UPTEC W11031
Examensarbete 30 hp
November 2011

Comparing Cork Filters to Conventional Sand Filters

A Pilot Study of Process Water Treatment

Ulrika Bohlin

Abstract

Comparing Cork Filters to Conventional Sand Filters: A Pilot Study of Process Water Treatment

Ulrika Bohlin

Process water is used for cooling and for transporting material in all kinds of industries. To clean the water for reuse, various types of filters can be used. Many conventional process water treatment plants incorporate sand filters, which readily clean the water from suspended matters. However, at some circumstances the sand filters do not remove high enough concentrations of metals.

This master thesis compares the water treatment abilities of activated cork, produced by Spikes & Cogs AB, to those of the sand filters used at steel making company Ovako Hofors AB in Hofors. As an on-site pilot study, the thesis investigates the cleaning capacity of three types of activated cork filters: Fats, Oils and Solvents (FOSS) filter, Fast Acting Digestive Enzymes (FADE) filter, and Metal Adsorption and Concentration (MAAC) filter.

The cork filters were compared to the sand filters during normal operation and, because of previous problems with the stability of the sand filter performance, during stress tests. The results show that the cleaning capacity of the sand filters is higher than the cleaning capacity of the cork filters at normal operation. At the conditions of the stress tests, at which the sand filters do not function, the cleaning capacity of the cork filters was somewhat lowered but was still well within acceptable limits.

An important result from the experiments is that the cork filters neutralize the pH. The sand filters are sensitive to changes in the pH, meaning that the cork filters could function as a buffering unit prior to the sand filters.

Keywords: sand filter, cork filter, stress experiment, cork, sorbent

Department of Information Technology, Uppsala University,
Box 337, SE-751 05 Uppsala, Sweden
ISSN 1401-5765

Referat

En jämförelse mellan korkfilter och konventionella sandfilter: Pilotstudie inom behandling av processvatten

Ulrika Bohlin

Processvatten används i alla typer av industrier. Processvattnets funktion kan vara att kyla eller att transportera material från olika industriprocesser. Oavsett syftet, måste vattnet vara rent nog för sitt ändamål. Processvattnet kan renas med bl. a. olika typer av filter. I många reningsverk används konventionella sandfilter. Sandfilter är framför allt bra på att ta bort suspenderat material, men även metaller och oljor.

Syftet med detta examensarbete är att jämföra reningsresultatet efter aktiva korkfilter från företaget Spikes & Cogs AB med konventionella sandfilter. Processvattnet som används under experimenten kommer från ståltillverkningen och bearbetningen på Ovako Hofors AB i Hofors. Försöket genomfördes som en pilotstudie på plats i Hofors.

Tre aktiverade korkfilter har använts: Fats, Oils and Solvents (FOSS) filter, Fast Acting Digestive Enzymes (FADE) filter och Metal Adsorption and Concentrating (MAAC) filter. Effektiviteten i korkfiltren jämfördes med effektiviteten i sandfilter vid normal drift. Störningar i sandfilterreningsprocessen på Ovako har inträffat under åren varför korkfiltren även testades under stressade förhållanden.

Resultatet visar att sandfiltrens reningsförmåga är högre än korkfiltrens reningsförmåga vid normal drift. Under stressexperimentet var korkfiltrens reningsförmåga något lägre än vid normal drift. Jämfört med sandfilter under stressade förhållanden kunde korkfiltren hålla en högre reningskapacitet. Korkfiltren har ett bredare funktionsspann vilket tyder på en större robusthet vid förändrat substratinnehåll i processvattnet. Ett viktigt resultat av experimenten är att korkfiltren neutraliserar pH. Sandfiltren är känsliga för förändringar i pH och korkfiltren kan fungera som en pH-utjämnare om de placeras före sandfiltren.

Nyckelord: sandfilter, korkfilter, stressexperiment, kork, sorbent

Institutionen för informationsteknologi, Uppsala Universitet,
Box 337, SE-751 05 Uppsala, Sverige
ISSN 1401-5765

Preface

This work is a master thesis of 30 ECTS within the Master of Science program in Aquatic and Environmental Engineering at Uppsala University, Sweden. The project has been carried out for Spikes and Cogs AB, in Stockholm, Sweden. Supervisor was Johan de Faire. Subject reviewer was Bengt Carlsson at the Department of Information Technology, the Division of Systems and Control, Uppsala University, Sweden. Examiner was Allan Rodhe, Department of Earth Sciences, Uppsala University, Sweden. The project was financed by Spikes & Cogs AB and Ovako Hofors AB.

Uppsala, 2011

Ulrika Bohlin

UPTEC W 11031, ISSN 1401-5765
Printed at the Department of Earth Sciences, Geotryckeriet, Uppsala University, Uppsala 2011

Populärvetenskaplig sammanfattning

En jämförelse mellan korkfilter och konventionella sandfilter: Pilotstudie inom behandling av processvatten

Ulrika Bohlin

Vatten har ett mycket brett användningsområde och många verksamheter skulle inte kunna genomföras utan vatten. Samtidigt är vatten livsnödvändigt för att möjliggöra de allra flesta former av liv på jorden. Därför är det extra viktigt att det vatten som används renas på ett adekvat sätt. I detta examensarbete har en ny vattenreningsteknik, där reningen sker med hjälp av aktiverad kork, utvärderats och jämförts med en befintlig sandfilterrening.

Utvärderingen av de två reningssystemen har skett på stålverket Ovako Hofors AB i Hofors. Filtren som har använts är framtagna av Spikes & Cogs AB och är av typerna Fats, Oils and Solvents (FOSS), Fast Acting Digestive Enzymes (FADE and Metal Adsorption And Concentration (MAAC).

FOSS-filter består av kork som har värmebehandlats för att på så vis skapa en större yta där absorption av oljor och fetter kan ske. FADE-filtret har en korkmatris som stomme och mikroorganismer som utsöndrar enzymer som bryter ned organiskt material. På så vis frigörs bl. a. metaller som finns bundna i det suspenderade organiska materialet. Vattnet med de frigjorda metallerna kan sedan filtreras genom ett MAAC-filter där metallerna adsorberas på den aktiverade korken. Resultatet efter denna behandling är ett vatten med lägre koncentrationer av oljor, fetter, organiskt material och metaller.

Sandfilter har använts i över hundra år för att rena vatten från suspenderat material. Sandfilter fungerar så att vatten pumpas eller får rinna genom en bädd av sand. Suspenderat material fastnar på eller mellan sandkornen och avskiljs på så vis från vattnet. De sandfilter som används i vattenreningen på Ovako i Hofors är av typen DynaSand och har en rörlig sandbädd där både vatten och sand pumpas runt.

Den jämförelse som gjorts inom ramen för detta examensarbete har fokuserat på att undersöka reningskapaciteten hos sandfiltren respektive korkfiltren. Detta har gjorts genom parallella experiment där vatten från normal drift har använts. Experiment där korkfiltren utsatts för stress i form av störningar som är kända för att orsaka minskad funktionalitet i sandfiltren har genomförts. De störningar som användes var högt och lågt pH samt förhöjda halter av suspenderat material, grafit, emulsion och avfettningsmedel. Varje störning provades en gång, men med två olika halter.

De slutsatser som gick att dra utifrån försöken var att vid normal drift fungerar sandfiltren bättre som renare av processvattnet än vad korkfiltren gör. Ett bättre reningsresultat med korkfiltren hade förmodligen kunnat uppnås med en större korkfiltervolym.

Utifrån stressexperimenten kunde ett antal slutsatser dras. Reningsresultaten från de stressade korkfiltren var aningen lägre än resultaten som uppnåddes under normal drift. Detta är dock fortfarande bättre än vad sandfiltren normalt presterar under likartade förhållanden. En annan viktig upptäckt var att korkfiltren neutraliserar pH, vilket gör att om korkfiltren placeras före sandfiltren skulle de kunna minska belastningen på sandfiltren samt fungera som en pH-buffert. Detta skulle kunna medföra en säkrare drift av sandfiltren. Vidare visade det sig att upptaget av molybden och nickel i korkfiltren var pH-beroende. En konsekvens av detta är att upptaget av molybden och nickel kan styras genom tillsats av syra respektive bas.

Till vattenreningen kommer ett specifikt flöde med vatten som har använts i stålkokningsprocessen. Efter att stålet har smälts och slaggbildare har tillsats avgasas stålet för att ge det rätt egenskaper. Under avgasningen används en vattendriven vakuumpump. Vattnet från vakuumpumpen kommer därefter till processvattenreningen. Prover tagna på stålavgasningsvattnet har visat att det har ett högt metallinnehåll. Ett försök att rena stålavgasningsvattnet med ett MAAC-filter gjordes med gott resultat. Ett par olika kontakttider, d.v.s. den tid vattnet är i kontakt med filtret, gjordes. Resultatet blev att det mesta av metallerna bands till filtret redan under de första 1-5 minuternas kontakttid. Om stålavgasningsvattnet skulle renas innan det förenas med det övriga vattnet i vattenreningen skulle metallbördan till sandfiltren kunna minskas.

Examensarbetet visar att korken är en stabil reningsteknik även om den inte når upp till riktigt samma reningsnivå som sandfiltren. Det finns dock en del kvar att göra. Mer utförliga pilotförsök på fler typer av vatten skulle ge mer kunskap om korkfiltertekniken. En ekonomisk analys av korkfiltertekniken jämfört med konventionella reningstekniker skulle vara intressant. Även livscykelanalys skulle kunna tillföra en del till kunskapen om korkfilter som ett alternativ till de vanliga reningsteknikerna.

Table of Contents

1 Introduction

Most industries have different types of process water running through their plants. The function of process water can be to transport residual products, solvent of chemicals or cooling. Regardless of the function of the water, it must be clean enough for its purpose. There are different kinds of cleaning technologies on the market, each suited for different applications.

Ovako Hofors AB, a Swedish steel company, uses a closed-circuit system for its process water. On site in Hofors, the process water undergoes several treatment procedures such as sedimentation, pH-adjustment, addition of flocculants, sand filters and lamella sedimentation. These are traditional treatment methods for this type of industry.

Partial flows of process water from different process steps finally connect at one common point, the process water treatment plant. The water contains a spectrum of pollutants; oils, fats, solvents, metals, heavy metals and suspended matter, that need to be removed before re-use.

Treatment methods applied at the plant generate process water of required quality for re-use. However, the final treatment step – the sand filters – are sensitive to certain variables; pH fluctuations and heavy loads of oils and suspended matters. To evaluate alternative treatment processes, the company Spikes & Cogs AB was asked to run a pilot study using their activated cork technologies for water treatment.

The scope of this thesis was to conduct a pilot study to compare the sand filters of Ovako Hofors AB to the Fats, Oils and Solvents (FOSS), the Fast Acting Digesting Enzymes (FADE), and the Metal Adsorption And Concentration (MAAC) technologies developed by Spikes & Cogs AB.

1.1 Spikes & Cogs AB

Spikes & Cogs AB (hereinafter called Spikes & Cogs) is a cleantech company specialized in treating industrial process water, effluents, leachates and wastewaters (J. de Faire, personal communication, May 17, 2011). The company was founded in April 2010 by Urban Falkmarken and Johan de Faire. The concept is to apply naturally occurring biochemical and biological processes to reduce organic matters, recover metal ions, absorb emulsified fatty matters and stabilize inorganic compounds. From an environmental point of view, the idea is to return treated fluids to the ecosystem without causing any additional environmental burden to the recipient. The treated water should be clean enough to be able to re-use as recycled process water, surface water, water for infiltration or water for irrigation.

The hardware used in Spikes & Cogs products are add-on units of plug-in type. They can be used as a complement to conventional water treatment methods or as a replacement for less cost-effective methods. During the summer of 2011, pilot studies of the technologies developed by Spikes & Cogs were conducted. One of the pilots was located at Ovako in Hofors and is the subject of this master thesis.

1.2 Ovako Hofors AB

Ovako in Hofors, Sweden, is represented by two companies within the same industrial area: Ovako Hofors AB and Ovako Tube & Ring AB (www.ovako.se). The forerunner to Ovako was SKF Steel. Today the Ovako group is composed of a number of companies and is owned by the private equity investor Triton. The main operation of Ovako Hofors AB is production of steel blanks and heavy bars. Steel is made in Hofors and some of it is further processed in the Ovako plant in Hällefors. The steel has high purity. About 70 % of the total steel production is used to make bearings and the rest is used in other applications with similar high demands on purity. Ovako Tube & Ring AB processes steel blanks to make tubes and rings.

1.2.1 Description of Processes

Ovako uses various qualities of steel scrap as raw material to the steelmaking process (Ovako steel). The scrap arrives by train or by truck and is loaded in scrap baskets before it is charged to the Electric Arc Furnace (EAF). The EAF process is run batchwise and the weight of one charge is approximately 100 tons. The steel is melted in the EAF. In the next step the molten steel is treated in the ladle furnace where the steel is alloyed and degassed. In the degassing process about 300 m^3 of process water is used. After the degassing, the steel is ingot-cast in 24 cast iron moulds per charge. The cast iron moulds are removed and the ingots put in a soaking pit furnace to be heat treated. After soaking, the ingots are rolled in the rolling mill to blanks in different dimensions.

Tube and Ring AB refines the blanks to tubes and rings. The steel is heated and processed to the desired dimensions. Tubes are hot rolled and may subsequently be cold processed to achieve desired properties. Depending on the dimensions, rings are rolled or forged. In a similar way blanks are refined to bars in Hällefors.

1.2.2 Process Water Treatment Plant

The process water treatment plant (PWTP) is situated in the south part of the industrial area of Ovako in Hofors (K. Pålsson, personal communication, June 16, 2011). Every hour, 550 m^3 of industrial process water flows through the PWTP, which yields a flow of approximately 5 000 000 m^3 a year.

After treatment the production units re-use the water in the manufacturing processes. In addition, the vacuum pump in the ladle furnace uses 600 m^3 of water per hour for the degassing process. The process runs between 30 and 40 minutes at each run and about 100 times per week. This yields an additional volume of approximately 1 560 000 m^3 per year to the total amount of process water flowing through the PWTP. Investigations indicate that a great part of the metal content in the incoming water to the PWTP come from the degassing water. The process water is returned after treatment in the PWTP to a closed circuit-system in the industrial area. The excess water from the PWTP overflows to the recipient, river Hoån.

In addition to the process water flows, it happens that vacuum loaders empty their burden in the pre-separator basin or in the sludge boxes outside of the PWTP depending on the water content in the load. The vacuum loaders collect waste all over the steel plant. Most often it is small amounts of sludge-blended water from maintenance of sewers. It is also common with wash water used to clean out the vacuum loaders after transport of solid bulk material like lime or mill scale. Even though the burdens are small in volume, they can cause disturbances to the PWTP. The most sensitive part is the sand filter process.

The technology and methods currently used for treating the process water works well under normal conditions, but when certain variations occur, the sand filters do not work efficiently.

The necessity of high-quality water in the process plant and environmental restrictions on overflowing water to Hoån motivate Ovako to take on a pilot study with technology from Spikes & Cogs. The pilot is done in order to evaluate if some of Spikes & Cogs technologies could match Ovakos requirements.

1.3 Description and Aim of Project

1.3.1 Purpose

The purpose of this master thesis was to analyze and compare the results of the sand filters at Ovako to the results of the FOSS, FADE and MAAC technologies. The purpose was also to compare the stability of the FOSS, FADE and MAAC technologies to the stability of the sand filters. The stability of the cork filters was tested through stress experiments. Parameters to be analyzed are:

- Oil concentrations
- Metal concentrations
- Concentration of suspended matters

1.3.2 Methodology

This master thesis was performed in the following steps:

- Perform literature study
- Conduct experiments
- Analyze test results
- Evaluate test results
- Write report

1.3.3 Limitations of Thesis

To limit the aspects evaluated during the experiments, some parameters were selected as more crucial than other. Also, the people responsible for the wastewater treatment plant at Ovako listed the problems they had encountered through the years. The following main disturbances to the incoming water system were stated:

- sudden changes in pH levels
- high loads of graphite
- high loads of emulsions
- high loads of degreasing agent
- high loads of suspended matters

The stress experiments were limited to cover the disturbances that are stated above.

The aspects evaluated were:

- The Spikes and Cogs filters during normal operation.
- The Spikes and Cogs filters at stressed operation beyond the sand filter limits of operation.

The parameters used for the evaluation were:

- Concentrations of suspended matters and oils.
- Concentrations of aluminum (Al), chrome (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), phosphorous (P), lead (Pb) and zinc (Zn).

2 Survey on Industrial Water Treatment

The following section gives a summary of some of the process water treatment and wastewater treatment technologies that are commonly available on the market. The function of sand filters is covered in more detail since it is the technique currently used at Ovako. Also, this section gives a background to the active processes of the FOSS, FADE and MAAC technologies. Process water is water used in different processes in industries. Wastewater is water that has been used in different applications and can be either industrial wastewater or municipal wastewater.

2.1 Conventional Methods for Heavy Metal Removal

Ahluwalia and Goyal (2007) discuss conventional methods for heavy metal removal from industrial effluents. Several processes have been developed to purify industrial and municipal wastewater. The most commonly used methods are precipitation, coagulation, ion exchange, cementation, electro-dialysis, electrowinning, electrocoagulation and reverse osmosis. The following sections briefly describe some of the methods.

2.1.1 Precipitation

The precipitation process is a commonly used method that can decrease the concentration of heavy metals in aqueous solutions to levels of parts per million (ppm). The process is usually cost effective but the treatment result is impaired at low pH. The precipitation process therefore depends on the addition of chemicals. The sludge produced in the treatment has high water content, which makes it expensive to dispose of. Precipitation can be done using lime, bisulphide or ion exchangers, but the process lacks the capacity to remove a specific metal and leave the others. Precipitation is ineffective at low concentrations of metals in the aqueous solution relative to the normal cleaning result.

2.1.2 Ion exchange

Ion exchange is another method frequently used with good results in the industry. An advantage of the ion exchange method is the possibility to decrease the concentration of metals to parts per billion (ppb) after treatment. The method can handle big volumes and still maintain low concentrations of pollutants in the water after cleaning. A disadvantage is the relatively high cost of the method compared to other methods.

An ion exchanger is a solid matrix that can change ions on the matrix surface with ions in the water surrounding the solid. A disadvantage is the ion exchanger’s dependence on the pH in the solution and its sensitivity to high loads of organic materials which easily clog the matrix. Also, ion exchange is very sensitive so salinity.

2.1.3 Electrowinning

Electrowinning is commonly used in the mining and metallurgical industry. The method is used to treat water from heap leaching and acid mine drainage. With electrowinning, metals like silver, gold, cadmium and chromium, and others, can be removed or recovered from industrial effluents. Recovery and removal are important in the metal transformation, electronics and electrical industries. Electrowinning is commonly used for refining of metals.

2.1.4 Electrocoagulation

Electrocoagulation is an electrochemical approach to water treatment. An electrical current is used to remove metals from the solution. In addition to metals, the electrocoagulation process also removes suspended solids, dissolved metals, tannins and dyes. Ions and other charged particles precipitate when they are presented with ions of the opposite electrical charges provided by an electrocoagulation system.

2.1.5 Cementation

Cementation is a variant of precipitation implying an electrochemical mechanism. A metal of higher oxidation potential is put into a solution together with a metal of lower oxidation potential. An example is a solution of copper. At the presence of solid iron the copper ions are reduced to atomic copper and the iron oxidizes to ions. Copper and other noble metals are the most frequently separated metals with the cementation method.

2.1.6 Reverse Osmosis

Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes. The membranes are used for recovery of metal ions from diluted wastewater. Selective membranes are used in electro-dialysis. An alternation of cation and anion membranes is put between the electrodes in an electrolytic cell. Under continuous electric current the ions migrate, allowing recovery of metals.

2.2 Sand filters

Following section describes sand filters and summarizes the *P72* publication of Svenskt Vatten (The Swedish Water & Wastewater Association) from 1992.

Filtration is a common method for water treatment. There are essentially two types of filters:

- Fast filters with a capacity of 5-10 m^3/m^2 for open filters and 10-15 m^3/m^2 for pressure filters.
- Slow filters with a capacity of 0.2-0.4 m^3/m^2.

The unit of measurement, m^3/m^2, describes the flow, m^3, through the top or bottom filter area, m^2. In the beginning, sand filters were used for separation of suspended matters. One of the first big sand filters went into production as early as 1830 for the purpose of filtrating water from river Thames before the water was distributed to the Londoners.

Use of the word filtration has changed over the years. In the beginning it was used to describe the process of separating suspended matters from water. Now, filtration describes all kinds of processes, not only with the purpose to separate suspended matters from a solution.

Sand filter construction normally consists of a bottom layer of gross particles with a layer of finer particles on top. The water infiltrates from the top and percolates down through the filter. A filter fouling is created at the contact area between the sand and the water. The filter fouling increases the cleaning capacity of the filter, but it also slows down the process upon increased pressure drop over the filter. Once saturated with suspended matters there is always a risk of leakage of suspended matters and the filter unit needs to be backflushed to remove such matters. To avoid loss of bed volume it is important to keep the backflushed flow at a rate where the sand stays in the filter instead of leaving with the rinse water. When a filter unit is being backflushed it has to be disconnected from the flow and therefore, to keep a continuous process running, at least two parallel filter units must be used.

It is not only the pore width between the sand particles that prevents the particles passing through the filter. Particles smaller than the pores can adsorb to the sand particles by electrostatic binding.

Figure 1: DynaSand filter (www.nordicwater.com)

A sand filter becoming more commonly used is the DynaSand filter which is also the technique used at Ovako. This technique makes it possible to have a continuous flow through the filter, because of the built-in backflush function. In a common fast sand filter the sand is stagnant. In a DynaSand filter the sand is moving through the filter at a constant speed and the flow through the filter is upstream, from the bottom to the top (bottom loaded). The water is injected about 1/3 from the bottom of the filter bed. The sand will therefore be most contaminated at the bottom of the filter. A mammoth pump, which is a pumped powered by air, lifts the sand from the bottom to the top while it is rinsed on its way up. At the top of the filter, the water and the sand will be clean.

In newer DynaSand filters the flow and the construction is reversed i.e. the water flows downwards and the sand upwards (top loaded).

2.3 Biosorbents

Biosorption is the process were a biological material, living or dead, adsorbs metals, dyes or different kinds of materials from aqueous solutions (Park et al., 2010). The first research article discussing a quantitative study on biosorption was published already in 1902, according to the work done by Park et al. (2010). The earliest application of biosorption for large scale use involved sewage and wastewater treatment. During the past 30 years thousands of articles discussing biosorption and about 70 review papers have been published (Park et al., 2010). The topics discussed in the articles mainly deal with biosorption phenomena, equilibrium and kinetic modeling, reactor operation and application in real industries (Park et al., 2010).

It is important to make a distinction between living and dead biosorbents. Living biosorbents are microorganisms that digest toxic pollutants and hence remove them from the wastewater. Dead biosorbents are different kinds of organic materials, for example rice straws, wheat bran, soy bean husks, plant residues, sawdust, tree barks and weeds only to mention a few (Park et al., 2010). The advantages of dead biosorbents are that they do not demand nutrient supplies and complicated bioreactor systems (Park et al., 2010) and are more tolerant to toxic environments (Matis et al., 2003). The organic material used as biosorbent is often common in the region where it is used (Das et al., 2008).

In a review by Babel and Kurniawan (2003), a wide range of different low cost adsorbents are described. Chitosan, a byproduct from cellulose, is a heavy metal adsorbent. Zeolites, naturally occurring crystalline aluminosilicates, are ion-exchangers. Zeolites are especially good at adsorbing strontium and cesium but also adsorb other heavy metals. Other kinds of clays have been studied for their ion-exchange capacities and have been found to adsorb zinc, lead and aluminum from aqueous solutions. Peat moss mainly consists of lignin and cellulose and is an ion-exchanger. The content of humic acids and fulvic acids in peat moss influences the uptake of metals. Over all peat moss is a good adsorbent for all metals. Natural oxides can be used as sorbents for heavy metals. Especially the uptake of arsenic and chromium has been studied. Industrial wastes such as iron(III) hydroxide, lignin, blast-furnace slag and saw dust adsorb metals. Other low-cost sorbents described by Babel and Kurniawan are rice husk carbon (RHC) and coconut shell. RHC removes chromium(VI) at pH 2.5. Coconut shell also removes chromium (VI) at pH below pH 7 and has a higher sorption capacity at low concentrations.

2.3.1 *Cork as Sorbent*

Cork bark contains high levels of the hydrophobic substance suberin. The function of suberin is to prevent water and minerals to pass through the plant wall (Campbell & Reece, 2005). The barrier is called the Casparian strip and works in two ways; the Casparian strip keeps water in the plant to prevent the plant from drying and it prevents too much water and minerals to pass into the plant (Campbell & Reece, 2005).

In a study conducted by Villaescusa et al. (2000), yohimbe bark and cork from the oak tree was used as sorbents. Yohimbe is a tropical tree used to extract yohimbine, an alkaloid with pharmacological properties. The aim of the study was to investigate the ability of cork and yohimbe bark wastes to remove Cu(II) and Ni(II) from an aqueous solution. The experiments were all carried out in a small laboratory scale with untreated cork and yohimbe bark. Samples of 0.1 g of the sorbent were put in contact with 10 cm^3 of different aqueous metal solutions and shaken until equilibrium was reached. The pH, the sodium chloride (NaCl) concentration and the metal concentration was varied. When pH was varied a maximum uptake was observed at pH values around 6-7. When the initial pH value was greater than 2.5-3 the pH increased to about neutral during the experiment. Villaescusa et al. (2000) also provided evidence for the theory that the metal uptake is dependent on the pH. The closer to a neutral pH value, the greater is the uptake of metals. The increased uptake at increased pH can be explained by the protons and metal cations competing for surface sites at low pH.

The experiment by Villaescusa et al. (2000) was continued as follows. When different concentrations of NaCl were added to the solution, the adsorption of metals decreased quickly. Especially the Ni adsorption to cork seemed to be sensitive to increased levels of NaCl. The adsorption process of the yohimbe bark was less sensitive and could keep a level of 90 % removal of Cu(II) at a NaCl concentration of 2.0 mol/dm^3. Cork, at the same concentration, has a 16 % removal of Cu(II).

The last aspect tried by Villaescusa et al. (2000) was how the initial metal concentration affects the metal uptake. Concentrations from 5 mg/dm^3 to 100 mg/dm^3 were applied. The result was that cork was a slightly less efficient sorbent than yohimbe bark. The uptake increased to 90 mg/dm^3 and became constant above that level.

A study of the adsorption of heavy metals by pre-treated cork was conducted by Chubar et al. (2004). The metals to be adsorbed were Cu, Ni and Zn. The cork used was in the fraction 50-100 μm. The pre-treatments of interest for this thesis are the Fisher esterification and the thermal activation process because similar methods are used to produce the cork used in the pilot study. The Fisher esterification was performed by Chubar et al. (2004) to confirm the important role of carboxylic groups in the metal binding process. Biomass of cork was treated with excess HPLC grade methanol using a solution of diluted hydrochloric acid as a catalyst. The cork was washed and dried after the treatment. The thermal activation process was carried out using steam. A porous carbon made of cork biomass was prepared and activated in steam with temperatures of 700 and 800 °C. The thermal treatment increases the surface of the cork.

The pre-treated cork and aqueous solutions containing Cu, Ni or Zn were placed in bottles. The flasks were stirred at 25 °C for a pre-set contact time of 24 or 48 hours. The solution was filtered and the metal concentration analyzed. Chubar et al. (2004) concluded that the Fisher esterification is important. Carboxylic groups are important binding sites for copper and nickel and the only binding sites for zinc. The sorption capacity of the thermally treated cork in a copper solution becomes four to six times higher than that for untreated cork.

2.3.2 Microorganisms in Municipal Wastewater Treatment

The following section describes the role of microorganisms in municipal wastewater treatment plants (WWTP) and summarizes the *U2* publication of Svenskt Vatten (The Swedish Water & Wastewater Association) from 2010.

A common setup of municipal WWTPs is to use an active sludge process. Active sludge contains microorganisms, most commonly different species of bacteria. The basic setup is an aerated and mixed basin, where active sludge and wastewater is blended. The microorganisms digest the nutrients of the incoming wastewater, multiply and build flocculants. The sludge-blended wastewater is transported to a settling basin where the active sludge settles. Clean water is decanted from the top of the settling basin. If flocculants are not built, the sludge will leave with the clean water to the next step. Some of the active sludge in the bottom of the sedimentation basin is pumped back to the aerated basin.

This process gives water with a concentration of suspended organic material and substances of 10-25 %. The water needs further processing, but the main part of the organic matter is gone.

A similar system for removal of nitrogen is composed of an aerated basin with oxidative bacteria, an aerated basin with nitrifying bacteria and an anoxic basin with denitrification bacteria. This is a system that is used to remove nitrogen from the outgoing water. Giving slightly different results, the basins can be put in different order.

It is also possible to use microorganisms to reduce the phosphorous load. The water must pass through an anaerobic basin that contains both nitrate and an excess of easily accessible carbon. The process can be designed to make all wastewater, or only parts of the flow, pass through the phosphorus strip basin.

2.3.3 Microorganisms as Sorbents

Many studies have been conducted on the topic of reducing metals and heavy metals from solutions by using microorganisms as sorbents. Matis et al. (2003) use a combination of *Penicillium chrysogenum* and fungi to adsorb metals from an aqueous solution in a two-step process. The contact time of this biosorption is 6 minutes. The experiment was conducted in laboratory scale. The result shows a 90-95 % uptake of Cu, a 50-95 % uptake of Ni and a 70-99 % uptake of Zn. Matis et al. (2003) draw the conclusion that the method can be used to adsorb metals but that it requires further improvement and optimization of the method.

In the extensive review conducted by Ahluwalia and Goyal (2007), a wide range of studies of metal uptake by bacteria and fungi was described. Three fungal, four algal and two bacterial biosorbents were presented as the best biosorbents in the studies. Ahluwalia and Goyal also draw the conclusion that it is very important to understand the mechanism by which microorganisms accumulate metals. If the mechanism is known it is possible to develop processes for concentration, removal and recovery of metals from the aqueous solution. An example is fungi that have, according to Ahluwalia and Goyal (2007) and Gupta et al. (2000), a variety of ligands on their cell walls involved in metal chelation bonding. A metal ion can also be adsorbed by building a complex with negatively charged reaction sites on the cell surface of the fungi. The cell surface of fungi can vary considerably between different species and the adsorption capacity therefore varies likewise. It is therefore important to choose the right fungi for adsorption.

3 Process water treatment plant at Ovako

A more in-depth description of the PWTP at Ovako follows in this section. The potential disturbances in the PWTP and their origin are described.

The process water from the processes in the industrial area is gravity fed through the whole process plant (T. Skoglund, personal communication, May 17, 2011). When the water reaches the PWTP it is 5 m below ground (1) and has to be pumped up to ground level. At the treatment plant the water first arrives in a pre-separator basin (2) where the large particles in the process water settle. In the next step, the process water is treated in one of two parallel settling basins (3) that are equipped with oil skimmers. The waterborne particles settle at the bottom of the basin forming sludge that bottom scrapes collect to one end where the sludge is pumped to a thickener (5) and on to a sludge storage (12). Skimmers collect the oil from the settling basin and move it to the other end of the basin where the oil is collected in an oil storage tank (4). The process water, now containing less oil and suspended matters, flows to a collection storage (6). From here, four pumps lift the process water (7) and aluminum chloride ($AlCl_3$), a flocculant, is added on the way to the sand filters (8). Studies made at Ovako show that most of the metals in the process water are bound to the suspended matters.

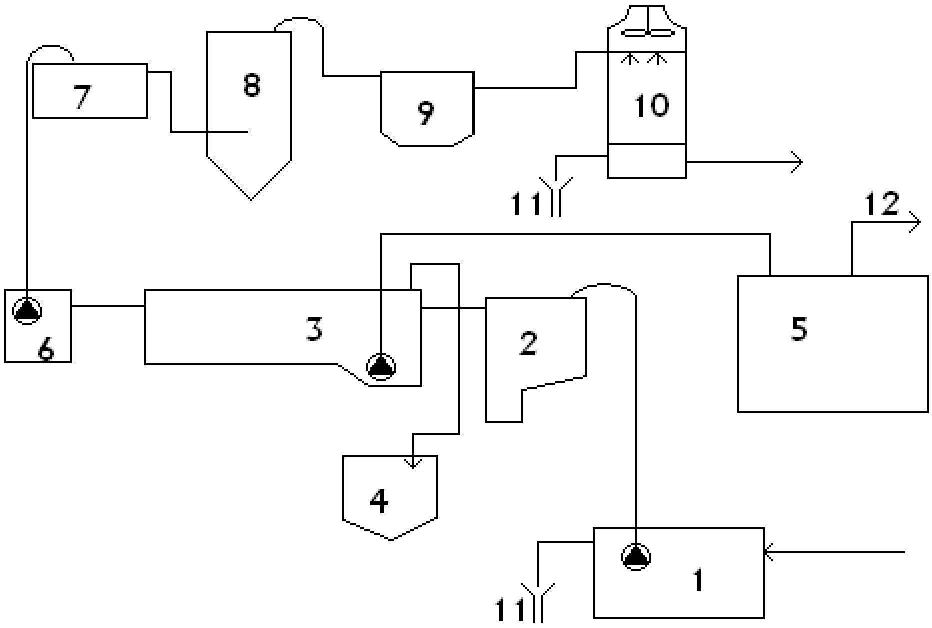

Figure 2: Schematic overview of the PWTP. 1. Collection storage for incoming wastewater. 2. Pre-separator basin. 3. Settling basin. 4. Oil storage tank. 5. Thickener. 6. Collector storage. 7. Collecting vessel. 8. Sand filter. 9. collecting vessel. 10. Cooling tower. 11. Outlet to recipient.12. To sludge processing.

There are 32 parallel DynaSand filters; 8 newer and 24 older. The newer sand filters were installed in the middle of the 90's and are top loaded. The old ones are bottom loaded. In each sand filter, a pump moves the water through the filter. After the sand filters, the clean water flows to a collecting vessel (9) onto two cooling towers (10) where the water is cooled to 25 °Celsius. From the cooling towers, pipes lead the water back to the production plant. If there is too much water at the same time in the PWTP, water can be decanted to recipient (11). The wash water from the sand filters, which contains all the pollutants and suspended matters, goes to a lamella sedimentation process. The lamella sludge goes to a sludge storage and onto a filter press. The water pressed from the sludge in the filter press flows back to the sedimentation basin. The water from the lamella flows to the pre-separator basin. During the summer months the need of cooling water is sometimes greater than the capacity of the PWTP. When this happens, additional water from the river Hoån is used to cool the processes in the steel plant.

3.1 Disturbances in the PWTP

In the following section the origins of the disturbances in the PWTP are described.

3.1.1 pH

The sand filters of the PWTP have a decreased efficiency at low and high pH. At normal operation, pH should be between 6.4 and 7.4. If the pH is lower or higher than the normal operational pH the amount of suspended matters in the filtrated water will increase.

In the steel mill, uncalcined lime is used as slag forming agent. When needed, a vacuum loader is used to remove excess or spilt lime from the site. After unloading the waste lime, the inside of the vacuum loader is washed. The wash water is sometimes emptied in the pre-separator basin at the PWTP which may result in an increased pH. The phenomenon of a decreased pH follow the same principles as that for an increased pH, only that the source is acid water remainings from the pickling. Independent of if the wash water increases or decreases the pH of the PWTP system, the water thereby disturbs the sand filters downstream from the pre-separator basin.

3.1.2 Graphite

Graphite is used as lubricant in some of the rolling processes. The residual graphite is collected in a trap, but some of it may accidentally overflow to the process water and end up in the PWTP where it clogs the sand filters. If this happens, the filter sand has to be replaced. Usually, very low concentrations of graphite will create disturbances to the filters. There are different kinds of graphite, some are dissolved in the aqueous phase, others are emulsified and others float on the surface. The one used in the experiment described in Section 5, is emulsified graphite.

3.1.3 Suspended Matters

On occasions, e.g. when loads have been emptied in the pre-separator basin, precipitated particles are stirred up and follow the flow to the sand filters. This causes a so-called penetration (i.e. leakage) as the sand filters cannot take the instant high load of particles.

3.1.4 Emulsions

Emulsions are for example used at the pilger mill at Tube & Ring to lubricate the tubes during cold rolling. The emulsions are meant to be trapped in an oil trap before the water leaves the production plant. Because emulsions do not float on the surface, but are emulsified in the water, they cannot be scraped off when they reach the PWTP. Instead, if emulsions get to the PWTP they will clog the filters. As a consequence, the sand bed has to be washed for one or two days, or in the worst case be replaced. The replacement is both time consuming and expensive.

3.1.5 Degreasing Agent

In the rolling mills, grease and oil are used to make the machines run smoothly. From time to time the machines need to be degreased and for this purpose degreasing agents are used. The mechanical parts are dismantled and brought to the building for degreasing. Normally, all degreasing agents are collected in this building. If small amounts of degreasing agent reach the PWTP, the flocculation process before the sand filters will be disturbed. The efficiency of the sand filters will decrease and the filtered water after the sand filters will contain too high concentrations of suspended matters.

3.2 Degassing water

In the steelmaking process, the steel must be degassed after being melted. During the degassing, oxygen is removed from the steel to give it a higher purity. The process water is used for the vacuum pumps that create a vacuum in the ladle to remove oxygen. Investigations of the water from the vacuum pumps have shown that it contains relatively high concentrations of metals. Therefore, it is of interest to see if the metals from the degassing water can be removed before the water reaches the PWTP.

4 Material

In this section a description of the equipment used for the experiment and the experimental setup will be given. All experiments were conducted according to the same setup. The following equipment was used during the pilot study:

- Submersible pump
- Water tank, 600 l
- Air Whirl Technology (AWT) unit
- Circulation pump
- Fats, Oils and Solvents (FOSS) filter, 60 l tank
- Fast Acting Digestive Enzymes (FADE) filter, 60 l tank
- Metal Adsorption AND Concentration (MAAC) filter, 60 l tank
- Orion5star Thermo Scientific meter

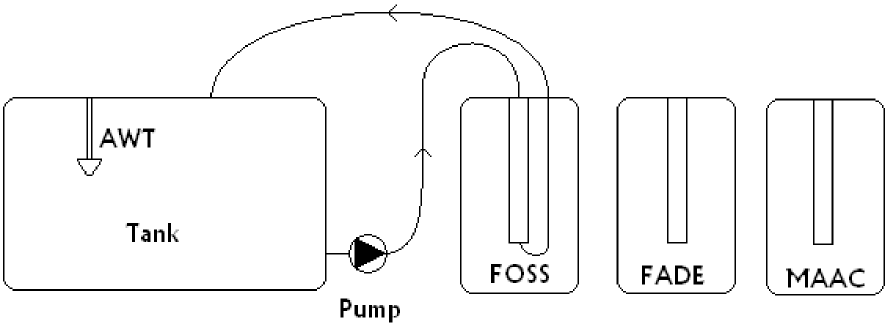

Figure 3: The experimental setup. An AWT unit mixes the water in the tank. A pump circulates the water through the filters, one filter at a time. When the desired contact time is reached in the first filter, the water is circulated through the next filter. Samples of the untreated water are taken from the tank before the circulation is started. Samples of the treated water are taken after the MAAC filter.

The process water was pumped to the tank from the collector storage, Figure 2, unit no 6, upstream of the sand filters before the addition of flocculants. The water was circulated through the FOSS filter until the desired contact time was reached. See section 5.1, for more information on the calculations of the contact time. When the desired contact time was reached in the first filter, the process water was pumped to the FADE filter and circulated to reach the desired contact time. Thereafter, the water was pumped to the MAAC filter. The water was stirred and aerated by the AWT unit throughout the whole process to facilitate the metal adsorption during the last step.

In a full scale application with all three filters, the filters are put in the same order as described above. The water will not be circulated, but pumped through the filters, see Figure 4.

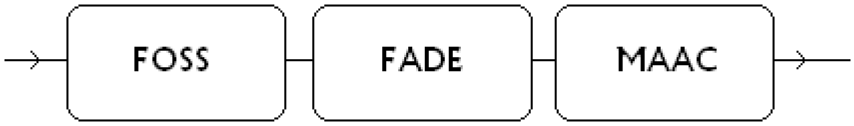

Figure 4: The flow of water through the filters in a full scale application. With enough filter volume, the water does not need to be re-circulated.

4.1 Filters

The FOSS, FADE and MAAC filters are all based on a cork matrix. The cork trees grow in Portugal and Spain and when the cork oak tree is 25 years old the cork bark is harvested for the first time. From then on the cork bark is harvested every ninth year. So far, most of the cork harvested goes to wine cork production. The process of making wine cork leaves 60-70 per cent rejects. Because cork contains suberin, a natural aliphatic fatty acid, it naturally absorbs oils and lipids. Oils, suspended matters and metal ions are adsorbed in the activated cork filters. To maximize the active surface, the cork is grated into granulates. It is then activated in different ways to lend it its specific characteristics.

4.1.1 The Fats, Oils and Solvents (FOSS) Filter

To improve the cork further it is heat-treated under pressure to expose more of the cells and thereby creating an even larger accessible surface (J.de Faire, personal communication, May 17, 2011). When the cork becomes more porous, i.e. a greater surface becomes accessible for oils and fatty matters to adhere to. The treated cork absorbs hydrocarbons and lipophilic compounds from C1, e.g. methanol, to C40, a compound containing 40 carbon atoms. During use, the saturated matrix gains high energy content. The used cork can be recovered by incineration.

4.1.2 The Fast Acting Digestive Enzymes (FADE) filter

In the FADE filter, enzymes that are excreted by microorganisms degrade suspended matters into stabilized fragments, e.g. natural nutrients (Spikes & Cogs, 2010). The active microorganisms in FADE are a lactic bacteria *Pediococcus pentosaceus* and two kinds of yeast; *Pichia farinose* and *Dekker bruxellenesis*. When in contact with water, the microbes will rapidly excrete biological metabolites, such as:

- Organic acids: lactic acid, acetic acid, succinic acid
- Digesting enzymes: amylase, galactosidase, proteinases
- Anti-microbial substances: “ pediocin” (bacteriocin)
- Vitamin B complex, D and growth factor

The benefits of the microbes are many (Spikes & Cogs, 2010). They have, among other, the ability of decomposing organic matter into substrates. They pre-activate organic materials for biogas and bioethanol production. During the process the microbes' activity lends the solution a pH of 6-7. Under anaerobic conditions the microbes have the ability to denitrificate. Under aerobic conditions foul smells and odors can be eliminated and nitrification and digestion will take place. The microbes' activity in the solution or material will create an unfriendly environment for pathogenic bacteria, viruses and fungi.

FADE is facultative anaerobic; if there is no oxygen present, compounds based on nitrogen, phosphorous and sulfur will be used in the microbial metabolism (Spikes & Cogs, 2010). By controlling the level of dissolved oxygen in the water, the process can be adapted to convert the nitrogenous, phosphorous and sulfurous compounds into compounds more friendly to the environment. More than 85 per cent of the suspended organic matter in contact with FADE is degraded in 6-48 hours (Spikes & Cogs, 2010).

4.1.3 The Metal Adsorption And Concentration (MAAC) filter

The binding mechanism used in the MAAC filter is based on chelating bonds (J. de Faire, personal communication, May 17, 2011). A chelating bond is formed when a single metal ion binds to two or more binding sites within the ligand (Hägg, 1989). When the metal ion has bound to the ligand, it cannot react with other elements or ions to form metal salts, precipitates or scale.

The MAAC filter matrix is based on cork that is enzymatically treated to expose more cells and to activate binding sites (J. de Faire, personal communication, May 17, 2011). Amines and carboxylic groups are allowed to form ligands that metal ions can bind to. When the filter is saturated, the matrix can be incinerated and the metals recovered by smoke-gas condensation. Another method is to desorb the metals from the matrix and evaporate them into dry powder. The metals can be reprocessed and re-used.

4.2 Air Whirl Technology

An AWT unit is used to aerate the water in the experimental tank (M.Bresell, personal communication, June 13, 2011). The aeration is achieved by adding air under vacuum, which differs from the commonly used strategy to add air at over-pressure. The technology is based on rotation. When the unit rotates at high speed, vacuum is created in the conical part of the unit. Air is sucked into the AWT unit through the drilled-through shaft. Water, in the form of a centripetal whirl, is sucked in through the bottom of the cone. The centripetal whirl in the water creates a fast and strong movement in the medium itself and the added air. When the water meets the air in the created vacuum in the cone, the two media implode. When this happens, microscopic air bubbles containing oxygen are created. The bubbles diffuse into the medium and binds to the water.

Microscopic bubbles have a longer dwell time in the medium and a greater total area compared to the result from other methods of aeration. A greater area and longer dwell time creates an environment that facilitates biological and chemical processes in the water. An AWT unit consumes an average of 1.5 kWh during operation. The effective aeration when the unit is in use is an average of 0.5 kg oxygen per hour. This means that 52 m^3 of water at a temperature of 18 °C can reach oxygen saturation within an hour.

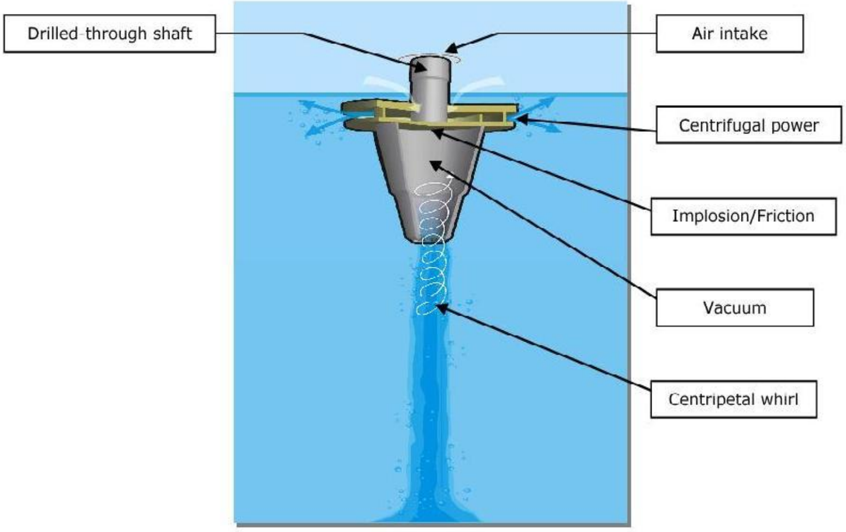

Figure 5: Air Whirl Technology unit

5 Method

In the following section, a method for calculation of contact time and experimental methodologies for parallel, stress and degassing water experiments are described. Also, measurement methods, methods for calculating reduction and historical data are described.

5.1 Contact time

The time that the water must be in contact with the filter to become clean is an indication of the efficiency of the filter and is called the contact time. The contact time was calculated by using the Empty Bed Contact Time (EBCT) method. The contact time was calculated by dividing the volume of the matrix by the flow rate through the filter. In the following experiments, a filter volume of 60 l was used. For example, if the flow rate through the filter is 8.45 l/min, the contact time per hour of operation is (60 l /(8.45 l/min=) 7.11 minutes per hour of operation. In the parallel experiments described below, different contact times were used. To achieve a contact time of 30 minutes, at the contact time per hour of operation in the example above, the equipment would have to run for (30 min / (7.11 min/hour) =) 4.21 hours.

5.2 Guidance Values

The guidance value is a value limiting the emissions to the recipient and the impact on the environment and is set by the authorities. The guidance values must be followed, and if they are exceeded, the company has to report to the Länsstyrelse (County Administrative Board) and present measures to come to terms with the emission. Specific guidance values for the PWTP at Ovako are given for the concentrations of suspended matters and oils. The guidance values are given as average concentrations per month.

- Suspended matters: 10 mg/l
- Oil: 5 mg/l

There is also a maximum allowed emission value (MAEV). If a MAEV is trespassed, the Länsstyrelse can take the company to court. The MAEV’s are too high to be important for this study.

A new general guidance value for emissions of P to recipients in the county of Gävleborg will be 0.4 mg/l, from January 1, 2012. As it is important for the company to follow the guidance values, the treatment results for the filters will be compared to the guidance values.

5.3 Experiments

To evaluate the chosen parameters experiments were conducted and samples were analyzed. In the following, the experimental methods of each experiment are described.

5.3.1 Parallel Experiments

To test the efficiency of the pilot equipment different contact times were used and the cleaning effects were compared to the results from the sand filters. The contact times analyzed were:

- 30 min with normal flow
- 15 min with normal flow
- 15 min with high flow
- 7.5 min with normal flow.

To reach the different contact times the flow of water through the filters was regulated. Low flow was set to 6-7 l/min and high flow was set to 11-13 l/min.

Depending on how many of the sand filters that were in use and the flow of the water through them, the contact time was calculated according to the EBCT method, see section 5.1. When the calculated time for the water to pass the old sand filters had passed, water samples were taken from the top of the old sand filters (bottom loaded). The newer sand filters have reversed inlets and the filtered water could therefore not easily be handled. The results from the sand filters were compared to the results from the pilot equipment.

5.3.2 Stress experiments

Different divergences were applied to the process water to allow analyses of the effects of the FOSS, FADE and MAAC filters. The applied divergences normally cause a loss of effect of the sand filters. This section describes how the divergences were applied.

5.3.2.1 pH

Two test rounds of extreme pH were conducted. The first round had a low pH of 5.6 and the second had a high pH of 8.9.

Hydrochloric acid, HCl, was used to lower the pH. The buffer capacity of the wastewater was measured in the laboratory and the amount of acid needed to lower the pH of the wastewater to the required level was calculated. 600 l of wastewater was put into the tank and the pH was adjusted to the desired level.

The same procedure was done with the added base. Sodium hydroxide, NaOH, was added to increase pH.

5.3.2.2 Graphite

6.5 g of graphite was added to get a concentration of approximately 10 mg/l graphite in the 600 l tank. To blend it properly with the water, the AWT unit was set at 50 Hz, without aeration.

5.3.2.3 Suspended Matters

Water was filled into the 600 l tank and the concentration of suspended matters in the water was measured at the laboratory. During the earlier parallel and stress experiments the concentration of suspended matters in the untreated water had been analyzed. Data shows that an amount of about 60 mg/l suspended matters seems to be the average concentration of suspended matters in the incoming wastewater. A concentration of three times the average concentration was chosen to simulate a high load. To reach the right level of suspended matters in the wastewater, dried and sifted sludge from the sludge boxes was added. 90 g of dried and sifted sludge was added to the total volume. During the second round, an amount of 85 g dried and sifted sludge was added to the total volume.

5.3.2.4 Emulsions

To make an estimation of a high load of emulsions the oil concentration was used. The guidance value of the oil concentration for the treated water from the PWTP was a monthly average of 5 mg/l. Twice the guidance value, 10 mg/l, was estimated as a high load for the sand filters. The normal load of oil in the incoming water during the experiments had an average concentration of 1.8 mg/l. To reach 10 mg/l a dose of 7 g was added under intensive stirring with the AWT unit. A series of samples was taken from the sample tank before the water was pumped to the filters, and another series from the water coming out from the filter.

5.3.2.5 Degreasing Agent

There is no previous analysis of the concentrations of degreasing agent in the incoming process water so an estimation of an appropriate high load concentration had to be made. As with the emulsion, the oil concentration was used to estimate a high load. A dose of 7 g degreasing agent was added to the tank while stirring with the AWT unit. A series of samples was taken from the sample tank before the water was pumped through the filter. Another series of samples was taken from the sample tank after the adding of degreasing agent. Finally, a third series was taken from the water leaving the MAAC filter.

5.3.3 Degassing Process Water

A sample of 600 l degassing process water was taken from the buffert basin upstream of the PWTP. The degassing process water contains metals, but no organic compounds, which is why this was circulated through the MAAC filter only. Different contact times were used to evaluate the purification; 1 min, 5 min, 10 min and 15 min.

5.4 Measurement Methods

Samples were taken using the same method for all trials. The first series of samples were taken from the untreated water in the tank (1). The second series of samples were taken from the tank after the divergence was added (1). The third series of samples were taken from the water leaving the last filter (2). When the emulsion and degreasing agents were used, a fourth sample was taken from the tube leading from the pump into the first filter. Three different samples were taken to analyze the concentration of oils, suspended matters and metals.

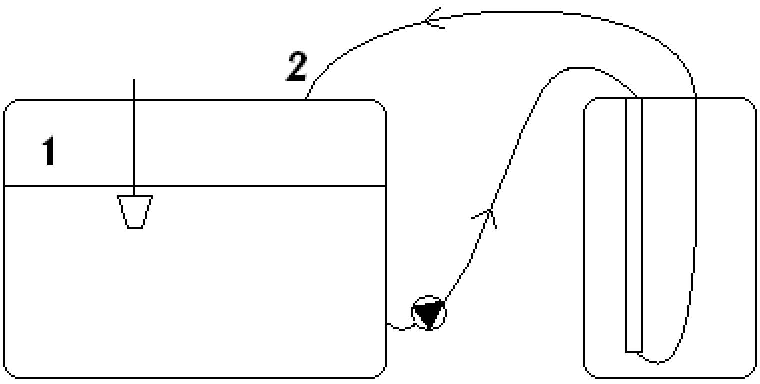

Figure 6: Sampling points. Point 1: Sampling point for untreated water and for water with added divergence. Point 2: Sampling point for treated water.

At the laboratory the concentration of oils was analyzed using the standard method ISO-9377-2, suspended matters were analyzed using the standard method SS-EN-872 and metals were acid digested and analyzed using Inductively Coupled Plasma (ICP) analysis. For measurements of temperature, conductivity, pH and dissolved oxygen (DO) an Orion5star Thermo Scientific meter and probes were used.

5.5 Calculations

The calculation of the contact time of the cork and the reject water was based on the contact time of the sand filters. The contact time of the sand filters was calculated from the volume of sand in the sand filters, the number of filters that was in use and the flow of the incoming water. The flow of the experimental system was measured manually.

5.6 Historical data

The efficiency of the sand filters has been measured by Ovako for a long time. The data used in this report are from April, 2010 and onwards. Important to notice is that the reduction is given in percent. The following equation was used:

$$reduction\ \% = \frac{c_{before} - c_{after}}{c_{before}} * 100$$

In Figure 7 the reduction of copper is shown.

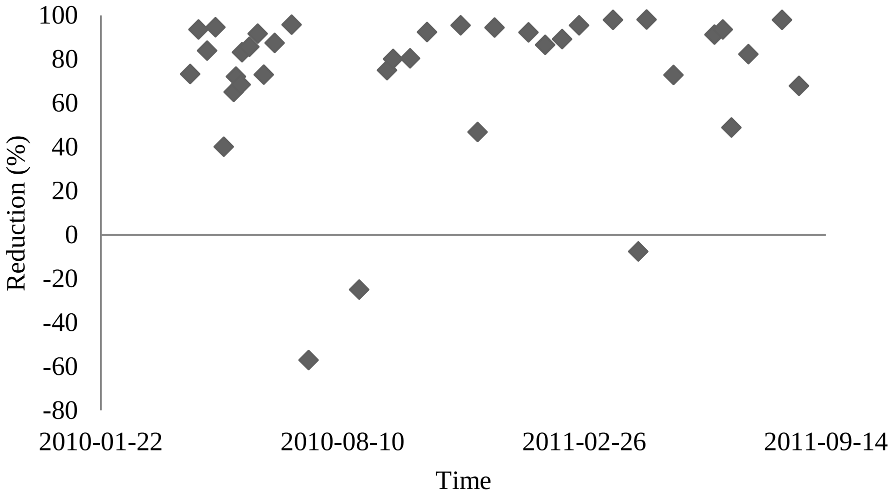

Figure 7: Reduction of Cu after sand filter

The values on the negative reduction axis show an increase of the metal in the effluent water from the sand filters. This was due to an overload of the sand filters which resulted in a penetration with increased levels of suspended matters, metals and oils to the filtered water. To enable comparison of the sand filters with the cork filters at normal operation, values from occasions with obvious disturbances in the PWTP were removed and an average and a maximum value were used for comparison. The points removed were 2010-05-04, 2010-07-13, 2010-08-24, 2010-11-30, 2011-04-12 and 2011-06-28. Figures of the reduction of Al, Zn, Cr and Fe after the sand filters are shown in Appendix A, Figure A1 – A4.

The calculated maximum and the average for the reduction of metals after sand filters are presented in Table 1.

Table 1: Calculated reduction maximum and mean values after sand filter. Reduction in (%).

	Cu	Al	Zn	Cr	Fe
Max	97.9	99.1	93.5	99.4	99.96
Average	85.4	85.7	67.2	89.2	91.5

6 Results

After the first two parallel experiments, it was decided to quit using the certified laboratory for the metal analyses that Ovako could do in their own laboratory. Samples for analyses of Antimonum (Sb) and of the concentration of oils were still sent to the certified laboratory. The analyses received from the certified laboratory had a higher reporting limit than the analyses received from the laboratory at Ovako. Also, the certified laboratory was slow at delivering the results from the analyses. For a summary, see Table 2.

Table 2: The table shows where each series of samples were analyzed. The external laboratory used for analyses of oil content was changed after the first six experiments. After the first two experiments, the concentration of metals was only analyzed at Ovako. After the ninth experiment Sb was not analyzed anymore because of its low content. After the sixth experiment the concentration of suspended matters was only analyzed at Ovako.

	Ext. Lab.1 Oil	Ext. Lab.2 Oil	Ext. Lab.1 Metals	Ext. Lab. 1 Sb	Ext. Lab.1 Susp	Ovako Metals	Ovako Susp
30 min	x		x	x	x	x	x
15 min	x		x	x	x	x	x
15 min H	x			x	x	x	x
7.5 min June	x			x	x	x	x
7.5 min September	x			x	x	x	x
pH 5.6	x			x	x	x	x
pH 8.9		x		x		x	x
Suspended matters, 10 mg/l		x		x		x	x
Suspended matters, 15 mg/l		x		x		x	x
Emulsions, 10 mg/l		x				x	x
Emulsions, 15 mg/l		x				x	x
Degreasing agent, 10 mg/l		x				x	x
Degreasing agent, 15 mg/l		x				x	x
Graphite, 10 mg/l		x				x	x

The data shown in the following sections are results from metal analyses that are made in an ICP at Ovako. After the stress experiments with suspended matters, results of the Sb levels arrived from the certified laboratory. Almost all data were under reporting limit. After that, no more samples were analyzed for Sb.

Samples for oil concentration analyses were sent to another certified laboratory (Eurofins) after the stress experiment with low pH. The reason to this was the long responding time at the first certified laboratory.

Duplicates of all samples were taken during the experiment with 30 minutes contact time. The analyses of the metal content in the duplicates were made by the

Ovako laboratory and showed almost identical results. To lessen the cost of the pilot study, the burden on the laboratory and the environmental impact only single samples were used for the following experiments.

Tables or figures of the concentrations and the reduction are presented for all experiment results. The reduction is calculated according to the procedure in section 5.6. The results focus on the reduction of Al, Zn, Cu, Cr, Fe, Pb, P, Mn, Mo, Ni, suspended matters and oil concentration.

Data of the concentrations of suspended matters and oils are compared to their guidance values.

6.1 Parallel experiments

Parallel experiments were conducted to compare the efficiency of the cork filters to the efficiency of the sand filters.

The radar diagram has an axis for every substance type. Note that, all radar diagrams use the logarithmic scale to enable visualization of all results in the same diagram. The concentration of each substance in the sample is plotted in the graph. All plotted concentrations are bound together by a line.

Values that are labeled “0 min” represent samples of the untreated water, which has not yet reached the sand filters or the cork filters. Values that are labeled “30 min” represent samples of water treated with 30 minutes contact time in the cork filters. Values that are labeled “15 min” represent samples of water treated with 15 minutes contact time in the cork filters. Values that are labeled “7.5 min” represent samples of water treated with 7.5 minutes contact time in the cork filters. Values that are labeled “Sand filter” represent samples of the water treated in the sand filters.

6.1.1 30 Minutes Contact Time

The first contact time to be tested was 30 minutes. Duplicates of all samples were taken. The duplicate samples “0 min” were by mistake taken with a two hour separation. It was obvious that some of the suspended matters had settled during the time passed.

The concentration of oils in all samples, both before and after the treatment, was below reporting limit, 0.1 mg/l. One of the samples for measuring suspended matters after the sand filter was reported below the reporting limit, 2.0 mg/l.

Figure 8 shows the concentrations at 30 minutes contact time.

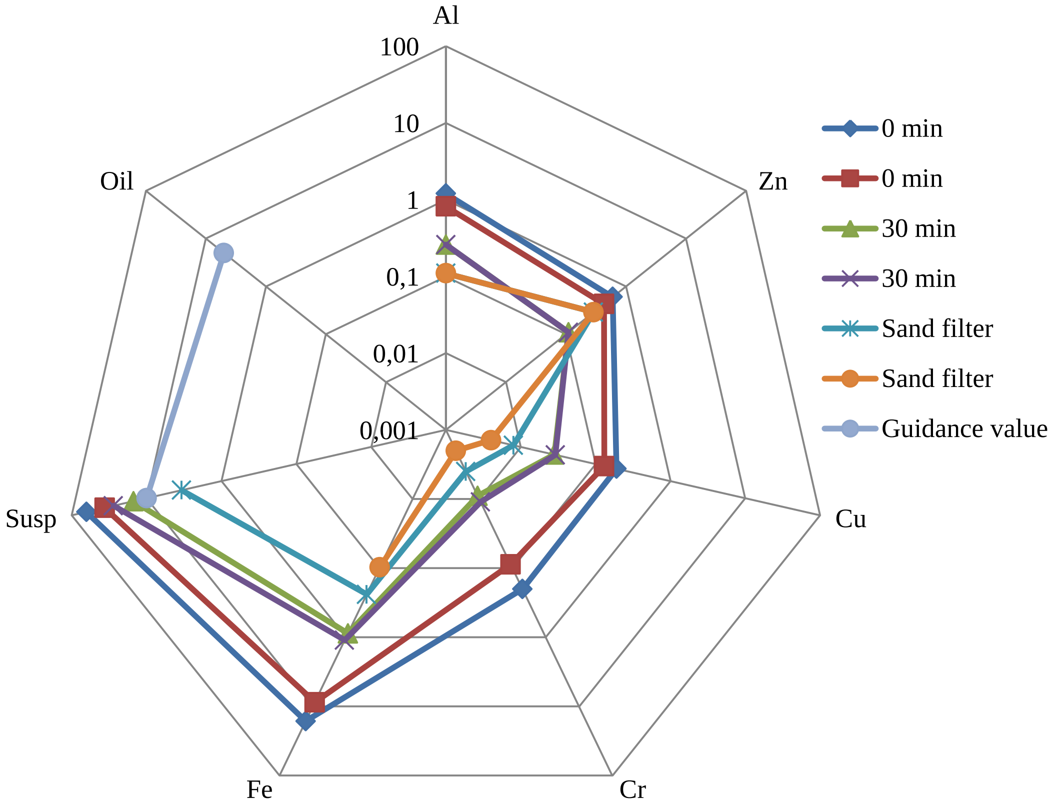

Figure 8: 30 minutes contact time. The table show both untreated and treated water before and after the sand and cork filters. Concentrations in mg/l

To calculate the reduction of suspended matters from the two duplicate samples, an average of the reported value and the reporting limit was used. The following is shown in Table 3:

- Except for Zn, the sand filters remove more of the substances.
- The reduction of Cr and Fe is 3-5 percentages lower in the cork filters than in the sand filters.
- The reduction of Al and Cu is 10 percentages lower in the cork filters than in the sand filters.
- The reduction of suspended matters is 20 percentages lower in the cork filters than in the sand filters.

Table 3: 30 minutes contact time. Reduction after cork and sand filters in percent.

	Al	Zn	Cu	Cr	Fe	Susp	Oil
Cork filter (%)	78.3	81.7	85.3	95.5	94.6	76.5	-
Sand filter (%)	90.8	51.7	96.8	98.5	99.0	95.8	-

In Figure 9, the reduction of Mo, Ni, Mn, Pb and P are shown.

- The reduction of Mo is 3 percentages lower in the cork filters than in the sand filters.
- The reduction of Ni is 6 percentages higher in the cork filters than in the sand filters.
- The reduction of Pb is 15 percentages lower in the cork filters than in the sand filters.
- The reduction of Mn is 25 percentages higher in the cork filters than in the sand filters.

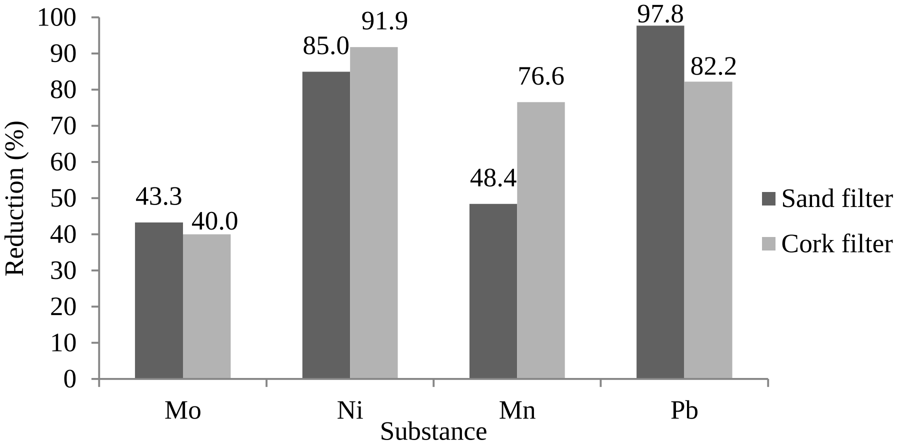

Figure 9: Reduction of Mo, Ni, Mn, Pb and P at 30 minutes contact time. Reduction in percent.

6.1.2 15 minutes contact time, normal flow

The parallel experiment with 15 minutes contact time was conducted in two batches. The first batch was run with a normal flow of 7 l/min. The results are shown in Figure 10. Note that the contact time of the sand filters could not be changed and is still 30 minutes.

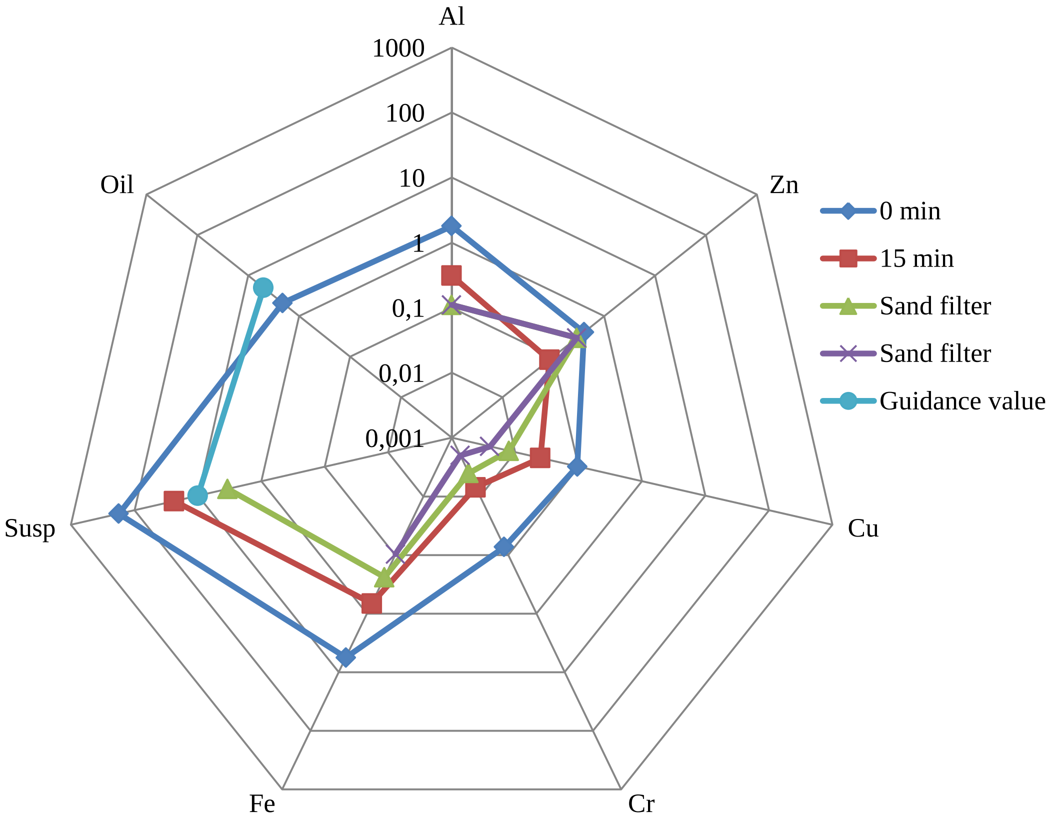

Figure 10: 15 minutes contact time, normal flow. The table show both untreated and treated water before and after the sand and cork filters. Concentrations in mg/l

The reduction of the concentration of oils in the filters, for both samples in Table 4, is calculated using the reporting limit of 0.1 mg/l. The reduction of suspended matters after the sand filters is calculated using the reporting limit of 2.0 mg/l.

- The reduction of Zn is 50 percentages higher in the cork filters than in the sand filters.
- The reduction of oil is identical in the cork and the sand filters because the calculation uses the reporting limit.
- The reduction of Cu is 20 percentages lower in the cork filters than in the sand filters.

- The reductions of Al, Fe and suspended matters are about 10 percentages higher in the cork filters than in the sand filters.
- The reduction of Cr is 5 percentages lower in the cork filters than in the sand filters.

Table 4: 15 minutes contact time, normal flow. Reduction after cork and sand filters in percent.

	Al	Zn	Cu	Cr	Fe	Susp	Oil
Cork filter (%)	82.8	79.0	74.0	90.4	88.0	86.6	95.2
Sand filter (%)	93.9	27.5	93.8	95.9	97.0	98.5	95.2

In Figure 11 the reduction of Mo, Ni, Mn, Pb and P are shown.

- The reduction of Mo is almost 20 percentages lower in the cork filters than in the sand filters.
- The reduction of Ni is almost 15 percentages higher in the cork filters than in the sand filters.
- The reduction of Mn is 25 percentages higher in the cork filters than in the sand filters.
- The reduction of Pb is about 15 percentages lower in the cork filters than in the sand filters.

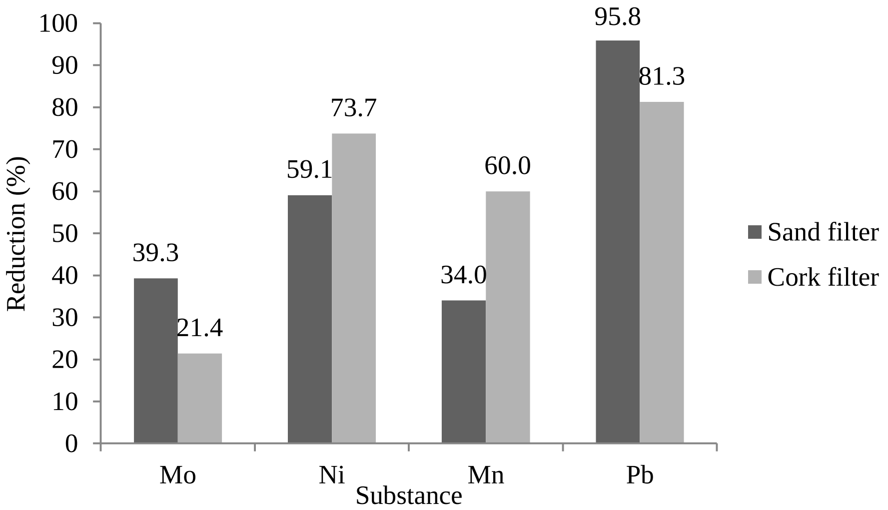

Figure 11:Reduction of Mo, Ni, Mn, Pb and P at 15 minutes contact time. Reduction in percent.

6.1.3 15 minutes contact time, high flow

In this experiment, a second contact time of 15 minutes was used. The difference from the other experiment with 15 minutes contact time is that a high flow of 12 l/min was used in this experiment. In Figure 12, the results are shown.

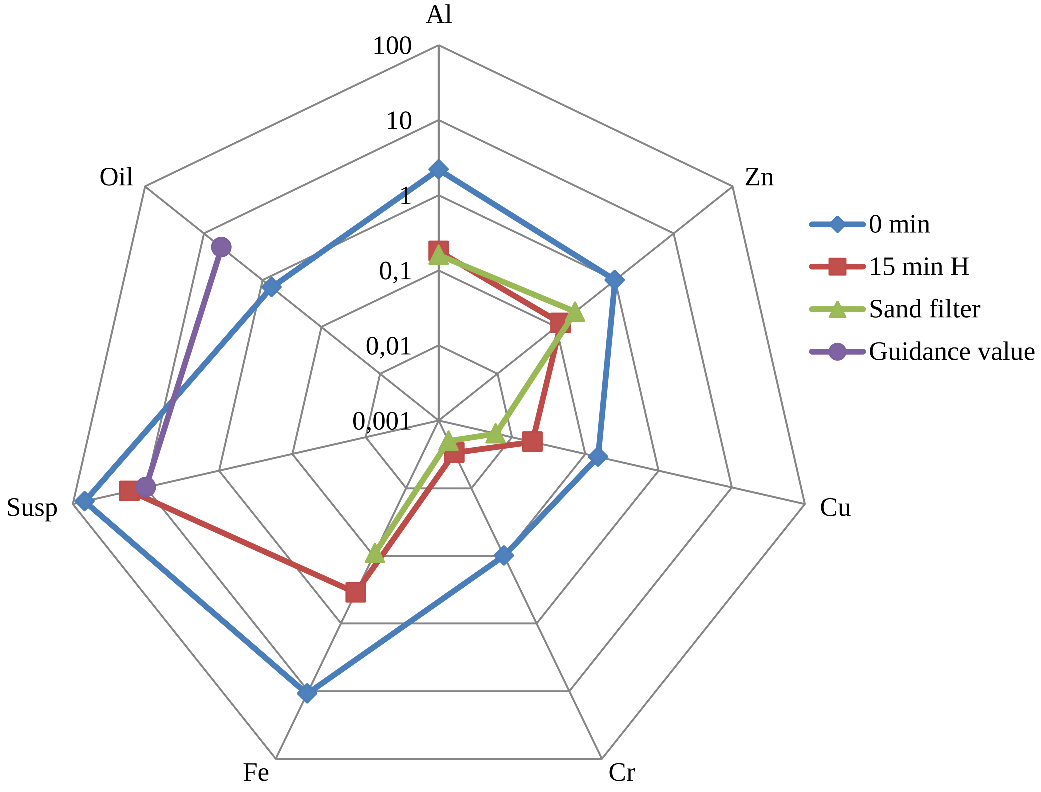

Figure 12: 15 minutes contact time with high flow. The table show both untreated and treated water before and after the sand and cork filters. Concentration in mg/l.

The reduction of the concentration of oils after the cork and the sand filters in Table 5 is calculated using the reporting limit of 0.1 mg/l. The reduction of suspended matters after the sand filters is calculated using the reporting limit of 2.0 mg/l.

- There are no big differences between the reduction of Al, Cr and Fe in the cork filters than in the sand filters.
- The reduction of Zn is 10 percentages higher in the cork filters than in the sand filters.
- The reduction of suspended matters is about 20 percentages lower in the cork filters than in the sand filters.

Table 5: 15 minutes contact time with high flow. Reduction after cork and sand filters in percent.

	Al	Zn	Cu	Cr	Fe	Susp	Oil
Cork filter (%)	91.8	88.0	87.3	97.0	96.8	75.8	85.7
Sand filter (%)	92.7	79.0	96.0	98.0	99.2	97.1	85.7

In Figure 13, the reduction of Mo, Ni, Mn, Pb and P are shown.

- The reduction of Mo is about 5 percentages higher in the cork filters than in the sand filters.
- The reduction of Ni is about 10 percentages lower in the cork filters than in the sand filters
- The reduction of Mn is about 10 percentages higher in the cork filters than in the sand filters.

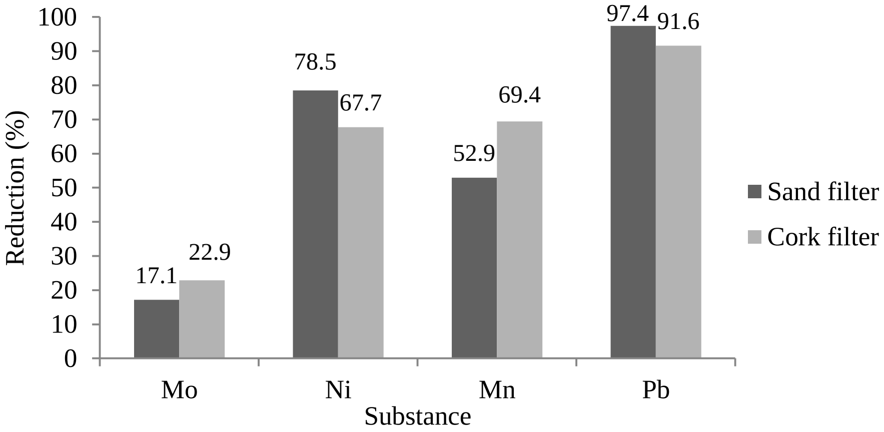

Figure 13: Reduction of Mo, Ni, Mn, Pb and P at 15 minutes contact time and high flow. Reduction in percent.

6.1.4 7.5 minutes contact time

The experiment with a contact time of 7.5 minutes was run two times, once in June and once in September. The reason for this was to analyze both if the water content had changed during the two months and if it would affect the results.

Concentrations of Al, Cu, Zn, Cr, Fe, suspended matters and oils can be seen in Figure 14:

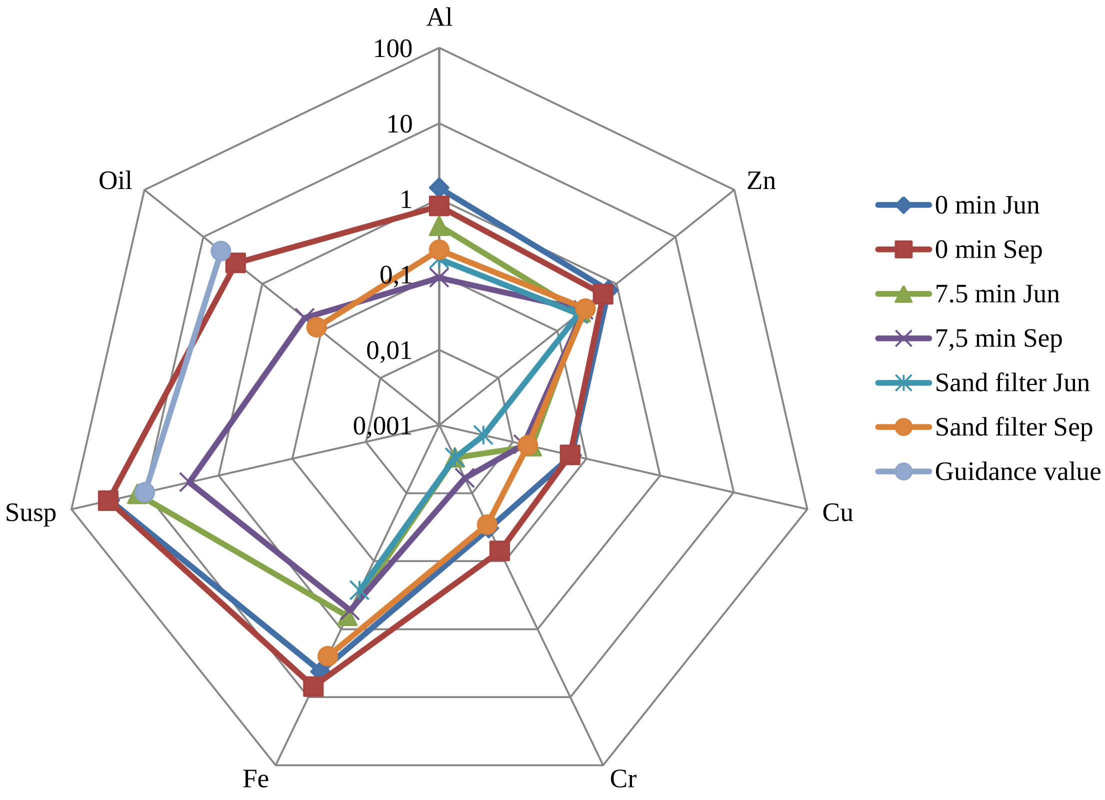

Figure 14: 7.5 minutes contact time. The table show both untreated and treated water before and after the sand and cork filters. Concentrations in mg/l.

In Table 6, the reduction of Al, Zn, Cu, Cr, Fe, suspended matters and oils are shown. The oil concentration cannot be calculated, because the concentrations before and after the filters are below the reporting limit. The reduction of suspended matters after the sand filters is calculated using the reporting limit.

- The reduction in the cork filters vary between the two experiments, especially the reduction of suspended matters.
- The reduction of Al is about 20 percentages lower in the cork filters than in the sand filters in June and is 15 percentages higher in the cork filters than in the sand filters in September.

- The reduction of Zn is 3 percentages lower in the cork filters than the sand filters in June and 3 percentages higher in the cork filters than in the sand filters in September.
- The reduction of Cu is 20 percentages lower in the cork filters than in the sand filters in June and about similar in the cork filters than in the sand filters in September.
- The reduction of Cr is similar in the cork filters and in the sand filters in June and almost 30 percentages higher in the cork filters than in the sand filters in September.
- The reduction of Fe is 10 percentages lower in the cork filters than in the sand filters in June and almost 30 percentages higher in the cork filters than in the sand filters in September.
- The reduction of suspended matters is 35 percentages lower in the cork filters than in the sand filters in June and almost similar in the cork filters than in the sand filters in September.
- The reduction of oils is almost similar in the cork filters than in the sand filters in September.

Table 6: 7.5 minutes contact time. Reduction after cork and sand filter

	Al	Zn	Cu	Cr	Fe	Susp	Oil
Cork filter (%) Jun	66.8	66.2	71.4	90.9	84.8	58,0	-
Sand filter (%) Jun	88.6	68.9	93.7	90.9	93.6	93.6	-
Cork filter (%) Sep	88.8	53.3	76.7	91.5	92.4	92	93.2
Sand filter (%) Sep	73.8	50.0	73.3	59.2	64.3	93.6	95.7

In Figure 15, the reduction for Mo, Ni, Mn, Pb and P are shown.

- The reduction of Mo and Ni is less than 10 percentages lower in the cork filters than in the sand filters.
- The reduction of Mn is almost 20 percentages higher in the cork filters than in the sand filters.
- The reduction of Pb is almost 25 percentages lower in the cork filters than in the sand filters.

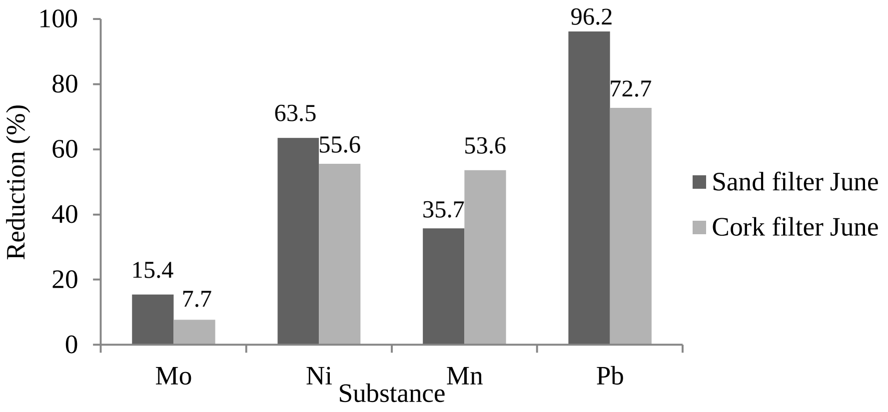

Figure 15: Reduction of Mo, Ni, Mn, Pb and P at 7.5 minutes contact time in June. Reduction in percent.

In Figure 16, the reduction for Mo, Ni, Mn, Pb and P at contact time 7.5 minutes in September are shown.

- The reduction of Mo is less than 5 percentages higher in the cork filters than in the sand filters.
- The reduction of Ni is 30 percentages higher in the cork filters than in the sand filters.
- The reduction of Mn is 15 percentages lower in the cork filters than in the sand filters.
- The reduction is less than 20 percentages lower in the cork filters than in the sand filters.

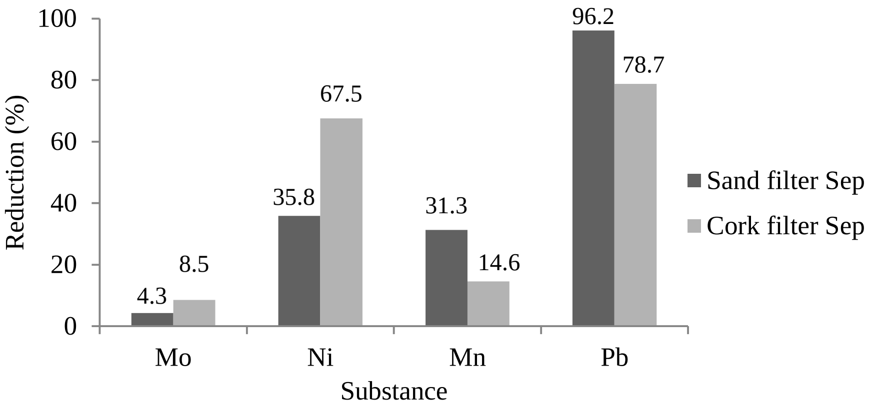

Figure 16: Reduction of Mo, Ni, Mn, Pb and P at 7.5 minutes contact time in September. Reduction in percent.

In Table 7 the concentrations of P before and after the sand filters and the cork filters are shown. Because of the increase of P in the water in the cork filters, the values are presented in a table. The concentration of P in the water after treatment is shown in times of the concentration of P before the filters. A value higher than 1 is an increase and a value lower than 1 is a decrease in concentration. The concentration of P in the sand filters is below the reporting value.

- The highest increase in concentration is during the experiment with the contact time 7.5 minutes in June. The concentration is increased 35 times.
- The highest decrease in the sand filters is 0.01 times and occurs during the experiment with 15 minutes contact time.
- The highest decrease in the cork filter is 0.18 times and occurs during the experiment with 15 minutes contact time.
- The decrease of P in the sand filters varies between 0.01 and 0.47 times.
- The increase of P in the cork filters vary between 5 and 35 times.

	Incomming water (mg/l)	Cork filter (mg/l)	Sand filter (mg/l)	Increase cork filter (times)	Increase sand filter (times)
30 min	0.16	0.87	<0.027	5	0.17
15 min	4.1	0.73	<0.027	0.18	0.01
15 min H	0.18	5.3	<0.027	29	0.15
7.5 min	0.075	2.6	<0.027	35	0.36
7.5 min	0.058	0.37	<0.027	6	0.47

Table 7:Concentration of P in the water before and after treatment with cork or sand filters. Concentrations in mg/l and increase of P after treatment in times of the concentration before treatment.

6.1.5 Comparison with historical data

To increase the statistical material, historical data from the sand filters (c.f. Section 5.6) were used for comparison. The reduction of each metal from each experiment shown in the radar diagrams was put into a diagram where it was compared to an historical average and a historical maximum value calculated from the historical sand filters sample data in Table 1. Because of the lack of historical data of Mo, Ni, suspended matters, oils, Mn, Pb and P no comparisons were made of these.

In Figure 17 the reduction of Cu is shown.

- The reduction is better than the historical average for the contact times 30 minutes and 15 minutes with high flow.
- For the three other contact times, the reduction is below the historical average.
- All values are above 70 % reduction of Cu.

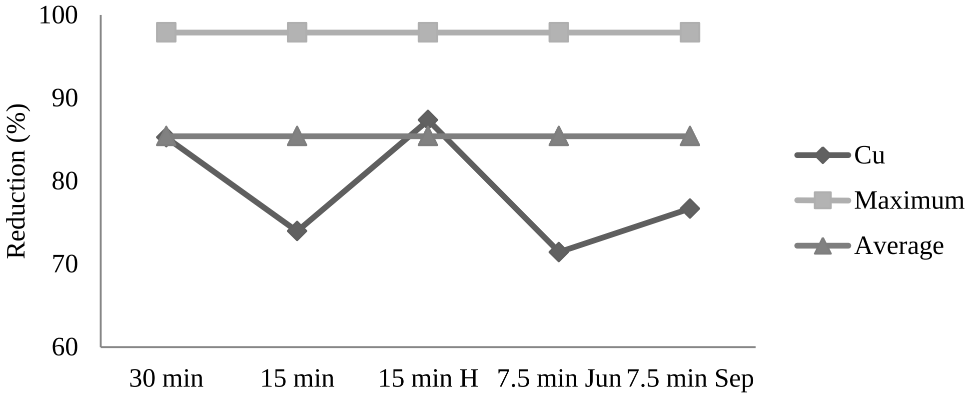

Figure 17: Reduction of Cu in cork filters, in percent, compared to historical data from the sand filters.

The reduction of Al is shown in Figure 18.

- At contact times 15 minutes with high flows and 7.5 minutes in September, the reduction is better than the historical average.
- The reduction is at its lowest at 68 % for 7.5 minutes contact time in June.
- The reduction is above 78% at 30 minutes and 15 minutes contact time.

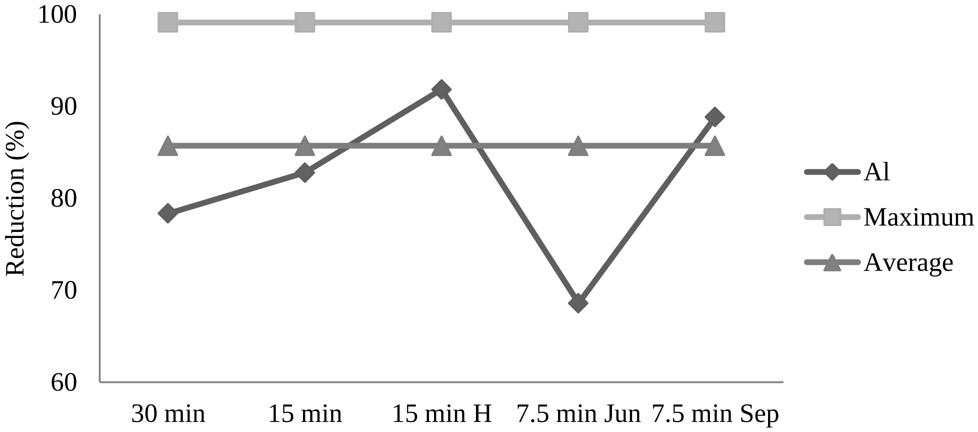

Figure 18: Reduction of Al in cork filters, in percent, compared to historical data from the sand filters.

The reduction of Zn is shown in Figure 19.

- The reduction is better than the historical average at 30 minutes contact time and at both the 15 minutes contact times.
- At 7.5 minutes contact time in June, the reduction is similar.
- At 7.5 minutes contact time in September the reduction is below the historical average.

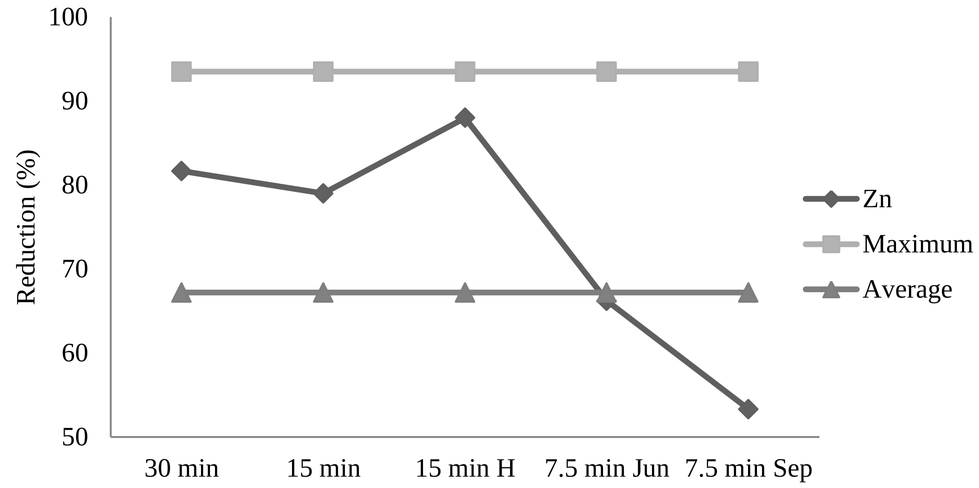

Figure 19: Reduction of Zn in cork filters, in percent, compared to historical data from the sand filters.

The reduction of Cr is shown in Figure 20.

- The reduction is better than the historical average at all contact times.
- The two highest reduction values were received for contact times 30 minutes and 15 minutes with high flows.
- The reduction of Cr is above 90 % for all samples.

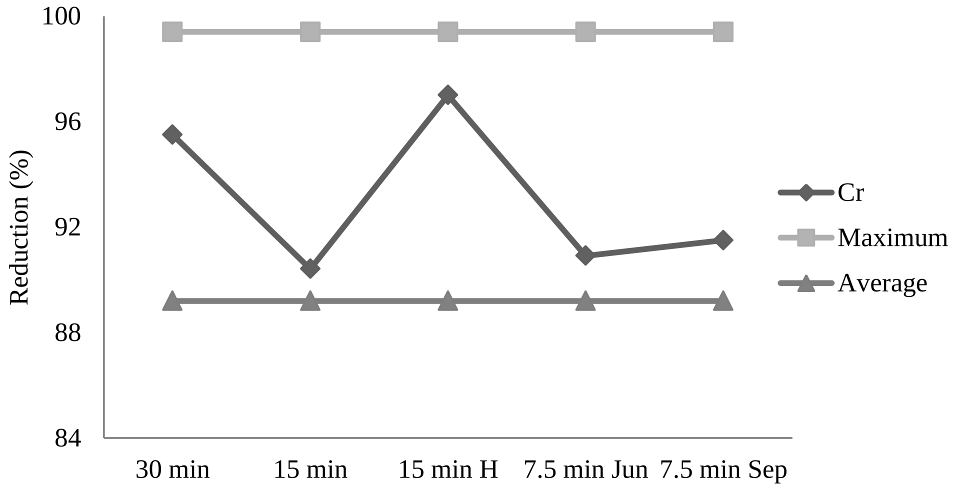

Figure 20: Reduction of Cr in cork filters, in percent, compared to historical data from the sand filters.

In Figure 21 the reduction of Fe is shown.

- 30 minutes, 15 minutes with high flow and 7.5 minutes contact time in September are better than the historical average, while the two other are below the historical average.
- The reduction of Fe is above 84 % for all contact times.

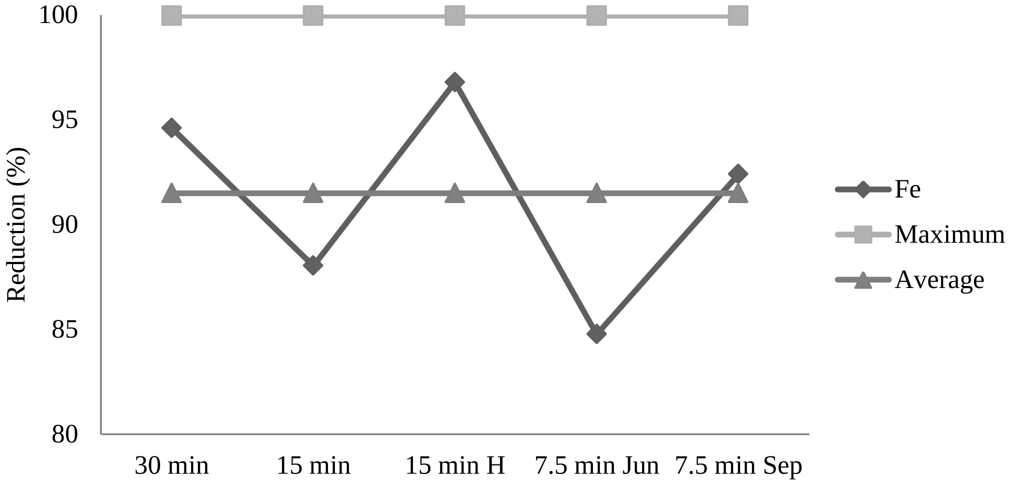

Figure 21: Reduction of Fe, in percent, compared to historical data from the sand filters.

To summarize, when the sand filters are functioning at their best, the cork filters do not match their results. For Zn, Cr and Fe the reduction is more often better than the average reduction of sand filters than it was below. The reduction of Al and Cu after the cork filter is more often below the average reduction after the sand filters than it is better than the reduction in the sand filters.

6.2 Stress Experiments

The stress experiments with pH and suspended matters were made before the service stop. The stress experiments with emulsions, degreasing agents and graphite were made after the service stop. The service stop was from July 11 to August 7.

The results of the stress experiments are compared to the normal operational data of 15 minutes contact time for cork filters from the parallel experiments. For the 15 minutes operational data the oil concentration was below reporting limit, 0.1 mg/l. To calculate the reduction in the cases the concentration is below reporting limit, the reporting limit is used. The oil sample from before the addition of the base in the experiment with a pH of 8.9 has been lost.

The bargraphs show the reduction for some substances. The exact reduction is put on top of each bar. To make the results more clear, the y-axis is shortened in some of the graphs. Radar diagrams for the concentration of Cu, Al, Zn, Fe, suspended matters and oils are found in Appendix B, Figure B1 – B9.

6.2.1 *Low pH*

Figure 22 shows the reduction at pH 5.6.

- The reduction of Cu, Al. Zn and Cr is about 3 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Al is similar in the stressed cork filters and in the cork filters at normal operation.
- The reduction of Fe is 10 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is 25 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is 20 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of suspended matters is 3 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of oils is almost 30 percentages lower in the stressed cork filters than in the cork filters at normal operation.

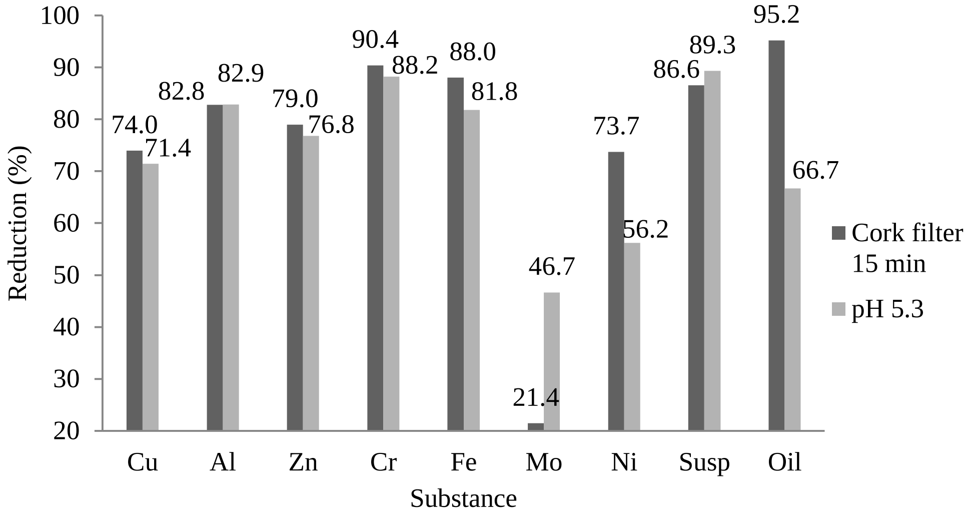

Figure 22: Reduction after divergence pH 5.6. Values in percent.

6.2.2 High pH

Figure 23 shows the reduction at pH 8.9.

- The reductions in percentages of Cu, Cr and Fe are almost similar in the stressed cork filters and in the cork filters at normal operation.
- The reduction of Al, Zn and suspended matters at pH 8.9 are 3-6 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is 5 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is 7 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- Nothing can be said of the oil concentration because the sample for 0 minutes untreated water was lost.

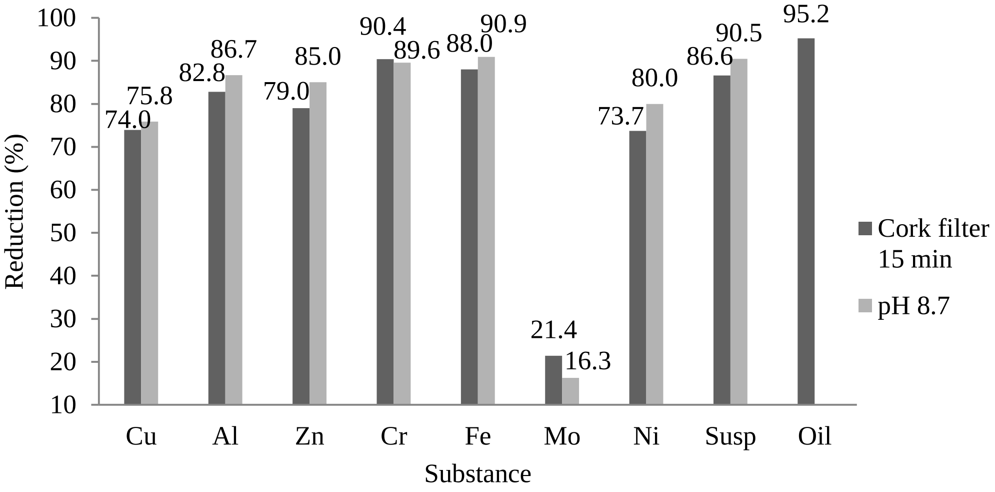

Figure 23:Reduction after divergence pH 8.9. Values in percent.

6.2.3 Graphite

In the stress experiment with graphite the concentration after the adding of 6 g graphite was about 10 mg/l of the substance. Figure 24 shows the reduction of metals, oils and suspended matters after treatment in the cork filters compared to the reduction in the sand filters.

- The reduction of Cu, Al, Fe and suspended matters are 4-7 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Zn is 30 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Cr is 3 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is 15 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is 10 percentages lower in the stressed cork filters than in the cork filters at normal operation.

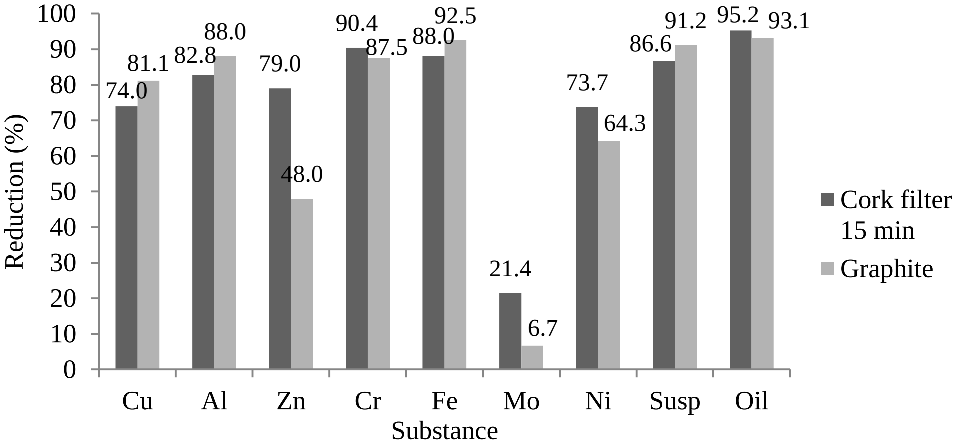

Figure 24: Reduction after divergence graphite 10mg/l. Values in percent.

6.2.4 Suspended Matters

In Figure 25 the reductions of metals, oil and suspended matters are shown.

- The reduction of oils is 20 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is about 10 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is about 10 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Cu is 7 percentages lower in the stressed cork filters than in the cork filters at normal operation.

- Otherwise, the reduction results vary between less than one percentage and up to 4 percentages in the stressed cork filters than in the cork filters at normal operation.

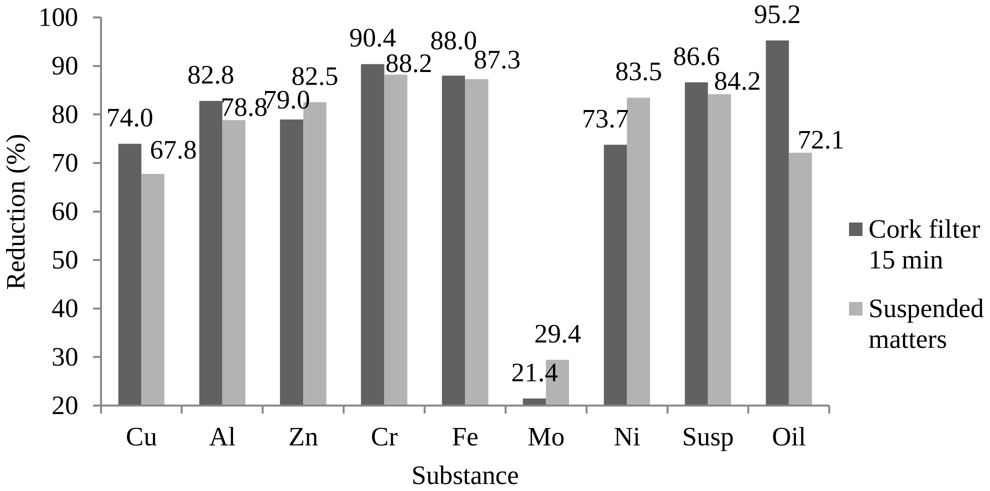

Figure 25: Reduction after divergence 10 mg/l suspended matters. Values in percent.

In Figure 26 the reduction, after increasing the concentration of suspended matters to 15 mg/l, is shown.

- The reduction of Al is about 20 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Zn, Cr and oils is about 5 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is about 7 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is about 10 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of suspended matters is about 5 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction in percentages of Cu and Fe is almost similar in the stressed cork filters than in the cork filters at normal operation.

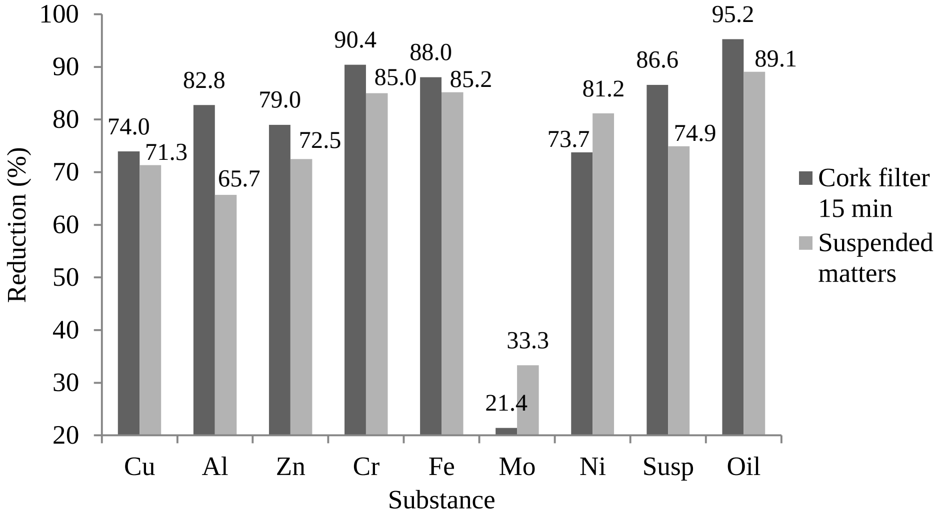

Figure 26: Reduction after divergence 15 mg/l suspended matters. Values in percent.

6.2.5 Emulsions

In Figure 27, the reduction of the concentrations of metals, oils and suspended matters in both the sand filters and the cork filters are shown.

- The reduction of Cu is 7 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of suspended matters and Al is 5 and 8 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- Zn and Cr have 3 percentages higher reduction in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Fe is almost similar in the stressed cork filters and in the cork filters at normal operation.
- The reduction of Mo is about 8 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of oils is 15 percentages lower in r the stressed cork filters than in the cork filters at normal operation.

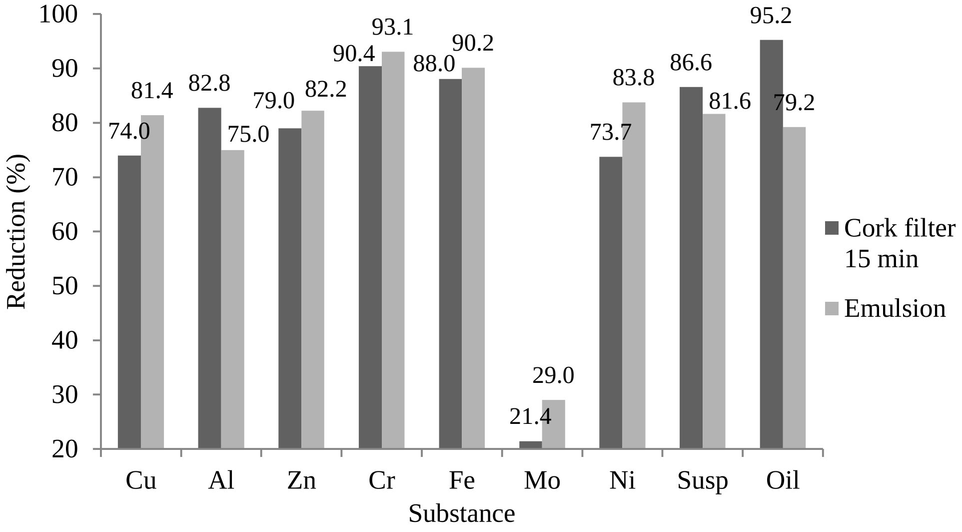

Figure 27: Reduction after divergence 10 mg/l emulsion. Values in percent.

Figure 28 shows the reduction with 15 mg/l of emulsions added to the water.

- The reduction of substances is almost similar or a little bit less in the stressed cork filters than in the cork filters at normal operation.
- The exception is Cr and Ni that has a slightly higher reduction in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is about 5 % lower in the stressed cork filters than in the cork filters at normal operation.

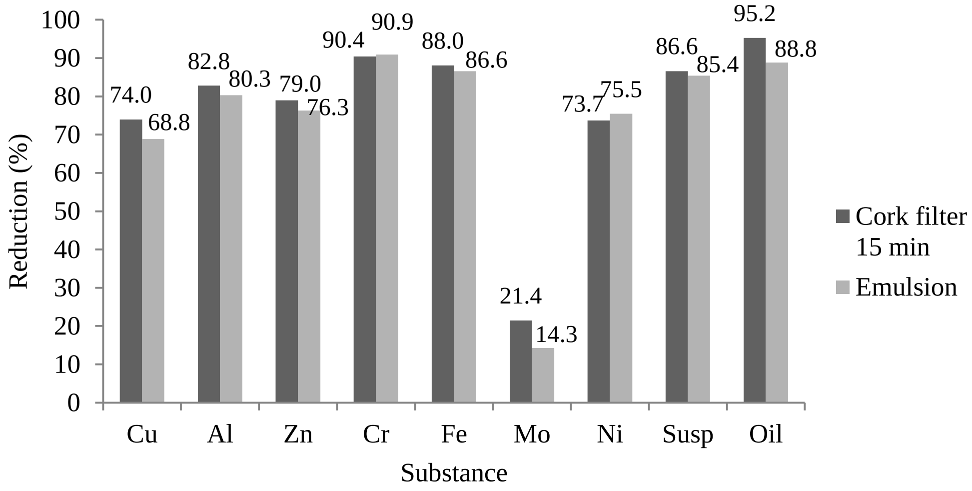

Figure 28: Reduction after divergence 15 mg/l emulsion. Values in percent.

6.2.6 *Degreasing agents*

Figure 29 shows the reduction with degreasing agent added to the water in the cork filters.

- The reduction of Cu is 7 percentages higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Cr and Fe is slightly higher in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is about 5 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is about 5 percentages higher in the stressed cork filters than in the cork filters at normal operation.

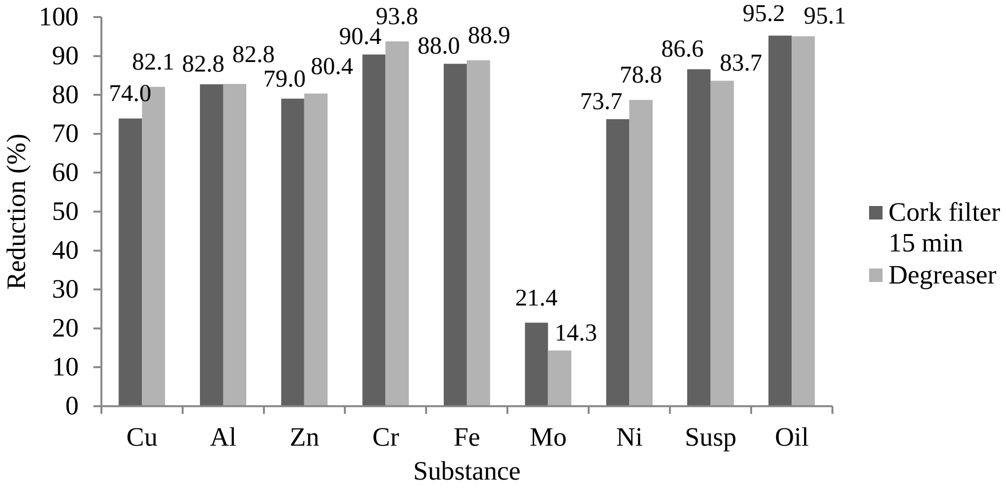

Figure 29: Reduction after divergence 10 mg/l degreasing agent. Values in percent.

Figure 30 shows the reduction after the adding of 15 mg/l of degreasing agent to the cork filter.

- The reduction of Cu and Al is almost similar in the stressed cork filters and after the cork filters at normal operation.
- The reduction of Zn is 6 percentages lower in the stressed cork filters than in cork filters at normal operation.
- The reduction of Cr is 30 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of suspended matters is 45 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Mo is about 12 percentages lower in the stressed cork filters than in the cork filters at normal operation.
- The reduction of Ni is about 25 percentages lower in the stressed cork filters than in the cork filters at normal operation.

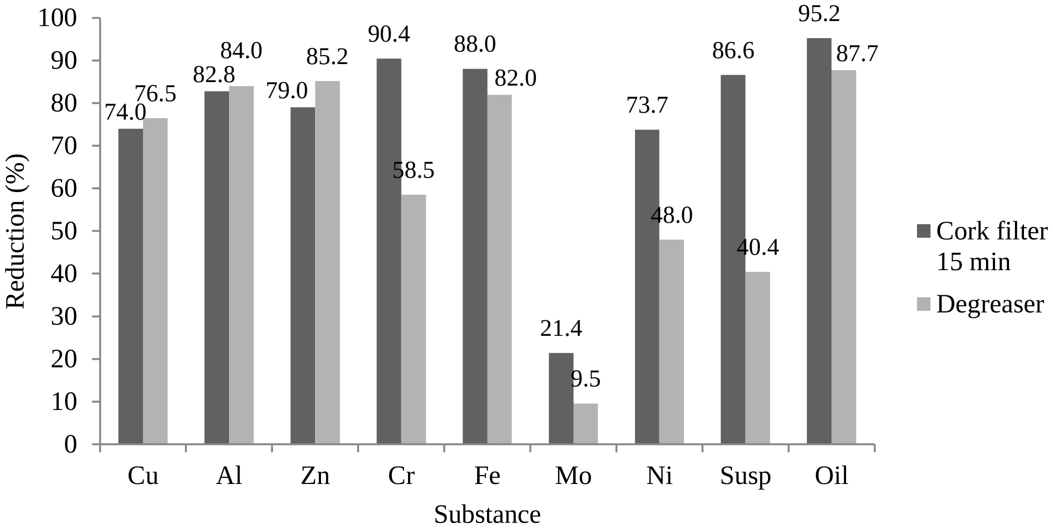

Figure 30: Reduction after divergence 15 mg/l degreasing agent. Values in percent.

6.3 Concluding Data for Stress Experiments

In Table 8, the pH for all stress samples has been collected. It is obvious that the cork filter treatment results in a more neutral pH, independent of if the original pH is over or below neutral. One value is missing. “Normal 15 min” did not have a divergence added why the change in pH is not applicable.

Table 8: pH for stress experiments compared with 15 minutes contact time with normal flow for cork filters.

	0 min unstressed	0 min + stress	15 min + stress	15 min normal flow in cork filter
pH 5.6	8	5.6	5.8	6.7
pH 8.9	8.4	8.9	6.8	6.7
Graphite 10 mg/l	7.9	8.1	7.2	6.7
Susp 10 mg/l	7.7	7.7	6.8	6.7
Susp 15 mg/l	7.8	7.4	7.3	6.7
Emulsion 10 mg/l	7.9	7.7	7.1	6.7
Emulsion 15 mg/l	7.8	7.9	7.2	6.7
Degreasing agent 10 mg/l	7.9	7.8	7.3	6.7
Degreasing agent 15 mg/l	7.9	7.9	7.2	6.7

In Table 9, the reduction of Mn and Pb in the cork filter is shown. The box marked with grey has been calculated using the reporting limit for the water after the cork treatment. The two values marked with a line were below the reporting limit both before and after the cork treatment.

Table 9: Reductions of Mn and Pb after cork treatment. Values in percent.

	Mn	Pb
pH 5.6	46.8	85.9
pH 8.9	59.4	97.4
Graphite 10 mg/l	15.5	74.5
Suspended matters 10 mg/l	70.3	83.1
Suspended matters 15 mg/l	57.0	84.9
Emulsion 10 mg/l	56.3	71.4
Emulsion 15 mg/l	31.3	-
Degreaser 10 mg/l	44.2	-
Degreaser 15 mg/l	51.1	67.7

To calculate the increase in concentration of P, a multiple of the concentration before the cork filter treatment was used. The values given are the times the concentration of the untreated water has to be multiplied to reach the concentration after the treatment.

As can be seen in Table 10, the concentration of P increases in all samples except after the experiment with 10 mg/l of suspended matters added to the water. The highest increases were for the experiments with low pH and with 15 mg/l of added degreasing agent.

Table 10: Increase of P after cork filter. The values in the table are the multiple of the concentration before each cork filter treatment to reach the concentration after each cork filter treatment.

	P
pH 5.6	13.3
pH 8.9	4.7
Graphite 10 mg/l	1.7
Suspended matters 10 mg/l	0.6
Suspended matters 15 mg/l	10.0
Emulsion 10 mg/l	5.8
Emulsion 15 mg/l	1.5
Degreaser 10 mg/l	9.6
Degreaser 15 mg/l	14.1

6.4 Degassing Water

The results from the degassing water with different contact times are shown in Figure 31. Only metals were analyzed.

- The concentrations are continuously diminishing for Cu and Zn.
- Al, Cr and Fe concentrations does not diminish continually.

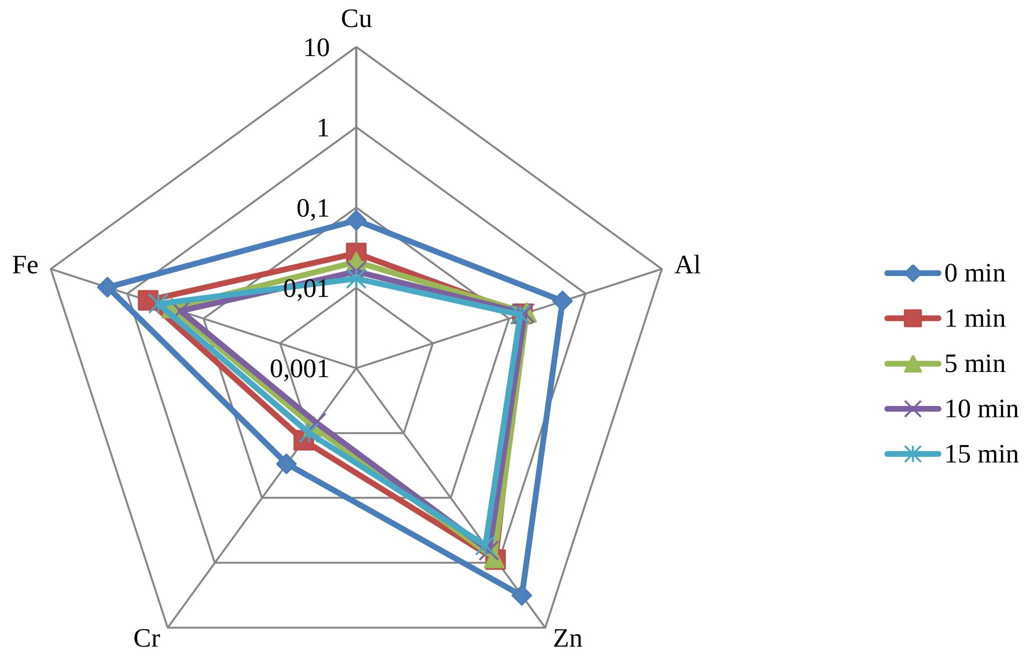

Figure 31: Concentrations of substances in the degassing water. Values in mg/l.

In Figure 32, the reduction is plotted against time.

- The reduction of Cu, Zn and Ni is increasing by contact time.
- The reduction of Fe and Cr increases during the first 10 minutes contact time to decrease during the last five.
- The reduction of Al is the opposite. The reduction decreases between the first and the fifth minute to increase from the fifth minute to the fifteenth.

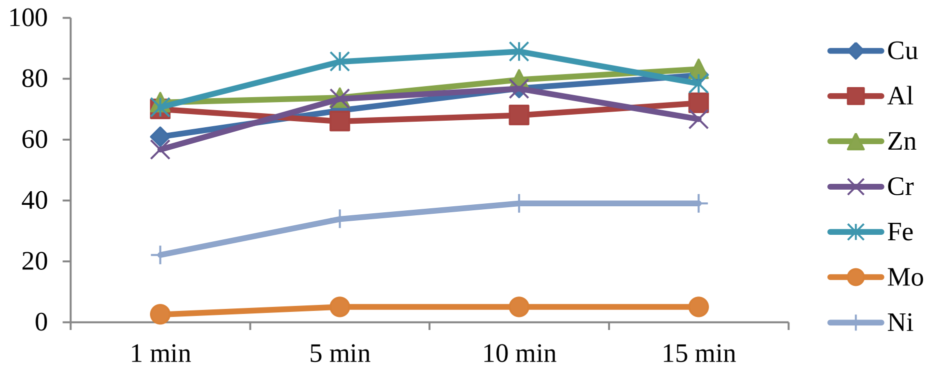

Figure 32: Reduction of metals in degassing water after cork filter treatment. Values in percent.

In Table 11, the reductions of Mn and Pb are shown for the degassing water samples after the cork treatment. Concentrations of Mn, Pb and P are shown in Appendix C, Figure C1.

- The reduction of Mn increases with the contact time.
- The reduction of Pb increases with the contact time. The largest increase is between 5 minutes contact time and 10 minutes contact time.

Table 11: Reduction of Mn, Pb and P in cork filters. Values in percent.

	Mn	Pb
1 min	44.7	67.3
5 min	45.3	73.6
10 min	49.3	83.2
15 min	50.7	88.2

As can be seen in Table 12, the concentrations of P increased in the cork filters. The concentration of P in the untreated water was 0.04 mg/l and was used as a reference value when comparing with the concentration after treatment. The highest increase was after the first minute. After that, the concentration of P decreased a little.

Table 12: Increase of P in the cork filter. The value of P in the untreated water is used as a reference value. Increase in multiples of the reference value.

	P
0 min	1.0
1 min	2.0
5 min	1.4
10 min	1.5
15 min	1.3

6.5 Concluding data for all experiments

Table 13 concludes the collected results from the experiments. The results from the cork filters in the parallel experiments are compared to the results from the sand filters in the same experiments. The results from the Stress experiments and the degassing experiments are compared to the results from the cork filters at 15 minutes contact time during the parallel experiments.

Table 13: Reduction of substances. The reduction in the cork filters during the parallel experiments is compared to the reduction in the sand filters during the same experiments. The reduction in the cork filters during stress experiments are compared to the reduction in the cork filters at 15 minutes contact time in the parallel experiments. The reduction in the cork filter during the degassing experiment is compared to the reduction in the cork filters at 15 minutes contact time in the parallel experiments.
--: difference is -15 % and lower, -: difference is -5 % to -15 %,0: difference is -5 % to +5 %, +: difference is +5 % to +15 %, ++: difference is +15 % or higher.

		Al	Zn	Cu	Cr	Fe	Mo	Ni	Mn	Pb	P	Susp	Oil
Parallell	30 min	-	++	-	0	0	0	+	++	--	--	--	x
	15 min	-	++	--	-	-	--	+	++	-	-	-	0
	15 min H	0	+	-	0	0	+	-	++	-	--	--	0
	7.5 min june	--	0	--	0	-	-	-	++	--	--	--	x
	7.5 min september	++	0	0	++	++	0	++	--	--	--	0	0
Stress	pH 5.6	0	0	0	0	-	++	--	-	-	--	0	--
	pH 8.9	0	+	0	0	0	-	+	0	0	--	0	x
	Suspended matters 10mg/l	0	0	-	0	0	+	+	+	-	--	0	-
	Suspended matters 15 mg/l	--	-	0	-	0	+	+	0	-	--	-	-
	Emulsions 10 mg/l	-	0	+	0	0	+	+	0	-	--	-	-
	Emulsions 15 mg/l	0	0	-	0	0	-	0	--	x	--	0	-
	Degreasing Agent 10 mg/l	0	0	+	0	0	-	+	--	x	--	0	0
	Degreasing Agent 15 mg/l	0	+	0	--	-	-	--	-	--	--	--	-
	Graphite 10 mg/l	+	--	+	0	0	-	-	--	-	--	0	0
Degassing	1 min	-	-	-	--	--	--	--	--	--	--	x	x
	5 min	--	-	0	--	0	--	--	-	--	--	x	x
	10 min	-	0	0	-	0	--	--	-	-	--	x	x
	15 min	-	0	+	--	-	--	--	-	-	--	x	x

7 Discussion

The discussion is divided into three parts:

- Discussions of the results from the parallel experiments
- Discussions of the results from the stress experiments
- Discussions of the results from treatment of the degassing water

Note that only one experimental round was run for each contact time and stress test. The exception was the parallel experiment with 7.5 minutes contact time, which was run two times.

The filters are constructed to have a continuous flow through them; this has not been the case during the pilot study. The experiments were run batch-wise and emptied after each round. The filters were used like this for about 4 days. Then, they were left for a weekend. After every experiment about 10 liters of filtered water were left in the bottom of the filters. This might have influenced the results as well. For example, the two pH stress experiments were run after each other and the left over water might have influenced the next experiment.

Some of the filters were exchanged during the pilot study. The first exchange was of a saturated FOSS filter after an unsuccessful experiment with added graphite. Therefore, the filter was new during the first experiment with suspended matters. At the same time the FADE and MAAC was reloaded. Furthermore, all filters were exchanged after the service stop. The first experiment with new filters was performed with increased concentrations of emulsions.

7.1 Parallel Experiments

The reductions of Cu, Al, Zn, Cr and Fe in the cork filters in Figure 17-Figure 21 vary in a similar way. The reduction was relatively high for all metals at 30 minutes contact time. At 15 minutes contact time the reduction decreased. At 15 minutes contact time with high flow the reduction was higher. At 7.5 minutes contact time in June the reduction decreased. Finally, the reduction at 7.5 minutes contact time in September increased compared to the other experiment with 7.5 minutes contact time. An interesting result is the reduction of suspended matters. Its curve is the opposite to the reduction of metals, except for the last two experiments at 7.5 minutes contact time. The metals have been thought to be bound to the suspended matters, so if the concentration of suspended matters decreased, so would the concentration of metals. Previous analyses made by Ovako on the water after the sand filters show this. The first three experiments with contact times of 30 minutes and 15 minutes showed the opposite behavior. The reduction of metals in the experiments with contact times of 7.5 minutes followed the reduction of suspended matters; when the reduction of suspended matters decreased, so did the reduction of metals.

The cause of the contradictory results of the reduction of metals and suspended matters might be that the metals were bound to inorganic materials in a higher extent in the first three experiments and to organic material to a higher extent in the last two. The microorganisms in the FADE filter can only digest organic material. Metals bound to inorganic material will pass through the cork filters. This implies that the suspended matters in the experiments with 7.5 minutes contact time were mainly of organic material that could be digested. The metals released could be reduced in the MAAC filters.

The reduction of Cu, Al, Zn, Cr and Fe during the parallel experiments compared to the historical data of the sand filters show that the historical data and the data from the experiment does not have to correlate. The reduction of Cr and Fe was lower in the cork filters than in the sand filters during the parallel experiments. The reduction of Cr and Fe in the cork filters compared to the historic reduction of Cr and Fe in the sand filters show that the reduction of Cr and Fe in the cork filters was better than the historical average reduction. This might be due to the fact that the sand filters were in good function during the experiments compared to the condition of the last 12 months. The reduction of Zn in the cork filters was higher than the reduction in the sand filters during the parallel experiment. Compared to the historical data the reduction of Zn in the cork filter was below the historical average reduction in the sand filters at two times. The behavior of Zn contradicts the assumption based on the behavior of Cr and Fe. Different properties in Cr and Fe compared to Zn might result in different binding capacities for the metals to the sand filters or the cork filters.

The normal assumption is that longer contact time gives a higher reduction. Figure 17- Figure 21 show the reduction in the parallel experiments. The figures show that this is almost true. There are two exceptions. The reduction of Al and suspended matters was lower at 30 minutes contact time than at 15 minutes contact time. The reason for the low reduction of suspended matters can be that the 30 minutes contact time was the first experiment to be done. There might have been small cork fragments that were washed out of the cork filters during the first experiment and made the reduction of suspended matters look lower than it was. Another reason might be the composition of the suspended matters. If most of the Al is bound to inorganic material it will not be reduced to the same extent as if it had been bound to organic matters.

An interesting thing is to see what happens when the flow was increased through the cork filters. When the flow was increased, the reduction was also increased. When the flow was increased, the time the filter has to be run was prolonged. Because the microorganisms in the FADE filter are so small, they slip out of the filter and are spread through the whole water volume. This gives the enzymes more time to digest organic suspended matters and thus solve metals. The metal adsorption in the MAAC filter happens almost momentarily as the water gets in contact with the matrix. The high flow does not affect the chelate binding. This also implies that the most part of the suspended matters were organic materials. Otherwise the FADE microorganisms would not been able to digest the suspended matters.

Except from Zn, the sand filters were better at removing most of the pollutants in the process water at normal operation. For all parallel experiments, except 7.5 minutes contact time in June, the concentration of Zn was lower after the cork filter treatment than after the sand filter treatment. The reduction of Zn varied between 69 % and 92 % in the sand filters. This was probably due to the Zn forming inorganic salts, like $ZnCl_2$, with the chloride from the flocculants added to the sand filters. The size of the salt particles is too small to fully stick in the sand bed. In the cork filters, the Zn did not form salts because of the lack of Cl ions and were thus adsorbed in the MAAC filter matrix. This caused the higher reduction of Zn in the cork filters compared to the sand filters. The lower reduction of Zn in the cork filters in June might be because of the MAAC filter becoming saturated.

Removing suspended matters from the process water was a problem for the cork filters. It was only the water from September, with a contact time of 7.5 minutes, which was below the guidance value of suspended matters. The reason to the relatively high concentrations of suspended matters after the cork filters was the incapacity of the cork filters to handle inorganic suspended matters. If the process water contains high loads of inorganic components, the reduction of suspended matters will be low. For some of the experiments the difference in reduction of the concentration of suspended matters was of one order of magnitude. The sand filters are good at reducing suspended matters because of their great volume that allow more of the suspended matters to stick to the filter masses. Also, the pores between the sand grains are small and suspended matters can get stuck.

The two experiments with 7.5 minutes contact time were supposed to show almost the same results. As can be seen in section 6.1.4, this was not the case. There were differences in the reduction of Al, Zn and suspended matters between the two experiments. The difference in the results between the two experiments may be due to the filters becoming saturated in June and that the filters were newly changed in September. The difference may also be due to differences in the incoming water. The concentration and composition of the suspended matters might be an explanation. If the suspended matters contained more inorganic material in June than in September the microorganisms in the FADE filter would not be able to solve metals in the same extent as if the suspended matter had been of organic origin. Zn does not seem to follow this pattern and the reason to this has been given above.

The reduction of oils varied between 85.7 % and 95.2 % after cork filter treatment. The sand filter reduction was higher and the concentration of oils after the sand filters was often below reporting limit. This is due to the size of the cork granulates, which are bigger than the sand particles. The bigger cork granulates will result in greater pores that the oil can slip through. The reduction in the cork filters could be increased with greater filter volumes.

The behavior of P is of interest. In four of the five parallel experiments the concentration of P is increased after the cork filters. The concentration of P in the process water before the cork filter treatment was low. Even though the concentration increased more than 30 times, the concentration after treatment in some cases was not extremely high, 2.6 mg/l. This was still much higher than the guidance value of 0.4 mg/l set by the authorities.

The source of the increase in concentration of P is probably the material the FADE microorganisms are bound to when they are put into the solution. The increase of P might be a problem in the long run if it continues to increase and accumulate in the system. P is an ending resource in nature. There are techniques for harvesting of P from water. These could be applied to the filter system to solve the problem with leaching of P. In the sand filters, P is in the form of a salt and is collected in the sand bed.

The reduction of Mo, Ni, and Mn were over all decreasing with decreasing contact time. Mo is highly soluble in water and is usually hard to collect in a filter. The reduction of Mo in the cork filters was sometimes higher than the reduction in the sand filters. The amount collected in the cork filters seems to be depending on the contact time more than the flow. The reduction of Ni in the cork filters was more often higher than the reduction in the sand filters. The reduction of Mn was higher in the cork filter than in the sand filters for all experiments except the experiment with 7.5 minutes contact time in September. This was probably due to the earlier mentioned digesting of organic material leading to a higher reduction of metals.

The reduction of Pb decreased with shortened contact time, but had two increases. One at 15 minutes contact time with high flow and the other at 7.5 minutes contact time in September. This was probably also due to the earlier mentioned digesting of organic material leading to a higher reduction of metals. The reduction of Pb was higher in the sand filters than in the cork filters during all experiments.

Cork filters at normal operation compared to sand filters at normal operation had a lower purifying efficiency according to these experiments. The exception was Mn, Ni and Zn that the cork filters were better at removing. All reductions could possibly be increased with increased filter volumes.

An advantage of the cork filters was their capacity of turning the pH towards neutral. This was due to the metal binding in the MAAC filter.

7.2 Stress Experiments

The point of the stress experiments was to see if the capacity of the cork filters was decreased when divergences were added.

There was no great difference in reduction of Cu, Al, Zn, Fe, Mo and suspended matters between the stress experiments and the parallel experiments. The reduction of Cr, Ni and Mn was about 10 % lower for the stress experiments than for the parallel experiments. The behavior of P was still most varying, but varied less than in the parallel experiments. The highest increase in concentration of P after treatment was 13 times the concentration of P in the incoming water for the stress experiments compared to about 34 times for the parallel experiments.

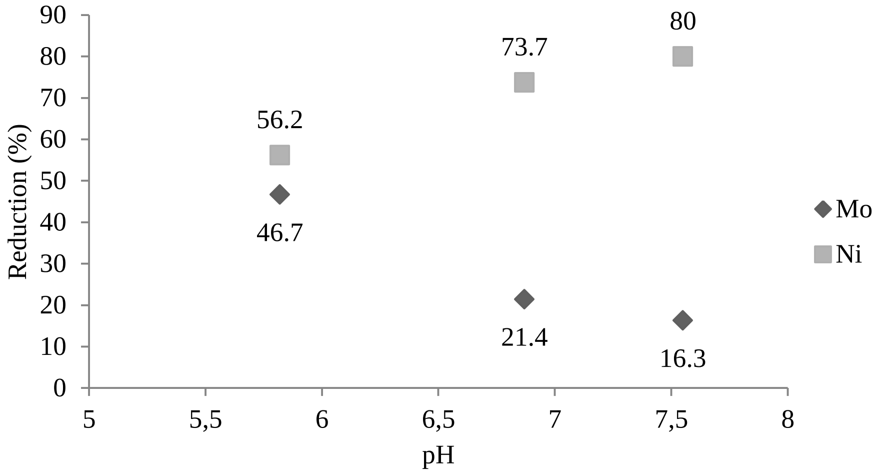

Figure 33: Reduction of Mo and Ni during stress experiment with low pH compared to pH at normal operation and 15 minutes contact time in the cork filters and compared to the reduction during stress experiment with high pH. Values in percent.

In Figure 33 the reduction of Mo and Ni are shown during the stress experiments with pH. The reduction of Mo was highest for the experiment with pH 5.6 and lowest at pH 8.9. It is known that Mo is sensitive for variations in pH so the result is not unexpected. The opposite behavior seems to be the nature of Ni. At low pH the reduction of Ni was low and at high pH the reduction of Ni was high. For the metals, except Mo and Ni, the reduction differed with about 10 % between the two experiments with low and high pH. The reduction of Cu, Al, Zn, Fe and Ni was higher in the stressed cork filters than in the cork filter at normal operation.

The leaching of P was about 4 times higher in the experiment with low pH than in the experiment with high pH. To make a comparison, the leaching of P from the cork filters at the experiment with graphite divergence was of the same magnitude as that with low pH. The pH for the graphite experiment was 7.9 in the untreated water and 7.2 in the treated water compared to the pH of the low pH experiment which was 5.6 in the untreated water and 5.8 in the treated water. The conclusion is that pH does not seem to control the leaching. As been discussed above in the parallel experiment, the constitution of the FADE matrix is more likely to affects the leaching of P.

If the lowest levels of reductions are analyzed for each substance, the lowest reduction of Cr, Ni, suspended matters and Pb and the next lowest reduction of Fe and Mo occurred during the experiment with 15 mg/l of degreasing agent. The experiment with 10 mg/l degreasing agent added to the water did not show the same low level of reductions. The presence of degreasing agent in the water might be the cause of the lowered reduction in the cork filters. The ability of the metals to bind to the lipophilic phase might be the cause of the different behavior. This could also be the cause why some metals had their top results at the same time.

The lowest reduction of Zn, Mo, Mn and P occurred during the experiment with 10 mg/l graphite added to the water. If the highest reductions in the cork filters of each substance are analyzed, the reduction of Cu, Al, Fe, suspended matters and oil occurred in the experiment with 10 mg/l of graphite added to the water. The graphite was supposed to absorb in the FOSS filter and the metals to adsorb to the MAAC filter. The content of graphite should therefore not influence the reduction of metals even though it seems to do so here.

To conclude the results discussed in this section, it can be observed that the cork filters were less sensitive for different kinds of stress than the sand filters. The stress experiments performed were of such nature that the sand filters would have had problem to operate normally during these circumstances. Cork filters could be applied before the sand filters to decrease the disturbances in the sand filters. Because of the operational robustness of the cork filters, they could be the solution to the problems accounted in the PWTP.

7.3 Degassing Experiments

Most of the reduction of metals in the degassing water happened during the first minute. This is due to the chelating bonds that form immediately between the metals and the chelates (Hägg, 1989). There were variations in the reduction; the reduction of Mo increased up to the fifth minute of contact time. The reduction of Ni increased from 20 % at 1 minute contact time to about 35 % at 5 minutes contact time. The reduction of Al decreased with about 5 % between 1 minutes contact time and 5 minutes contact time.

Not much happened after 5 minutes contact time. There were small increases in the reduction for Zn, Al, Cu, Pb and Ni, decreases for Fe and Cr. Mo and Mn was keeping the same level of reduction after 5 minutes contact time. The increase in the concentration of P was twice as high as in the untreated water after 1 minutes contact time and the concentration decreased after that. After 5 minutes contact time the concentration of P after treatment was 1.4 times the concentration in the untreated water and continues on about that level.

If the degassing water should be pretreated before it reaches the PWTP, the contact time would only need to be between 1 and 5 minutes. The total metal concentration in the degassing water before treatment with MAAC filter was 14 mg/l at the time of the experiment. After one minute contact time with the cork filter the metal content was 8.7 mg/l in the treated water. The total metal reduction in the degassing water was 38 %. The concentration of Zn in the degassing water was higher than in the process water. If a MAAC filter was applied the reduction of Zn could be increased and the burden on the sand filters could be lowered.

An advantage of the degassing water is its low content of organic material and oils. If a MAAC filter was applied about 40 % of the metals in the degassing water could be collected before the degassing water reaches the PWTP. The concentrations of metals in the degassing water during the performed experiment were quite similar to the concentration of metals in the incoming process water.

7.4 In context

When searching for new organic materials for water treatment use, materials common in the close surroundings are often used (Das et al., 2008). Cork is grown in Portugal and Spain, and has been so for many years. Since the wine producers started to use plastic materials instead of cork to seal wine bottles, the cork industry have been desperate to find new use for their raw material. If the cork can be used in filters for water treatment, job opportunities are saved and even created in Portugal and Spain where such initiatives are of great need. This, and the good sorption capacities of cork, might compensate for the long transportation route to get the cork to Sweden. Cork is a renewable resource, which sand is not, and is therefore a good alternative to conventional sand filters. As have been shown in the experiments, the reduction capacity of the cork filter was lower than the reduction capacity of the sand filters. The reduction capacity of the cork filters can be enhanced. The experiments done have led to the development of a new MAAC filter with better reduction capacity.

A consequence of the cork filters being separated into three units is the possibility to customize the cleaning process for different use. Thus, the cork filters can be applied to a varying range of waters for treatment. As was shown with the stress experiments, the cleaning capacity was still high for most of the compounds, which is more than can be said of the sand filters at the same conditions. Cork filters might be an important complement to sand filters to make the water treatment process more stable. During such conditions, where sand filters cannot be used, cork filters could be of good use. An example is water with high or low pH and a metal content that needs to be removed. Sand filters cannot do the job, but cork filters could do it.

8 Conclusions

- In general, the reduction of substances in the cork filters was lower than in the sand filters at normal operation. The exception was Zn that has a higher reduction in the cork filters than in the sand filters. The reduction of suspended matters was lower in the cork filters than in the sand filters at normal operation.

- The reduction of Mo and Ni is pH dependent. This makes it possible to control the uptake of these metals.

- The cork filters neutralized the pH.

- At extreme conditions the reduction in the cork filters was only slightly lower than the reduction at normal operation. It is known that the efficiency of the sand filters is decreased during these circumstances.

- If the degassing water is pretreated with a MAAC filter before it reaches the PWTP, the contact time for the degassing water in the cork filters would only have to be 1-5 minutes. The lowered metal concentration would decrease the metal load to the sand filters.

- A combination of cork filters and sand filters would reduce the incidence of costly disturbances to the sand filters. The sand filters would have a final polishing effect on the process water.

9 Further work

The work done in this thesis is only a beginning of what could be done. To really evaluate the FOSS, FADE and MAAC technologies, an in-depth pilot study has to be done on different types of process water.

To be able to really compare the Spikes & Cogs technologies an economic analysis should be done.

A life cycle assessment on the cork and sand filters might give interesting insights in the pros and cons of cork and sand filters.

10 Acknowledgements

Great thanks to Johan de Faire who has answered all my questions and been a good supervisor. Also, great thanks to Kjell Pålsson who has been an informal supervisor at Ovako and helped me a lot with input on the project, contacts on site and the structure of the report.

Heléne Bergwall and Pernilla Sellfors-Forsling in the laboratory at Ovako, you are the best! Great thanks to both of you for all help with the samples, your encouragement and input on all kinds of chemical questions I have had during these months.

Thanks also to all the nice people working at the process water treatment plant at Ovako. I would especially like to thank Lars Bengtzén, Rasmus Mohlén and Anders Rosengren at Maintpartner AB for the time you have taken to show me how the treatment plant works, answer my questions and helping me with the materials I needed. Without you the work with the experiment would have been so much more complicated.

I would also like to show my gratitude to Torbjörn Skoglund, who have answered my questions and helped me get in the contact with the right persons around the plant. Thanks also to Torbjörn Pettersson who have come by the experiment site and chatted about the results and given me valuable input on the subject of water treatment. Thanks to Mirja Sonestad for all help with the lodging in Hofors. I appreciate the efforts you have put in to get me somewhere to sleep. Thanks to Tommy Fors for a never ending will to help me out with material and knowledge of the steel plant.

Thanks to Bengt Carlsson for the input on my master thesis, Patrik Sternudd for the support throughout the work and to all others who have been part of this project either through answering questions, supporting, helping out with practicalities, being friendly or encouraging.

11 References

Ahluwalia SS, Goyal D. 2007.Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, **98**:2243–2257.

Babel S, Kurniawan TA. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, **97**:219–243.

Campbell NA, Reece JB. 2005. *Biology*. 7th edition, Pearson Benjamin Cummings, San Francisco.

Chubar N, Carvalho JR, Correia MJN. 2004. Heavy metals biosorption on cork biomass: effect of the pre-treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **238**:51–58.

Das N, Karthika P, Vinodhini V. 2008. Use of natural products as biosorbent of heavy metals. an overview. *Natural Product Radiance*, **7**:133–138.

Gupta R, Ahuja P, Khan S, Saxena RK, Mohapatra H. 2000. Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions. *Current Science.* **78**:967-973.

Hägg G. 1989. *Allmän och oorganisk kemi.* 9th edition. Almqvist & Wiksell, Uppsala.

Matis KA, Zouboulis AI, Lazaridis NK. 2003. Heavy metals removal by biosorption and flotation. *Water, Air and Soil Pollution: Focus*, **3**:143–151.

Ovako Steel. Welcome to Ovako Steel at Hofors and Hällefors.

Park D, Yun YS, Park JM. 2010. The past, present, and future trends of biosorption. *Biotechnology and Bioprocess Engineering*, **15**:86–102.

Svenskt vatten. 1992. *Dricksvattenteknik. Ytvatten.* Publikation P72. Svenskt vatten AB. Stockholm.

Svenskt Vatten. 2010. *Avloppsteknik 2. Reningsprocessen.* Publikation U2. Svenskt vatten AB. Stockholm.

Spikes & Cogs AB. 2010. Product information. FADE. Spikes & Cogs AB.

Nordic water. DynaSand.
WWW article 2011: http://www.nordicwater.com. Downloaded 20110920.

Ovako.
WWW article 2011:http://www.ovako.se. Downloaded 20110616

Appendix A

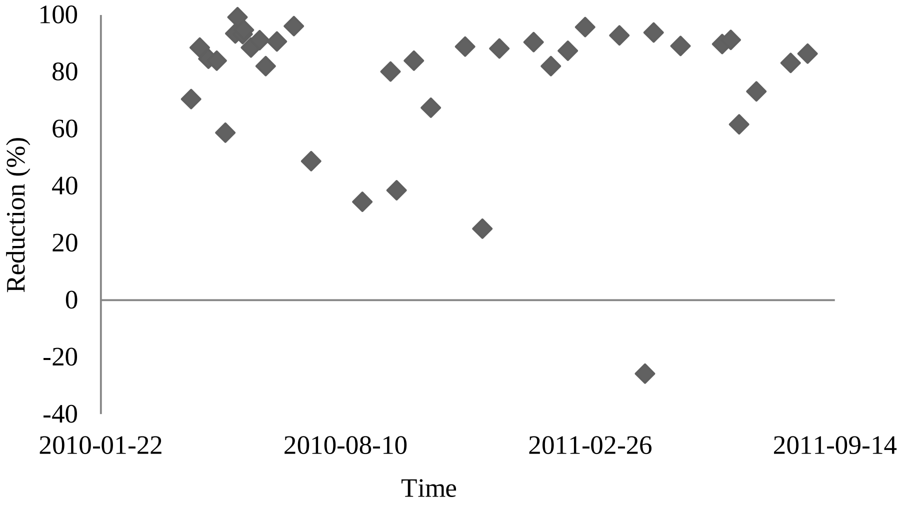

Figure A1: Reduction of Al after sand filter

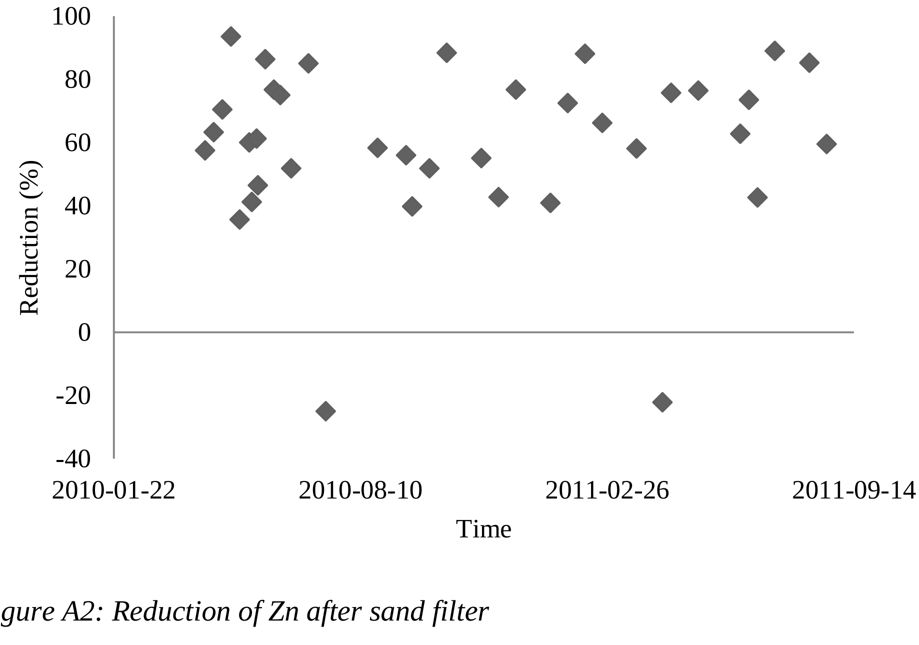

Figure A2: Reduction of Zn after sand filter

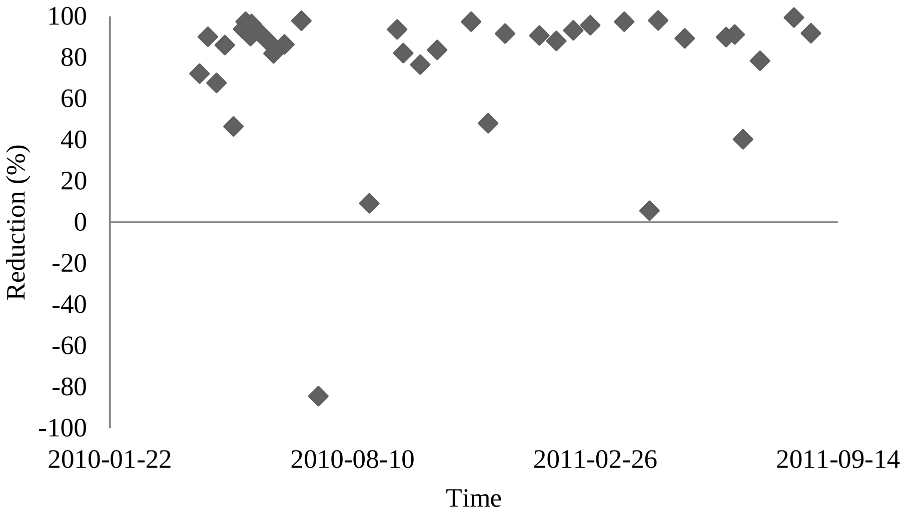

Figure A3: Reduction of Cr after sand filter

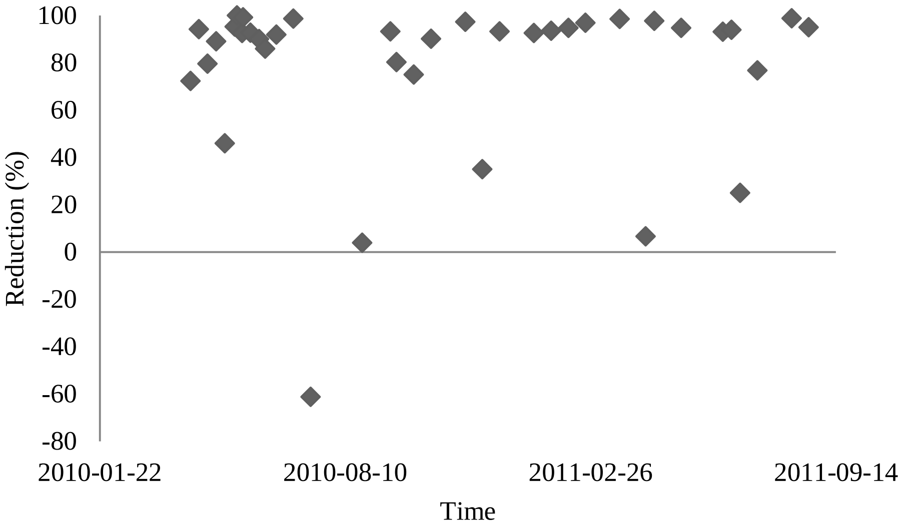

Figure A4: Reduction of Fe after sand filter

Appendix B

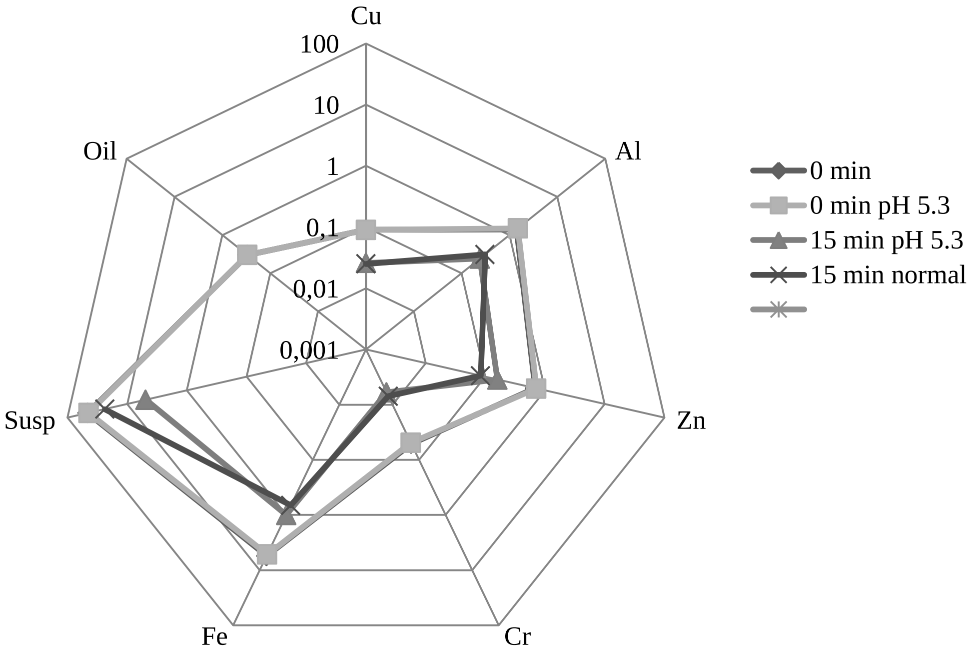

Figure B1: Reduction at low pH. Concentrations in mg/l.

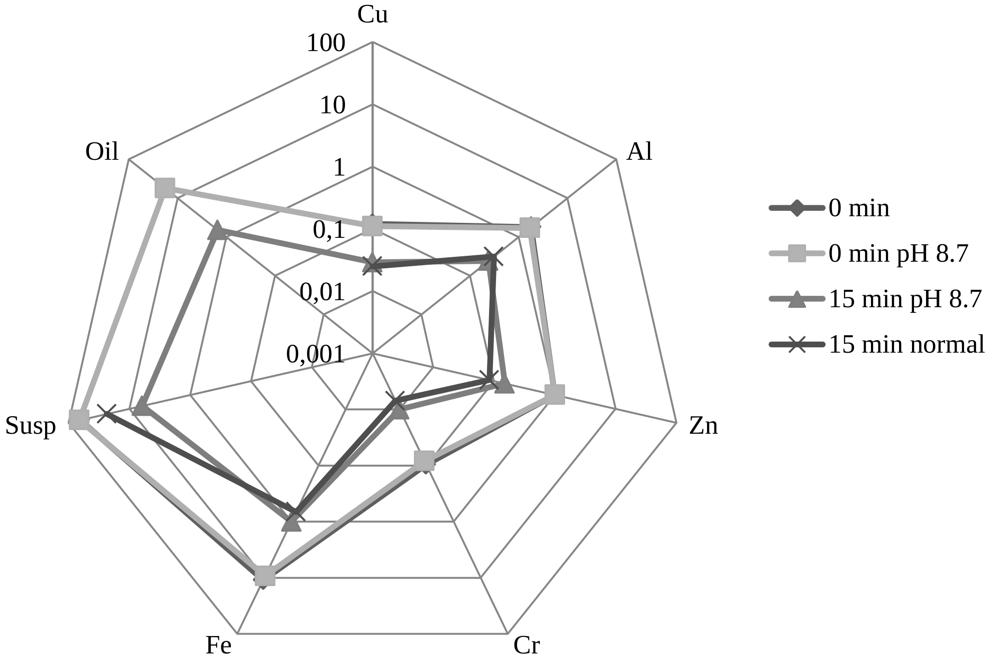

Figure B2: Reduction at high pH. Concentrations in mg/l.

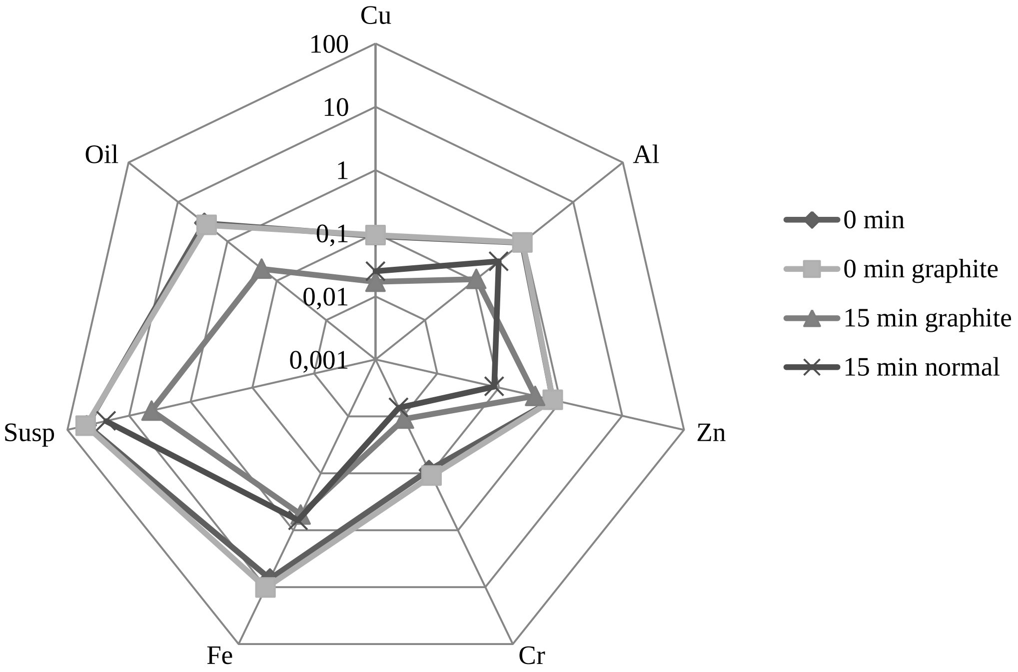

Figure B3: Reduction at a graphite concentration of 10 mg/l. Concentrations in mg/l.

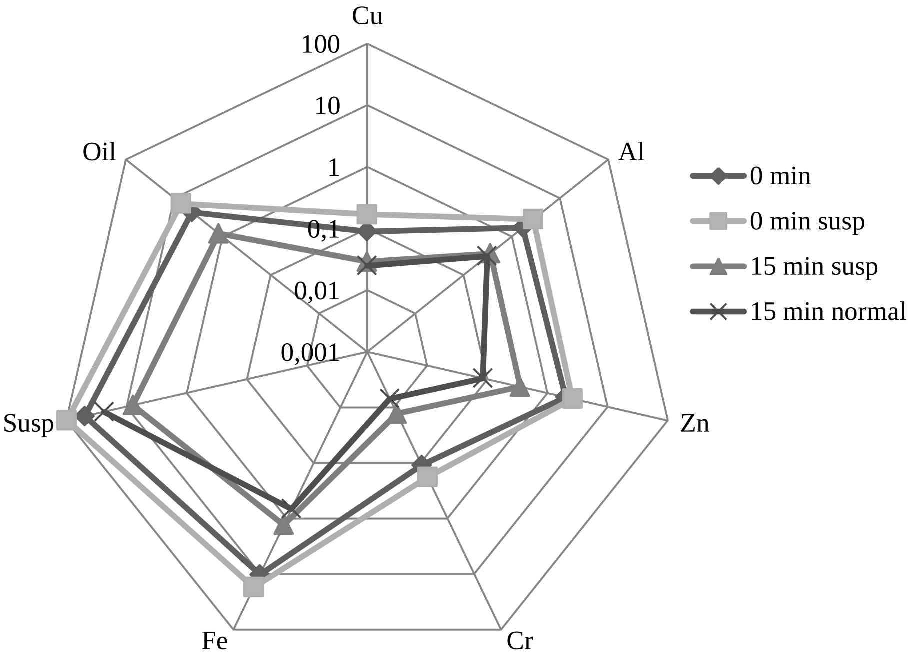

Figure B4: Reduction at a concentration of suspended matters of 10 mg/l. Concentrations in mg/l.

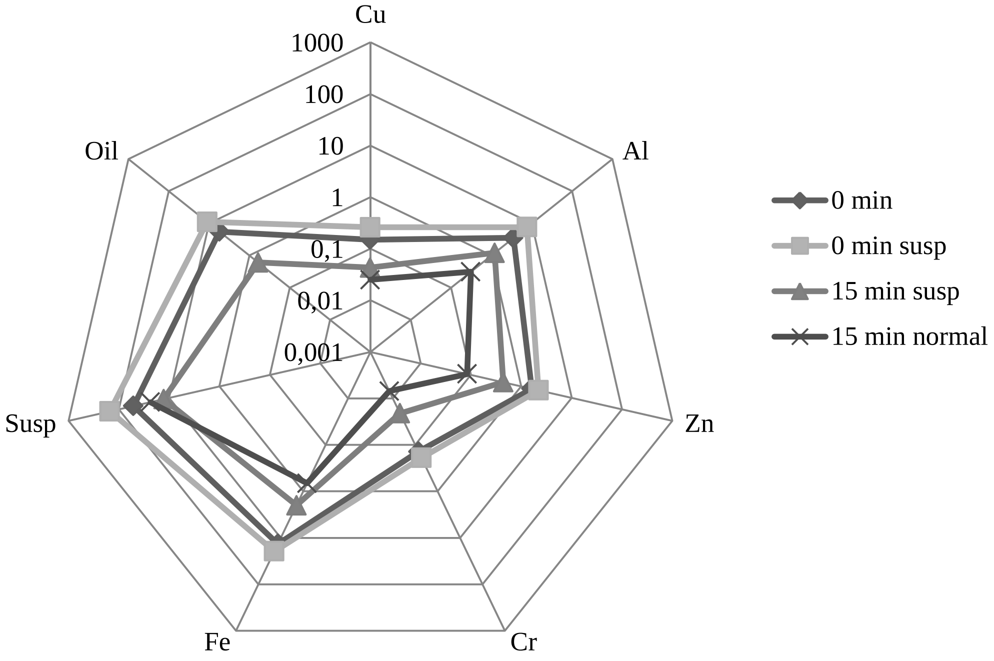

Figure B5: Reduction at a concentration of suspended matters of 15 mg/l. Concentrations in mg/l.

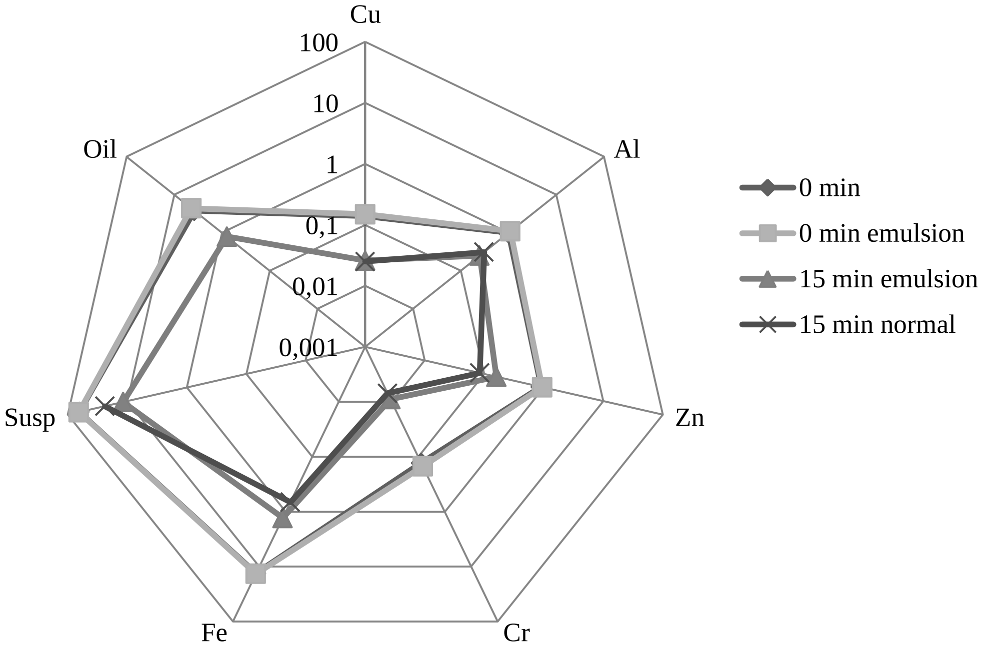

Figure B6: Reduction at a concentration of emulsion of 10 mg/l. Concentrations in mg/l.

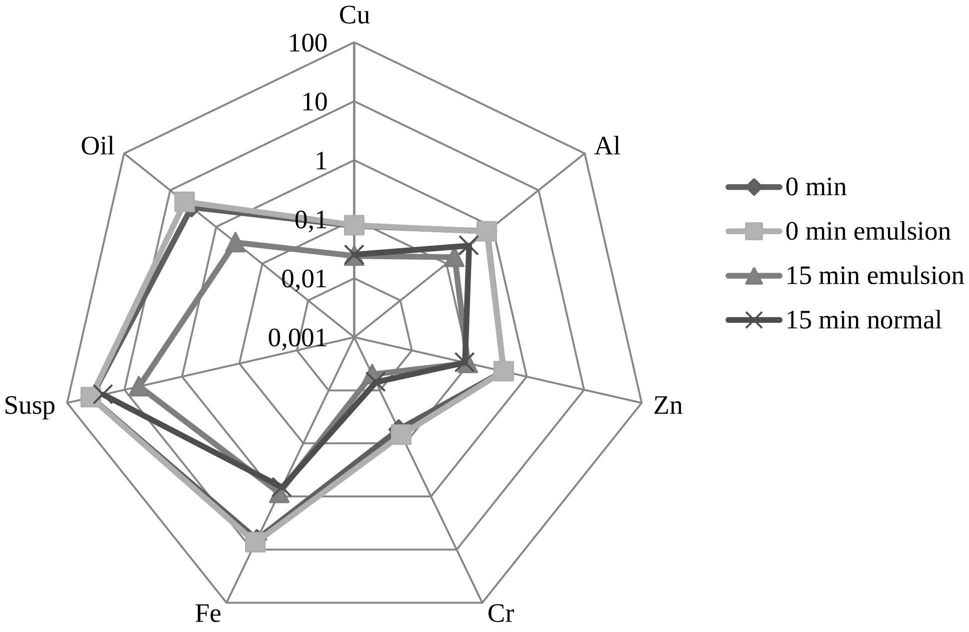

Figure B7: Reduction at a concentration of emulsion of 15 mg/l. Concentrations in mg/l.

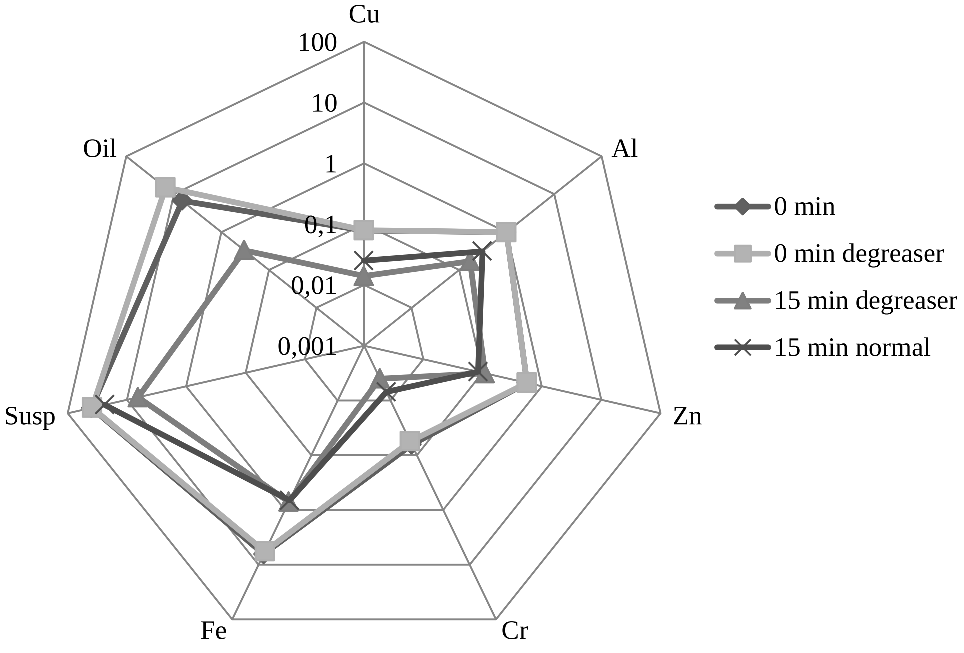

Figure B8: Reduction at a concentration of degreasing agent of 10 mg/l. Concentrations in mg/l.

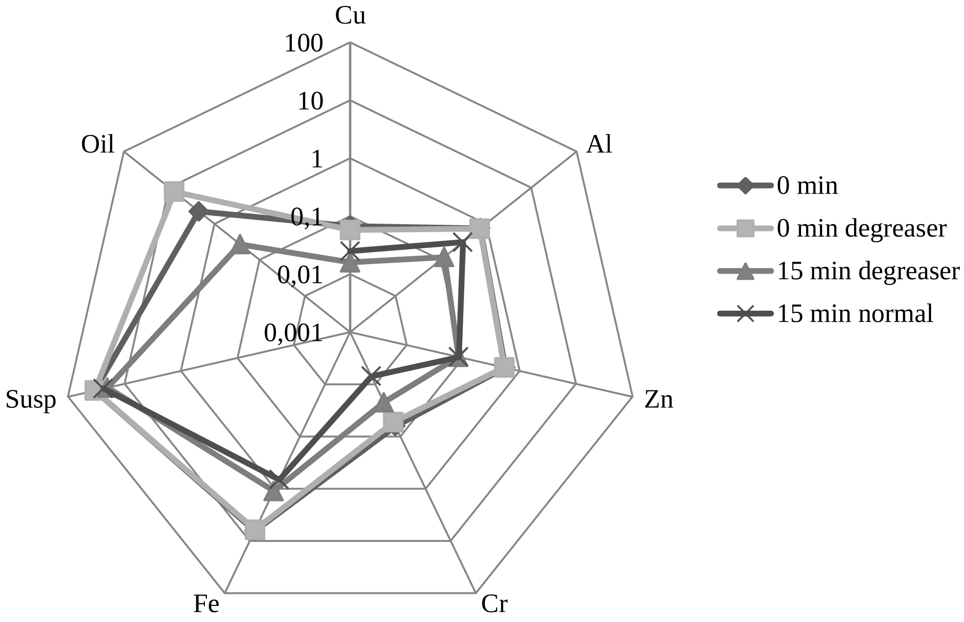

Figure B9: Reduction at a concentration of degreasing agent of 15 mg/l. Concentrations in mg/l.

Appendix C

Table C1: Concentrations of Mn, Pb and P after treatment with cork. Concentrations in mg/l.

	Mn (mg/l)	Pb (mg/l)	P (mg/l)
1 min	0.83	0.072	0.08
5 min	0.82	0.058	0.056
10 min	0.76	0.037	0.058
15 min	0.74	0.026	0.053