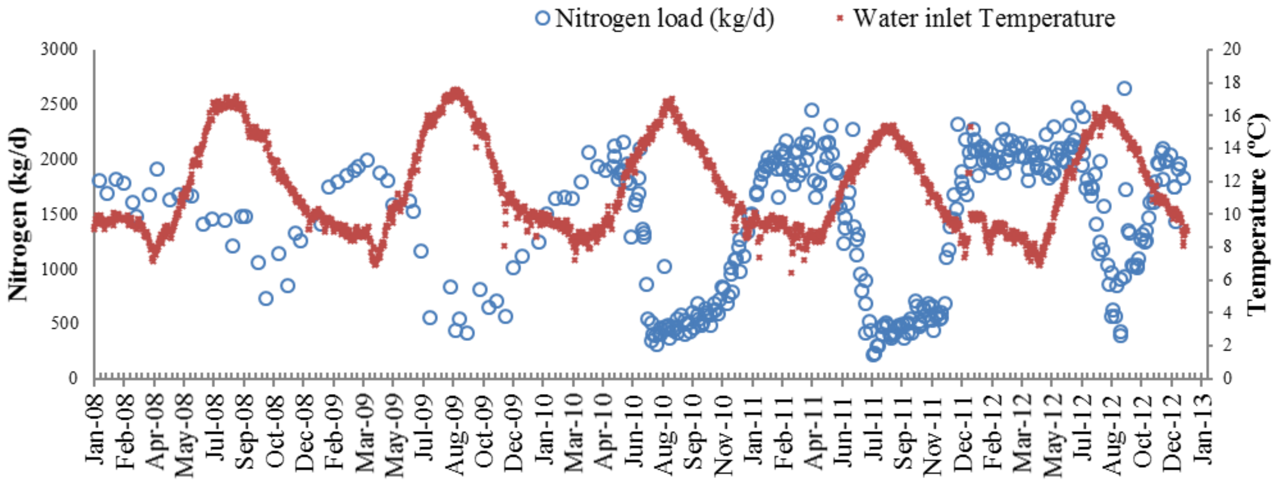



***Figure 20*** *Daily discharge and N load for the interval 2008-2012 in Oulu WWTP.*

The N outgoing load followed a similar pattern, which in the months of March/April/May the load was high (reaching the maximum in March 2012) and in August/September/October is low (reaching the lowest in August 2012). This is also related with the efficiency of the N removal that is higher when the load is low being always between 46% and 81%. In spring the wastewater contain high levels of P and N and that cause several problems, and it is therefore necessary to remove such substances from wastewaters in order to reduce their harm to the environment.

The temperature of the incoming water, affect the N removal as it is possible to observe in the graphic below (Figure 21). In Oulu WWTP, the N removal is working in summer months when the process temperature is over 12°C (Oulun Vesi Oy, 2008). In some of the years, when the incoming water temperature reach the maximum (16°C) the N removal efficiency is higher reaching at 80%. Every time that temperature overcomes 12°C the N removal efficiency is more than 20%. This question, confirms that for the process to be more efficient, the incoming water temperature should be controlled, however it just depend on the ambient temperature.




*Fi**gure 21** -Water inlet Temperature and Nitrogen load in Oulu WWTP in 2008-2012*

The model predictions for the N load in the years 2008-2012 obtained good results. (Figure 22). The success of the fitting was good ($R^2$=0.6805) and also the quality (Adjusted R-square=0. 6779). Although, the total deviation of the response values from the fit to the response values have a random error (SSE=5.004$e^7$) and a standard error of the regression (RMSE=363. 4) The residuals bars show the differences between the response data and the fit to the response data at each predictor value and in this study the bars are randomly distributed which suggest that the model fits to the data.

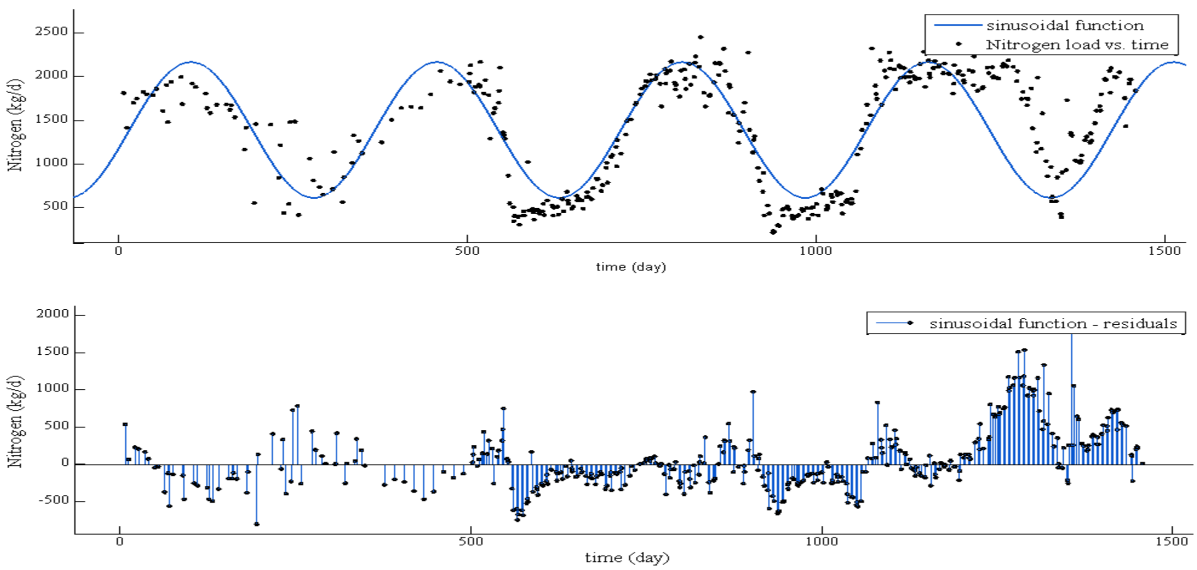



***Figure 22** Fitting process of Nitrogen load in Oulu WWTP 2008-2012.*

The representation of the trend of the N load from Oulu WWTP will follow the sinusoidal evolution, which will be represented in the equation 7.

***Equation 7****-Sinusoidal equation for the nitrogen load in Oulu during the studied period of 2008-2012.*

$$W(t) = 1386 + 774.4 * \sin(0.01788 * t - 12.86)$$

The coefficients of the model are the mean load ( $\overline{W}$), amplitude of the loading ($W_a$), angular frequency (ω) and phase shift (θ). Each one can vary between a range: $\overline{W}$ -[(1349, 1423)], $W_a$ -[721.7, 827], and ω-[0.01771, 0.01805] and θ- [12.69, 13.02].

### 4.1.3 Kempele

Treatment process of Kempele´s WWTP was different from the others plants due the wetland as final treatment. During the years 2004-2012, the daily discharge oscillated between 2 644$m^3$/d and 10 772$m^3$/d (Figure 23). Those variations were following a pattern, which increase the discharge in spring and afterwards decrease. The high discharge can be explained by snow melting as in the other WWTPs. In 2006, the discharge increased due the sewer that started coming from Hailuoto (Figure 23).

The results of the treatments were good and fulfilled the conditions of the permissions except for N. The requirements for N removal started in 2011 and just for the months June to August. During those months the outgoing N concentration should be under 20mg/l and removal efficiency over 70%. For the interval 2008-2012, the annual average of load was for P an average of 0.52kg/d, $BOD_7$ of 18.5kg/d and N 230.21kg/d. The reduction was 31%, 99%, 99% for N, P and $BOD_7$ respectively. After the implementation of the N requirements in 2011, the monthly concentration of N increased in the referred months and also the annual average.

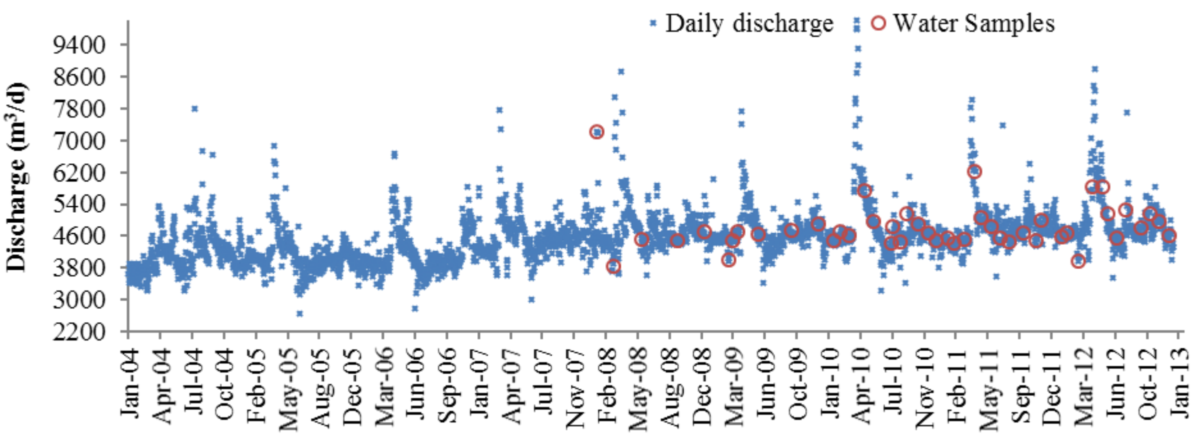



***Figure 23****- Daily discharge in Kempele WWTP and water samples*

The N concentration is measured in the point of discharge of the wetland once a month. Observing the Figure 24 the load seems to have a sinusoidal patter that varies between 182kg/d and 562kg/d. In some of the months there are no data due to lack of samplings. In the years 2008 and 2009 the N load is not enough to understand the behaviour so for that reason, it was chosen just focus the study starting in 2010 and ending in 2012.

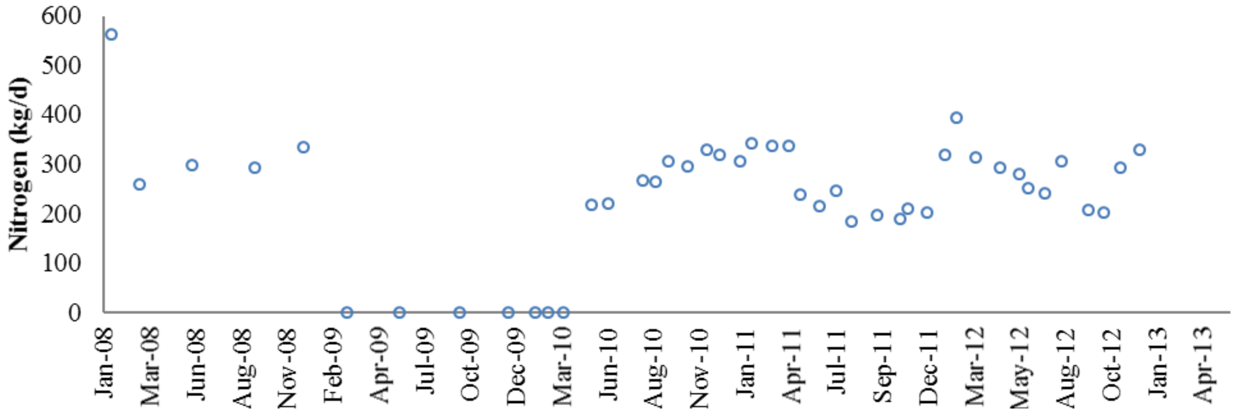



***Figure 24****- Nitrogen load from Kempele WWTP in the years 2008-2012.*

Sinusoidal curve fitting showed that the modeling process had an acceptable success ($R^2$=0. 4896) and also a reasonable quality (Adjusted $R^2$=0. 4349). The deviation of the total response has a random error (SSE=4.8831e$^4$) and a standard error of the regression (RMSE=41.76) which that means that the fit was good (Figure 25). The residuals bars were also randomly distributed, meaning that the model can be used to predict the N load.

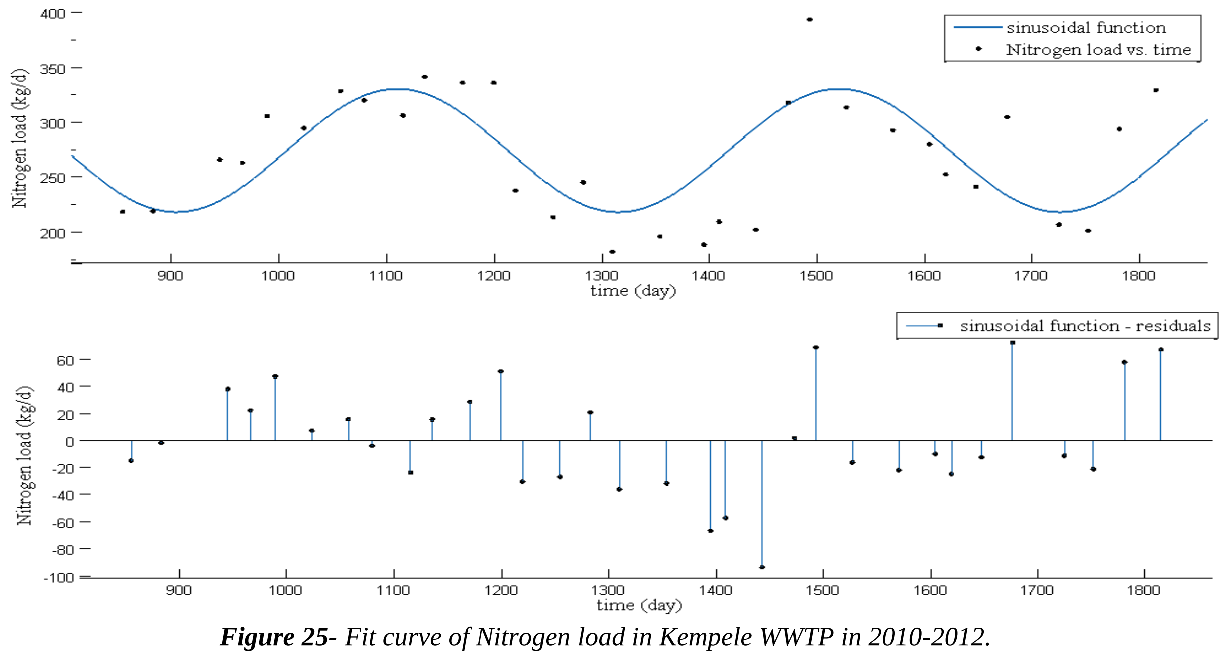



***Figure 25****- Fit curve of Nitrogen load in Kempele WWTP in 2010-2012.*

The results of the process in the wetland are related to the type of the vegetation that can affect the nitrifying and denitrifying bacteria (Bastviken, 2006). The annual N efficiency removal after 2011 decreased changing from 38% to 29%. It is not possible to observe the N removal in the summer months because Kempele's WWTP did not provide the monthly average N incoming to be possible to calculate the percentage removal.

The trend of the N load from Kempele WWTP followed the sinusoidal function, which will be represented in equation 8:

***Equation 8**- Sinusoidal equation for the nitrogen load in Kempele during the studied period of 200-2012.*

$$W(t) = 273.9 + 55.9 * \sin(0.01534 * t - 9165)$$

The coefficients of the model are the mean load, amplitude of the loading, angular frequency and phase shift.  Each one can vary between a range: $\overline{W}$ [(258.6; 289.2)], $W_a$ [33.7; 78.11], ω [0.01398; 0.0167] and Ɵ [7.289; 11.04].

The N removal was related with water inlet temperature which was higher during the summer and lower in winter. For Kempele's WWTP the mean temperature was 6.9°C, but can varied from 0°C to 22°C (Figure 26). When the temperature was high, the N load was lower which means a higher percentage of removal nitrogen. However, it is not possible to compare the monthly temperature with monthly N removal, due to lack of incoming N is not possible to check the N percentage removal. Therefore, is not possible to calculate the monthly percentage removal and compare with monthly temperature.

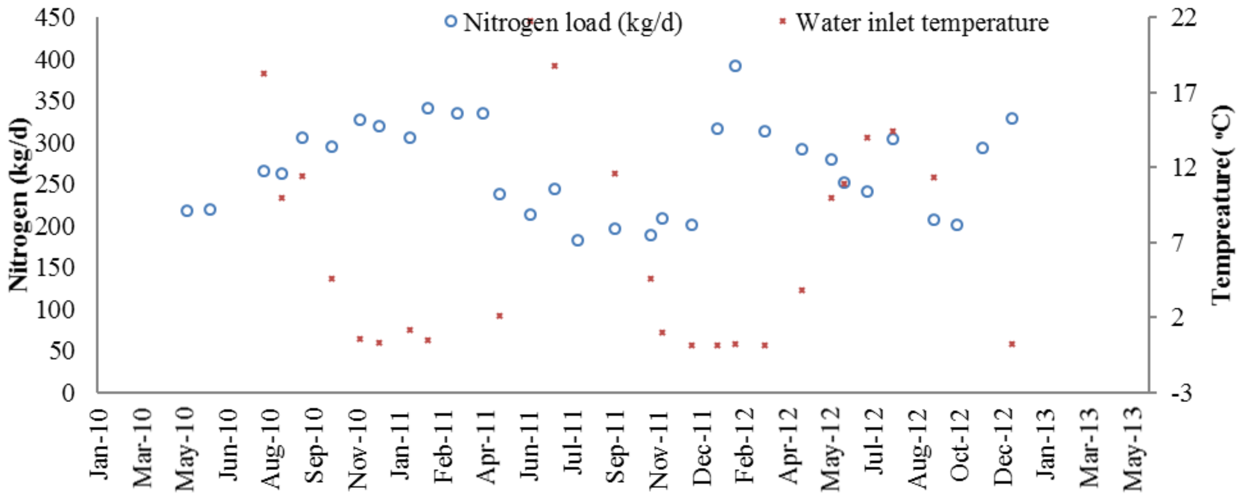



***Figure 26** Water inlet temperature and Nitrogen load in Kempele WWT.*

### 4.1.4 Raahe

In Raahe´s WWTP, the average daily discharge was 4 981m$^3$/d from July of 2008 until the end of 2012, which had a range from 3 129m$^3$/d to 39 440m$^3$/d. The variation of the discharge follows the same normal pattern as the other plants. In spring increases due the snow melting and rain, then back to constant flow (Figure 27). The annual average discharge increased about 200m$^3$/d every year and this was due to the wastewater in 2007 started coming from Vihanti to Raahe.

WWTP in Raahe has permit regulation just for $BOD_7$ and P removal and for those the limit need to be at least 90%. For the studied period, the annual average of $BOD_7$ load was 36.6 kg/d, P was 1.5kg/d and N 199.6kg/d. The removal percentages of $BOD_7$, P and N were 96%, 96% and 21% respectively. These results showed that the set out requirements are being met accomplished. The control parameters were measured in the samples taken, which was randomly distributed during the years 2008- 2012 (Figure 27).

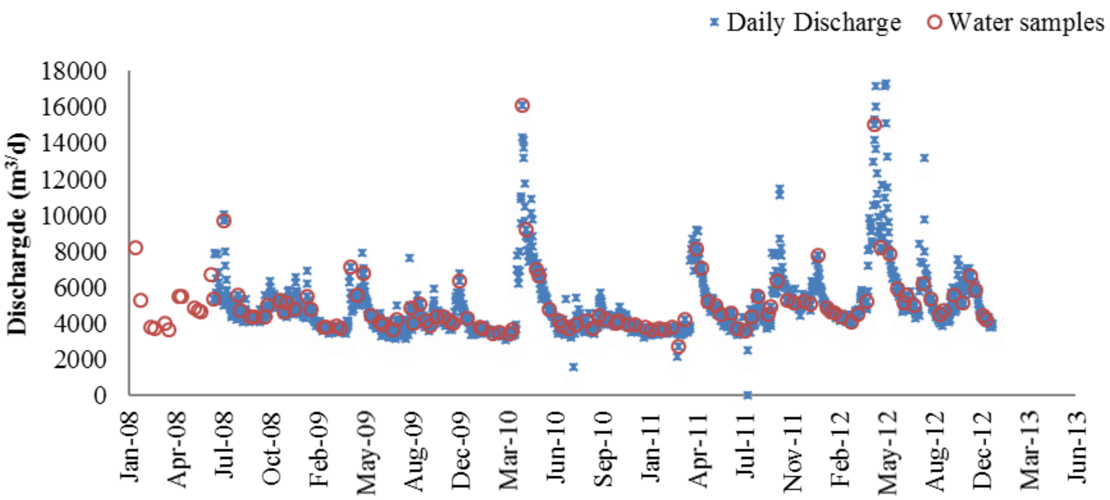



***Figure 27*** *Daily discharge and water samples in Raahe WWTP*

The successive study of N load demonstrated a linear behaviour during the interval 2008-2010 and then a continuous load in 2011-2012. (Figure 28) The linear model of the study, in the period 2008-2010, follow this relation presented in equation 9 and $R^2$=0.4264 with adjusted $R^2$=0.4095. The total deviation of the response values from the fit to the response values have a random error of (SSE=5946) and a standard error of the regression (RMSE= 13.2243) (Figure 28).

***Equation 9****-Linear equation of nitrogen load in Raahe for the studied period of 2008-2010.*

$$W(t) = 11.335*t+193.6$$

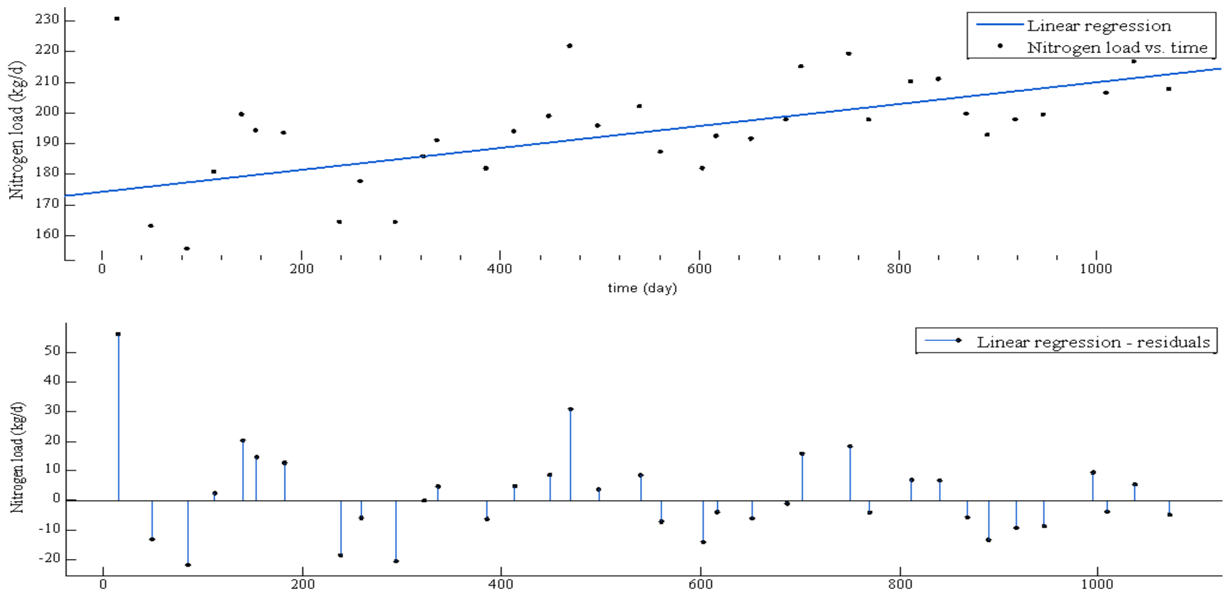



***Figure 28***- *Fitting process of N load in Raahe WWTP in the period of 2008-2010.*

As indicated, the N load increase with the time in a linear relation. The coefficients of the linear equation have a range of m (6.786; 15.87) and b (189.2; 198.1). For the next study period from 2011 to 2012, the N load had a continues evolution as it was verified (Figure 29). Although, to exclude any doubts, sinusoidal fitting gave only poor results ($R^2$=0.0855), weak quality (adjusted $R^2$= -0.05166), a random error of (SSE=1.104$e^4$) and a standard error of the regression (RMSE= 23.49). The results show that the best way to describe the N load was to use the constant load function. Therefore, if the process does not change or the incoming nitrogen load does not increase in the future the N outgoing load will be always around the median value which was 209kg/d and with 21% of N removal.

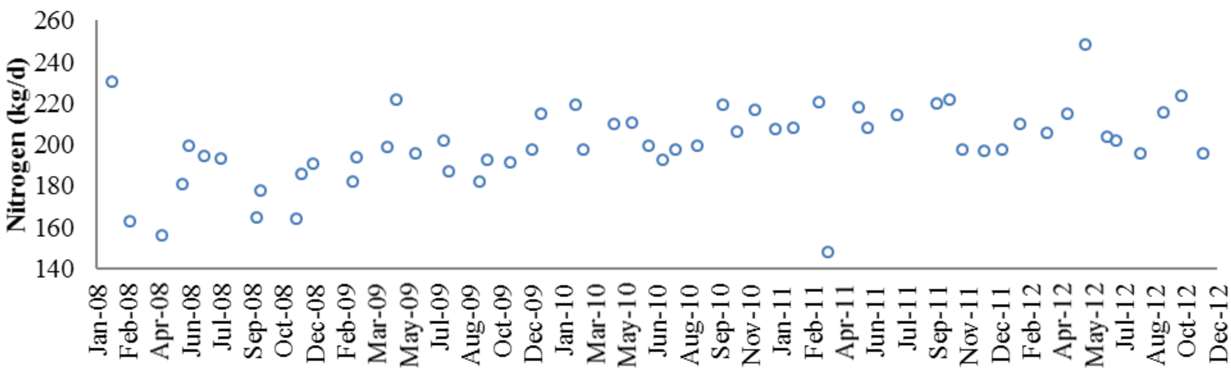



***Figure 29*** *Nitrogen load in Raahe WWTP for period 2008-2012.*

In Raahe WWTP, the inlet water temperature did not varied so much than in the other plants. The average temperature was 7°C for the studied period, reaching a maximum of 11°C in summer and a minimum of 3°C in winter. With this information, it is not possible to see the relation between temperature and the percentage removal (Figure 30). Although, when the temperature was 12°C the percentage removal was also high being around 20%.

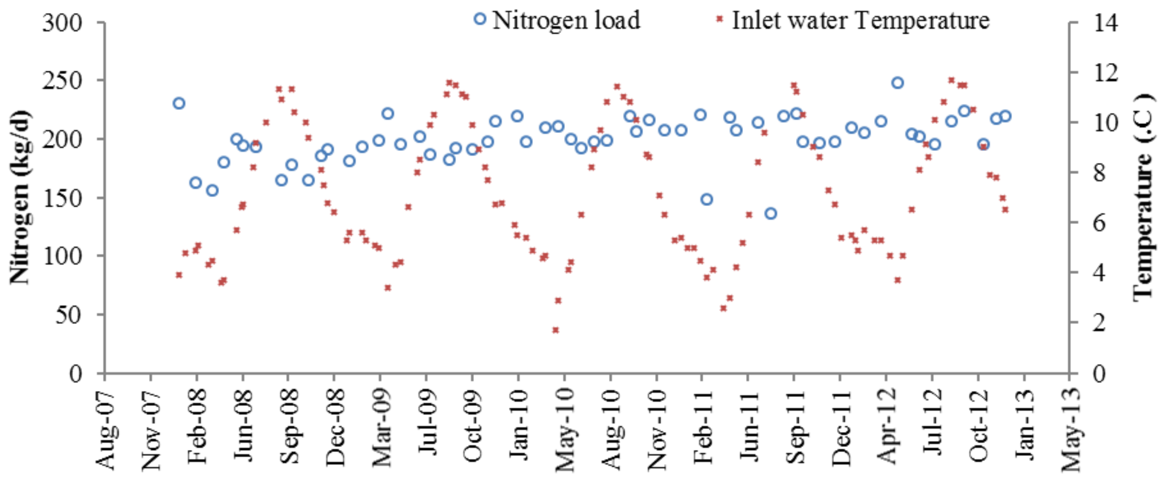



***Figure 30****- Nitrogen load of Raahe WWTP from years 2008 to 2012.*

### 4.1.5 Kokkola

In the city of Kokkola, the WWTP received a daily discharge of 8 421$m^3$/d in average in the interval of 2006-2012 (Figure 31). In the months of spring, the discharge is usually higher, reaching its maximum in April 2008 with 11 393$m^3$/d and a lower in cold months which happened in February of 2011 with 5 966$m^3$/d. In 2011, the treatment process has changed from biological-chemical to activated sludge. In this year there was an increase of the average daily discharge about 580$m^3$/d. The new process of the treatment, accomplishment a better efficiency of the requirements imposed by the plant in 2012.

The required license conditions in Kokkola was implemented in 2012 and it state only removal requirements to $BOD_7$ (95%) and P (95%). For N, there is just a target level of 60% which mean that is not necessary to be achieved. The parameters were obtained by water samples, which were collected once per month randomly (Figure 31). In the years before the implementation of the requirements the removal percentage in average was for 84%, 97%, and 14% for $BOD_7$, P and N respectively. In 2012, the efficiency was 97%, 91%, and 34% for $BOD_7$, P and N in that order. The P reduction was lower than the previous average, although the N removal was much higher rising from 15% to 34%. In 2012, the condition the requirements of WWTP became into force enforcing a $BOD_7$ not more than 10 mg/l with 95% efficiency removal and for P 0.3mg/l with 95% respectively. Before 2011, the process scarcely reached these values reflecting on changing the process to obtaining the requisites. All over the years, the outgoing P concentration does not have any relation with the N concentration, increasing and decreasing randomly. After 2010, the annual percentage removal of P started being higher than the previous years and in 2012 it reached 97% with concentration of 0.6mg/l. The water quality of the discharge, related with $BOD_7$ parameter, it was always with a concentration higher than the limit (30mg/l) but after the changing of the process in 2011 to 10mg/l they manage to reach values bellow it being the year 2012 the best one until now.

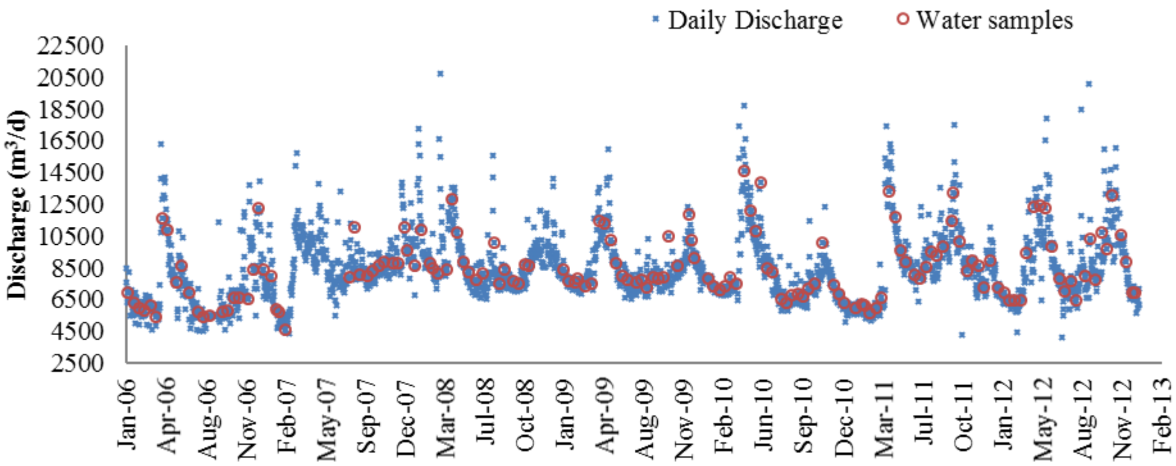



***Figure 31***- *Daily discharge in Kokkola WWTP and the water sample of wastewaters*

The studied of N load was made in two parts, having the year 2011 as transition and being when the wastewaters started going to the new WWTP. The study periods were 2006-2010 and 2011-2012 (Figure 32). When the new treatment plant was started, the load comportment changed and started decreasing. The results of study of the new process show that in the following years the load had a linear relation with the time.

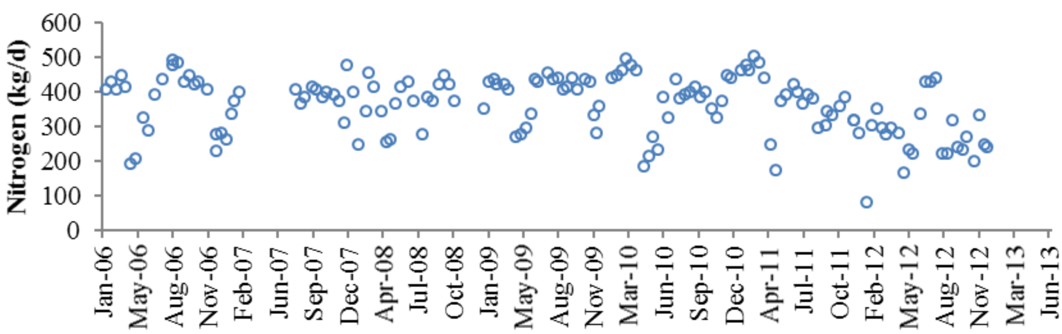



***Figure 32*** *Nitrogen load of Kokkola WWTP during 2006-2012*

The model prediction of the N load in Kokkola after 2011 showed a linear relation (Figure 33). The success of the fitting is poor ($R^2$=0. 2952) and also the quality (Adjusted $R^2$=0. 2799). The random error (SSE=2. 912$e^5$) and the standard error of the regression (RMSE=79. 57) are significant. The residuals bars show the differences between the response and the predict value and the randomness of the distribution, which suggest that the model fits well to the data. The linear relation, is represented in the equation 10 and the coefficients of the equation are in a range of (-0.349; -0.1296) and 849.6 (607.8; 1091) respectively.

***Equation 10*** *Linear equation for nitrogen load in Kokkola for studied period 2011-2012.*

$$W(t) = -0.2393*t+849.6$$

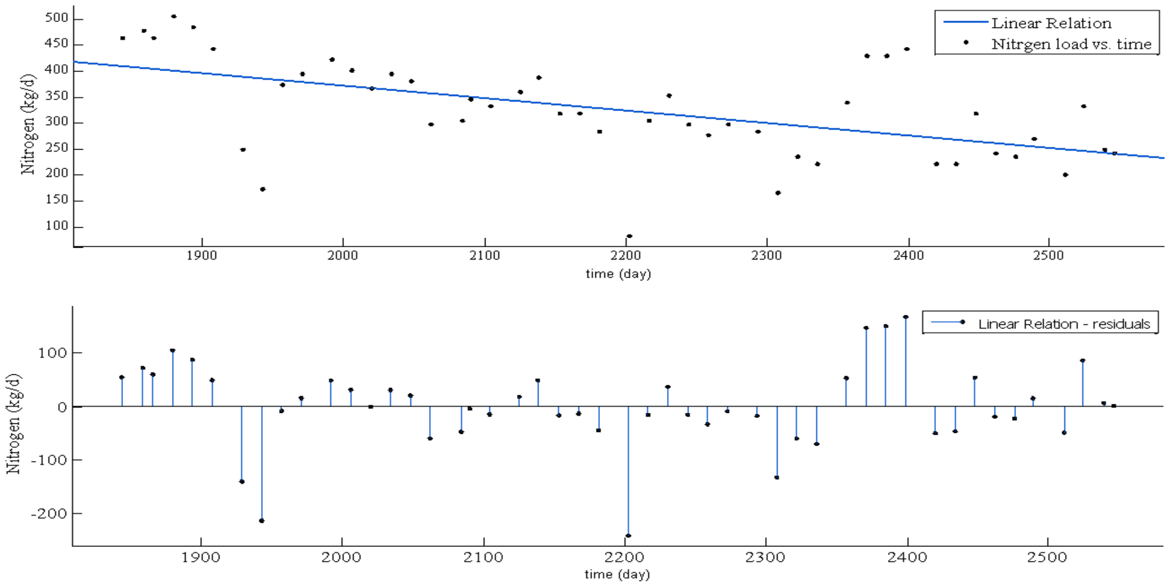



***Figure 33****- Fitting process of N load of Kokkola WWTP during the years 2011-2012.*

The temperature of the process is related with the N removal, as it is possible to observe in the next graphic, when the temperature start to increase the N load begins to decrease (Figure 34). The new plant, implemented in October 2011 a target of 70 % for N removal, meaning that it shall not necessarily to be achieved. The percentage removal in 2011 and 2012 was 15% and 34% respectively, according with these percentages, the difference between the incoming and outgoing concentrations of N will be higher in 2012, which mean that also the incoming water of the sewer increased and the efficiency of the process improved (Figure 34). In the following years the behavior of the N load will be the same with a constant percentage of N removal if the process does not suffer a change. In Kokkola WWTP, the N removal efficiency is a function of the process temperature.

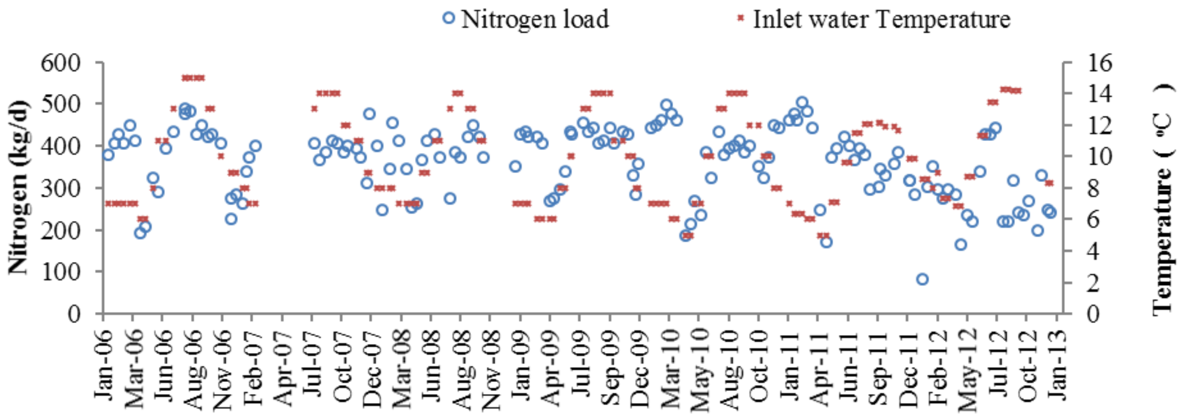



***Figure 34*** *-Nitrogen load and Water Inlet Temperature in Kokkola WWTP in 2006-2012*

### 4.1.6 Pietarsaari

In Pietarsaari's WWTP, the treatment suffered some changes through the years although they were not relevant for the efficiency of the process. The daily discharge during this time had an average of 8 741m$^3$/d and increased 3 961m$^3$/d from 2003 to 2012 (Figure 35). The maximum daily discharge was reached in 2008 with 22 058m$^3$/d and the lowest in 2006 with 4 352m$^3$/d.

In 2010, the requirements for N removal were set as a target level of 60% and for $BOD_7$ and P were already been set in 2003 as 90% both. The outgoing concentration it is 20mg/l for $BOD_7$ and P is 0.7mg/l. The average outgoing load of N during the period time of 2003 and 2012 had an average of 303kg/d representing 31% of removal. In 2006 the load had reached a minimum with 258kg/d and the highest in 2012 with 360kg/d. The P load has been 3.7kg/d during the years, with a 95% of removal, and average higher in the months of April/ May (5.5kg/d) and lower in July (1.9kg/d).

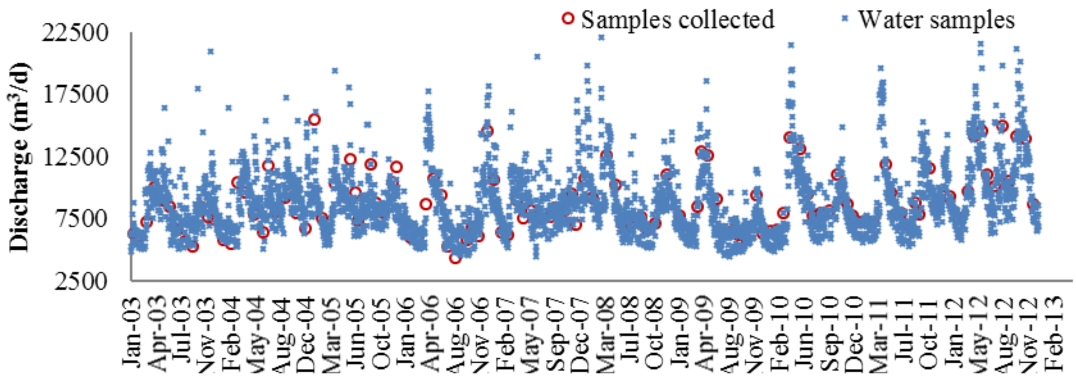



***Figure 35-*** *Daily discharge in Pietarsaari WWTP in 2003-2012*

The N load variation is represented in the Figure 36. The N load was constant until the end of 2007 with an average of 283kg/d. Since 2008 the load increased as also the discharge and the best description of the load after 2008 until 2012 is a linear relation.

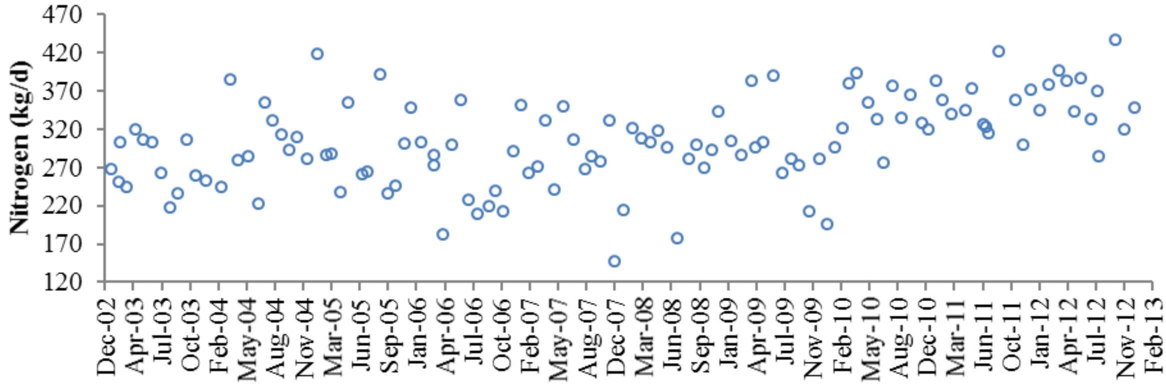



***Figure 36***- *Nitrogen load in Pietarsaari WWTP in 2003-2012.*

The results of the study period 2008-2012 showed a linear performance. The success of the fitting is poor ($R^2$=0.2839) and also the quality (Adjusted $R^2$=0.2715). The random error (SSE=1.163e$^5$) and the standard error of the regression (RMSE=744.77) are significantly small. The linear model has the following range of coefficient: m = 0.05271 (0.03071; 0.07472), b = 180.8 (119.5; 242.1). The residual bars appear to have a randomly evolution so the model fits well to the data. The representation of the trend of the N load in Pietarsaari WWTP will follow the linear relation, which will be represented in equation 11.

***Equation 11*** *Linear equation for nitrogen load in Pietarsaari for studied period 2011-2012.*

$$W(t) = 0.05271 * t + 180.8$$

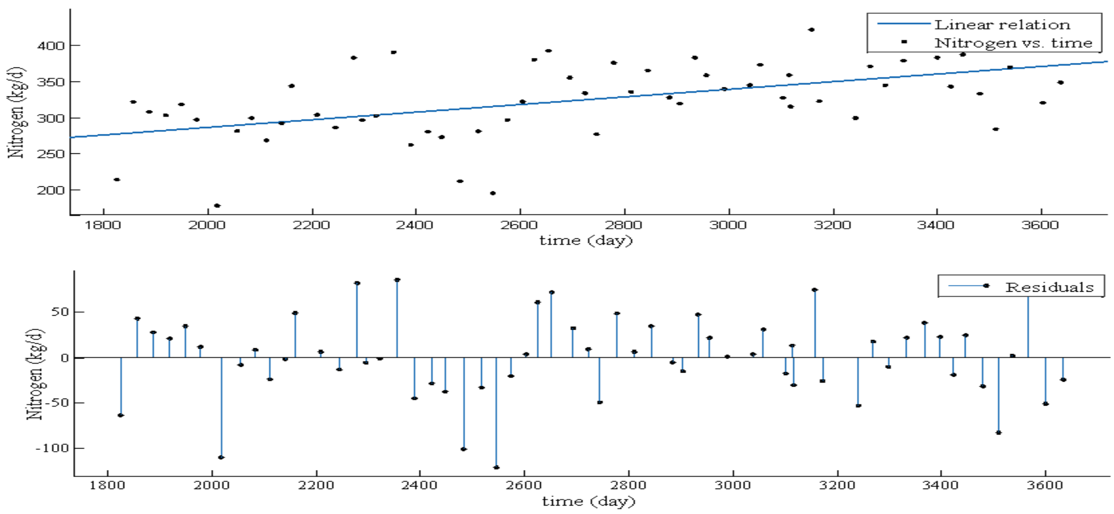



***Figure 37***- *Fitting process of Nitrogen load for 2008-2012.*

The efficiency of processes, as it was notices in the previous studied WWTPs, is related with temperature (Figure 38). When the temperature increases, the load decrease and so the efficiency is higher reaching in maximum 43%.

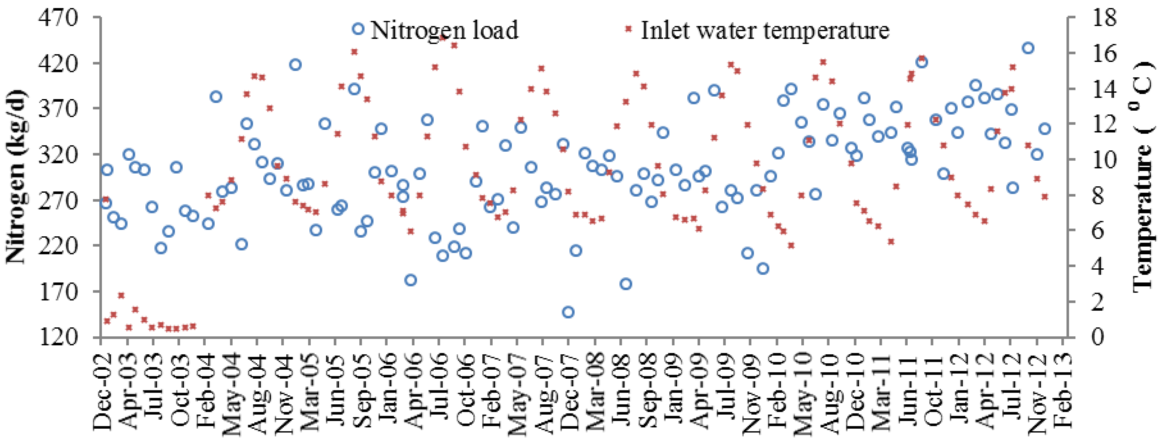



***Figure 38****- Nitrogen load and Water Inlet Temperature in Pietarsaari WWTP in 2003-2012.*

## 4.2 Discussion

The results of all modeling process of outgoing N from the studied WWTPs are present in Table 8. Among them, the new WWTP was established in Kokkola during those years. Currently, two of them have biological treatment (Kemi and Raahe WWTPs) and the others have activated sludge processes (Oulu, Kempele, Pietarsaari and Kokkola WWTPs) sometimes mixed with chemical treatment. Although, they have slightly different stages on the processes between them, like sedimentations and flocculation stage. Also, Kempele have an additional process, wetland that was not considered in the N modeling process.

The plant that removed the most N, in average of the study period, it was Oulu with 40% followed by Kempele and Pietarsaari´s WWTPs with 31% and last Kokkola´s WWTP in 2012 with 35%. These results, are the best ones for N removal even without, in some of them, the implementation of N removal processes. Oulu and Kempele are the two plants that had the implementation of N removal in summer time and it was clear increased of N removal percentage during that period. However, they exceed the implemented limits of 20mg/l set by the Finnish environmental authorities. It is not possible to compare the concentration of N in summer months of Kempele with Oulu, because Kempele do not have data of monthly average just the exact days of samples. Although, with the annual average of N concentration in Kempele and Oulu's WWTPs it is possible to conclude that in Oulu the concentration of the outgoing N was lower over the times as being always around 33mg /l and in Kempele´s WWTP over 52mg/l. The implementation of the N removal, in Oulu´s WWTP, during summer months made the difference in the outgoing N concentration, even though it happened only 3 times in 2010, 2011, and 2012. The referred years, are after the renovation of the treatment plant that showed being a good deed. The minimum N concentration value was 11.3mg/l and the low percentage removal in that period (2010-2012) was 50%.

In Kemi, Raahe and Kokkola WWTPs (before 2011), the treatment process has been biological and chemical with screening, sand separator, primary sedimentation, aeration tank, and secondary settlement as main steps. Amongst all the WWTPs, those were the ones who had the lowest N removal in average of the studied period. Kemi's WWTP had the worst result with 14% and also Kokkola before 2011 and for Raahe 21%. These plants do not have any N removal and just Kokkola had a target level in summer but it never reaches the 70% N percentage removal. In the modeling process, their N load were a constant function not being possible to predict if they are going to continue in the same way or not. However, when Kokkola's changed the treatment process the load started to became liner and the N load decreased. The changed of the process was a benefit for the N target level.

***Table 8***- *Modeling results for WWTPs studies with fitting parameters: SSE, $R^2$, Adjusted $R^2$, RMSE and also the type of treatment and period time and requirements of nitrogen removal.*

| WWTP | Time period | Type of Treatment | Type of Model | SSE: | $R^2$ | Adjusted $R^2$ | RMSE | Nitrogen Removal | Exceed Limit |
|---|---|---|---|---|---|---|---|---|---|
| **Kemi** | [2008-2012] | Biological Chemical | Constant 255kg/d | – | –- | –- | –- | No | yes |
| **Oulu** | [2005-2007] | Activated Sludge | Constant 1665kg/d | – | – | – | – | No | yes |
| | [2008-2012] | | Sinusoidal | $5.004e^7$ | 0.6805 | 0.6779 | 363.4 | Since 2008 (June-August) | yes |
| **Kempele** | [2008-2009] | Activated Sludge | No sufficient data | | | | | | |
| | [2010-2012] | | Sinusoidal | $4.883e^4$ | 0.4896 | 0.4349 | 41.76 | Since 2011 (June-August) | yes |
| **Raahe** | [2008-2010] | Biological Precipitation | Linear | 5946 | 0.4264 | 0.4095 | 13.22 | No | yes |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | [2011-2012] | | Constant 209kg/d | – | – | – | – | | yes |
| **Kokkola** | [2006-2010] | Biological-Chemical | Constant 280kg/d | – | – | – | – | target level(2009) | yes |
| | [2011-2012] | Activated Sludge | Linear | $2.912e^{5}$ | 0.2952 | 0.2799 | 79.57 | target level | yes |
| **Pietarsaari** | [2003-2007] | Activated Sludge | Constant 283kg/d | – | – | – | – | No | yes |
| | [2008-2012] | | Linear | $1.163e^{5}$ | 0.2839 | 0.2715 | 744.77 | target level (2011) | yes |

## 5. Conclusions

Modeling outgoing N load showed that implementation of N removal processes and the nature of wastewater treatment affect the percentage removal of N. All studied WWTPs exceed required limit values for N (20mg/l), which has given by the Finnish environmental authorities. The models had different results between the WWTPs and that presented different impacts on the environmental water quality.

The modeling N load in Kemi´s WWTP, led to a continuous behaviour of an outgoing N concentration over the years around 30mg/l, which results in a 14% of N removal for the period 2008-2012. Not having implemented the requirements of N removal, the average outgoing N concentration is always higher than the limit implemented by environmental authorities. Despite this, the quality of the discharge water has been consistent with the other parameters set by the authorities. In Oulu's WWTP, after the sewage reparation (in 2008), the behaviour of the outgoing N load became sinusoidal showing a pattern with lower concentration in summer months and higher during the rest of the year. Although, it did not reach the set limit required of 20mg/l but it is in the right direction to reduce every year a little bit more than the previous one. Kempele, it was also a WWTP that showed a sinusoidal pattern presenting a lower concentration of N in summer months and higher in spring. After 2011, when implemented the N removal, the N concentration decreased annually in average a little bit but in summer months increase. This might have happened due the process is still under stabilizing and require more time to steadying. These results show that both are on the right way to bring a decrease of the eutrophication problem in the discharge set point.

In Raahe, Kokkola and Pietarsaari's WWTPs, the modeling processes have similarities which mean that the load did not show any seasonal trend. Raahe´s WWTP started with a linear relation with the load in function of time and then changed to a constant relation. During the years 2008-2010, the relation was linear showing a proportional increasing the N load. The outgoing N concentration started with 37mg/l and reached the maximum in 2010 with 48mg/l reflecting a decreasing percentage N removal. When the load became constant, the outgoing N concentration started to decrease and reflecting a higher removal percentage. When the load increased, the concentration decreased also because of the discharge also increases with them. If Raahe's WWTP aims to have a better efficiency, it should introduce N removal process and also warm up the incoming wastewater, in the way to become more efficient process. Also, in Kokkola's WWTP, the N load was constant by the 2010 and started decline since 2011 following linear trend. The change of N load also decreased the outgoing N concentration, being related with the expansion of the sewer network in 2011 as well as the process treatment. Pietarsaari's WWTP proved being worked in the same way as Kokkola´s WWTP. However the linear relation is growing instead of decreasing. Starting in 2003, as a constant N load and in 2008 became a linear relation in function of time. The outgoing N concentration before 2008 were in the same range of values of the next years as 36mg/l, even though the percentage reduction was higher in the constant relation than in the linear relation interval 2008-2012. In 2010, the implementation of the target level of 60% was never accomplished.

The results of the modeling process showed that some of the WWTPs could do something about the N removal to decrease their outgoing N concentration. Kemi, Raahe, Kokkola and Pietarsaari's WWTPs are among the studied who not have any kind of control and are contributing to the eutrophication problem. Nonetheless, Oulu and Kempele's WWTP are the only ones that in the near future they are going to accomplish the set limit and will be an example to follow. The best treatment process to accomplish those results is the ASP, which was revealed in the percentage of N removal, also by WWTPs that do not have N removal requirements like Pietarsaari and Kokkola 31% and 35% respectively during the studied period. ASP has increasingly gained popularity, and today it is most widely used. The process is a biological process in which microorganisms oxidize and mineralize organic matter (Fatihah et all., 2012). In the activated sludge process, the temperature of the process is also a relative parameter that is related with rate of the kinetic bacteria. Low temperatures might be the problem that the set requirements are normally unreached biological process based upon suspended biomass are effective for organic carbon and nutrient removal from WWTPs.

## 5.1 Limitations and future work

In general, the results given in this thesis were good and the modeling of N load was accomplished with a good approximately to the reality. However, for future work it could be interesting study small intervals and use other equations to fit the models. It is also important to create a model, where it is possible to observe the level of eutrophication with the depth of water and the amount of DO relating with the temperature of the water. Also, the parameters of organic quality of water could be an important characteristic to evaluate water quality. One widely used model is called Streeter Phelps models which investigated some of water quality parameters in streams and estuaries. It would be interesting to use that model to understand how the water quality is affected by the discharge of these loads.

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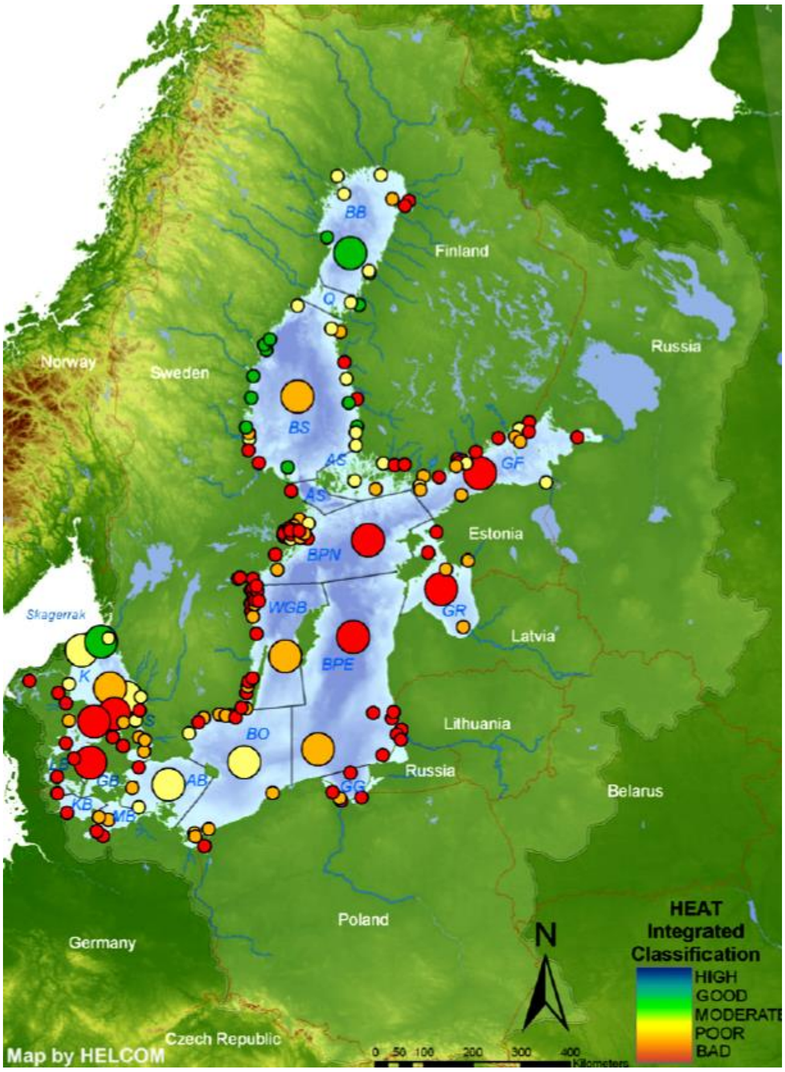
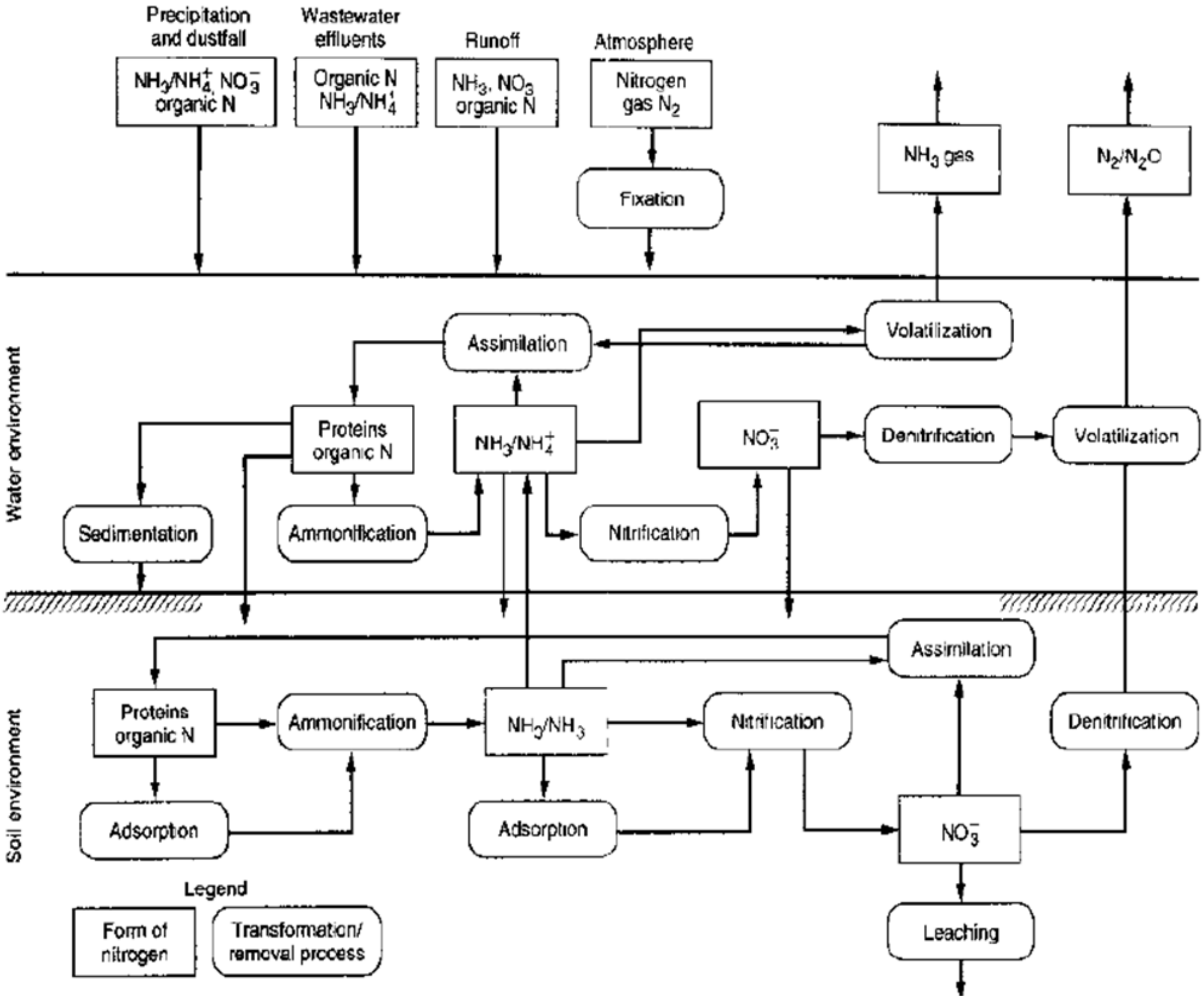
## 7. Annex I - Integrated classification of eutrophication status based on 189 areas.




Integrated classification of eutrophication status based on 189 areas. Good status is equivalent to ‘areas not affected by eutrophication’, while moderate, poor and bad are equivalent to ‘areas affected by eutrophication’. Large circles represent open basins, while small circles represent coastal areas or stations. HEAT = HELCOM Eutrophication Assessment Tool. Abbreviations: BB=Bothnian Bay, Q=The Quark, BS=Bothnian Sea, AS=Archipelago Sea, ÅS=Åland Sea, BPN= Northern Baltic Proper, GF=Gulf of Finland, BPE= Baltic Proper, Eastern Gotland Basin, GR=Gulf of Riga, WGB=Western Gotland Basin, GG=Gulf of Gdansk, BO=Bornholm Basin, AB=Arkona Basin, MB=Mecklenburg Bight, KB=Kiel Bight, GB=Great Belt, 4 LB=Little Belt, S=The Sound, K=Kattegat.

## 8. Annex II- Generalized nitrogen cycle in the aquatic and soil environment. Source: Metcalf and Eddy



## 8.1 Annex III- Modeling and Simulation software

| **Name of the *software*** | **What it does?** |
| --- | --- |
| Activated Sludge Model No. 1 (ASM1) | ASM1 was published in its final form in 1987. In ASM1 two kinds of substrate, readily and slowly biodegradable COD (RBCOD and SBCOD), are introduced and a hydrolysis process is included. In ASM1 it is also assumed that slowly biodegradable substrate consists fully of particulate substrate (XS). ASM1 includes nitrogen and organic matter removal with simultaneous consumption of oxygen and nitrate as electron acceptors; however, it does not contain biological phosphorous removal. ASM1 was developed mainly for municipal activated sludge plants (Henze *et al.*, 2002; Henze *et al.*, 2008). |
| Activated Sludge Model No. 2 (ASM2) | Was published in 1995; additionally, the model included both nitrogen removal and biological phosphorus removal. The role of denitrification in relation to biological phosphorus removal was still unclear, and Task Group decided not to include that element. However, the development in research was fast, and denitrifying PAOs (phosphorus accumulating organisms) were needed for simulation of many results from research and practice. Because of this, the ASM2 model was expanded in 1999 into the ASM2d model, where denitrifying PAOs were included (Henze *et al.*, 2002). |
| Activated Sludge Model No. 3 (ASM3) | Describes the same processes as ASM1; however, ASM3 was introduced to correct the deficiencies of ASM1. The most important reason for introducing ASM3 was the recognition of importance of three rates of oxygen consumption in the process: the rapid rate of oxygen consumption for degradation of RBCOD, slow rate associated with degradation of SBCOD, and even slower endogenous oxygen uptake rate (OUR). In ASM1 there is only one oxygen consuming process, which makes calibration of the model very difficult. Calibration of ASM3 should be easier mainly because of converting the circular growth death growth (death regeneration) model by endogenous respiration model (Henze et al., 2008). |
| EFOR by Danish Hydraulic Institute (Denmark) | Software tool to use in the modeling of WWTP. Includes ASM1 and ASM2 model, which is modified to include biological phosphorous removal. |
| Bio Win by EnviroSim Associates Ltd | Process simulator that makes use of linked process units to simulate biological wastewater treatment systems. BioWin is a Microsoft Windows based simulator used in the analysis and design of WWTP. BioWin Version 3.0 contains an integrated biological model for biological nutrient removal (BNR) activated sludge, fermenters, Moving Bed Biofilm Reactor (MBBR) & Integrated Fixed Film Activated Sludge (IFAS) systems, and anaerobic digesters. |
| GPS-X by Hydromantis Inc, Canada, | Is a modular, multipurpose modeling environment for the simulation of wastewater treatment systems. GPSS Version 5.0 is supplied with over 50 preconfigured layouts covering most of the unit processes found in wastewater treatment plants. The simulator |

| | |
|---|---|
| | is built on the ACSL simulator, that provides powerful integration and general simulator features. Six standard biological models e.g. temperature dependent versions of ASM1, ASM2d and ASM3 are available in GPSX. The biological unit processes include carbon, N and P removal, in various suspended growth and fixed film configurations. |
| SIMBA-SIMulation programs für die Biologische Abwasserreinigung | Developed at the Institut für Automation und Kommonikation (IFAK) in Germany. It can be considered a custom made version of Simulink for wastewater treatment applications; with its latest version SIMBA 5, allows the holistic consideration of sewer system, WWTP, sludge treatment and rivers. It extends Matlab/Simulink using block libraries for biological and chemical treatment processes. SIMBA includes several default models including ASM1, ASM2d, ASM3, the BioP Model and several settler models. |
| STOAT<br>Sewage Treatment Optimization and Analysis over Time | Developed by Water Research Center (UK) is a Windows based computer modeling tool designed to dynamically simulate the performance of a wastewater treatment works including sludge treatment processes. STOAT includes an implementation of ASM1, called IAWQ No.1, and the Takács settler model, called Generic. The software can be used together with commercial sewerage and river quality models. |
| WEST-Wastewater treatment plant Engines for Simulation and Training): | an interactive dynamic simulator. It is developed mainly at the University of Gent. WEST includes a number of modules and features that enables the user to model and evaluate almost and kind of wastewater treatment plant application that exists. Most of the models in WEST simulator are open source and open code; thus, the models can be modified if necessary. WEST mainly has been used in the context of wastewater treatment research. |

## 9. Annex IV- Requirements for discharges from urban wastewater treatment plants subject to Articles 4 and 5 of the Directive 91/271/CEE.

The values for concentration or for the percentage of reduction shall apply.

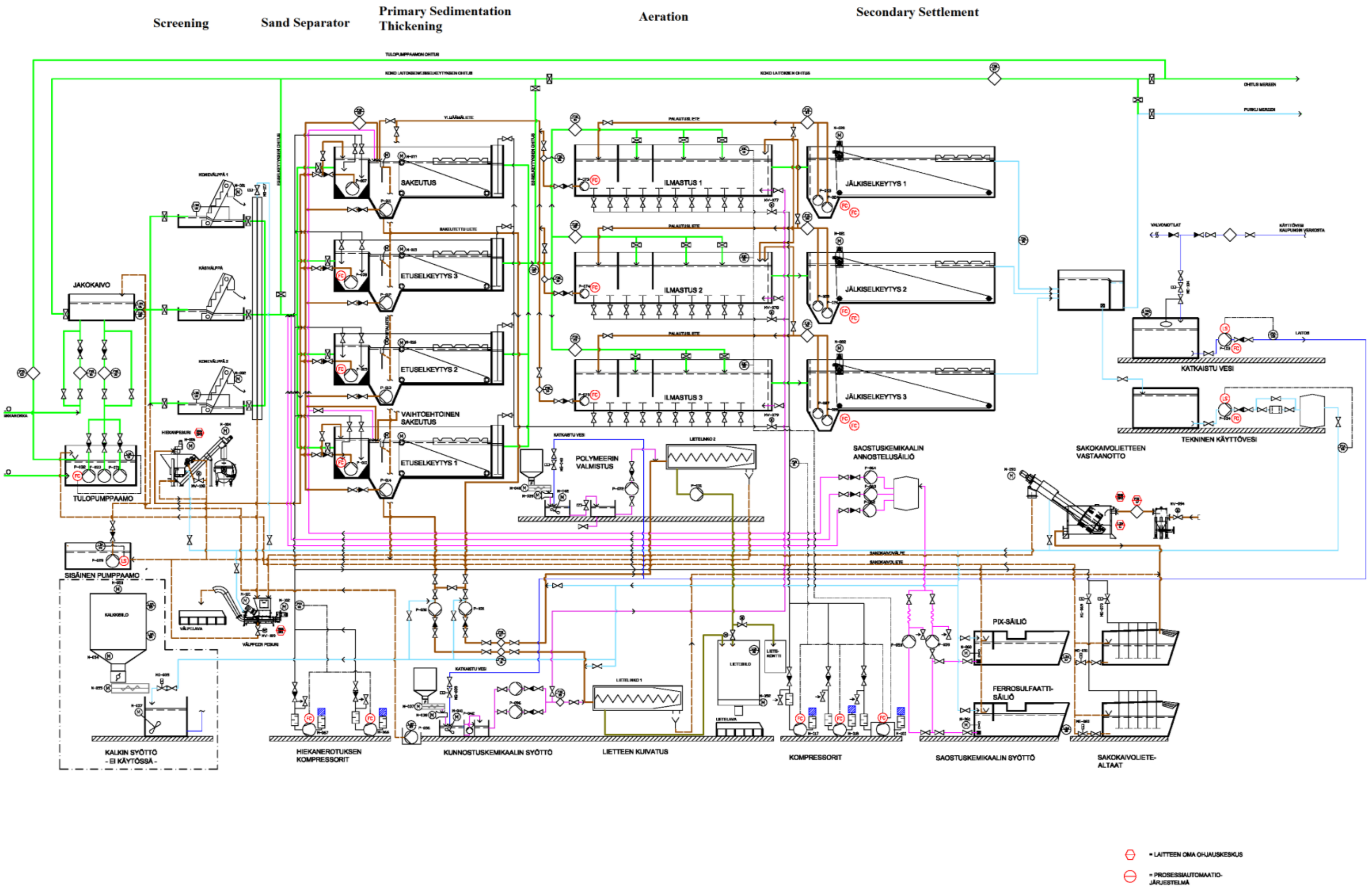
| Parameters | Concentration | Minimum percentage of reduction (1) | Reference method of measurement |
|---|---|---|---|
| Biochemical oxygen demand (BOD5 at 20 °C) without nitrification (2) | 25 mg/l $O_2$ | 70-90<br><br>40 under Article 4 (2) | Homogenized, unfiltered, undecanted sample. Determination of dissolved oxygen before and after five-day incubation at 20 °C ± 1 °C, in complete darkness. Addition of a nitrification inhibitor |
| Chemical oxygen demand (COD) | 125 mg/l $O_2$ | 75 | Homogenized, unfiltered, undecanted sample Potassium dichromate |
| Total suspended solids | 35 mg/l (3)<br><br>35 under Article 4 (2) (more than 10 000 p.e.)<br><br>60 under Article 4 (2) (2 000-10 000 p.e.) | 90 (3)<br><br>90 under Article 4 (2) (more than 10 000 p.e.)<br><br>70 under Article 4 (2) (2 000-10 000 p.e.) | — Filtering of a representative sample through a 0,45 μm filter membrane. Drying at 105 °C and weighing<br>— Centrifuging of a representative sample (for at least five mins with mean acceleration of 2 800 to 3 200 g), drying at 105 °C and weighing |

(1) Reduction in relation to the load of the influent.
(2) The parameter can be replaced by another parameter : total organic carbon (TOC) or total oxygen demand (TOD) if a relationship can be established between BOD5 and the substitute parameter.
(3) This requirement is optional.

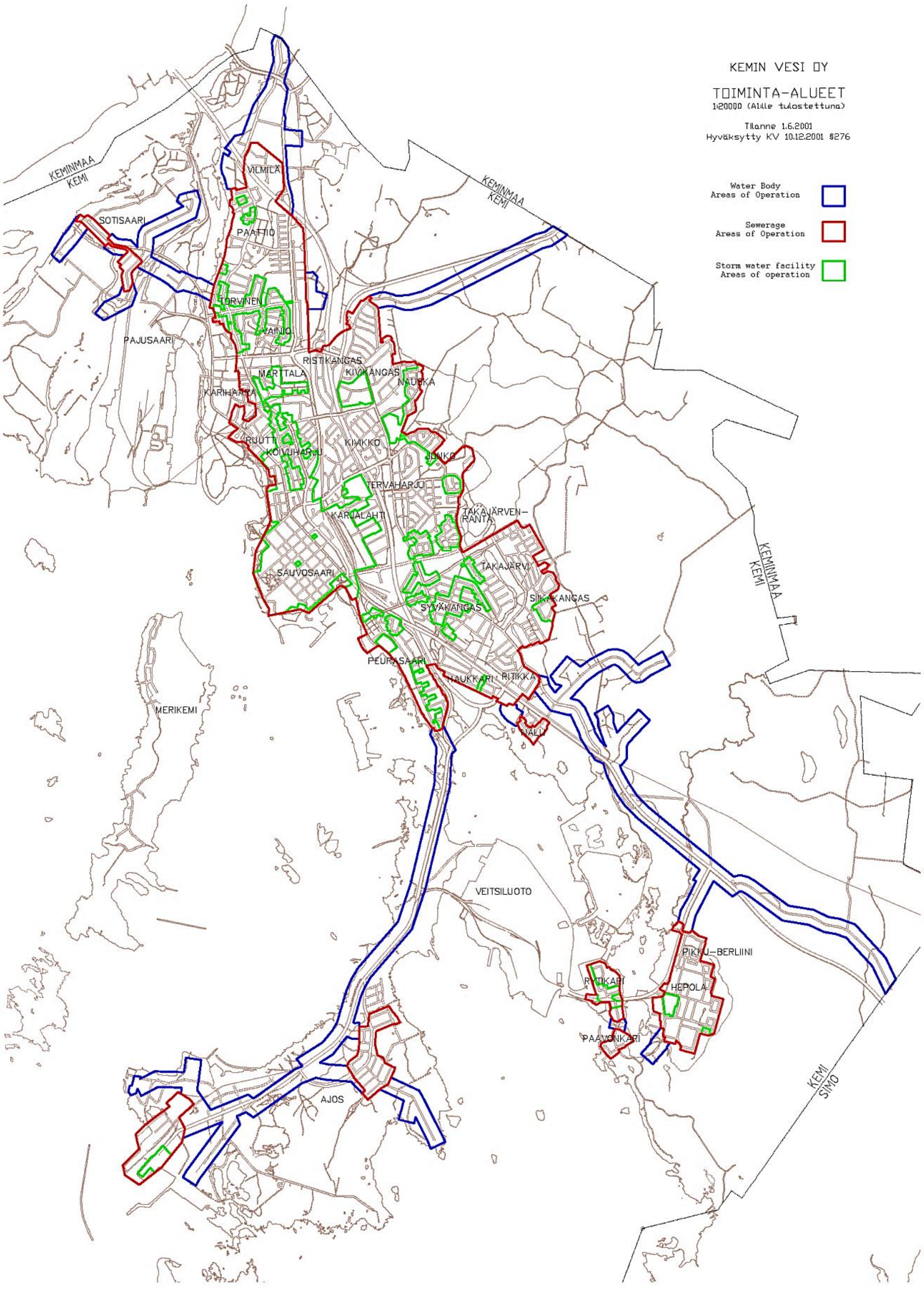
| Parameters | Concentration | Minimum percentage of reduction (1) | Reference method of measurement |
|---|---|---|---|
| Total phosphorus | 2 mg/l P (10 000 - 100 000 p. e.)<br>1 mg/l P (more than 100 000 p. e.) | 80 | Molecular absorption spectrophotometry |
| Total nitrogen (2) | 15 mg/l N (10 000 - 100 000 p. e.)<br>10 mg/l N (more than 100 000 p. e.) (3) | 70-80 | Molecular absorption spectrophotometry |

(1) Reduction in relation to the load of the influent.
(2) Total nitrogen means : the sum of total Kjeldahl-nitrogen (organic N + $NH_3$), nitrate ($NO_3$)-nitrogen and nitrite ($NO_2$)-nitrogen.
(3) Alternatively, the daily average must not exceed 20 mg/l N. This requirement refers to a water temperature of 12° C or more during the operation of the biological reactor of the waste water treatment plant. As a substitute for the condition concerning the temperature, it is possible to apply a limited time of operation, which takes into account the regional climatic conditions. This alternative applies if it can be shown that paragraph 1 of Annex I.D is fulfilled.

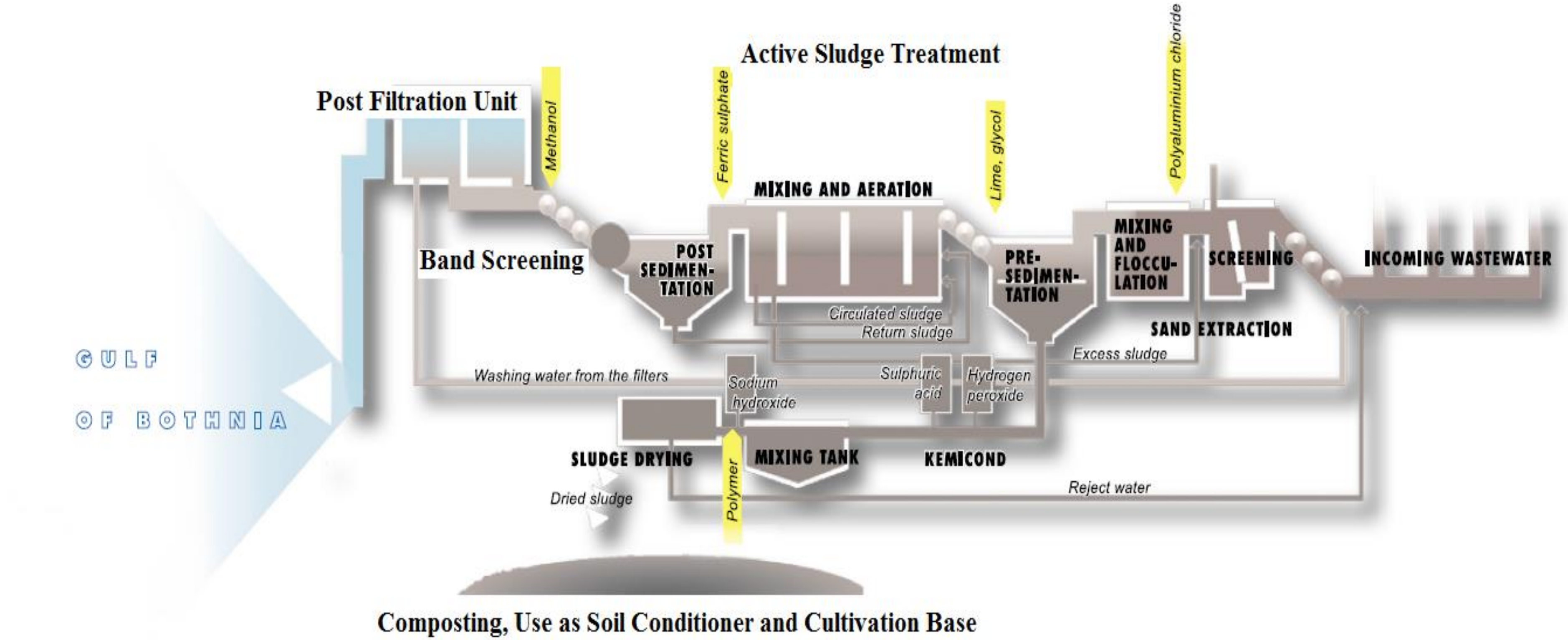
## 9.1 Annex V – Kemi´s WWTP process chart



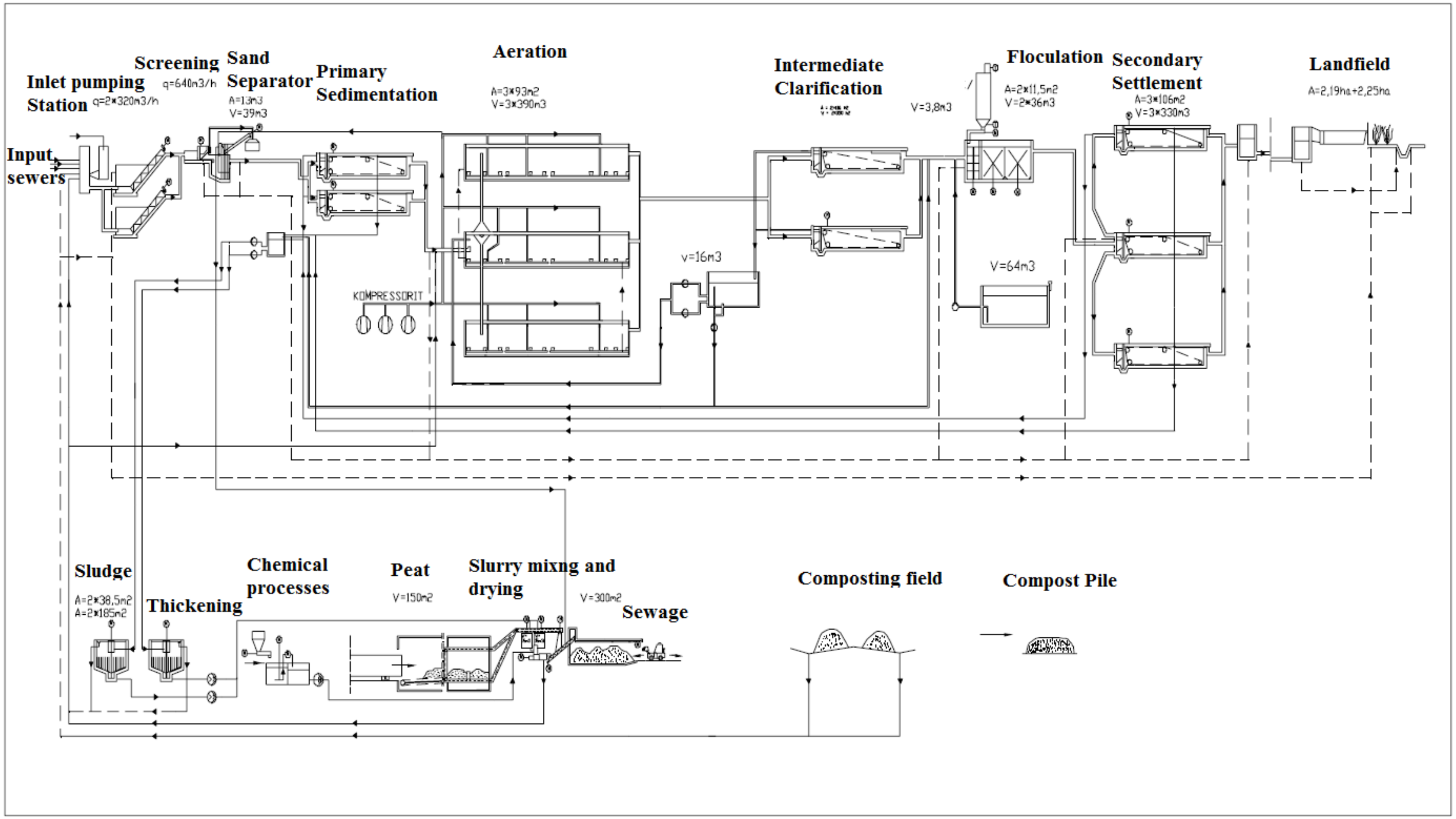
## 9.2 Annex VI- Network of Kemi´s WWTP



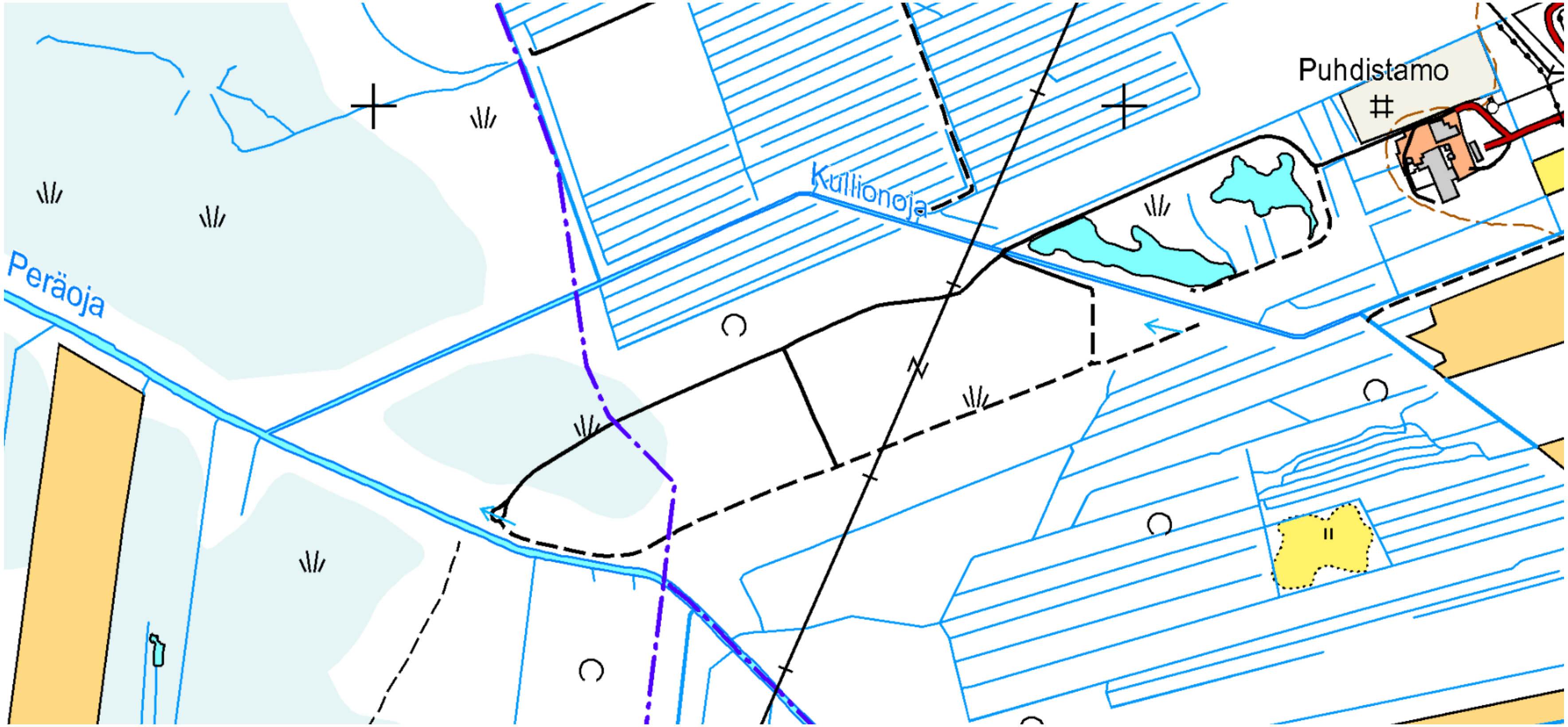
## 9.3 Annex VII- Oulu's WWTP process chart



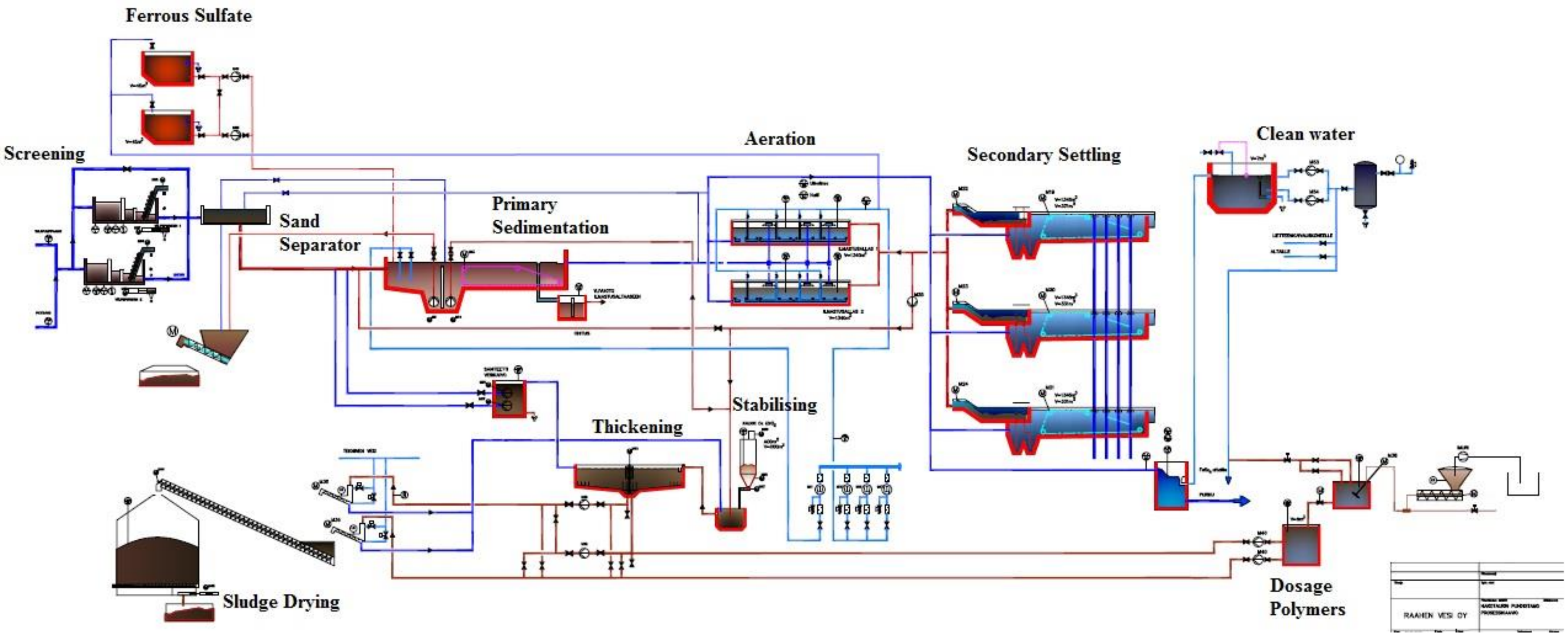
## 9.4 Annex VIII- Kempele´s WWTP process chart



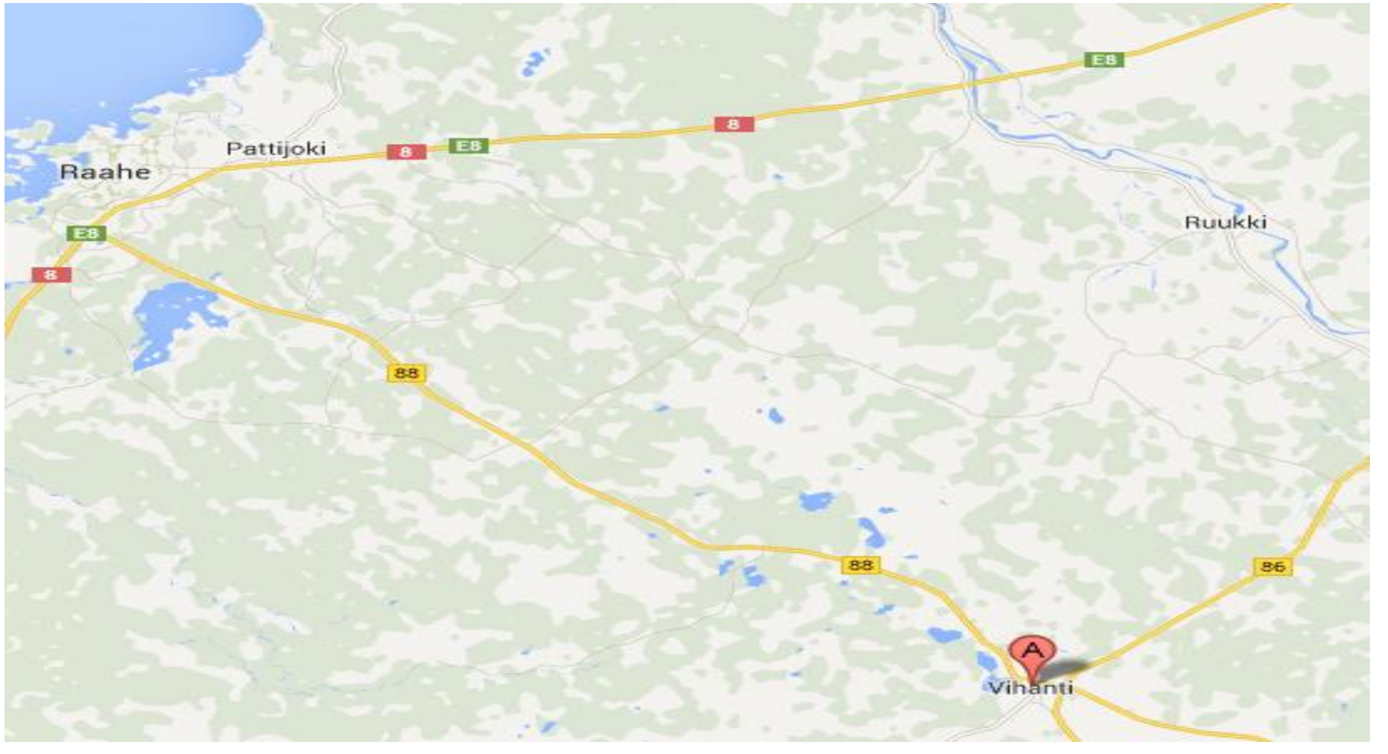
## 9.5 **Annex IX- Ditches where Kempele WTTP discharges**.



## 9.6 Annex X – Raahe´s WWTP process chart.

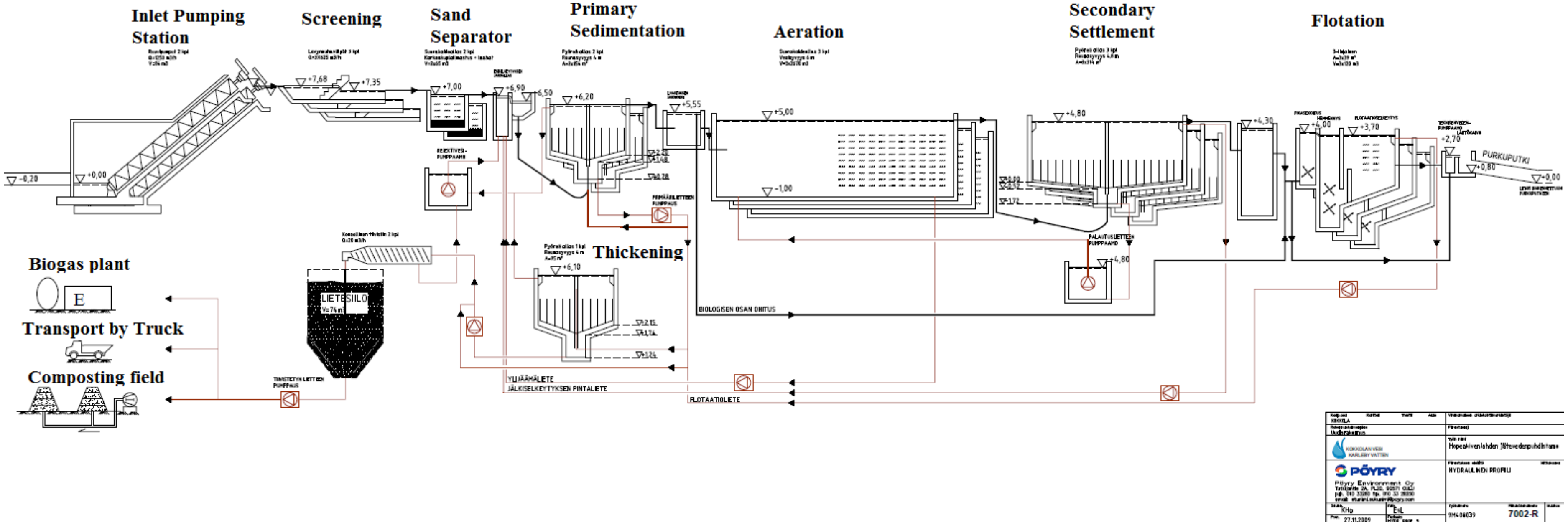


## 9.7 Annex XI- Wastewater piped from Vihanti to Raahe WWTP.

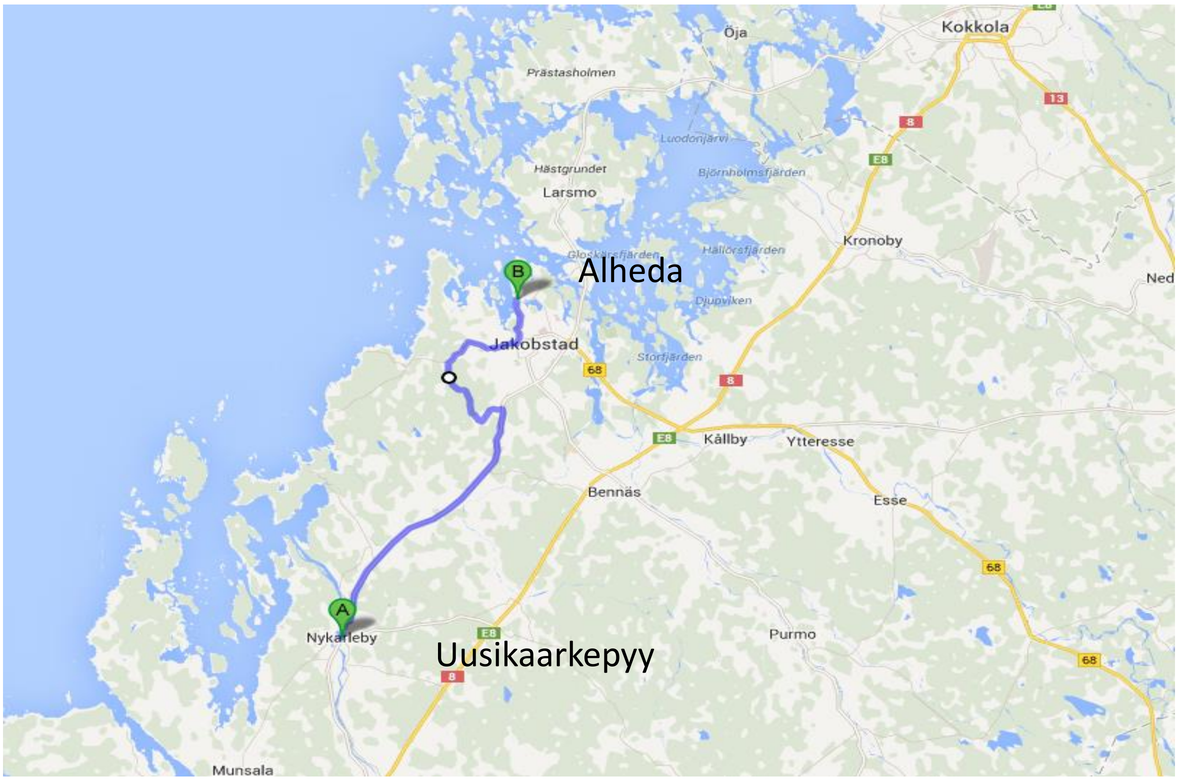



Source:Google Maps. 24/08/2013

# 9.8 Annex XII- Kokkola´s WWTP process chart

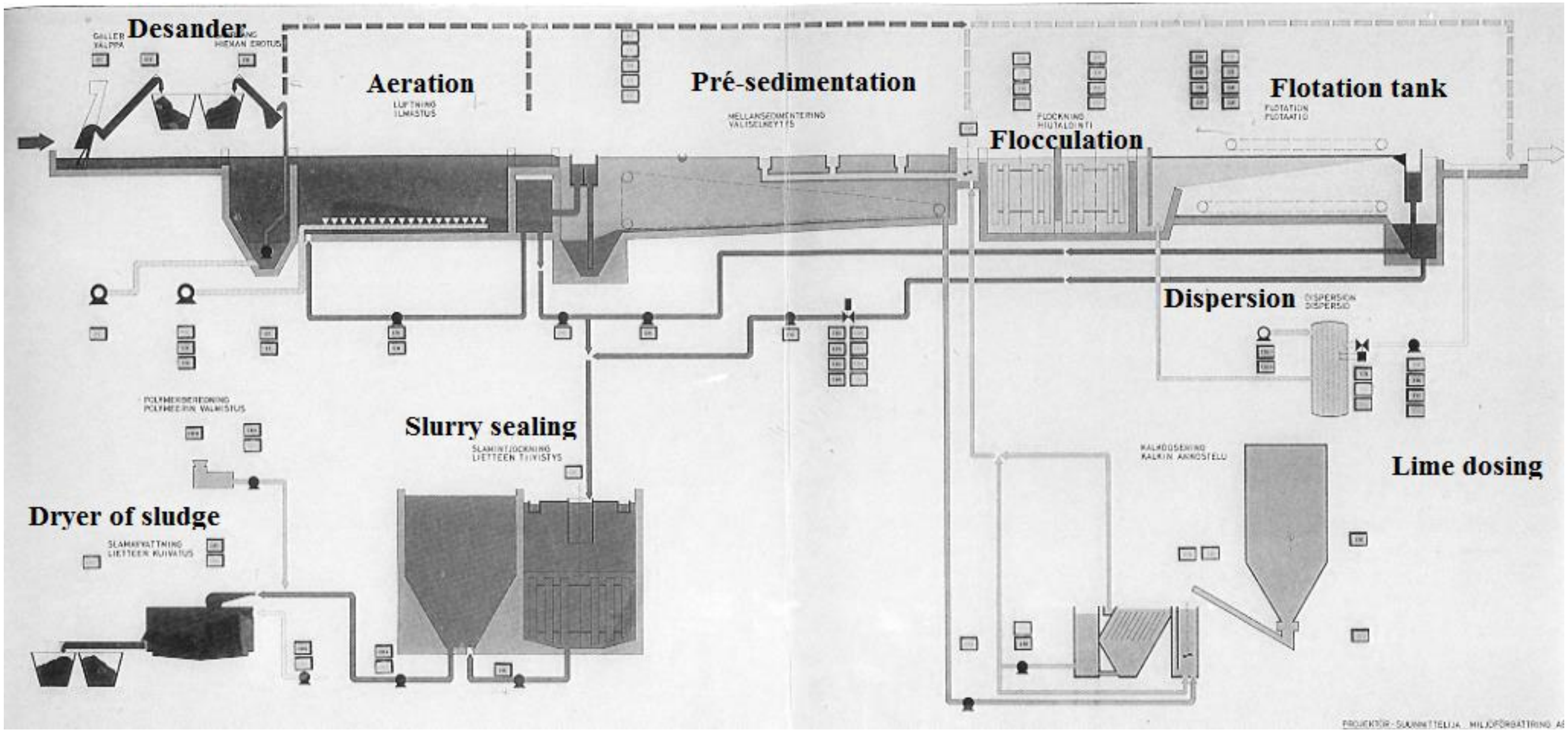


# 9.9 Annex XIII- Sewages coming from Uusikaarkepyy to Alheda.




*Google maps 24/8/2013.*

## 9.10 Annex XIV- Pietarsaari´s WWTP process chart



## 9.11 Annex XV- Matlab code (script) for

### 1. Kemi

```
%Kemin Vesi Oy
data=xlsread('kemiNoutgoing.xlsx'); % going to y=func(t,N);

t=data(:,1);% Time in days
N=data(:,2);%Nitrogen outgoing load kg/d

M=248.58;

plot (t,N,'-o')
xlabel('Time (days)');
ylabel('Nitrogen Load (kg/d)')
legend('Nitrogen Outgoing Load in Kemin between 2008 and 2012' )
title('Kemin Vesi Oy')
```

### 2. Oulu

**2.1 Constant load**

```
Oulun Vesi Oy before 2008

% this period of time is for 3 years

data=xlsread('oulubefore.xlsx'); %going to read the datas before 2008

t1=data(:,1);%time in days
N2=data(:,2);%load of nitrogen kg/d
N3=data(:,3);% nitrogen load in the summer time

% CONSTANT LOAD
W1=1675.539;          % Median value kg/d


plot (t1,N2,'b', t1,N3,'-o')
xlabel('Time (days)');
ylabel('Nitrogen Load kg/d')
legend('Nitrogen Load before 2008' )
title('Oulun Vesi Oy')
```

**2.2 Sinusoidal load**

```
%Oulun Vesi Oy after 2008

data=xlsread('ouluafter2008.xlsx'); %going to read the datas before 2008
t1=data(:,1);   %time in days
```

```
N=data(:,2);   %load of nitrogen kg/d

%constant load
W1=1603.264; % kg/d median before 2008

%sinusoidal loading
W_av=1303.264; %mean loading (kg/d) MT-1 , the mean value for the sine wave
W_a=780.12;%amplitude of the loading kg/d MT-1 , how high the oscillation swings vertically
omega=0.01668;%angular frequency of the oscillation (radians T-1) , how frequently the sine wave oscillates  , 2Pi/Tp
theta=11.899;%teta phase shift (radians), how much the function is shifted horizontally relative to the standard sine wave
x=(omega*t1-theta); %argumento do seno

W2=W_av+W_a*sin(x); %sinusoidal function mathematically represented

plot (t1,N,'-o',t1,W2,'b')
xlabel('Time (days) ');
ylabel('Nitrogen Load (kg/d)')
legend('Nitrogen Load after 2008 "including"' )
title('Oulun Vesi Oy')
```

### 3. Kempele

```
%Kempele
 data=xlsread('kempeleNoutgoing.xlsx');

t1=data(:,1);%time in days
N=data(:,2);%load of nitrogen kg/d

plot (t1,N,'-o')
xlabel('Time (days)');
ylabel('Nitrogen Load kg/d')
legend('Nitrogen Load ' )
title('Kempele ')
```

### 4. Raahe

```
% Raahe
 data=xlsread('load2008210.xlsx');

t=data(:,1);%time in days
N=data(:,2);%Daily discharge m3/d


alfa=0.495;%Slope of the line
W=alfa*t; %Linear load function

plot (t,N,'b' , t,W,'o')
```

```
xlabel('Time (days)');
ylabel('Nitrogen (kg/d)')

% Raahe
 data=xlsread('load20112012.xlsx');

t1=data(:,1);%time in days
N1=data(:,2);%Daily discharge m3/d


plot (t,N,'b' )
xlabel('Time (days)');
ylabel('Nitrogen (kg/d)')
```

5. **Kokkola**

```
%Kokkola
 data=xlsread('kokkolaNoutgoing.xlsx');

t1=data(:,1);%time in days
N=data(:,2);%load of nitrogen kg/d

plot (t1,N,'-o')
xlabel('Time (days)');
ylabel('Nitrogen Load kg/d')
legend('Nitrogen Load ' )
title('Kokkola ')



%Kokkola
 data=xlsread('Nitrogen2011_2012.xlsx');

t3=data(:,1);%time in days
N3=data(:,2);%load of nitrogen kg/d

plot (t3,N3,'-o')
xlabel('Time (days)');
ylabel('Nitrogen Load kg/d')
legend('Nitrogen Load ' )
title('Kokkola ')
```

6. **Pietarsaari**

```
%PIETARSAARAN
 data=xlsread('nitrogen20032008.xlsx');
```

```
t=data(:,1);%time in days
N=data(:,2);%Nitrogen outgoing kg/d

plot (t,N,'-o' )
xlabel('Time (days)');
ylabel('Nitrogen kg/d')
legend('Nitrogen load ' )
title('Pietarsaarin ')

%PIETARSAARAN
 data=xlsread('nitrogen20082012.xlsx');


t1=data(:,1);%time in days
N1=data(:,2);%Nitrogen outgoing kg/d

plot (t,N,'-o' )
xlabel('Time (days)');
ylabel('Nitrogen kg/d')
legend('Nitrogen load ' )
title('Pietarsaarin ')
```

# 10.Annex XVII.