Carbon utilisation for extended nitrogen removal and resource savings

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Carbon utilisation for extended nitrogen removal and resource savings

TOBIAS HEY
DEPARTMENT OF CHEMICAL ENGINEERING | LUND UNIVERSITY, SWEDEN
Carbon utilisation for extended nitrogen removal and resource savings

Tobias Hey

LICENTIATE DISSERTATION
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To be defended at lecture hall K:G at the Center for Chemistry and Chemical Engineering, Getingevägen 60, Lund. Date 10\textsuperscript{th} June 2013 and time 13:15.

\textit{Opponent}

PhD Dines Thornberg, Copenhagen Wastewater Innovation, Denmark.
A full-scale in-line primary sludge hydrolysis experiment was conducted in one out of four primary settlers at the Klagshamm Wastewater Treatment Plant (WWTP) to test if the wastewater quality can be improved in terms of providing easily accessible carbon for possible pre-denitrification and the reduction of external carbon sources. The amount of easily accessible carbon produced, in the form of the volatile fatty acid (VFA), alkalinity and ammonium concentrations, was measured throughout the entire full-scale experiment at the outlet of the hydrolysis tank and that of the ordinary primary settler, which served as a reference line. VFA concentrations were measured in wastewater and hydrolysate samples using three analytical methods: the 5 and 8 pH point titration methods and gas chromatography. A calibrated model was established to fit data regarding the Klagshamm WWTP's annual activated sludge operation of its secondary settler and wastewater composition. For modelling purposes and due to the small amount of data available, a linear regression method was established and used to complete the annual data set of the wastewater entering the Klagshamm WWTP. The full-scale data were incorporated into the calibrated model to simulate different scenarios of the activated sludge process with the purpose of saving energy (electricity) and resources (ethanol). Furthermore, an environmental (CO2-emissions) and economic evaluation was performed based on the data gathered from the full-scale experiment.

A VFA concentration of 43 mgCOD\textsubscript{VFA}·l\textsuperscript{-1} with no release of ammonium was achieved in the full-scale hydrolysis experiment; this amount was shown, by simulation, to substitute for 50% of the concentration of ethanol currently used. The amount of ethanol saved represents an equivalent electricity saving of 19 MWh for ethanol production, and the operation of fewer nitrification zones, while still maintaining full nitrification over two summer months, could ensure an additional electricity saving of 177 MWh. The evaluation and comparison of the results obtained using the three techniques showed that the 5 pH point titrimetric method was adequate and sufficiently accurate in this context to monitor VFA concentrations below 100 mg·l\textsuperscript{-1} at an alkalinity of 300 mgCa\textsubscript{CO3}·l\textsuperscript{-1}. The method can be easily implemented in the routine laboratory of the WWTP, and the measured VFA concentrations are equivalent to those obtained by gas chromatography.

For the Klagshamm WWTP, the modelling results and further evaluations showed that in-line primary sludge hydrolysis can decrease the dependence on external carbon utilization and can thereby reduce chemical costs and carbon dioxide emissions.

Key words primary sludge hydrolysis, carbon source, energy, resources, denitrification, environment, economy, volatile fatty acids, multiple pH point titration, wastewater treatment, activated sludge simulation.

Classification system and/or index terms (if any)
Carbon utilisation for extended nitrogen removal and resource savings

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Preface

This thesis is the result of an industrial PhD project between VA SYD and Water and Environmental Engineering at the Department of Chemical Engineering, Lund University.

The work has been conducted within the frame of VA-Teknik Södra with financial support from Svenskt Vatten (The Swedish Water & Wastewater Association).

The study focused on the potential of full-scale primary sludge hydrolysis for the generation of an internal carbon source to replace external sources for denitrification. An in-line, full-scale primary sludge hydrolysis experiment was conducted at the Klagshamn wastewater treatment plant (WWTP).

Activated sludge modelling was utilised to investigate the treatment capacity for nitrogen removal in the activated sludge tank at Klagshamn WWTP.

Furthermore, a chemical analysis method for monitoring and measuring volatile fatty acids was tested and compared with two other analytical methods.

The results of this thesis can be applied to wastewater treatment plants aiming to either decrease operational carbon supplements or even to replace them entirely for biological nutrient removal. Furthermore, a chemical analysis method is suggested that can be easily implemented into a routine laboratory at a WWTP.
Summary

Council Directive 91/271/EEC was the first European directive aimed at protecting the water environment from adverse effects by imposing strict regulations on the discharge of urban wastewaters. Since its implementation in 1991, several wastewater treatment plants (WWTPs) have been obliged to upgrade existing processes or even introduce new ones related to total nitrogen removal and stricter phosphorus removal to comply with the new discharge demands.

Consequently, in the 1990s, the municipal Klagshamn WWTP, situated in the south of Sweden, underwent several upgrades following a series of full-scale experiments. The efforts were focused mainly on removing nitrogen to make the plant’s operation as technically and economically feasible as possible. These experiments and process upgrades were initiated due to population increase and, above all, due to the demand of total nitrogen removal with very diluted wastewater entering the WWTP at very low concentrations of utilizable carbon for denitrification during the activated sludge process. Today, chemical pre-precipitation for phosphorus removal and post-denitrification with ethanol as a carbon source are applied at the plant. However, the market price for external carbon sources has gradually increased and has become one of the major wastewater treatment costs at the Klagshamn WWTP.

The biological degradation of primary sewage sludge, referred to as primary sludge hydrolysis, improves wastewater quality by making inaccessible carbon accessible for biological nutrient removal (BNR). Internal carbon sources can be easily utilized by microorganisms, which obviates the need to adapt to a new substrate. This process can be operated either ‘in-line’ within the main-stream of the primary settler or ‘off-line’ as a side-stream in an additional reaction tank separate from the main-stream process.

A full-scale in-line primary sludge hydrolysis experiment was conducted in one out of four primary settlers at the Klagshamn WWTP to test if the wastewater quality can be improved in terms of providing easily accessible carbon for possible pre-denitrification and the reduction of external carbon sources. The produced volatile fatty acid (VFA), alkalinity and ammonium concentrations were monitored throughout the entire full-scale experiment at the outlet of the hydrolysis tank and that of one of the ordinary primary settlers, which served as a reference line.
VFA concentrations were measured in wastewater and hydrolysate samples using three analytical methods: the 5 and 8 pH point titration methods and gas chromatography. The evaluation and comparison of the results obtained using the three techniques showed that the 5 pH point titrimetric method was adequate and sufficiently accurate in this context to monitor VFA concentrations below 100 mg·l$^{-1}$ at an alkalinity of 300 mgCaCO$_3$·l$^{-1}$. The method can be easily implemented in the routine laboratory of the WWTP, and the measured VFA concentrations are equivalent to those obtained by gas chromatography.

Dynamic wastewater treatment simulations are widely used to analyse altered process scenarios for possible upgrades and/or to provide improved insight into the dynamic behaviour of the activated sludge process at different wastewater compositions and temperatures. A calibrated model was established to fit data regarding the Klagshamn WWTP’s annual activated sludge operation of its secondary settler and wastewater composition. For modelling purposes and due to the scarce amount of data available, a linear regression method was established and used to complete the annual data set of incoming wastewater. The combination of full-scale experimental results with wastewater treatment modelling allows for rapid evaluation and provides an indication of the potential for resource and energy savings without full-scale experiments.

The full-scale data obtained were incorporated into the calibrated model to simulate different scenarios of the activated sludge process with the purpose of saving energy (electricity) and resources (ethanol).

A VFA concentration of 43 mgCOD$_{VFA}$·l$^{-1}$ with no release of ammonium was achieved in the full-scale hydrolysis experiment; this amount was shown, by simulation, to substitute for 50% of the amount of ethanol currently used. The amount of ethanol saved represents an equivalent electricity saving of 19 MWh that would otherwise be spent on ethanol production. Furthermore, the operation of fewer nitrification zones, while still maintaining full nitrification over two summer months, could ensure an additional electricity saving of 177 MWh.

The environmental and economic evaluation showed that in-line primary sludge hydrolysis could annually reduce the amount of ethanol (100%) by 76.5 m$^3$, which corresponds to a cost reduction of 692 000 SEK today. Furthermore, carbon dioxide (CO$_2$) emissions could be decreased by 285 tonnes per year.

For the Klagshamn WWTP, the modeling results and further evaluations showed that in-line primary sludge hydrolysis can decrease the plant’s dependence on external carbon utilization and can thereby reduce chemical costs and carbon dioxide emissions. Another important highlight of the present work is the lack of a negative impact on the methane potential in pre-precipitated primary sludge. Indeed, similar specific methane yields were obtained with raw and hydrolysed sludges.
Scope of the thesis

The present licentiate thesis is a compilation of work on the subject of carbon utilisation for extended nitrogen removal and resource savings. This work was performed during 2008-2013 at Water and Environmental Engineering at the Department of Chemical Engineering, Lund University and at the wastewater department of VA SYD at Klagshamn WWTP, Malmö.

A full-scale experiment was conducted in the summer of 2010 to investigate the implementation and efficacy of biological primary sludge hydrolysis in a primary settler at Klagshamn WWTP. Three analytical methods for measuring and monitoring the produced volatile fatty acids during the full-scale experiment were applied, and the results were evaluated and compared. Activated sludge modelling was applied to investigate different strategies for extended nitrogen removal, and energy and resource savings were evaluated by comparing outlet concentrations from the activated sludge system with and without inlet data from the full-scale experiment.

The results have been summarised in four scientific publications, including one peer-reviewed conference paper and three peer-reviewed articles in international journals.

Paper I demonstrates that pre-precipitated primary sludge from Klagshamn can undergo biological hydrolysis and that the resulting supernatant is of high quality for nitrogen removal. The paper also reports that no difference in the specific methane potential between raw and hydrolysed primary sludge was found.

Paper II describes the set-up and approach for performing full-scale, in-line primary sludge hydrolysis and investigates the potential of improved denitrification through the production of volatile fatty acids.

Paper III presents the calibration of a dynamic model for predicting the potential of combined in-line hydrolysis with predenitrification at a full-scale plant based on annual measurements at Klagshamn WWTP. The constructed model was applied in Paper II to investigate the potential energy and resource savings by implementing the results of the full-scale primary sludge hydrolysis experiment and different process configurations.
Paper IV provides a comparison among three analytical methods for measuring volatile fatty acids.
Acknowledgements

I express my deep gratitude to Karin Jönsson and Jes la Cour Jansen for accepting me as a PhD student. I am very thankful for your great support and valuable discussions and input, which enabled this study to progress. I am also very thankful for your encouragement that I attend conferences and seminars and particularly for counselling patience.

I also express my deep gratitude to VA SYD for financing my PhD and for enabling me to perform full-scale experiments.

My thanks also to Svenskt Vatten (Swedish Water & Wastewater Association) for their financial support.

Furthermore, I am very thankful to the technical and laboratory staff at VA SYD for their support and contributions to the full-scale experiment in 2010 and the data provided for my computer simulations.

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About the papers

This thesis comprises the following original papers which will be referred to in the text by their Roman numerals I-IV.


My contributions to the publications

**Paper I**: I wrote the Materials and Methods section, statistically evaluated the methane potential test and created the figures. Karin Jönsson wrote the rest of the paper. The experiments were designed by Karin Jönsson and performed by Helena Norlander. The article is based on Helena Norlander’s Master of Science thesis from 2008.

**Paper II**: I planned the experiment together with Karin Jönsson, Jes la Cour Jansen and Ulf Nyberg. I was responsible for the design, installation and functioning of the full-scale equipment used in the experiment performed at the Klagshamn municipal wastewater treatment plant. I performed the activated sludge simulations and evaluated the results. I wrote the paper with input from Karin Jönsson and Jes la Cour Jansen. The full-scale experiment analyses were performed by Disa Sandström.

**Paper III**: I planned and performed the calibration of the activated sludge model tool with Jes la Cour Jansen. I wrote the paper with input from Jes la Cour Jansen and Karin Jönsson. All analyses were performed by the staff at Klagshamn WWTP at VA SYD.

**Paper IV**: I planned the experiment together with Karin Jönsson. I set up and programmed the titration equipment, including the supply of the evaluation tools. I wrote the paper with input from Karin Jönsson, Victor Ibrahim and Disa Sandström. The analyses and titration procedures were performed by Disa Sandström.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AD</td>
<td>Anaerobic digestion</td>
</tr>
<tr>
<td>Alk.</td>
<td>Alkalinity</td>
</tr>
<tr>
<td>AS</td>
<td>Activated sludge</td>
</tr>
<tr>
<td>AUR</td>
<td>Ammonia utilisation rate</td>
</tr>
<tr>
<td>BNR</td>
<td>Biological nutrient removal</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>BSAP</td>
<td>Baltic Sea Action Plan</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DN</td>
<td>Denitrification</td>
</tr>
<tr>
<td>EBPR</td>
<td>Enhanced biological phosphorus removal</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionisation detection</td>
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<tr>
<td>FT-IR</td>
<td>Fourier transform infra-red</td>
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<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>HAc</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>HYPRO</td>
<td>Hydrolysis process. A process concept for primary sludge hydrolysis</td>
</tr>
<tr>
<td>LCFA</td>
<td>Long chain fatty acid</td>
</tr>
<tr>
<td>MBBR</td>
<td>Moving bed biofilm reactor</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>MWh</td>
<td>Megawatt hour</td>
</tr>
<tr>
<td>N/DN</td>
<td>Nitrification/Denitrification</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>Nitrite plus nitrate</td>
</tr>
<tr>
<td>NUR</td>
<td>Nitrate utilisation rate</td>
</tr>
<tr>
<td>OUR</td>
<td>Oxygen uptake rate</td>
</tr>
<tr>
<td>p.e.</td>
<td>population equivalents</td>
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<tr>
<td>pK\textsubscript{a}</td>
<td>Logarithmic acid dissociation constant</td>
</tr>
<tr>
<td>SCFA</td>
<td>Short-chain fatty acid</td>
</tr>
<tr>
<td>SEK</td>
<td>Swedish kronor</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended solids</td>
</tr>
<tr>
<td>SSH</td>
<td>Side-stream hydrolysis</td>
</tr>
<tr>
<td>TITRA5</td>
<td>5 pH point titration method</td>
</tr>
<tr>
<td>TITRA8</td>
<td>8 pH point titration method</td>
</tr>
<tr>
<td>TN</td>
<td>Total nitrogen</td>
</tr>
<tr>
<td>TP</td>
<td>Total phosphorus</td>
</tr>
<tr>
<td>WAS</td>
<td>Waste activated sludge</td>
</tr>
<tr>
<td>VFA</td>
<td>Volatile fatty acid</td>
</tr>
<tr>
<td>VSS</td>
<td>Volatile suspended solids</td>
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<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
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1 Introduction

1.1 Background

In 1991, the first European directive [91/271/EEC] concerning the discharge of urban wastewater to protect the water environment from adverse effects described as cultural eutrophication was introduced. This phenomenon occurs when an overload of nutrients, e.g., nitrogen and phosphorus, from untreated wastewater enters a water body and causes a rapid increase in the density of photosynthetic organisms. Hence, large blooms of algae and cyanobacteria become common mostly in the summertime. This condition destabilizes the aquatic ecosystem and threatens the survival of almost all aquatic living organisms, including fish (Campbell et al., 2005). Therefore, the European directive imposed quite stringent demands on nutrient release into receiving waters, and the restrictions are expected to be strengthened in the future.

For wastewater treatment plants (WWTPs), the discharge requirements take into account the sensitivity of the receiving water body and the number of connected persons and industries, which is expressed as population equivalents (p.e.) and can be classified as follows: (i) \( \leq 2 \, 000 \) p.e., (ii) \( 2 \, 000 \) to \( 10 \, 000 \) p.e. and (iii) \( \geq 10 \, 000 \) p.e. One population equivalent refers to an organic biodegradable load with a five-day biochemical oxygen demand (BOD\(_5\)) of 60 g of oxygen per day. WWTPs discharging treated wastewater into a sensitive water body, e.g., a river or an estuary, can have more stringent discharge requirements than WWTPs discharging into a less sensitive receiving water body such as the sea [91/271/EEC].

The manner in which wastewater is treated to fulfil the effluent requirements is primarily determined by the characteristics of a given stream of wastewater; for the Scandinavian climate in particular, wastewater temperature plays a major role (Ericsson, 1994). Wastewater composition itself is influenced by not only the number of connected inhabitants and industries but also the corresponding sewage systems’ configuration and retention times (Henze, 1992; Bixio et al., 2001).

Municipal WWTPs generally treat wastewater through mechanical, biological and chemical steps. The mechanical step comprises a screen, grit chamber and primary clarification for the removal of coarse material entering the WWTP.
A chemical treatment process is applied to improve the removal of suspended solids (SS), biological oxygen demand (BOD), phosphorus containing coagulant(s), e.g., metal salts, polymers or lime, from wastewater. Precipitation, can be employed at different locations within the main-stream process, typically described as pre-precipitation, simultaneous precipitation and/or post-precipitation.

Pre-precipitation involves the addition of a coagulant to raw wastewater, where the precipitant is removed in the primary settler of a WWTP and is thus described as primary sludge. If, for example, an activated sludge process is applied as the subsequent process, a remaining phosphorus concentration of $\approx 1 \text{ mgTP·l}^{-1}$ is required for bacterial growth.

Simultaneous precipitation is achieved by adding a coagulant to entering wastewater during an activated sludge process. The settled sludge in the secondary clarifier of a WWTP is then partially removed as waste activated sludge, and the remaining sludge is pumped back into the activated sludge process and is thus referred to as return sludge.

During post-precipitation, a coagulant is added to the secondary settled wastewater to remove the remaining phosphorus, SS and BOD, which requires an additional settling unit, a tertiary settler. The precipitated sludge is denoted as chemical or tertiary sludge.

For biological nutrient removal, the activated sludge process is the most commonly applied process among trickling filters and moving bed biofilm reactors (MBBRs). For total nitrogen removal, the activated sludge process requires two biological steps. First, ammonium is converted in the presence of free molecular oxygen to nitrate via nitrite; this process is described as nitrification. Second, nitrate is removed during the denitrification process (DN), where easily degradable carbon functions as an energy source for heterotrophic bacteria and nitrate is used as the terminal electron acceptor (Henze et al., 2002; 2008). Furthermore, the denitrification process depends on the concentration and ratio of available utilizable carbon and nitrate. During denitrification with scarce amounts of easily degradable carbon, an external carbon source, e.g., ethanol or methanol, can function as a supplement for carbon utilization and as an energy source (Christensson et al., 1994; Ericsson, 1994; Andersson et al., 1998). However, external carbon sources require natural resources and energy to be produced and transported, which contributes to increased carbon dioxide emissions and environmental pollutions (e.g., electricity required for the production of external carbon sources, fuel for transportation, traffic load, exhaust and air particles in cities and rural areas), in addition to increased wastewater treatment costs. However, the aforementioned directive dictated stricter discharge demands, which urged some wastewater treatment plants that perform only carbon and phosphorus removal to introduce extended nitrogen removal in their processes. The increased removal of nutrients not only entails changes in the
process configuration to treat wastewater but also requires increased energy for aeration during the activated sludge process and, if necessary, additional external resources (e.g., precipitant and/or organic carbon) for the removal of carbon, phosphorus and nitrogen. As the degree of nutrient removal that is demanded increases so does the amount of energy and resources and consequently costs required.

To increase the amount of easily accessible carbon in wastewater for biological nutrient removal (BNR), biological primary sludge hydrolysis has been demonstrated in several full-scale experiments and applications to be a cost-efficient process (Ericsson, 1994; Bixio et al., 2001) and an excellent source of organic carbon substituting external carbon (Barnard, 1984; Abufayed and Schroeder, 1986; Henze and Harremoës, 1990; Brinch et al., 1994; Ericsson, 1994; Isaacs and Henze, 1995; Canziani et al., 1995, 1996; Andreasen et al., 1997; Banister and Praetorius, 1998; Barajas et al., 2002; Bouzas et al., 2002; Elefsiniotis et al., 2004, 2006; Tykesson 2005, 2006; Jönsson et al., 2008; Ji et al., 2010; Yuan et al., 2010). Hence, the in-line primary sludge hydrolysis process should definitely be taken into consideration as a potential process to adopt when upgrading WWTPs for BNR (Rabinowitz and Oldham, 1986; Andreasen et al., 1997).

The modelling and simulation of activated sludge WWTPs has proved to be a valuable tool to evaluate process optimisations, process alternatives for WWTP upgrades and extended nutrient removal (Hoffmann and Klute, 1990; la Cour Jansen et al., 1993; Finnson, 1993; Dupont and Sinkjær, 1994; Hatziconstantinou et al., 1996; Funamizu et al., 1997; Brdjanovic et al., 2000; Carrette et al., 2001; Gernaey et al., 2004). In addition, primary sludge fermentation models have been developed to obtain the desired VFA concentration and fermenter behavior (Ribes et al., 2002; Chanona et al., 2006; Yasui et al., 2008; Donso-Bravo et al., 2009, 2010).

Furthermore, by dynamically simulating different activated sludge process configurations at a WWTP, the combination of full-scale in-line primary sludge hydrolysis experimental data and wastewater treatment plant simulation could be used to investigate to what extent energy and resources can be saved.
1.2 Hypothesis and objectives

The main hypothesis of this thesis is as follows: *In-line primary sludge hydrolysis can be applied for the production of VFAs as an internal carbon source to replace external carbon sources for extended biological nutrient removal and decrease the costs of chemical and carbon dioxide emissions.*

The broad objective of this study was to investigate the outcome of full-scale in-line primary sludge hydrolysis.

Emphasis was placed on determining the potential for pre-denitrification in an activated sludge tank to decrease external carbon source amendments and to save energy.

The following tasks were performed to complete this objective:

- Conducting in-line primary sludge hydrolysis on a full scale and comparing the measured concentrations of volatile fatty acids, alkalinity and ammonium-nitrogen between a normally operated primary settling tank and an in-line primary sludge hydrolysis tank.
- Testing, comparing and evaluating three different analytical methods for measuring and monitoring volatile fatty acids in wastewater and hydrolysate on a full scale for possible implementation at routine laboratories.
- Calibrating a dynamic wastewater treatment model and incorporating the full-scale experimental results into the calibrated model and later simulating different activated sludge scenarios to evaluate the potential for energy and resource savings.
- Evaluating the annual environmental (in CO₂ emissions) and economic (in Swedish kronor) impact of in-line primary sludge hydrolysis compared to the use of an external carbon source at the Klagshamn WWTP.
1.3 Thesis outline

The present thesis is composed of 6 chapters covering concepts, fundamentals and analyses concerning the findings reported in the four papers that are appended at its end.

Chapter 1 provides a general introduction to wastewater treatment and the main conventional processes applied at WWTPs where nitrogen removal is required. The problem of extended total nitrogen removal demand and carbon deficiencies is described. Primary sludge hydrolysis as a potential carbon source is introduced, as well as activated sludge modelling for evaluating purposes.

The first section of Chapter 2 defines hydrolysis in general terms and focuses on the definition within the wastewater community. In the second part of Chapter 2, volatile fatty acids (VFAs) are defined, and the different analytical methods for measuring VFAs are described, including a detailed description of the titrimetric methods. The chapter ends by presenting the principle of biological anaerobic sludge hydrolysis, in addition to enumerating other available sludge hydrolysis methods.

Chapter 3 begins with a presentation of the Klagshamn WWTP and a description of full-scale studies and process upgrades that have been conducted over the past 25 years. The full-scale in-line primary sludge experiment carried out at the Klagshamn WWTP in the summer of 2010 and a comparison of three analytical methods for measuring VFAs are further described. The chapter proceeds by evaluating the potential for energy and resource savings at Klagshamn by integrating the 2010 full-scale experimental results into a dynamic wastewater treatment simulation model. The model was calibrated to mimic the annual operation and performance of the activated sludge tank and secondary settler step. A linear regression method was established to compile an annual data set regarding wastewater composition and model the activated sludge process based on a small amount of available data. An environmental and economic feasibility study of in-line primary sludge hydrolysis was performed based on the results obtained from the full-scale experiment.

Chapter 4 discusses the main findings with respect to factors affecting VFA production by full-scale in-line primary sludge hydrolysis. Moreover, the applicability and reliability of the 5 pH point acid titrimetric measurements of VFAs and alkalinity are integrated into the study. The chapter also reflects on the need to merge in-line primary sludge hydrolysis with subsequent activated sludge modelling to simulate the overall behaviour of both processes. The implications of sludge hydrolysis for methane potential, savings in electricity and chemicals and biological nutrient removal are discussed at the end of this chapter.
Chapter 5 presents the major conclusions reached to improve the accessibility of easily degradable carbon for biological nutrient removal and reduce the utilization of external carbon sources and thereby cost and carbon dioxide emissions. Suggestions for future research are provided in Chapter 6, where different anaerobic sludge hydrolysis concepts are illustrated and incorporated into the Klagshamn WWTP process layout.
2 Definitions of hydrolysis and volatile fatty acids and the use of hydrolysis for biological nutrient removal

2.1 Hydrolysis

The word hydrolysis is derived from the Greek root words hydro, meaning “water”, and lysis, meaning “to break”; thus, hydrolysis literally means to break down using water. Figure 1 shows a polymer consisting of long chains of linked molecules being broken into smaller units by the addition of water (Campbell et al., 2005; Madigan et al., 2009). This process is a chemical reaction in which the bonds between the building blocks, shorter carbon molecule chains, are broken by the addition of water molecules. A hydrogen atom (-H) from the water attaches to one end of the broken molecule, and a hydroxyl group (-OH) binds to the adjacent departing molecule.

![Figure 1](image_url)

Figure 1.
Hydrolysis of a polymer into its constitutive monomers by addition of water (Campbell et al., 2005). Reprinted by permission of Pearson Education, Inc. Upper Saddle River, NJ.
Definition of hydrolysis by the wastewater community

Biological hydrolysis occurs in wastewater, which is a matrix rich of biopolymers and other macromolecules present in both soluble and suspended forms. The phenomenon is commonly referred to by the wastewater community as the generation of volatile fatty acids rather than simply the breakdown of polymeric substance into monomers (Morgenroth et al., 2002). Two definitions have been proposed to explain the term hydrolysis based on the following concepts: particle degradation and substrate degradation.

Particle degradation

The hydrolysis process in wastewater was described by Hobson (1987) as particle degradation. Hobson defined the process in terms of the available substrate-surface area (spherical, cylindrical and plate form) for degradation rather than in terms of the concentration of dissolved substrates. Hobson’s degradation model uses rates of 0.005 mm thickness per unit time for spherical, cylindrical and plate particle degraded from the outside only. The main mode of degradation considered is that in which a particle covered by bacteria is degraded at a constant rate per unit area of surface independently of the weight of the remaining substrate. Furthermore, Hobson (1987) stated that particles in the feed to a digester treating industrial waste or biomass specially prepared for biogas production may be relatively uniform compared to particles of human or animal faeces. On the other hand, Hobson (1987) also mentioned that only a part of the outer faecal surface may be degradable, whereas the rest may have already been degraded. Based on Hobson’s model (Hobson, 1987), Vavilin et al. (2008) developed a surface-related kinetic and two-phase model of hydrolysis of particulate (spherical and cylindrical) substrates. In the two-phase model, the first phase consists in bacterial colonization, in which the surface of a solid particle is covered by hydrolytic bacteria. Bacteria, whether in direct contact with or surrounding the particle’s surface, release enzymes and produce the monomers that are utilized by the hydrolytic bacteria (synergistic effect). The hydrolytic bacteria divide, and the daughter cells fall off into the liquid phase to attach to a new particle surface. The second phase occurs when an available surface is covered with bacteria and the surface is degraded at a constant depth per unit time (Hobson 1987; Vavilin et al., 2008).

Substrate degradation

For wastewater applications, Morgenroth et al. (2002) defined hydrolysis as the breakdown of an organic substrate into smaller products that can subsequently be taken up and degraded by bacteria.

A similar definition was provided by Ristow et al. (2006), who described hydrolysis as the extracellular enzymatic breakdown of polymers (particulate) into soluble monomers and dimers, which enter the subsequent acidogenesis stage of anaerobic
digestion. Furthermore, Morgenroth *et al.* (2002) differentiated hydrolysis into two types: (1) hydrolysis in which the primary organic substrate present in the original wastewater is broken down and (2) hydrolysis in which the secondary substrate, the substrate produced by bacteria, is broken down. The latter substrate can be composed of either intracellular macromolecules stored during normal metabolism or the cellular debris of decayed bacteria (Morgenroth *et al.*, 2002). Hydrolysis is the first step toward the generation of volatile fatty acids, which are discussed in the following section.
2.2. Volatile Fatty Acids

Volatile fatty acids (VFAs), also known as short-chain fatty acids (SCFAs), are a class of aliphatic carboxylic acids having six or fewer carbon atoms ($C_{n \leq 6}$) per molecule, including formic ($C_1$), acetic ($C_2$), propionic ($C_3$), butyric ($C_4$), valeric ($C_5$) and caproic ($C_6$) acid and their respective isomers, all of which are presented in Table 1 (Sansone and Martens, 1981; Scrimgeour, 2005).

Table 1.
Volatile fatty acids: nomenclatures, structural formula, molecular weights and acid dissociation constants.

<table>
<thead>
<tr>
<th>Systematic name</th>
<th>Common name</th>
<th>Structural formula</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanoic</td>
<td>Formic</td>
<td>H-COOH</td>
<td>CH$_2$O</td>
<td>46.02</td>
<td>3.75</td>
</tr>
<tr>
<td>Ethanoic</td>
<td>Acetic</td>
<td>CH$_3$-COOH</td>
<td>C$_2$H$_4$O$_2$</td>
<td>60.05</td>
<td>4.76</td>
</tr>
<tr>
<td>Propanoic</td>
<td>Propionic</td>
<td>CH$_3$-CH$_2$-COOH</td>
<td>C$_3$H$_6$O$_2$</td>
<td>74.08</td>
<td>4.86</td>
</tr>
<tr>
<td>n-Butanoic</td>
<td>n-Butyric</td>
<td>CH$_3$-(CH$_2$)$_2$-COOH</td>
<td>C$_4$H$_8$O$_2$</td>
<td>88.11</td>
<td>4.83</td>
</tr>
<tr>
<td>iso-Butanoic</td>
<td>iso-Butyric</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentanoic</td>
<td>n-Valeric</td>
<td>CH$_3$-(CH$_2$)$_3$-COOH</td>
<td>C$<em>5$H$</em>{10}$O$_2$</td>
<td>102.13</td>
<td>4.84</td>
</tr>
<tr>
<td>iso-Pentanoic</td>
<td>iso-Valeric</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexanoic</td>
<td>Caproic</td>
<td>CH$_3$-(CH$_2$)$_4$-COOH</td>
<td>C$<em>6$H$</em>{12}$O$_2$</td>
<td>116.16</td>
<td>4.85</td>
</tr>
<tr>
<td>iso-Hexanoic</td>
<td>iso-Caproic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Furthermore, all VFAs ($C_1$-$C_6$) are described as monocarboxylic acids having one carboxyl group (-COOH), as compared to di- and tricarboxylic acids, which contain two and three carboxyl functional groups, respectively.
The total amount of VFAs or individual VFA compounds (C$_1$-C$_6$) can be measured using different analytical methods. Biosensors are used to measure the total VFA concentration in samples to be analysed (Rozzi et al., 1997; Vanrolleghem and Lee, 2003). Individual VFA compounds can be quantified using different techniques such as vacuum and steam distillation (Zijlstra et al., 1977), fluorescence (Vanrolleghem and Lee, 2003), Fourier transform infrared (FT-IR) spectroscopy (Steyer et al., 2002; Vanrolleghem and Lee, 2003), high performance liquid chromatography (HPLC) in conjunction with ultraviolet (UV) detection (Freguia et al., 2010), gas-solid chromatography (Eastman and Ferguson, 1981), gas chromatography (GC) in conjunction with flame ionization detection (FID) (Wilson and Novak, 2009) and mass spectrometry (MS) (Hamlin et al., 2008).

Another analytical method for measuring volatile fatty acids and/or alkalinity is titrimetry. This method has been advantageous over other conventional techniques such as HPLC, GC-MS, GC-FID and FT-IR due to its ease of use, low running cost, robustness and equivalent accuracy.

The method allows for the direct titration of raw samples without any pretreatment and has the ability of determining more than one parameter (VFA and alkalinity) with the same accuracy as that achieved with a more sophisticated instrument. To provide a better understanding of this method, some historical background up to the state of art in this field will be provided.

In 1961, a titrimetric method for measuring VFAs in raw feed and in digested sludge was published. Using this method, the sample to be analysed had to be acid titrated to pH 4 and then further titrated to pH 3.3. Thereafter, the sample was boiled for 3 minutes and titrated back with a base to pH 4 and finally to pH 7 (Dilallo and Albertson, 1961).

Since then, efforts have been made to facilitate the laboratory procedure but also to improve the accuracy of the method compared to that achieved by more sophisticated instruments, e.g., gas chromatography. Consequently, in 1993, Moosbrugger et al. (1993a) investigated previously published titrimetric methods and concluded that they were either too elaborate or too approximate or both to be applicable and reliable for analysing and monitoring VFAs and alkalinity during, for instance, anaerobic digestion. Therefore, the researchers introduced the 4 and the 5 pH point titration methods, presented in Table 2, which were described as being simple, straightforward and accurate (Moosbrugger et al., 1993a, b, c). The 4 and 5 pH point methods are acid titrations in which, e.g., 0.1 M HCl is used as a titrant, starting from the initial pH of the sample ($\geq$6.7) down to either 3 or 4 pre-defined lower pH points (6.7, 5.9, 5.2 and 4.3) depending on the parameter to be analysed (alkalinity and/or VFA content).
The first pair of selected pH levels (6.7 and 5.9.) was selected due to its symmetrical location around the first dissociation constant of the carbonate weak acid/base buffer system \( \text{H}_2\text{CO}_3/\text{HCO}_3^- \), whereas that of the second pair (5.2 and 4.3) occurs approximately at the pK\(_a\) of the acetate weak acid/base buffer system \( \text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^- \); these two systems represent alkalinity and VFA content, respectively. Hence, the 4 pH point titration method is only capable of measuring alkalinity, whereas the 5 pH point titration method measures both alkalinity and volatile fatty acid content. Total measured volatile fatty acids are expressed as acetic-acid equivalents (mgCH\(_3\)COOH·l\(^{-1}\)) comprising all volatile fatty acid compounds, whereas alkalinity is expressed in units of calcium-carbonate equivalent (mgCaCO\(_3\)·l\(^{-1}\)).

The 5 pH point titration method was designed to monitor the VFA content and alkalinity in anaerobic digesters with VFA contents ranging from 100 to 1000 mgVFA·l\(^{-1}\) and high alkalinity (1990-2488 mgCaCO\(_3\)·l\(^{-1}\)). However, it was mentioned that this method is not applicable at VFA concentrations higher than half the total carbonate concentration (Lahav et al., 2002). Accordingly, Lahav et al. (2002) re-investigated the 5 pH point titration method and performed experiments at VFA concentrations below 100 mgVFA·l\(^{-1}\) at an alkalinity of 1000 mgCaCO\(_3\)·l\(^{-1}\). In the same study, an empirical investigation of the impact of high phosphorus, ammonium and sulphate concentrations on the determination of VFA and alkalinity was carried out. The authors concluded that the 5 pH point titration method was sensitive to sulphate concentrations higher than approximately 100 mg S·l\(^{-1}\), resulting in less accurate VFA measurements, whereas extremely high phosphorus and ammonium concentrations did not affect the results. Furthermore, either the loss of H\(_2\)S or inaccurate measurements of phosphate or sulphide, or a combination of both, contributed to significant errors in the carbonate alkalinity measurement. Therefore, Lahav et al. (2002) proposed an improved approach and calculation matrix (based on their empirical findings) for measuring the VFA concentration and total alkalinity more accurately. The improvement was made by including three additional pH points (2.7, 2.7<x<2.4 and 2.4) and the measurement of sulphide, which resulted in the development of the 8 pH point titration method presented in Table 2.

However, Ai et al. (2011) criticized the proposed 5 and 8 pH point titration methods by claiming that they do not account for all of the buffer subsystems that could introduce error into the calculation of total alkalinity. Therefore, the researchers considered that one additional pH point had to be added to take into account all weak acid/base subsystems (carbonate, acetate, nitrogen and phosphorus) in their mathematical model, which resulted in the 9 pH point titration method (Table 2). This method was designed and tested to measure low VFA (10 to 50 mgVFA·l\(^{-1}\)) and low alkalinity (20 to 100 mgCaCO\(_3\)·l\(^{-1}\)) concentrations more accurately. In the study by Ai et al., the VFA/total carbonate ratio ranged between 0.5 and 1, which is
above the critical ratio (VFA/alk. ≤ 0.5) for obtaining accurate and reliable results with the 5 and 8 pH point titration methods. On the other hand, Ai et al. (2011) did not state whether VFA and alkalinity concentrations higher than 50 mgVFA·l⁻¹ and 100 mgCaCO₃·l⁻¹, respectively, at concentration levels below or over 100 mgS·l⁻¹ could still be measured more accurately with their method than with the 5 and 8 pH point titration methods. Table 2 provides an overview of all previously discussed multiple pH point titration methods and the corresponding pH titration points utilized.

Table 2.
Multiple pH-point titration methods for VFA, alkalinity or simultaneous VFA and alkalinity measurements.

<table>
<thead>
<tr>
<th>pH-points</th>
<th>Parameter</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 Initial, 6.7, 5.9, 5.2</td>
<td>Alk.</td>
<td>(Moosbrugger et al., 1993b, c)</td>
</tr>
<tr>
<td>5 Initial, 6.7, 5.9, 5.2, 4.3</td>
<td>VFA, alk.</td>
<td>(Moosbrugger et al., 1993a)</td>
</tr>
<tr>
<td>8 Initial, 6.85, 5.85, 5.25, 4.25, 2.7&lt;x&lt;2.4</td>
<td>VFA, alk.</td>
<td>(Lahav et al., 2002)</td>
</tr>
<tr>
<td>9 Initial, 6.85, 6.35, 5.85, 5.25, 4.75, 4.25, 2.7&lt;x&lt;2.4</td>
<td>VFA, alk.</td>
<td>(Ai et al., 2011)</td>
</tr>
</tbody>
</table>

2.3. Biological primary sludge hydrolysis for VFA production

The organic matter found in raw wastewater typically consists of proteins (40-60%), carbohydrates (25-50%) and lipids (8-12%) (Tchobanoglous et al., 2003). The removal of carbon from municipal wastewater can be achieved by chemical precipitation and/or the biological activated sludge process. The sludges that occur must be separated from the main stream and transferred to a sludge treatment facility. The most common way to handle these sludges at WWTPs is via anaerobic digestion (AD) at an optimal temperature of 37°C (mesophilic) or 55°C (thermophilic) or a combination of both. The biogas produced during AD consists mainly of methane (65%) and carbon dioxide (35%), which can be utilized for energy-related purposes (e.g., heat, electricity or gas fuel for vehicles) (Henze et al., 2002).

The AD process can be described as the decomposition of organic matter by a complex microbial ecosystem in the absence of oxygen, through parallel sequences of metabolic pathways involving different kinds of interacting trophic groups (Cirne, 2006). The main steps of AD with biogas as the end product are
(1) hydrolysis, (2) acidogenesis, (3) acetogenesis and (4) methanogenesis. These processes are described in the following subsections.

**Hydrolysis**

The molecular size of removed carbon, e.g., in primary sludge, is too large for the carbon to pass through anaerobic microorganisms’ cell membranes and cannot be directly utilized. Thus, the molecular size must be reduced and the carbon must be converted into a more accessible form. This is achieved by enzymatic hydrolysis, which is the first step in the anaerobic digestion process. According to the degradation mechanism described by Morgenroth *et al.* (2002), anaerobic microorganisms produce and release their hydrolytic enzymes either in solution or directly onto the surfaces of the organic polymers (particulate substrate) to which they adhere. The degradation of various proteins, carbohydrates, lipids and cellulose is achieved by the hydrolytic enzymes protease, amylase, lipase and cellulase, respectively. The hydrolysis step has often been identified as the rate-limiting step in the anaerobic digestion process, especially when the substrate occurs in particulate form (Eastman and Ferguson, 1981; Vavillin *et al.*, 1996).

**Acidogenesis**

Acidogenesis, also described as fermentation (Tchobanoglous *et al.*, 2003; Cirne, 2006), is the second step of the AD process, in which hydrolysis products are further converted within bacterial cells (Cirne, 2006). The organic substrates from the hydrolysis step serve as both electron donors and acceptors (Tchobanoglous *et al.*, 2003), obviating the need for external electron acceptors (Cirne, 2006). The principal fermentation products in this step are acetate, hydrogen gas, carbon dioxide and single-carbon compounds, which can be directly utilized by methanogenic bacteria.

The degradation pathways of proteins, carbohydrates and lipids are mentioned below but are not explained or discussed in detail. All of the pathways depend on the substrate and microorganisms involved.

The hydrolysis products of proteins are amino acids, which can be further metabolized via the Stickland reaction to VFAs (C₂-C₅) or via anaerobic oxidation linked to hydrogen, which can lead to the production of acetic, butyric and propionic acid (Elefsiniotis and Oldhamn, 1994), valerate, ammonia, sulphide, carbon dioxide and hydrogen (Cirne, 2006) and valeric and iso-valeric acid (Chen *et al.*, 2007).

The Embden-Meyerhof-Parnas (EMP) pathway plays a major role in the fermentation of glucose (derived from the hydrolysis of carbohydrates), with pyruvic acid as the intermediate product. The fermentation of pyruvic acid can lead to the production of formate (C₁), acetate (C₂), propionate (C₃), butyrate (C₄), lactate, alcohols, ketones and aldehydes (Elefsiniotis and Oldhamn, 1994; Cirne, 2006).
The hydrolysis of lipids generates glycerol, which is mainly fermented to acetate, whereas long-chain fatty acids are further degraded via β-oxidation, which is achieved not by acidogenic but by syntrophic acetogens. Some specific acidogens can undergo β-oxidation and produce acetate and propionate (Elefsiniotis and Oldhamn, 1994; Cirne, 2006) and butyrate (Elefsiniotis and Oldhamn, 1994). The acidogenesis step is considered the fastest step in the AD process; however, it is limited by hydrolysis as the rate-limiting step (Cirne, 2006).

**Acetogenesis**

In the acetogenic step, obligate hydrogen-producing acetogens produce acetate, hydrogen and carbon dioxide from the degradation of long-chain fatty acids and volatile fatty acids.

**Methanogenesis**

Strictly anaerobic methanogenic bacteria convert carbon dioxide, hydrogen, formate, methanol, acetate and other available compounds to either methane only or methane and carbon dioxide (biogas).

Volatile fatty acids generated in the acidogenic step can also be employed for denitrification. Table 3 presents the stoichiometric reaction of various VFA components (C₁-C₆) and commonly used external carbon sources: ethanol and methanol. However, if only VFA must be anaerobically produced, the anaerobic digestion process must be terminated at the acidogenic stage, which Brinch et al. (1994) achieved by controlling the sludge residence time (12-24 hours) at ambient temperature (15-25°C) and pH (≤ 6).

Table 3.
Stoichiometric denitrification reactions with VFAs (C₁-C₆), ethanol and. The stoichiometric reactions do not include biomass (C₅H₇O₂N) formation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stoichiometric denitrification reaction without biomass formation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>2 NO₃⁻ + 5 HCOOH + 2 H⁺ → N₂ + 6 H₂O + 5 CO₂</td>
</tr>
<tr>
<td>Acetic</td>
<td>8 NO₃⁻ + 5 CH₃COOH + 8 H⁺ → 4 N₂ + 14 H₂O + 10 CO₂</td>
</tr>
<tr>
<td>Propionic</td>
<td>14 NO₃⁻ + 5 C₃O₂H₆ + 14 H⁺ → 7 N₂ + 22 H₂O + 15 CO₂</td>
</tr>
<tr>
<td>Butyric</td>
<td>20 NO₃⁻ + 5 C₄O₂H₈ + 20 H⁺ → 10 N₂ + 30 H₂O + 20 CO₂</td>
</tr>
<tr>
<td>Valeric</td>
<td>26 NO₃⁻ + 5 C₅O₂H₁₀ + 26 H⁺ → 13 N₂ + 38 H₂O + 25 CO₂</td>
</tr>
<tr>
<td>Caproic</td>
<td>32 NO₃⁻ + 5 C₆O₂H₁₂ + 32 H⁺ → 16 N₂ + 46 H₂O + 30 CO₂</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12 NO₃⁻ + 5 C₅H₅O + 12 H⁺ → 6 N₂ + 21 H₂O + 10 CO₂</td>
</tr>
<tr>
<td>Methanol</td>
<td>6 NO₃⁻ + 5 CH₃OH + 6 H⁺ → 3 N₂ + 13 H₂O + 5 CO₂</td>
</tr>
</tbody>
</table>

33
The type of carbon source used for denitrification has a direct effect on the denitrification rate. Endogenous carbon yields the slowest denitrification rate (expressed in units of, e.g., mgNO$_3$-N·gSS$^{-1}$·h$^{-1}$), whereas higher denitrification rates can be obtained by using carbon found in raw wastewater; moreover, some of the highest denitrification rates can be obtained with acetic acid, methanol or ethanol. Acetic acid is the substrate preferred by denitrifying bacteria due to its natural occurrence in wastewater, which implies that no substrate adaptation is required (Henze et al., 2002; Elefsiniotis et al., 2004). In contrast, some VFAs seem to have a partial or complete inhibitory effect on denitrification. The most inhibiting compound is isovaleric acid, followed in descending order of degree of inhibition by isobutyric, n-valeric, propionic and caproic acid. Volatile fatty acids of the iso-configuration are more inhibitory than acids of the n-configuration. The inhibition is always dependent on the concentration of the inhibition compound (Eilersen et al., 1995).

If utilisable carbon is not available in raw wastewater, ethanol or methanol is commonly used as an external carbon source. However, the use of methanol for denitrification entails a longer adaptation time for the growth of a specific type of bacterium, *Hyphomicrobium*, compared to the use of ethanol (Nyberg et al., 1992). Nyberg et al. (1996) showed that denitrification rates with ethanol (10 mgNO$_3$-N·gSS$^{-1}$·h$^{-1}$) were more than two times higher than with methanol (4.2 mgNO$_3$-N·gSS$^{-1}$·h$^{-1}$) with a substrate-adapted sludge. Furthermore, Æsøy et al. (1998) showed that the hydrolysate achieves the same denitrification rate as ethanol, whereas a lower COD/N-ratio was required for ethanol utilization (4.5 gCOD·gNO$_3$-N$^{-1}$) than with the produced hydrolysate (8-10 gCOD·gNO$_3$-N$^{-1}$). Elefsiniotis et al. (2004) reviewed the denitrification rates obtained with various organic carbon substrates (methanol, acetate, propionate, acetate and propionate, butyrate, valerate, mixed VFA and effluent VFA) and concluded that VFAs are excellent carbon sources, with acetic acid as the preferred VFA species. If acetic acid is completely utilized, butyric and propionic acid are then the most preferred.

**The generation of VFAs during full-scale primary sludge hydrolysis**

The biological removal of nitrogen requires appropriate amounts of easily accessible carbon for utilization. For denitrification, the carbon source can be either internal (e.g., in raw wastewater) or external (e.g., ethanol or methanol). External carbon source is mostly applied for denitrification and in cases in which the amount of easily utilisable carbon is insufficient. Internal carbon sources, produced on-site at a WWTP, can improve the quantity and quality of easily accessible carbon. One way to establish an internal carbon source is through primary sludge hydrolysis. Operational factors that can affect the production of volatile fatty acids through full-scale primary sludge hydrolysis are described in the following subsections.
**Sludge retention time**

The tested sludge retention times (SRT) in an acid fermenter reported were 2 days (Skalsky and Daigger, 1995), 2.5 to 4 days (Eastman and Ferguson, 1981), 1 to 5 days (Henze and Harremoës, 1990) and up to 6 days (Banister and Pretorius, 1998; Nicholls et al., 1986). The most reported and applied (anaerobic) SRT on a full scale with good VFA production was between 3 to 5 days (Henze and Harremoës, 1990; Barajas et al., 2002). However, the required SRTs are also dependent on the ambient temperature and solids concentration (Henze and Harremoës, 1990). It has been reported that a higher SRT entails a higher risk for methane gas development. In that case a lower VFA release, due to the VFA consumption in the acetogenic and methanogenic phase, can be expected.

**Solid concentration**

Various solid concentrations ranging from 0.5% – 2% (Banister and Pretorius, 1998) and to 6-7% (Eastman and Ferguson, 1981; Nicholls et al., 1986) have been investigated. The study of Banister and Pretorius (1998) demonstrated that a total solid (TS) concentration of more than 2% did not improve the VFA production per initial TS.

**Temperature**

The anaerobic sludge hydrolysis process is a biological enzymatic process and is therefore temperature-dependent. The optimal temperature for this process was determined to be 37°C (Eastman and Ferguson, 1981); nevertheless, this temperature cannot be expected in municipal wastewaters experiencing seasonal variations (summer/winter), especially not in temperate climates. The annual average wastewater temperature occurs between psychrophilic and mesophilic temperatures. Jönsson et al. (2008) reported that the initial hydrolysis rate (mg sCOD·gVSS⁻¹·h⁻¹) and the average VFA/soluble COD ratio in the hydrolysate of pre-precipitated hydrolysed sludge at 10°C and 20°C were 0.73 and 46% and 2.3 and 60%, respectively.

**pH**

The production of VFAs depends on the pH in a given hydrolysis reactor. Ahn and Speece (2006) observed that the highest extents of hydrolysis/acidification occurred under neutral pH conditions and diminished with decreasing pH. Eastman and Ferguson (1981) showed that the development of methane gas can be suppressed at pH levels below 6.8 because the AD process operates optimally under neutral pH conditions (Ahn and Speece, 2006).

**Oxidation reduction potential (ORP)**

The oxidation reduction potential provides a general indication of the oxidative status of a system being monitored. The ORP electrode can provide information
about the biological processes occurring under anoxic and anaerobic conditions (Vanrolleghem and Lee, 2003). Moreover, the production of VFAs in a primary settling tank is related to the oxidation reduction potential (ORP) (Chu et al., 1994; Barajas et al., 2002; Chang et al., 2002). The ORP measurement procedure was described and explained by Vanrolleghem and Lee (2003). The acidogenic fermentation takes place above -300 mV (Chu et al., 1994), whereas methanogenic fermentation occurs below -550 mV (Barajas et al., 2002). However, Vanrolleghem and Lee (2003) stressed that processes should not be controlled based on the absolute ORP.

**Release of nutrients**

In addition to the generation of VFA, the phenomenon of nitrogen and phosphorus release (Christensson et al., 1998) could increase the nutrient load during the activated sludge process. Although N and P release has been observed to be negligible in several studies, it must still be considered and monitored (Abufayed et al., 1986).

The wastewater entering a WWTP varies dynamically in terms of flow and temperature. These variations entail varying pollutant loads, hydraulic retention times, surface loading rates, sludge blanket heights and water velocities in the primary settler. To precisely control the sludge retention time in an in-line primary sludge hydrolysis tank, the amount of suspended solids that enter and exit (at the outlet and underflow) the hydrolysis tank and the amount of SS degraded must be measured and monitored, which can be achieved by either (preferably) on-line measurements or by taking daily composite samples. As in wastewater analyses, the amount of degraded suspended solids (e.g., VFA or soluble COD) must be measured during AD, where e.g., the amount of methane gas produced corresponds to the amount by which the volatile suspended solids content is reduced (0.45-0.60 m$^3$ CH$_4$·kgVSS$^{-1}$; Henze et al., 2002).

However, the production of VFAs depends on temperature and pH, which cannot be controlled on-site at a low cost and must be accepted as they are. Furthermore, it can be either very difficult or too costly to perform in-line primary sludge hydrolysis using advanced controllers to achieve a more stable process and optimal VFA production.

The main purpose of in-line primary sludge hydrolysis is to achieve simple and robust VFA production for BNR rather than optimisation for maximal VFA production. The excess production of VFAs (which can no longer be utilized in the DN process) would unnecessarily increase the oxygen demand in the activated sludge process, which would consequently require more energy and higher sludge production. In summary, the discussed parameters for the operation of in-line primary sludge hydrolysis can considered a framework and recommendations that
can lead to the reasonable and robust production of VFAs with a low risk of methane production.

Technical problems and risks associated with the operation of full-scale primary sludge hydrolysis

The operation of primary sludge hydrolysis on a full scale could cause a variety of technical problems and risks. In the study of Teichgräber (2000), the clogging of pumps and/or pipes was observed and an odour developed due to H$_2$S formation. These two problems can be definitely attributed to primary sludge hydrolysis when operated on a full scale. Furthermore, Teichgräber (2000) hydrolysed primary sludge in a closed reactor and assessed the risks of explosion, asphyxiation and/or poisoning due to the lethal effect of H$_2$S upon inhalation. H$_2$S is actually lethal at concentrations between 100 and 800 ppm, and immediate death will occur at concentrations above 800 ppm. Therefore, precautionary measures for developed gases must be seriously taken into consideration when primary sludge hydrolysis is operated with a hood on a reactor. Moreover, in the study by Teichgräber (2000), the condensate that formed in the hood was classified as being highly/very highly corrosive to concrete. However, the acidified primary sludge in the reactor was classified to be slightly corrosive to concrete but not to structural steel elements. The classifications were made according to the German standard DIN 4030 and 50930.

Other sludge degradation methods

The degradation of sludge for the production of VFAs can be achieved not only through biological anaerobic hydrolysis but also through other methods that could contribute to higher sludge degradation. The main purposes of the reported methods are to improve sludge degradation (less handling costs) and to increase biogas production. However, a few studies have focused exclusively on nutrient release and recovery.

These pretreatment methods are categorized as follows: (1) thermal, (2) mechanical, (3) chemical and (4) biological (beside anaerobic hydrolysis) or (5) combinations of different treatment methods.

Thermal

Thermal treatment is mostly applied at high temperatures ranging from 35 to 180°C and low sludge retention times of 1 minute to 10 hours (Davidsson et al., 2008; Carrère et al., 2010; Ge et al., 2010). Furthermore, high-pressure thermal hydrolysis (HPTH) at 100 kPa (1 bar) has been tested by Aravinthan et al., (2000).

Mechanical

Sludge can be mechanically degraded through sonication at low frequency (20-40 kHz) with a TS content between 2.3% and 3.2%. A collision plate in which
A sludge collides at a speed of 30-100 m·s⁻¹ at a pressure of 3000-5000 kPa (3-5 bar) has been tested. Furthermore, a high-pressure homogenizer can be applied for degradation and operates at a pressure of 900 000 kPa. Grinding with stirred ball mills can also be used for improved degradation (Carrère et al., 2010).

**Chemical**

The pH level has a direct effect on the enzymatic degradation of sludge. Therefore, the degradation and/or fermentation of sludge was tested under acidic (Ahn and Speece 2006; Ge et al., 2010) and alkaline conditions (Aravinthan et al., 2000; Ahn and Speece, 2006; Wu et al., 2010).

The degradation of sludge can be enhanced by applying (wet) oxidation. This can be done by adding either ozone (0.045-0.16 gO₃·gTS⁻¹) or hydrogen peroxide (2 gH₂O₂·gTS⁻¹) at 90°C for both reactions, with a retention time between 24-60 hours (Carrère et al., 2010).

**Biological degradation with the addition of specific enzymes**

The biological degradation of sludge proceeds by the action of hydrolytic enzymes. Several studies have reported on the addition of specific enzymes to improve the degradability of sludge (Aravinthan et al., 2000; Yang et al., 2010).

**Combined treatment**

The abovementioned degradation methods can also be combined to achieve higher degradation rates and possibly higher biogas production.

Ultrasound treatment with the addition of a base (mechanical-chemical), the addition of chemicals at high temperature (chemical-thermal) and ultrasound treatment at high temperature with the addition of enzymes (mechanical-thermal-biological) have been tested. These treatment methods, in addition to anaerobic biological hydrolysis, were summarized and reviewed in Davidsson et al., 2008 and Carrère et al., 2010.
3 Carbon, nitrogen and resource savings - The case of Klagshamn WWTP

3.1 Klagshamn WWTP description and process developments over the last 25 years.

In addition to nitrogen and phosphorus, carbon is one of the most important parameters in wastewater treatment that determines whether biological nutrient removal (BNR) can be naturally applied at ambient temperatures.

In wastewater, carbon appears in organic or inorganic bound forms. Both forms contribute to biological nutrient removal either as a substrate for bacterial metabolism or by increasing alkalinity (carbonate system).

The Klagshamn wastewater treatment plant was commissioned on February 1, 1974, for treating wastewater, and since then, energy savings have been a primary focus for its operators.

The Klagshamn municipal WWTP was originally designed and built for 90,000 person equivalents (p.e.) in southern Malmö with the Öresund Strait\(^1\) as the receiving water body. The incoming wastewater is mainly from households and was originally treated as depicted in Figure 2.

For mechanical treatment, two fine step-screens were installed to remove coarse debris and larger items coming from the sewer system that could damage the subsequent processing equipment and therefore reduce the overall treatment reliability and effectiveness. Thereafter, the wastewater flow was split into two parallel trains, which remained split until the outlet of the secondary settler. In total, two aerated grit chambers were built to remove grit consisting of sand, gravel, cinders or other heavy solid materials. Subsequently, primary sedimentation, which occurred in four rectangular tanks, was applied to remove readily settable solids and

\(^{1}\) The Öresund Strait connects the North Sea and the Baltic Sea.
floating material, thereby reducing the suspended solids content. This process was followed by two rectangular, aerated activated sludge tanks for carbon removal only, with eight subsequent rectangular sedimentation tanks. The treated water was then released into the Öresund with discharge demands of 80% for BOD and 30% for phosphorus removal (Vattendomstolen, 1968).

![Diagram of wastewater treatment process]

**Figure 2.**

The primary and waste-activated sludges were thickened in a gravity thickener before being pumped into a mesophilic anaerobic digester (37°C) for concomitant sludge treatment and biogas production. The digested sludge was then thickened in a gravity thickener and dewatered through centrifugation. The supernatants from both thickeners, termed ‘reject water’, were recirculated directly back to the inlet of the WWTP. The produced biogas was first utilised for heating the buildings and digesters in combination with an oil boiler that was later exchanged for a natural gas boiler. In the 1980s, a commercial greenhouse for vegetable growth was established next to the Klagshamn WWTP, and it was directly supplied with the produced heat. Heating pumps were also installed at the wastewater flow outlet to utilise part of the remaining wastewater heat for further energy savings. Nevertheless, due to the low annual average wastewater temperature (12°C), it was not economically sustainable to continue to operate these pumps after 15 years.
In the late 1980s, the Öresund Strait around Klagshamn was considered to be a sensitive ecological area, and therefore, additional and more stringent discharge demands were expected to be set for Klagshamn WWTP’s outlet water, including limits of 8-12 mgN·l$^{-1}$ and 0.3 mgP·l$^{-1}$. At that time, the activated sludge system was exclusively designed for biological carbon removal; thus, the expected demands for total nitrogen removal necessitated that the system include not only nitrification but also denitrification processes.

For the introduction of biological nitrogen removal, each activated sludge tank was subdivided into eight zones, and a new bottom aeration system was installed. These installations enabled each zone to be operated as either aerated or un-aerated. In addition, the installation of specialised stirrers enabled half of the activated sludge-tank to be operated under anoxic conditions.

The composition and ratio of the various components of the incoming wastewater are considered a key parameter for the selection and functioning of wastewater treatment processes, including biological nitrogen removal. Table 4 provides an overview of the wastewater characteristics at the Klagshamn WWTP between 1984 and 1992 (Nyberg 1994) and 2011 (VA SYD, 2012). The wastewater type was described as either very diluted (very dil.), diluted (dil.), moderate (mod.) or concentrated (conc.) according to the definitions in Henze et al. (2002, 2008).
Table 4.
Characteristics of the incoming wastewater to Klagshamn WWTP: Flow volumes; concentrations (TN, NH₄-N, TP and chloride); ratios; and loads of carbon, nitrogen and phosphorus (Nyberg, 1994; VA SYD, 2012).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>m³·d⁻¹</td>
<td></td>
<td>15 150*</td>
<td>23 822</td>
<td>25 550**</td>
<td></td>
</tr>
</tbody>
</table>

Concentration

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>COD₇</td>
<td>gO₂·m⁻³</td>
<td>420</td>
<td>441</td>
<td>-</td>
<td>Dil.</td>
</tr>
<tr>
<td>BOD₇</td>
<td>gO₂·m⁻³</td>
<td>118*</td>
<td>147</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>gSS·m⁻³</td>
<td>204*</td>
<td>207</td>
<td>251</td>
<td>Dil.*</td>
</tr>
<tr>
<td>TN</td>
<td>gN·m⁻³</td>
<td>33*</td>
<td>38</td>
<td>41</td>
<td>Dil.*</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>gN·m⁻³</td>
<td>-</td>
<td>19</td>
<td>27</td>
<td>-</td>
</tr>
<tr>
<td>TP</td>
<td>gP·m⁻³</td>
<td>7.7*</td>
<td>5.0</td>
<td>5.5</td>
<td>Dil.*</td>
</tr>
<tr>
<td>Chloride</td>
<td>gCl·m⁻³</td>
<td>-</td>
<td>300-900</td>
<td></td>
<td>Mod.-</td>
</tr>
</tbody>
</table>

Ratio

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1984-1992</th>
<th>2011</th>
<th>Load increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD₇/BOD₇</td>
<td>2.7-4.5 (3.6*)</td>
<td>3.9</td>
<td>Low*</td>
</tr>
<tr>
<td>BOD₇/TN</td>
<td>2.9</td>
<td>3.6</td>
<td>Low</td>
</tr>
</tbody>
</table>

Load

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>1984-1992</th>
<th>2011</th>
<th>Load increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₇</td>
<td>kgO₂·d⁻¹</td>
<td>1 788*</td>
<td>3 502</td>
<td>96%</td>
</tr>
<tr>
<td>SS</td>
<td>kgSS·d⁻¹</td>
<td>3 091*</td>
<td>4 931</td>
<td>60%</td>
</tr>
<tr>
<td>TN</td>
<td>kgN·d⁻¹</td>
<td>500*</td>
<td>905</td>
<td>81%</td>
</tr>
<tr>
<td>TP</td>
<td>kgP·d⁻¹</td>
<td>117*</td>
<td>119</td>
<td>2%</td>
</tr>
</tbody>
</table>

*Annual average value (1984-1992). **Incoming wastewater including internal loads at Klagshamn WWTP.

The values in Table 4 show that the incoming wastewater between 1984 and 1992 was very diluted for BOD₇ and diluted for SS, TN and TP, and therefore, a low BOD₇/TN ratio was obtained. According to the literature (Henze et al., 2002), this low ratio does not support enhanced denitrification.

Furthermore, beginning with the introduction of COD₇ measurements at Klagshamn WWTP, a high COD₇/BOD₇ ratio was obtained, indicating that the incoming organic matter is difficult to degrade and inaccessible for denitrification.

A low BOD₇/TN ratio and high COD₇/BOD₇ ratio indicate that an increased amount or improved quality of the incoming carbon in the wastewater has not occurred during the last 25 years at the plant. In this case, 'improved quality' refers to the increase in easily accessible and utilisable carbon for denitrification.
However, to fulfil the more stringent outlet demands in the 1990s, the nitrification and denitrification processes became a necessity despite the relatively limited volumes of the activated sludge tank (Table 5). To implement and improve these processes, different full-scale tests were performed to determine the most appropriate upgrading technology by taking only the existing basin volumes into consideration. The aim was to avoid extending the activated sludge system and the associated high construction costs.

Hence, four different process strategies (1-4) were applied as shown in Figure 3. Strategies 1 and 2 investigated whether the amount and quality of the incoming carbon was sufficient for predenitrification, whereas strategies 3 and 4 applied post-denitrification with the addition of methanol or ethanol as an external carbon source to comply with the discharge demands. These strategies were implemented between 1990 and 1992 at Klagshamn WWTP (Nyberg, 1994).

The strategies are briefly described as follows:

1. Primary sedimentation with subsequent predenitrification in the activated sludge tank.
2. Bypassing of the primary sedimentation tank, with the wastewater from the outlet of the grit chamber pumped directly into the activated sludge tank for predenitrification.
3. Pre-precipitation with FeCl₃ with subsequent nitrification and post-denitrification with methanol as an external carbon source.
4. Ethanol used instead of methanol as in strategy 3.
Pre-precipitation with FeCl$_3$ greatly improved suspended solids and phosphorus removal (Figure 3, strategies 3 and 4). As a consequence, a very low BOD$_7$/TN ratio of 1 in the activated sludge system was obtained, which was far less than the ratio needed for denitrification in practice (5-9 gBOD$_7$·gN$^{-1}$, Nyberg, 1994). However, this low ratio also resulted in a significantly improved ammonia utilisation rate (AUR) from 2 mgN·gVSS$^{-1}$·h$^{-1}$ to 4-5 mgN·gVSS$^{-1}$·h$^{-1}$ (Andersson et al., 1992). Thus, the results from the above-listed strategies revealed that nitrification could be established, whereas the requirements for predenitrification remained unlikely to be fulfilled. Therefore, the use of external carbon was determined to be unavoidable (Andersson et al., 1992; Nyberg et al., 1992, 1994).

The decision to apply an external carbon source was further motivated by the high nitrate utilisation rates (NUR) that were achieved using methanol (3-4 mgNO$_3$-N·gVSS$^{-1}$·h$^{-1}$) and ethanol (8.5 mgNO$_3$-N·gVSS$^{-1}$·h$^{-1}$) compared to the obtained NUR using the raw incoming wastewater as the sole carbon source (1-2 mgN·gVSS$^{-1}$·h$^{-1}$) (Andersson et al., 1992; Nyberg, 1994). In addition, the market price for ethanol (EtOH) and methanol (MeOH) at that time was much lower than today’s price. The final configuration and operation of Klagshamn WWTP in 1997 is illustrated in Figure 4.

**Figure 3.**
Four different full-scale process strategies investigating nitrification and denitrification at Klagshamn WWTP. Reproduced with permission from Ulf Nyberg (Nyberg, 1994).
Figure 4.

At the start of the construction of the Öresund Bridge between Denmark and Sweden, a population increase of up to 90,000 p.e. within Klagshamn’s catchment area was predicted. Andersson et al. (1998) estimated that the existing activated sludge capacity would not be enough to handle the increasing hydraulic and nutrient load. Therefore, a solution that could maintain a stable carbon, phosphorus and nitrogen removal process had to be found.

As a result, pre-precipitation was maintained for suspended solids and phosphorus removal in the primary settlers to maintain a high nitrification rate and capacity in the activated sludge tanks. The activated sludge system was employed only for nitrification with subsequent secondary clarification. Post-denitrification in four moving-bed biofilm reactors (MBBR) with ethanol as a carbon source and five subsequent dual-media sand filters were selected for denitrification and polishing, respectively (Andersson et al., 1998).
Currently, Klagshamn WWTP operates according to the process layout in Figure 5.

![Figure 5. Present process scheme of Klagshamn WWTP. Reproduced with permission from Ulf Nyberg (Nyberg, 1994).](Image)

### Table 5.
Current number, area and volumes of each process section at Klagshamn WWTP.

<table>
<thead>
<tr>
<th>Process Section</th>
<th>Number</th>
<th>Area (m²)</th>
<th>Volume (m³)</th>
<th>MBBR-carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grit chambers</td>
<td>2</td>
<td>2×200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary clarifiers</td>
<td>4</td>
<td>4×250</td>
<td>4×550</td>
<td></td>
</tr>
<tr>
<td>Activated sludge basins</td>
<td>2</td>
<td>2×2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary clarifiers</td>
<td>8</td>
<td>8×170</td>
<td>8×612</td>
<td></td>
</tr>
<tr>
<td>MBBR</td>
<td>2</td>
<td>2×550</td>
<td></td>
<td>36% filling degree</td>
</tr>
<tr>
<td>Dual media filters</td>
<td>5</td>
<td>5×44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In summary, by comparing the inlet data in Table 4 from 1984-1992 with those from 2011, the incoming wastewater flow has increased by 57%, and the concentrations of BOD₇, SS and TN have increased by 25%, 1% and 15%, respectively. However, total phosphorus decreased by 35%, which is attributed to the fact that since March 1, 2007, in Sweden, the allowable amount of phosphorus in laundry and
dishwasher detergents has been limited to 0.2 and 0.5% (in weight-weight percentage), respectively (SFS 2007:1304).

As a result of the higher inflow in combination with increased concentrations over the last 30 years, the loads of BOD₇, SS, TN and TP increased by 96%, 60%, 81% and 2%, respectively. Nevertheless, all compound concentrations from 2011 remained low due to the high infiltration of seawater, as indicated by the high chloride concentration varying between 300 and 900 gCl·m⁻³ (Table 4), and by the infiltration of groundwater and high water consumption of the connected households (Table 6).

Table 6.
Water balance at Klagshamn WWTP and water usage per capita from 2011.

<table>
<thead>
<tr>
<th>Water type</th>
<th>m³·year⁻¹</th>
<th>% of wastewater</th>
<th><strong>Per capita (l·d⁻¹)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater</td>
<td>9 497 000</td>
<td></td>
<td>355</td>
</tr>
<tr>
<td>Freshwater usage*</td>
<td>4 828 000*</td>
<td>51</td>
<td>181</td>
</tr>
<tr>
<td>Stormwater</td>
<td>593 690</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td>Drainage and leakage</td>
<td>4 075 000</td>
<td>43</td>
<td>152</td>
</tr>
</tbody>
</table>


Despite the increased hydraulic and nutrient loads for Klagshamn WWTP, the wastewater characteristics maintained a low BOD₇/TN ratio and a high COD₅/BOD₇ ratio. This finding demonstrates that an improvement in the wastewater quality has not been achieved over the last 25 years at Klagshamn WWTP, and pre-denitrification is still not favoured with today’s wastewater composition.

Since ethanol has been utilised for post-denitrification in the MBBR, it has become one of the major expenses as a result of its steadily increasing market price. Alternative solutions must be found to treat wastewater more economically. This cost reduction could be achieved by decreasing the nitrogen load in the MBBR and subsequently reducing the ethanol requirement.

The outlet concentrations from 2011, discharge demands and nutrient removal at Klagshamn WWTP are shown in Table 7.
Table 7.
Inlet and outlet concentrations including internal load, and discharge demands, loads and removal at Klagshamn WWTP in 2011 (VA SYD, 2012).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg·l⁻¹)</th>
<th>Load (kg·d⁻¹)***</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
<td>Discharge demand</td>
</tr>
<tr>
<td>BOD₅</td>
<td>150</td>
<td>4.8</td>
<td>10*</td>
</tr>
<tr>
<td>TP</td>
<td>5.5</td>
<td>0.17</td>
<td>0.3*</td>
</tr>
<tr>
<td>TN</td>
<td>41</td>
<td>7.6</td>
<td>12**</td>
</tr>
</tbody>
</table>

*Monthly average values; **Annual average value; ***Based on 25 550 m³·d⁻¹ (2012).

3.2 In-line primary sludge hydrolysis

Earlier studies carried out at Klagshamn WWTP concluded that the incoming wastewater was not sufficient as the sole carbon source for denitrification, and the addition of external carbon was necessary. Different studies have shown that on-site biological hydrolysis of primary sludge can improve the carbon quality, e.g., increase the soluble COD concentrations to a certain degree (Brinch et al., 1994; Canziani et al., 1995, 1996; Bixio et al., 2001; Barajas et al., 2002). The perception of total carbon has changed from that of a waste product that needs to be removed to an internal potential and cheap resource for process applications, such as denitrification and EBPR (Pitman et al., 1992; Skalsky and Daigger, 1995; Jönsson et al., 1996; Andreasen et al., 1997; Christensson et al., 1998).

For these reasons, Jönsson et al. (2008) investigated in a laboratory-scale experiment whether the pre-precipitated primary sludge could be biologically hydrolysed and used as an internal carbon source for denitrification to decrease the amount of dosed external carbon present in the MBBR. The authors proposed the activated primary tank concept (Barnard, 1984) to generate volatile fatty acids, and this was implemented in one of the primary sedimentation basins in 2010 (as depicted in Figure 6) at Klagshamn WWTP. This change was made by recycling the primary settler’s underflow to the influent to increase the sludge retention time in the primary settler, a process described as 'in-line primary sludge hydrolysis' in Papers II, III and IV. For the same process, different nomenclatures, such as 'main stream primary sludge hydrolysis' (Janssen et al., 2002) or 'activated primary settling tank' (Ribes et al., 2002), are used. The main idea of this process is to generate VFA under anaerobic conditions for nutrient removal and to make use of the existing units in the treatment plant, which would be more economical compared to building an additional basin (Barnard, 1984).
The study by Jönsson et al. (2008) showed that the hydrolysate was of good quality, with 16% of the total COD solubilised, of which 60% was VFA. The hydrolysate obtained denitrification rates equivalent to those achieved using acetate (3.1 mgNO$_3$-N·gVSS$^{-1}$·h$^{-1}$). The amount of hydrolysate that could be produced at full scale was predicted to decrease the required external carbon source by 50% and result in a decrease of 270 kgN·d$^{-1}$ in the MBBR; this was accompanied by using up to 25% of the activated sludge volume for predenitrification.

Norlander (2008) investigated the VFA production by hydrolysing pre-precipitated primary sludge, waste-activated sludge and mixed sludge (primary and waste-activated sludge). The release of ammonium and phosphorus accompanied by hydrolysis and the influence of stirring during the experiment were also observed. Thereafter, the hydrolysis rates for these sludges were calculated. Furthermore, an experiment was conducted to investigate the impact on the specific methane production of primary sludge and hydrolysed primary sludge. The same study confirmed the findings of Jönsson et al. (2008) that 50% of the external carbon source can be saved and further showed that there was no difference in VFA production between pre-precipitated and mixed sludge. Interestingly, no difference was found in VFA production between stirred and unstirred sludge hydrolysis.

The achieved data from Norlander (2008) were further analysed and are evaluated in Paper I. The hydrolysate produced from pre-precipitated primary sludge was shown to have low phosphorus content (release) and could therefore be applied directly for post-denitrification into the MBBR despite the stringent outlet demands for phosphorus at Klagshamn. The results also showed that there was no significant difference in the specific methane production between raw and hydrolysed primary sludge.

A full-scale, in-line primary sludge hydrolysis experiment was conducted in the summer of 2010 by transforming one primary settler into an in-line hydrolysis tank, as shown in Figure 6, to investigate the full-scale potential of VFA production. The alteration was achieved by decreasing the primary sludge outtake and constantly pumping the underflow, which was released just below the water surface to wash out the produced VFA with the incoming wastewater. The full-scale experiment is described in detail in Paper II.
Figure 6.
Process layout of Klagshamn WWTP during the full-scale experiment in the summer of 2010. Primary sludge hydrolysis is applied in one of the sedimentation basins in line 1. The other sedimentation basin is used as a reference.

The concentration of volatile fatty acids, ammonium-nitrogen and alkalinity were monitored at the outlet of both primary in-line settlers over the entire experimental period of 66 days. The produced VFA was measured with three different analytical methods: the 5- and 8-pH point titrations and gas chromatography (GC). The results achieved from these methods were compared and statistically evaluated in Paper IV.

The full-scale experiment in 2010 showed that a stable net production of 20 gCOD\text{HAc}\cdot{m}^{-3} was achieved, and no additional ammonium release was measured at the outlet of the in-line hydrolysis tank compared to the primary settler tank without in-line hydrolysis over a period of 28 days. No change in alkalinity was observed during the entire experiment, as discussed in Paper II.

The comparison among the three analytical methods showed that the titrimetric methods slightly overestimated the VFA concentrations compared to GC. Nevertheless, the 5 pH-point titration method was sufficient and accurate enough to monitor the full-scale primary sludge hydrolysis, whereas the 8 pH-point titration method did not always measure accurately.
3.3 Wastewater treatment modelling

Wastewater treatment models have been shown to provide rapid insight into the dynamic response of the process behaviour by changing operational factors that can later be evaluated and quantified without testing at full scale.

For these reasons, wastewater treatment modelling has already been applied for Klagshamn WWTP both to evaluate possible activated sludge process configurations for denitrification with an external carbon source (Aspegren et al., 1992) and to investigate whether ammonium-nitrogen peak flows in the activated sludge system caused by supernatant from the anaerobic digester can be circumvented (la Cour Jansen et al., 1993). These studies have shown that wastewater treatment modelling tools can avoid unnecessary costs and time consumption and minimise the risks of process disturbances related to full-scale testing.

Norlander (2008) tested and combined batch experiment results and used sludge modelling to predict and solve potential operational problems associated with primary sludge hydrolysis at Klagshamn WWTP. For these reasons, one of the two activated sludge systems with four subsequent clarifiers was set up at Klagshamn in a dynamic wastewater treatment tool EFOR (DHI, 2003). The activated sludge system was subdivided into eight zones that can be operated aerated or un-aerated. Norlander began collecting and implementing data into the model from the Öresundsverket WWTP in Helsingborg, which operates with main-stream hydrolysis. However, the chosen data were shown to be unreasonable and not reflective of Klagshamn’s primary clarified wastewater because pre-precipitation is applied for phosphorus removal and accompanied by a higher suspended solids removal compared to Öresundsverket, which operates with biological nutrient removal only. Hence, data from a hydrolysis batch experiment with three days of retention time and inlet wastewater concentrations of total nitrogen, ammonium-nitrogen, total phosphorus, suspended solids, total and soluble COD from Klagshamn were combined and shown to be more realistic than the earlier data from the Öresundsverket (Norlander, 2008). All simulations were conducted in steady state with a wastewater temperature of 18°C to evaluate the potential of implementing main-stream hydrolysis with subsequent predenitrification. Different inlet concentrations of suspended solids (70 and 76 mgSS·l⁻¹) and different numbers of denitrification zones (1-3) in the activated sludge tank were simulated. The resulting simulated data from the outlet of the secondary clarification tank under these different conditions were then compared and evaluated. Norlander (2008) concluded that main-stream hydrolysis with subsequent predenitrification can only be operated if the suspended solids concentration in the activated sludge tank is at least 4100 mgSS·l⁻¹ with two anoxic zones or 5200 mgSS·l⁻¹ with three anoxic zones,
maintaining full nitrification with a concentration of 0-1 mgNH₃-N·l⁻¹ in the outlet of the biological process. It was also found that the most suitable process configuration for main-stream hydrolysis was one un-aerated activated sludge zone removing 180-200 kgNOₓ-N·day⁻¹.

Notably, Norlander’s simulations were conducted at constant parameters, which provided indications that predenitrification could be achieved with main-stream hydrolysis and under full nitrification. However, dynamic and seasonal variations in wastewater flow, temperature and composition and/or in activated sludge operation, including suspended solids concentration, the amount of aerated and un-aerated zones, return and waste-activated sludge pumping, could all contribute to improved predenitrification evaluations and thus create additional opportunities to change operational factors, e.g., the number of anoxic zones in the activated sludge tank.

In Paper III, Klagshamn’s physical properties (Table 5), dynamic variations and laboratory data from the outlet of the primary settler until the outlet of the secondary clarifier were extracted and implemented in the same wastewater treatment tool (DHI, 2003) that Norlander (2008) used. The dynamic operation of the activated sludge process (varying amounts of anoxic zones and suspended solids concentrations) and subsequent clarifiers were calibrated to reflect one operational year at Klagshamn WWTP. However, the available data from different wastewater compositions obtained by routine laboratory analyses were not sufficient for modelling purposes.

As a result, a proper data treatment method was presented to obtain a complete annual time series of the incoming wastewater composition based on scarce measured laboratory values. Moreover, by comparing the simulated and actual data, a calibrated wastewater treatment model was created that reflected the annual overall performance of the activated sludge system and subsequent settlers at Klagshamn WWTP (Paper III). The calibrated model was established to function as a basis for further evaluations by, for instance, changing the wastewater characteristics and/or process strategies in the activated sludge system.

In general, routine measurements at WWTPs are not carried out under optimal conditions for modelling (e.g., sampling time intervals and wastewater composition). Paper III presents an effective treatment method for completing an annual data set by calculating the component ratio, e.g., COD/SS, and applying linear regression. The resulting equation can be used to calculate either the COD or SS (if only one of them is measured).

The calibrated model has proven valuable to quickly evaluate operational changes, including seasonal factors, over a one-year period at Klagshamn WWTP (Paper III).
Thereafter, the results of the full-scale experiment were applied to the calibrated model to evaluate the potential for total nitrogen removal by testing different process strategies for energy and resource savings, which is presented in Paper II.

This evaluation was conducted by modifying the wastewater characteristics in the originally calibrated model to mimic primary sludge hydrolysate by, for example, increasing the VFA-concentration with 20 mgCOD$_{\text{HAc}}·l^{-1}$. Furthermore, the activated sludge process operation was modified by increasing the number of anoxic zones up to half of the available activated sludge tank volume while maintaining the requirement for full nitrification.

Four different scenarios were simulated in the calibrated model with the results from the full-scale in-line primary sludge hydrolysis experiment (Paper II). The process configurations and strategies were configured in relation to the inlet wastewater temperature as described below.

The activated sludge process operated with the following conditions:

1) one anoxic zone at wastewater temperatures $\leq 11^\circ\text{C}$ and two anoxic zones at $\geq 12^\circ\text{C}$
2) one anoxic zone at wastewater temperatures $\leq 11^\circ\text{C}$, two anoxic zones at 12-14°C and three anoxic zones at $\geq 15^\circ\text{C}$
3) one anoxic zone at wastewater temperatures $\leq 11^\circ\text{C}$, two anoxic zones at 12-14°C, three anoxic zones at 15°C and four anoxic zones at 16°C
4) one anoxic zone at wastewater temperatures $\leq 11^\circ\text{C}$, two anoxic zones at 12-14°C and four anoxic zones at $\geq 15^\circ\text{C}$

The simulated data, including the total nitrogen load from the outlet of the secondary settler, were then compared with data from the original calibrated model simulated without hydrolysate.

Jönsson et al. (2008) estimated that 50% of the external carbon source (ethanol) in the MBBR could be replaced if all four primary settlers were operated as in-line hydrolysis tanks. Moreover, 25% of the activated sludge volume could be used for predenitrification during at least the summer period. These estimations were confirmed in Paper II, and in addition, two anoxic zones could be operated for up to seven months (May-November), and four anoxic zones could be operated for two months in the summer-autumn period (mid-August to mid-October).

Total energy and resource savings of 196 MWh of electricity and 76.5 m$^3$ of ethanol were calculated in Paper II. These savings were achieved by rapidly increasing from two to four anoxic zones for two months in the summer, which required less aeration and less ethanol. Thus, a total net saving of 177 MWh of electricity due to
decreased aeration in the activated sludge tanks and 19 MWh of electricity due to decreased production of ethanol could be obtained.

The simulations also showed that an annual average capacity increase of 120 kgN·d\(^{-1}\) could be established without the need to increase the filling degree in the MBBR or to extend the volume of the activated sludge system.

### 3.4 Environmental and economic evaluations

The full-scale experiment demonstrated that 40 mgCOD\(_{\text{HAc}}\)·l\(^{-1}\) can be achieved through primary sludge hydrolysis under summer conditions (Paper II). However, the VFA production is expected to vary, as has been observed since the introduction of in-line primary sludge hydrolysis at the Öresundsverket (Tykesson et al., 2005) in the 1990s. Therefore, an average VFA concentration of 30 mgCOD\(_{\text{HAc}}\)·l\(^{-1}\) with hydrolysis in the primary settler outlet at Klagshamn WWTP was assumed. To evaluate the environmental and economic feasibility for operating in-line primary sludge hydrolysis at Klagshamn WWTP, calculations 1 and 2 were applied to calculate the total amount of COD produced and the corresponding volume in pure ethanol (EtOH) per year. The factor 2.09 kgCOD·kgEtOH\(^{-1}\) in calculation 2 was applied according to literature (Henze et al., 2002).

Calculation 1, the annual production of hydrolysate in COD:

\[
\frac{9 497 000 \text{m}^3 \cdot 30 \text{gCOD}_{\text{HAc}} \cdot \text{kg}}{\text{year} \cdot \text{m}^3 \cdot 1000 \text{g}} = \frac{284 910 \text{kgCOD}_{\text{HAc}}}{\text{year}}
\]

Calculation 2, conversion of the annual hydrolysate (COD) into ethanol.

\[
\frac{284 910 \text{kgCOD}_{\text{HAc}} \cdot \text{kgEtOH} \cdot \text{EtOH} \cdot \text{year}}{2.09 \text{kgCOD} \cdot 1.65 \text{kgEtOH} \cdot \text{year}} = \frac{82 618 \text{litre EtOH}}{\text{year}}
\]

The annual VFA amount resulted in \(\approx 285\) tonnes COD\(_{\text{HAc}}\) equivalent to \(\approx 83\) m\(^3\) EtOH, comparable with data from Paper II, which found a value of 76.5 m\(^3\) EtOH. Furthermore, Klagshamn WWTP receives ethanol from two suppliers, who deliver ethanol at different purities and at different prices, denoted as EtOH-1 and EtOH-2. The annual consumption from 2011 and the market price from 2013 (Dimitrova, 2013), as well as the CO\(_2\)-equivalents (Gustavsson and Tumlin, 2012) for FeCl\(_3\) and ethanol, are presented in Table 8.
Table 8.
Annual cost and CO₂ equivalents of chemicals added to the wastewater treatment process.

<table>
<thead>
<tr>
<th>Product</th>
<th>Annual consumption</th>
<th>CO₂-equivalent</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃ (40%)</td>
<td>355 000 kgFeCl₃</td>
<td>0.145 kgCO₂·kgFeCl₃⁻¹</td>
<td>0.92 SEK/kgFeCl₃ (40%)</td>
</tr>
<tr>
<td>EtOH-1</td>
<td>347 000 kgCOD</td>
<td>1 kgCO₂·kgCOD⁻¹</td>
<td>0.87 SEK/kgCOD₇₀OH</td>
</tr>
<tr>
<td>EtOH-2</td>
<td>219 000 kgCOD</td>
<td>1 kgCO₂·kgCOD⁻¹</td>
<td>2.90 SEK/kgCOD₇₀OH</td>
</tr>
</tbody>
</table>


As noted above, Klagshamn applies pre-precipitation using iron (III) chloride (FeCl₃, 40% v/v) to maintain a stable concentration of suspended solids and a lower concentration of phosphorus in the outlet of the primary settlers corresponding to values of 5.1 mgFe³⁺·l⁻¹ of received wastewater and 0.92 mgFe³⁺·mgTP⁻¹, corresponding to ≈ 0.5 mole-Fe³⁺·mole-TP⁻¹. An annual total amount of 566 tonnes of COD was utilised in the MBBR for post-denitrification. The C/N-ratio was calculated to range from 2 to 6 gCOD·gN_removed⁻¹ in the MBBR and sand filters (Dimitrova, 2013).

The environmental and economic feasibility of in-line primary sludge hydrolysis was evaluated. Normal operation without in-line primary sludge hydrolysis is presented in Table 9, and operation with in-line primary sludge hydrolysis is shown in Table 10.

Without in-line primary sludge hydrolysis, the equivalent amount of CO₂ emission for FeCl₃ and EtOH production was calculated to be 617 tonnes of CO₂, and the cost of chemicals was ≈ 1.4 million SEK (Table 9).

Table 9.
Annual carbon footprint and cost analysis at normal operation.

<table>
<thead>
<tr>
<th>Product</th>
<th>Total amount in 2011</th>
<th>kgCO₂eqv.·year⁻¹</th>
<th>SEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃ (40%)</td>
<td>355 000 kg</td>
<td>51 475</td>
<td>461 500</td>
</tr>
<tr>
<td>EtOH-1 (COD)</td>
<td>347 000 kg</td>
<td>347 000</td>
<td>301 890</td>
</tr>
<tr>
<td>EtOH-2 (COD)</td>
<td>219 000 kg</td>
<td>219 000</td>
<td>635 100</td>
</tr>
<tr>
<td>Total</td>
<td>617 475</td>
<td>1 398 590</td>
<td></td>
</tr>
</tbody>
</table>

If in-line primary sludge hydrolysis is applied and no phosphorus release occurs, the carbon dioxide emission and chemical costs would decrease by 285 tonnes of CO₂ and 692 000 SEK (Table 10), respectively, compared to normal operation (Table 9).
Table 10.
Annual carbon footprint, chemical costs and savings with in-line primary sludge hydrolysis provided that no phosphorus release occurs.

<table>
<thead>
<tr>
<th>Product</th>
<th>Total amount in 2011</th>
<th>kgCO$_2$eqv·year$^{-1}$</th>
<th>SEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_3$ (40%)</td>
<td>355 000 kg</td>
<td>51 475</td>
<td>461 500</td>
</tr>
<tr>
<td>EtOH-1 (COD)</td>
<td>347 000 kg</td>
<td>347 000</td>
<td>301 890</td>
</tr>
<tr>
<td>EtOH-2 (COD)</td>
<td>219 000 kg</td>
<td>219 000</td>
<td>635 100</td>
</tr>
<tr>
<td>EtOH-1 (COD-VFA)</td>
<td>-65 910 kg</td>
<td>-347 000</td>
<td>-57 342</td>
</tr>
<tr>
<td>EtOH-2 (COD-VFA)</td>
<td>-219 000 kg</td>
<td>-219 000</td>
<td>-635 100</td>
</tr>
<tr>
<td>Total</td>
<td>332 565</td>
<td>760 048</td>
<td></td>
</tr>
</tbody>
</table>

Nevertheless, possible drawbacks related to in-line hydrolysis could include a greater release of phosphorus and suspended solids entering the activated sludge system, which could jeopardise the discharge demands, especially for phosphorus.
4 Discussion

Full-scale, in-line hydrolysis experiment at Klagshamn WWTP

The full-scale experiment with a production of 40 mgCOD\(_{\text{HAc}}\)·l\(^{-1}\) and no ammonium-nitrogen release showed that the hydrolysate can be a suitable carbon source for pre-denitrification at Klagshamn WWTP (Paper II). However, the primary sludge hydrolysis experiment took place during the summer of 2010, which means that the warm wastewater temperature enhanced the hydrolysis rate and thus the VFA production (Ferreiro and Soto, 2003; Jönsson and la Cour Jansen, 2006). To monitor and evaluate the in-line primary sludge hydrolysis process under more variable wastewater flow rates and temperatures, a longer experimental run would be necessary to measure variations in the hydrolysate compositions, e.g., VFA, total and soluble COD, suspended solids, ammonium-nitrogen, total phosphorus, alkalinity and pH. However, conducting a longer run was not possible due to operational problems at Klagshamn WWTP, and therefore, the full-scale experiment had to be abruptly stopped. Due to this circumstance, the time given (67 days) was too short to perform any optimisation of the hydrolysis process in terms of on-line monitoring, control and observing a possible increase in VFA production.

The Öresundsverket WWTP in Helsingborg was the first plant in Sweden to be designed for extended nitrogen removal and for operating enhanced biological phosphorus removal at full scale (Jönsson et al., 1996). Further, the operation of in-line primary sludge hydrolysis for biological nutrient removal has been applied for the VFA supply at the Öresundsverket since the beginning of the 1990s (Jönsson et al., 1996; Tykesson et al., 2005, 2006). In comparison, the influent average VFA concentration for both WWTPs was \(\approx 20 \text{ mg·l}^{-1}\), whereas the outlet concentrations from the primary settlers varied between 10 and 60 mgHAc·l\(^{-1}\) at the Öresundsverket (Tykesson et al., 2005, 2006) and levelled off at 42 mgHAc·l\(^{-1}\) during the hydrolysis experiment at Klagshamn WWTP (Paper II). The observed variations in VFA concentration at Öresundsverket can be mainly attributed to the high hydraulic loads that introduce dilutions and cause possible wash-out of the primary tank’s underflow. At regular hydraulic loads, the average outlet VFA concentration from the hydrolysis tank used to be \(\approx 50 \text{ mg·l}^{-1}\) (Jönsson, 1995; Tykesson et al., 2005, 2006). This level of variation (in flow and VFA concentration) was not observable at Klagshamn WWTP due to the short experimental duration and the beneficial weather conditions at that time. For more than six years, Öresundsverket has been a
good example of the application and use of in-line primary sludge hydrolysis to support and maintain the BNR process without any addition of external resources, e.g., FeCl₃ or an external carbon source (Jönsson et al., 2007).

**Comparison of the analytical methods for VFA determination**

The comparison study among three chemical analytical methods, including i) 5 pH-point titration (TITRA5), ii) 8 pH-point titration (TITRA8) and iii) gas chromatography (GC) for the determination of volatile fatty acids, has shown that TITRA5 was sufficient and accurate enough (within the 95% confidence interval) to monitor VFA (and alkalinity) in primary sludge hydrolysate (Paper IV).

The findings in Papers II and IV agree with those reported by Jönsson (1995) and Tykesson et al. (2006), where VFA concentrations in wastewater of less than 50 mgVFA·l⁻¹ at an average alkalinity of 300 mgCaCO₃·l⁻¹ (Papers II and IV) were analysed. These results promote the applicability of TITRA5 for analysing wastewater and primary sludge hydrolysate at lower VFA concentrations, which is in contrast to Lahav et al. (2002) and Ai et al. (2012), who reported that the 5 pH-point titration method is not able to accurately measure VFA concentrations below 100 mgVFA·l⁻¹.

**Wastewater treatment modelling**

Dynamic wastewater treatment modelling was applied to investigate possible predenitrification with the hydrolysate from in-line primary sludge hydrolysis. Different process configurations were established to evaluate the extent to which the amount of the external carbon source could be decreased.

However, problems were encountered during the calibration of the dynamic model at Klagshamn WWTP (Paper III). The available laboratory data were scarce (especially during bank holidays), which made it problematic to achieve a complete data set for one operational year. In general, most of the laboratories at WWTPs measure compounds that are most relevant for monitoring the biological and chemical process (e.g., COD₅₅, BOD₇, NH₄-N, PO₄-P, SS, etc.) and are directly related to the discharge demands (BOD₇, TN and TP). Furthermore, biological process rates, such as the oxygen uptake rate (OUR), AUR, NUR and hydrolysis rate, are not commonly measured at WWTPs, but these would contribute to a more accurate model. To increase the amount of available data for modelling purposes, either daily measurements, e.g., composite samples, need to be introduced or data from on-line instruments could be used. However, the data from on-line instruments could only be useful if maintenance is carried out on a regular basis. The analysis of additional compounds depends on the intentions and financial resources of the modeller.

The calibrated model and the full-scale results were merged, and four different process scenarios were tested at a constant VFA concentration of 43 mgCOD₃₅₅·l⁻¹
However, the VFA generation is affected by the ambient temperature (Ferreiro and Soto, 2003; Jönsson and Janssen, 2006), which could result in high VFA production in the summer but low production in the winter, and by the hydraulic variations, as described in the studies conducted at Öresundsverket by Tykesson et al. (2005, 2006). High variations are not expected to occur often due to the very long wastewater pipeline to Klagshamn WWTP and an inlet equalisation tank at the plant. Despite this, the constant VFA concentration in the model could be questioned, as VFA variations influence the decision regarding the number of anoxic zones operated in the activated sludge tank and, subsequently, the amount of external carbon needed to fulfil the discharge demands for total nitrogen.

Nevertheless, the calibrated model provided good insight into the potentials for predenitrification in the activated sludge system but not into the behaviour of the biological process in the in-line primary settler tank. To simulate in more detail in-line primary sludge hydrolysis, Ribes et al. (2002) developed a dynamic activated primary tank model from a pilot plant study. This model was meant to simulate outlet concentrations of the following: VFA and suspended solids at different sludge retention times (3.7-4.7 days), total solids concentration, biological hydrolysis rates and VFA generation, the recirculation rate of the underflow and settling behaviour due to elutriation of the VFA. The model constructed by Ribes et al. (2002) could indicate the risks for sludge wash-outs and improve VFA generation. It would have been favourable to merge both models (Ribes et al., 2002; DHI, 2003) to improve the VFA generation prediction and to predict the dynamic behaviour of the total solids concentration and sludge blanket height in the primary settler outlet with the available dynamic data from Klagshamn WWTP.

Environmental and economic feasibility

The environmental feasibility of applying in-line primary sludge hydrolysis has been mainly assessed through the minimisation of carbon dioxide emissions. In all presented scenarios, i.e., normal operation and in-line primary sludge hydrolysis, carbon dioxide emissions could be decreased. Nevertheless, possible drawbacks with in-line hydrolysis include a higher release of phosphorus and suspended solids entering the activated sludge system, which could jeopardise the discharge demands, especially for phosphorus. Therefore, the amount of precipitant might need to be increased. In the case of Klagshamn WWTP, increased pre-precipitation might be advantageous compared to post-precipitation. This advantage may be present because the sand filters might overload faster, in which case the high energy-demanding backwashing step would be required more often to remove the accumulated particles. By increasing the amount of FeCl₃ in the inlet, problems in the activated sludge process might arise due to low alkalinity, low pH and phosphorus deficit. This, in turn, would entail disturbances and periodically inhibit
the activated sludge process, which could lead to increased nutrient release into the receiving water body and promote eutrophication or algae blooms.

The economic feasibility of in-line primary sludge hydrolysis has been shown to be dependent on the varying market price for FeCl₃ and ethanol and on the amount of VFA produced. It is possible to reduce the expenses related to the external carbon source by achieving higher VFA amounts through process optimisation. Under stable production of sufficient amounts of VFA, in-line primary sludge hydrolysis could even compete with external carbon sources purchased at low market prices. However, despite the minimal contribution of FeCl₃ to the total chemical cost (< 10%) at Klagshamn WWTP, the increasing bulk prices could render in-line primary sludge hydrolysis less attractive for WWTPs with high phosphorus content in the hydrolysate. The release of ammonium-nitrogen, and the consequent higher energy consumption for nitrification, was not considered in this study because during the full-scale experiment in the summer of 2010, no ammonium-nitrogen release was noticed, and no additional release was anticipated to occur at lower wastewater temperatures.

**Impact on gas potential of in-line primary sludge hydrolysis**

*Paper I* shows that there was no significant difference in the specific methane production between fresh primary sludge (or raw sludge) and biologically hydrolysed primary sludge. No studies were found that focused specifically on the optimal carbon distribution for BNR and the effects on biogas production. To evaluate at full-scale whether hydrolysing primary sludge affects the methane production in the mesophilic digester, all four primary settlers should be operated as in-line hydrolysis tanks with subsequent predenitrification.

Furthermore, the question of whether biological primary sludge hydrolysis could increase the treatment capacity for anaerobic digestion and thus improve the digestion process becomes valid. This possibility is raised by the fact that the first and second anaerobic digestion process steps already take place in the activated primary tank, and therefore, either a lower anaerobic reaction volume might be required or a higher organic load of hydrolysed sludge might be accommodated. This potential might be of interest for WWTPs that have a high organic load but short sludge retention time in the digester.
Future aspects for higher total nitrogen removal

This thesis focused not only on replacing external carbon sources to decrease the wastewater treatment costs but also investigated whether more nitrogen could be removed with the present plant layout at Klagshamn WWTP.

The Swedish Environmental Protection Agency (Naturvårdsverket) stated that more total nitrogen must be removed to improve the water quality in the Baltic Sea starting in 2016, which is detailed in the Baltic Sea Action Plan (BSAP). The goal is to diminish the annual amount of released total nitrogen into the Baltic Sea by 3000 tonnes. Furthermore, a nutrient emission trade market for nitrogen will be established that will allow the purchase and sale of certificates for 1 kg of nitrogen. Under this scheme, wastewater treatment plants that remove more total nitrogen than is required (≥82%) will be able to sell 1-kg nitrogen certificates for each extra kg they remove to WWTPs that have a lesser degree of total nitrogen removal (Naturvårdsverket, 2009).

Klagshamn’s receiving water body is the Öresund Strait, and 80% of the total nitrogen was removed in 2011, which is 5% more than the removal demand set by the EU directive (91/271/EEC, article 5). However, with the BSAP coming into effect, the effluent discharges are expected to be more stringent for total nitrogen. The increased removal of nitrogen could lead to the increased utilisation of external carbon sources and higher treatment costs, which could increase the wastewater levy to the consumer. However, in-line primary sludge hydrolysis has been shown to be a potential candidate to treat wastewater with increased nitrogen removal demands at a low cost (Paper II). The more total nitrogen that can be removed with in-line primary sludge hydrolysis, the more rewarding it could become to trade nitrogen certificates with the potential to additionally decrease the treatment costs.
5 Conclusion

The total carbon in the incoming wastewater can undergo hydrolysis to improve the accessibility of easily degradable carbon for nitrogen removal.

Biological in-line primary sludge hydrolysis is an inexpensive process that is easy to implement at full-scale WWTPs and has the potential to produce internal utilisable carbon at low costs.

Biological in-line primary sludge hydrolysis for the production of VFA with subsequent predenitrification has the potential to decrease the total nitrogen load in the MBBR and to decrease by 50% the external carbon amount and costs. At the same time, this process could increase the treatment capacity for total nitrogen at Klagshamn WWTP.

Combining full-scale experiment results with wastewater treatment modelling can provide a rapid evaluation of the behaviour of the activated sludge process and indications of the potential for resource and energy savings without performing full-scale tests.

Compared to sophisticated instruments, the 5 pH-point titration method is cheap to operate, robust and could easily be implemented at WWTP laboratories. Total VFA and alkalinity can be measured in primary sludge hydrolysate with the 5 pH-point titration method even at low concentrations, and the resulting total VFA concentrations are equivalent to the results obtained with GC.

Despite the low VFA and alkalinity concentrations in the hydrolysate, the 5 pH-point titration method delivers reliable results even though the method was originally designed to monitor anaerobic digesters with high VFA and alkalinity concentrations.

The costs for external carbon sources could be reduced by sludge hydrolysis depending on the nutrient release and additional associated costs.
6 Further suggestions and studies

6.1 Different anaerobic sludge hydrolysis concepts

This thesis has shown that resource usage, electricity and carbon dioxide emissions could be diminished through in-line primary sludge hydrolysis by modifying the primary settler’s function and activated sludge process strategy. Nevertheless, in-line primary sludge hydrolysis is one of many process applications that can improve the BNR. In addition to this process, other full-scale process concepts based on anaerobic biological hydrolysis are presented and described briefly, and these are integrated into the illustrations of Klagshamn’s plant layout. The selection criteria were based on the highest likelihood of being established at Klagshamn WWTP. Furthermore, all suggested process configurations in this chapter are of hypothetical character and are designed for the production and extended production of VFA for BNR.

The HYPRO concept

The HYdrolysis PR Occess concept was developed through a concerted action between research institutions and companies from Norway, Sweden and Denmark (Henze and Harremoës, 1990). In Figure 7, Line 1 presents in-line primary sludge hydrolysis, where the primary settler is altered to be an activated primary tank. Line 2 presents the HYPRO concept, where the underflow from the primary settler is hydrolysed in an additional reactor. The HYPRO concept could be applied at Klagshamn WWTP if the hydrolysis process needs to be operated under more controlled conditions or if eliminating the risk for primary sludge wash-out at a high flow rate is considered important. However, to implement this configuration at Klagshamn WWTP, a slight modification of the original concept was made, where the primary sludge underflow can be bypassed from the HYPRO tank directly to the gravity thickener for possible maintenance or if operational problems occur (Figure 7).
Side-stream hydrolysis of waste-activated sludge

The production of volatile fatty acids from waste-activated sludge (WAS) via side-stream hydrolysis (SSH) has been shown to function well. However, the hydrolysis yield is strongly dependent on whether primary sedimentation is applied (Jönsson and la Cour Jansen, 2006). WAS without primary sedimentation has higher initial hydrolysis rates and higher soluble/total COD-ratios. However, the time to reach the maximum soluble COD is twice as long compared to WAS with pre-sedimentation (Jönsson and la Cour Jansen, 2006). Two different types of SSH are presented in Figure 8 as follows: Line 1, SSH is fully implemented into the return sludge stream; Line 2, only part of the WAS stream is hydrolysed in a bypass reactor, and the hydrolysate is released back into the WAS stream.

Figure 8.
Side-stream hydrolysis configuration of waste-activated sludge. The SSH-configurations were reproduced with permission from Karin Jönsson and Jes la Cour Jansen (Jönsson and la Cour Jansen, 2006).
In-line primary-sludge hydrolysis in combination with side-stream hydrolysis

In-line primary sludge hydrolysis is applied in all four primary sedimentation tanks, and either side-stream hydrolysis in the main-return-sludge stream (Line 1) or in a bypass reactor (Line 2) could be applied to increase the total VFA production (Figure 9).

**Figure 9.**
Combinations of primary-sludge hydrolysis with side-stream hydrolysis of WAS for increased VFA production.

The HYPRO concept in combination with side-stream hydrolysis

For the same reasons as described for in-line primary sludge hydrolysis with SSH, the HYPRO concept could be applied in combination with the two different SSH alternatives (Figure 10).

**Figure 10.**
Combinations of the HYPRO-concept with side-stream hydrolysis of WAS for increased VFA production.
The production of VFA in the primary settlers has been shown to have the potential to replace 50% of the annual amount of external carbon source at Klagshamn WWTP. To increase the amount of produced VFA and consequently decrease further external carbon utilisation, the presented concepts in Figure 7 and Figure 8 were combined and integrated into the plant layout of Klagshamn WWTP; see Figures 9 and 10.

In Figures 7 and 9, the HYPRO hydrolysate enters together with the primary settled wastewater directly into the activated sludge tank with predenitrification and subsequent nitrification. However, it is assumed that the HYPRO hydrolysate contains a high amount of suspended solids, which could cause lower nitrification rates and therefore require a greater (nitrification) volume; thus, predenitrification cannot be applied. If predenitrification cannot be operated in the activated sludge tank, the HYPRO concept might become useless in that sense. To maintain high denitrification and nitrification rates with the HYPRO hydrolysate, filtration is necessary to remove the suspended solids. However, activated sludge modelling might be needed to simulate and later evaluate the maximal tolerated suspended solids concentration entering the activated sludge tank for maintaining full nitrification and predenitrification.

Among all the presented process configurations presented in Figures 7 to 10, the most controllable process is found to be the HYPRO concept in combination with the bypass SSH (Figure 10). This process configuration provides the opportunity to control the flow and thus the retention time in the reactors. Furthermore, primary sludge wash-outs that could cause disturbances in the subsequent treatment process are more or less eliminated. However, this configuration requires extra volume that might need to be built and requires space and extra equipment (pumps, pipes) as well as instruments that might need to be installed. All of these additions are associated with higher costs compared to the simple alteration of a primary tank. Mechanical treatment in terms of disc or drum filtration or centrifugation to achieve a higher quality of supernatant was not taken into account in the plant layouts, but it is certainly a necessity.
6.2 Further studies

**Set-up of a plant-wide modelling tool for the evaluation of different process configurations and optimal distribution of the incoming carbon**

In general, Sweden and Denmark have different approaches to treating wastewater at WWTPs that serve up to 100 000 p.e.; primary sedimentation is used in Sweden, and no primary sedimentation is used in Denmark.

In Denmark, raw wastewater without primary sedimentation enters the AS process, which requires higher AS volumes and longer retention times compared to pre-sedimented wastewater. However, more biomass is produced that could be hydrolysed for VFA production to maintain BNR, and the excess carbon may be utilised for biogas. In Sweden, WWTPs mostly have primary sedimentation to remove the incoming carbon for anaerobic digestion. However, the extensive carbon removal in a primary settler could lead to an insufficient amount of carbon for the BNR process, in which case external carbon would need to be applied. Both countries show that both concepts work to fulfil the EU directive for discharging wastewater. However, it is unclear which plant-wide process configuration is the better option in terms of environmental impact and economic sustainability considering the release of CO₂, N₂O, NO and CH₄ and energy and resource requirements. Therefore, a plant-wide modelling tool to evaluate these parameters is of interest. One recently published study has begun to examine these plant-wide parameters (Arnell and Jeppsson, 2013).

**Robustness and accuracy of the titrimetric method with different compounds and wastewaters**

Studies have shown that the titrimetric method for VFA and alkalinity determination becomes less accurate or completely useless in the presence of lactic (Anderson and Yang, 1992) and citric acid (Lahav *et al.*, 2005). However, neither study discussed the concentrations of lactic or citric acid at which the method begins to become inaccurate. Therefore, a continuity study to investigate the method’s limitations and interferences in, for example, industrial wastewater samples containing lactic and/or citric acid, needs to be carried out. Furthermore, other organic compounds (mono-, di- or tricarboxylic acids) similar in structure to lactic or citric acid could be investigated. Such a study could provide answers to the question of whether the 5 pH-point titration method could also be applied for wastewater types (e.g., landfill leachate and wastewaters from food and pulp industries) containing different compounds that could potentially disturb the VFA and alkalinity measurements. These compounds include organic acids with pKₐ values within one unit of the pKₐ of the acetate or carbonate weak acid/base buffers.
7 References


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