



Linnæus University

Faculty of Health and Life Sciences

Bachelor Project Work

Effects of Heat Transfer Fluid from District Heating Networks on Activated Sludge

-A respirometric analysis using a dilution series to assess disruption of biological treatment processes in wastewater treatment facilities

Victor Bergseije
2014-04-29
Subject: Environmental Science
Level: Ground level
Nr:

1 Table of Contents

1	Introduction.....	1
1.1	Function and Formation of a District Heating System.....	1
1.2	Contamination and Treatment of the Heat Transfer Fluid.....	2
1.3	Leakage of the Heat Transfer Fluid and Exposure to Recipients	3
2	Materials & Methods.....	6
2.1.1	Respirometric Bioassay	6
2.1.2	External Analysis of Metals.....	12
3	Results and Discussion	13
3.1	Results from Respirometric Bioassay of Kalmar Energi DH Water.....	14
3.1.1	Oxygen Uptake Rate	14
3.1.2	Inhibition Percentage.....	17
3.2	Results from Respirometric Bioassay of Vaxjo Energi DH Water.....	18
3.2.1	Oxygen Uptake Rate	18
3.2.2	Inhibition Percentage.....	21
3.3	Results from External Analyses of Metals	22
3.4	Further Discussion of Risk Factors Associated with an Exposure of DH Water to Activated Sludge in a WWTP	22
4	Conclusions.....	24
5	Further studies.....	26
6	Acknowledgements	27
7	References.....	28

Bachelor of Science

Assessment of Inhibition on Activated Sludge Caused by Heat Transfer Fluid from District Heating Distribution Networks

Victor Bergseije

Bachelor of Science, *Environmental Science 15 ECTS*

Supervisors:

Fil. Dr., Fabio Kaczala Linnaeus University (Faculty of Health and Life Sciences)

Curt Tappert QTF Sweden AB

Björn Carlsson QTF Sweden AB

Examiner:

Fil. Dr., Per Woin Linnaeus University (Faculty of Health and Life Sciences)

The Examination Project Work is included in the study program *Miljöanalytiker 180 ECTS*

Abstract

Det är vanligt med läckage av fjärrvärmevatten och detta väntas öka i framtiden eftersom distributionsnäten blir allt äldre. Läckor leder till förorening av vattnet vilket orsakar ytterligare skador och korrosion som resulterar i mer läckage. Av den anledningen tillsätts kemikalier till nätet för att rena värmebäraren och skydda rören. Man vet att några av kemikalierna som används kan vara skadliga i vattnekosystem och att fjärrvärmevatten hamnar i reningsverk. Därför genomfördes en respirometrisk analys för att bedöma hur fjärrvärmevatten påverkar aktivt slamprocessen. Utförandet baserades på en standardiserad metod utformad av Organization for Economic Co-operation and Development (OECD) kallad OECD standard 209; OECD Guidelines for the Testing of Chemicals. Vissa ändringar gällande exponering och mättid gjordes för att det minskar risken för feltolkningar. Vatten från två fjärrvärme nät, Kalmar och Växjö, testades på slam hämtat från Tegelviken vattenreningsverk i Kalmar. Hämmningen på total oxidation, oxidation av kol och kväve mättes genom att använda en spädningsserie av fjärrvärmevatten (6.25%, 25% och 100%). Toxicitetsgraden uppskattades genom att jämföra med en lösning med enbart aktiv slam. En metallanalys gjordes för att bedöma om eventuell toxicitet uppkom av korrosionsprodukter i vattnet. Det påträffades att fjärrvärmevattnet från Kalmar hämmade nitrifikationen med ca 20% för alla testade koncentrationer, trots stora skillnader dem emellan. Fjärrvärmevattnet från Växjö uppvisade en negativ korrelation mellan en ökning i koncentration och ökning av toxicitet, 74 % (6.25%) -11 % (100 %). Metallanalysen uteslöt korrosionsprodukter som trolig källa till toxicitet, därför drogs slutsatsen att kemikalierna sannolikt är orsaken till hämmningen. Störning av nitrifikation i reningsverk är allvarligt i områden kring Östersjön då eutrofiering är ett stort problem och till stor del orsakas av kvävedeposition.

Summary

District heating has a long standing tradition in Sweden and today it is the most common way of producing and transporting heat. A District heating system (DH system) is divided into three parts: a production facility, distribution network (DH network) and one more heat stations. The heat produced in the facilities is distributed to the customers via a heat transfer medium, usually water (DH water), in piping networks that make up the DH network. The heat is transferred to the customers via the heat exchanger at which point they can use it as heated tap water or for heating purposes. The DH networks are often constructed in steel as it is cheap and a relatively resistant material. However it has the disadvantages of corrosion and expansions when it is exposed high temperatures which lead to damages in the DH network resulting in loss of the DH water, this is an unavoidable occurrence in any DH network. This results in addition of pollutants by leakages into the DH network or with the water that is used to compensate for the losses. The pollutants cause further corrosion, leading to metal contamination, and more damages on the DH network meaning there is a continuous degradation. Therefore various treatments are used to clean and ascertain an acceptable chemical environment in the DH systems. These treatments are effective but not at a level which is required so many chemicals are used to enhance the treatment of the water. Some of these are known to be toxic to humans and water ecosystems.

As leakages are abundant and often end up in the WWTPs of the concerned municipality, which often have troubles with disturbances of the biological treatment, it was decided that an assessment of the toxic effects that DH water pose on activated sludge was to be investigated. This was done by testing water from two DH networks, Växjö and Kalmar, on the same activated sludge obtained from Tegelviken WWTP in Kalmar. A respirometric bioassay approach established by the Organization for Economic Co-operation and Development (OECD), OECD standard 209; OECD Guidelines for the Testing of Chemicals was used with changes made to exposure and measuring time as this decrease the risk of misinterpretation of the results. A dilution series using different concentrations (6.25%, 25% and 100%) of DH water was tested and compared to a blank control samples containing only activated sludge. Assessment of toxicity on total oxidation, oxidation carbon and oxidation of nitrogen was made. To get some idea of what might cause toxic effect samples of the waters was sent to outside laboratories for analyses of metals. The result from the bioassay and metal analysis was used to formulate risk factors associated with a DH water spill and exposure to WWTPs.

It was found that both DH waters have a significant inhibition on nitrification in WWTPs. The DH water from Kalmar exhibited similar toxicity dynamics, roughly 20% inhibition, despite large differences in concentration. The DH water from Växjö showed a negative correlation between an increase in concentration of DH water and toxicity, 74% for the lowest concentration and 11% for the highest. The metal analysis concluded that there was no abundance of metal contamination which led to the inference that toxicity is probably caused by the chemicals used for treatment. This poses a great risk for the Baltic Ocean as many WWTPs release their treated water directly into water courses with a short detention time before reaching the sea.

1 Introduction

1.1 Function and Formation of a District Heating System

Building of district heating systems (DH system) was first started in Stockholm during 1909 and started spreading to other Swedish cities during the early 1950s meaning they have a long standing tradition (Frederiksen & Werner, 1993, p. 406). Today district heating (DH) is the most common way of producing and transporting heat energy. According to the Swedish trade organization, Svensk Fjärrvärme, approximately 53 TWh was delivered in 2012. This accounts for roughly 60% of the market (Magnusson, 2012).

Although sometimes widely different in shape and design any DH system can be divided into three main segments;

1. A production facility,
2. A distribution network,
3. A heat exchanger (heat substation).

The production of heat in a DH system is attributed to one or a few production facilities. These can be facilities constructed with the sole purpose of producing heat and electricity or facilities where excess heat is used, for example industrial facilities. The heat produced in the facilities is distributed to the customers via a heat transfer medium, usually a fluid, in piping networks (distribution networks, DH networks) that are often buried in the ground at an approximate depth of the one meter (Svenskt Vatten AB, 2013). The most common design of the DH networks is a traditional 2-way pipe system consisting of one feeding pipe for delivering heat to the customers from the production facility and one return pipe for recirculation (Frederiksen & Werner, 1993, p. 138). These are divided into ever-smaller networks of varying age and composition. The heat exchanger, or heat station, is the final component in a district heating system and it is stationed at or close to the customer. In some cases heat exchangers are used within in the networks and acts as a divider between different network circuits. The heat stations are the place where the heat that is produced in the production facility is transferred from the DH network to the internal network of the customer. When the heat has been transferred the customer can finally use the heat directly in the tap as heated water or for heating purposes in radiators.

The materials used in DH systems vary as do the materials within a specific DH network since they have gone through additions and renovations over the years during which time the technology has improved. One difference in the materials used in the DH network is seen on the casing, the insulating pipe that surrounds the internal transportation pipe that house the heat carrier. In recent years there has been a steady increase in the use of plastics for insulation. The preferred plastic by the industry is usually polyethylene (Frederiksen & Werner, 1993, pp. 142-151) . In general terms old piping is insulated with concrete and new pipes are insulated with plastics. (Svenskt Vatten AB, 2013).

The internal pipe that houses the heat carrier is usually constructed in steel even though copper and plastics are sometimes used. Steel pipes are used because they are:

- Cheap in comparison with materials that exhibit similar properties.
- Easy to handle and is well suited for welding which simplifies repair and renovation.
- Has a high resistance against wear and tear that can arise during installation, pressure variation or other circumstances such as changes in temperature.

However steel also has the disadvantages of corrosion and expansions when it is exposed high temperatures which causes damages on the pipes (Frederiksen & Werner, 1993, p. 154). This leads to leakages into and from the DH network which pollute the heat transfer fluid causing further damage leading to more leakages and even more pollution. This is an unavoidable occurrence in any DH system and today it seems to become increasingly more common.

1.2 Contamination and Treatment of the Heat Transfer Fluid

The most common heat carrier, medium for transporting heat, used in Sweden is water (DH water). As it is transported around the network the DH water is constantly polluted which results in an increase of damage causing factors such as corrosion and coating formation. Corrosion is an inescapable threat to all piping networks and can arise due to many different reasons. Corrosion attacks from the outside of the DH network are caused by contact with water and oxygen in the atmosphere which in turn is caused by damages on the insulating material (Svenska värmeverksföreningen, 1985, p. 147). For corrosion attacks from inside the system the most contributing factor is the amount of dissolved oxygen (Bjurström & Carlsson, 2001). Key factors affecting the amount of dissolved oxygen are temperature, pressure and salinity. Increased pressure increases the solvability of oxygen to liquid and higher temperatures and salinity lessens the solvability. Other factors that increase corrosion processes are use of metals with different electrode potential, increased conductivity, increased chloride concentration, temperature fluctuation, low pH and high ratios of bicarbonate and sulfate and other common ions. The most significant corrosion threats besides the above mentioned is particular matter as this triggers erosion-corrosion and increase in carbonic acid concentration, by dissolvent of CO₂, as this lowers the pH of the water (Svenska värmeverksföreningen, 1985, pp. 20-34). Coatings lessen the efficiency of the system by forming on heat transferring surfaces and increase the risk of erosion and corrosion attacks within the system. Coatings are usually caused by calcium (Ca²⁺) and magnesium (Mg²⁺) which is added by leakage into the network or when the water in the network is resupplied due to water losses (Frederiksen & Werner, 1993, p. 306; Svenska värmeverksföreningen, 1985). The water used for dilution is raw water taken from the municipal drinking water network. Raw water houses a number of chemical properties that are not suitable in a DH network. Among other things the water used for dilution contain lime, oxygen, dissolved ions and organic substances. When a large amount of dilution water is required treatment is necessary to maintain an adequate chemical environment. The main practices for treating the dilution water are; filtration, desalination, degassing and softening. These are effective methods that give great results and lengthens the life expectancy of the system if managed properly (Bjurström & Carlsson, 2001).

However not all undesirable constituents can be entirely removed so several chemical additives are used to enhance the treatment of the circulating water DH water. Also chemicals are sometimes used to ascertain an acceptable chemical environment, for instance pH adjustment, and to protect the surface of pipes by reducing friction. The main functions sought to achieve by use of chemicals are mainly:

- Adjustment of pH in dilution- or DH water
- Reduction of dissolved oxygen
- Corrosion inhibition
- Reduction of friction
- Leak detection

Wide spread common corrosion is usually negligible if the pH in the system is kept at 9 so a buffer, ammonia or sodium hydroxide, is added (Bjurström & Carlsson, 2001). Dissolved oxygen is usually

removed by adding a chemical that reacts or binds with oxygen. Previously the most common was hydrazine (N_2H_4) as it was deemed most effective. Hydrazine reacts with dissolved oxygen and the residues are nitrogen and water which are both relatively harmless to the DH network and to the environment or organisms. Unfortunately Hydrazine itself is known to be transdermal and carcinogenic also it can cause several allergic reactions and long term damage to e.g. lung tissue due to long term exposure. When released into surface water it is known to kill fish and algae (Svenska värmeverksföreningen, 1985, p. 160). This has led to a transition away from hydrazine to similar chemicals with less toxic properties, this has resulted in increasing costs as Hydrazine is cheaper than the other alternatives. Several nations in Europe, for instance Holland and Denmark, have decided to completely ban the use of Hydrazine but in Sweden it is still allowed in low concentrations with a permit issued by Yrkesinspektionen (Falk, 1998). As a result there are several other oxygen reducing agents that are commonly used in DH systems, for instance: sodium sulfite, carbonylhydrazide and some organic chemicals as diethylhydroxylamine (DEHA), sodium erythorbate, metyletylketoxim (MEKO) and tannins (Bjurström & Carlsson, 2001). The organic oxygen reducing agents produce organic acids and later carbon dioxide when they react with oxygen. As mentioned carbon dioxide decrease the pH of the DH water which increase corrosion. Carbonylhydrazide produces only carbon dioxide as it reacts, however it decomposes into Hydrazine at high temperatures, 135-150°C. Dosing with sulfites has in some cases been associated with an increase in corrosion attacks on copper surfaces in DH systems and networks, stimulation of growth of sulfate reducing bacteria has been specified as a primary cause (Bjurström & Carlsson, 2001). Corrosion inhibitors are organic- or inorganic chemicals that are added to reduce corrosion by forming a protective film on metallic surfaces. Examples of inorganic corrosion inhibitors are phosphates, silicates, chromates and nitrites. Some inorganic inhibitors can be treacherous in the DH systems as they can cause pitting corrosion, very aggressive form of corrosion, if some metallic surfaces are left unprotected. Organic inhibitors are sodium benzoate, phthalates and acetate or similar forms (Bjurström & Carlsson, 2001). Friction reduction is done by adding chemicals that lessens the resistance of the DH water and pipe wall. One group of chemicals that can be used for this purpose is surfactants (Bjurström & Carlsson, 2001). Surfactants are organic chemicals that are poisonous to all water living organisms (Svenskt Vatten AB, 2009). To detect leakages a dye is added to the water in many systems. In Sweden a salt named Pyranine with sharp green color and fluorescent properties is used. Pyranine is a commonly used chemical in for instance hygiene products and cosmetics and its toxicity is less than that of ordinary table salt (Bauer, Carlsson, & Persson, 1989).

As explained the chemicals used in DH systems are sometimes harmful in different circumstances and they are not universal for the treatment purposes required, meaning that a chemical used to decrease a certain damaging factor can enhance dynamics that are favorable to another. For instance some chemicals produce acids as they are broken down which decrease the pH of the water (Svenska värmeverksföreningen, 1985, p. 119). This leads to complex relationship that is hard to control and more use of different chemicals is could be the result.

1.3 Leakage of the Heat Transfer Fluid and Exposure to Recipients

Despite the actions that are taken to reduce the underlying factors losses of the heat transfer fluid always occur. These can be divided into two varieties, intentional and unintentional loss.

Intentional loss, release, often occurs when actions such a reparation or addition is necessary, this is sometime done by releasing water to the regular drainage system and the local WWTP is the final recipient (Bjurström & Carlsson, 2001). It is difficult to give a complete and entirely accurate record of release of DH water from systems as it is suspected that many unrecorded releases and undocumented withdrawals are carried out. A release of DH water directly into a recipient requires

approval from the environmental office in the specific municipality (Svenskt Vatten AB, 2009), practices for this vary from one region to another.

Unintentional loss, leakage, is caused by damages on the DH network or other parts in the DH system. Leakages are mainly attributed to mechanical damages during e.g. renovation, settling in the ground or corrosion on pipes and other parts (Sjökvist, Ren, & Ahlberg, 2012). Concrete piping in dry conditions have a life expectancy of 50-100 years while piping in wetter conditions only last for 20-30 years (Fjärrsyn, 2012). Leakages can also happen from newer pipes due to settling or substandard setup of the pipes (Sjökvist, et al., 2012). In one study performed by a company called Termisk Systemteknik together with Svensk Fjärrvärme IR-photography was used to identify leakages from DH networks. It was found that some leakages release up to 150 m³/day and that smaller leakages can be several years old (Sjökvist, et al., 2012). Even a DH network with good chemical environment and little problem with corrosion could exchange all of its DH water during the course of a year (Carlsson, 2013). Leakages are expected to increase since the DH networks are getting increasingly old (Sjökvist, et al., 2012). Today there is roughly 700 km of old piping insulated with concrete buried beneath the ground in Sweden. This is not much relative to the fact that a specific network can at least 1000 km long or that the entire length of all piping in Sweden is roughly 16 000 km of paired piping. However the renewal process of old pipes in Sweden only exchanges approximately 50 km of pipes in one year (Fjärrsyn, 2012).

There is always loss of DH water and it is not quite clear exactly how much water is lost and where it ends up. However the first recipient of a leakage is the nearby surrounding environment but since the burial is not very deep the water can also end up above ground in for instance streets or ditches. When this occurs the water could end up in the drainage system directly as storm water or by infiltration. Then the local watercourses or sometimes constructed wetlands but also potentially the local waste water treatment plant (WWTP) becomes the final recipient (Baker, 2009, p. 183; Stockholmvatten AB, 2005). DH water can also leak from one closed circuit in the DH system to another, for instance through damaged heat exchangers. This means that the water could end up in the tap water system of the customer (Bjurström, Grönholm, & Nystrand, 1994). DH water is old water and contains contaminants and therefore it is not appropriate for use as drinking water or in showers. If the DH water ends up in the tap water system the WWTP is the primary recipient.

Constructed wetlands are artificial water areas where biological process has been enhanced to treat waste water from sources otherwise not treatable in a WWTP, e.g. farmland or storm water. WWTPs use biological processes to treat primarily carbon and nutrients in household water even though water from other recipients is sometimes treated. Since the DH water could contain chemicals known to be toxic in water environments and possibly corrosion products, metals, it could disrupt these biological processes and undo much of the efforts made to ensure a viable water treatment infrastructure (Cai, Xie, Yang, & Arcangeli, 2010; Feng et al., 2013). All waters that end up in WWTPs or wetlands located near the coast line often have a short detention time before it is released to lakes or rivers that has openings towards the ocean. Disturbances of the biological processes in WWTPs or wetlands increase release of nutrients, nitrogen and phosphorus, into rivers and oceans leading to eutrophication if the amount released is larger than the capacity of the water bodies to assimilate them (Office of Wastewater Management, 2004). Disturbance of biological processes around the Baltic Ocean could be particularly severe since eutrophication is abundant in that region. Nitrogen derivatives are perceived to be the limiting factor for primary production in the Baltic and a disturbance of nitrification is therefore even more severe. Nitrification is particularly low during winter since the nitrifying microorganisms are sensitive to the colder weather (Bydén, Larsson, & Mikael Olsson, 2003). In summertime regions around the coastline of the Baltic Ocean are more populated and WWTPs

therefore loaded with more water (Svenskt Vatten AB, 2011). Nitrifying biological processes has also been proven to be more sensitive to toxic presence than biological respiration processes (Feng, et al., 2013). To combat release of nitrogen to water courses Naturvårdsverket (The Swedish EPA) and Svenskt Vatten AB (Swedish Water AB) have established absolute threshold values for inhibition of nitrification for industrial waste water when it is diluted with household. These are a 20% inhibition with a mixture of 20% concentration of industrial water into household water or a 50% inhibition for a concentration of 40% (Svenskt Vatten AB, 2009). Further the environmental efforts undertaken in Sweden are joined together in environmental goals enacted by the Swedish parliament. There are particularly two of these goals that cover nitrogen release into the Baltic Ocean:

- 7: No Eutrophication¹.
- 10: A balanced marine environment, flourishing coastal areas and archipelagos².

Much effort has been put into treating nutrients in leachate and storm water from farmlands and other polluting sources, for instance the erection of constructed wetlands is increasing. Also tougher legislation aiming to increase treatment in WWTPs has been put into place. Despite this there has been no decrease in the supply of nitrogen into Swedish water courses for 40 years. Today there is no sign that either of the environmental goals will be fulfilled until the target time of 2020 is reached.

Due to the exposure pathways and the potentially hazardous constituents it is suspected that DH water have the potential to do severe harm to the processes in WWTPs or wetlands if and when a leakage occurs under any of the above mentioned circumstances. Treatment of nitrogen was considered to be of special concern since these processes are more sensitive. It is the perception that DH water is forgotten or overlooked in studies using upstream tracking to identify possible disruption sources of biological processes in WWTPs even though it is known to be a big outlet of water. Effluents to WWTPs are complex mixtures with varying interactive effects. Monitoring effluents entering WWTPs with bioassays can be used to identify waters likely to reduce the efficiency biological treatment (Dalzell et al., 2002). On behalf of Quality Transfer Fluids AB (QTF), a technical company specialized in thermal degassing of heat transferring fluids based in Kalmar, Sweden, and in cooperation with Linnaeus University (LNU) a screening toxicity test using activated sludge was performed to try and address these suspicions concerning DH water. QTF was interested in a study into DH networks, corrosion, leakages and the chemicals that are used as they believe that other methods of water treatment could prove to be more effective, cheaper and friendlier to the environment than the methods that are used today.

A study using a screening risk assessment approach used by the U.S Environmental Protection Agency (EPA) focusing on the hazards (chemicals and corrosion products) and the exposure pathways (releases and leakages) of DH water described above with dose-response assessment (concentration-effect relationship) being addressed by a respirometric bioassay on activated sludge was performed. Respirometric analyses are most effectively used when assessing effects on activated sludge systems (Gutierrez, Etxebarria, & de las Fuentes, 2002) however the same bacteria are found in wetlands as in activated sludge so the biological degradation is in many ways similar (Kadlec & Wallace, 2009, p. 279). The respirometric analysis in this assay was based upon the standardized approach formulated by the Organization for Economic Co-operation and Development (OECD), OECD standard 209;

¹ Link to webpage with information on environmental goal no.7 <http://www.miljomal.se/sv/Miljomalen/7-Ingens-avgodning/>

² Link to webpage with information on environmental goal no.10 <http://www.miljomal.se/sv/Miljomalen/10-Hav-i-balans-samt-levande-kust-och-skargard/>

OECD Guidelines for the Testing of Chemicals³. The wide spread use of the OECD standard makes it appropriate for replication, however it has been reported with misinterpretation of results (Talinli & Tokta, 1994). Therefore it was decided to prolong the time of exposure and measuring to assess the overall inhibition effects instead of assessing precisely timed measurements which is the OECD method. In addition the approach for reagents and solutions (2.1.1) recommended by James C. Young and Robert M. Cowan in *Respirometry for Environmental Science and Engineering* was used as it, for practical reasons, suited the Pulse Flow Batch Respirometer that was utilized (Young & Cowan, 2004).

The toxic effects of DH water on total oxidation (respiration and nitrification), carbon oxidation (respiration) and oxidation of ammonia (nitrification) was assessed using a dilution series with different concentrations of DH water that were compared to a control mixture with zero concentration of DH water. As the microorganisms in the activated sludge use dissolved oxygen for oxidation the relationship between the oxygen consumption and the volume of oxygen input needed to maintain a constant air pressure in the respirometer vessels is used in respirometry to assess biological activity. A decrease in the volume of oxygen input in a reactor vessel compared to the control mixture is interpreted as the biological activity being inhibited. The inhibition is assumed to be equivalent to the degree of toxicity.

Questions aimed to address were:

- 1) Does the heat transfer fluid from distribution networks in district heating systems disrupt biological processes in waste water treatment plants.
- 2) Does variance in concentration of heat transfer fluid effect toxicity dynamics on activated sludge from WWTPs.
- 3) Is there a substantial presence of metals in the heat transfer fluid indicating corrosion.
- 4) Are corrosion products the source of expected toxicity.

The results from the bioassay and the external metal analysis combined with the reports of hazards and exposure pathways described above (1.2) was used to formulate risk factors associated with loss of heat transfer fluid from DH networks.

2 Materials & Methods

2.1.1 Respirometric Bioassay

Apparatus and Equipment

- Headspace gas pulse flow respirometer with water bath capacity connected to an aeration device, oxygen measuring equipment and a computer,
- 8 reactor vessels to contain 500 mL of final test mixture,
- Magnetic stirrers and followers,
- pH-meter,
- Scales and other equipment suitable for laboratory work

³ Link to webpage containing OECD standard 209
<http://www.oecd.org/env/ehs/testing/oecdguidelinesforthetestingofchemicals.htm>

Reagents and Solutions

Test Substance

In this assay DH water, heat transfer fluid, from the primary DH distribution network in Kalmar and Växjö were gathered from Kalmar Energis facility Moskogen and VEABs facility in Växjö. They use Ferrolix 560 (sodium sulfite) as an oxygen reducing agent and Adjunt CL (Pyranine) as dye a for leak tracing. Växjö uses 7300 m³ of dilution water each year which is produced in a countercurrent generated anion/cation exchanger. The distribution network in Växjö houses roughly 50 000 m³ of water.

The water samples were collected in acid washed air tight containers to avoid contamination. As to not affect the waters in any way they were kept away from sunlight and were stored, if necessary, in a refrigerator for up to two days before being used (Figure 1). After being sampled pH of the waters was measured. The DH water from Kalmar had a pH of approximately 9.2 and the DH water from Växjö had a pH of approximately 9.4.



Figure 1 Description of the sampling procedure for heat transfer fluid from the primary distribution network in Kalmar, Sweden.

Microbial Inoculum

Activated sludge was obtained from the municipal waste water treatment plant (WWTP) in Tegelviken, Kalmar (). The WWTP is a 3-stage treatment facility that treats domestic and industrial waste water. That is a WWTP with aerobic treatment using activated sludge combined with anaerobic treatment of nitrogen using a denitrification stage. The main part, about 90%, of the municipality's private housing is connected to the WWTP. Each year roughly 6 million m³ of waste water is treated, a third of the volume ending up in the WWTP is represented by waters originating from industrial and public facilities around the municipality. The sludge used in the test was obtained from one of the first pools with high aeration as it has high concentration of microorganisms. If the sludge was not used on the same day as it was collected, then 50 ml of synthetic sewage (see synthetic sewage feed) was added for approximately each liter of sludge and it was aerated and kept at constant temperature overnight.



Mineral Base I

Mineral base I was prepared by was prepared by dissolving the following reagents in 400 mL of distilled water and diluted to 500 mL. 5 mg/L of EDTA was used to keep minerals in solution.

- $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Cobalt (II) chloride hexahydrate0,125 g
- $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, Iron (III) chloride tetrahydrate2,50 g

Figure 2 Sampling procedure of activated sludge for a respirometric bio-assay at Tegelviken waste water treatment facility in Kalmar, Sweden.

- $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Manganese (II) chloride tetrahydrate0,025 g
- $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, Sodium molybdate dihydrate0,0025g
- NiCl_2 , Nickel (II) chloride0,0125g
- CuCl_2 , Copper (II) chloride0,0035g
- ZnCl_2 , Zinc chloride0,0125g
- H_3BO_3 , Boric acid0,0125g
- Na_2SeO_4 , Sodium selenate0,0125g

Mineral Base II

Mineral base II was prepared was prepared by adding and dissolving the following reagents in in 800 mL of distilled water and diluted to 1.0 L.

- CaCl_2, Calcium (II) chloride27,7 g
- $\text{MgCl}_2 \cdot 7\text{H}_2\text{O}$, Magnesium (II) chloride heptahydrate101 g

Nutrient Base

Mineral base II was prepared by dissolving the following reagents in 800 mL of distilled water and pH neutralized to 7.0 ± 0.2 using 50% NaOH. When the reagents were completely dissolved the solution was diluted to 1 L.

- NH_4Cl , Ammonium chloride38,2 g
- Na_2SO_4 , Sodium sulfate15,0 g

Buffer Base

A Buffer Base was prepared by adding and dissolving the following reagents in 800 mL distilled water and the pH was adjusted to 7.0 ± 0.2 using NaOH. When pH was neutralized the solution was diluted to 1 L.

- KH_2PO_4 , Potassium dihydrogen phosphate204 g

Inhibitor solution

A 2.32 g/L solution of N-allylthiourea (ATU) to inhibit nitrification was prepared using distilled water.



Figure 3 Experimental setup and materials used to prepare mineral-, nutrient, buffer base and inhibitor solutions used in the respirometric bioassay.

Test procedure

Preparation of Test Mixtures and Dilution Series

Test solutions containing synthetic sewage, sludge, distilled water and test substance in varying concentrations following a dilution series was prepared as seen in table 1. In this test a dilution series with a ratio of test substance, district heating water, at 1:4 was used. The final test mixtures were prepared in a manner to obtain equal volumes in the test vessels. Reactor vessels with a volume of 500 ml were used. A blank control mixture containing synthetic sewage, sludge but no test substance was prepared. The blank controls were diluted with distilled water to the same final volume as the test solutions. A duplicate of each concentration, including the blank control, was created to increase the security of the test. As the purpose of the test in this report was to evaluate the inhibition on total, heterotrophic and nitrogen oxidation a second dilution series was prepared in the same manner but which also contained 2.5 mL of a stock solution of 2,32 g/L ATU in order to inhibit nitrifying reactions (Table 1). This dilution series was used to measure oxygen uptake as a result of heterotrophic oxidation, the result was later used to calculate the oxygen uptake caused by nitrification reactions (Calculation 1). The pH in all solutions was adjusted to 7.0 ± 0.5 .

Table 1 Dilutions series of test mixtures used to measure total oxidation and heterotrophic oxidation

nr	Name	Synthetic Sewage Feed	Microbial Inoculum	Test substance	Dest. water	ATU*
1	Blank 1	16 ml	250 ml		234 ml	2,5 ml
2	Blank 2	16 ml	250 ml		234 ml	2,5 ml
3	100% 1	16 ml	250 ml	234 ml		2,5 ml
4	100% 2	16 ml	250 ml	234 ml		2,5 ml
5	25% 1	16 ml	250 ml	58,5 ml	175,5 ml	2,5 ml
6	25% 2	16 ml	250 ml	58,5 ml	175,5 ml	2,5 ml
7	6,25% 1	16 ml	250 ml	15 ml	219 ml	2,5 ml
8	6,25% 2	16 ml	250 ml	15 ml	219 ml	2,5 ml

*ATU was only added to solutions intended to test heterotrophic oxidation of carbon.



Figure 4 Description of the systematic test procedure for preparing test mixtures with varying concentrations of heat transfer fluid from district heating distribution networks.

Preparation of Apparatus and Test Conditions

A Pulse Flow Respirometer with two reactor chambers, each containing 8 slots for reactor vessels, was set up. The reactor chambers were filled with water and connected to a temperature control device as to keep the test temperature constant as it is related to dissolved oxygen concentration. The temperature was set up, as described by OECD, to be kept at $20 \pm 2^\circ\text{C}$ during the entire length of the test procedure. The reactor vessels, containing the final test mixture, were connected to a controlled aeration device with flow measuring capacity that compensates for the loss of oxygen in the vessels. To keep the microbial inoculum in suspension the test mixtures were continuously mixed at constant speed using a magnetic stirring device. To remove carbon dioxide that is produced during oxidation a CO_2 -scrubber containing potassium hydroxide was inserted into a slot at the top of the reactor vessels and the slots were thoroughly sealed. A computer was connected to the flow measuring device to acquisition data on the oxygen uptake. Every input of oxygen was measured and summed to give a cumulative measurement of oxygen uptake. The cumulative measurement was later used to calculate the rate of oxygen uptake.



Figure 5 Setup of batch respirometer and connection of pressure regulated aeration device for oxygen input and computer used to measure the input.

Data Acquisition and Calculations

Cumulative Oxygen Demand

The respirometer used in this test operates according to the concept that the oxygen that is consumed by the microbial inoculum is replaced in small injections by the controlled aeration device. The sum of all oxygen injections are considered to be equal to the cumulative oxygen uptake occurring in the reactor vessels. A curve was produced by plotting the concentration of oxygen uptake with time passed, giving a curve showing the steadily increasing oxygen consumption. As two samples of each

concentration, original and duplicate, were used in this test a mean value was calculated and used to plot the curve. This mean value was used for all other calculations following in this report.

Oxygen Uptake Rate

The oxygen uptake rates, OUR, was calculated as described by OECD from the mean of all measured values falling within the linear part of the graph showing cumulative oxygen demand. This was done to avoid misinterpretation of the results caused by the stabilizing or in any other way changing oxygen uptake, illustrated by non-linear sections of the graph showing oxygen uptake versus time. OUR was expressed in milligrams per liter per hour (mg/Lh) as described by OECD. The OUR (R) was calculated according to Equation 1:

$$1. \quad R = Y_n / (V * t) \quad \text{mg O}_2/\text{Lh}$$

where;

Y_n = value for the selected point on the linear part of the cumulative curve

V = volume of test mixture

t = time of measurement in parts of hours

Oxygen Uptake Due to Nitrification

The oxygen uptake rate caused by nitrification is an estimated nominal value based on the measured oxygen uptake caused by the heterotrophic oxidation. Oxygen uptake caused by nitrification was calculated as instructed by OECD by subtracting the cumulative oxygen values for heterotrophic oxygen uptake from corresponding values for the total oxidation. This is described in Equation 2:

$$2. \quad Y_N = Y_{CN} - Y_C \quad \text{mgO}_2/\text{L}$$

where;

Y_N = is the cumulative oxygen demand for nitrification

Y_{CN} = is the cumulative oxygen demand for heterotrophic oxidation and nitrification

Y_C = is the cumulative oxygen demand for heterotrophic oxidation

Percentage Inhibition

The inhibition of oxygen consumption for all concentrations and oxidizing reactions was calculated for and expressed as a percentage in the way described by OECD. The percentage inhibition was expressed as a curve by plotting it against the logarithm of the test substance concentration. Which test substance concentration that inhibits the oxygen uptake by 50% was interpolated or calculated from the resulting graphs. Suitable values that mark the beginning and end of inhibition was also interpolated in the same manor.

$$3. \quad I_{N,H,T} = 100 - (Y_{N,H,T} / Y_B) * 100$$

where:

$I_{N,H,T}$ is the inhibition as a percentage of blank control for any type of oxidation

$Y_{N,H,T}$ is the OUR for the type of oxidation and the concentration of test substance

Y_B is the mean OUR for the blank controls for either type of oxidation

2.1.2 External Analysis of Metals

Both the water from Kalmar Energi and Växjö Energi was sent for analysis of appropriate parameters such as metals, pH, hardness, nitrogen and phosphorus. This was done to help with interpretation of the results and to assess the level of corrosion. The waters from Kalmar were sent to Eurofins Environment Sweden AB (Lidköping). Unfortunately due to unforeseen circumstances and trouble with funding the waters from Växjö could not be sent to the same laboratory. Instead it was sent to ALS Scandinavia AB (Luleå). Both samples that were sent to outside laboratories were collected at the same time as the samples used in the respirometry assay as to ensure representative interpretation. The result from the external analysis was compared with industry standards and the guidelines recommended for release of industrial waste water to WWTPs. These facts and figures of industry standards were formed by Värmeforsk and Svensk Fjärrvärme and published at Värmeforsks database. The only recommended values for corrosion assessment presented are Fe mg/L < 0,1 and Cu mg/kg < 0,02 (Bjurström & Carlsson, 2001). The threshold values for release of industrial waste water to WWTPs were formulated by Svenskt vatten AB and Naturvårdsverket and found in Naturvårdsverkets internet accessible database.

Table 2. Highest recommended values for mixture of a industrial waste water into ordinary household waste water going to a WWTP.

Substance	Warning Value
Lead, Pb	0.05 mg/L
Cd	There should be none at all
Cu	0.2 mg/L
Cr	0.05 mg/L
Hg	There should be none at all
Ni	0.05 mg/L
Ag	0.05 mg/L
Zn	0.2 mg/L
Hazardous organic substances	There should be none at all

3 Results and Discussion

Page left blank on purpose.

3.1 Results from Respirometric Bioassay of Kalmar Energi DH Water

3.1.1 Oxygen Uptake Rate

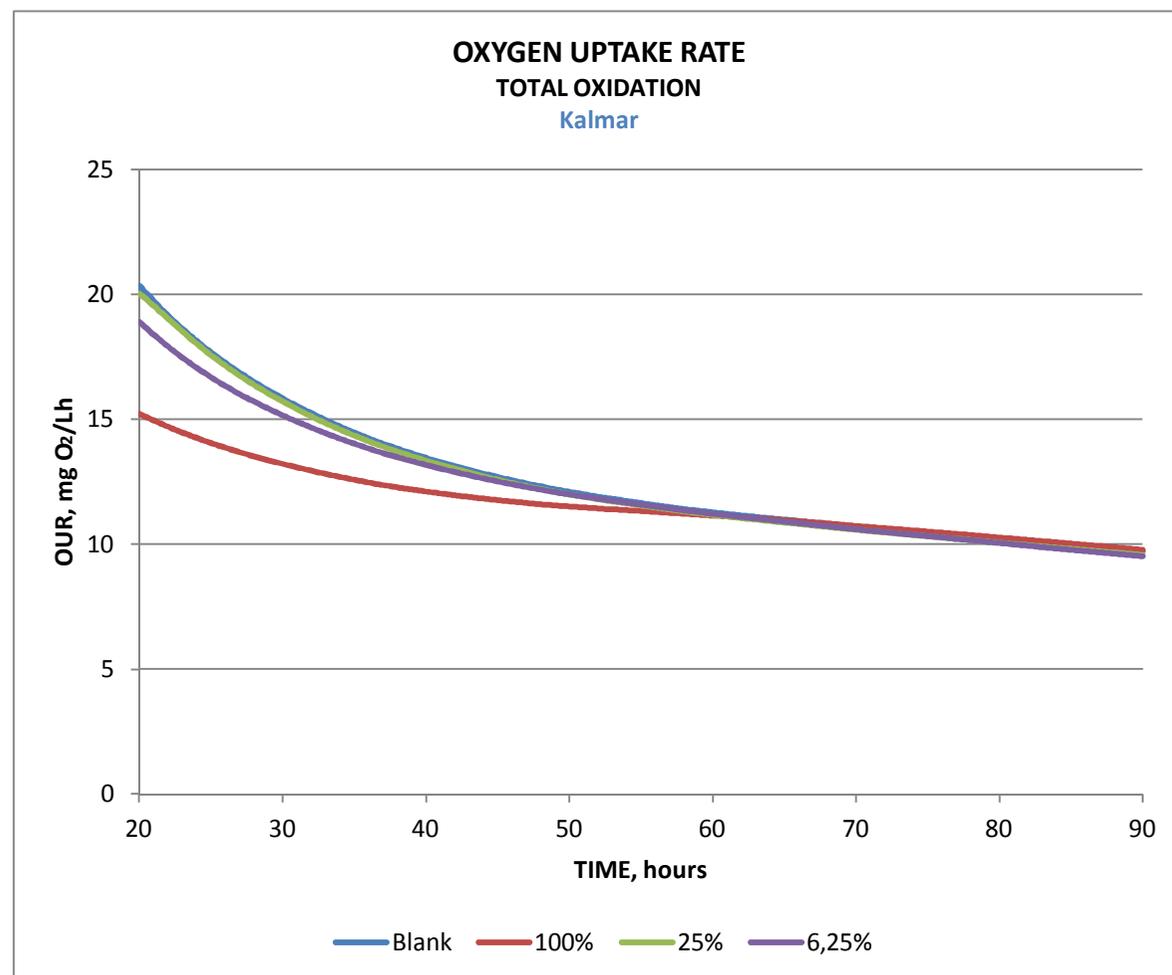


Figure 6 Effects on the oxygen uptake rate (OUR) due to biological oxidation reactions of carbon and ammonia carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid from the primary distribution network in Kalmar, Sweden. The blue curve symbolize a blank test mixture with 0% heat transfer fluid representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

Total Oxidation

The OUR graph of total oxidation (Figure 6) shows an initial inhibitory effect that is strongest for the for the 100% test mixture. This is a sign that the DH water from Kalmar has an inhibitory effect on the biodegradation processes of activated sludge. Noteworthy is that the inhibition on total oxidation is interdependent from increasing concentration. Meaning there is no correlation between inhibition and increasing concentration, the 6.65% solution shows more inhibition than the 25% solution which has almost no sign of inhibition. The curves are showing similar signs of decreasing activity as the blank solution, after about 50-60 hours all curves approaches the same level of oxygen uptake indicating that the inhibitory effect caused by the DH waters has surpassed. The normalization of the OUR, movement towards the levels of the blank test mixture, is faster for the 6.25% test mixture than for the 100%. This indicates that the recuperation from inhibition is sustained for a longer period of time when activated sludge is exposed to higher concentrations for the waters from Kalmar DH network.

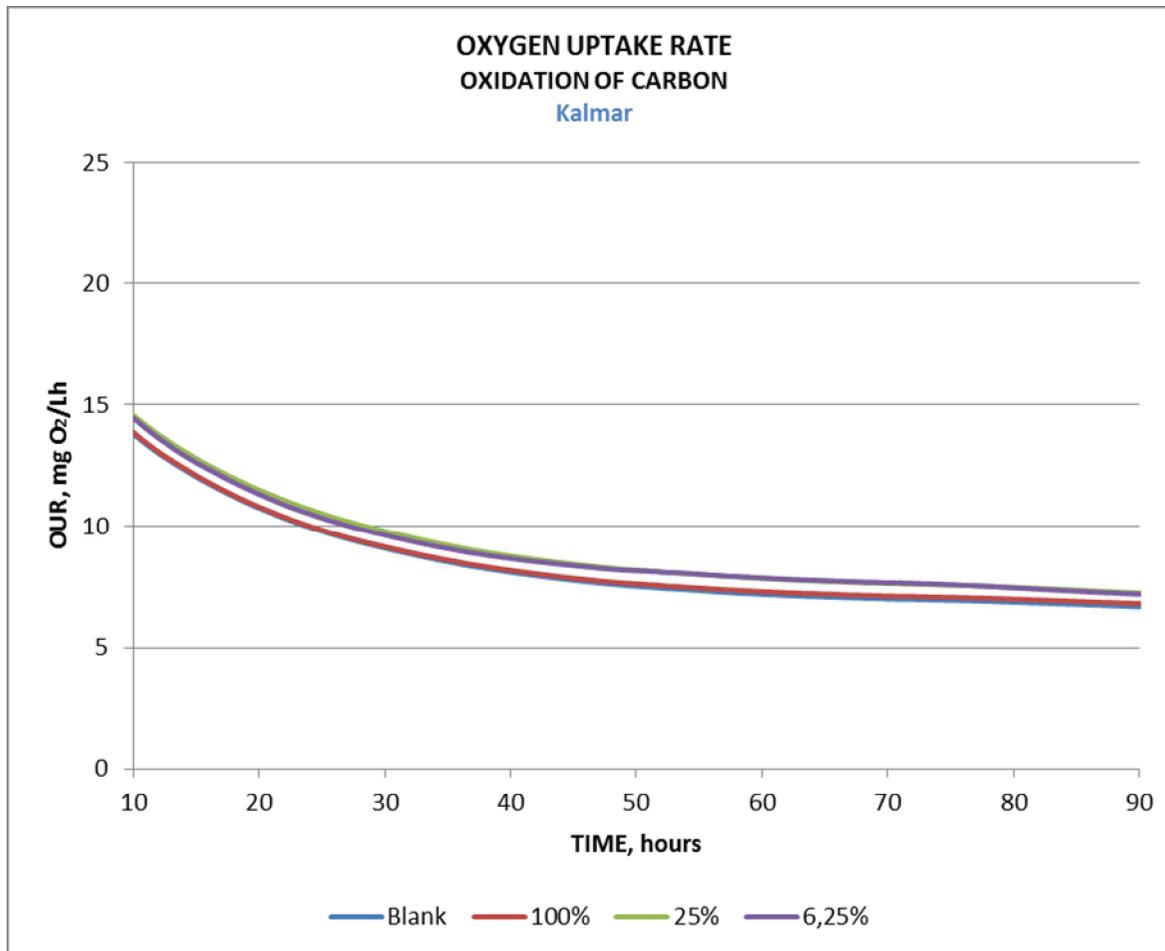


Figure 7 Effects on the oxygen uptake rate (OUR) due to oxidation reactions of carbon carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid from the primary distribution network in Kalmar, Sweden. The blue curve symbolize a test mixture with 0% heat transfer fluid representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

Carbon Oxidation

The OUR graph for oxidation of carbon (Figure 7) shows no significant sign of inhibition for any of the solutions. This excludes the effects on carbon oxidation as a source for the inhibition seen on total oxidation (Figure 6). The OUR measured for the 100% test mixture is weakest of the test mixtures containing DH water. It is seemingly the same as the OUR for the Blank test mixture. The 6.25% test mixture and the 25% solution shows small sings of stimulation with the latter having a slightly stronger OUR profile. This indicates that stimulation is somewhat dependent on concentration. Noteworthy is that the 100% solution do not follow the same pattern which could mean that the substance causing stimulation is less stimulating in higher concentrations or that the DH water contain one or more substances that hinder stimulation from manifesting itself in concentrations higher than 25%. The decrease in OUR is similar for all tested test mixtures and the stimulation for the two lesser ones, 6.25% and 25%, is sustained through the entire length of the measurement.

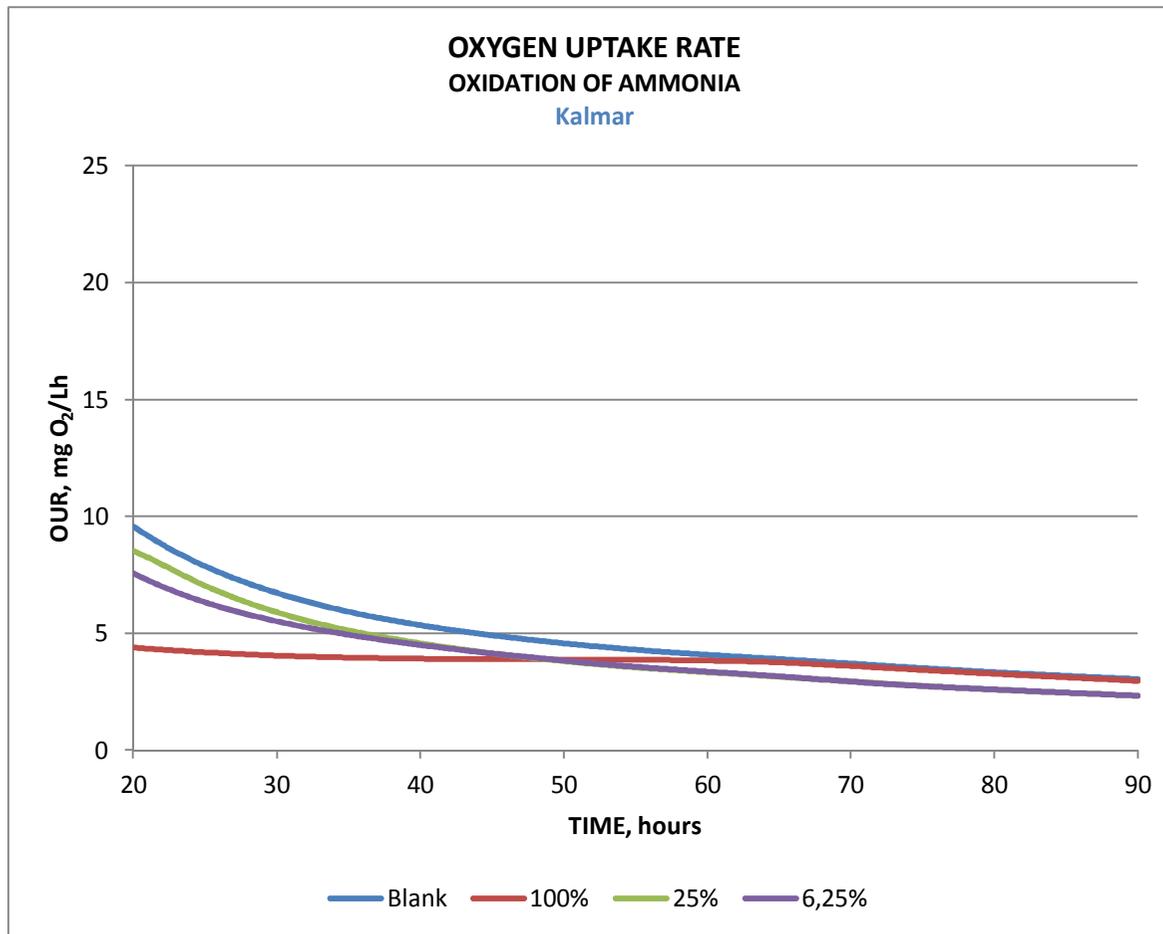


Figure 8 Effects on the oxygen uptake rate (OUR) due to oxidation reactions of ammonia carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid from the primary distribution network in Kalmar, Sweden. The blue curve symbolize a test mixture with 0% heat transfer fluid representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

Ammonia Oxidation

The graph of oxidation of ammonia, nitrification, shows a drastic inhibition for all measured test mixtures. The 100% test mixture is initially the most inhibited followed by the 6.25% and the 25% respectively. The OUR measured for the 6.25% and the 25% solutions approaching each other and after roughly 35 hours it is similar in both samples. This illustrates that the inhibition in the 6.25% test mixture is ending, however none of the 6.25% or 25% has a movement towards normalization indicating that the inhibition caused by DH water in these concentrations is present for at least 90 hours. Noteworthy is that after about 50 hours the OUR in those test mixtures are less than for the 100% solution which had a higher inhibition initially but shows signs of a movement towards normalization. After about 40-50 hours the OUR for the 100% test mixture is still around 4 mg O₂/Lh which is about the same as in the beginning of the measurement indicating a sustained inhibition for high concentrations. However after about 60-70 hours the OUR profile for the 100% solution is approaching that of the blank control and the decline in nitrification is similar between the two after 70 hours. Indicating that the OUR of the sludge is sustained in higher concentrations. This could be because of a population adaptation to tougher living conditions or that the DH water contains one or more stimulatory substances for nitrifying bacteria.

3.1.2 Inhibition Percentage

The calculations of inhibition percentage (Table 3) of total oxidation show that there is a small inhibition of total oxidation in all test solutions although it is not very strong. The 100% test mixture has the strongest inhibition of nearly 8%. The analysis of inhibition percentage for carbon oxidation shows that a slight stimulation is present in all test mixtures. Interestingly the two lower mixtures have a stronger effect than the 100% test mixture, this is illustrated further in the OUR profile for carbon oxidation (Figure 7). The result of the inhibition percentage calculation on ammonia oxidation shows that the inhibition is strongest, 22.40%, for the 100% solution and that inhibition it is not directly correlated to increasing concentration (Table 3). The inhibition viewed in percentages follows the same pattern as the OUR profiles for all test mixtures despite the fact the OUR profile for the 100% test mixture is sustained and eventually higher than for the two lesser concentrations (Figure 8). The test mixture containing 6.25% DH water has an inhibition of 18.60% and the 25% test mixture has an inhibition of 15.97% (Table 3). This despite the fact that the OUR profiles are almost identical after roughly 35 hours of measurement (Figure 8).

Table 3 Inhibition percentage, degree of inhibition throughout the entire measurement (90 hours), on microorganisms in activated sludge exposed to varying amounts of test substance, heat transfer fluid, from the primary distribution network in Kalmar, Sweden. The percentages were derived by comparing the test mixtures with varying amounts of test substance with a test mixture containing 0% test substance which represents the normal oxygen uptake of the microorganisms in the activated sludge.

INHIBITION PERCENTAGE FOR DH WATER FROM KALMAR			
Concentration	Total oxidation	Carbon oxidation	Ammonia oxidation
100%	7.83	-1.16*	22.40
25%	0.90	-8.08	15.97
6.25%	2.35	-7.26	18.60

* Negative values indicate stimulation of oxygen consumption due to biological oxidation reactions.

3.2 Results from Respirometric Bioassay of Växjö Energi DH Water

3.2.1 Oxygen Uptake Rate

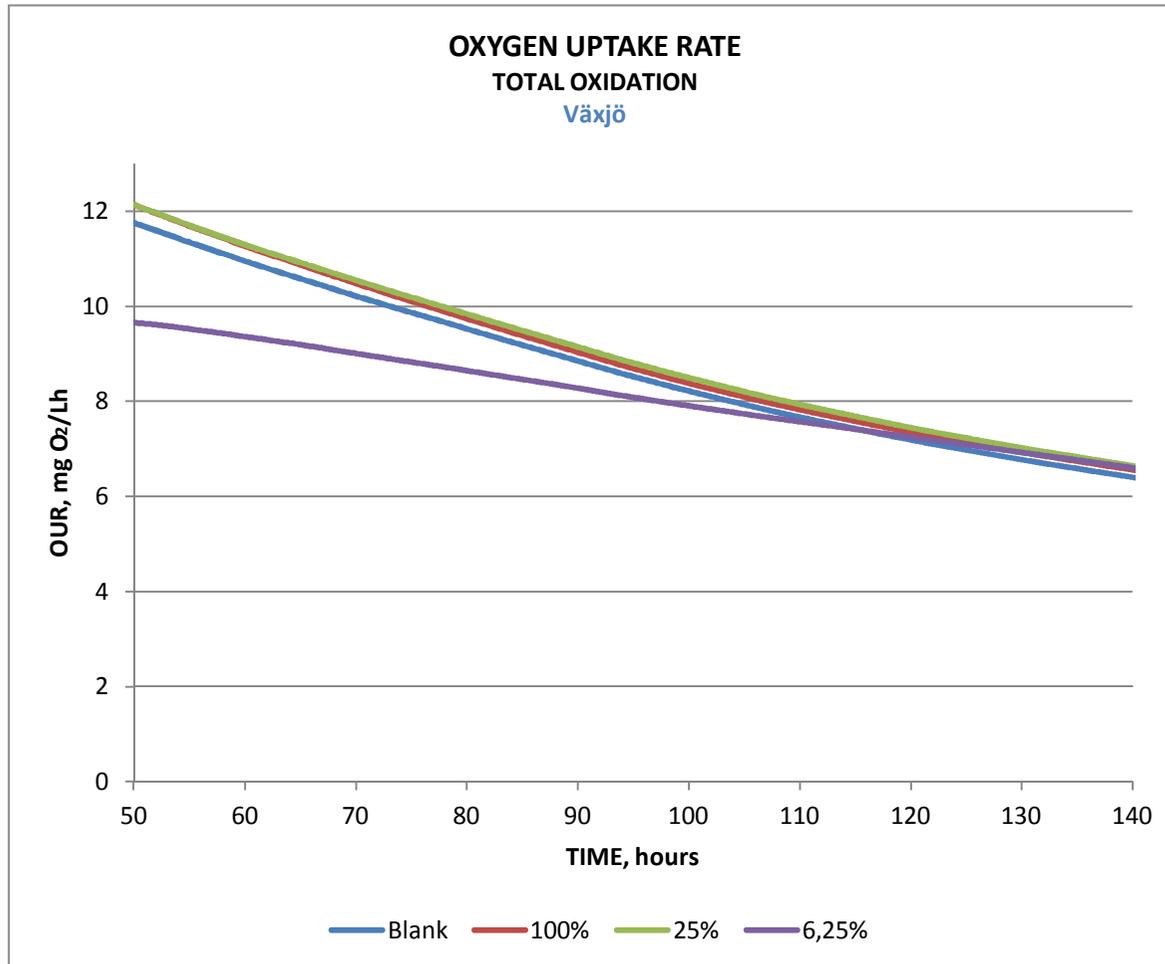
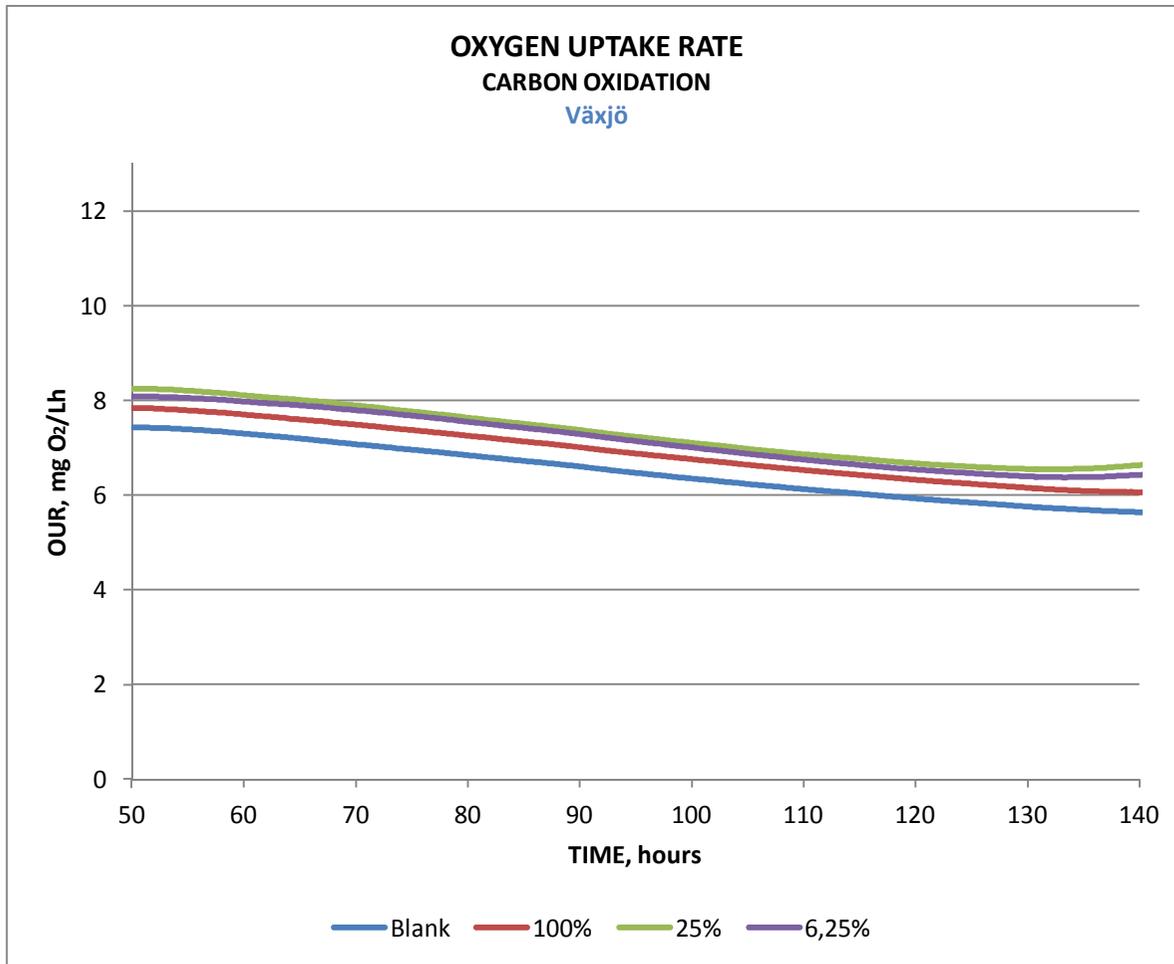


Figure 9 Effects on the oxygen uptake rate (OUR) due to biological oxidation reactions of carbon and ammonia carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid, test substance, from the primary distribution network in Växjö, Sweden. The blue curve symbolize a blank test mixture with 0% test substance representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

Total Oxidation

The OUR profile for total oxidation evaluated with DH water from Växjö (Figure 9) shows that the 6.25% test mixture has a strong initial inhibition that last for roughly 110 hours. There is a movement towards normalization of the OUR profile for the 6.25% test mixture. At roughly 110 hours the profile is the almost the same as for the other dilutions and the blank control test mixture. This indicating that the inhibition as surpassed and that the microorganisms have recovered from the inhibition. It also indicates that small concentrations can have a long lasting inhibitory effect. The OUR profiles for the 100% and the 25% test mixtures show a slight stimulation. This is first sign that DH waters from different systems have substantially different effects as the waters from Kalmar showed a substantial inhibition when activated sludge is exposed to 100% concentration (Figure 6).



Carbon Oxidation

The OUR profile for carbon oxidation assessed with DH water from Växjö (Figure 10) shows that all test mixtures are associated with stimulatory effects on carbon oxidation. This excludes effects on carbon oxidation being the source of inhibition seen on total oxidation (Figure 9). This also indicates that the DH waters from both networks have similar effects on carbon oxidation as the waters from Kalmar also stimulate carbon oxidation in the same concentration pattern, with the 100% test mixture having the least followed by the 6.25% and the 25% respectively (Figure 6). Just as the OUR profile of carbon oxidation for the Kalmar DH water the same OUR profile for the Växjö DH water shows that the 25% test mixture has the strongest stimulation followed by the 6.25% test mixture but a comparison between the two shows that the differences are not as strong in the Kalmar OUR profile.

Figure 10 Effects on the oxygen uptake rate (OUR) due to oxidation reactions of carbon carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid from the primary distribution network in Växjö, Sweden. The blue curve symbolize a test mixture with 0% heat transfer fluid representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

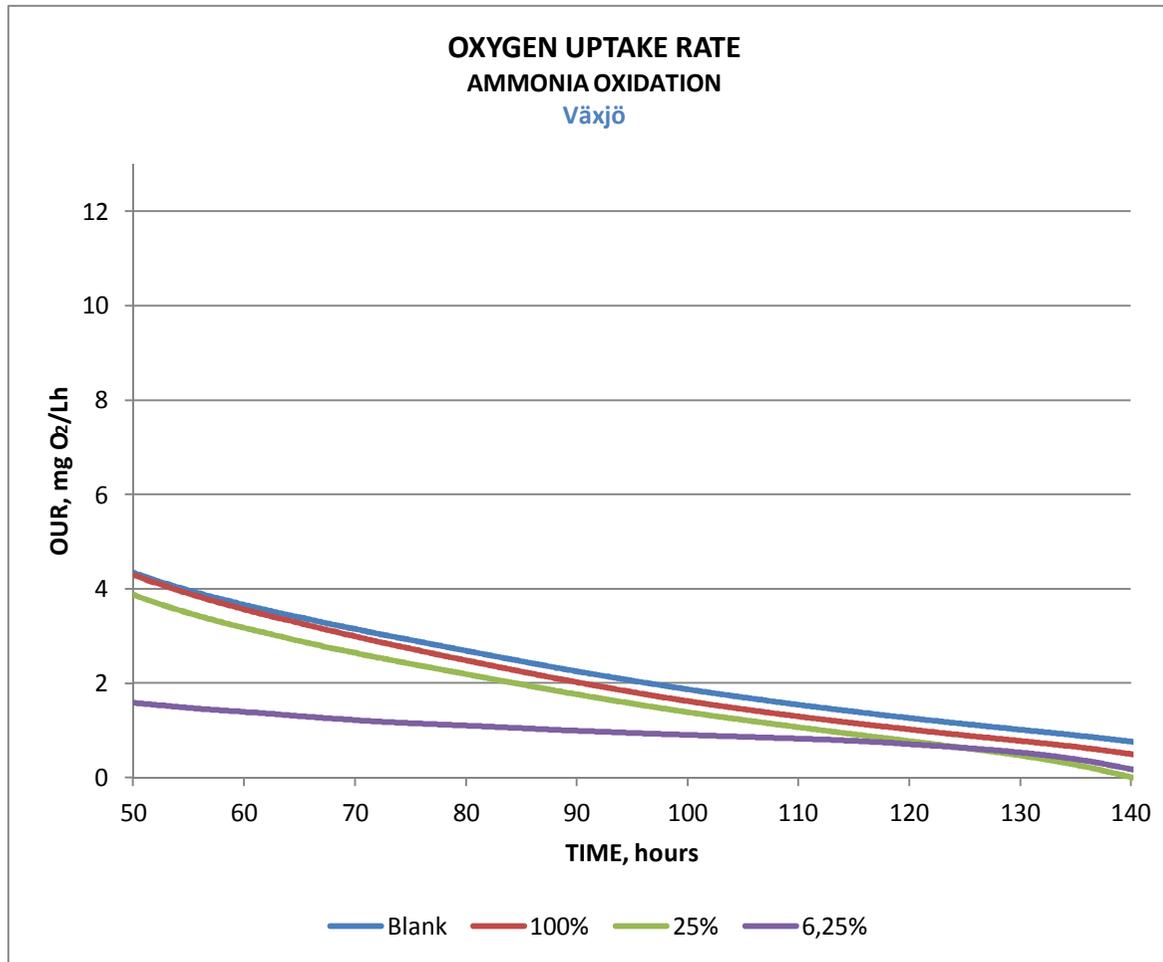


Figure 11 Effects on the oxygen uptake rate (OUR) due to oxidation reactions of ammonia carried out by microorganisms in activated sludge exposed to varying concentrations of heat transfer fluid from the primary distribution network in Växjö, Sweden. The blue curve symbolize a test mixture with 0% heat transfer fluid representing the normal OUR of the activated sludge. This has been used as a reference to establish the OUR state for the other test mixtures.

Ammonia Oxidation

The Växjö OUR curve for ammonia oxidation (Figure 11) shows that all concentrations have an inhibition on nitrification. This attributes the inhibition seen in total oxidation to inhibition caused to nitrifying microorganisms. This also indicates, as the Kalmar OUR profile (Figure 8) shows similar patterns, that the DH water from both networks is toxic to nitrifying bacteria in activated sludge. Noteworthy is that for the Växjö DH water the 6.25% test mixture has the most inhibition and the 100% the least. Another sign that DH waters from different systems have different inhibition properties, since the water from Kalmar affect nitrification more with a 100% concentration (Figure 8). Also the OUR profiles for Kalmar DH water shows no direct relationship to an increase or decrease in concentration which is not the case for the Växjö water shows a negative correlation between inhibition and an increase in concentration. Further the OUR profiles of the Växjö water shows that after about 120 hours the measured nitrification of the 25% solution and the 6.25% approach each other and after 130 hours the 25% solution has lower OUR than the 6.25% (Figure 8).

3.2.2 Inhibition Percentage

The analysis of inhibition percentage for total oxidation of DH water from Växjö (Table 4) verifies that the 25% and the 100% solutions have slight stimulatory effect, 2.32% and 3.37% respectively, the 6.25% solution shows a slight inhibition, 3.90%. This differs from the corresponding results from the water from Kalmar that showed a slight inhibition for all test mixtures (Table 3). The inhibition percentage calculations for carbon oxidation show that all solutions have a slight stimulation, 10.19%, 12.38%, and 6.07% as concentration increase (Table 4). The lower concentrations have a stronger stimulation than the 100% solution. Perhaps indicating a biphasic relationship for any inhibitory substances that are present in the waters. The inhibition percentage analysis for ammonia oxidation shows that the Växjö waters have an inhibitory effect that is positively correlated to a decrease in concentration. The inhibition for the solutions 6.25%, 25%, and 100% is 74.13%, 44.21%, 11.35%, respectively. This differs from the corresponding analysis for the Kalmar water that showed an inhibition in all test mixtures but no consisting concentration/inhibition relationship (Table 3). Both waters however have a substantial toxicity to nitrifying microorganisms in activated sludge.

Table 4 Inhibition percentage, degree of inhibition throughout the entire measurement (140 hours), on microorganisms in activated sludge exposed to varying amounts of test substance, heat transfer fluid, from the primary distribution network in Växjö, Sweden. The percentages were derived by comparing the test mixtures with varying amounts of test substance with a test mixture containing 0% test substance which represents the normal oxygen uptake of the microorganisms in the activated sludge.

INHIBITION PERCENTAGE FOR DH WATER FROM VÄXJÖ			
Concentration	Total oxidation	Carbon oxidation	Ammonia oxidation
100%	-2,32*	-6.07	11.35
25%	-3.37	-12.38	44.21
6.25%	3.90	-10.19	74.13

* Negative values indicate stimulation of oxygen uptake due to biological oxidation reactions.

3.3 Results from External Analyses of Metals

The overall levels of metal in both waters are low compared to the warning values issued by Naturvårdsverket (Table 2) and the levels of Fe and Cu used for corrosion approximation by Värmeforsk and Svensk Fjärrvärme (Section 2.1.2). The pH for both waters is at a level that is good for hindering wide spread corrosion in the networks, this was expected since it is closely monitored. The low concentration of metals in both waters excludes metals as a source of any observed toxicity seen in the respirometric bioassay. This leading to the deductive conclusion that any toxic effects, primarily seen on nitrification, could be caused by the chemicals that are used to treat the DH waters.

Table 5 Results of metal analyses conducted on the heat transfer fluid from the primary distribution networks in Växjö and Kalmar to evaluate level of corrosion and metal contamination. Vacant boxes means that the parameter was not analyzed.

Analysis	Växjö*	Kalmar**	Unit
pH	9.2***	9.5	
Ca, Calcium	2.89	-----	mg/L
Fe, Iron	0.0259	0.031	mg/L
K, Potassium	0.61	-----	mg/L
Mg, Magnesium	0.927	-----	mg/L
Na, Sodium	24.8	-----	mg/L
S, Sulfur	1.33	-----	mg/L
Si, Silicon	0.00153	-----	mg/L
Al, Aluminum	0.0203	-----	mg/L
As, Arsenic	0.0005	-----	mg/L
B, Boron	0.00873	-----	mg/L
Ba, Barium	0.0125	0.020	mg/L
Cd, Cadmium	0.00002	0.00010	mg/L
Co, Cobalt	0.00005	<0.0010	mg/L
Cr, Chromium	<0.1000	<0.0010	mg/L
Cu, Cupper	<0.0010	<0.0010	mg/L
Hg, Mercury	<0.0010	-----	mg/L
Mn, Manganese	-----	0.0021	mg/L
Pb, Lead	-----	<0.0005	mg/L
Li, Lithium	-----	<0.050	mg/L
Ni, Nickel	-----	<0.0010	mg/L
Zn, Zink	-----	<0.0050	mg/L
* Analyzed by ALS Scandinavia AB (Luleå).			
** Analyzed by Eurofins Environment Sweden AB (Lidköping).			
*** Measurement was performed internally at LNU			

3.4 Further Discussion of Risk Factors Associated with an Exposure of DH Water to Activated Sludge in a WWTP

DH production is despite some negative aspects that will be discussed further down in this section a good way of producing and transporting heat energy. The risk assessments are based on the bioassay and the findings of the exposure pathways and the hazard assessment conducted in connection with the bioassay. The assessment of risks that are made is done out of hypothetical and worst case scenarios. The risk assumption are drawn with the soul intention of improving factors that otherwise could increase environmental aspects or result in negative economic effects for concerned actors on the DH market.

The findings of the bioassay conducted in this study confirm the suspicions that DH water inhibits biological degradation in WWTPs, primarily nitrification (Figure 8, Figure 11). The metal analysis conducted excludes corrosion products from being the source of the toxic effects. This leads to the

inference that the chemicals used for treatment of the DH water is the likely source of toxicity to activated sludge (Table 5). The chemicals are at this point identified as the hazardous agent as there being any unknown hazardous agent causing the effects is deemed unlikely due to the uninterrupted monitoring of the DH water conducted by the companies (Bjurström & Carlsson, 2001). Further a definite dose-response effect can be seen but there is no clear sign of correlation between an increase in concentration and an increase in toxicity, or the reverse. This is due to the dissimilar degree of inhibition caused by different concentrations of the two DH waters. It is the supposition based on the findings of dose-response seen in the assay that larger concentrations can be just as inhibitory as smaller concentrations. The waters from Kalmar show a strong toxicity compared to the values issued by Naturvårdsveket (20% inhibition for a 20% concentration). They also display similar degree of toxicity for all tested concentrations despite there being large concentration differences between the test mixtures. The waters from Växjö exhibits strong toxicity of both large and small concentrations. There is a negative correlation between an increase in concentration and toxicity for the waters from Växjö with the 6.25% concentration of test mixture having an inhibition of 74%! The exposure pathways identified in relationship with this study (1.2) are deemed to be of a secure nature despite the lack of coherent accounting of loss from the distribution networks. The potential exposure pathways of DH water to activated sludge appear with a controlled release, leakage that dilutes DH water with storm water, a leakage between closed circuits of the network and unlicensed and undocumented withdrawals, the latter obviously having a speculative nature. Small leakages (in perspective of the size of DH systems) are certain and an uninterrupted occurrence that can proceed for several years, the frequency of these relatively small leakages is at least 1000/year. Even smaller leakages that are almost impossible to identify are likely to occur uninterrupted for an unforeseeable time. Larger leakages are usually found and dealt with quickly as the green pyranine used makes these leakages very noticeable. However the magnitude of larger leakages are apparent, as mentioned leakages up to 150 000 L have been identified, the frequency of these leakages are less but will likely increase in the future. (Sjövist, et al., 2012). The exposure to activated sludge is deemed to be certain mostly due to dilution to storm water that is diverted to WWTPs and controlled with release.

These assessments of hazard, exposure and dose-response raise concerns of some risk factors that will be discussed from this point.

- Many leaks are old, some are big and there is a great amount of uncertainty in the actual number. This result in a risk factor around the magnitude of chemical exposure to activated sludge. The potential amount of chemicals that are released over a period of time is potentially very big even if the amount used in the networks is low percentage wise. Difficulties in detecting leakages advance this risk further.
- The waters tested in this report only contain one oxygen reducing chemical additive but companies add chemicals for a series of other purposes. This is a risk factor since cocktail effects are not considered.
- The reports of substantial leakages from DH networks combined with the result from the respirometric assay carried out in this report illustrates the risk factors that could arise when DH water ends up as storm water and is lead directly into streams, rivers, wetlands or into the drainage system and then the WWTP. Storm water has varying properties depending on site conditions, time of year, weather conditions etc. leading to the fact that DH water will be diluted with other forms of waste water. Interaction with constituents in the storm water could enhance the toxic effects of the DH water to activated sludge or lessening the intended treatability for the storm water leading to a discharge of hazardous materials form a WWTP.

- Wetlands are constructed areas where biological degradation has been enhanced to treat among other things storm water. That DH water seems to inhibit nitrifying biological reactions is a risk factor for wetlands. A discharge into a wetland could decrease the treatability in these areas causing greater release of e.g. nutrients such as nitrogen or phosphorus from these areas.
- An exposure of DH water to a WWTP or wetland that releases its treated water to streams, rivers or lakes that has a short detention time before reaching the Baltic Ocean is a great risk factor for the entire Baltic Ocean. If nitrification is inhibited this will cause a great amount of nitrogen derivatives being released. Since nitrogen is the limiting growth factor for primary production in the Baltic Ocean this will cause an increase in eutrophication that is already a great threat to the ocean.
- The fact that DH water is overlooked in studies using upstream tracking poses further risk factors for the Baltic Ocean. If DH water is not addressed as a major source of nitrification inhibition discharge will continue, disruption will endure and eutrophication will increase.
- The results in this report indicate that the water from both DH systems has larger or pretty much the same inhibition in smaller concentrations than in larger ones. This is a risk factor since the current priority of the actors involved on the DH market seems to be on larger leakages. Many smaller leakages add up however and the final amount could possibly be, as shown in this report, of environmental concern.
- Larger leakages still pose a great risk factor since it increases the likelihood of the DH water spreading from the source of the leakage into streams, rivers, wetlands, storm drains and finally the WWTP where it will cause inhibition.
- Leakages can be caused by temperature variations, changes in pressure and external damage. Seasonality can surely impact these factors. In summer, low season for usage of district heating, a leakage to a WWTP could impact nitrification reactions that are higher during this time of year. In some areas the load on these recipients are higher during summer time which could result in large amounts of nitrogen derivatives to be released to other recipients if nitrification is inhibited. This will result in more algae production in the Baltic which is already a great problem in some areas during summer time.
- Risk factors also exist during winter as a discharge could also have severe impacts on nitrification that is usually low during times when the weather is cold. A leakage of even small amounts could impact the nitrification severely and result in a discharge of large amounts of nitrogen during long periods of time since the bacterial culture would most likely have a hard time recuperating which is shown in this study.
- One risk factor is posed by the older pipes that still exist and is being exchanged at an alarmingly slow rate. Older pipes are usually existent in areas hard to access for renovation, this means cities. As leakages are more associated with those pipes a discharge of DH water that dilutes with storm water from the city are likely and as a result the risk of exposure to a WWTP increases.

4 Conclusions

As no metal contamination was found the toxicity observed is attributed to the chemical additives that are used. Reduction of the use of chemicals for treatment and release of DH water to WWTPs should therefore be considered. As technological methods have improved greatly in recent years these should be given more consideration as a possible treatment option instead of chemicals. Especially since pollution of the DH water is expected to increase and give rise to more need for treatment of the DH water. This fact will likely contribute to more chemicals being used if the current course of action is

followed, to avoid further use of chemicals and decrease environmental impact, primarily eutrophication in the Baltic Ocean, other options need to be further reflected upon. This could also result in economic favor since the cost for chemical use is steadily increasing. However compared with the cost of increase in leakages chemical use is cheap. This is probably one factor leading to a substantial increase of the use of chemicals for treatment. By removing the use of chemicals it could jeopardize the entire system causing more leakages and increase cost due to increasing losses of heat. Use of chemicals is justified by these factors and any method that aims to replace them must be readily available, cheap and just as effective as to insure the continued wellbeing of the system. QTF Sweden AB has a lot of expertise and is very skilled at treating technical fluid systems and will hopefully be able to address these issues with time.

5 Further studies

- It is strongly recommended that a study that takes place over a longer period of time is carried out to further assess the inhibitory effects of the DH waters on activated sludge.
- Effects of seasonality on leakages, properties of activated sludge and exposure to DH water should be investigated.
- It is recommended that how effects change as the water is diluted with water from other sources is investigated.
- It is important to perform further studies on waters from more DH systems. No system is alike in terms of age, use of materials, size, connected customers and so forth. As the overall age, degree of enlargement and reconditioning also show varying features the treatment methods and use of chemicals also vary considerably.
- The recipients change from one place to another and especially WWTPs show varying properties in their activated sludge. Therefore it is recommended to test activated sludge from different recipients in combination with testing DH water from other systems.
- Testing of more dilutions is strongly recommended.
- A study addressing the dilution with storm water that occurs with a particular rainfall situation can be made by either approximation of a DH water spill or by direct measure of a spill. Storm water runoff can be calculated using the relationship:

$$4. \quad Q = CIA$$

where;

Q= storm water runoff

C=coefficient of runoff based on surface type

I= average rainfall in inches/h

A= drainage area, acres

- A respirometry inhibition test using uniformly grown microorganisms instead of activated sludge from a WWTP should be carried out.
- Upstream tracking when an inhibition on activated sludge is detected in a WWTP should be carried out to see if DH water could be the likely source.

All of these suggestions that are made above should in the ideal case wrap up into a study that addresses the real life situation. A sampling of at least one, preferable more, actual leakages should be made and a test using the method described in this report and others if it has been proven necessary should be carried out. In these tests questions concerning amount and degree of dilution in the recipient should be given special importance as it would answer many of the additional questions concerning these issues that have been generated by the results in this report.

6 Acknowledgements

Lastly I would very much like to extend a big "THANK YOU!" to all people that have been involved in this bachelor thesis and helped to get it started and to see it through to the end.

Especially I would like to thank Fabio Kaczala qua mentor for the guidance, inspiration and experience that has been extended. Big thanks also go out to Curt Tappert and Björn Carlsson for arranging meetings, providing expertise and sending feedback throughout the process, it has been invaluable. Professor William Hogland is also given special thanks most of all for showed interest but also for the time and effort that has been given during meetings even though there was no obligation on his part, it was encouraging. Annika Wall and Robert Stensson are well deserved of special gratitude for arranging a tour of the two district heating facilities, answering all the necessary questions and providing the waters that were tested.

Many thanks to all, it has been very educational!

7 References

- Baker, L. A. (2009). *The water environment of cities*. New York: Springer.
- Bauer, T., Carlsson, B., & Persson, F. (1989). Färgämne för läckageindikering i fjärrvärmesystem (Vol. 343). Stockholm: Värmeforsk.
- Bjurström, H., & Carlsson, B. (2001). *Handbok i vattenkemi för energianläggningar*.
- Bjurström, H., Grönholm, S., & Nystrand, B.-Å. (1994). *Friktionsnedsättande tillsatser inverkan på miljön* Stockholm.
- Bydén, S., Larsson, A.-M., & Mikael Olsson. (2003). *Mäta vatten : undersökningar av sött och salt vatten* (3., rev. och utök. uppl. ed.). Göteborg: Institutionen för miljövetenskap och kulturvård, Göteborgs universitet.
- Cai, B. J., Xie, L., Yang, D. H., & Arcangeli, J. P. (2010). Toxicity evaluation and prediction of toxic chemicals on activated sludge system. [Article]. *Journal of Hazardous Materials*, 177(1-3), 414-419.
- Carlsson, T. (2013). Planera fjärrvärmeunderhåll från luften. (NOVEMBER 2013/JANUARI 2014). Retrieved from http://omvarldsbevakning.byggstjanst.se/Global/Byggstj%C3%A4nstPM/1%C3%B6sa%20artikel/PM4-2013/PM%204_2013-planera-fj%C3%A4rrv%C3%A4rmeunderh%C3%A5ll-fr%C3%A5n-luften.pdf
- Dalzell, D. J. B., Alte, S., Aspichueta, E., de la Sota, A., Etxebarria, J., Gutierrez, M., et al. (2002). A comparison of five rapid direct toxicity assessment methods to determine toxicity of pollutants to activated sludge. [Article]. *Chemosphere*, 47(5), 535-545.
- Falk, I. (1998). *Sammanställning och utvärdering av konsekvenser vid användning av hydrazin respektive organiska syrereduktionsmedel*.
- Feng, B., Fang, Z., Hou, J. C., Ma, X., Huang, Y. L., & Huang, L. Q. (2013). Effects of heavy metal wastewater on the anoxic/aerobic-membrane bioreactor bioprocess and membrane fouling. [Article]. *Bioresource Technology*, 142, 32-38.
- Fjärrsyn. (2012). *STATUSBEDÖMNING AV BETONGKULVERT*.
- Frederiksen, S., & Werner, S. (1993). *Fjärrvärme Teori, teknik och funktion*. Lund: Studentlitteratur.
- Gutierrez, M., Etxebarria, J., & de las Fuentes, L. (2002). Evaluation of wastewater toxicity: comparative study between Microtox (R) and activated sludge oxygen uptake inhibition. [Article]. *Water Research*, 36(4), 919-924.
- Kadlec, R. H., & Wallace, S. D. (2009). *Treatment wetlands* (2nd ed.). Boca Raton, FL: CRC Press.
- Magnusson, D. (2012). Swedish district heating-A system in stagnation: Current and future trends in the district heating sector. [Article]. *Energy Policy*, 48, 449-459.
- Office of Wastewater Management. (2004). *Primer for Municipal Wastewater Treatment Systems*.
- Sjökvisst, S., Ren, J., & Ahlberg, J. (2012). *KVANTIFIERING AV VÄRMELÄCKAGE GENOM FLYGBUREN IR-TEKNIK Ó EN FÖRSTUDIE*. Stockholm: Svensk Fjärrvärme AB.
- Stockholmvatten AB. (2005). *DAGVATTENSTRATEGI FÖR STOCKHOLMS STAD*
- Svenska värmeverksföreningen. (1985). *Kemi för fjärrvärmesystem : Råd och anvisningar*: Stockholm : Material- och korrosionsgruppen, Värmeverksfören. (VVF), 1985 ;.
- Svenskt Vatten AB. (2009). Råd vid mottagande av avloppsvatten från industri och annan verksamhet. Stockholm: Svenskt Vatten AB.
- Svenskt Vatten AB. (2011). *Nyckeltal för reningsverk ó verktyg för effektivare resursanvändning*.
- Svenskt Vatten AB. (2013). *Ny metod för läcksökning*.
- Talinli, I., & Tokta, S. (1994). OXYGEN-UPTAKE RATE INHIBITION TEST - A MODIFIED METHOD FOR PRIORITY POLLUTANTS. [Article]. *Environmental Technology*, 15(10), 979-988.
- Young, J. C., & Cowan, R. M. (2004). *Respirometry for environmental science and engineering*. Springdale, Ark.: SJ Enterprises.

SE-391 82 Kalmar
+46 480 446200
Lnu.se



Linnæus University