SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Suomen Soodakattilayhdistys ry

Non-process elements in the recovery cycle of six Finnish kraft pulp mills

Camilla Karlemo, Åbo Akademi
1.11.2019

Raportti 6/2019

16A0913-E0199

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Master's Thesis
Åbo Akademi University
Faculty of Science and Engineering
Camilla Karlemo
2019

Abstract

KARLEMO Camilla: Non-process elements in six Finnish Kraft pulp mills
Master's Thesis in Chemical Engineering,
Faculty of Science and Engineering at Åbo Akademi University, Turku 2019

The work reported in this Master's thesis was carried out in collaboration with Soodakattilayhdistys (the Finnish Recovery Boiler Committee). The objective of this work is to obtain a better understanding of pulp mill non-process elements. In this work, NPE concentration data from six Finnish pulp mills are analyzed and compared to data available in literature. This work aims to address the following research questions:

i) Does the geographic location (north vs. east) influence the Finnish mill NPE levels?
ii) How have the NPE levels changed in Finnish pulp mills since the 1990s?
iii) How do the present data compare to literature data on pulp mill NPE levels in North America (geographic location) as well as South America (geographic location and pulping wood species eucalyptus)?

All six pulp mills collected three samples from seven sample points in the recovery cycle. Eight NPEs (Al, Si, Ca, P, Mg, Mn, Cl and K) and the liquor chemicals Na and S were analyzed by a commercial laboratory (Eurofins Labtium) in this project. The observed distribution and accumulation of the elements can mainly be explained with the theory found in literature on NPE behavior in the recovery cycle.

When comparing the mills based on their geographic location, relatively small differences could be identified. In roughly 10% of the data, there was a significant ($p < 0.05$) difference due to geographic location, with the majority of these significant differences being due to lower NPE levels in the northern mills.

The level of phosphorous has increased in the recovery cycle, when comparing the results from this study to NPE data from Finnish pulp mills in the 1990s. However, the non-process element levels in white liquor have stayed generally at the same level compared to Finnish mills in the 1990s. The mills are also removing NPEs more efficiently based on this project's results compared to the North American results. The pulp wood and the process water quality also have an impact on the non-process element concentration. Al, Cl and Si results were found to be higher in South American results compared to this project's results.

The waste streams ending up in landfill from Finnish pulp mills have been reduced by over 90% since 1992. Yet most of the non-process elements in the recovery cycle have not changed much in the mills compared to present data. This is a clear indication that mills have become better in removing NPEs, using makeup chemicals and makeup lime that entail less NPEs and concurrently minimize the waste discarded from mills.

A recommendation for future work would be to look in more detail into the impact of biofuels or other NPE rich side streams. These streams could possibly have a larger impact on the overall process when the processes are becoming more closed, as the effluent and waste streams are reduced to minimize the environmental footprints of the pulp mills.

Keywords: Non-process elements, Kraft pulp mill, recovery cycle, effluent stream closure, green liquor dregs removal

Acknowledgements

This Master's thesis is as a collaboration between the Laboratory of Inorganic Chemistry at Åbo Akademi University and Soodakattilayhdistys (the Finnish Recovery Boiler Committee).

Firstly, I would like to thank the members of Soodakattilayhdistys (the Finnish Recovery Boiler Committee) for giving me the opportunity to write this incredibly interesting thesis and for financing this project.

The topic of this thesis included a considerable amount of work and I would not have been able to complete this thesis without all the help I recieved from Lipeätyöryhmä (the Black Liquor Sub-committee). Thank you for the support, patience and insightful ideas. Your guidance and inputs during the whole process have been extremely helpful and motivated me to do my best.

I would like to extend my gratitude to my supervisor D.Sc. Markus Engblom. This thesis included connecting numerous people, committees and companies together. Your guidance, support and help on how to work with so many different partners and still be able see the bigger picture of the thesis helped me to gain so much insightful knowledge about this industry. Your support during all the mill visits, meetings and feedback on the thesis was irreplaceable.

I would also like to thank all the six Kraft pulp mills who participated in this project. Thank you for taking the time to invite my supervisor and me to the mill sites and for the very insightful conversations we had. I am very grateful for your genuine interest in this topic, open-minded approach and all the industry knowledge I received during this project.

Finally, I would like to thank my family, friends and partner for the encouragement and support they have given me during my thesis work.

Camilla Karlemo
Turku, May 2019

Abbreviations

ABL	As-fired black liquor
ADt	Air dry ton of pulp
AOX	Adsorbable Organic Halides
BAT	Best available technology
df	Degrees of freedom
ds.-%	Dry solids content in percentage
ESP A	ESP ash
GL	Green liquor
GL D	Green liquor dregs
IC-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LM	Lime mud
n_A	The sample size in sample A
n_B	The sample size in sample B
NPE	Non-process element
s	Standard deviation
s_A	The standard deviation of sample A
s_B	The standard deviation of sample B
SEM	Scanning Electron Microscope
t	The t-test value
TGA	Thermogravimetric analysis
WBL	Weak black liquor
WL	White liquor
$\bar{x}_A$	The mean of group A
$\bar{x}_B$	The mean of sample B

Dictionary

English	Finnish	Swedish
Ash conveyor	Tuhkakuljetin	Asktransportör
Black liquor	Mustalipeä	Svartlut
Calcining	Kaustisointi	Kausticering
Causticizing tank	Kaustisointisäiliö	Kausticerings kärl
Chemical cycle	Kemikaalikierto	Lutcykel
Chemical recovery rate	Kemikaalien talteenottoaste	Återvinningsgrad
Clarifier	Selkeytin	Grönlutsklargörare
Dead load	Kuollut kuorma	Barlast
Density	Tiheys	Densitet
Dissolving tank	Sulaliuottaja	Smältlösare
Dregs	Viherlipeäsakka	Grönlutsslam
Dregs filter	Sakkasuodin	Grönlutslamfilter
Dry matter content	Kuiva-ainepitoisuus	Torrhalt
Dry solids	Kuiva-ainemäärä	Torrsubstans-mängd
Electrostatic precipitator	Sähkösuodin	Elfilter
Emergency shut down	Hätäpysäytys	Forcerad nedeldning
Emission	Ilmapäästö	Emission
Evaporation plant	Haihduttamo	Indunstning anläggning (station)
Feed liquor	Syöttölipeä	Blandlut
Filtering	Suodatus	Filtering
Flue gas	Savukaasu	Rökgas
Fluegas handling	Savukaasun käsittely	Rökgasrening
Fly ash	Lentotuhka	Flygaska
Fuel silo	Polttoainesiilo	Bränslesilo
Fume	Sähkösuodintuhka	Stoft
Green liquor	Viherlipeä	Grönlut
Green liquor clarifier	Viherlipeäselkeytin	Grönlutklarnare
Green liquor filter	Viherlipeäsuodin	Vitlufilter
Hardwood	Lehtipuu	Lövträd
Heat efficiency	Hyötysuhde	Verkningsgrad
Heat surface	Lämpöpinta	Värmeyta
Heavy liquor	Vahvalipeä	Tjocklut
Lime	Kalkki	Kalk
Lime Bin	Uunikalkkisiilo	Kalksilo
Lime kiln	Meesauuni	Mesaugn
Lime mud drier	Meesan savukaasukuivain	Cyklontork
Lime mud filter	Meesasuodin	Mesafilter
Lime mud storage tank	Meesasäiliö	Mesatank
Lime mud wash filter	Meesan pesusuodin	Mesatvättfilter
Lime stone equipments	Kalkkikiven käsittely	Kalksten handling
Limeburning, calcining	Kalsinointi	Kalk förbränning, kalcinering
Lime kiln	Meesauuni	Mesaugn

Make up chemicals	Korvauskemikaalit	Tillskottskemikalier
Mix tank	Tuhkan sekoitussäiliö	Sulfatmixer
Multiple evaporation	Monivaihehaihdutus	Flerstegsin dunstning
Non process-proces elements	Vierasaineet	Process främmande grundämnen
Pre coat	Pre-coat	Precoat
Precipitation	Saostuminen	Utfällninig
Precoat filter	Precoat-suodin	Pre coat filter
Purging of chemicals	Kemikaalien ulosotto	Utstötning
Recovery boiler	Soodakattila	Sodapanna
Residual alkali	Jäännösalkali	Rest alkali
Scaling	Likaantuminen lämpöpinnoilla	Inkrustbildning
Scrubber	Kaasupesuri	Skrubber
Semi-thick liquor	Välilipeä	Mellanlut
Sludge press	Lietepuristin	Slampress
Slurry tank	Meesan liettosäiliö	
Smelt	Sula	Smälta
Soap	Suopa	Svartlutsåpa
Soap skimming	Suovan kuorinta	Såpavskiljning
Softwood	Havupuu	Barrträd
Sootblowing	Nuohous	Sotblasning
Strong black liquor	Vahvalipeä	Tjocklut
Sulfur-sodium ratio	Rikki-natrium -suhde	Svavel-natrium-förhållande
Superheater	Tulistin	Överhettare
Vacuum pump	Tyhjöpumppu	Vakuumpump
Weak liquor	Pesulipeä	Tunnlut
Weak wash	Heikkolipeä	Svaglut
Weak-black liquor	Laihalipeä	Tunnlut
White liquor	Valkolipeä	Vitlut
White liquor filter	Valkolipeäsuodin	Vitlutfilter
White liquor separation	Valkolipeän erotus	Vitlutsseparering
White liquor storage tank	Valkolipeäsäiliö	Vitluttank
Virgin black liquor	Mustalipeä	Svartlut

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1. Introduction

Environmental issues regarding acceptable emission levels have become stricter during the past decades. Numerous industry sectors are trying to create new, more environmentally friendly products and optimize their processes to minimize their environmental footprint, and the pulping industry is no exception to this.

Changes towards greener processes in the pulping industry are expected to be made without negatively affecting the mill's economy. To achieve this, the pulp mills have created more closed systems and are trying to reuse and recover as much chemicals, energy and heat as possible from the pulp production. This has led to decreased water, chemical and energy waste, a positive result that has made the industry more environmentally friendly. However, this has led to new problems in pulp mills, such as accumulation of non-process elements (NPEs) in the pulping process and especially in the recovery cycle. NPEs are defined as those elements that do not actively participate in the pulping process and some of them, if let to accumulate, can cause severe operating problems in the Kraft pulp mills. The decreased use of fresh water and the increased use of biofuels might raise the NPE levels, too. (Salmenoja, et al., 2009)

Better fundamental knowledge to address how, where and when the NPEs accumulate in the system is therefore needed. The NPEs tend to accumulate in the recovery cycle, where they usually cause the most harm as well. The operating problems caused by NPEs are often expensive to repair and create unnecessary costs for pulp mills. The attempt to understand the NPEs behavior in the process has turned out to be an interesting and important subject, since mills want to remove the elements in a cheap and effective way.

Effective ways to reduce NPEs are therefore needed to avoid the accumulation of the elements. There are some natural ways, also called kidneys, where NPEs are removed through several purging places of the cycle. Green liquor dregs in the recovery cycle is the most important and most used purging point for removing NPEs. (Richardson, et al., 1998; Svensson, 2012)

Studying and understanding the behavior of the NPEs in the pulping process is already something mills are looking into and are trying to address in effective ways. Accumulation of unwanted elements in processes is only going to become more central, not only in the pulping process, but in several other industry sectors as well, as industries are trying to decrease their environmental footprint by reducing their waste and moving towards greener solutions.

2. Objective of this work

The objective of the work reported in this master thesis is to answer the following questions:

- Are there NPE differences due to the mill location in Finland (north vs. east)?
- How have NPE levels changed in Finnish pulp mills since the 1990s?
- How do the present data compare to literature data on pulp mill NPE levels in North America (geographic location) as well as South America (geographic location and pulping wood species eucalyptus)?

Data are assembled from six pulp mills in Finland, in the form of chemical analysis and mill interviews. Each pulp mill took samples at seven sample points in the recovery cycle. Eight NPEs (Al, Si, P, Ca, Mn, Mg, Cl and K), as well as the liquor chemicals Na and S are examined in this project to obtain a better understanding of the behavior and accumulation of the NPEs. In addition, Mercury (Hg) and Fluorine (F) are examined in the as-fired black liquor sample.

The NPEs tend to behave in a certain way in the recovery cycle, either precipitating in process units or staying soluble in the alkali liquor. Factors such as the element concentrations, temperature, pH and other NPEs influence the element's solubility in the system. This project maps where the NPEs tend to accumulate in the six Finnish pulp mills.

The pulp mills are located in two different parts of Finland, which may also give a good insight into how the NPE levels in the mills differ depending on their geographic location. In addition, the different process steps, equipment, chemicals and fuels used in the mills vary and studying these might give a better picture of which parameters affect the accumulation of the NPEs.

Finally, the results will be compared to older and similar literature studies from Finland, North America and South America. The NPE values tend to be very mill specific and, therefore, not optimal to compare with other mills, but overall trends are expected to be seen when comparing the results.

3. Kraft pulping process

The Kraft pulping process is today used as the globally dominant process to remove lignin chemically from pulp. A chemist named Dahl discovered in Germany in 1879 that one could replace the makeup chemicals in the soda process with a cheaper version, crystalline decahydrate sodium sulfate, which led to the invention of the sulfate process. (Gustafsson, et al., 2011)

The Kraft pulping process is divided into a fiber line and a chemical recovery line. The fiber line contains the wood chip handling, bleached of pulp and drying of the pulp, and the recovery cycle line covers the recovery of liquor chemicals concurrently supporting the mill with heat and energy. A simplified process flow sheet of the Kraft pulp process is shown in Figure 1.

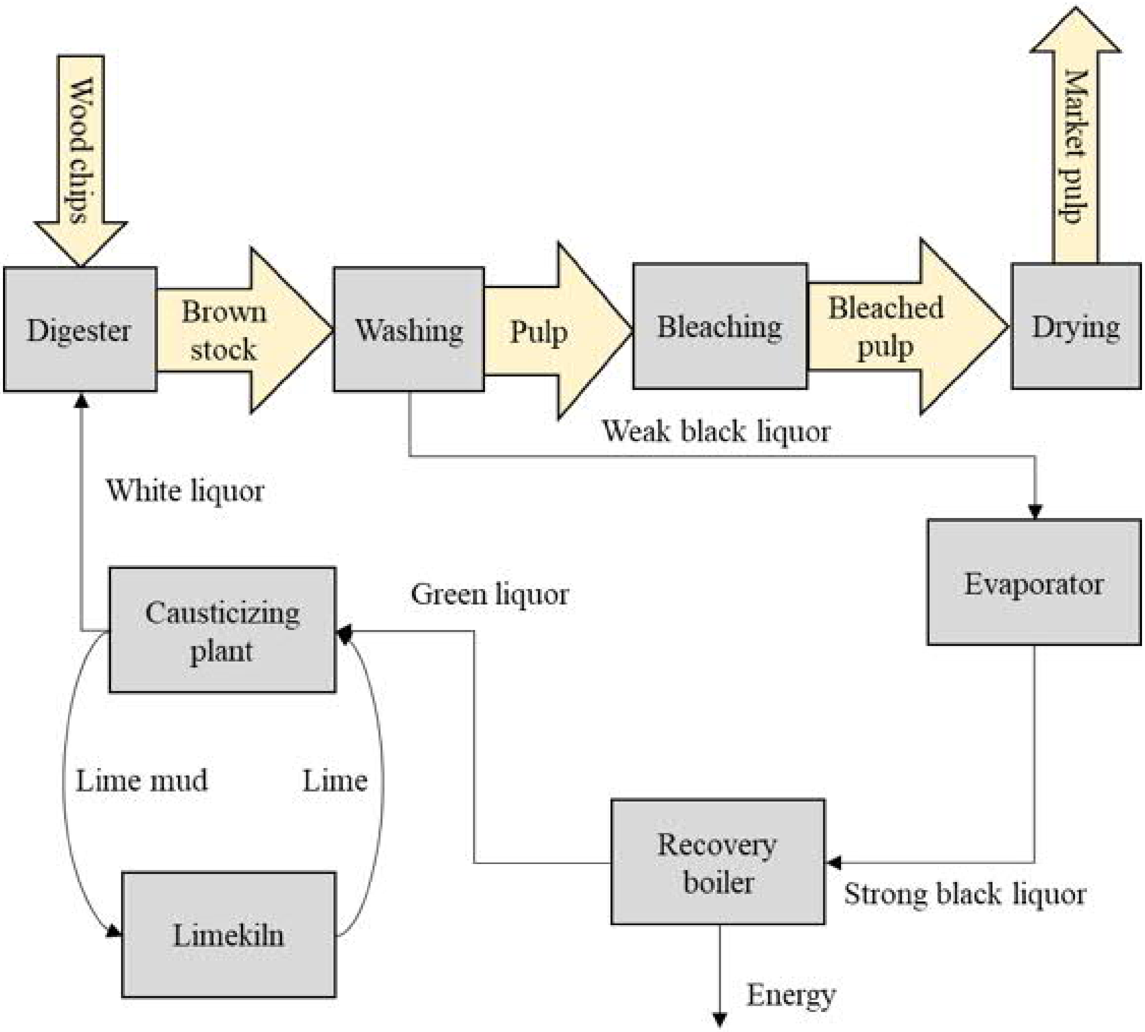

Figure 1 Block flow diagram outline of the Kraft pulping process (Green & Hough, 1992).

The incoming wood processing starts with being debarked, chipped and screened. A good debarking step is important because traces of bark could potentially increase NPE levels in the system, if not removed properly. The screening eliminates too small and over-sized chips from the raw material before it enters the digester, where the cooking process starts. (Gustafsson, et al., 2011)

3.1. Digester

Kraft pulp cooking in the digesters is divided into three basic types of cooking options: batch cooking, continuous-flow cooking and conveyor cooking. The conveyor cooking process is not widely used, because of its limited capacity. Batch cooking technology is divided further into conventional batch cooking and the more modern displacement batch cooking version. The displacement batch cooking was introduced in the 1980s and is today preferred over the conventional batch cooking, because of its lower energy consumption compared to the conventional cocking. The continuous-flow cooking is also divided into a more conventional continuous cooking and some more modern modifications. (Gustafsson, et al., 2011)

The incoming wood chips react with white liquor in a large pressurized vessel called digester in order to remove lignin. White liquor is an aqueous solution consisting of sodium sulfide (Na_2S) and sodium hydroxide ($NaOH$). The wood chips and white liquor cook together in the digester for around two hours in 170 ◦C. The temperature and time might vary, depending on the Kraft pulp mill, the digester and the cooking type. (Gustafsson, et al., 2011)

In the delignification, white liquor anions react with lignin. The white liquor fragmentates lignin polymers into smaller water/alkali- soluble parts (Gellerstedt and Lindfors, 1984). The carbon-carbon linkage of cellulose is more stable than the lignin's ether-bonds and therefore tends to survive the cooking and stay intact during the cooking. This results in the cellulose, i.e. the pulp, not degrading in the digester and the liquor removing only lignin from the wood. (Chakar & Ragauskas, 2004; Gustafsson, et al., 2011)

After the delignification, the brown stock is washed and screened in order to remove incompletely de-lignified wood residues as well as separating pulp from the used liquor. The washing usually consists of multistage counter-current washing systems. Screening separates solid impurities from the pulp, after which the pulp can be bleached. (Tervola, et al., 2011)

3.2. Bleaching process

After washing, the pulp enters the oxygen delignification or the first bleaching stage. If no bleaching is required, the pulp heads to the last process step where paper and boards are produced. Bleaching usually happens in a sequence of several bleaching stages in a row. The bleaching reagents are applied as solutions or in gas form into the pulp. (Chirat, et al., 2011)

Many modern Kraft pulp mills have stopped using chlorine as a bleaching chemical, due to environmental aspects. Mills have instead started to use elemental chlorine free (ECF) or totally chlorine free (TCF) bleaching processes, to lower the environmental impact of the bleaching process. (Chirat, et al., 2011)

As opposed to the cooking chemicals, the bleaching chemicals cannot be recycled or reused. After the bleaching chemicals are washed out from the pulp, the effluent must either be treated and cleaned, combusted or sent back to the recovery boiler. If the bleaching effluents is recycled into the recovery cycle, the mill's effluent load significantly decreases, but it might also enhance the concentration of unwanted NPEs in the system. (Chirat, et al., 2011)

Some Kraft pulp mills add magnesium sulfate ($MgSO_4$) to the washing stage of the pulp, in order to protect the fibers during the oxygen and bleaching stages. Especially softwood benefits from the addition of $MgSO_4$ (Robert, et al., 1964; Skerker, et al., 1989). The effluents up until the oxygen stage is usually recycled, meaning that magnesium sulfate can enter the recovery cycle from this incoming source. (Vakkilainen, 2008)

3.3. Chemical recovery process

Kraft pulping was invented in the 1870s. At that time, black liquor was simply discarded after its use. Even though the recovery processes had been around for a while, it was first in the 1930s and 1940s when the use of chemical recovery systems became more widespread and mills started to implement a recovery process. The regeneration of spent liquor was more economically feasible than to buy new chemicals constantly, especially when the mill sizes started to grow in the 1930s and increasing the recovery process's popularity. (Boniface, 1992; Vakkilainen, 2008)

The two main objectives of the recovery cycle are to recycle the liquor chemicals and to produce heat and energy for the pulp mill. The modern Kraft pulp mills reuse 95 – 97% of these chemicals. The losses occur when makeup chemicals leave the system through ashes, dregs and grits alongside with the NPEs (Green & Hough, 1992).

A recovery system usually consists of:

- Evaporators, for evaporating black liquor
- Recovery boiler, to combust black liquor
- Causticizing, to causticize sodium carbonate to sodium hydroxide
- Lime kiln, where lime mud is regenerated in a lime kiln

Some minor operations that are interesting regarding NPEs and part the recovery cycle are:

- Removal of tall soap in the black liquor
- Addition of makeup chemicals
- Removal of fly ash from the recovery boiler and lime kiln
- Disposal of dregs and grits (Green & Hough, 1992)

The principal unit operations of the Kraft recovery process are shown in Figure 2.

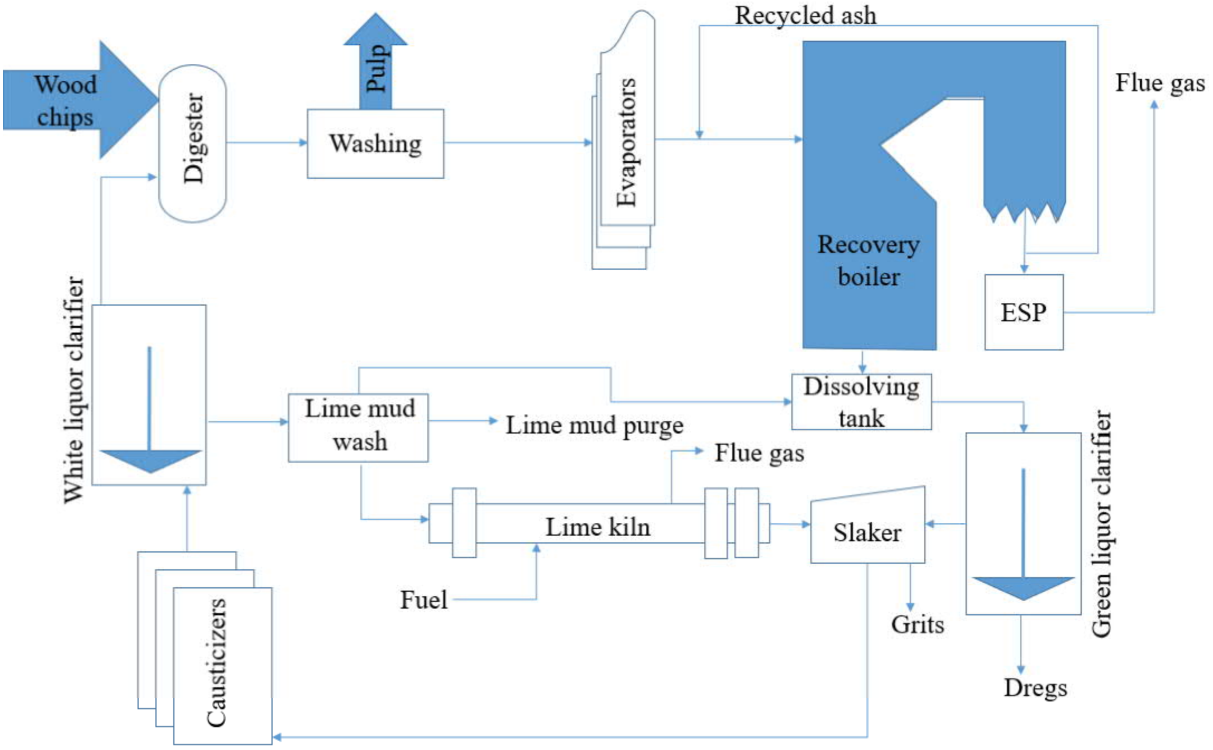

Figure 2 An overview of the chemical recovery cycle (Green & Hough, 1992).

NPEs accumulate in process units and create various problems in the system, thereby increasing the importance to know which NPE accumulates where and what kind of problems they might cause. Mapping the accumulation of NPEs is a good way to gain a better understanding of where and why the NPEs accumulate in different parts of the cycle. It is also important to remember, not just to move the problem around from one unit to another, but instead focus on the interaction between these unit operations and truly trying to solve the problems caused by the NPEs and remove them systematically from the cycle instead. (Green & Hough, 1992; Bialik, et al., 2014)

The sections below explain briefly the main unit operations in the recovery cycle i.e. evaporation, recovery boiler, green liquor handling, causticizing and lime kiln and chemical reactions essential to recycling of the liquor chemicals.

3.3.1. Evaporation

White liquor converts into weak black liquor (Na_2SO_4 and Na_2CO_3) after cooking in the digester and reacting with lignin from the wood. Weak black liquor is thereafter separated through washing from the pulp. The weak black liquor consists 12 – 20% of dry solids, both organic and inorganic and it needs to be concentrated to a dry solids concentration above 60% before it is combusted. (Adams, 1997; Tran, 1997; Parviainen, et al., 2008)

The evaporation usually happens in a multi-stage vacuum evaporator train i.e. a build of several heat transfer units that are connected in series with a heating medium, such as steam, and the black liquor that is being concentrated. The evaporation step separates water from the black liquor, to generate concentrated black liquor and condensate. (Green & Hough, 1992; Parviainen, et al., 2008)

Wood extractives and other components are separated from black liquor too. A major portion of the resin and fatty acids suspend and dilute in the black liquor after the cooking phase. When the black liquor reaches a total solids concentration of 25 – 28%, the extractives are diluted in the liquor separately from the aqueous phase. This phenomenon is called soap skimming (Krotscheck & Sixta, 2006). The rise of the dissolved solids content makes the soap components insoluble in the liquor and they start to float on the surface of the liquor. Soap removal is important, since good soap removal reduces the NPE levels and toxicity in the recovery cycle as well. (Foran, 1992)

Biosludge can be added at this stage of the recovery cycle. Some mills prefer to burn biosludge simultaneously with the liquor in the recovery boiler. This minimizes the amount of sludge having to be discarded by the mills. Tall oil effluents and other side streams can similarly be added to the liquor, in order to burn them in the recovery boiler. These side streams can contain many unwanted NPEs and the side streams have to be properly analyzed before they are added to the system. (Hyvönen, 2009)

3.3.2. Recovery boiler

The recovery boiler has several purposes in the pulping process. It acts as a chemical reactor to convert black liquor to smelt and further to green liquor. It is also a fuel combustor, a steam generator and abolishes dissolved organic matter from the recovery cycle by burning them. Before the black liquor enters the recovery boiler, recycled ESP ash is mixed into the liquor. The liquor before ash addition is called virgin black liquor and after the addition of the ash, it is referred to as as-fired black liquor. The ash is recycled to the liquor stream, in order to minimize pulping chemical waste. (Tran, 1997; Krotscheck & Sixta, 2006)

As-fired black liquor is sprayed into the boiler in the form of droplets by a liquor gun. The black liquor is either combusted in the air while falling to the char bed or combusted at the char bed on the bottom of the recovery boiler. Black liquor typically contains 3 – 5% sulfur (S) and 20% sodium (Na) by weight. Both elements distribute among various organic and inorganic compounds of decomposed lignin. (Green & Hough, 1992)

Modern, high load and high temperature boilers have plenty of Na in the liquor in order to bind S from the black liquor. A reduction reaction occurs during char combustion. The main products from the reaction in the char bed are sodium carbonate and Na_2S as well as small amounts of Na_2SO_4. The main products from the combustion reaction is water and carbon dioxide.

The recovery boiler contributes with steam to the pulping process. Burning black liquor can generate enough heat and power for the whole pulp mill and therefore making mills often self-sufficient regarding heat and energy consumption (Green & Hough, 1992). Black liquor higher heating value is typically 14 MJ/kg (Vakkilainen, 2008).

Flue gases leaving the recovery boiler go through an electrostatic precipitator (ESP), which removes the Na and sulfate fumes that are in the flue gas system. The recovered salts then rejoin with the black liquor before entering the recovery boiler again, in order to reduce the loss of makeup chemicals. Other chemicals and NPEs might reach the ESP as well. Mostly K and Cl accumulate in the ESP ash. Thus, good purging systems connected to the ESP are important and help the mill to control the accumulation of Cl and K in the recovery cycle. (Green & Hough, 1992)

3.3.3. Green liquor handling and causticizing

The smelt from the recovery boiler, thereafter, enters the smelt dissolving tank, where weak white liquor is introduced to the stream. The weak white liquor dissolves with the smelt and produces green liquor. The green liquor consists mainly of Na_2S and Na_2CO_3.

Unburned carbon, insoluble inert materials from the smelt and other undesired components can contaminate green liquor and end up being carried around in the liquor if not removed. Some components can be detrimental for the recovery cycle, if not removed properly and, therefore, a good green liquor clarification step is vital for mills. These undesired materials are often referred to as dregs. (Krotscheck & Sixta, 2006)

Green liquor is clarified in the green liquor clarification system. This purging point removes most of the NPEs from the cycle (Arpalahti, et al., 2008). The green liquor is purified either with a clarifier or with filters. The more conventional method is to use a clarifier. A clarifier purifies the liquor by sedimentation of the dregs. The density difference of green liquor and the solid particles in the liquor drive the solid particles to settle on the bottom of the clarifier forming a sludge. A rake at the bottom of the clarifier moves the sediments towards an opening in the middle of the tank, where the sludge is removed from the clarifier (Arpalahti, et al., 2008). Filters are better in removing dregs than clarifiers are, since filters retain smaller particles from the liquor. The filter operates by creating a pressure difference in a filter medium that drives the green liquor into the filtration. There are several different filters on the market with and without lime mud filter-aid. The medium used can be a lime mud cake, a filter cloth or a dregs cake. Example of filters used today in the industry are candle filters, cassette filters, disk filters or crossflow filters. (Arpalahti, et al., 2008; Krotscheck & Sixta, 2006)

The separated dregs are washed, in order to minimize the loss of valuable cooking chemicals. Rotary drum filters with a lime mud pre-coat are usually used as dregs washers. The amount of lime mud used in the filter is roughly the same amount as the quantity of dregs removed with the filter. The purge of lime mud is, however, a good way for mills to remove NPEs from their lime cycle, and therefore not seen as an unnecessary loss. (Krotscheck & Sixta, 2006)

The clean green liquor is then mixed with water and lime in a slaker. The reaction that occurs in the slaker is the production of slaked lime, which is a fast and exothermic reaction as presented in reaction R1.

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \qquad \text{(R1)}$$

Sand, over burned lime and other insoluble particles settling in the slaker are called grits. Grits are dumped once they are removed (Krotscheck & Sixta, 2006). The causticizing reaction starts immediately after the slaking has begun. The mixture enters the causticizers, where the slaked lime reacts with the green liquor as shown in reaction R2.

$$Na_2CO_3 + Ca(OH)_2 \leftrightarrow 2NaOH + CaCO_3 \qquad \text{(R2)}$$

This reaction is slightly exothermic. The solution properties such as temperature affects the reaction's equilibrium. The causticizing reaction is reversible, which means that a conversion rate of 100% cannot in practice be achieved. NPEs can for instance change the conversion rate or physical properties of the chemicals. The causticizer-train usually consists of three causticizers. The formed calcium carbonate achieved from the reaction is then precipitated and filtered out from the liquid, which has now transformed into white liquor (Na_2S and $NaOH$). (Arpalahti, et al., 2008)

Pressure disk filters or candle (pressure tube) filters are used to remove the lime mud from white liquor. The use of clarifiers for this purpose is slowly declining (Krotscheck & Sixta, 2006). Lime mud $CaCO_3$ is further washed and separated into weak white liquor and lime mud, which enters the lime kiln (Mehtonen, 2013; Arpalahti, et al., 2008). The washing is usually done with a rotary drum filter. The weak wash is used further to dissolve the smelt in the dissolving tank to produce green liquor, whereas the lime mud, now with 75 – 85% dry solids enters the lime kiln. (Krotscheck & Sixta, 2006)

3.3.4. Lime kiln

The purpose of the lime kiln is to recycle lime to the causticizing process and to maintain the lime circulation process in the recovery cycle as free from impurities as possible. This way the amount of added makeup lime reduces. The lime mud enters the lime kiln where it burns and transforms from calcium carbonate into calcium oxide. The conversion happens by burning the moist lime mud. The lime kiln uses an externa fuel source, in order to reach the required temperature for the reaction to occur. The calcination reaction shown in reaction R3 is endothermic.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(R3)}$$

The lime kiln is typically a rotary furnace or a fluidized bed reactor. The burning produces dust and flue gases that require cleaning and fume capture e.g. gas scrubbers or ESPs. The fuel used in the lime kiln is usually natural gas or heavy fuel oil. Today mills are also using environmentally friendly fuels such as biofuels instead of fossil fuels. The biofuels can, however, cause complications because they can increase the concentration of various NPEs in the system. (Arpalahti, et al., 2008)

3.4. Effect of how closed or open a cycle is

Kraft pulp mills are today expected to dump and discard waste according to stricter waste limits. Simultaneously when mills keep closing their cycle, problems with NPEs will start to arise in mills. Therefore, complete closure is difficult and nearly impossible to reach, especially with chlorine-based bleaching sequences. The concept to a zero-effluent mill is, however, an attractive concept and mills are keen to invest in new technologies to perfect their systems to fit better these standards. (Bajpai, 2018; Ikonen, 2012)

Natural purge points for NPEs have in the past been green liquor dregs, grits, effluent streams, ESP ash, lime kiln ESP ash and removal of lime mud. The effluent flow ranges from 10 to 30 m^3/ADt in modern Kraft pulp mills. The effluent flow in many European mills are around 15 to 25 m^3/ADt. When mills reach high degree of system closure (around 15 m^3/ADt), the mills have to start to use special methods and techniques in order to purge NPEs effectively from the system. (Bajpai, 2018)

The degree of closure at the mill has a major impact on how aggressively the NPEs might create problems. The closure of wastewater flow, reduction of air emissions and waste to landfills all help the mill to create a more closed system. (Suhr, et al., 2015)

4. Non-process elements

Non-process elements (NPEs) are classified in literature as those elements that do not actively participate in the pulping process (Salmenoja, et al., 2009). In other words, not all NPEs are harmful. However, some NPEs can become quite damaging and cause harm or needless dead load in the process, if let to accumulate.

NPEs enter the pulping process mainly with wood, makeup lime, makeup chemicals and process water. Bark contains more NPEs than the stem wood, consequently making it important to have a well-functioning barking process to reduce the intake of NPEs as much as possible. (Svensson, 2012)

The most harmful NPEs are phosphorous (P), silicon (Si), aluminum (Al), magnesium (Mg), iron (Fe), calcium (Ca), chlorine (Cl), potassium (K) and manganese (Mn). Even though Ca has an active role in the lime cycle, it is seen as an NPE because it is not an active chemical elsewhere in the process.

NPEs can cause operating problems such as,

- Fouling, scaling and plugging
- Corrosion
- Poor efficiency
- Dead load, low solid content in lime mud and poor mud settling
- Gaseous and particulate emissions
- Na and S imbalance in the recovery cycle. (Ulmgren, 1997; Svensson, 2012)

The operating problems caused by NPEs are often expensive to repair, thus, creating unnecessary expenses for the pulp mills (Svensson, 2012). An effective way to avoid the accumulation of these elements is to purge them from the system. Natural purge points remove NPEs naturally from the process. Green liquor dregs in the recovery cycle is the most important and used purging point for the removal of NPEs (Richardson, et al., 1998; Svensson, 2012). Other kidneys are grits, lime mud, recovery boiler ESP ash, lime kiln ESP ash and pulp (Doldán, et al., 2011).

Mills today move towards more closed systems, which makes it easier for NPEs to accumulate in the system; hence, they will not be purged out from the process as before and therefore start to accumulate. As stated before, the pulping process already has existing “natural kidneys” (purge points) and the amount of NPE in the system can effectively be minimized by utilizing these purge points to remove NPEs as well. A few alkali soluble elements require other purge methods, since they are not easily precipitated in the green liquor sludge. (Salmenoja, et al., 2009)

NPEs can roughly be divided into two groups: elements that could be purged via green liquor dregs and those elements that accumulate in liquor and lime cycle. The insoluble elements are more insoluble in alkali solutions. The insoluble elements are quite effectively purged with green liquor dregs. NPEs such as Mg, Ca, Mn, Fe, Pb and other transition metals belong to this group. This only applies if the NPEs enter the system with the raw material. However, if they enter via lime kiln fuel, they might enrich in lime or white liquor and bypass the clarification step. (Ulmgren, 1997; Hogebrandt, et al., 2017)

The more complex elements are those, which are soluble in alkali solutions. These elements usually accumulate in the liquor and lime cycle. Elements such as Al, Si, K and Cl typically accumulate in the liquor cycle and Mg, Al and P (and small amounts of Mn, Fe and Si) accumulate in the lime cycle. These elements have to accumulate significantly before they precipitate and can purge from the system (Ulmgren, 1997). Table 1 presents the categorization of NPEs.

Table 1 Categorization of NPEs according to their accumulation and purging from the recovery system (Ulmgren, 1997)

Purged via green liquor dregs	Accumulate in liquor cycle	Accumulate in lime cycle
Mg	Al	Mg
Ca	Si	Al
Mn	K	P
Fe	Cl	(small amounts of Mn, Fe and Si)
Pb		
Other transition metals		

4.1. Input of NPEs

NPEs enter mainly via wood into the system. Over 70 elements have been detected from wood. Around 80% of all the NPEs in wood consist of the four NPEs K, Ca, Mg and P. The element concentration might vary depending on the season and the geographical location of the tree and of the tree species in question.

Table 2 presents approximate concentration levels of several elements in softwoods and hardwoods, excluding carbon, hydrogen, nitrogen and oxygen. (Willför, et al., 2011)

Table 2 Approximate concentration levels of various elements in dry stem wood of soft- and hardwoods (Willför, et al., 2011)

Range, ppm	Elements
400 – 1000	K, Ca
100 – 400	Mg, P
10 – 100	F, Na, Si, S, Mn, Fe, Zn, Ba
10 – 1	B, Al, Ti, Cu, Ge, Se, Rb, Sr, Y, Nb, Ru, Pd, Cd, Te, Pt
0.1 – 1	Cr, Ni, Br, Rh, Ag, Sn, Cs, Ta, Os
<0.1	Li, Sc, V, Co, Ga, As, Zr, Mo, In, I, Hf, W, Re, Ir, Au, Hg, Pb, Bi, Sb

The amounts of NPE can differ in summer and winter wood. The species of the wood and the location where it has grown also has an impact on the NPE levels. The wood-parts contain rather small amounts of inorganic components. The highest concentration of inorganics is in the living parts of the tree where the tree can transport minerals and nutrients via the root system up to the leaves. This means that, in contrast to stem wood, the highest content of inorganics is often in needles, leaves, bark, branch wood, and root wood. (Willför, et al., 2011)

NPE concentrations also depend a lot on the wood species. The dominant Kraft pulping raw materials in Finland are pine, spruce and birch. Eucalyptus is also a widely used raw material especially in South American Kraft pulp mills. Table 3 presents the typical composition of Finnish pine, spruce and birch, Polish birch and Uruguayan eucalyptus.

Table 3 Typical elemental compositions found in pine, spruce, birch and eucalyptus (Saarela, et al., 2002)

Element		**FIN Pine**	**FIN Spruce**	**FIN Birch**	**PL Birch**	**UY Eucalyptus**
Ash	%	0.34	0.38	0.32	0.26	0.50
P	ppm	75	103	144	79	126
S	ppm	70	80	125	81	161
Cl	ppm	152	158			
K	ppm	656	753	619	440	1010
Ca	ppm	774	915	847	709	1246
Mn	ppm	86.1	93.5	121	37	82.4
Fe	ppm	12	6.7	3.3	2.7	15.7
Ni	ppm	0.14	0.22	0.28	0.21	0.53
Cu	ppm	0.9	0.82	1.16	0.54	0.95
Zn	ppm	6.97	6.64	35	11	2.46
Pb	ppm	0.11	0.17	1.23	0.29	0.28
Rb	ppm	2.5	3.3	3.9	1.5	3.3
Sr	ppm	3.2	6	5.7	1.9	13.1
Ba	ppm	2.4	10.7	11.3	7.4	23.1

Eucalyptus is known to have high K and Ca concentrations. Pulp raw material can thus create different problems depending on the wood species used in the mill. (Doldán, et al., 2011)

NPEs also enter the system with process water, process chemicals and from equipment corrosion. Iron (Fe) concentration in the recovery cycle is known to increase if the process equipment has started to corrode. Process makeup chemicals such as lime, bleaching chemicals, $MgSO_4$, EDTA and DTPA may also contribute to higher NPE levels. If the wood used for pulping happens to be contaminated with a lot of dirt, the sand and clay might enter the system as well. Clay and sand mainly consist of Al and Si. NPEs entering with the process water are mainly Fe, Al and Si. Due to the more closed effluent systems in pulp mills, mills are recycling their process waters from the fiber line i.e. bleach plant effluents and brow stock washers' effluents to the recovery cycle. NPEs such as Ca, Mg and Mn might enter the system due to bleaching effluents. Low-quality lime rock can also increase the accumulation of NPEs. (Taylor & McGuffie, 2007)

The biofuels in the lime kiln can contribute with an increase of NPEs. Clear NPE specifications for lime rock, fuel oil, salt cake and clarified green liquor is, thus, important in order to decrease the accumulation of these elements (Taylor, 2007).

The burning of biofuels in lime kilns can increase the amount of P in the recovery cycle, as the biofuel's impurities react directly with the lime in the lime kiln. The biofuel could unintentionally also transfer Si, Al and transition metals like Mn and Fe into lime and later into white liquor. If such enriched NPE liquor is used in delignification and bleaching, the transition metals can decompose the bleaching chemicals and the pulp quality might decrease. These elements contribute with a lot of problems in the recovery cycle as well. (Bialik, et al., 2014)

Table 4 shows the input and output of the most common NPEs in the recovery cycle.

Table 4 Input and output of a few of NPEs (Milanez, 2007)

NPE	Input	Output
Cl	Wood and makeup chemicals	ESP ash
K	Wood	ESP ash
Si	Wood, makeup lime, process water, clay and sand	Dregs, lime sludge and pulp
Ca	Wood	Dregs, bleaching filtrates and pulp
Mg	Wood, makeup lime, process water and $MgSO_4$	Dregs, lime sludge, grits, bleaching filtrates
P	Wood, biosludge	Lime sludge, grits
Mn	Wood	Dregs
Fe	Wood, makeup lime and corrosion from equipment	Dregs, lime sludge, pulp, bleaching filtrate
Al	Wood, makeup lime, clay and sand	Dregs, lime sludge, pulp bleaching filtrate

Extractives in wood can also cause problems to the Kraft pulping process, if not removed efficiently. Extractives contain more NPEs than cellulose or hemicellulose in wood. The number of extractives found in wood depends on several factors. The latitude of where the tree is growing effects the number of extractives produced in the tree. When the growth conditions turn out to be more unfavorable, i.e. in northern latitudes, trees tend to have a higher lignin production. Trees tend to accelerate their lignin production, if they have a harsher growing environment. (Routa, et al., 2017)

4.2. Distribution of NPEs between fiber line and recovery cycle

Chemicals present in the brown stock distribute between the fiber line and black liquor after brown stock washing. Depending on the NPE, it will enrich either in the fiber line or in black liquor. The distribution depends on the NPE's solubility in into black liquor or, if it tends to sorb onto the pulp fibers. (Järvinen, et al., 1995)

A significant fraction of metal ions sorbs or precipitates on the pulp and are carried forward to the bleach plant. Pulp fibers have carboxylic acid and phenolic hydroxyl sites that can bind metals via ion exchange with hydrogen ions. Acidic bleaching removes the metals and replaces them with hydrogen ions and alkaline bleaching helps the metals to resorb or re-precipitate on the fibers once they reach the bleaching process of the pulp mill. (Frederick, et al., 2000)

Järvinen, et al., 1995 studied the distribution of NPEs in Kraft mill fiber lines, where they concluded that different NPEs distribute unevenly between the fiber line pulp and black liquor. Approximately 80% of Ca proceeds with the pulp. The amount of Ca is however vast in wood and the amount of Ca ending up in the recovery cycle is quite large. Mg tends to distribute rather evenly between the pulp and liquor. Mn, Fe, P, Al and Si tend to dissolve to the liquor a little bit more than to the pulp after the washing, thereby winding up in the recovery cycle more frequently. Cl is one of the elements that dissolves nearly 100% into the liquor. (Järvinen, et al., 1995)

4.3. Problems caused by NPEs

Most of the NPEs can be categorized depending on what operational problems they might cause to the pulp mill. Table 5 below presents some of the most common problems NPEs can cause.

Table 5 Operational problems and the contributing NPEs. The red color indicates that the element is more soluble in the liquor and tends to accumulate in lime and liquor cycle. The blue color indicates that the element can be purged more easily from green liquor dregs (Ulmgren, 1997)

Operational problem	**Contributing NPEs**
Recovery boiler corrosion	Cl, K
Evaporator scaling	Si, Al, Ca, Fe
Poor green liquor filterability	Si, Mg
Poor mud settling	Si, Mg, Al, Fe
Higher dead load in mud	Si, Mg, Al, Fe, P, Mn

The color-coding in the table indicates if the NPE is more insoluble (blue) or soluble (red) in alkali solutions. The insoluble elements are more easily removed from the system than the red (more soluble) ones. The problems listed in Table 5 are the most common and severe operational problems caused by NPEs. Figure 3 summarizes locations and types of damage caused by NPEs. The blue color represents element known to be insoluble in alkali solutions and therefore more easily purged from the system with green liquor dregs. The red color is for elements more soluble in alkali solutions and tend to accumulate in the system more easily. They are harder to remove from the system.

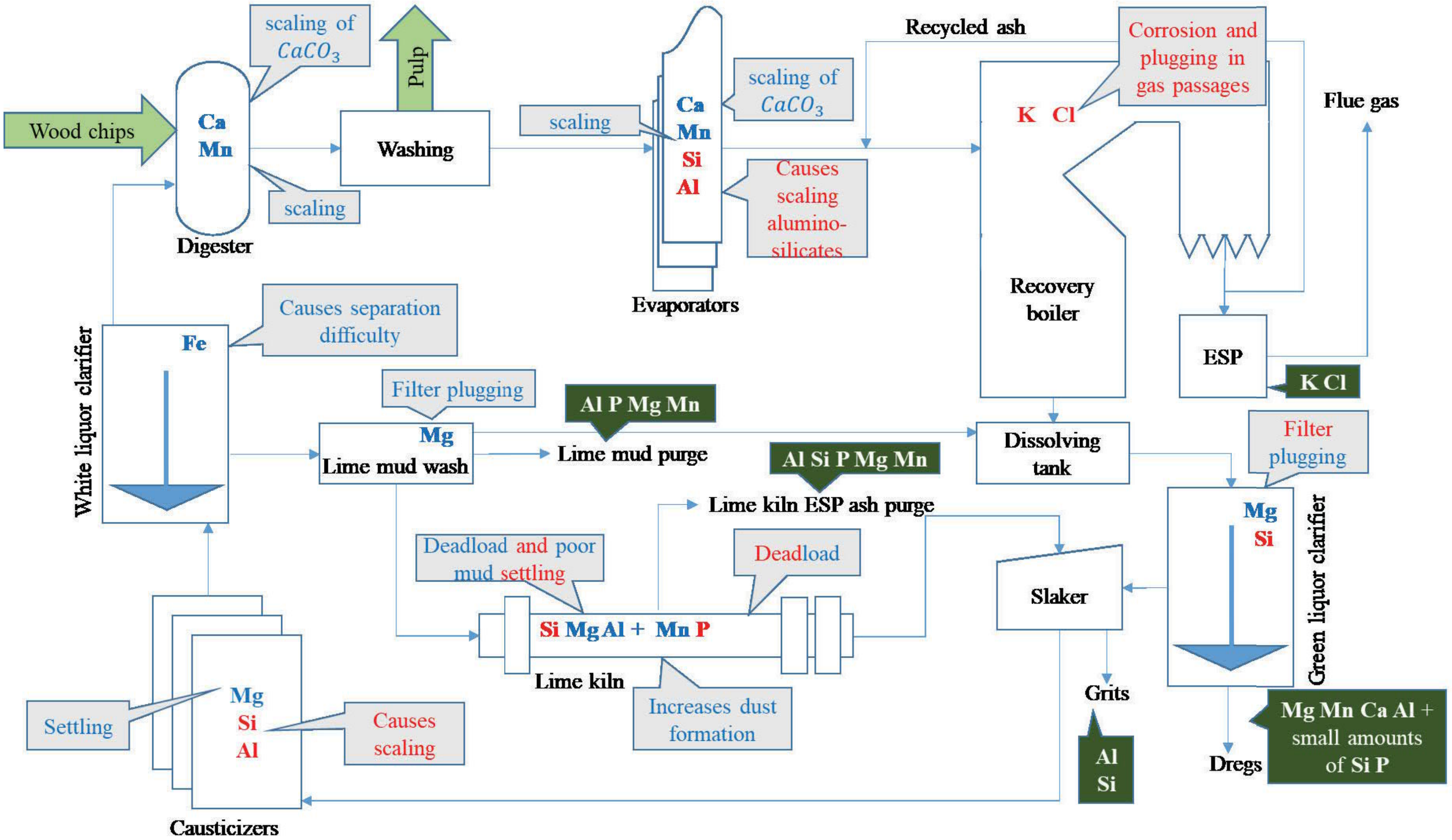

Figure 3 A summary of operating problems caused by NPEs. (Adams, et al., 1997) (Arpalahti, et al., 2008) (Backman, et al., 1996) (Bialik & Jensen, 2017) (Bialik, et al., 2014) (Bialik, et al., 2014) (Doldán, et al., 2011) (Empie, et al., 1999) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Hogebrandt, et al., 2017) (Järvinen, et al., 1995) (McGuffie & Taylor, 2007) (Milanez, 2007) (Parthasarathy & Krishnagopalan, 1999) (Salmenoja, et al., 2004) (Salmenoja, et al., 2009) (Svensson, 2012) (Taylor, 2007) (Taylor & Bossons, 2006) (Taylor & McGuffie, 2007) (Ulmgren, 1987) (Ulmgren, 1997) (Wannenmacher, et al., 2005) (Wolf, et al., 2017)

4.4. Description of individual NPEs

All NPEs tend to behave differently in the recovery cycle. The sections below review several harmful NPEs individually. The elements described in this section are P, Si Al, Mg, Mn, Ca, K and Cl.

4.4.1. Phosphorous

Phosphorous (P) is one of the most harmful NPE in the recovery cycle. P is difficult to remove from the recovery cycle because of its nature to change its solubility during recausticizing. P enters the Kraft pulp mill mainly from the wood raw material, but also with lime kiln fuel, if a biofuel is used. If biosludge is added to the recovery cycle, it may also contribute with P to the system. Lime can also contain some trace amounts of P, if the pulp mill uses low-quality makeup lime. (Mehtonen, 2013; Bialik, et al., 2014)

P accumulates typically in lime mud, mostly in the form of calcium phosphate compounds, such as hydroxyapatite $Ca_5(PO_4)_3(OH)$. The reason why P accumulates in the lime cycle is, because of its good solubility in green liquor (Ulmgren, 1997). P has been shown in numerous different mills to be the major contributor of dead load (Taylor, 2007). One weight percent of P can bind five weight percent of active calcium oxide (CaO), which reduces the amount of available calcium oxide in the lime and thereby contributes with an inert dead load (Mehtonen, 2013). Increased dead load also increases the energy consumption in the lime kiln burner (Bialik, et al., 2014).

Recent research has identified new chemical forms of P-based dead loads, compared to the apatite and hydroxyapatite known from before. Silicobernanite $Ca_2Na_2(PO_4)SiO_4$ is one newly identified compound (Bialik, et al., 2014). The presence of Ca seems to have a positive effect on P precipitation in lime mud, whereas the occurrence of Mg has a negative inhibiting effect (Wolf, et al., 2017).

The removal methods of P are limited because it accumulates in white liquor and lime mud and is very soluble in green liquor. Purging lime mud from the circulation is a good way to get rid of P easily (Mehtonen, 2013). Lime mud is commonly used in pre-coat filters for dregs, which makes it easier to remove P from the system concurrently. P can also be removed from the ESP ashes of the lime kiln (Doldán, et al., 2011).

4.4.2. Silicon

Silicon (Si) is also a more problematic NPE. Like P, it is also more soluble in green liquor compared to white liquor. Si mainly enters the system through wood, talc, makeup chemicals, Si based defoamers, process water, burning of a biofuel in the lime kiln and from dust (sand). (Mehtonen, 2013; Bialik, et al., 2014; Salmenoja, et al., 2009)

Si can be found all over the recovery cycle and in several possible purge places. Si causes scaling on evaporators in the form of aluminosilicates and it increases the dead load in the lime kiln, therefore, contributing with a negative effect on the mill's energy balance as well. (Salmenoja, et al., 2009)

High concentrations of Si present in white liquor can lead to unwanted accumulation of aluminosilicates in the black liquor evaporators. Aluminosilicates form scales on the surface of the heat exchanger tubes and reduce the heat transfer efficiency of the evaporators. The scales are usually very hard and glossy in their context and therefore very difficult to remove. (Taylor, 2007; Ulmgren, 1997)

Si is alkali-soluble in lime thus causing Si to be found in different concentrations in black, green and white liquors. Green liquor can have varying amounts of Si in soluble and insoluble forms. (Milanez, 2007)

Si occurs in various forms such as soluble, suspended and colloidal forms in the recovery cycle. Si typically is in its amorphous calcium silicate and calcium silicate hydrate forms in lime mud. The gel-like silica structure accumulates in the lime mud, contributing to the lime kiln's dead load and reduces the available amount of free Ca in lime mud (Mehtonen, 2013). The formed aluminosilicate i.e. kaolinite $Al_2O_3 * 2SiO_2 * (OH)_4$, in lime mud has a high surface area and a small particle size, which leads to low solids content in lime mud causing filter plugging (Taylor, 2007). The presence of kaolinite changes the lime mud to a more greenish color. This is because the sulphide species combines with the aluminosilicate mineral to form the colored pigment green (Taylor, 2007). Other dead load compounds found in lime containing Si are ghelenite $2CaO * Al_2O_3 * 2SiO_2$ and silicobernanite $Ca_4Na_2(PO_4)_2SiO_4$ (Bialik, et al., 2014). Fe may contribute to the creation of aluminosilicate compounds as well. (McGuffie & Taylor, 2007)

Lime mud purging is an effective way to discard Si, because it tends to accumulate in the lime mud (Taylor, 2007). The addition of Mg to the dissolving tank is found to benefit the removal of Si from the green liquor dregs (McGuffie & Taylor, 2007). Si has not been traditionally purged with green liquor sludge, due to the assumption of its high solubility in green liquor. New data, however, suggests that Si can be precipitated alongside with Al, Mg and P from the green liquor sludge, as an unknown and complex Mg-Al-Si compound. The removal is however not as effective as the addition of Mg. (Bialik, et al., 2014)

The solubility of Si is affected by other present cations in the solution, for instance the solubility of Si will decrease in the presence of Ca (Salmenoja, et al., 2009).

4.4.3. Aluminum

Aluminum (Al) enters the cycle with the wood, makeup lime and process water or when burning biofuels in lime kilns (Mehtonen, 2013). The highest removal of Al occurs with green liquor dregs and grits removal. A significant part of Al also accumulates in lime mud. (Milanez, 2007)

Al is found in the liquor as well as in the lime cycle. Temperature and the presence of cations affect the solubility of Al (Salmenoja, et al., 2009).

Al can precipitate as aluminosilicates and vermiculite in green liquor. Aluminosilicates create scales on hot surfaces and are very difficult to remove once they have precipitated. When compared to each other, Al and Mg behave quite similarly and share similar chemistry in the recovery cycle. Mg and Al react with each other to form together an insoluble double salt called hydrotalcite $Mg_6Al_2CO_3(OH)_{16} * 4(H_2O)$ (Mehtonen, 2013). The precipitation of hydrotalcite is increased, if weak white liquor's OH^- level decreases. Weak white liquor's hydroxide levels decrease by lowering the temperature, decreasing the concentration of HS^- and Si, and by increasing the concentration of CO_3^{2-}. (Doldán, et al., 2011)

4.4.4. Potassium and chlorine

Potassium (K) and chlorine (Cl) usually create the most damage in the recovery boiler, if they precipitate as sticky dust on the equipment (Bialik, et al., 2014). Both have high solubility and have, therefore, no natural kidneys in the pulp mill. (Doldán, et al., 2011)

K causes ring formation in the lime kiln and changes the melting behavior of the ash by lowering the first melting point. K can contribute to fouling problems and causes corrosion on recovery boiler superheaters. (Salmenoja, et al., 2009; Taylor, 2007)

K stays quite unreactive and is not too capable of ionic exchange with fibers, meaning it will gradually accumulate in the recovery cycle instead of continuing with the fiber line. (Milanez, 2007)

Cl also changes the melting properties of ash. Cl increases the fouling of the heat transfer surfaces in the recovery boiler and causes superheater corrosion (Salmenoja, et al., 2009). The corrosion rate increases if the pH decreases at high Cl levels (Ulmgren, 1997).

Cl enters the system via wood, makeup chemicals, bleaching chemicals, biosludge, spent acid and process water. K enters mainly via wood raw material. Due to their high solubility, both are found in the entire pulping process. The enrichment of Cl in ESP is mainly dependent on the temperature of the lower furnace and the content of SO_2 in the flue gas. Sodium dioxide drives Cl into the gas phase by sulfating $NaCl$ to $NaSO_4$. (Salmenoja, et al., 2009)

K and Cl are very difficult to remove from the process. The only output place from the cycle today is the ESP ash from the recovery boiler. The best method available for removing Cl and K from the system is probably the discharge and cleaning of the recovery boiler dust (Ulmgren, 1997). Purging of ESP ash, however, causes high Na and S losses. Sometimes it is nevertheless wanted in a mill to purge ESP ash. The sulfidity level in the recovery cycle is for instance controlled by purging ESP ash. However, if a lot of ash has to be removed, it increases the cost of makeup chemicals to the pulp mill. To minimize Na and S losses, ash leaching processes, installed for the ESP, can remove K and Cl with high efficiency and simultaneously decrease the makeup lime cost to the pulp mill. (Doldán, et al., 2011)

4.4.5. Calcium

Calcium (Ca) causes the most problems in the digester and evaporation plants. Ca dissolves in acidic solutions. It is mostly found as calcium hydroxide or calcium sulphate and calcite in green liquor and white liquor. No evident enrichment of Ca is, therefore, found in the recovery cycle except in the evaporator plants. It will, however, enrich in the brown stock and bleaching plant instead. (Doldán, et al., 2011)

The main sources of Ca are wood and makeup lime (Salmenoja, et al., 2009). Ca also enters with bark traces to the process if the debarking has not been efficient enough (Milanez, 2007). Ca precipitates mostly as calcium carbonate in green liquor. Factors affecting the precipitation of calcium carbonate is the temperature. The precipitation increases with decreasing temperature (Hyvönen, 2009). Ca can usually be removed in the form of $CaCO_3$ with the green liquor dregs (Milanez, 2007).

Brown stock containing even a slight amount of Ca ions can cause severe scaling of $CaCO_3$ on washing, knotting and screening equipment and thereby cause incremental damage to the equipment. Ca can be removed with acidic effluents. Acid dissolves practically all the Ca compounds, which therefore are discharged with acidic effluent. (Doldán, et al., 2011)

4.4.6. Magnesium

Magnesium (Mg) behaves similarly to Ca in the pulp systems, but in much lower quantities (Milanez, 2007). Mg enters the system mostly with wood and stays adsorbed on the fibers after brown stock washing. Mg is often added in the oxygen phase, because it protects the fibers (especially softwood fibers) from degradation from the bleaching chemicals. Mg can also enter with traces of bark, from the Mg sulfate addition and makeup lime. (Milanez, 2007)

Mg's solubility in green liquor is low, however, it increases in white liquor. Mg precipitates together with Al as hydrotalcite in green liquor dregs, if their ratio is favorable for complex formation.

Mg causes filter plugging problems due to poor dewatering of green liquor sludge or lime mud (Bialik, et al., 2014). This decreases the solids content in lime mud and therefore increases the energy demand of the lime kiln (Mehtonen, 2013). Mg dissolves poorly in white liquor and decreases lime mud's filterability as $Mg(OH)_2$ compounds (Bialik, et al., 2014). Mg hydroxide is a gelatinous material and has poor settling properties in green liquor clarification (Salmenoja, et al., 2009) (Milanez, 2007). Mg is however, more easily handled than P or Si and is nearly entirely removed from the recovery cycle in green liquor dregs, grits and lime mud. This is only possible provided that efficient green liquor filtration or clarification are installed in the Kraft pulp mill (Salmenoja, et al., 2009). Sodium dioxide drives chloride into the gas phase by sulfating $NaCl$ to $NaSO_4$ (Salmenoja, et al., 2009).

4.4.7. Manganese

Manganese (Mn) enters the system mainly with wood in the range of 50 – 200 g/ADt (100% dryness) for Scandinavian softwood species (Ulmgren, 1997). A lot of Mn is present in the bark, where the concentration is up to six times higher than in the stem wood, meaning that contamination of bark residues may cause an increase of Mn in the recovery cycle. Some Mn may also enter the system with the process water and makeup lime. (Bialik, et al., 2014; Holamo, 2000)

Mn is effectively removed via green liquor dregs. Mn is easily purged with green liquor dregs and it does not therefore accumulate heavily in the recovery cycle. This is only if the Mn is introduced before the green liquor clarification step. If Mn enters via lime kiln fuels or make up lime, then it might tend to accumulate in white liquor as well. Its presence in the fiber line, especially in the bleaching process, causes some severe problems. (Bialik, et al., 2014)

Mn might cause scale formations in the fiber line, in digesters and black liquor evaporators (Bialik, et al., 2014). Mn is detrimental to the peroxide bleaching process. If Mn is present in the bleaching process, it decomposes the catalyst needed for the peroxide bleaching. (Salmenoja, et al., 2009; Ulmgren, 2005)

Hard black scales caused by Mn can be found clogging brown stock washing equipment. The amorphous scales correspond to manganese oxide MnO_2 or/and manganese hydroxide $MnO(OH)$ (Ulmgren, 2005). Scales found in digesters and evaporators contain mainly Mn in the form of MnS (Bialik, et al., 2014).

Mn is rather inert during black liquor combustion in the recovery boiler and therefore not enriched in the ESP dust. Mn forms MnS and $Mn(OH)_2$ in the smelt dissolving tank and are thereafter easily removed by the green liquor dregs. (Bialik, et al., 2014)

If the dregs removal is executed poorly, traces of Mn can enter the lime cycle and accumulate as MnS dead load or transform to various Mn oxides in the recalcination step (Bialik, et al., 2014). Mn can be removed from the process by acidic washing. High concentrations of Mn can also color the lime, but this is not harmful for the process only an esthetic problem (Salmenoja, et al., 2009).

4.5. Common corrosion, deposit, scaling and dead load problems encountered in mills

The problems with NPEs start to arise when they begin to precipitate and fall out from the liquor in unintended places in the cycle, and not in their natural purge points. If they behave like inert elements, not reacting with anything or precipitating in the process, they do not cause any harm to the recovery cycle. All elements, however, start to cause problems once their solubility limit has been reached. The elements start to generate deposits, scales or dead load to the system. The elements can corrode surface materials and the deposits can start to plug up tubes, filters and pipes, when let to accumulate. Several studies have been conducted, where various scales and deposits found in the recovery cycle. For instance, Taylor and McGuffie have created a thorough data bank on several deposits found in Elk Falls mill, explaining what deposits are found in which locations of the recovery cycle. (Taylor & McGuffie, 2007)

Table 6 presents data from several sources about the operational problems NPEs can cause in the recovery boiler and the corresponding NPE components causing the damage.

Table 6 A summary of operational problems caused by various NPE compositions. (Bialik, et al., 2014) (Doldán, et al., 2011) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Holamo, 2000) (McGuffie & Taylor, 2007) (Milanez, 2007) (Järvinen, et al., 1995) (Pöllänen, 1994) (Richardson, et al., 1998) (Salmenoja, et al., 2004) (Salmenoja, et al., 2009) (Svensson, 2012) (Taylor, 2007) (Taylor & Bossons, 2006) (McGuffie & Taylor, 2007) (Ulmgren, 1997) (Wannenmacher, et al., 2005) (Wolf, et al., 2017) (Zakir, et al., 2013)

Operational problems	**Corrosion**	**Plugging scaling and deposit formation**	**Dead load**
Digester		$CaCO_3$ Aluminosilicates Burkeite Barium carbonate	
Bleaching plant		$CaCO_3$ CaC_2O_4 $CaSO_4$ $BaSO_4$ Aluminosilicates Burkeite Barium sulphate Calcium oxalate Ba, Ca and Mg	
Evaporators	Magnesium silicate hydrate	Aluminosilicates $CaCO_3$ Burkeite	
Recovery boiler	KCl NaCl	KCl NaCl K_2SO_4 K_2CO_3 K_2S Magnesium potassium silicates	
Green liquor treatment system		Bemenite Magnesium hydroxide Pirssonite $CaCO_3$ Thermonatrite Quartz Graphite Erdite Sulfur, elemental (S) Calcium sulphate Diopside Aluminosilicates pargasite Vermicullite Hydrotalcite Calcium phosphate Lepidocrocite Clinochlore	
Causticizer		Aluminosilicates $Mg(OH)_2$ Bemenite	Aluminosilicates Hydroxyapatite $Mg(OH)_2$ Mn, Fe, Cu (hydroxides) Si, Al, P, Mg, Mn, Fe Calcium silicate
Lime kiln		Bemenite Diopside Graphite Fe Calcite Portlandite Lime Pirssonite Thermonatrite Hydroxyapatite Silicorbenanite Quartz Gypsum	Kaolinite Gehlinite Silicorbenanite Hydroxyapatite Si, Al, P, Mg, Mn, Fe and Cu Calcium silicate
Cool surfaces (melt dissolving tank, green liquor lines, pumps, filters)		$Mg(OH)_2$ Pirssonite Barium sulphate Calcium oxalate Quartz Lepidocrocite Clinochlore	

Problems such as scaling, and deposit formation greatly depend on when the NPE exceeds its solubility limit and starts to precipitate in the system. The fouling out usually happens, due to significant temperature changes. For instance, if the solubility decreases with higher temperature, then the precipitation of scales will occur on the warmest position that usually is the heat transfer surface. Calcium carbonate is a well-known compound to precipitate on hot surfaces in the digester, as well as in the evaporator's heat transfer surfaces. (Wannenmacher, et al., 2005)

Other compounds that cause scaling problems on black liquor evaporators are Na_2CO_3-Na_2SO_4-type solids like burkeite $Na_2CO_3 * 2Na_2SO_4$ and decarbonate $Na_2SO_4 * 2Na_2CO_3$ (Bialik & Jensen, 2017). Aluminosilicates, such as kaolinite $Al_2O_3 * 2SiO_2 * (OH)_4$ and ghelinite $2CaO * Al_2O_3 * SiO_2$ also form scales on the black liquor evaporators (Taylor & McGuffie, 2007).

NPEs that promote corrosion and plugging of the gas passages in the recovery boiler are Cl, K and Mg. K and Cl are highly soluble in alkali solutions and accumulate, therefore, without limit in the recovery process. K and Cl cannot, therefore, be purged with the green liquor dregs. Cl and K lower the melting temperature of fly ash, increasing sticky deposits formation on tubes, superheaters and furnace walls, which will ultimately lead to corrosion and fouling. (Ulmgren, 1997)

Pirssonite scales form on cool surfaces and are usually found in the green liquor treatment system of mills. Pirssonite $Na_2CO_3 * CaCO_3 * 2H_2O$ precipitates, when the sodium carbonate concentration in green liquor exceeds the solubility of pirssonite. Green liquor piping and other cool surfaces are therefore typical locations for pirssonite scale formation (Ulmgren, 1997). Calcium oxalate precipitates on cool surfaces such as in the bleach plant, in pumps, on the walls of bleach towers and on the washing filters (Ulmgren, 1997). Pirssonite is believed to be the main contributor in Kraft pulp mills for hard scale build up in green liquor handling systems. Increasing concentrations of sodium carbonate and other sodium salts decrease the solubility of pirssonite, and its solubility increases with temperature. (Zakir, et al., 2013)

Other problems encountered in the green liquor handling system is the presence of $Mg(OH)_2$. Magnesium hydroxide reduces dregs settling properties and filterability in green liquor.

All NPEs present in green liquor after the clarification step will end up accumulating in the lime cycle. Lime mud is easily contaminated, if traces of dregs end up in the clarified green liquor. P, Mg, Al and Si decrease the filtration efficiency and settling in the recausticizing step, as well as produce inert dead load in the lime cycle. When the elements are in a soluble form, it is not possible to purge them easily from the system. When the NPEs react with Ca, they decrease the causticizing capacity to produce CaO.

NPEs are also effective in bringing alkali and moisture to the lime kiln. NPEs can cause severe deposits like diopside, graphite and bermenite in lime kilns or plugging filters. (Taylor & McGuffie, 2007; Doldán, et al., 2011)

Al and Si have been studied to decrease in a 1:1 ratio in green and white liquor solutions to form aluminosilicates. Aluminosilicates can be found in carbonate, hydroxide, or sulfate form in the liquor, depending on the solution's concentration (Wannenmacher, et al., 2005). Al and Si are removed sometimes from the green liquor dregs as the compounds of diopsides, pargasite $\mathrm{NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2}$ and vermiculite $\mathrm{Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}(OH)_2 * 4(H_2O)}$. (Taylor & McGuffie, 2007)

Scales and deposits can be removed by periodic washing cycles (Bialik & Jensen, 2017). However, several NPEs interacting with each other, create new scales that can contribute to new unknown problems compared to if they would be present alone (Bialik, et al., 2014). The chemistry and behavior of NPEs, therefore tends to be quite complex and mill specific.

4.6. Pulp mill NPE levels reported in literature

NPE levels are highly mill specific. Large amounts of studies conducted in the past decades have mapped several non-process elements in different Kraft pulp mills and in the recovery cycle. These NPE values can give a somewhat better picture of how much the values can fluctuate between mills and if some elements seem to behave similarly in several mills. Because the NPE levels tend to be so mill specific, no conclusions can be made on whether a mill with higher NPE values experiences more problems due to the elements compared to a mill with lower concentrations of NPEs. Therefore, no conclusions can be made solely on comparing the results with literature studies. Literature data can however function as a good base for finding some trends and similarities on how elements behave in the recovery cycle and what concentration levels have been found in the past.

Studies from Scandinavia, North and South America are presented in the following tables (Table 7, Table 8, Table 9, Table 10, Table 11 and Table 12). The raw materials used are pine, spruce, birch and eucalyptus in the upcoming results. The mills in South America use almost exclusively eucalyptus as their raw material in these literature studies. Only the NPEs relevant for this study have been presented in the following tables (Table 7, Table 8, Table 9, Table 10, Table 11 and Table 12). The results are shown both in mg/l, mg/kg, ppm or g/ADt, depending on the literature reference.

4.6.1. Weak black liquor, as-fired black liquor and ESP ash reported results

NPE levels in weak black liquor, as-fired black liquor and ESP ash from several sources from Finland, US and Canada are shown in Table 7. Cl and K have the highest concentration in all the sample points. The concentrations of Cl and K increase significantly in the ESP ash compared to the black liquor samples. This is because K and Cl accumulate in the recovery boiler ash. The reason for this is that K and Cl are both soluble in alkali solutions, which leads to the elements not being purged efficiently out via dregs or grits, and because they both are volatile, they tend to end up in the ESP ash.

The comparison of weak black liquor and as-fired black liquor conducted by McGuffie and Taylor in 2007, shows a slight increase in concentration of the majority of the NPEs towards as-fired black liquor. This could be due to the addition of some side streams to the liquor and concentration differences of the liquor compared to weak black liquor.

Table 7 A summary of weak black liquor (WBL), as-fired black liquor (ABL) and ESP ash (ESP A) from several literature sources (Järvinen, et al., 1995) (Holamo, 2000) (Frederick, et al., 2000) (McGuffie & Taylor, 2007) (Salmenoja, et al., 2004). The result shows an average of (Avg.) samples. All of the mills use softwood and hardwood as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
FIN	Järvinen	1995	37	WBL	mg/kg	30	267	146	85	128	68	2481	17776
FIN	Holamo	1999	5	WBL	mg/kg	44	375	233	76	138	67	1545	27080
US	Frederick	2000	6	WBL	mg/kg	8	47	35	7	14	11	131	2183
CA	McGuffie Taylor	2007	1	WBL	mg/kg	75	368	279		156	82		7770
FIN	Salmenoja	2004	5	ABL	mg/kg	33	284	219	71	154		1600	27800
CA	McGuffie Taylor	2007	1	ABL	mg/kg	85	465	440		239	92		7500
FIN	Holamo	1999	3	ESP A	mg/kg							10533	61633
FIN	Salmenoja	2004	5	ESP A	mg/kg	6	105	77	25	46		6800	47600
US	Frederick	2000	6	ESP A	mg/kg	14	120	116	18	34	34	1525	38902

Data on eucalyptus weak black liquor and ESP ash NPEs are shown in Table 8. Si, Ca and Cl show a tendency to be much higher in eucalyptus Kraft pulp mills as compared to e.g. birch, pine and spruce Kraft mills, based on the results shown in Table 8, in the weak black liquor samples. This goes in line with the fact that eucalyptus has high Ca, Cl and K concentrations. (Doldán, et al., 2011)

Table 8 A summary of weak black liquor (WBL), as-fired black liquor (ABL) and ESP ash (ESP A) from literature sources such as (Doldán, et al., 2011) (Milanez, 2007) The result shows an average (Avg.) of sample points found in literature. The South American mills in this table use eucalyptus as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
S Am	Milanez	2007	2	WBL	ppm	70	498	632		199.6	67.2	4719	
S Am	Milanez	2007	1	ESP A	ppm	78	375	144		49.0	13.5	79800	
S Am	Doldan	2009	2	ESP A	g/adt	0.45	5.95	6.5	1.1	2.2	1.05	2161	2947

4.6.2. NPE levels in green liquor and white liquor

Table 9 presents literature data on green liquor and white liquor NPEs.

It can be noted that in Table 9, especially Mn and Mg concentrations, are significantly lower in green and white liquor, compared to concentrations in black liquor (Table 8). Mn and Mg seem to be effectively removed from green liquor during its clarification step. The concentration level of Ca seems to have decreased, but to a lesser extent than Mg and Mn.

P and Al show a tendency to decrease during green liquor clarification. However, because the elements tend to be soluble in alkali solutions they do not decrease as much as Mg, Mn and Ca do. Cl is also soluble in alkali solutions and behaves similarly to P and Al.

Si does not show any clear signs of decreasing in green liquor and it is one of the elements with highest concentrations in green and white liquor. K is one of the elements with a high concentration in green and white liquor. However, when comparing the concentration levels in black liquor, K has decreased to some extent as well. This is because it tends to enrich in ESP ash. Table 9 presents the literature values found for white and green liquor in Scandinavian and North American mills. Table 10 presents corresponding data from an eucalyptus mill.

Table 9 A summary of clarified green liquor (GL) and clarified white liquor (WL) from several literature sources (Holamo, 2000) (Bialik, et al., 2014) (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor & McGuffie, 2007) (Järvinen, et al., 1995). The result shows an average of (Avg.) samples conducted from the literature reference. All the mills use softwood and hardwood as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
FIN	Holamo	1999	9	GL	mg/l	10	164	11	31	2.1	4.7		9788
SWE	Bialik	2014	4	GL	mg/kg	15	172	12	36	2.3	1.7		
US	Richardsson	1998	4	GL	mg/kg	9	118	15		7.0	2.7		7803
US	Frederick	2000	6	GL	mg/kg	10		36	22	3.4	3.6	500	6011
US	Gu	2002	1	GL	mg/l			71		35	8.2		2075
CA	Taylor	2006	1	GL	mg/l	28	280	12	25	0.2	4.0		
CA	McGuffie Taylor	2007	1	GL	mg/l	30	282	10	26	0.4	4.2		3790
FIN	Järvinen	1995	30	WL	mg/l	17	154	29	12	1.0	4.2	1259	7794
FIN	Holamo	1999	7	WL	mg/l	15	148	13	14	0.4	4.0	1167	9907
SWE	Bialik	2014	6	WL	mg/kg	20	203		10	0.7	1.7		
US	Richardsson	1998	4	WL	mg/kg	8				1.0	3.0		6910
US	Frederick	2000	5	WL	mg/kg	18	127	220	7	3.5	2.2	464	5815
US	Gu	2002	1	WL	mg/l			71		4.0	4.2		2000
CA	McGuffie Taylor	2007	2	WL	mg/l	30	289	10	8	0.7	4.5		3585

Table 10 A summary of clarified green liquor (GL) and white liquor (WL) from one literature source (Milanez, 2007) The result shows an average (Avg.) of sample points found in literature. The South American mills in this table use eucalyptus as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
S Am	Milanez	2007	1	GL	ppm	62	782	18		0.1	2.3	13085	
S Am	Milanez	2007	1	WL	ppm	90	886	31		2.7	4.1	19975	

4.6.3. Lime mud and green liquor dregs

Table 11 shows a summary of literature data on lime mud and green liquor dregs. K does not accumulate in the lime cycle and its concentration level is the lowest in the lime mud, compared to the other sample points.

P, Si and Al tend to accumulate in the lime cycle. Al concentration is the highest in lime mud compared to the other sample points, as well as Si concentration level. Al, Si and P react with the lime mud causing dead load and turn out to be more difficult to remove from the process.

The alkali insoluble elements show high concentrations in lime mud as well, even though they can be removed quite effectively during green liquor clarification. However, if the elements are not removed thoroughly, they can cause problems in the causticizers, white liquor handling and lime cycle. These elements can also enter the cycle through other side streams, such as the fuel used in the lime kiln, make up lime and process water.

Ca concentration is naturally high in lime mud, since most of the lime mud consists of Ca. In this situation, Ca is not seen as a NPE, since it actively participates in the process chemistry. However, Ca is not wanted in the rest of the process steps and therefore it is seen as an NPE there.

Green liquor dregs are the main purging point for the NPEs. Ca, Mg and Mn as stated before can be effectively removed via dregs as presented in Table 11.

Table 11 A summary of lime mud (LM) and green liquor dregs (GL D) from several literature sources (Holamo, 2000) (Bialik, et al., 2014) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor & McGuffie, 2007) (Richardson, et al., 1998). The result shows an average of (Avg.) samples conducted from the literature reference. All of the mills use softwood and hardwood as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
FIN	Holamo	1999	9	LM	mg/kg	287	1155	381889	6959	6987	379		378
SWE	Bialik	2014	7	LM	mg/kg	520	1514		5714	4843	243		54
US	Frederick	2000	6	LM	mg/kg	35		49860	662	598	76		5719
CA	Taylor	2006	1	LM	mg/kg	900	2200		7500	3400			
CA	McGuffie Taylor	2007	1	LM	mg/kg	737	1750	380000		2820	221		22
FIN	Holamo	1999	9	GL D	mg/kg	3881	6914	174667	2315	33812	16150		7013
SWE	Empie	1993	5	GL D	mg/kg	6040	2220	209000	2075	30200	19800	275	
SWE	Bialik	2014	3	GL D	mg/kg	13667	14667		667	61667	16667		
US	Richardsson	1998	4	GL D	mg/kg	2276	1908	188875		25034	11174		10136
US	Empie	1995	5	GL D	mg/kg	4760	6700	154980	100	24480	15700	2700	6125
CAN	Taylor	2006	2	GL D	mg/kg	1860	5285	19600	88	10065	4965		10715
CA	McGuffie Taylor	2007	1	GL D	mg/kg	2050	5190	20700		12100	5950		11600

Even though Al and Si are more alkali soluble, they are also purged out with green liquor dregs to some extent. This is because they will precipitate in green liquor if they exceed their solubility concentration or if they have reacted with other compounds and are purged simultaneously with these elements from the system. There seems to be some variation in literature data on P, depending on the literature source.

Relatively little data on green liquor Cl was found but based on the data available Cl tends to be soluble in green liquor and therefore harder to purge with dregs.

Table 12 shows data on lime mud and green liquor NPEs in eucalyptus mills.

Table 12 A summary of lime mud (LM) and green liquor dregs (GL D) from literature sources (Doldán, et al., 2011) (Milanez, 2007) The result shows an average (Avg.) of sample points found in literature. The South American mills in this table use eucalyptus as their raw material

Loc.	Author	Year	Avg.	Sample		Al	Si	Ca	P	Mg	Mn	Cl	K
S Am	Milanez	2007	1	LM	ppm	535	1047			2426	16	14010	
S Am	Doldan	2009	1	LM	g/ADt	170	1000		5600	2100	130		58
S Am	Milanez	2007	1	GL D	ppm	7568	3791	192942		17401	4380		

4.7. NPE removal

This section discusses NPE removal techniques currently used. The complexity of the connections between the NPEs is a relatively new topic and is not fully understood yet. If the NPEs interactions were clearly and better known, one could more precisely predict how they accumulate in the recovery system.

4.7.1. Most common removal techniques

Effective removal of NPEs is preferred in mills. The elements can be controlled with keeping the cycle open and removing waste and effluents from the process. The closing of waste streams makes the removal more challenging and new ways to remove NPEs more effectively with minor waste streams are needed. The most common and effective ways are still to purge dregs and ESP ash from the process.

The raw material is known to be the major contributor of NPEs to the system. Some mills remove the NPEs by leaching the chips before the digester stage. Chelating agents such as EDTA are also widely used. The chelating agents chemically isolate the NPEs in a dissolved state, after which they are removed in the washing stages of the pulp with filters. (Bajpai, 2018)

There are existing natural ways in the pulping process, also referred as kidneys, where NPEs can easily be removed from the cycle. Green liquor dregs in the recovery cycle is the most important purging point. (Ulmgren, 1997; Richardson, et al., 1998; Svensson, 2012)

Al, Mg, Mn, Fe and small amounts of Si and P are purged with the green liquor dregs. If lime mud is removed from the process, it also removes NPEs such as Al, P, Mg, Mn, and Fe. Recovery boiler is the best kidney for purging K and Cl. Grits can purge small amounts of Al and Si as well (Ulmgren, 1997). An effective way to remove lime mud is to use it in dregs filters to remove green liquor dregs. Removing lime mud decreases the amount of P and other accumulating NPEs from the lime cycle. (Gu & Edwards, 2004)

Separation of Si with green liquor dregs has in the past thought to be unsuccessful, but new studies are contradicting these statements (Wolf, et al., 2017). The change in Si's behavior could be due to the concentrations of NPEs being higher in the liquor system than when studied in the past (Wolf, et al., 2017).

Green liquor separation is the most important purge point for many NPEs. Many troublesome NPEs precipitate here and can be removed with a filter or a clarifier. Cross flow filters are known to be more efficient than clarifiers. The Samoa Pacific mill did for instance install filters and a pre-coat dregs filter in April 1996, to improve their dregs removal (Taylor & Bossons, 2006). They had used a clarifier before the installation. Their measurements showed significantly lower NPE concentrations in their white liquor and better lime mud quality after starting the use of the filters. However, nearly a year had to pass in order for the changes to be seen, hence, the time for the NPEs to be purged from such a large system takes a long time. (Taylor & Bossons, 2006)

The formation of hard and extremely difficult to remove aluminosilicate scales in evaporation is an example of complex compounds that can cause a lot of problems and may contribute to serious problems in the white liquor and other process stages. That is why, the concentration of Al and Si in white liquor should be kept low. If the formation of aluminosilicates occurs, mills should control their lime makeup quality and check if the separation of Al and Si could be improved in the green liquor sludge. (Bialik, et al., 2014)

The removal of NPEs can be improved for instance by adding a polymer to the suspended dregs or use a decanter centrifuge as a final dewatering step of green liquor sludge (Svensson, 2012). Scaling on evaporator surfaces could be minimized by coating the evaporator with glass. The surface properties of the equipment used in the process has been stated to influence the formation of scales. (Bialik & Jensen, 2017)

4.7.2. NPEs in bleaching plants

NPEs do not only cause problems in the recovery cycle, but also in the bleaching plant of the pulp mill. For instance, in TCF-bleaching (total chlorine free) many harmful NPEs (i.e. the transition metals such as; Mn, Fe and Cu) can deactivate the hydrogen peroxide catalyst. The transition metals are known to decompose oxygen-based bleaching chemicals (Bialik, et al., 2014). However, the bleaching point is also a good purging point for some NPEs like Ca, Mn, Cu and Barium. (Ulmgren, 1997)

4.7.3. The complexity of NPE removal

As explained earlier, common techniques work effectively enough to remove most of the NPEs. However, as the closing of the effluent streams becomes more relevant, the mills might get more problems with the NPEs, since their behavior and accumulation rate can change.

The difficulty in purging NPEs rises when the elements should be removed concurrently. Some NPEs can increase or decrease the solubility of other NPEs, and different factors such as pH and temperature affect NPEs properties as well. This makes it nearly impossible to control and precipitate several NPEs at the same time. (Wolf, et al., 2017)

The NPEs interact with each other and the change in one or two parameters in green liquor can affect the NPEs in a different way, making it even harder to purge them all concurrently from the green liquor.

Earlier studies usually only focused on one or two NPEs at a time. It is today assumed that the NPEs can also create bigger complex compounds together, changing the properties of the precipitate, which makes it harder to keep track on the NPEs and how to purge them from the system. The complex compounds can consist of up until 4 – 5 different NPEs, thus, making the NPE research of solely one NPE insignificant. (Bialik, et al., 2014)

5. Experimental

Six Finnish Kraft pulp mills participated in this project. The purpose was to obtain a better understanding of the NPE status in Finnish pulp mills. Three of the mills are located in north Finland and three mills in east Finland. Sampling was carried out by the mills and samples were sent to an outsourced commercial laboratory Eurofins Labtium for analysis. The experimental part of this thesis included two parts: i) the coordinating of the sampling on site at the pulp mills, and ii) interviews at the mills. This chapter describes the differences between the mills, how the sampling was carried out, how the interviews were held and how the samples have been analyzed as well as sampling errors to be considered, when analyzing the results. Data handling techniques and other necessary calculation steps are also described at the end of this chapter.

5.1. Kraft pulp mills

The Kraft pulp mills that agreed to be part of this project, are located in northern and eastern Finland. The location of the harvesting of the raw material could affect the NPE concentration. The main raw materials the mills are using is pine, spruce, and birch. A more detailed description of the mills' raw materials and location are presented in Table 13.

Table 13 An introduction to the mills, showing their location and raw material

Pulp Mill	Wood species	Location
Mill A	Softwood	North
Mill B	Softwood & Hardwood	North
Mill C	Softwood & Hardwood	North
Mill D	Softwood	East
Mill E	Softwood & Hardwood	East
Mill F	Softwood & Hardwood	East

The raw material is the main source of NPEs and has the largest impact on the concentrations of NPEs in the process. The three main raw materials the six pulp mills use are birch, spruce and pine, which are divided in this thesis into hardwood and softwood. Softwood contains more extractives than hardwood. Softwoods also contain more lignin and less hemicellulose compared to hardwood. The cells in softwood are mainly fibrous while hardwood on the other hand has a broader diversity of specialized cells and has larger pores, which helps the pulping liquor to enter the structure more easily during Kraft pulping. (Willför, et al., 2011)

5.2. Sampling

The sampling for this project was carried out in fall 2018. Table 14 presents the more specific weeks when each mill took their samples. The sampling was planned to take place during a period when no disturbances or mill shut downs would affect the process and the sampling. The guidelines and instructions given to the mills, were to take three samples in a period of three days to generate trustworthy results that represent the mills' normal steady state. This was, however, not possible for all mills to carry out and therefore are the samples taken during a time span of one to five days instead. From each collected sample three replicate analysis were carried out by a commercial laboratory.

Table 14 Sampling executed at Mills

Pulp Mill	Sampling week in 2018
Mill A	48
Mill B	42
Mill C	44
Mill D	43
Mill E	42
Mill F	50

All mills were provided with an instructional document describing where in the recovery cycle to take the samples, how often samples had to be taken and how much sample was needed.

The initial guidelines were to have seven sample points for this project, which were;

1. Weak white liquor
2. As-fired black liquor
3. ESP ash
4. Clarified green liquor
5. Green liquor dregs
6. White liquor
7. Lime mud

The elements analyzed from each sample point are presented below in Table 15. In addition to the NPEs, fluorine (F) and mercury (Hg) were analyzed in the as-fired black liquor sample point. Fluorine and mercury were in all mills under the detection limits <0.01 mg /kg for Hg and <20 mg/kg for F. The seven sample points are shown in Figure 4. For some of the mills the process included parallel process lines. For these mills additional sampling was carried out as compared to the seven sample points indicated in Figure 4.

Table 15 Description of the sample points and the elements analyzed from each sample point

Sample point		Analyzed element
1. Weak black liquor	mg/kg	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca
2. As-fired black liquor	mg/kg	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca + F, Hg
3. ESP ash	mg/kg	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca
4. Clarified green liquor	mg/l	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca
5. Green liquor dregs	mg/kg	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca
6. White liquor	mg/l	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca
7. Lime mud	mg/kg	Na, S, K, Cl, Al, Si, P, Mg, Mn, Ca

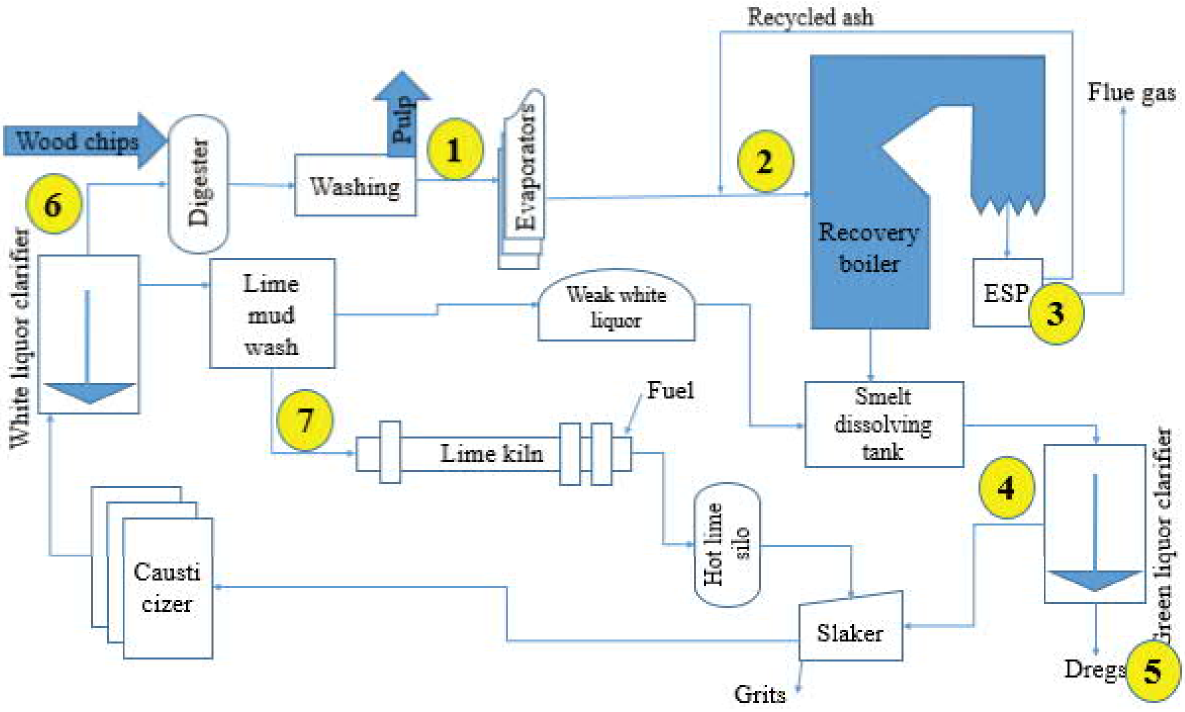

Figure 4 Illustration of the seven sample points at the mills.

The second sample point (as-fired black liquor) transforms rapidly into a thick sluggish liquor after sampling, which makes it difficult to mix the sample properly afterwards. That is why, only one sample was taken at this sample point. The sample points differed to some extent between the mills, because the mills did not have identical processes nor sampling points. The differences in sampling between mills had some impact on the results, including differences in green liquor dregs removal which resulted in some dregs samples containing lime mud used as dregs filter pre-coat or weak black liquor samples without tall soap. These differences are further described in section 5.4.1. Sampling and interview errors.

5.3. Sample analysis

Sample analysis was carried out by a commercial laboratory. From each collected sample, three replicate analysis were carried out. For a more concrete picture, this resulted in (6 mills) × (7 sample points/mill) × (3 replicate analysis/sample point) = 126 sample analyses. Additional samples were taken for some mills, which increased the total number of sample analysis. Each sample analysis covered the ten elements (Al, Si, Ca, P, Mg, Mn, Cl, K, Na, S), as well as Hg and F in as-fired black liquor.

All elements except Cl was analyzed with the IC-OES method. The pretreatment method for the samples however varied, depending on which sample point was concerned.

Weak black liquor and as-fired black liquor samples were pretreated with the SCAN-N 38:10 method. The samples are decomposed with hydrogen peroxide and nitric acid in a microwave before analyzing.

ESP ash, white liquor and green liquor do not have a standardized pretreatment method. In this project the samples were decomposed with hydrogen peroxide and nitric acid.

Green liquor dregs and lime mud do not have a standardized pretreatment method. The samples are decomposed with hydrogen peroxide and nitric acid in a microwave, after which the dissolved samples are analyzed.

Chlorine was pretreated and analyzed with a different method.

In weak black liquor and as-fired black liquor chlorine was analyzed with AOX-analyzer. The sample is heated up to 1000 °C and the freed chlorine is analyzed with a coulometric titration method.

In white and green liquor, the samples were analyzed with the SCAN-N 4:78 method. The sample is dissolved in water and a silver nitrate solution is used to potentiometric titrate the solution with a silver nitrate solution.

The ESP ash does not have a standardized method, however, it is handled similarly as the SCAN-N4:78 method. The sample is dissolved in water, after which it is potentiometrically titrated with silver nitrate.

Green liquor dregs and lime mud are dissolved in water and the dissolved chlorine is thereafter analyzed with ion chromatography.

The dry solids content, except for green and white liquor, were determined at 105 °C.

The raw data, as received from the laboratory, for all six pulp mills is summarized in Appendix A.

5.4. Mill interviews

During this project, all six mills were visited, and interviews were carried out with the mill personnel to gain a better picture of the long-term NPE situation at the mills. The interview included questions about the process steps, what equipment they use and what operational problems they have had in the process due to the enrichment of NPEs.

Each visit took around three hours. The interview was carried out quite freely and not all questions in the prepared questionnaire were necessarily answered. The main purpose with the interview was to clarify what their process looked like and if they had encountered any NPE derived problems. The dates of the mill visits are summarized in Table 16.

Table 16 The date of visit and interviews conducted by each mill

Pulp Mills	Date of visit/interview
Mill A	24.01.2019
Mill B	28.11.2018
Mill C	14.11.2018
Mill D	12.12.2018
Mill E	13.12.2018
Mill F	13.12.2018

The interview can be divided into three categories according to the type of questions asked. One category was questions about their process equipment. The second category was questions about the process parameters. The third category were questions about if the personnel had encountered any problems with NPEs in the mill. The answers to the third-category questions are more subjective and cannot be compared in a straightforward way to each other, since there seemed to be different opinions about what is considered a problem, what problems are caused by NPEs instead of other factors and what is labeled just as normal wear of the equipment.

The information gained from the interviews was used to identify unreliable sample analysis results. The data collected from the interviews was also used to explain and understand better differences in results, when an answer could not be found from other sources. One mill had experienced a kaolin contamination, which was explained during the interview.

The answers also give good insight into what the pulp mills see themselves as problems that need to be solved or if the concentrations of the NPEs do not affect their production in such an extent that their presence would be a problem. However, it should be kept in mind that these opinions may also vary depending on the mill and person interviewed.

5.4.1. Sampling and interview errors

Samples were taken three days in a row, one sample each day and mixed together to create a collected sample. This was done for all sample points, except for the as-fired black liquor sample point. This sampling method was chosen to provide more trustworthy values, due to representing a longer period compared to if only one random sample would have been taken.

The six mills in this project use different raw materials, their production capacity varies, their process steps differ, and the equipment used in the process are not the same. Therefore, some variations that have nothing at first hand to do with NPEs can be expected in the results. The results can thus not be compared between mills, without considering factors that might cause the values to differ.

All the samples were taken in fall of 2018 between the weeks 42 to 50, which should be close enough for not causing too much differences between mills, due to seasonal changes. A factor that may affect the sampling results is whether the sample was taken right before or right after a shutdown. Even though the mills that took samples after the shutdown waited until their process reached a steady state for the sampling, it may still have affected the results.

The green liquor handling system differs between the mills. Three of the mills use a clarifier and the rest have invested in crossflow filters. In the clarifier, the dregs sink to the bottom of the tank, where it is removed. In these mills, the dregs sample was taken from the dregs coming out from the clarifier tank. The dregs filter sometimes uses lime mud as a pre-coat on the filter to precipitate the dregs on them more effectively. All mills with filters were able to take the sample without lime mud present except Mill B, which has lime mud present in its green liquor dregs sample.

Mill A was not able to take a weak black liquor sample before the tall soap was removed, which means that its values are going to differ from the other mill’s results as well. All the other mills were able to take samples of the weak black liquor still including the tall soap.

Other factors creating further variations in the results are mill specific problems during the sampling time. Mill C had a kaolin spill and the kaolin was introduced into the recovery cycle creating scales and plugging in their evaporator plant. The mill was clearly not in its normal process state during the sampling and this can be seen in the results too.

The results from the interviews are all based on subjective opinions and the answers vary much depending on whom you ask. The answers might give an insight into how the mills respond to the NPEs being in the system and if it even is something that they actively follow the levels at the mills.

5.5. Mill Balances

Pulp mill mass balance calculations in this study were performed using the MillFlow program. Professor Esa Vakkilainen from Lappeenranta University of Technology, School of Energy Systems, provided in this study all the Millflow mass balance calculations for the six pulp mills.

Millflow software is based on standard engineering methods for dimensioning pulp mills. The software is a mill spreadsheet that has been gradually developed at LUT Energy to dimension pulp mills. The software includes detailed mass and energy balances to provide detailed results of the mill design and its mass and energy balances. (Hamaguchi, et al., October/December 2011)

5.6. Hypothesis tests

In statistical hypothesis testing, the student's t-test is a commonly used method for comparing two means and to tell, if they are different from each other or not. The t-test values from sample analysis in this work are summarized in Appendix B. The t-test also analyses how significant the differences are. The t-test inspects the so-called null hypothesis. The null hypothesis is that the means of two populations are said to be equal as shown in Equations 1.

$$H_0: \mu_1 - \mu_2 = 0 \qquad (1)$$

The t-test indicates, if the difference seen between the two groups is a result of chance or not. In other words, if the t-test is significant then the difference between the two groups is due to the population's characteristics, rather than being just a sampling error or due to chance.

The t-score tells the ratio between the difference between the two groups tested and the difference within the groups. A large t-score indicates that the difference between the group is big and a low t score means that the groups are more like each other.

If the populations are assumed to have unequal variances an adaption of the student's test can be used, called Welch's t-test.

The t-value is calculated as presented in Equation 2 if the populations are assumed to have unequal variances.

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_A^2}{n_A} + \frac{s_B^2}{n_B}}} \qquad (2)$$

Where, t is the t-test value,

$\bar{x}_A$ is the mean of group A,

$\bar{x}_B$ is the mean of sample B,

s_A is the standard deviation of sample A,

s_B is the standard deviation of sample B,

n_A is the sample size in sample A,

and n_B is the sample size in sample B.

The calculation of standard deviation (s) is presented in Equation 3.

$$s_x = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}} \quad (3)$$

where, n is the number of data points,

x_i is each of the values of the data

and $\bar{x}$ is the mean of the population x_i.

Degrees of freedom (df) is the number of observations in the population which can be varied independently under constraint. Welch–Satterthwaite equation is used to approximate the degrees of freedom (Satterthwaite, 1946). The degrees of freedom approximation is shown in Equation 4.

$$df \approx \frac{(\frac{s_A^2}{n_A}+\frac{s_B^2}{n_B})^2}{\frac{s_A^4}{n_A^2*(n_A-1)}+\frac{s_B^4}{n_B^2*(n_B-1)}} \quad (4)$$

where, s_A is the standard deviation of sample A,

s_B is the standard deviation of sample B,

n_A is the sample size in sample A,

and n_B is the sample size in sample B.

The t-test value measures 'strength of evidence' that a real difference can be seen. The t-value is, thereafter, compared according to its degrees of freedom to a t-test table as presented in Appendix C. The table value defines how high the t-test value could be by chance alone. If the t-test value is greater than the t-test table value, the observed difference is defined not have happened by chance.

The p-value tells the probability that the results from the comparison occurred by chance. The p-value ranges from 0% to 100% and a p-value below 5% is seen as significant. A low p-value of 5% also written as 0.05 indicates that there is a 5% probability that the results gained happened by chance. A p-value of 0.05 is generally used in the test. (Boddy & Smith, 2009) (Tiemann, 2012)

This study used Microsoft Excel 2017 for carrying out the t-tests. To study the comparisons of several NPEs, a two-tail t-test assuming unequal variances was applied. The p-value 0.05 was used. The results are presented in Appendix B.

6. Case studies

During the interviews, two cases connected to the presence of NPEs in the cycle were observed. The first case was concurrent with the sampling for this project, which means that the NPE problem can be seen in the sampling results as well. The second case was not during the sampling period, which means that the problems cannot be linked with the results gained from the sampling. These two cases are good examples on what kind of real problems the NPEs can cause in the recovery cycle.

6.1. Kaolin contamination

In the fall of 2018, Mill C had experienced an abnormal amount of scaling and plugging in their evaporators. This was a direct cause of the risen concentration of Al and Si in their weak black liquor due to a contamination caused by external factors. The reason was a spill of kaolin that leaked into their wastewater treatment unit. Kaolin is commonly used as a surface chemical for cardboards. Al and Si precipitated in the wastewater treatment center alongside with the dead microbes to the bottom of their tanks creating sludge, which resulted in kaolin being able to enter the recovery cycle via the recycling of biosludge to the evaporator plant in the pulp mill.

Aluminosilicates, such as kaolinite $Al_2Si_2O_5(OH)_4$ and ghelinite $2CaO * Al_2O_3 * SiO_2$, are known to cause scales in black liquor evaporators. They cause many operational problems in the recovery cycle, such as plugging and unnecessary dead load (Taylor & Bossons, 2006). Aluminosilicates are difficult to remove, because the scales are very hard and glossy in their structure and tend to stick well on the tube walls. Aluminosilicates have a low conductivity and a high surface area, meaning that a thin layer is enough to decrease the evaporator's efficiency a great deal. (Ulmgren, 1987)

Literature studies claim that if Al concentration surpasses 0.02% of the black liquor's dryness, it starts to cause problems in mills (Pöllänen, 1994). Another study showed that if the weak black liquor's Al concentration exceeds 40 mg/l and Si concentration 60 mg/l, the elements start to precipitate. (Pöllänen, 1994; Ulmgren, 1987)

6.2. Ring formation

One of the mills had experienced ring formation in its lime kiln. A sample of both the good and bad lime was collected during the mill visit. Figure 5 below shows the difference in appearance of good and bad lime. The lime samples were taken after the lime kiln.

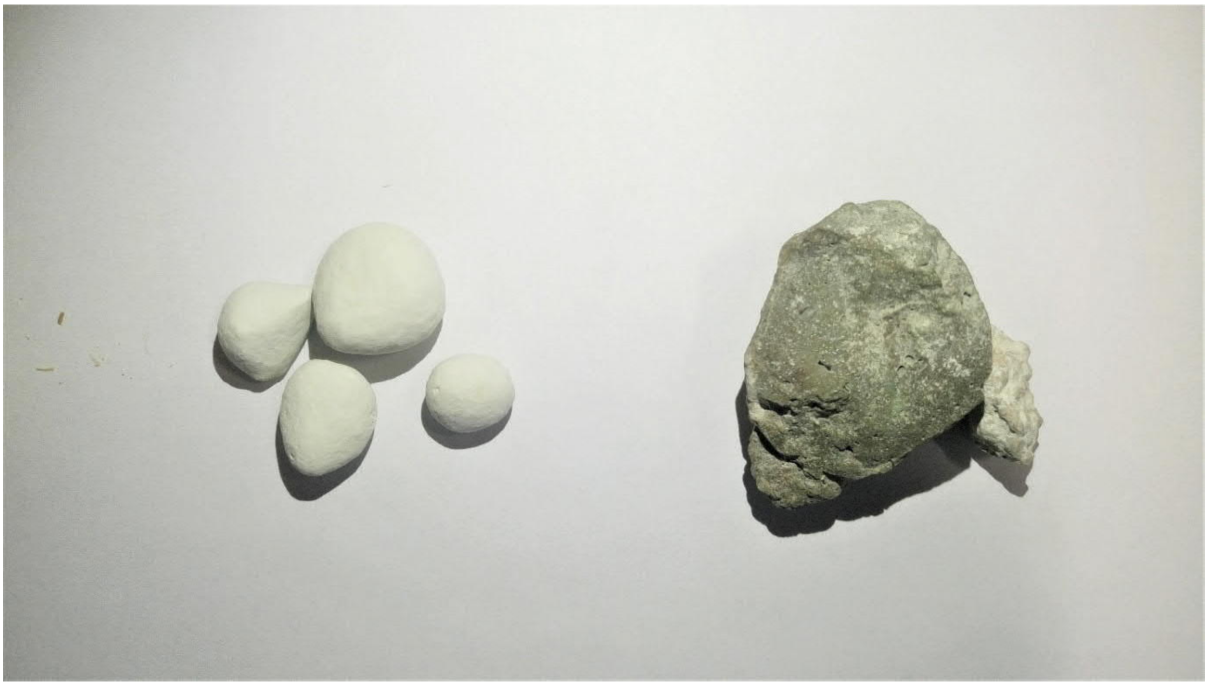

Figure 5 Samples of the good (left) and bad (right) lime.

The samples, when analyzed with a scanning electron microscope (SEM), showed an increase of Al, Si, P and Fe, in the bad lime sample compared to the good lime sample. This indicates that for some reason, some NPEs had started to accumulate in the lime kiln. The rise of NPE levels can also be a side effect of some other problems and imbalances in the lime kiln.

Ring formation usually appears when lime particles adhere to the kiln wall, become hard and resistant after a while, and do not fall off the wall. The adherence and stickiness of the lime particles to the kiln wall is partially because of the melting of $\mathrm{Na_2CO_3}$ and $\mathrm{Na_2SO_4}$ in the lime mud. The ring usually becomes harder due to recarbonation of the deposit. Recarbonation occurs when the ring temperature is below the lime mud calcination temperature. During recarbonation, a chemical reaction between lime CaO and $\mathrm{CO_2}$, $\mathrm{SO_2}$, $\mathrm{O_2}$ in the flue gas forms $\mathrm{CaCO_3}$ and $\mathrm{CaSO_4}$. $\mathrm{CaCO_3}$ and $\mathrm{CaSO_4}$ form a layer over the lime particles, joining them together to larger and harder deposits on the kiln wall. (Tran & Mao, 1993)

Table 17 and Figure 6 present SEM results for good and bad lime.

Table 17 The SEM results of the good and bad lime

Component		Good lime	Bad lime
C	wt - %	3.57	4.38
O	wt - %	42.39	39.99
Na	wt - %	1.42	0.98
Mg	wt - %	1.08	1.46
Al	wt - %	0.13	7.33
Si	wt - %	0.16	2.88
P	wt - %	0	0.66
Ca	wt - %	51.25	41.83
Fe	wt - %	0	0.5

As seen in Table 17 and Figure 6, Al and Si have accumulated in the bad lime, compared to the normal lime. The source of Al and Si is however not known. Aluminosilicate-complexes form hard and sticky deposits that are extremely difficult to remove and could be one reason for the hard stone-like lime. The ring formation did not occur during sampling period of this project and cannot be linked to the sample results gained in this study.

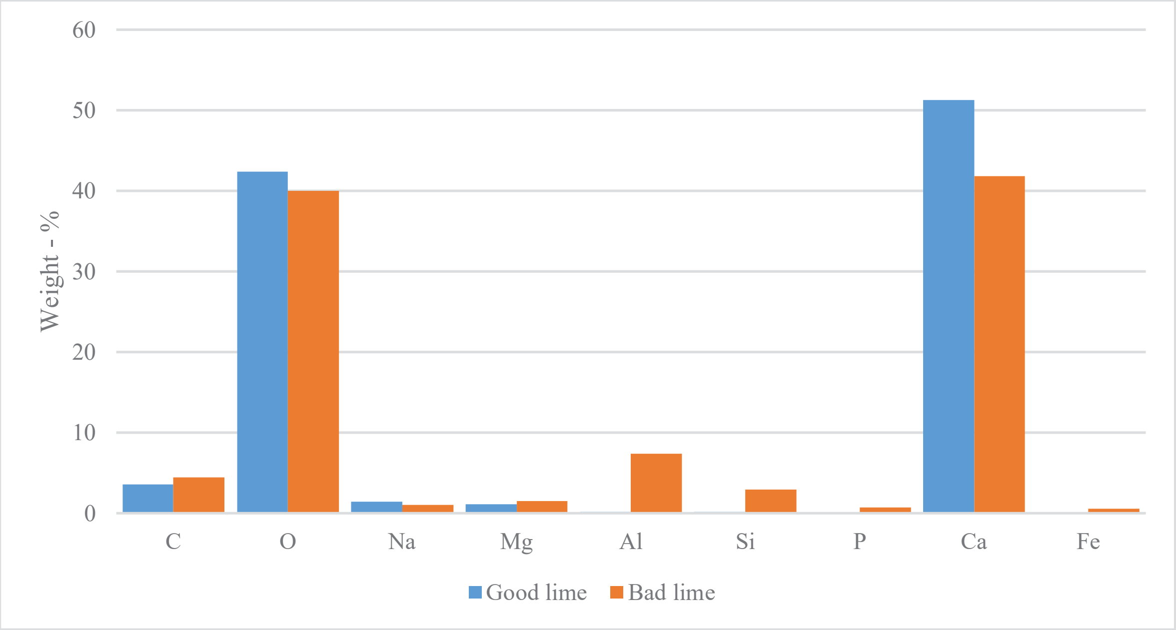

Figure 6 SEM results of good and bad lime.

7. Results and discussions

The results shown in the next section are all based on the data presented in Appendix A. All results are presented as either mg/kg dry solids or mg/l. All sample points are shown individually in the first section of this chapter. One of the goals is to examine if the elements behave similarly as literature references.

The data gained from this study is in the second half of this section compared to older similar data from Finland, North America and South America. One main objective is also to see if the NPE values correlate to the mill equipment, raw material, and geographic location of the mill.

7.1.NPE results for the sampling points

Seven sampling points were examined in this study (weak black liquor, as-fired black liquor, ESP ash, clarified green liquor, green liquor dregs, white liquor and lime mud) at six Finnish Kraft pulp mills. This section shows all sample points individually and present the mean values each mill had in the sample points. All results are based on the raw data presented in Appendix A.

7.1.1. Weak black liquor

Figure 7 presents the results of weak black liquor. The weak black liquor sample at Mill A does not contain any tall soap, whereas all the other Mill samples contain. Al, Si and Ca levels are much lower for Mill A compared to the other mills and could be because of the unintended removal of tall soap but also be due to other circumstances.

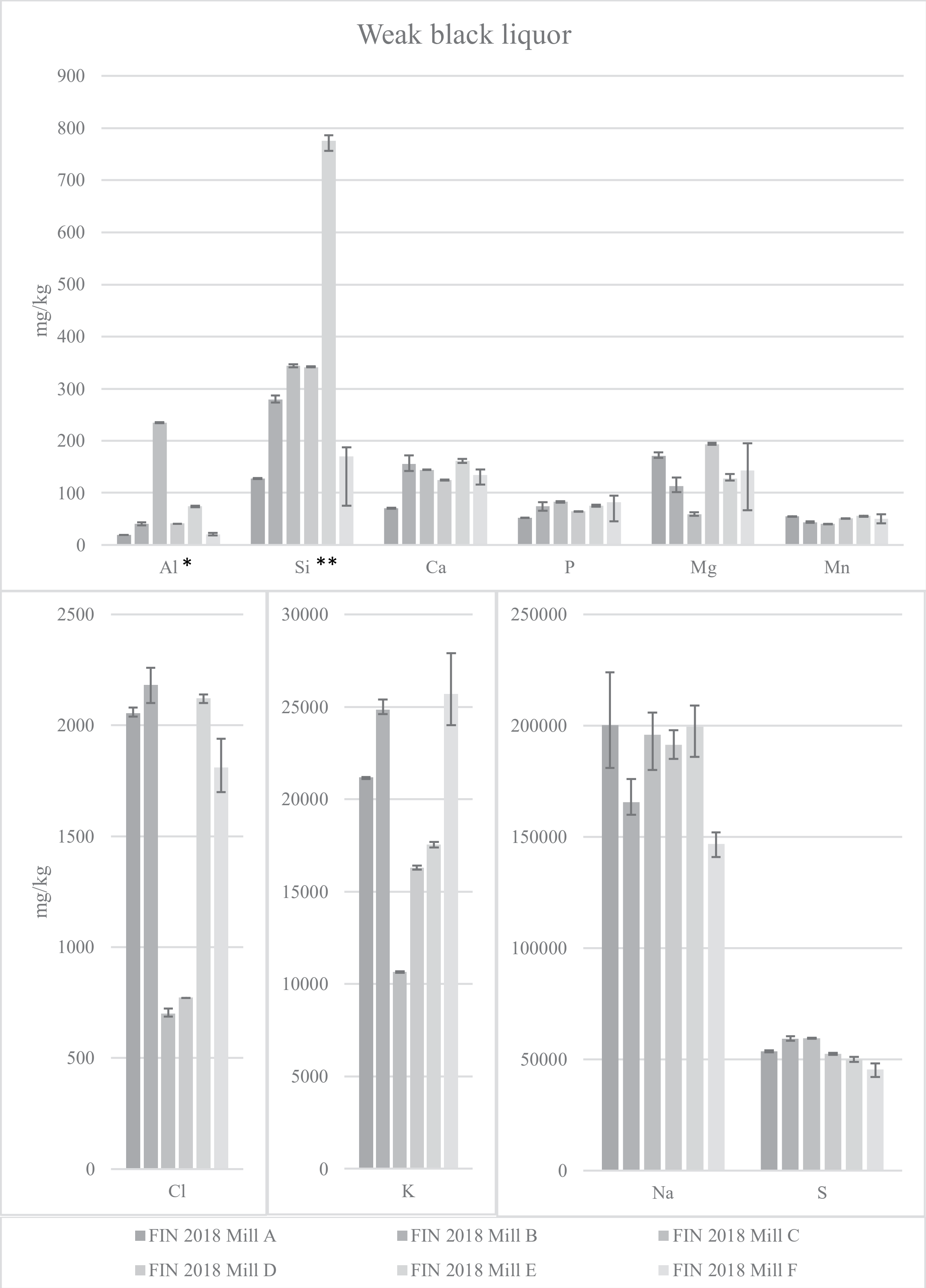

*Figure 7 Weak black liquor results. The error bars show the minimum and maximum level. The column represents the average of the results. Mill A has not tall soap in its sample * Mill C has abnormal amount of Al in sample. ** Abnormally high Si value for Mill E.*

Mill C has an abnormal Al peak (235 mg/kg) compared to the other mills. This is due to the kaolin contamination case. Mill C does not seem to have high Cl or K levels, 699 mg/kg and 10 633 mg/kg, respectively. Its Mg level is low as well. Mill D has low Cl value too, compared with the others. Mill D has a very low chlorine content in all sample points, throughout the cycle.

Mill E also shows high Si values, but the reason for this is unknown. Especially when the Si value in as-fired black liquor shows no indication of high Si levels anymore. The high Si value can be due to an error in sampling or analyzing or due to other factors.

7.1.2. As-fired black liquor

Figure 8 presents the results of as-fired black liquor samples. The as-fired black liquor sample contains recycled ash. The kaolin case in Mill C is still noticeable as its Al and Si values are exceptionally high, 355 mg/kg and 550 mg/kg, respectively. Since kaolin entered the recovery cycle via biosludge in the evaporator step, it is natural that the highest value of kaolin is found in the as-fired black liquor sample.

Biosludge and other side streams are usually added in the evaporator step in the recovery cycle to be burnt alongside with the liquor in the recovery boiler. It is in many ways economically feasible to burn biosludge and other streams, because dumping them in landfills is the more expensive alternative.

Mill E has the highest Ca concentration 403 mg/kg and Cl level 3 250 mg/kg. Its Ca level increased from 162 mg/kg to 403 mg/kg and Cl from 2 120 mg/kg to 3 250 mg/kg.

Mill A seems to have lower Al, Si and Ca levels compared to other mills. Mill A's P levels are quite low as well. Mill D and Mill C have high Mg levels. Both mills use only softwood as raw material, and this could be one reason for the high Mg concentration.

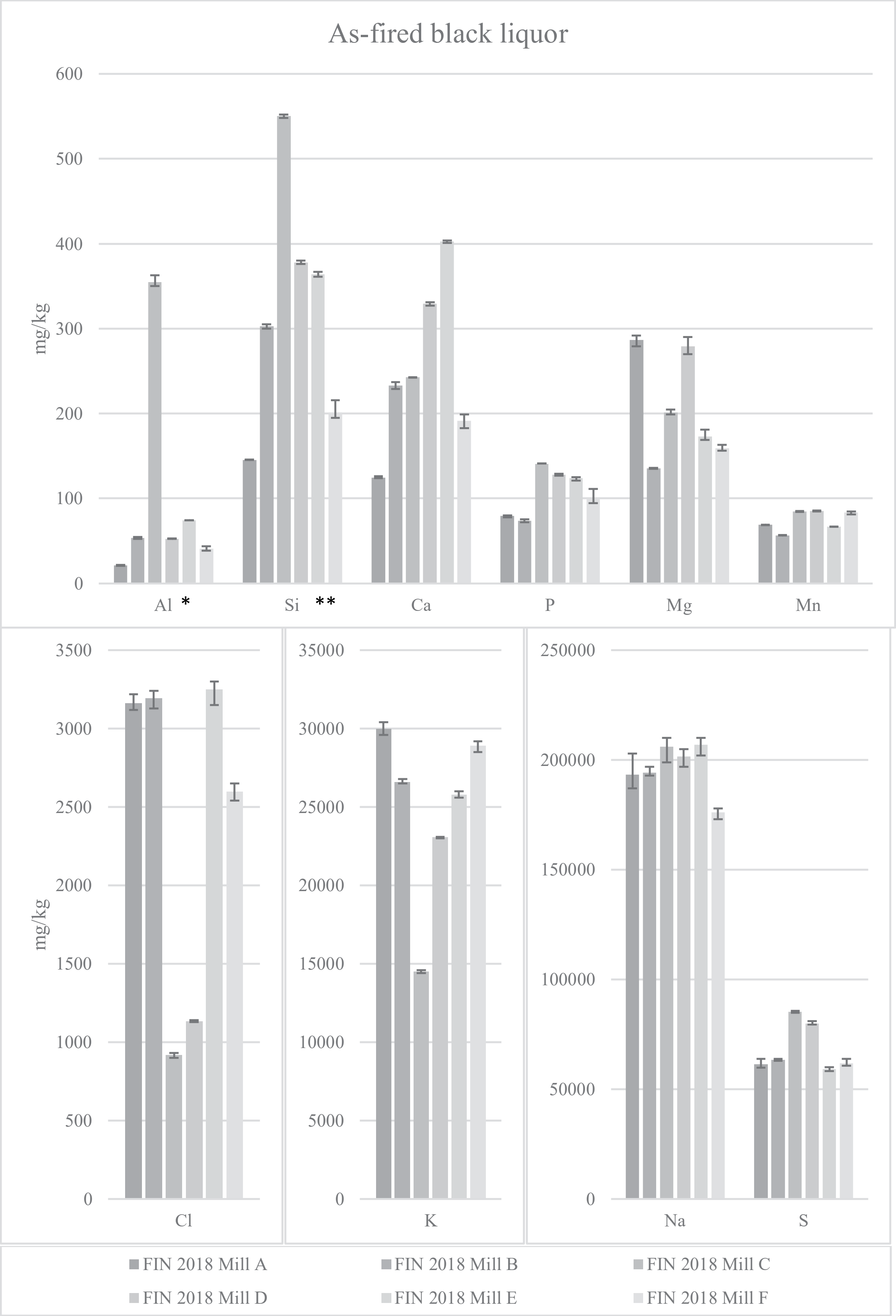

*Figure 8 As-fired black liquor results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill C has abnormal amount of Al in sample. **Mill C has abnormal amount of Si in sample.*

7.1.3. ESP ash

Figure 9 shows the results gained from ESP ash samples from the six Finnish pulp mills. Mill C and Mill D have the highest Si (316 mg/kg and 269 mg/kg), Ca (154 mg/kg and 255 mg/kg), Mg (113 mg/kg and 144 mg/kg) and Mn (77 mg/kg and 92 mg/kg) levels, compared with the rest of the mills. Quite interestingly, Mill C and Mill D’s Cl values are the lowest at the same time (3 300 mg/kg and 4 070 mg/kg). The high Ca level for Mill D can also be seen in the as-fired black liquor sample, where it is 330 mg/kg. The high Ca value is also spotted in ESP ash sample for Mill D.

By purging ESP ash, the mills usually regulate the sulfidity and levels of Cl and K in the recovery cycle. If, however the purging opportunity is removed, K and Cl have to find new purging routes out.

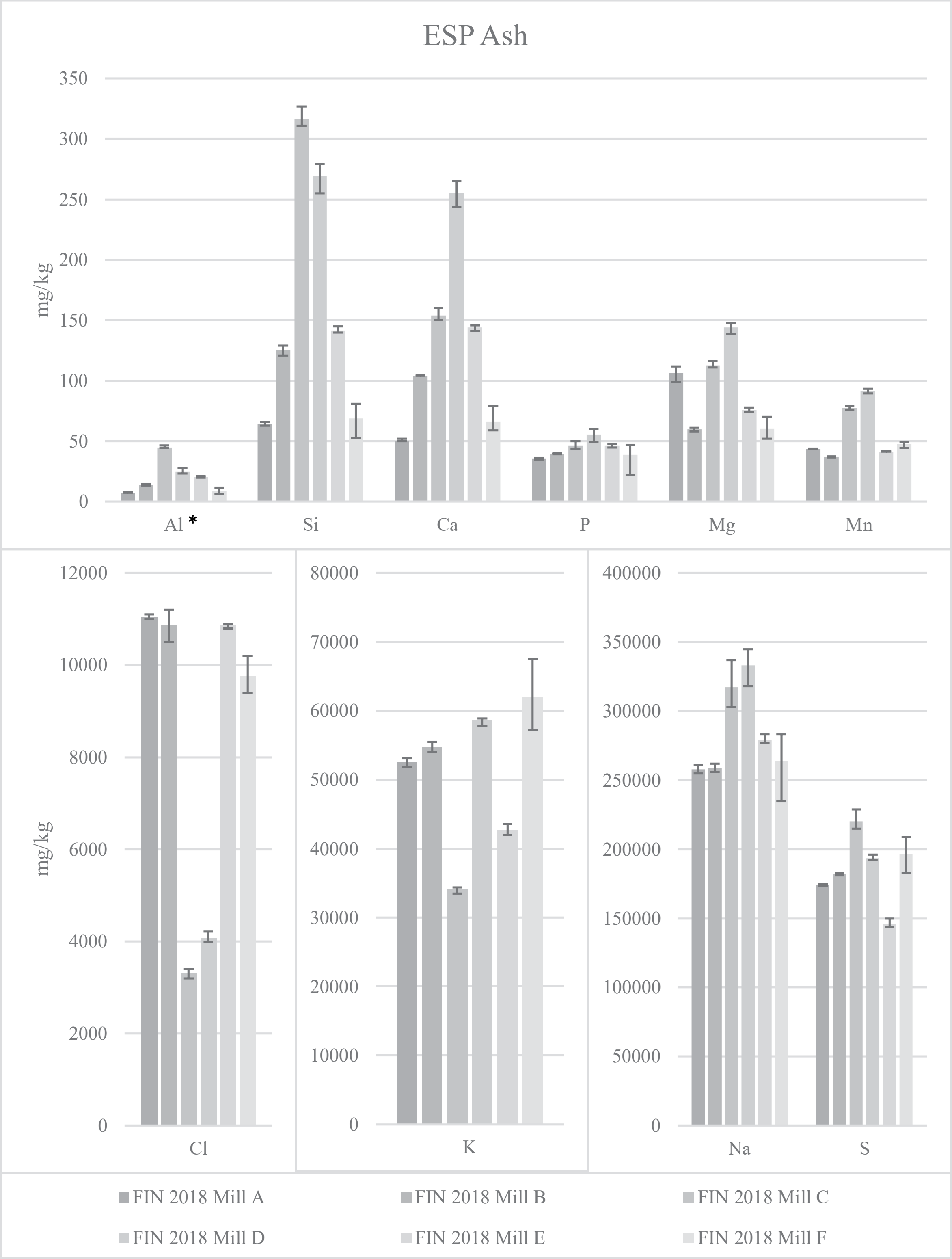

*Figure 9 ESP ash results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill C has abnormal amount of Al in sample.*

The enrichment factor for the ESP ash relative to as-fired black liquor results are shown in Figure 10.

The enrichment factor for K is between 1.2 – 1.5. One of the mills had two recovery boilers. A mean value for the enrichment factors was therefore calculated for the mill. The enrichment factor for Cl is between 2.1 and 2.6.

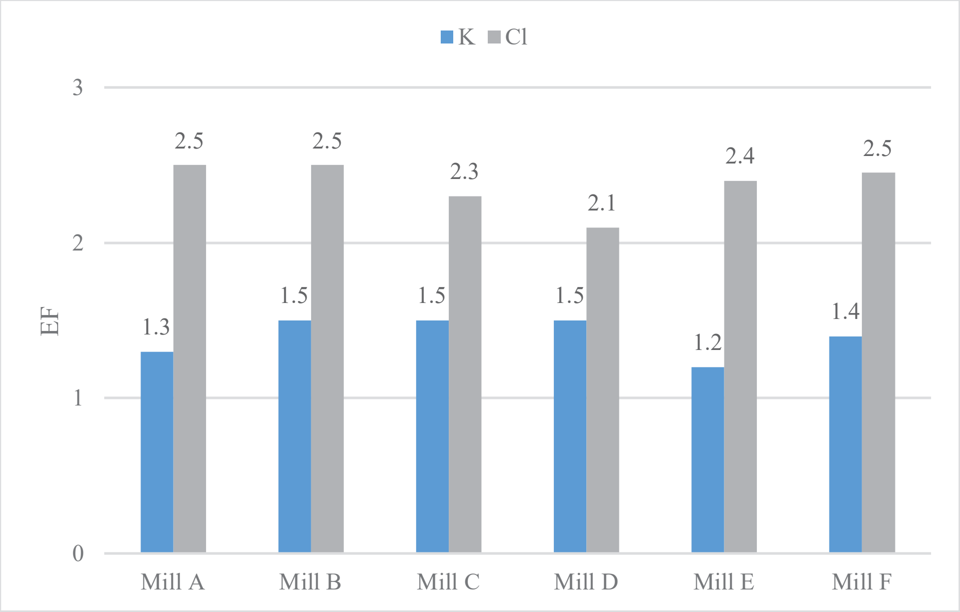

Figure 10 Enrichment factor for K and Cl in ESP ash results.

Several literature studies have been conducted on the enrichment factor of Cl and K in the ESP ash. Backman et.al 1996 researched the flue gas and dust chemistry in recovery boilers and reported enrichment factors for Cl between 1.9 to 2.5 and K between 1.5 and 2.0 (Backman, et al., 1996). Further studies have as well concluded that the Cl enrichment factor typically ranges from 1.5 to 3 and K from 1.5 to 3 as well (Hupa, 1997).

Salmenoja also conducted a study, where he calculated the enrichment factors of Cl and K for six Finnish pulp mills (Salmenoja, et al., 2004). The results are presented in Figure 11.

Salmenoja's Cl results seem to be much higher than the values calculated for this project. The K levels, however, seem to agree with Salmenoja's results. A low Cl and K level suggest low fouling and corrosion propensities in the recovery boiler (Salmenoja, et al., 2004). Salmenoja described that due to the lack of parallel analyses the reason for such high Cl values could not be confirmed.

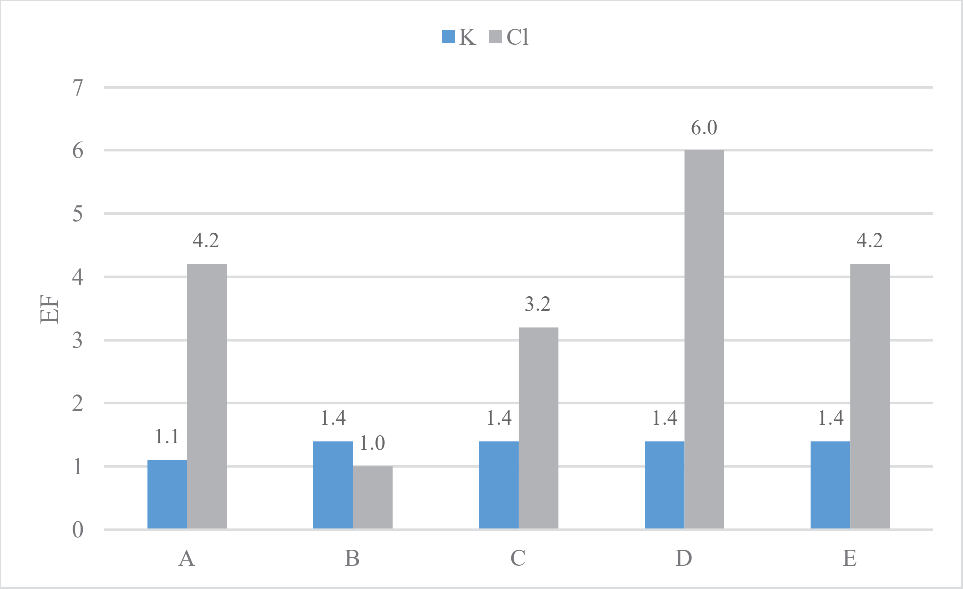

Figure 11 Enrichment factor for K and Cl from Salmenoja et al., 2004.

According to Salmenoja, a high enrichment factor implies that highly volatile compounds are formed during combustion. Cl is present as KCL or $NaCl$ in ESP ash. A recovery boiler with high temperature in the lower furnace and low SO_2 emissions favor the formation of KCL and $NaCl$. (Hupa, 1997) (Salmenoja, et al., 2004)

7.1.4. Clarified green liquor

Figure 12 presents the clarified green liquor results. The mills in this study use either crossflow filters or a clarifier to remove dregs from the liquor.

Mill C still has higher Si and Al values compared to the other mills, even after the clarification step. Si is not effectively removed with dregs and accumulates easily in the liquor and lime cycle. Al precipitates better than silica in green liquor dregs and is more effectively removed. Ca, Mg and Mn seem to have decreased much from the as-fired black liquor and ESP ash values for all six mills as expected.

Mill C and Mill D continue to have very low Cl concentrations in green liquor as well. Mill C has low K too. Mill F has the highest Mn, Mg and Ca levels in clarified green liquor. Mill F uses a clarifier to remove dregs, which could be one of the reasons it has higher NPE levels in green liquor.

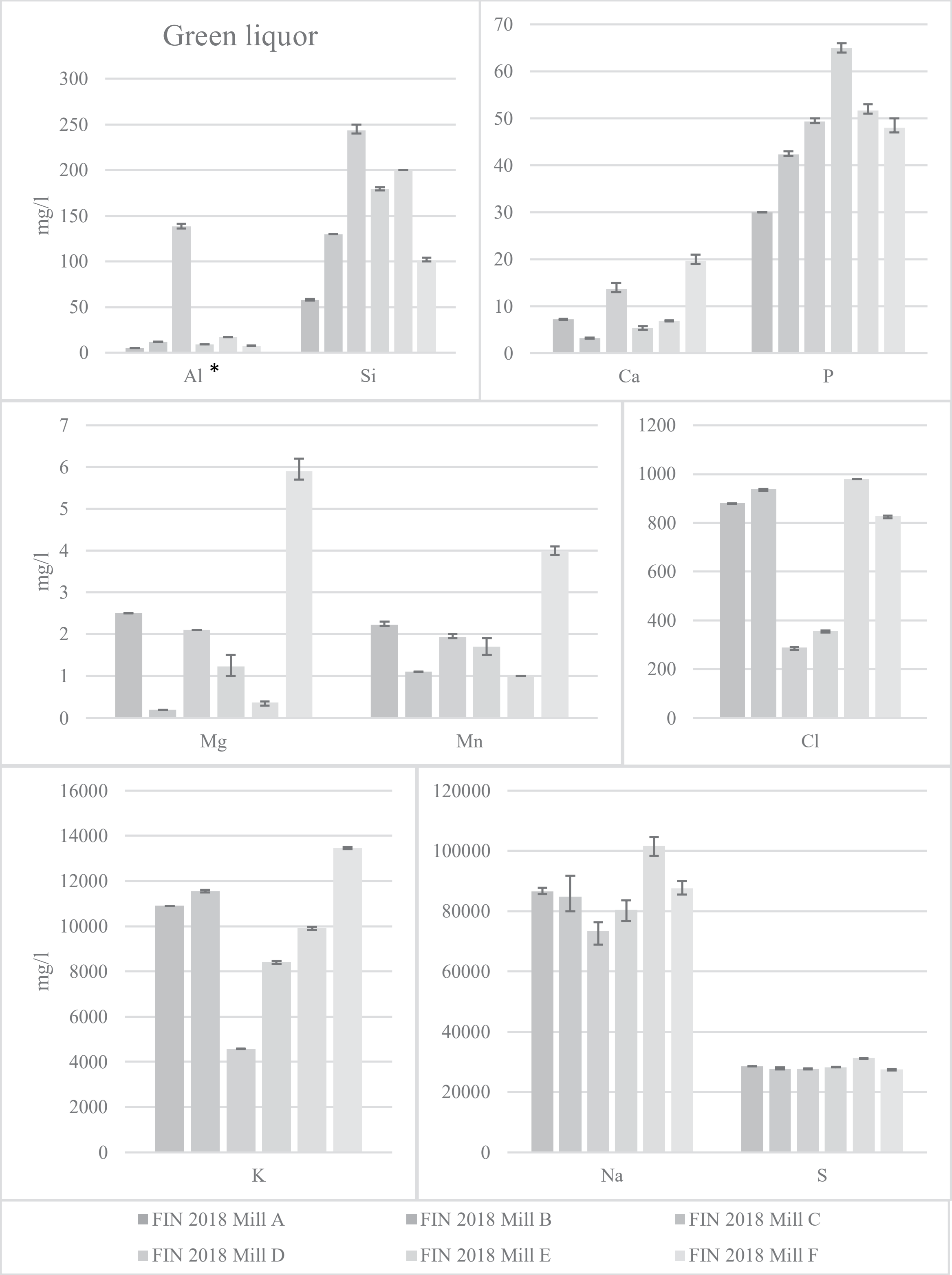

*Figure 12 Clarified green liquor results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill C has abnormal amount of Al in sample.*

7.1.5. White liquor

Figure 13 presents white liquor results from the six Finnish pulp mills. The high Al content in Mill C can still be spotted in white liquor as well, being 140 mg/kg, whereas the other mills have values no higher than 23.3 mg/kg for Al. Si level in white liquor ranges from 61 mg/kg (in Mill A) to 243 mg/kg (in Mill C). Si is more difficult to remove from the cycle and accumulates therefore in the liquor. Mill C has low P concentration in white liquor. This difference could not be spotted in green liquor nor in the other sampling points. Mill A and Mill F have the highest P concentrations around 22 mg/kg.

K and Cl levels do not seem to differ a lot from green liquor results, which is expected since those NPEs tend to be soluble in alkali and not easily removed.

Mn level of Mill D has increased going from green liquor to white liquor. This could be due to NPEs entering with makeup lime or the NPE's entering the system with lime kiln fuel. The P level has decreased in white liquor sample compared to green liquor sample. P prefers lime mud and accumulates in lime mud over white liquor.

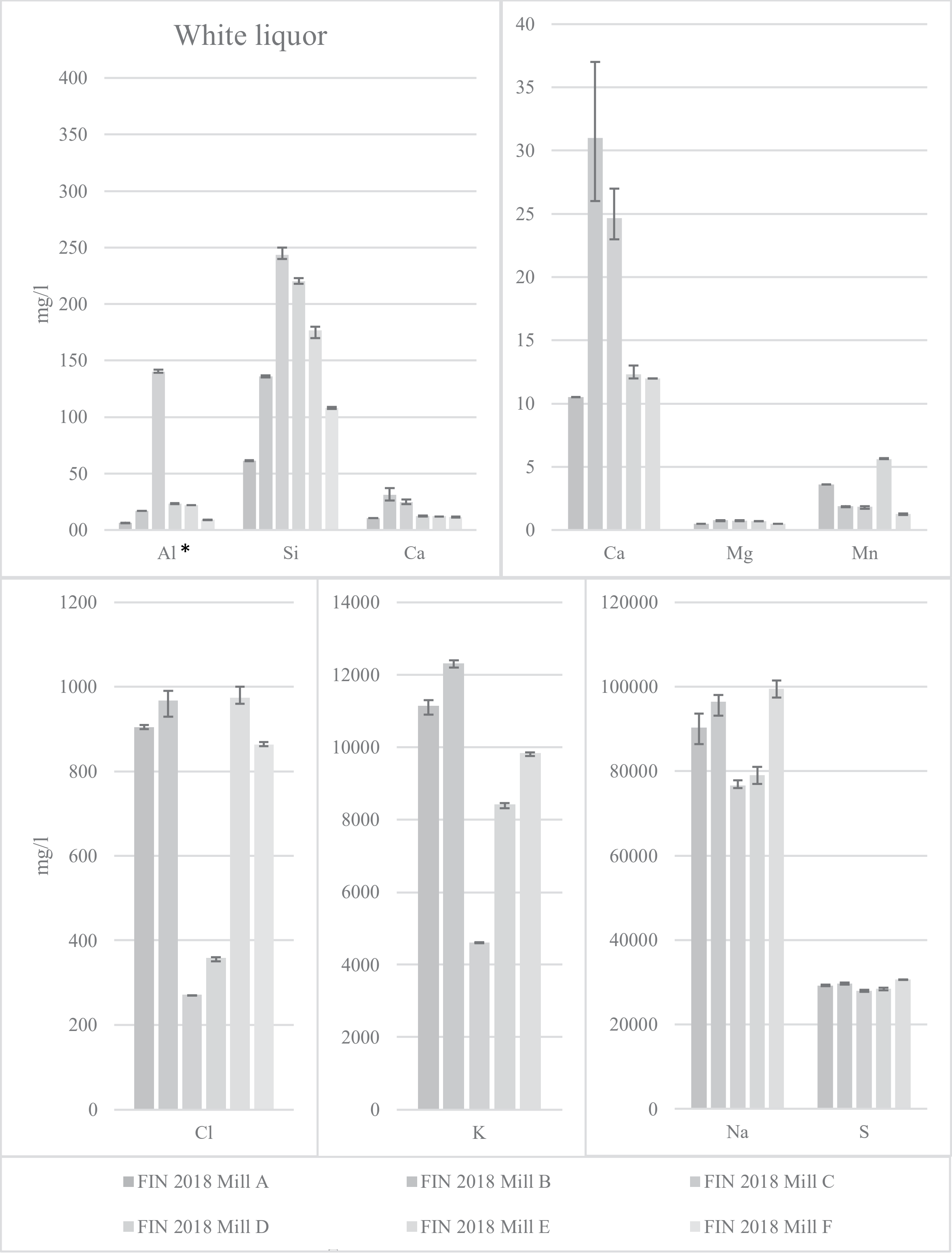

*Figure 13 White liquor results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill C has abnormal amount of Al in sample.*

7.1.6. Lime mud

Figure 14 shows lime mud results from the six Finnish pulp mills. P, Mg, Al and Si accumulate in the lime mud as seen in Figure 14. Mill A has a very low Si concentration compared to others. It also has a lower Ca concentration. Mill E has exceptionally low P concentration. Mill E's P concentration is 2 160 mg/kg, which is about one quarter of the P level in the rest of the mills. The reason could be a detection error or linked to other side streams or lime kiln fuel.

Mg and Mn levels seem to mirror each other. This could be a coincidence. Other factors that could possibly contribute to this is if both elements originate from the same source. The lime mud results also show that Mill A, Mill D and Mill F all have slightly higher Mg and Mn levels as compared to Mill B, Mill C and Mill E. This could be linked to the raw material use but could also be connected to other factors.

Mill A has a low Si concentration in lime mud, in line with low Si in other Mill A sampling points.

As expected, the concentration levels of K and Cl are very low in lime mud for all mills. 436 mg/kg is the highest K value and 12.5 mg/kg for Cl in lime mud.

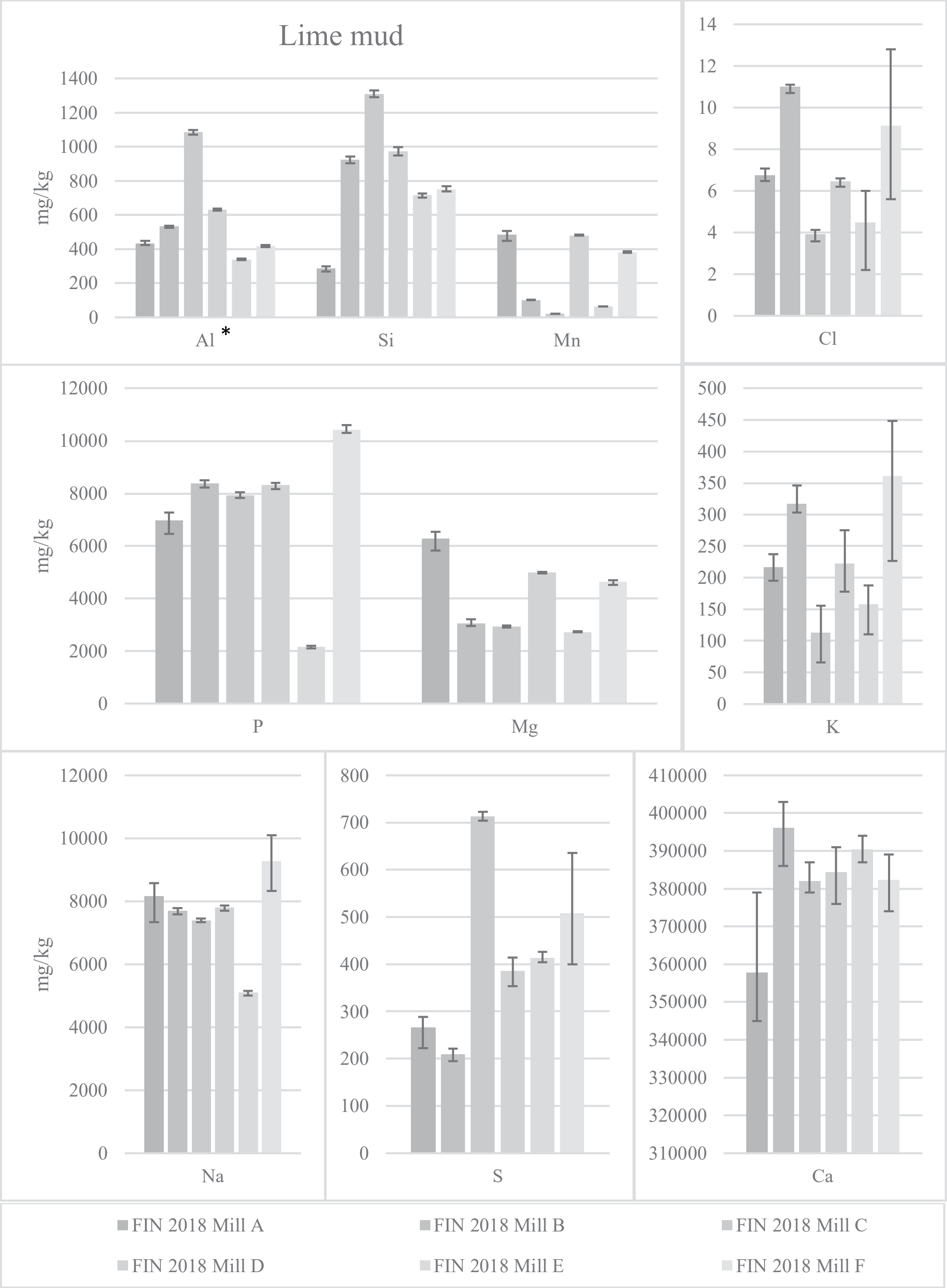

*Figure 14 Lime mud results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill C has abnormal amount of Al in sample.*

7.1.7. Green liquor dregs

Figure 15 shows green liquor dregs results from the six Finnish pulp mills. When looking at the results, it is evident that the NPE composition in green liquor dregs varies a lot.

Mill A and Mill F have very low Al and Si concentrations in the dregs sample. Mill A and Mill F also have the lowest Al and Si values in white liquor, however the mills difference in white liquor compared to the rest of the mills was not as large as in the dregs result. The concentrations of Al and Si have been low for Mill A in all samples however, which is also reflected in the dregs.

Mill A has the highest K and Cl concentrations within these six mills and Mill F has very low Mg and Mn levels in its dregs sample. Mill D has exceptionally high Si concentration in its dregs sample. Its Si value was 27 200 mg/kg and the second highest were Mill C with 8 360 mg/kg of Si. Mill D has in other sampling points high Si values but is not ranked as the highest for Si in any other sample point. The higher Si value in Mill D could be due to lime kiln fuel choice, other added side streams or makeup lime or makeup chemical quality.

Mill B has lime mud in its green liquor dregs sample which affects its dregs results. Ca is 285 700 mg/kg and P is 3 650 mg/kg, which are higher that the corresponding values in the other mills.

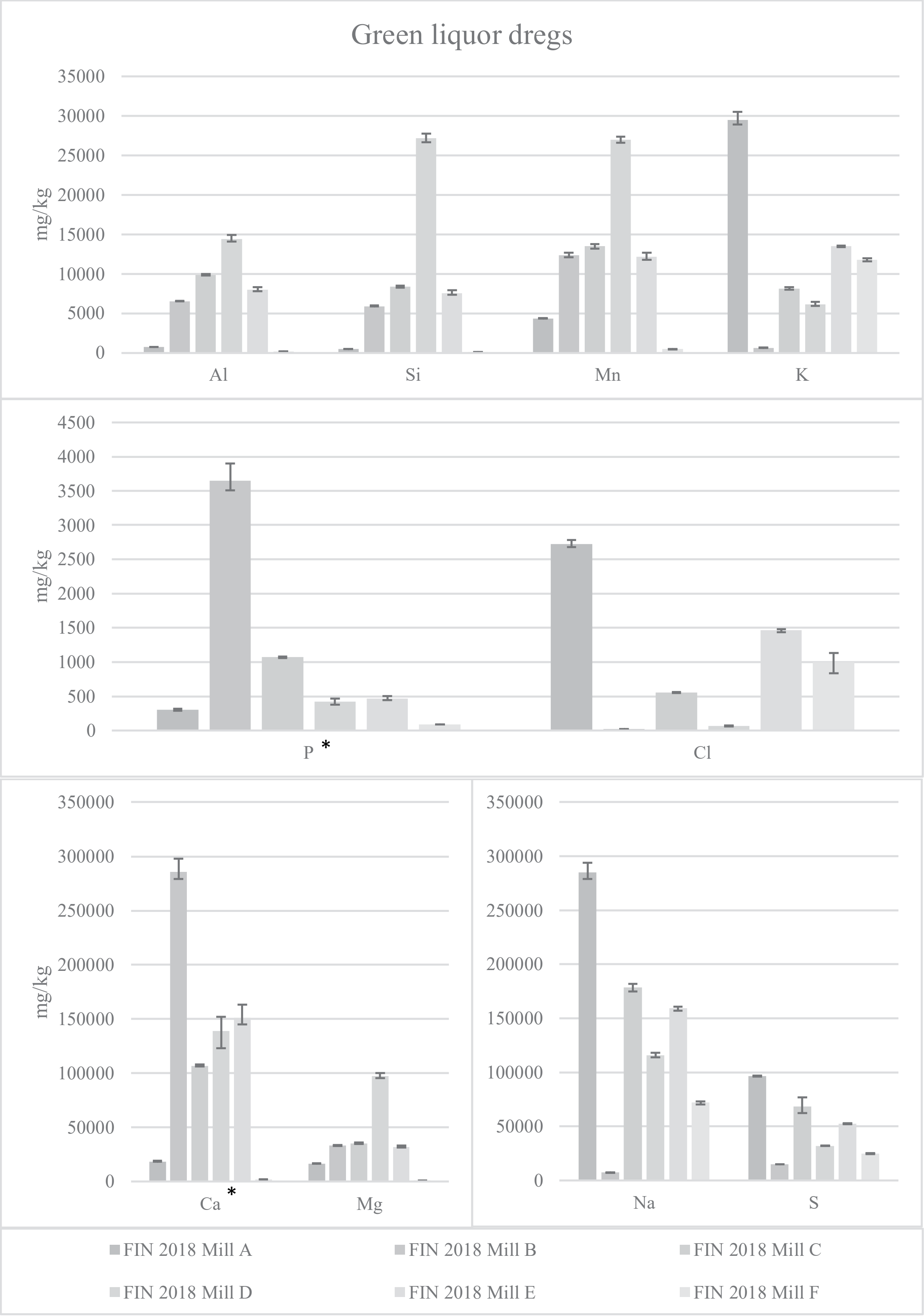

*Figure 15 Green liquor dregs results. The error bars show the minimum and maximum level. The column represents the average of the results. * Mill B has lime mud in its dregs sample.*

7.2. Element behavior of the NPE results

The NPEs can roughly be divided into two groups. The first group contains elements that are more insoluble in the liquor and lime cycle and can be purged with the green liquor dregs from the system. It includes elements like Mg, Mn and Ca. If, however, Mg and Mn pass the green liquor clarification step or enter the system after the clarification, they can also start to accumulate in the lime cycle.

The other group consists of elements that tend to accumulate in the liquor and lime cycle. These elements include Al, Si and P. They are very soluble in alkali solutions and, therefore, not easily purged with green liquor dregs. Cl and K are also part of the second group and tend to accumulate in the liquor cycle and especially in the ESP ash. Cl and K do not however accumulate in the lime cycle.

This section reviews all the elements individually and analyzes their behavioral patterns. If some mills have had several sampling points for one sample, an average of these values is used in this section figures. Mill mass balances provided by Professor Esa Vakkilainen were used to convert concentration data into pulp-production specific values (element/ADt pulp).

The labels used in the figures are abbreviations of weak black liquor (WBL), as-fired black liquor (ABL), green liquor (GL), white liquor (WL), lime mud (LM) and green liquor dregs (GL D). Green liquor and white liquor results are shown in mg/l and the others as mg/kg. In the figures presenting pulp-production specific data, all values are in g/ADt. The difference of the soluble and insoluble NPEs in alkali solutions are color-coded to blue (insoluble) and red (soluble) in alkali solutions.

7.2.1. Elements removed with green liquor dregs

Mg, Mn and Ca are NPEs that are effectively purged together with dregs removal and are shown in removal and are discussed in the section to follow. These elements have a blue color in the figures.

7.2.1.1. Magnesium

Figure 16 presents what concentration levels of Mg in weak black liquor (WBL), as-fired black liquor (ABL), green liquor (GL) and white liquor (WL) for the six Finnish pulp mills. Even though Mg is effectively removed from the green liquor, it will accumulate in the lime cycle if it has a chance to enter the lime cycle. Mg can enter the lime cycle with the green liquor or with makeup lime, process water and lime kiln fuel. Much of Mg is removed with the dregs when comparing this study’s results. Mg is the second most common NPE found in dregs, right after Ca. It ranges from 988 mg/kg to 97 400 mg/kg in the dregs sample conducted in this study. The Mg concentration level in lime mud is around 5 000 mg/kg.

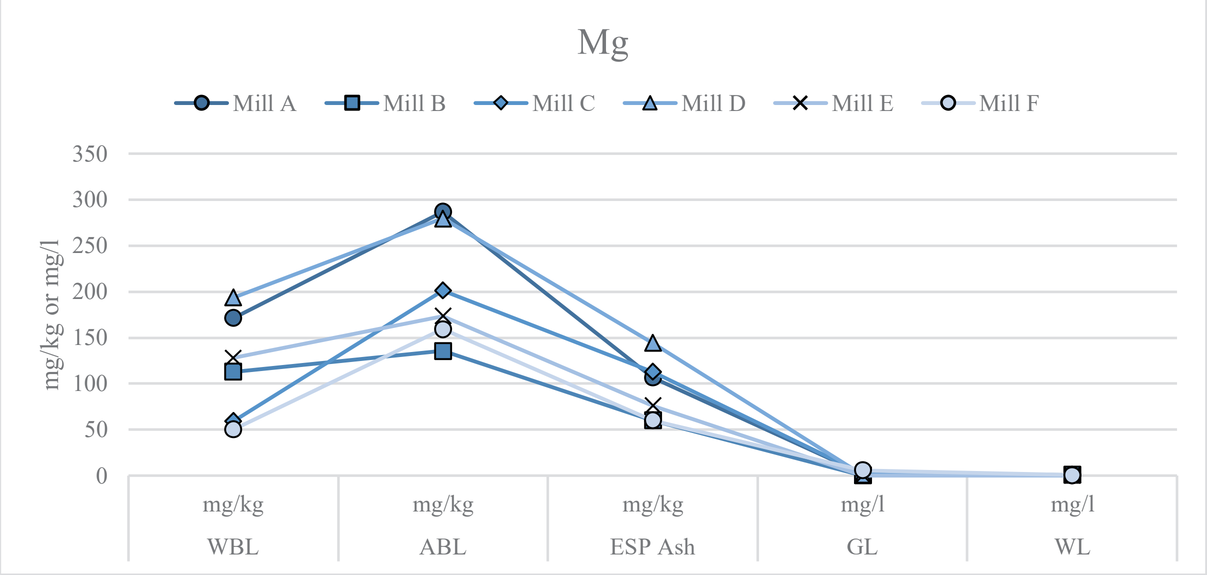

Figure 16 Mg results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

Figure 17 presents Mg per pulp production. Mg tends to accumulate in the lime mud. Mill D removes 974 g/ADt Mg with the dregs, the remaining mills are all under 500 g/ADt.

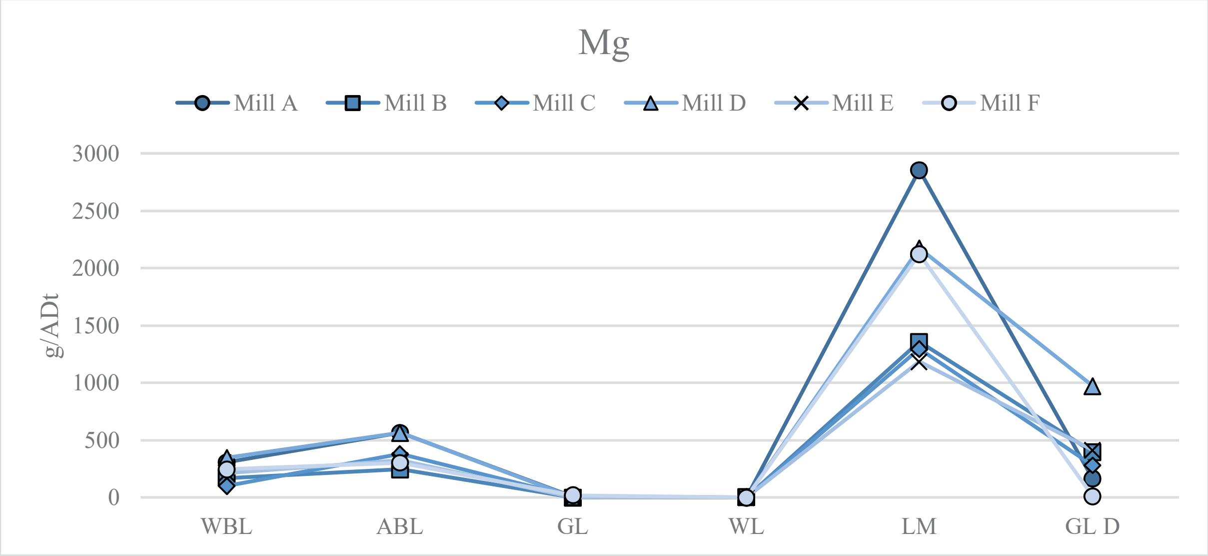

Figure 17 Mass balance for Mg in all the sample points.

7.2.1.2. Manganese

Figure 18 presents Mn concentration in weak black liquor (WBL), as-fired black liquor (ABL), green liquor (GL) and white liquor (WL), for the six Finnish pulp mills in this study. Mn is also removed relatively well with the dregs.

The Mn value found in dregs range from 460 mg/kg to nearly 27 000 mg/kg. Mn ranges in lime mud from 20 mg/kg to 500 mg/kg. The concentration level of Mn in lime mud is lower compared to Mg. The concentration level of Mn decreases remarkably after the green liquor dregs clarification step as it did with Mg. Mill C and Mill D have higher Mn values compared to the other mills in the ESP ash sample point.

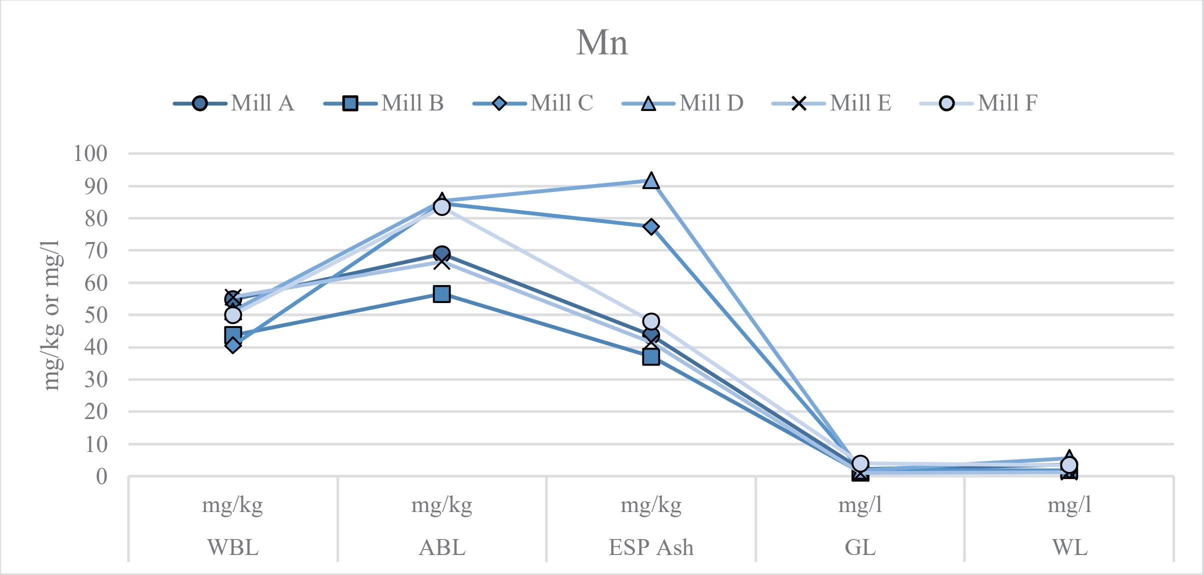

Figure 18 Mn results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

Figure 19 presents Mn per pulp production. A smaller amount of Mn accumulates in the lime mud compared to Mg. This is because Mg tends to accumulate easily in lime mud compared to Mn. Mill A, Mill D and Mill F clearly accumulate in lime mud compared to Mill B, Mill C and Mill E. The reason for this is however unknown.

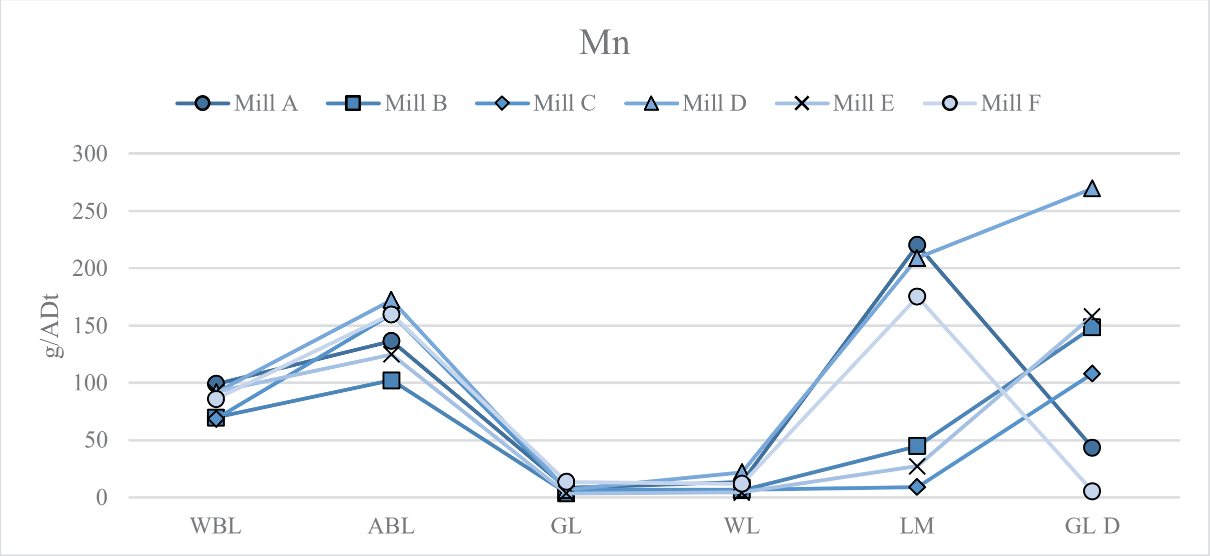

Figure 19 Mn per pulp production in all the sample points.

7.2.1.3. Calcium

Ca is seen as a NPE in all the other parts of the recovery cycle, excluding the lime cycle, because it tends to cause a lot of damage if it is found in other parts than the lime cycle. Figure 20 shows concentration of Ca in weak black liquor (WBL), as-fired black liquor (ABL), green liquor (GL) and white liquor (WL), for the six Finnish pulp mills.

The Ca concentration found in lime mud for the six pulp mills ranges from 360 000 mg/kg to 400 000 mg/kg. Ca is the main component in lime and the high Ca value found in the samples is expected. Ca is also effectively removed with dregs, ranging from 2 000 mg/kg to 150 000 mg/kg. Mill B has an abnormally high Ca concentration in its dregs sample, because its sample contained lime mud.

The Ca amount found in green and white liquor is as expected low, indicating that Ca is purged with green liquor dregs.

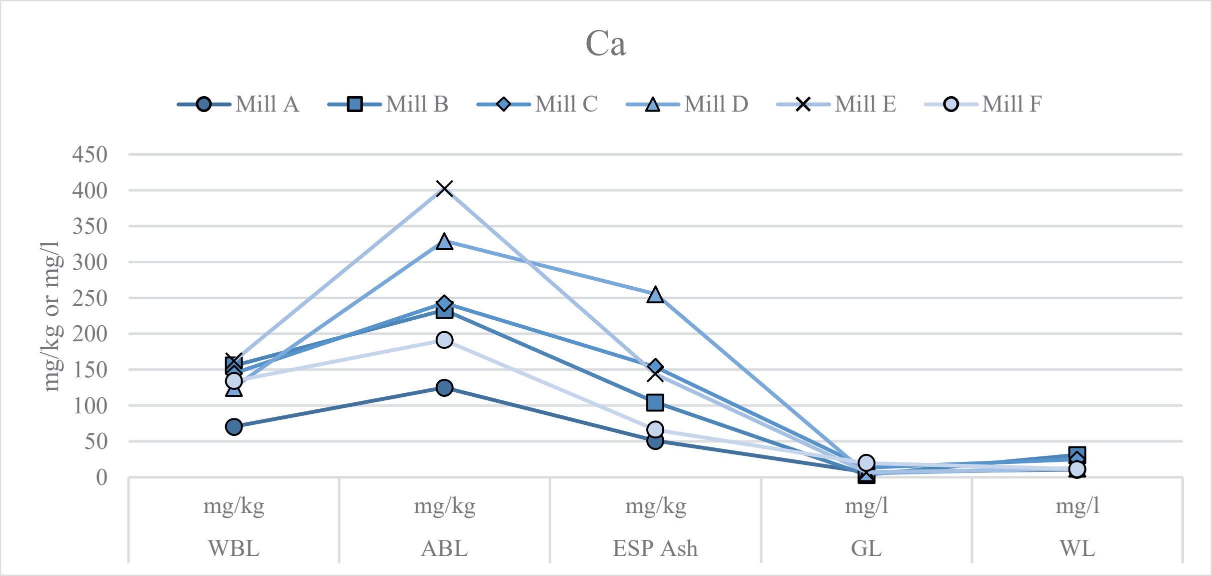

Figure 20 Ca results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

Figure 21 presents Ca per pulp production.

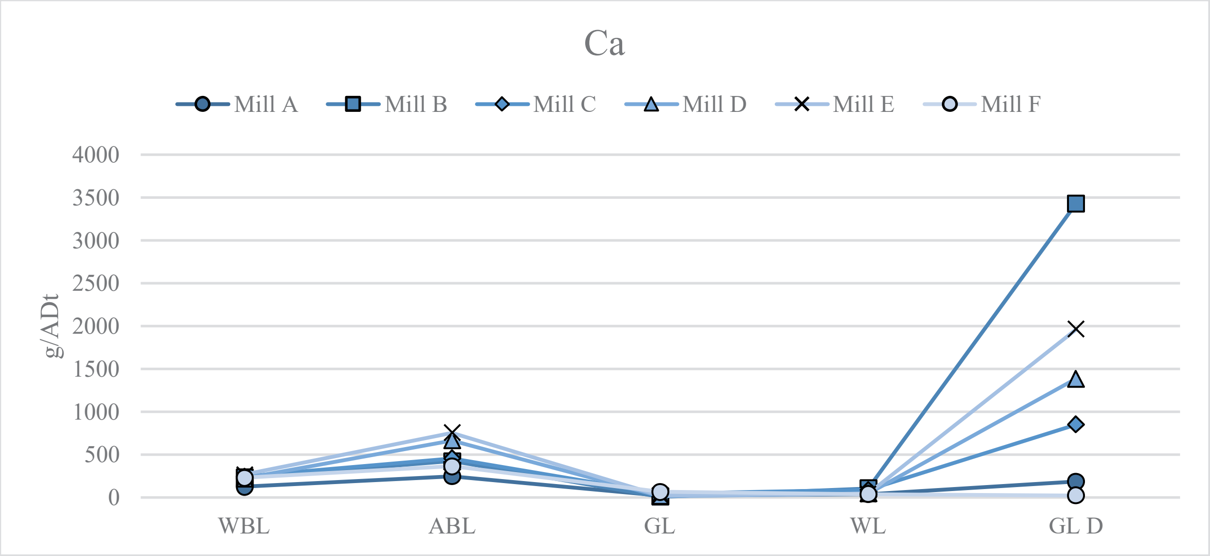

Figure 21 Ca per pulp production in all the sample points.

7.2.2. Elements accumulating in the liquor and lime cycle

The elements accumulating in the liquor and lime cycle can roughly be divided into two groups. Out of the elements analyzed for this project Cl and K are elements that tend to accumulate merely in the liquor cycle. Because of their volatile nature, they tend to accumulate in the ESP ash of the recovery boiler. Al, Si and P are NPEs that are soluble in alkali solutions and therefore found in the liquor cycle. They also accumulate in the lime cycle, especially P, which reacts with the lime mud creating unnecessary dead load in the lime cycle.

The labels used in the figures presented in the next chapters are abbreviations of weak black liquor (WBL), as-fired black liquor (ABL), green liquor (GL), white liquor (WL), lime mud (LM) and green liquor dregs (GL D). Green liquor and white liquor results are shown in mg/l and the others as mg/kg. In the mass balance figures, all the values are converted to show elements in g/ADt.

7.2.2.1. Chlorine

Cl accumulates in the ESP ash, as shown in Figure 22. The concentration level in white and green liquor does not change. On the other hand, 10 mg/kg was the highest concentration of Cl found in lime mud. The low Cl value is probably because Cl is soluble in alkali solutions. The reason why Mill C and Mill D had remarkably lower Cl and K concentrations in ESP ash. In order to identify the factors that contribute these lower Cl values it would have to be further studied.

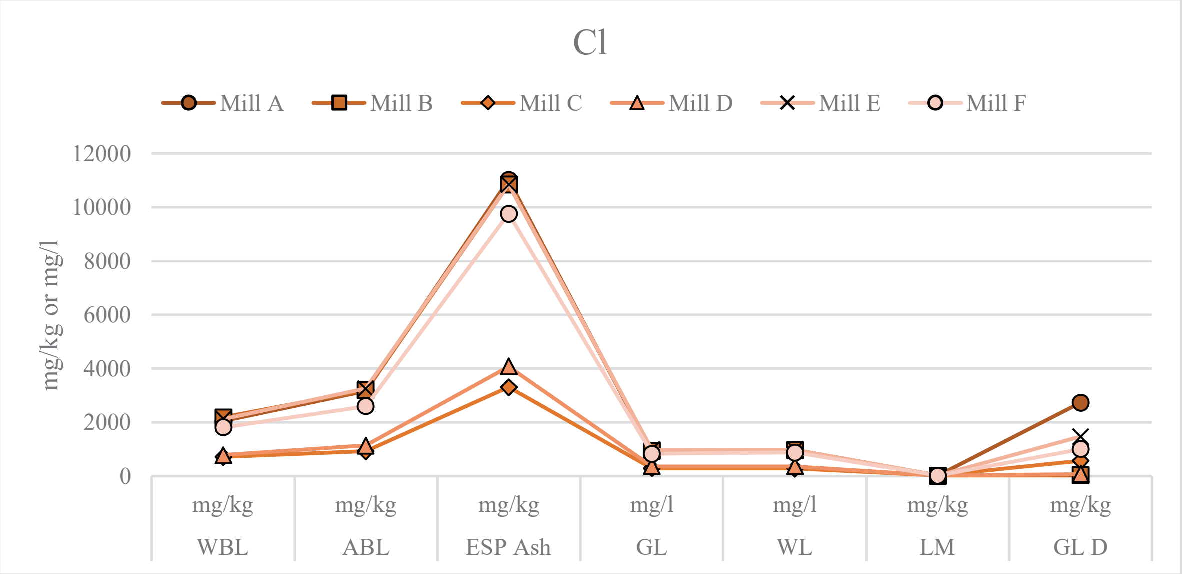

Figure 22 Cl results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor, white liquor, lime mud and green liquor dregs sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

Figure 23 presents Cl per pulp production. Here the accumulation rate of Cl in lime mud and green liquor dregs becomes even clearer. Cl too follows the same kind of pattern for all the mills, even though two of the mills have lower concentrations.

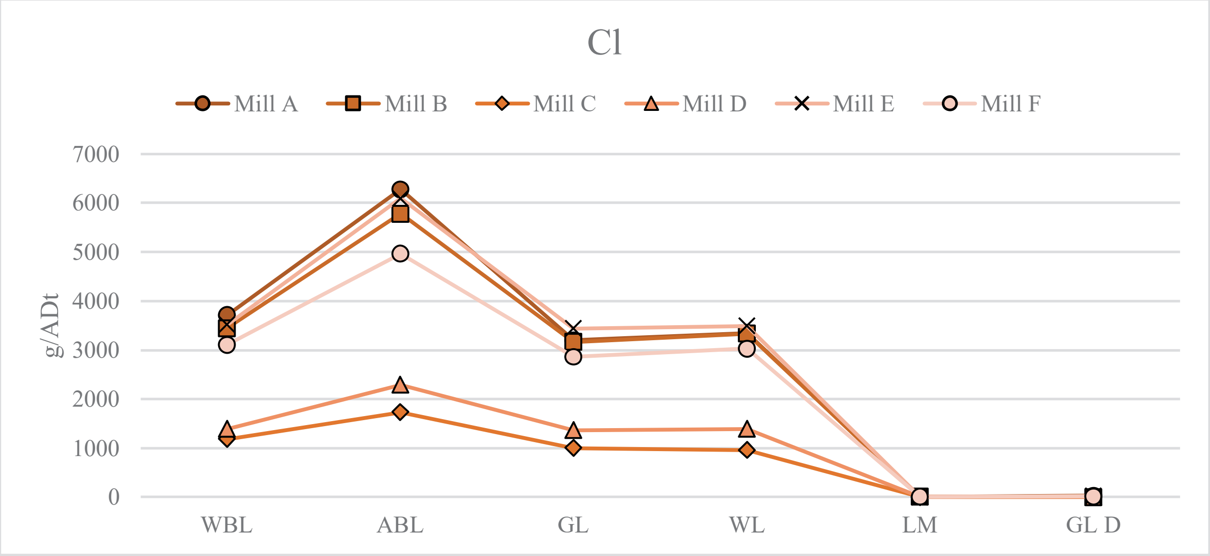

Figure 23 Cl per pulp production in all the sample points.

7.2.2.2. Potassium

Like Cl, also K accumulates in the ESP ash. K and Ca are the most common NPEs found in wood. Figure 24 presents concentration in the sample points.

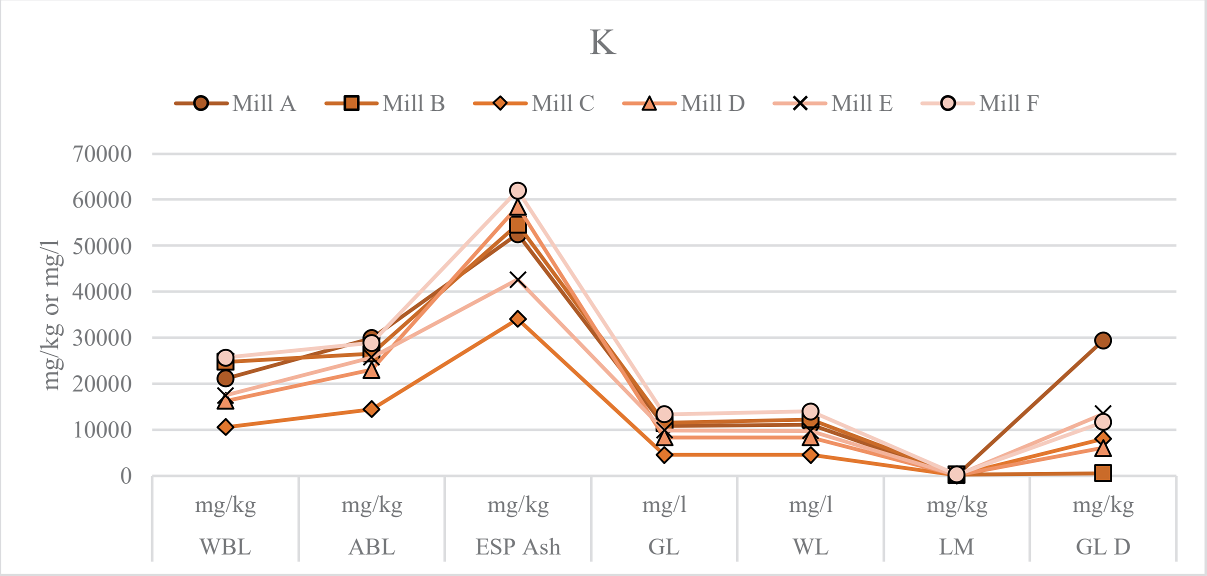

Figure 24 K results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor, white liquor, lime mud and green liquor dregs sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

K purges to some extent with the green liquor dregs as well. It is however very low in lime mud as expected, since it is alkali soluble. The concentration of K in white and green liquor is between 4 500 mg/kg and 14 000 mg/kg. As seen in Figure 24, there are practically no differences in K between green and white liquor. Figure 25 presents K per pulp production.

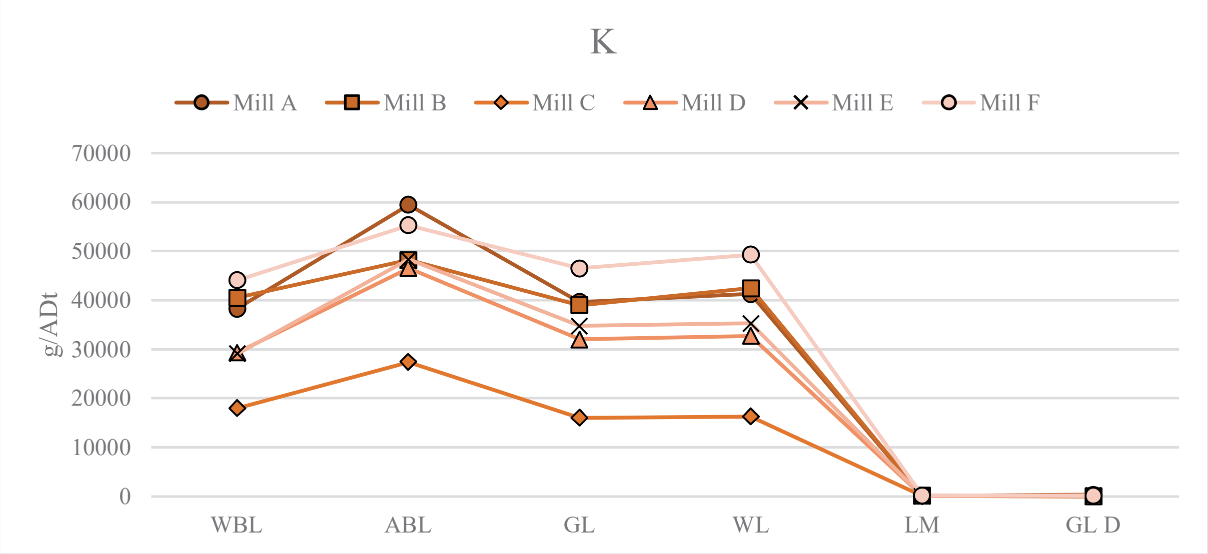

Figure 25 K per pulp production in all the sample points.

Figure 25 clearly shows how K accumulates in the liquor cycle. K values range from 16 300 g/ADt to 59 400 mg/kg in the sample points from weak black liquor to white liquor. K in lime mud ranges from 50 g/ADt to 165 g/ADt. In green liquor dregs the values range from just below 8 g/ADt to nearly 300 g/ADt.

7.2.2.3. Aluminum

Figure 26 presents all sample points for Al excluding green liquor dregs and lime mud. As stated in the literature, Al does accumulate in the lime cycle. Al can also be purged from the cycle with dregs. The concentration found in dregs ranges from 173 mg/kg up to 14 433 mg/kg. Mill C is not shown in Figure 26 because of its abnormally high Al caused by the kaolin contamination.

Al concentration found in lime mud ranges between 340 mg/kg to 630 mg/kg. Mill C’s abnormal value is around 1 010 mg/kg in lime mud.

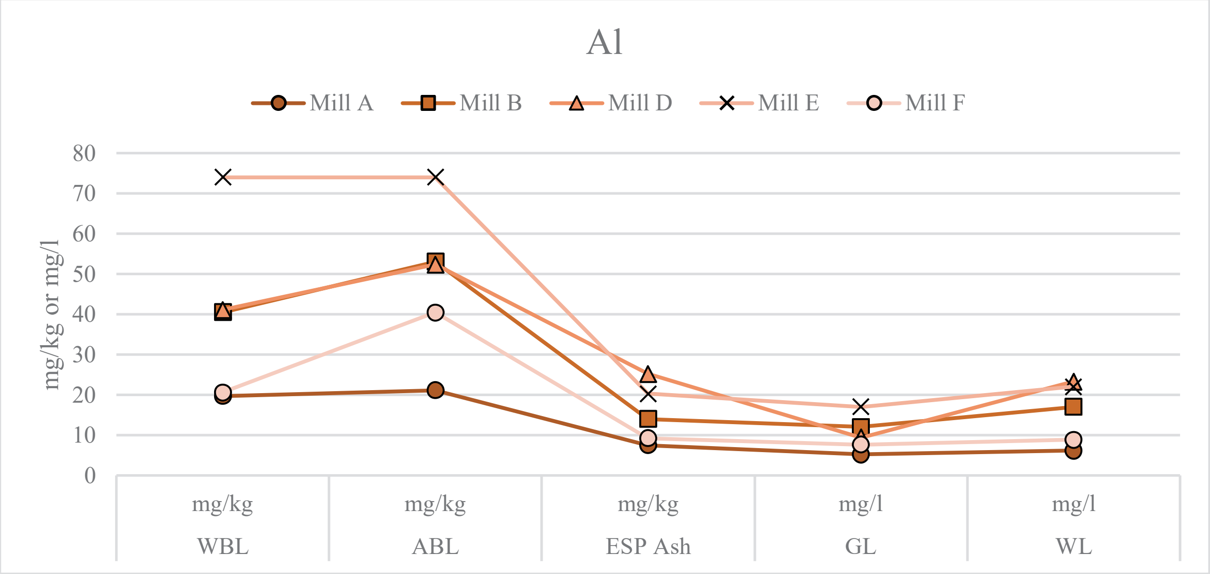

*Figure 26 Al results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg. * Mill C is not included in this picture.*

Al does not change much in its concentration level between weak black liquor and as-fired black liquor. It gets removed to a certain extent during green liquor clarification and a concentration between 5 mg/l to 22 mg/l of Al is found in green and white liquor afterwards. Figure 27 presents Al per pulp production.

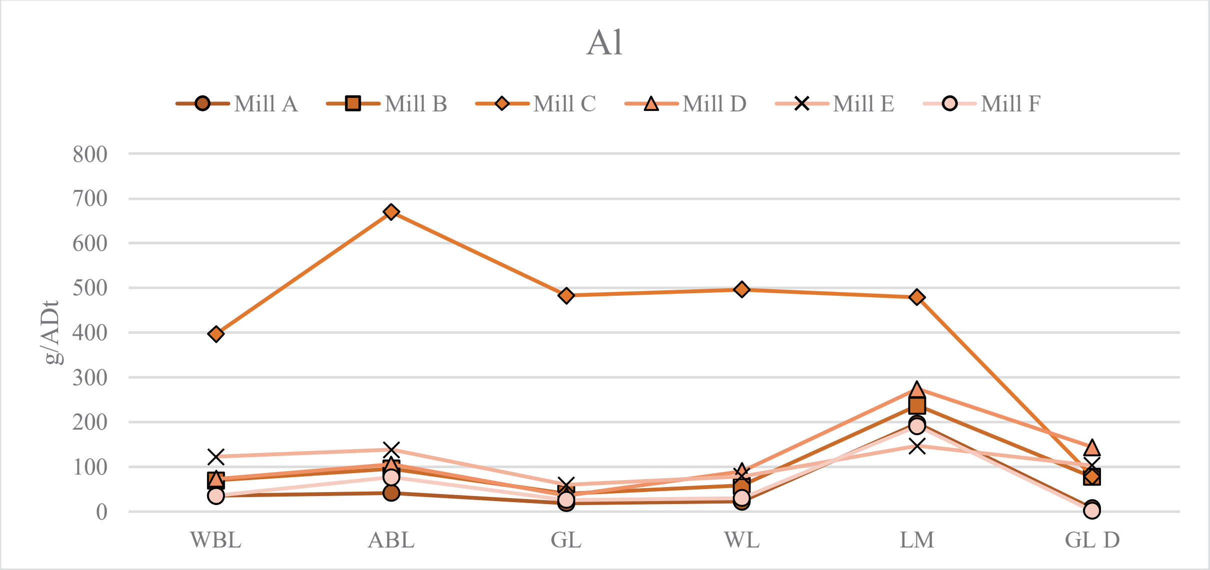

Figure 27 Al per pulp production in all the sample points.

7.2.2.4. Silicon

The highest concentration of Si is found in green liquor dregs. Mill A and Mill F have low concentration of Si in dregs, 492 mg/kg and 108 mg/kg respectively. Mill D on the other hand purges Si 27 200 mg/kg and the remaining three mills are in a range between 5 910 mg/kg to 7 520 mg/kg.

Mill E has an abnormal peak of Si in weak black liquor. This value could be due to analyzing error or something else. The Si level seems to decrease to the same level as the remaining mills in the rest of the points, which could support the idea that the high Si in weak black liquor is a detection error.

The Si concentration ranges between 57 mg/kg to 243 mg/kg in green and white liquor as shown in Figure 28. This adds up with literature statements that Si is harder to remove and can stay in the cycle more easily. Si concentration in lime mud ranges between 288 mg/kg to 1 310 mg/kg. Mill A has the lowest Si concentration in lime mud and Mill C the highest. The high Si concentration in Mill C can be linked to the kaolin contamination.

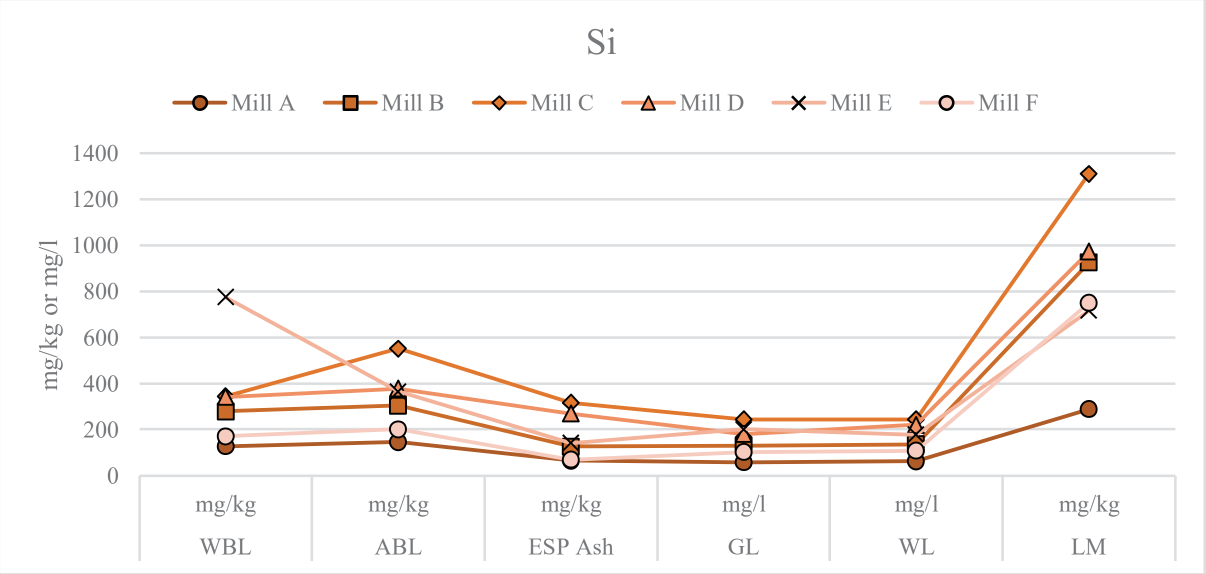

Figure 28 Si results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

As seen in Figure 29 (Si per pulp production), it is clear that Si accumulates in liquor and lime cycle

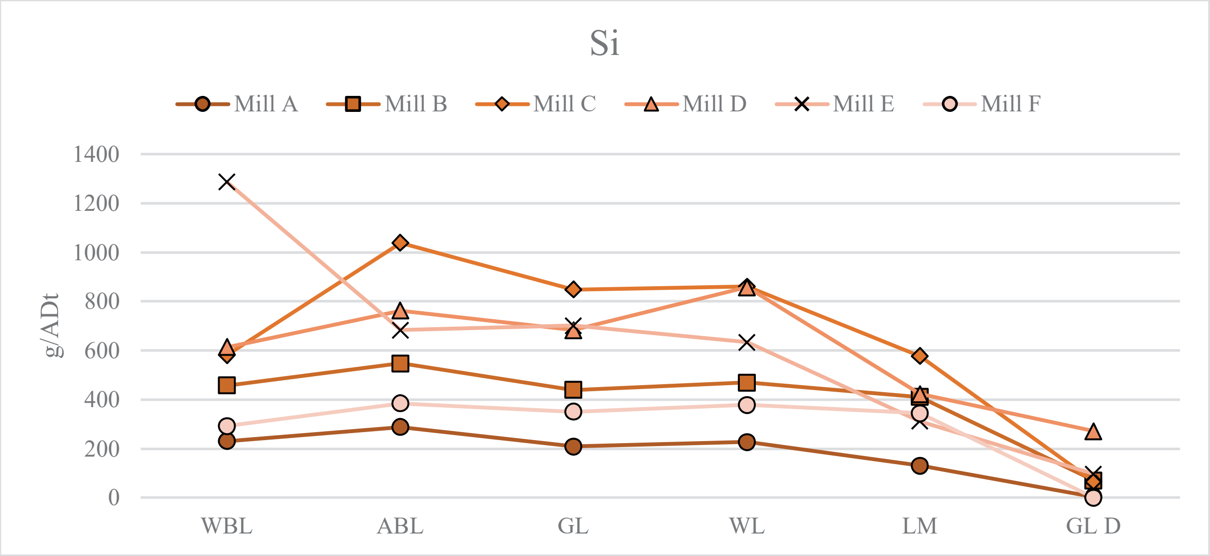

Figure 29 Si per pulp production in all the sample points.

her clarifier or filter has a link to how much NPEs can be removed with dregs. The addition of other side streams such as biosludge and the choice of lime kiln fuel could affect the amount of NPEs increasing in the recovery cycle.

7.2.2.5. Phosphorous

P tends to accumulate in lime mud. Mill E has a value of 2 631 mg/kg P in lime mud, whereas the other Mills are in a range of 6 970 mg/kg to 10 417 mg/kg. The concentration of P found in green liquor dregs is lower than in lime mud and varies between 90 mg/kg to 1070 mg/kg. Mill B has 3 650 mg/kg P in the dregs sample, which is probably due to the presence of lime mud in the dregs sample.

Figure 30 presents the P levels found in weak black liquor, as-fired black liquor, ESP ash, green liquor and white liquor. P levels in weak black liquor are between 52 mg/kg to 82 mg/kg. The level rises in as-fired black liquor for all the other mills, except Mill B. The reason for this is unknown and could also be a sampling or analysis error. P is higher in green liquor (30 mg/kg to 65 mg/kg) compared to white liquor (8.5 mg/kg to 21.7 mg/kg), which is in line with literature data that P prefers to accumulate in lime mud instead of white liquor.

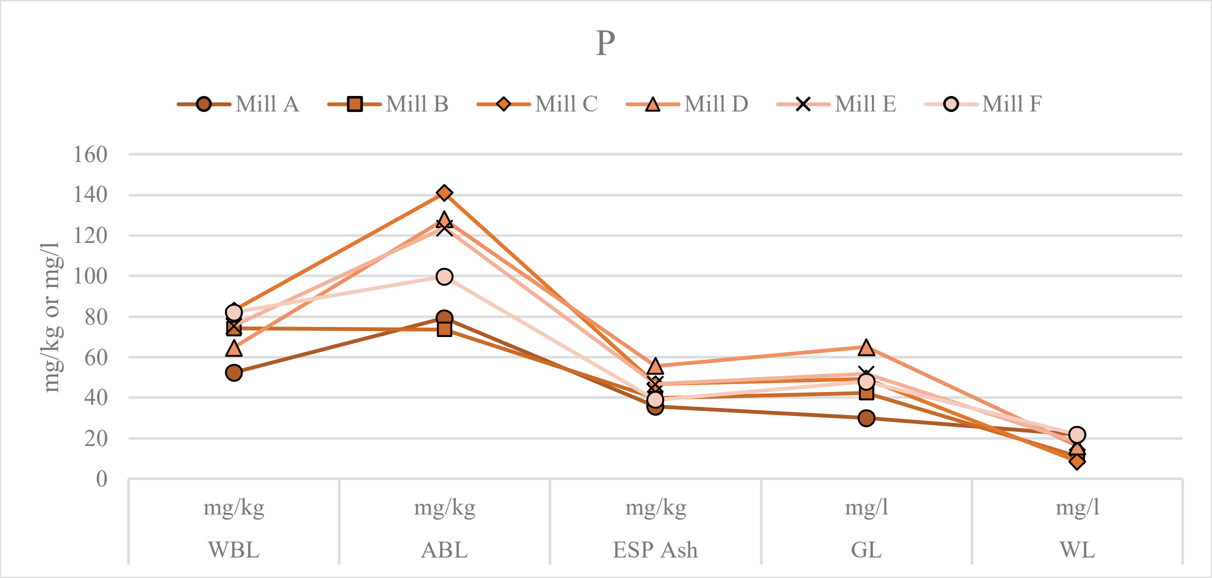

Figure 30 P results from the six pulp mills shown in weak black liquor, as-fired black liquor, ESP ash, clarified green liquor and white liquor sample points. The unit is displayed in the x-axis to be either mg/l or mg/kg.

Figure 31 presents P per pulp production. The mass balance calculation showed a clear buildup in lime mud (942 g/ADt to 4779 g/ADt). The P results for lime mud is not shown in Figure 31. P is the lowest in green liquor dregs, because of its nature of not accumulating in the dregs.

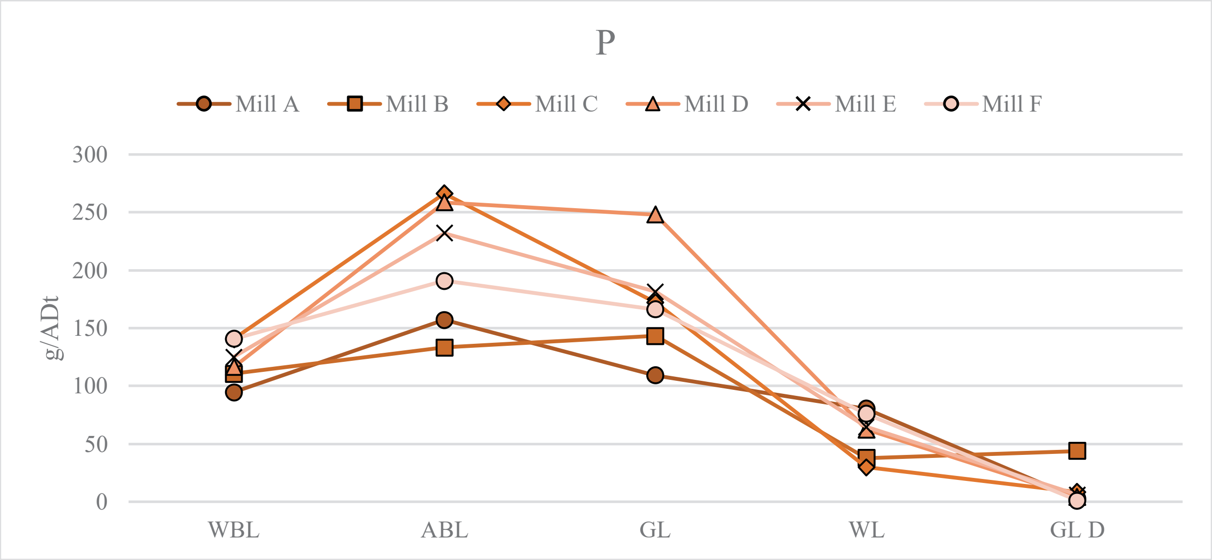

Figure 31 P per pulp production in all the sample points.

7.3. Mill location

The section that follows reports analysis done on the present data. The data is analyzed for similarities and differences compared to literature data and when comparing the six pulp mills with each other.

In this part, the so-called t-test statistical analysis is used to determine if the differences are statistically significant or not. The difference between the two averages from the comparison is seen as significant if the p-value is below 0.05. The t-test is described more thoroughly in the experimental part in section 5.6. Hypothesis test. The complete t-test results are summarized in Appendix B.

7.3.1. North versus east Finland

One of the goals of this project was to determine if the geographical location had an impact on the NPE concentrations found in Finnish mills. Three of the mills are located in the northern part on Finland and three in eastern Finland.

Altogether 56 t-tests were conducted in this comparison. All sample points NPE values were grouped according to their location north/east and all elements (Al, Si, Ca, P, Mg, Mn, Cl and K) were compared. The t-test showed that 6 out of 56 t-tests were significant. Not representing a normal operational situation, the Mill C abnormally high Al concentrations were not included in the t-tests. The complete t-test results for the north vs east comparison can be found in Appendix B.1. Table 18 presents an overview of all the t-tests made for comparing the east and north location. The color describes, which one has a lower value in the sample point. Green stands for lower NPE value and red for a higher NPE value. The exception is green liquor dregs, where the one removing more NPE has a green color. The means are first presented for both north and east mill results for all the NPEs, after which the p-value is presented underneath to indicate if the value is significant or not. A p-value of 0.05 was chosen, and only values smaller than 0.05 are seen as significant in this/these two-tail t-tests.

*Table 18 T-test hypothesis results for comparing the mill location (north vs. east). The mean for each element is shown for both north and east results. The color indicates that the t-test had a significance level over 0.05. The green color means that the mean value was significantly lower compared to the other mean and the red color indicates that the mean was significantly higher compared to the other mean value. * Mill C's high Al concentrations are not included in this t-test*

		Al *	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
WBL	North	30	250	124	70	115	46	1645	18878
	East	45	429	140	74	155	52	1567	19841
	p-value	0.122	0.091	0.273	0.438	0.054	**0.032**	0.806	0.715
ABL	North	37	333	200	98	208	70	2425	23689
	East	56	314	308	117	204	78	2327	25911
	p-value	0.059	0.783	**0.011**	0.129	0.895	0.114	0.844	0.394
ESP A	North	11	169	103	41	93	53	8400	40444
	East	18	160	155	47	93	60	8233	49017
	p-value	**0.020**	0.858	0.120	0.064	0.975	0.455	0.921	0.221
GL	North	9	144	8	41	2	2	701	9004
	East	11	160	11	55	3	2	721	10582
	p-value	0.218	0.602	0.363	**0.002**	0.355	0.354	0.888	0.258
WL	North	12	147	22	14	1	2	713	9347
	East	18	168	12	19	1	3	731	10757
	p-value	0.077	0.503	**0.013**	0.051	0.125	0.178	0.905	0.352
LM	North	484	841	378556	7762	4091	202	7	215
	East	462	813	385611	6969	4117	308	7	247
	p-value	0.669	0.862	0.331	0.544	0.969	0.283	0.680	0.493
GL D	North	3638	4921	136955	1675	28400	10078	1100	12754
	East	7528	11609	97281	328	43474	13198	844	10479
	p-value	0.136	0.146	0.405	**0.030**	0.326	0.464	0.589	0.622

The northern mills had five sample points which were significantly lower compared to east Finland. For instance, Mn in weak black liquor was 46.4 mg/kg lower compared to 52.2 mg/kg in east Finland, with a p-value of 0.0316. Green liquor dregs sample showed a higher P level of 1674.8 mg/kg in north Finland compared to east Finland 327.7 mg/kg. The p-value is 0.0299. Northern Mills tend on the other hand to have more Ca in white liquor than eastern Mills (22.1 mg/l and 11.9 mg/l respectively).

Overall, most of the t-test results were not significant, and the mill location (north vs. east Finland) seems to have only a small impact on NPE levels.

7.3.2. Older versus present Finnish results

Studies reported in literature cover Scandinavian, North American and South American mills. The South American mills use mainly eucalyptus as their raw material, instead of pine, spruce and birch, which are used mostly in Scandinavian and North American Kraft pulp mills.

Finnish data from 1995, 1999 and 2004 cover similar sampling points as in the present work (Järvinen, et al., 1995) (Holamo, 2000) (Salmenoja, et al., 2004). Some of the data dates back to over two decades ago. It is, therefore, interesting to compare the old data with the present one.

18 out of 51 t-test results showed a significant difference. All t-test hypothesis results comparing older Finnish data to the present data are summarized in Appendix B.2.

Figure 32 shows Finnish values from 1995, 1999 and 2004 for weak black liquor and as-fired black liquor, along with data from this study. The p-value is also presented in the x-axis of the figure. The high concentration of Al for Mill C has not been included in the t-tests.

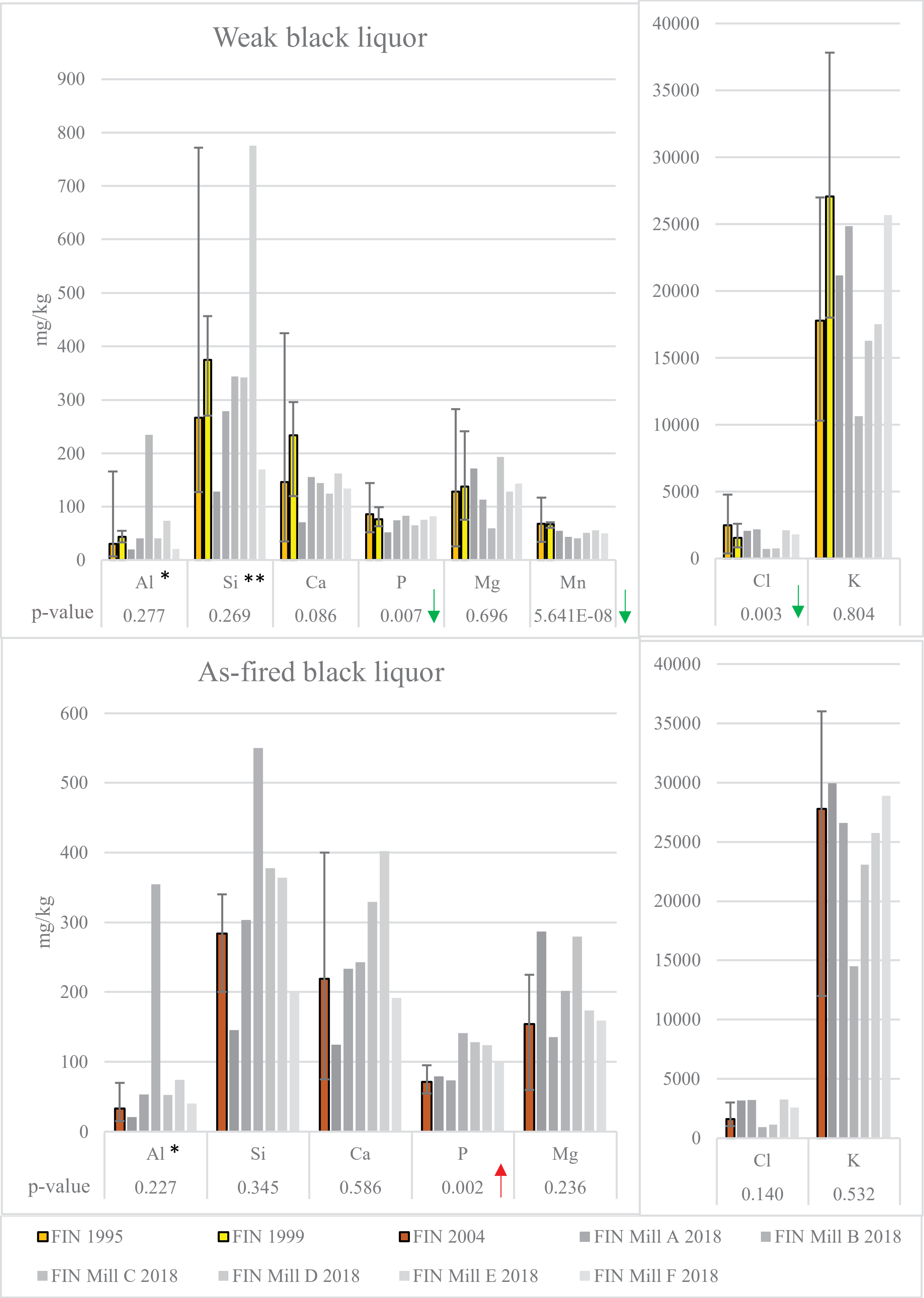

*Figure 32 Weak black liquor and as-fired black liquor comparisons between older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) (Salmenoja, et al., 2004) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * The abnormally high Si values from Mill C are not included in the t-test. **The abnormally high Si value from Mill E is included. The t-test was performed with and without the high Si value and t-test was both times insignificant.*

The weak black liquor values seem to be lower for some elements in the present results compared to the literature data from 1995 and 1999. Factors that could possibly contribute to lower NPE levels in the present results are better removal of NPEs, better lime quality and chemical quality. P levels are higher in the as-fired black liquor for the present results. The reason for the higher P values in the present results could be due to the addition of more side streams to the cycle, such as biosludge, and if the waste streams have been decreased a lot.

Figure 33 shows the results for ESP ash. The ESP ash NPE values are for Al, Si, Ca, P and Mg higher in the present results compared to the older results, according to the t-test. Cl and K do not seem to have changed. The literature values used in ESP ash are from 2004 and for Cl and K data from 1999 was available as well.

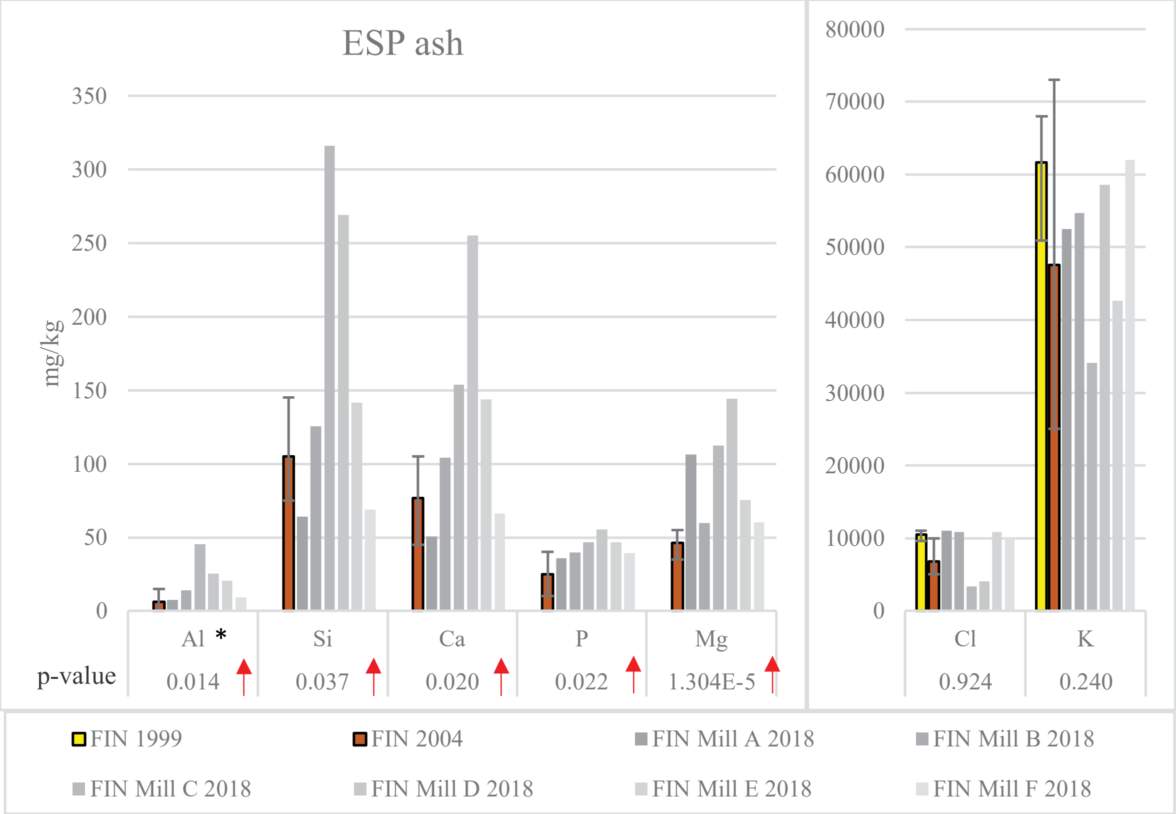

*Figure 33 ESP ash comparison between older Finnish results (Holamo, 2000) (Salmenoja, et al., 2004) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. A green arrow indicates that the data from the present work are significantly lower, and a red arrow indicates that the data from the present work are significantly higher as compared to data from literature sources. * Mill C's Al value is not included in the t-test result.*

Figure 34 shows the values for green liquor and Figure 35 for white liquor.

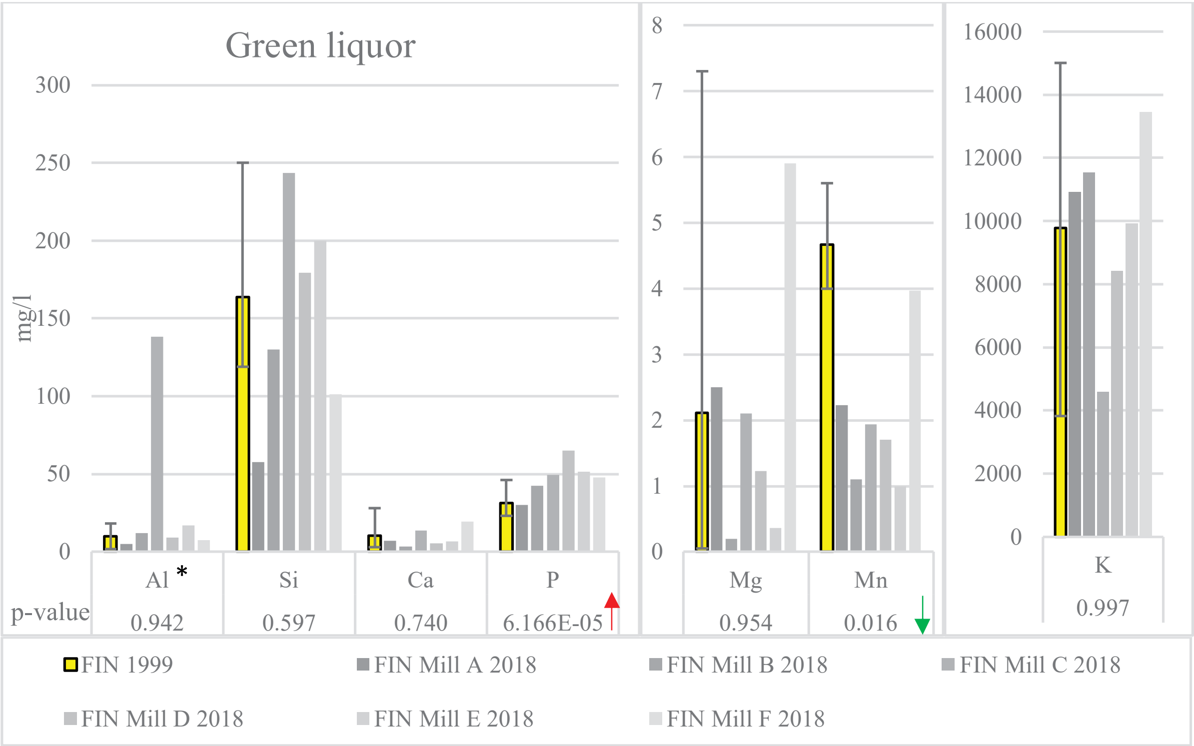

*Figure 34 Green liquor comparison between older Finnish results (Holamo, 2000) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * Mill C's high Al value is not included in the t-test results.*

The green liquor has more P compared to older Finnish results. The Mn concentration seems to be consistently lower in weak black liquor, green liquor and white liquor in the present results. The white liquor results are also interesting because the present results seem to have less Mg, Mn and Cl present. This could indicate that the removal techniques of NPEs have changed to be more efficient today, compared to older results. P, however, seems to just be a bit higher in 2018 results compared to older results.

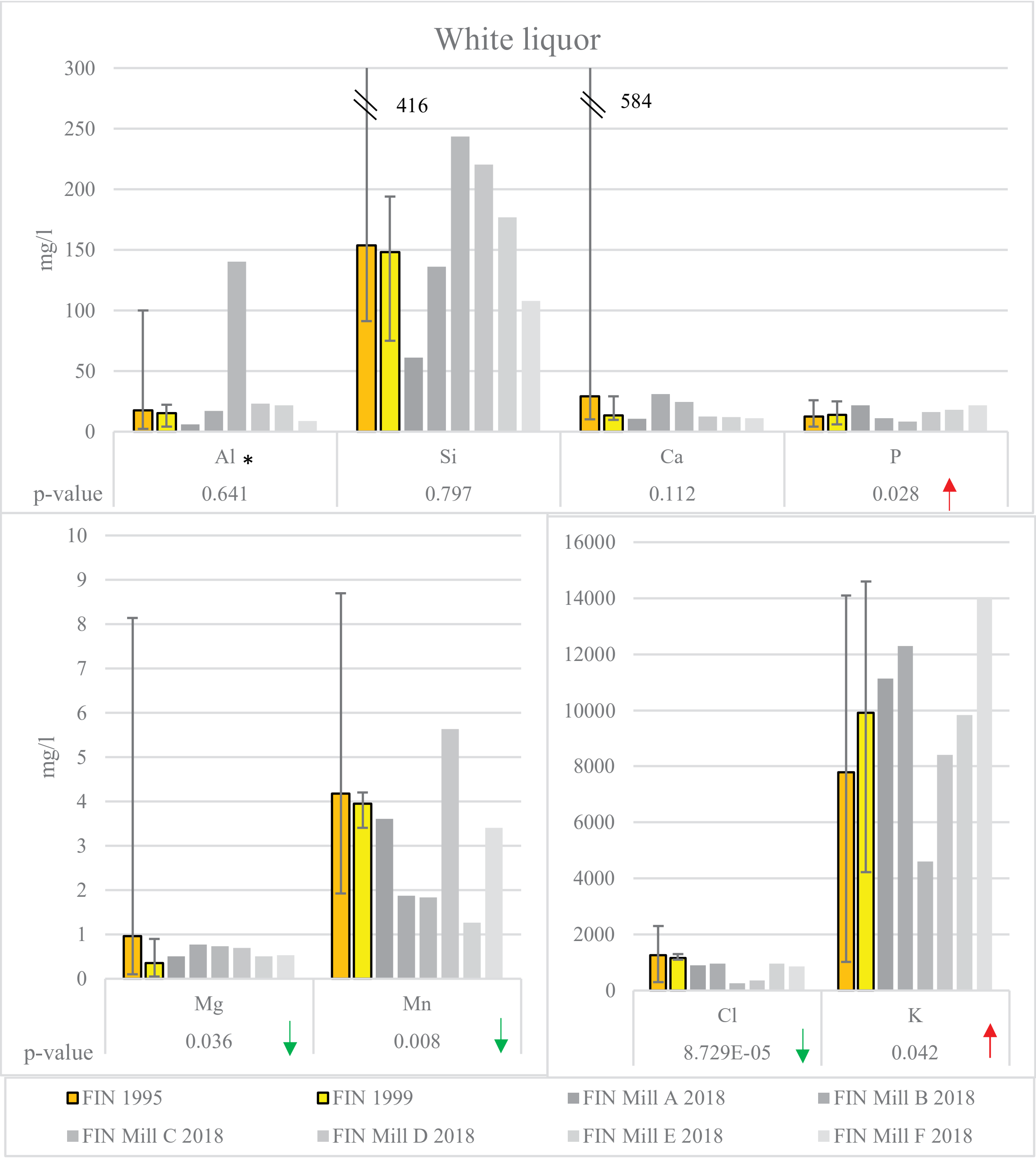

*Figure 35 White liquor comparison between older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * Mill C's abnormally high Al values are not included in the t-test.*

Figure 36 presents similar results for lime mud and green liquor dregs compared to Finnish results from 1999 (Holamo, 2000).

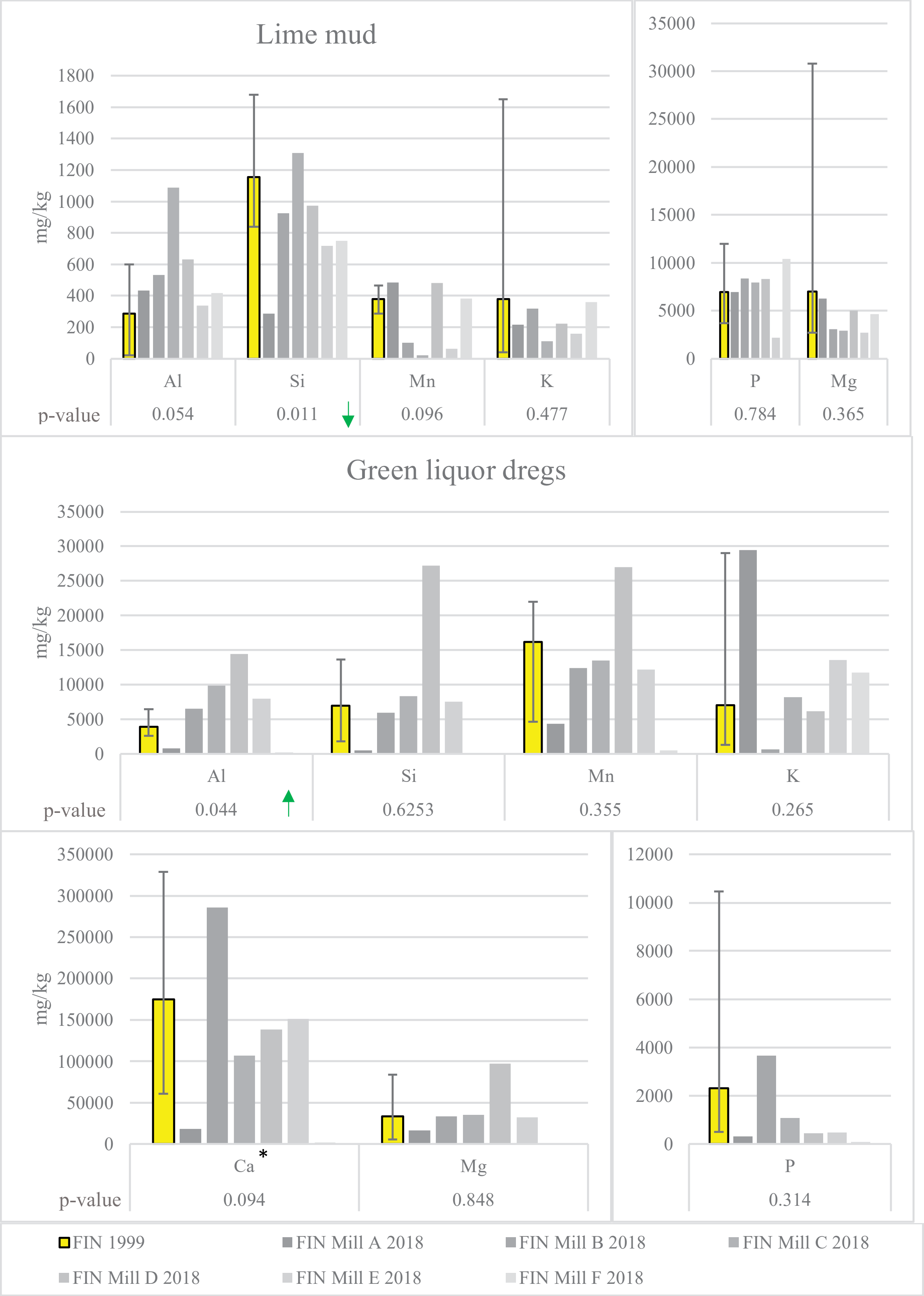

*Figure 36 Lime mud and green liquor dregs comparison between older Finnish results (Holamo, 2000) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly higher, and the red color indicates that the present values are significantly lower in this case with green liquor dregs. * Mill B has lime mud in its green liquor dregs sample.*

Al is significantly higher for this project's lime mud results compared to the older Finnish results. Si has lower values in lime mud than older studies. Table 19 summarizes the t-tests conducted when comparing older Finnish values to present this project's NPE values.

*Table 19 T-test hypothesis results for comparing older Finnish results (Holamo, 2000) (Järvinen, et al., 1995) (Salmenoja, et al., 2004) to this project's results. Seven sample points were compared and eight NPEs. No color indicates that the t-test had a significance level over 0.05. The green color means that the mean value was significantly lower and red color means that the mean value was significantly higher. No values at all means that no t-test could be done because literature data was not available. * Mill C's high Al concentrations are not included in this t-test*

		Al *	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
WBL	Older FIN	32	277	156	84	129	68	2351	18969
	FIN 2018	39	340	132	72	135	49	1606	19359
	p-value	0.277	0.269	0.086	**0.007**	0.696	**5.64E-08**	**0.003**	0.804
ABL	Older FIN	33	284	219	71	154	1600	27800	
	FIN 2018	48	324	254	108	206	2376	24800	
	p-value	0.227	0.345	0.586	**0.002**	0.236	0.140	0.532	
ESP A	Older FIN	6	105	77	25	46		8200	52863
	FIN 2018	15	164	129	44	93		8316	44731
	p-value	**0.014**	**0.037**	**0.020**	**0.022**	**1.30E-05**		0.924	0.240
GL	Older FIN	10	164	11	31	2	5		9788
	FIN 2018	10	152	9	48	2	2		9793
	p-value	0.942	0.597	0.740	**6.17E-05**	0.954	**0.016**		0.997
WL	Older FIN	17	153	26	13	0.9	4	1250	8194
	FIN 2018	15	158	17	16	0.6	3	722	10052
	p-value	0.641	0.797	0.112	**0.028**	**0.036**	**0.008**	**8.73E-05**	**0.042**
LM	Older FIN	287	1155	381889	6959	6987	379		378
	FIN 2018	471	827	382083	7366	4104	255		231
	p-value	0.054	**0.011**	0.989	0.784	0.365	0.096		0.477
GL D	Older FIN	3881	6914	174667	2315	33812	16150		7013
	FIN 2018	6618	8265	117118	1001	35937	11638		11616
	p-value	**0.044**	0.625	0.094	0.314	0.848	0.355		0.265

When comparing the present data to older Finnish NPE values, 18 out of the 51 t-test (results) were significant, with a p-value less than 0.05. This is ca. 35% of all the t-tests in this comparison. K values do not seem to have changed much during the past decades. The K value found in white liquor was the only one higher in the present results, compared to the older ones, except in white liquor. Weak black liquor seems to have lower values for P, Mn and Cl compared to older results. P increases much in as-fired black liquor. One reason could be that mills today add more side streams such as biosludge to the liquor, which adds P to the recovery cycle. When looking at the ESP ash results, all NPEs, except Cl and K (excluding manganese, where no literature references were available) have increased in the present results. Cl and K are known to accumulate in ESP ash, but those elements did not increase as the others did.

Mn was lower in the present results in weak black liquor, green liquor and white liquor. Cl was also lower in weak black liquor and white liquor. Overall, one could say that the NPE amount found in white liquor is lower in the present results, at least for Mg, Mn and Cl. The exception is P, which is higher. Overall this means that less NPEs reach the digester with the liquor. This is a good indicator on that the removal of the NPEs has developed compared to the past.

7.3.3. Finnish versus North American NPE data

In this section, North American mills are compared with the results conducted from this project. No t-tests could be made for as-fired black liquor and weak black liquor due to the lack of sample point data in literature.

Figure 37 presents weak black liquor, as-fired black liquor results with similar North American results from Canada (McGuffie & Taylor, 2007).

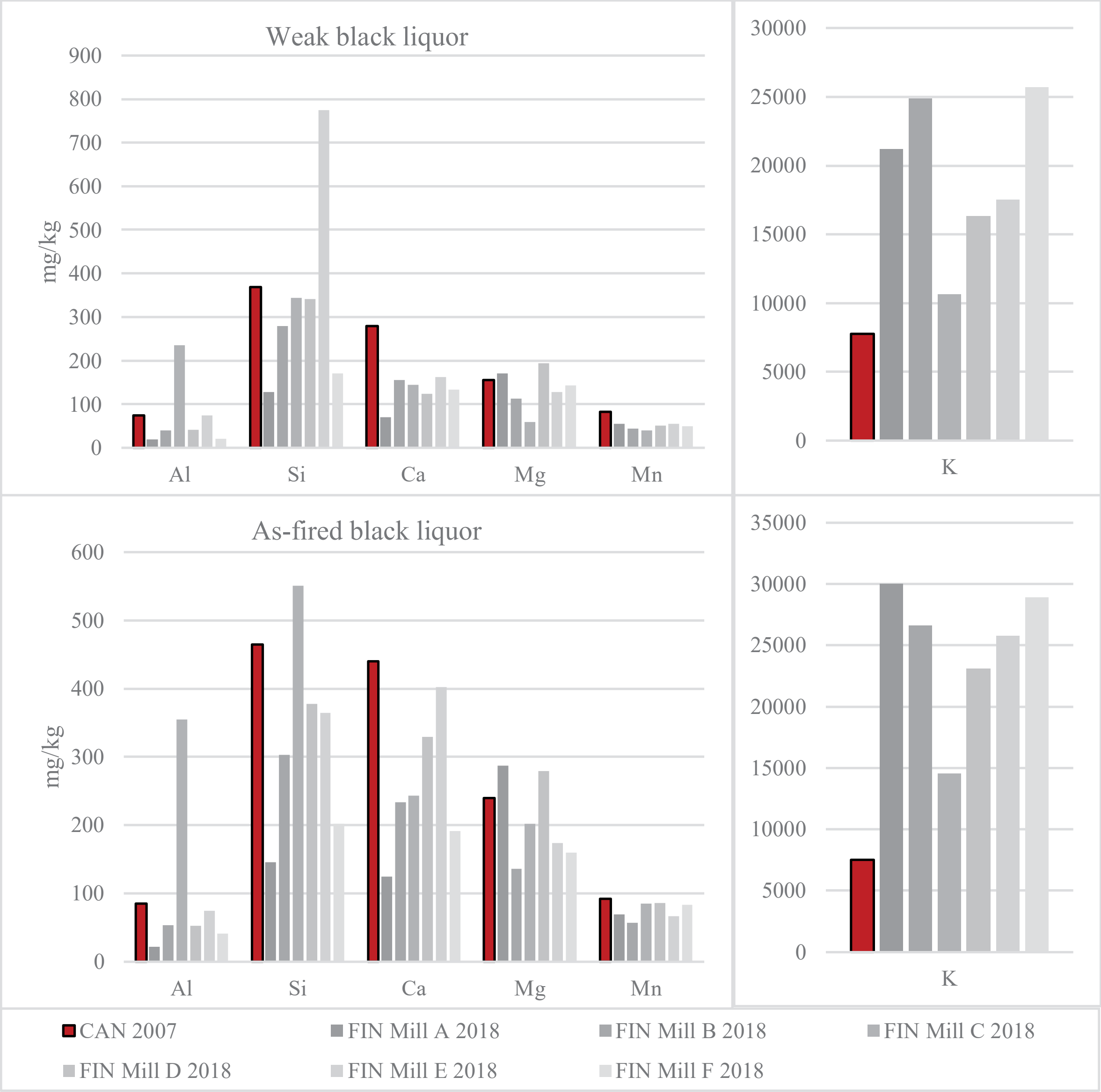

Figure 37 Comparison between North American results (McGuffie & Taylor, 2007) and this project's results in weak black liquor and as-fired black liquor. The colored column represents the literature value and the grey columns are the average of the six Finnish pulp mills participating in this project.

K is much lower in the North American samples for weak black liquor and as-fired black liquor. The Canadian values gathered by McGuffie and Taylor 2007 contained only a single value, meaning that the K value could be contain some error, from sampling or from analysis.

Figure 38 presents ESP ash comparisons of North American and this project's results. The p-value is shown in the x-axis of the reference and the t-tests.

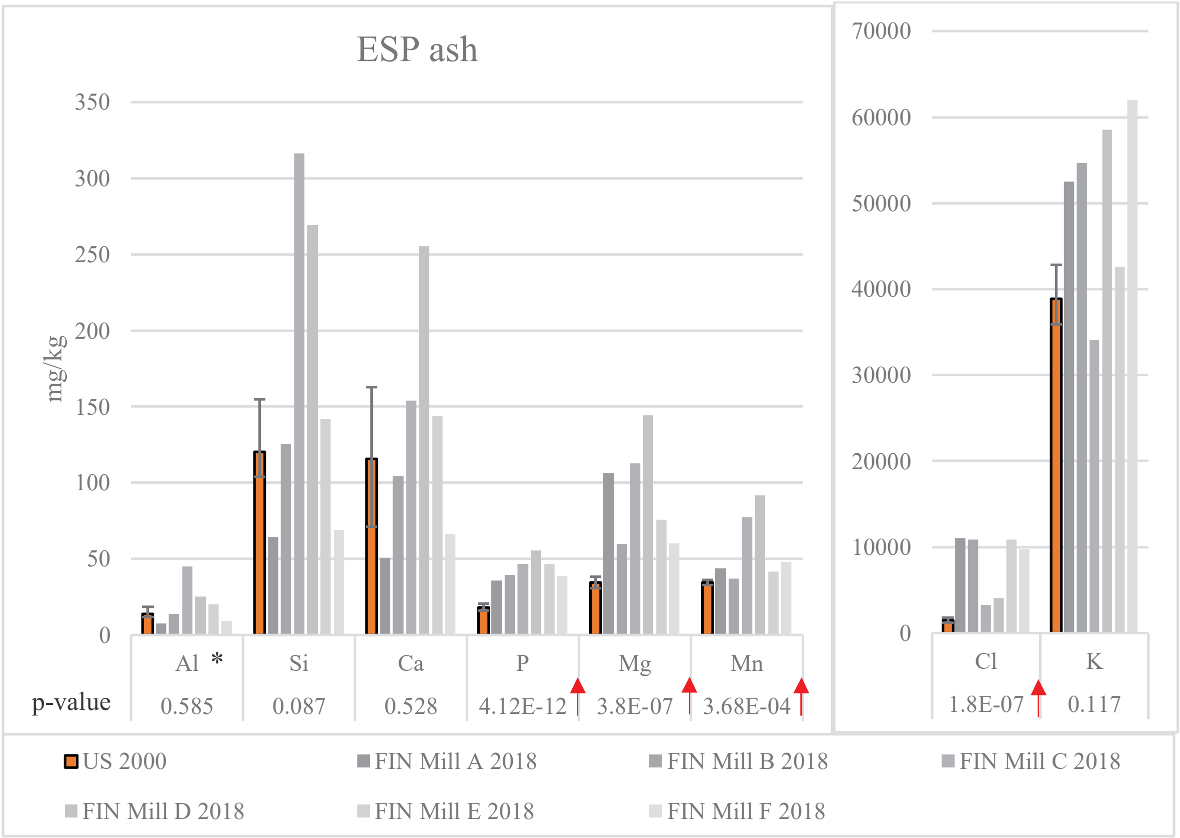

*Figure 38 ESP ash comparison between older North American results (Frederick, et al., 2000) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * The abnormally high Al values from Mill C are not included in the t-test.*

The NPE values in ESP ash seem to be higher for P, Mg, Mn and Cl in the 2018 Finnish results compared to North American results from 2000. The same trend could be seen when this project's results were compared to older Finnish results. In Finland Al, Si, Ca and Mg have increased since the 1990s.

For green and white liquor, some literature results were shown as mg/kg. The literature data was converted into mg/l to compare the results to the present ones. The literature the density of green liquor ranges from 1.12 kg/l – 1.2 kg/l (Arpalahti, et al., 2008). In this work's figures, the density value 1.15 kg/l was used for green and white liquor. Sensitivity of the results was also tested and t-tests with a density of 1.1 kg/l and 1.2 kg/l were therefore conducted. The conversions using different densities did not affect the significance of the t-test results, except for Cl in green liquor. If the density of 1.1 kg/l for green liquor was used, then the Finnish results were seen as higher, with a p-value of 0.036 compared to North American results. Green and white liquor results are shown in Figure 39 and Figure 40. The p-value is shown in the x-axis.

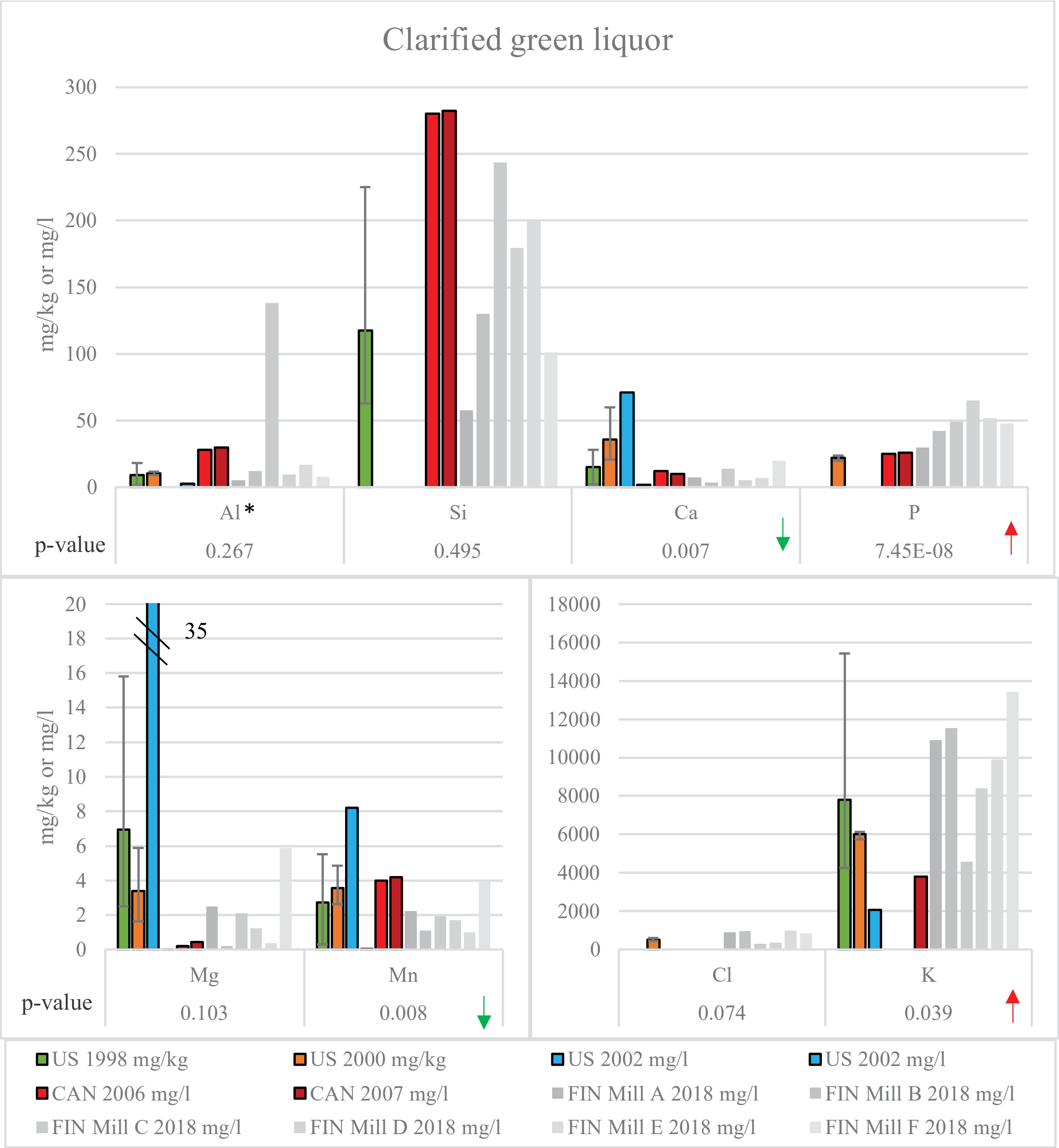

*Figure 39 Clarified green liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. The legend also describes if the values shown are in mg/l or mg/kg in the figure. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * The abnormally high Al values from Mill C are not included in the t-test.*

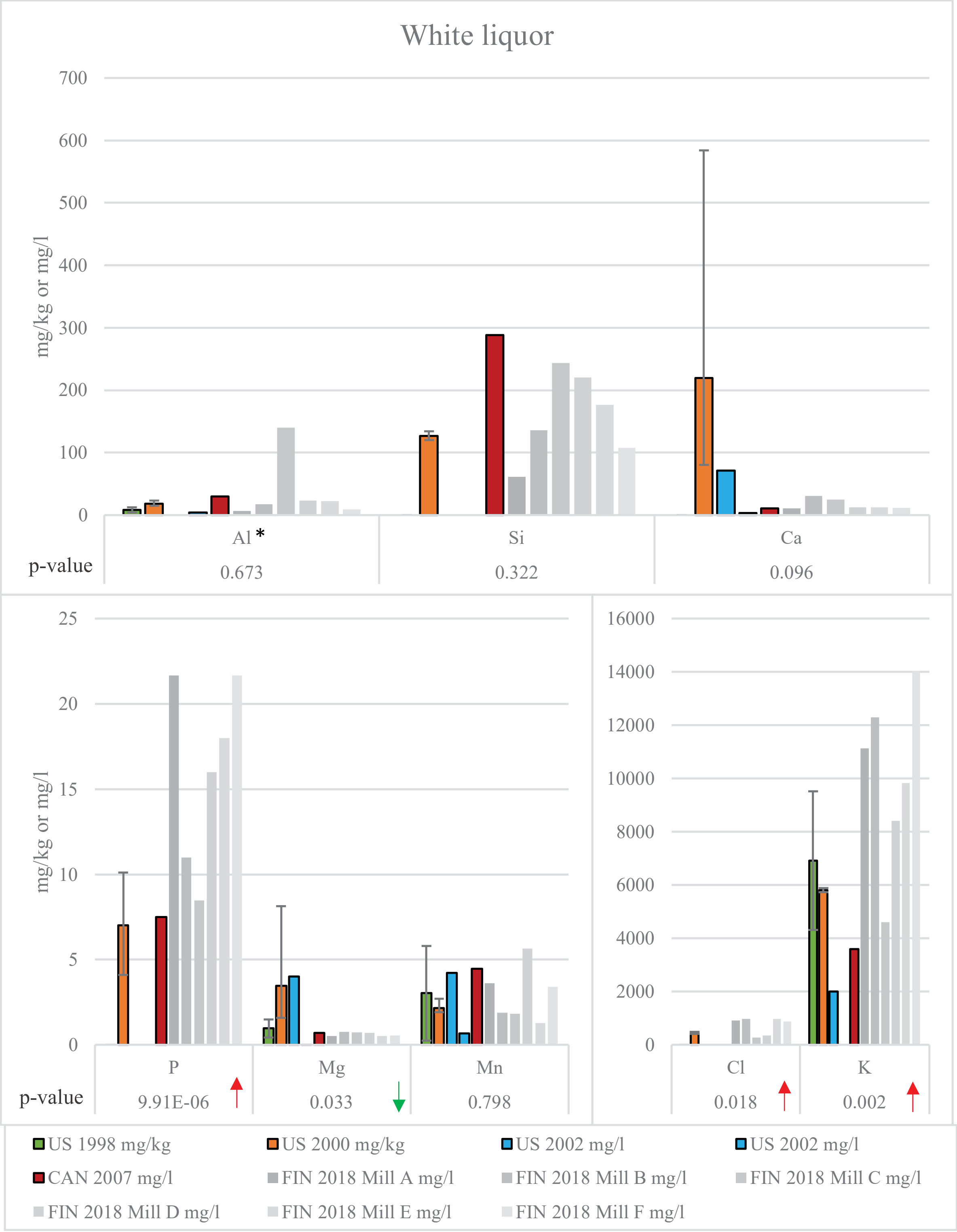

*Figure 40 White liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (McGuffie & Taylor, 2007)and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. The legend also describes if the values shown are in mg/l or mg/kg in the figure. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the present values are significantly lower, and the red color indicates that the present values are significantly higher. * The abnormally high Al values from Mill C are not included in the t-test.*

Ca and Mn are lower in Finland in clarified green liquor with a p-value of 0.011 and 0.008 respectively. In white liquor, P, K and Cl have a higher concentration in Finland. Mg is only significantly lower in white liquor in Finland. Finnish mills in this study seem to have higher NPE values for all NPEs except K when compared to older North American data.

Figure 41contains t-test comparisons for lime mud and green liquor dregs.

*Figure 41 Lime mud and green liquor dregs comparisons between older North American results (Empie, et al., 1999) (Richardson, et al., 1998) (Frederick, et al., 2000) (Taylor & Bossons, 2006) (McGuffie & Taylor, 2007)and this project's results from 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates in lime mud that the present values are significantly lower, and the red color indicates that the present values are significantly higher. In green liquor dregs, the green arrow indicates that the present value has higher NPE concentration. * The abnormally high Al values from Mill C are not included in the t-test. ** The literature reference (Frederick, et al., 2000) has very high values in some of the sample points and has to be taken into account when analyzing the results. *** Mill B has lime mud in its green liquor dregs sample.*

Ca is not seen as an NPE in lime mud. The Finnish mills tend to accumulate more NPEs in their lime mud than North American mills do. Mn, P and Mg were higher in Finnish mills, whereas K was lower in Finnish mills compared to the literature references from North America.

On the other hand, the Finnish mills tend to have more NPEs present in green liquor dregs, at least for NPEs like Al, Si, P and K. Factors that could possibly contribute to this is that Finnish mills are present and therefore have better clarifying systems. The North American results are also older, which could also affect the results and does not give an overview of the present situation in North America. Table 20 summarizes the t-tests conducted when comparing North American values with Finnish values.

*Table 20 T-test hypothesis results for comparing North American results to this project's results. Seven sample points were compared and eight NPEs. No color indicates that the t-test had a significance level over 0.05. The green color means that the mean value was significantly lower and red color means that the mean value was significantly higher. No values at all means that no t-test could be done because literature data was not available. In white and green liquor, the density of 1.15 kg/l is used to convert those literature values that had their values in mg/kg in white and green liquor. * Mill C's high Al concentrations are not included in this t-test*

		Al *	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
ESP A	North America	14	120	116	18	34	34	1525	38902
	FIN 2018	15	164	129	44	93	57	8316	44731
	p-value	0.585	0.087	0.528	**4.22E-12**	**3.81E-07**	**3.68E-04**	**1.83E-07**	0.117
GL Density 1.15 kg/l	North America	13	184	29	25	7	4	575	6936
	FIN 2018	10	152	9	48	2	2	711	9793
	p-value	0.267	0.495	**0.007**	**7.45E-08**	0.103	**0.008**	0.074	**0.039**
WL Density 1.15 kg/l	North America	17	193	151	8	2	3	533	6199
	FIN 2018	15	158	17	16	1	3	722	10052
	p-value	0.673	0.322	0.096	**9.91E-06**	**0.033**	0.798	**0.018**	**0.002**
LM	North America	231	1975		1639	1226	97		4905
	FIN 2018	471	827		7366	4104	255		231
	p-value	0.107	0.130		**4.00E-04**	**7.27E-05**	**0.008**		**1.30E-03**
GL D	North America	3165	3114	176000	233	20278	11249	799	5861
	FIN 2018	6618	8265	117000	1001	35937	11638	972	11616
	p-value	**0.018**	**0.036**	0.115	**0.022**	0.058	0.883	0.726	**0.039**

From the t-test 20 out of 38 tests gave a significant result, which means that over 50% of the results had a significant difference when comparing the present data to North American data from 1995-2007. All t-test results can be found in Appendix B.3.

7.3.4. Impact of raw material on NPE levels

The raw material has a significant impact on the NPE levels found in mills. Mill A and Mill D use only softwood (pine and spruce) as their raw material. The remaining four mills use both hardwood (birch) and softwood (pine and spruce) as their raw material source. In lime mud, white liquor and green liquor Mg levels seem to be higher for mills using only softwood compared to the other mills. Mill F has also high Mg levels which could be explained by them using also more softwood compared to hardwood.

When comparing the results to literature studies conducted at a mill using eucalyptus (Milanez, 2007), clear differences can be seen between this project's results and the eucalyptus mills results. However, the comparison is qualitative, since t-test could not be made due to too few data. The values conducted from Milanez study were an average of four samples, individually collected in different and consecutive production days. The Milanez results are shown as ppm. The raw data was not available, so the data used is the average shown in Milanez et al., 2007. Due to the lack of data points, t-test could not be made. Figure 42 shows the results for the six Finnish pulp mills and a South American mill (Milanez, 2007) using eucalyptus as its raw material.

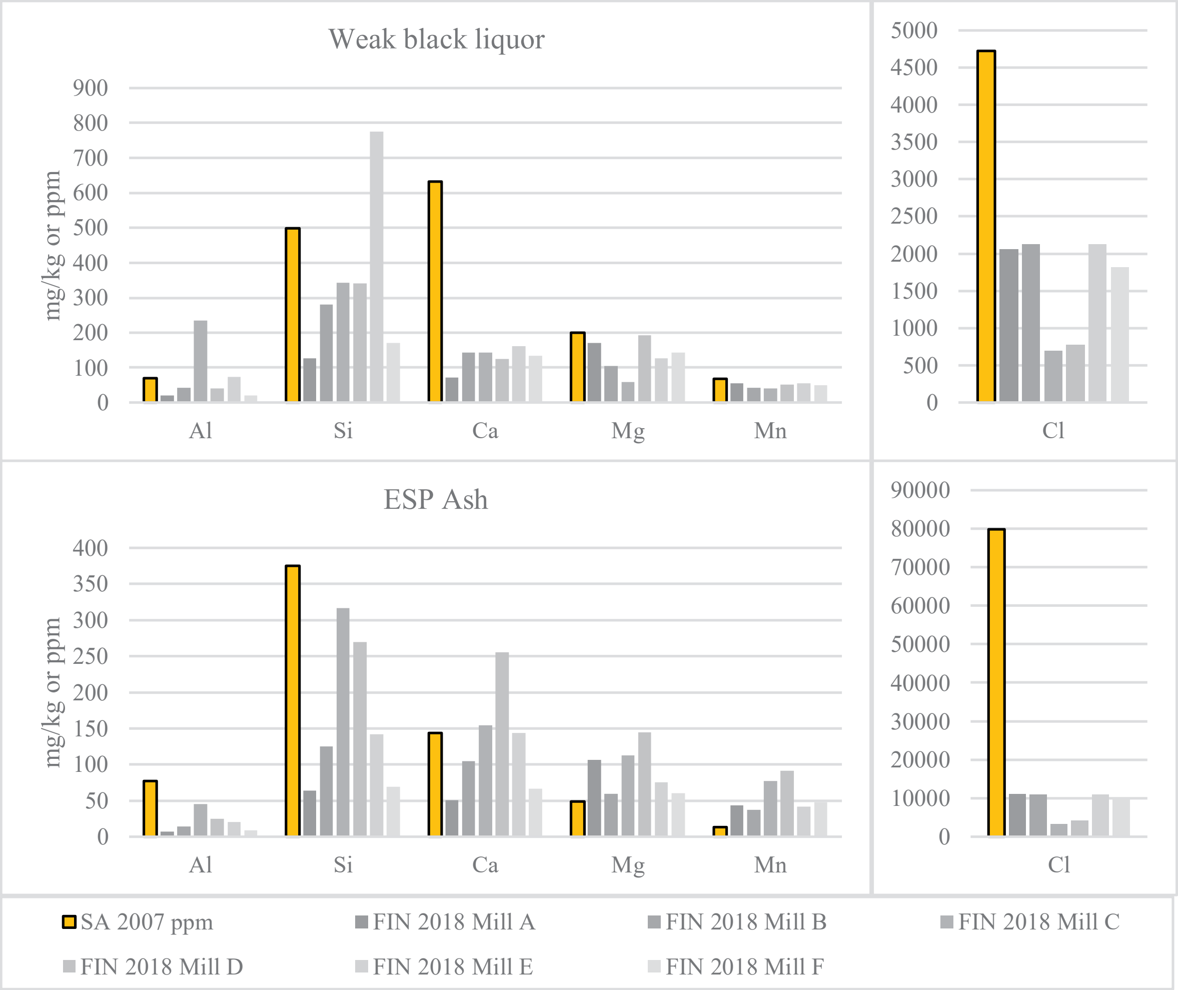

Figure 42 Weak black liquor and ESP ash results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

Cl is higher in the study conducted by Milanez. Si seems also to be higher in the eucalyptus samples, but Mn seems to be lower in the ESP ash for eucalyptus.

The high Cl value can be due to the process water. Ca is known to stay sorbed on the pulp fibers during cooking and often ending up in the fiber line. However, if calcium dissolves in the digester it could enter the liquor cycle, which could be one factor that a higher Ca concentration can be spotted in Figure 42 for weak black liquor.

Figure 43 presents clarified green liquor and white liquor results. Here too Si and Cl seem to be much higher at the eucalyptus mill compared to the Finnish pulp mill results. If Mill C's kaolin contamination is disregarded, the South American mill seems also to have higher Al levels in green and white liquor. As stated in literature Al prefers to precipitate with Mg in green liquor dregs as hydrotalcite. If not enough Mg or Al is present in the liquor, they cannot precipitate from the cycle as easily. When looking at the green liquor results in Figure 43, it becomes evident that the Al concentration is high whereas the Mg concentration is low for the South American mill. One possible explanation for this could be that hydrotalcite is not formed to the extent it is formed in the Finnish mills (present data from 2018) and, thus, hydrotalcite is not purged from the eucalyptus mill of Milanez.

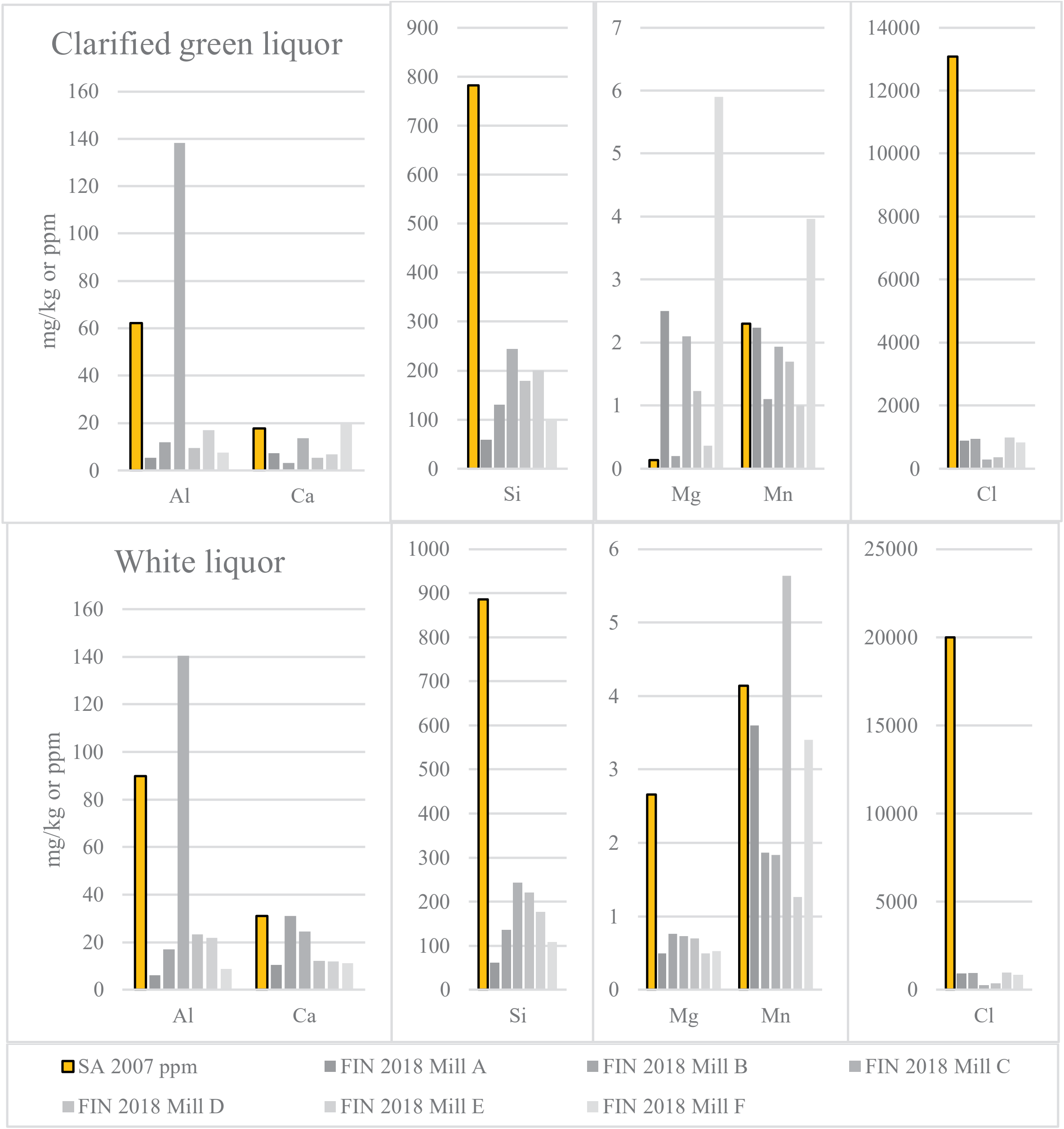

Figure 43 Clarified green liquor and white liquor results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

Figure 43 shows lime mud and green liquor dregs results. The greatest difference in lime mud is the higher Cl amount in Milanez's eucalyptus mill.

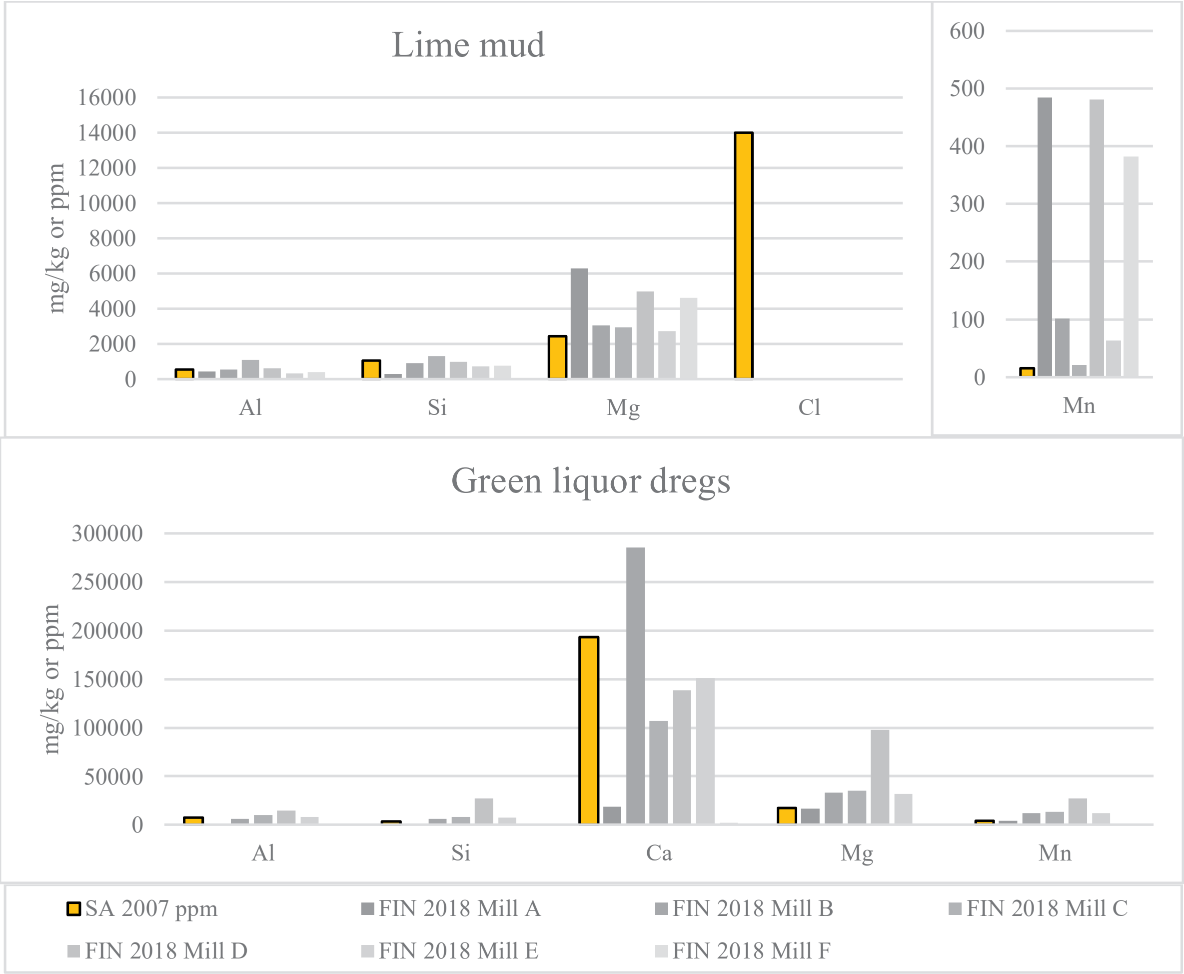

Figure 44 Lime mud and green liquor dregs results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

Lime mud seems also to contains more Cl in the South American mill. The high Cl concentration could be due to the process water. The conclusion from the comparison is that Cl seems to be generally higher in a eucalyptus mill as compared to Finnish mills using birch, pine, and spruce. Also, Al and Si seem to be higher in the eucalyptus mill.

7.4. Comparison of equipment and side streams

This section discusses the six Finnish mills participating in this study by considering differences in equipment and process side streams between the mills. The use of either clarifier or filter has a link to how much NPEs can be removed with dregs. The addition of side streams, such as biosludge and the choice of lime kiln fuel could affect the amount of NPEs increasing in the recovery cycle.

7.4.1. Green liquor handling

There are different ways for a mill to purify their raw green liquor. The two most common methods are usage of a clarifier or filters. Three of the Finnish mills in this project use a clarifier and the remaining three mills use crossflow filters. Studies have been conducted to compare efficiencies of clarifiers and filters (Gu & Edwards, 2004). Table 21 and Table 22 present values as mass balances in the six mills in the present work.

*Table 21 Green liquor dregs mass balance for the mills. Three of them use a clarifier and three mills use crossflow filters. The blue color describes those elements that are more easily purged with dregs and the red the opposite. * The Ca value 3428 g /ADt is higher than normal because this mill had lime mud in its sample*

Green liquor dregs		**Ca**	**Mg**	**Mn**	**Al**	**Si**	**P**	**Cl**	**K**
Clarifier	g/ADt	185	166	44	8	5	3	27	295
Clarifier	g/ADt	853	281	108	79	67	9	4	65
Clarifier	g/ADt	26	12	6	2	1	1	12	141
Filter	g/ADt	3428*	401	148	78	71	44	0	8
Filter	g/ADt	1387	974	270	144	272	4	1	61
Filter	g/ADt	1963	416	158	104	98	6	19	176

Table 22 Clarified green liquor mass balance for the mills. Three of them use a clarifier and three mills use crossflow filters. The blue color describes those elements that are more easily purged with dregs and the red the opposite

Clarified green liquor		**Ca**	**Mg**	**Mn**	**Al**	**Si**	**P**	**Cl**	**K**
Clarifier	g/ADt	26	9	8	19	210	109	3200	39632
Clarifier	g/ADt	48	7	7	483	849	172	1000	15975
Clarifier	g/ADt	68	20	14	26	351	166	2862	46506
Filter	g/ADt	11	1	4	41	440	143	3167	38994
Filter	g/ADt	20	5	6	36	684	248	1360	32059
Filter	g/ADt	24	1	4	60	702	181	3438	34741

Ca, Mg and Mn are elements conventionally purged with the dregs. These elements precipitate in alkali solutions more effectively and are therefore removed with the clarifier and filters from green liquor. In Table 21, a clear distinction for Ca, Mg and Mn can be seen when comparing the dregs results for the mills using a clarifier or filter.

A low value in clarified green liquor in Table 22, implies that the dregs removal has efficiently removed NPEs from green liquor. The mills using filters have here an advantage as well and score lower values for Ca, Mg and Mn. This is in line with literature that filters remove NPEs more efficiently from green liquor than clarifiers (Gu & Edwards, 2004).

The removal of more alkali soluble elements does not follow the same trend as Ca, Mg and Mn. P, Cl and K. This does not seem to have any correlation to the use of filters or clarifiers. When looking at Table 22, with the clarified green liquor results no connection between the green liquor handling method and amount of Al, Si, P, Cl and K is detectable.

7.4.2. Other factors that can impact the NPE values

The next section describes which side streams could influence the NPE levels found in pulp mills and will describe more thoroughly the participating mill's side streams and purging points.

7.4.2.1. Addition of biosludge

Conventional techniques to discard biosludge, such as dumping it in landfills or combusting it in solid fuel boilers, are expensive for mills. Therefore, combusting biosludge with the liquor in the recovery boiler is an attractive alternative for many mills. Biosludge, however, is known to contain many NPEs and could, therefore, be a potential source of unwanted corrosion, scaling or plugging in the recovery cycle. (Harila & Kivilinna, 1999; Knuutila, et al., 1999; Hyvönen, 2009)

Biosludge is the side product from the biological wastewater treatment plant. The sludge has to be pretreated and dried to around 10 – 15% of dry solids before it is mixed together with weak black liquor in a mixing tank, where the weak black liquor has a concentration of about 40% dry solid. The biosludge flow in black liquor is usually 1 – 2% of the total dry solids content. (Hyvönen, 2009)

Two mills from this project have decided not to add biosludge to the liquor. The addition of biosludge is expected to increase the NPE levels found in the liquor, but when studying the results from this project no obvious differences can be spotted between the mills that add biosludge and those that do not. The impact of biosludge can increase the NPE levels, but it would have to be studied more thoroughly in order to be able to make statements on their impact in the recovery cycle.

7.4.2.2. Addition of dispersion chemicals

Some mills in this project have decided to use dispersion chemicals in their recovery cycle. Dispersion chemicals are often used to target the formation of pirssonite in the green liquor handling systems. Pirssonite precipitates on cold surfaces, such as pipes, filters and in the bottom of tanks.

The NPE levels found in green liquor dregs and clarified green liquor are difficult to connect to the use or absence of dispersion chemical. The impact from dispersion chemicals on the NPE levels was not studied in this project and would need future research in order to make conclusions of their impact.

7.4.2.3. Lime kiln fuel choice

Almost all lime kilns use heavy fuel oil or natural gas according to literature. They tend to have the required stability and high enough temperature to be good candidates as fuels. Mills prefer also other fuels like tall oil, pitch oil and methanol. The fuels can mostly be mixed with fossil fuels to reach the desired properties of the fuel. (Arpalahti, et al., 2008)

The mills participating in the project use a wide range of different fuels. The fuel choices in the mills were natural gas, heavy fuel oil, pitch oil, gasified bark and hydrogen. Some mills mix biofuels and fossil fuels in their lime kilns. The impact from the fuel use is difficult to analyze. No exact conclusions can be made, with the information gathered with this study and further analyzing is needed in order to make conclusions on the impact the lime kiln fuels have on the NPE amount found in the six pulp mills.

7.4.2.4. Comparison of the degree of closure of the cycle

Determining and comparing the openness or closeness of the recovery cycle is very challenging, because the term itself is very imprecise and many factors can have an impact on it. Factors such as the usage of fresh water, wastewater disposal, removing lime mud, removing ESP ash from the recovery boiler and lime kiln are some of the variables that affect the openness of the cycle. Mills strive to minimize their environmental footprint. The side effects of this can be seen as the rise of more NPE problems in mills than before. The problems might not yet be too harmful, but if the effluent system and other waste streams decreases, it might start to cause problems in the future.

Mills use in general some main effluent and waste streams to discard NPEs. Dregs removal is often seen as the main purging point to remove unwanted elements. Grits can be removed from the slaker and this is also commonly used as a good purging point. A third way to open the mill cycle is to remove lime mud. Lime mud is usually used as a pre-coat on dregs filters or in filters intended for green liquor purification. This opens the lime cycle, where P, Mg, Al and Si are known to accumulate. ESP ash both from the recovery boiler and lime kiln can be removed. K and Cl accumulate in the recovery boiler ESP ash, meaning that mills can influence Cl and K levels by removing ESP ash.

One of the mills, participating in this project, does not dump recovery boiler ESP ash from the process at all and recycles everything back to the cycle. When comparing this mill's Cl and K results, no detectable difference can be seen that could be linked to the mill not removing ash.

Two mills out of the six Finnish pulp mills do not use lime mud in dregs filters. Half of the mills have also decided to remove lime kiln ESP ash. The removal of lime mud and ESP ash are optimal ways for P, Al and Si to get out of the recovery cycle. It would be interesting to analyze if the removal of lime mud and ash creates a difference in the result. This was, however, not studied in this project.

8. Summary and conclusions

The objective of this work is to obtain a better understanding of pulp mill non-process elements. In this work, NPE concentration data from six Finnish Kraft pulp mills are analyzed and compared to data available in literature. This work aims to address the following research questions:

i) Does the geographic location (north vs. east) influence the Finnish mill NPE levels?
ii) How have NPE levels changed in Finnish pulp mills since the 1990s?
iii) How do the present data compare to literature data on pulp mill NPE levels in North America (geographic location) as well as South America (geographic location and pulping wood species eucalyptus)?

The NPE results from the mills in this project are in line with literature data. Some variations and peak values are detectable, but the elements seem overall to behave as described in literature.

Most of the NPE levels are relatively similar between the six Kraft pulp mills, however, some noteworthy differences between the mills were identified.

Mill A stood out from the other mills, because it tends to have very low concentrations for elements such as Ca, Al, Si and P throughout the cycle.

In most of the sampling points Mn and Mg seem to mirror each other, meaning that the mills having high Mn values also have higher Mg values. A possible reason for this could be that Mg and Mn originate from the same source in the process. This could explain why the elements behave similarly in the mills.

One observation made from the Cl and K results, is that Mill C and Mill D have exceptionally low Cl values throughout the cycle. Mill C has also the lowest K values. The reason for the lower value was, however, not studied further in this project.

Mill C had a kaolin contamination during the sampling period and has, therefore, the highest values for Al and Si in its samples. Mill E has a strange Si peak in weak black liquor, which could be due to sample or analysis errors. Mill B had lime mud in its green liquor dregs sample, which is why its P and Ca values were higher in the sample than for the other mills.

The geographical location (north vs. east) of the mill does not seem to have an impact on the NPE values in the mills participating in this study. At least in Finland, it would seem that the location of the raw material does not have a large impact on the NPE concentrations overall. For north vs. east, only roughly 10% of the performed t-test results were significant.

When comparing the results of this study with Finnish results from the ‘90s and early ‘00s, some interesting observations can be made. The landfill waste material from pulp mills has decreased by about 90% from 1992 (Heikkinen, 2018). The NPE levels found in Finnish pulp mills today, have not, however, changed much compared to the older results. This indicates that the mills are able to remove NPEs more effectively with less dregs. A factor that could contribute to the NPE concentration in mills today as well, is better quality makeup lime and makeup chemicals, with less NPEs in them.

When comparing older and present Finnish results, the share of significant t-test results was about 35%. Some NPEs were systematically lower in weak black liquor and white liquor, compared to older Finnish results. However, in the present data, P was consistently higher in as-fired black liquor, ESP ash and green liquor. One reason could be that mills in this study add more side streams to the cycle, for instance the addition of biosludge could increase the amount of P in the recovery cycle. The results from the ESP ash sample point tends to have higher NPE values in this project's results compared to older Finnish results.

When comparing this project's results to older North American results, over 50% of the t-tests had a significant result. The Finnish values are lower for some NPEs in weak black liquor compared to North American results. The ESP ash results were higher in the present Finnish results compared to North American data. The lime mud NPE levels were also higher for some elements in the present Finnish results, as compared to the references found from North America.

P and K are also higher in the Finnish results. One reason for the higher K level could be because of the raw material. Another interesting reflection is that more NPEs were found in the dregs sample at Finnish mills compared to North American results. This could indicate that the removal of NPEs with dregs is more efficient in the Finnish mills participating in this study.

When comparing the Finnish mills to South American mills with eucalyptus as their raw material, t-tests were not done, due to too few data available. However, qualitatively, Cl, Al and Si were higher in the mills using eucalyptus. The higher concentrations of these elements could possibly be due to the raw material. The South American mills might also have more Cl in their process water, which could be one possible explanation for its higher Cl values.

Future work includes further studies of the impact of the openness/closeness of the chemicals cycle in the mills participating in this study. All mills in this study have different ways, how they operate and how much waste they discard from the system in order to keep the NPE levels low. The addition of biosludge, ash removal, usage of makeup lime and chemicals, removal of dregs, removal of lime mud and the choice of lime kiln fuel can all have an impact on the NPE level found in the cycle. However, in this work, it was not possible to find any clear connections between these factors and mill NPE levels.

All six mills have stated that normal wear of the equipment and pipes are common. NPEs might attribute to the damage, but their presence is not seen as the sole reason for the wear of apparatuses. No severe and long-lasting NPE problems seem to be found in mills. These statements about the mill conditions are made from the perceptions gained from the interviews that were conducted with the mills personnel and are solely based on their subjective opinions.

An observation made from the interviews was that sudden changes in NPE levels, for instance, found in side streams, could create severe problems in mills. The kaolin case in Mill C, is a good example on how sudden peaks of some NPE levels in the recovery cycle can quickly cause damage to the process.

When mills know which parameters and factors increase NPE levels, resulting in increased scaling, corrosion and deposit formation, they can prepare themselves better for the impact and damage the NPEs might create. The best and cheapest way, would be to prevent and control the accumulation of NPEs and formation of scales, deposits and dead load, before they become too severe.

As the mills effluent closure increases, in order to meet stricter emission and waste regulations, and as mills want to become more environmentally friendly, the symptoms that can be seen in today's mills caused by NPEs, could potentially become a more severe problem in the future. According to the mill interviews, Finnish mills do not seem to have any consistent severe problems with the NPEs during normal steady state operation of the process. The exception is process disturbances. All the mills are aware of the negative impact the NPEs can have on their process and seem to actively follow the concentration levels of several NPEs regularly, in order to know when they could start to cause problems.

9. Swedish summary – Processfrämmande ämnen i sex finska cellulosafabriker

Utsläppskrav från myndigheterna på finska cellulosafabriker har blivit allt mer strikta under de senaste årtionden. Strängare miljökrav har även motiverat cellulosafabriker att minska sina utsläpp för att kunna bli miljövänligare i sin verksamhet. Finska cellulosafabriker har effektivt minimerat sina utsläpp under de senaste tjugofem åren, då deras avfall har minskat med över 90% sedan 1992 (Heikkinen, 2018).

Minimeringen av avfallsströmmar har dock orsakat nya utmaningar i fabriker, då den har lett till att processfrämmande ämnen anrikas allt mer i kemikalieåtervinningscykeln. Processfrämmande ämnen är de ämnen som inte aktivt deltar i cellulosaframställningsprocessen och kan i vissa fall vara skadliga ifall de anrikas i processen. Även användningen av biobränslen och minskningen av färskvatten i fabrikerna kan orsaka en ökning av dessa ämnen. Dessa oorganiska komponenter kan orsaka mycket problem i fabrikerna då de kan korrodera och skada ytorna på apparaturen. Processfrämmande ämnen kan även öka barlasten i processen eller stocka filter och rör. (Salmenoja, et al., 2009) (Svensson, 2012)

Syftet med detta arbete är att kartlägga hur processfrämmande ämnen fördelas inom processen vid sex finska cellulosafabriker. Avsikten är att jämföra ifall fabrikernas geografiska läge utgör en skillnad på hur mycket processfrämmande ämnen förekommer i kemikalieåtervinningscykeln i cellulosafabrikerna. Tre av de sex fabrikerna är stationerade i norra Finland och tre är stationerade i östra Finland. En inblick ges även i vilka andra faktorer så som användning av olika råmaterial, bränslen och olika apparaturval i fabriker påverkar anrikningen av dessa ämnen. Resultaten från detta arbete jämförs även med äldre studier från både Finland, Nordamerika och Sydamerika.

Inom ramen av arbetet utfördes det provtagningar hos de sex deltagande fabrikerna. Sju provtagningsställen i återvinningscykeln analyserades för åtta processfrämmande ämnen och för lutkemikalierna. Prov togs från följande punkter i återvinningscykeln: tunnlut, svartlut, ESP aska, grönlut, grönlutsslam, vitlut och mesa. Ämnena som analyserades var fosfor (P), aluminium (Al), kisel (Si), kalcium (Ca), magnesium (Mg), mangan (Mn), kalium (K) och klor (Cl) samt lutkemikalierna natrium (Na) och svavel (S). Fabriksintervjuer vid varje deltagande fabrik utfördes under arbetets lopp. Syftet med intervjuerna var att få en bättre helhetsbild av vilka problem processfrämmande ämnen orsakat vid fabrikerna.

Eftersom processfrämmande ämnen beter sig varierande i återvinningscykeln kan de grovt delas in i två olika grupper: de ämnen som fälls ut i grönlut och rensas från processen med grönlutsslammet och de ämnen som är lösliga i alkaliska lösningar och ackumuleras istället i lutcykeln och mesacykeln. Ämnenas komplexitet har dock orsakat att det inte är lätt att bli av med elementen snabbt och effektivt från processen. Elementen kan reagera med varandra och bilda stora komplexa komponenter vars löslighet kan också ändras, vilket gör det mer komplicerat att avlägsna processfrämmande ämnen från processen. (Ulmgren, 1997) (Wolf, et al., 2017)

Dessa ämnen kommer främst med råmaterialet d.v.s. med veden in i processen. Andra strömmar som ämnena kan komma in i processen genom är med processvattnet, kemikalietillskottet, kalktillskottet, bränslet i mesaugnen och förbränningen av slam från vattenreningsverket i sodapannan. (Gu & Edwards, 2004) (Salmenoja, et al., 2009)

I och med att avfallsströmmarna stryps ned kommer andelen sidoströmmar och kvalitén av bränsle i mesaugnen att ha en större påverkan på vilka halter av processfrämmande ämnen som förekommer i återvinningscykeln. Därför kommer det att bli allt viktigare för fabriker att aktivt följa med halterna av processfrämmande ämnen.

I arbetet jämfördes fabrikerna i norra Finland med fabrikerna i östra Finland. Resultatet av jämförelsen var att den geografiska positionen i Finland inte påverkar mycket på halten av processfrämmande ämnen.

När man jämför detta projekts resultat med data från äldre finska vetenskapliga artiklar kan man dock utskilja större skillnader (Holamo, 2000) (Järvinen, et al., 1995) (Salmenoja, et al., 2004). Halten av fosfor var klart högre i data från detta projekt jämfört med äldre data. Orsaken kan vara att fabriker nuförtiden tillför processen flera sidoströmmar som kan innehålla fosfor, exempelvis biobränslen eller förbränning av slam i sodapannan. Halterna av de resterande processfrämmande ämnena uppvisade inte lika stora skillnader. När man tar i beaktande att avfallet från fabrikerna har minskat sedan 1992 med över 90% är det dock positivt, att halterna inte stigit ytterligare. Detta tyder på att fabriker nuförtiden är kapabla att avlägsna mera slaggämnen från processen med mindre avfall, vilket är en mycket positiv utveckling. Orsaken kan även vara att fabrikerna använder bättre tillskotts kemikalier och kalk än vad de gjorde innan.

Även i jämförelse med data från amerikanska fabriker kunde man se att fosforhalten var högre överlag i detta projekts resultat. Resultaten från detta projekt visade dock mera processfrämmande ämnen i grönlutsslammet, vilket tyder på att fabrikerna i Finland nuförtiden kan avlägsna slaggämnen bättre från processen.

Apparaturen i fabriken kan också påverka halterna i processen. När fabrikernas grönlutsrening jämfördes var användningen av filter i grönlutsreningen bättre än användningen av en grönlutsklargörare. De fabriker som använde filter kunde effektivare avlägsna processfrämmande ämnen och hade således lägre halter av dessa ämnen i den renade grönluten. Andra väsentliga skillnader mellan fabrikerna kunde inte fastställas, utan kräver vidare forskning.

Processfrämmande ämnens negativa och ackumulerande påverkan på processen blir aktuellt då fabrikerna minskar på sina utsläpp och processflödena koncentreras. Ökad användning av biobränslen i fabrikerna kommer även att påverka halterna av dessa oorganiska komponenter i processen. Därför krävs det bättre teknologier för att rena flödena i återvinningscykeln från processfrämmande ämnen och en bättre förståelse för hur ämnena egentligen beter sig i processen.

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Appendix A

Raw sample data for Mill A, Mill B, Mill C, Mill D, Mill E and Mill F. Tables A1- A6 contain data for each pulp mill at the seven sample points, weak black liquor, as-fired black liquor, ESP ash, green liquor, green liquor dregs, white liquor and lime mud. The elements analyzed were aluminum, silicon, calcium, phosphorous, magnesium, manganese, chlorine, potassium, sodium and sulfur. The tables contain minimum, maximum and the average value for each sample point and element.

Table A7 contains the average value for Hg and F in as-fired black liquor sample point. All F and Hg values were under the detection limit.

Table A 1 Mill A sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill A		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	20.7	mg/kg	19.7	127.7	70.5	52.3	171.3	54.9	2053.3	21166.7	200333.3	53533.3
WBL	Min	20.6	mg/kg	19.6	127.0	70.7	51.9	167.0	54.8	2040.0	21100.0	181000.0	53200.0
WBL	Max	20.9	mg/kg	19.9	129.0	71.2	52.7	178.0	55.4	2080.0	21200.0	224000.0	54000.0
ABL	Avg	78.9	mg/kg	21.1	145.3	124.7	79.2	286.7	68.8	3163.3	29966.7	193333.3	61400.0
ABL	Min	78.5	mg/kg	20.7	145.0	124.0	77.5	279.0	68.3	3120.0	29600.0	187000.0	59800.0
ABL	Max	79.2	mg/kg	21.5	146.0	126.0	80.2	292.0	69.3	3220.0	30400.0	203000.0	63800.0
ESP A	Avg	100.0	mg/kg	7.5	64.3	50.7	35.7	106.3	43.6	11033.3	32533.3	258000.0	174000.0
ESP A	Min	100.0	mg/kg	7.3	63.0	50.0	35.0	98.9	43.3	11000.0	31800.0	255000.0	173000.0
ESP A	Max	100.0	mg/kg	7.6	66.0	52.0	36.0	112.0	44.0	11100.0	33200.0	261000.0	175000.0
GL	Avg		mg/l	5.2	57.7	7.3	30.0	2.5	2.2	880.0	10900.0	86500.0	28566.7
GL	Min		mg/l	5.1	57.0	7.1	30.0	2.5	2.2	880.0	10900.0	85600.0	28500.0
GL	Max		mg/l	5.4	59.0	7.4	30.0	2.5	2.3	880.0	10900.0	87800.0	28600.0
GL D	Avg	24.6	mg/kg	758.3	492.0	18533.3	304.3	16633.3	4366.7	2723.3	29466.7	285000.0	96600.0
GL D	Min	24.5	mg/kg	749.0	486.0	18200.0	289.0	16500.0	4330.0	2680.0	28900.0	279000.0	95900.0
GL D	Max	24.7	mg/kg	774.0	503.0	19100.0	322.0	16900.0	4430.0	2780.0	30500.0	294000.0	97200.0
WL	Avg		mg/l	6.2	61.3	10.5	21.7	0.5	3.6	903.3	11133.3	90366.7	29233.3
WL	Min		mg/l	6.1	61.0	10.5	21.0	0.5	3.6	900.0	10900.0	86400.0	29100.0
WL	Max		mg/l	6.2	62.0	10.5	22.0	0.5	3.6	910.0	11300.0	93700.0	29400.0
LM	Avg	85.5	mg/kg	434.0	287.7	357666.7	6970.0	6276.7	484.0	6.7	216.0	8153.3	265.7
LM	Min	85.1	mg/kg	423.0	269.0	345000.0	6460.0	5820.0	447.0	6.5	195.0	7330.0	222.0
LM	Max	85.7	mg/kg	447.0	300.0	379000.0	7280.0	6540.0	506.0	7.1	237.0	8580.0	289.0

Table A 2 Mill B sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill B		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	15.8	mg/kg	40.6	279.0	155.8	74.1	113.2	43.7	2181.7	24833.3	165666.7	59200.0
WBL	Min	15.7	mg/kg	38.0	274.0	142.0	66.0	102.0	42.3	2100.0	24600.0	160000.0	58300.0
WBL	Max	15.9	mg/kg	43.5	287.0	172.0	82.1	130.0	45.4	2260.0	25400.0	176000.0	60500.0
ABL	Avg	75.3	mg/kg	53.1	303.0	233.3	73.6	135.7	56.5	3193.3	26600.0	194333.3	63500.0
ABL	Min	75.1	mg/kg	52.2	300.0	229.0	71.8	135.0	56.3	3130.0	26500.0	193000.0	63100.0
ABL	Max	75.4	mg/kg	54.5	305.0	237.0	75.7	136.0	56.8	3240.0	26800.0	197000.0	63800.0
ESP A	Avg	100.0	mg/kg	14.0	125.3	104.3	39.7	59.8	37.1	10866.7	54700.0	259000.0	182000.0
ESP A	Min	100.0	mg/kg	13.5	121.0	104.0	39.0	58.3	36.8	10500.0	54000.0	256000.0	181000.0
ESP A	Max	100.0	mg/kg	14.5	129.0	105.0	40.0	61.0	37.3	11200.0	55500.0	262000.0	183000.0
GL	Avg		mg/l	12.0	130.0	3.3	42.3	0.2	1.1	936.7	11533.3	84900.0	27700.0
GL	Min		mg/l	12.0	130.0	3.1	42.0	0.2	1.1	930.0	11500.0	80000.0	27400.0
GL	Max		mg/l	12.0	130.0	3.4	43.0	0.2	1.1	940.0	11600.0	91800.0	28100.0
GL D	Avg	55.4	mg/kg	6516.7	5910.0	285666.7	3650.0	33400.0	12366.7	21.1	641.3	7326.7	14833.3
GL D	Min	55.3	mg/kg	6490.0	5870.0	279000.0	3510.0	33000.0	12100.0	19.8	591.0	7140.0	14800.0
GL D	Max	55.6	mg/kg	6560.0	5980.0	298000.0	3900.0	33900.0	12700.0	22.9	681.0	7550.0	14900.0
WL	Avg		mg/l	17.0	136.0	31.0	11.0	0.8	1.9	966.7	12300.0	96466.7	29733.3
WL	Min		mg/l	17.0	135.0	26.0	11.0	0.7	1.8	930.0	12200.0	93200.0	29500.0
WL	Max		mg/l	17.0	137.0	37.0	11.0	0.8	1.9	990.0	12400.0	98100.0	29900.0
LM	Avg	75.8	mg/kg	533.3	924.7	396000.0	8383.3	3056.7	101.3	11.0	317.3	7700.0	209.0
LM	Min	75.1	mg/kg	526.0	904.0	386000.0	8230.0	2950.0	101.0	10.7	303.0	7590.0	195.0
LM	Max	76.6	mg/kg	538.0	942.0	403000.0	8500.0	3210.0	102.0	11.1	346.0	7790.0	221.0

Table A 3 Mill C sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill C		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	16.0	mg/kg	234.7	343.7	144.3	83.0	59.3	40.6	699.0	10633.3	196000.0	59533.3
WBL	Min	16.0	mg/kg	234.0	341.0	144.0	81.7	58.6	39.9	687.0	10600.0	180000.0	59600.0
WBL	Max	16.0	mg/kg	236.0	347.0	145.0	84.6	63.3	40.9	723.0	10700.0	206000.0	59700.0
ABL	Avg	77.5	mg/kg	354.7	550.3	242.7	141.0	201.3	84.6	917.0	14500.0	206000.0	85200.0
ABL	Min	77.2	mg/kg	350.0	548.0	242.0	141.0	199.0	84.1	900.0	14400.0	199000.0	84900.0
ABL	Max	78.0	mg/kg	363.0	552.0	243.0	141.0	205.0	85.0	932.0	14600.0	210000.0	85800.0
ESP A	Avg	100.0	mg/kg	45.0	316.3	154.0	46.7	112.7	77.4	3300.0	34100.0	317333.3	220333.3
ESP A	Min	100.0	mg/kg	44.3	311.0	150.0	44.0	111.0	76.0	3200.0	33500.0	303000.0	215000.0
ESP A	Max	100.0	mg/kg	46.4	327.0	160.0	50.0	116.0	79.1	3400.0	34400.0	337000.0	229000.0
GL	Avg		mg/l	138.3	243.3	13.7	49.3	2.1	1.9	286.7	4580.0	73333.3	27600.0
GL	Min		mg/l	136.0	240.0	13.0	49.0	2.1	1.9	280.0	4560.0	68900.0	27400.0
GL	Max		mg/l	141.0	250.0	15.0	50.0	2.1	2.0	290.0	4590.0	76300.0	27800.0
GL D	Avg	17.3	mg/kg	9850.0	8360.0	106666.7	1070.0	35166.7	13500.0	556.7	8153.3	178333.3	68366.7
GL D	Min	17.1	mg/kg	9770.0	8260.0	106000.0	1060.0	34600.0	13200.0	550.0	7990.0	175000.0	62200.0
GL D	Max	17.6	mg/kg	10000.0	8540.0	108000.0	1080.0	36000.0	13800.0	560.0	8300.0	182000.0	77000.0
WL	Avg		mg/l	140.3	243.3	24.7	8.5	0.7	1.8	270.0	4606.7	76633.3	27933.3
WL	Min		mg/l	139.0	240.0	23.0	6.7	0.7	1.7	270.0	4590.0	76000.0	27700.0
WL	Max		mg/l	142.0	250.0	27.0	10.0	0.8	1.9	270.0	4620.0	77800.0	28200.0
LM	Avg	81.1	mg/kg	1086.7	1310.0	382000.0	7933.3	2940.0	20.9	3.9	112.3	7386.7	712.3
LM	Min	81.1	mg/kg	1070.0	1290.0	379000.0	7820.0	2890.0	20.6	3.6	66.0	7340.0	704.0
LM	Max	81.1	mg/kg	1100.0	1330.0	387000.0	8040.0	2970.0	21.1	4.1	156.0	7460.0	722.0

Table A 4 Mill D sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill D		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	18.0	mg/kg	41.1	341.7	124.7	64.7	193.7	51.1	770.7	16300.0	191333.3	52366.7
WBL	Min	17.9	mg/kg	41.0	341.0	124.0	64.1	192.0	50.7	770.0	16300.0	185000.0	52100.0
WBL	Max	18.1	mg/kg	41.2	343.0	126.0	65.4	196.0	51.6	771.0	16400.0	198000.0	52900.0
ABL	Avg	83.9	mg/kg	52.4	377.7	329.3	128.0	279.3	85.4	1133.3	23066.7	201666.7	80000.0
ABL	Min	83.8	mg/kg	52.1	376.0	327.0	127.0	270.0	84.6	1130.0	23000.0	197000.0	79500.0
ABL	Max	84.0	mg/kg	52.7	380.0	331.0	129.0	290.0	86.1	1140.0	23100.0	205000.0	81000.0
ESP A	Avg	100.0	mg/kg	25.2	269.3	255.3	55.7	144.3	91.8	4070.0	58533.3	333000.0	193666.7
ESP A	Min	100.0	mg/kg	23.1	255.0	244.0	49.0	139.0	89.4	3990.0	57800.0	318000.0	192000.0
ESP A	Max	100.0	mg/kg	27.7	279.0	265.0	60.0	148.0	93.2	4210.0	58900.0	345000.0	196000.0
GL	Avg		mg/l	9.4	179.3	5.4	65.0	1.2	1.7	356.7	8410.0	80533.3	28233.3
GL	Min		mg/l	9.3	178.0	5.0	64.0	1.0	1.5	350.0	8320.0	76700.0	28100.0
GL	Max		mg/l	9.4	181.0	5.8	66.0	1.5	1.9	360.0	8460.0	83600.0	28400.0
GL D	Avg	47.5	mg/kg	14433.3	27200.0	138666.7	425.0	97400.0	26966.7	67.2	6136.7	115666.7	32000.0
GL D	Min	47.2	mg/kg	14100.0	26700.0	123000.0	378.0	95400.0	26600.0	61.6	5970.0	114000.0	31800.0
GL D	Max	47.9	mg/kg	14900.0	27800.0	152000.0	464.0	100000.0	27400.0	71.6	6460.0	118000.0	32400.0
WL	Avg		mg/l	23.3	220.3	12.3	16.0	0.7	5.6	356.7	8410.0	79100.0	28466.7
WL	Min		mg/l	23.0	218.0	12.0	15.0	0.7	5.6	350.0	8320.0	77000.0	28100.0
WL	Max		mg/l	24.0	223.0	13.0	17.0	0.7	5.7	360.0	8460.0	81000.0	28700.0
LM	Avg	76.5	mg/kg	630.7	972.7	384333.3	8326.7	4993.3	480.0	6.4	221.7	7796.7	384.3
LM	Min	76.1	mg/kg	624.0	949.0	376000.0	8170.0	4950.0	478.0	6.2	178.0	7700.0	353.0
LM	Max	76.7	mg/kg	638.0	998.0	391000.0	8410.0	5020.0	484.0	6.6	275.0	7870.0	414.0

Table A 5 Mill E sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill E		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	18.0	mg/kg	74.0	775.3	162.0	75.4	128.0	55.5	2120.0	17533.3	199666.7	50100.0
WBL	Min	17.8	mg/kg	73.0	756.0	158.0	73.3	124.0	54.4	2100.0	17400.0	204000.0	48900.0
WBL	Max	18.2	mg/kg	75.1	786.0	165.0	77.7	136.0	56.1	2140.0	17700.0	209000.0	51100.0
ABL	Avg	77.6	mg/kg	74.0	364.3	402.7	123.7	173.3	66.6	3250.0	25766.7	207000.0	59266.7
ABL	Min	77.4	mg/kg	74.0	361.0	401.0	121.0	169.0	66.5	3150.0	25600.0	202000.0	58300.0
ABL	Max	77.7	mg/kg	74.1	367.0	404.0	125.0	181.0	66.6	3300.0	26000.0	210000.0	60000.0
ESP A	Avg	100.0	mg/kg	20.3	141.7	144.0	46.7	75.7	41.6	10866.7	26500.0	279333.3	146333.3
ESP A	Min	100.0	mg/kg	19.8	140.0	141.0	45.0	74.5	41.4	10800.0	25900.0	277000.0	144000.0
ESP A	Max	100.0	mg/kg	21.1	145.0	146.0	48.0	77.9	41.9	10900.0	27300.0	283000.0	150000.0
GL	Avg		mg/l	17.0	200.0	6.9	51.7	0.4	1.0	980.0	9903.3	101533.3	31200.0
GL	Min		mg/l	17.0	200.0	6.8	51.0	0.3	1.0	980.0	9830.0	98300.0	31000.0
GL	Max		mg/l	17.0	200.0	7.0	53.0	0.4	1.0	980.0	9970.0	104600.0	31300.0
GL D	Avg	39.5	mg/kg	7976.7	7520.0	151000.0	467.7	32033.3	12166.7	1463.3	13533.3	159333.3	52400.0
GL D	Min	39.0	mg/kg	7800.0	7330.0	145000.0	443.0	31400.0	11800.0	1440.0	13400.0	157000.0	51900.0
GL D	Max	39.7	mg/kg	8310.0	7900.0	163000.0	506.0	33200.0	12700.0	1480.0	13600.0	161000.0	52800.0
WL	Avg		mg/l	22.0	176.7	12.0	18.0	0.5	1.3	973.3	9826.7	99566.7	30633.3
WL	Min		mg/l	22.0	170.0	12.0	18.0	0.5	1.2	960.0	9760.0	97500.0	30600.0
WL	Max		mg/l	22.0	180.0	12.0	18.0	0.5	1.3	1000.0	9860.0	101500.0	30700.0
LM	Avg	80.3	mg/kg	337.7	716.7	390333.3	2163.3	2723.3	62.5	4.5	157.3	5093.3	412.3
LM	Min	80.1	mg/kg	334.0	703.0	387000.0	2100.0	2710.0	62.2	2.2	110.0	5000.0	404.0
LM	Max	80.5	mg/kg	344.0	725.0	394000.0	2200.0	2750.0	62.7	6.0	188.0	5150.0	426.0

Table A 6 Mill F sample data for the seven sample points. An average, minimum and maximum values on the sampler results are calculated

Mill F		ds.-%	Unit	Al	Si	Ca	P	Mg	Mn	Cl	K	Na	S
WBL	Avg	17.7	mg/kg	20.6	170.2	134.2	82.0	143.4	50.0	1808.9	25688.9	146777.8	45466.7
WBL	Min	16.7	mg/kg	18.8	144.0	116.0	60.9	115.0	41.9	1700.0	24000.0	141000.0	42200.0
WBL	Max	19.1	mg/kg	22.9	188.0	145.0	95.2	195.0	59.5	1940.0	27900.0	152000.0	48300.0
ABL	Avg	72.1	mg/kg	40.5	201.3	191.3	99.8	159.3	83.5	2596.7	28900.0	176166.7	61866.7
ABL	Min	71.8	mg/kg	38.3	195.0	183.0	94.6	156.0	81.1	2540.0	28500.0	173000.0	60700.0
ABL	Max	72.4	mg/kg	43.6	216.0	199.0	111.0	163.0	84.7	2650.0	29200.0	178000.0	63800.0
ESP A	Avg	100.0	mg/kg	9.3	68.8	66.5	39.0	60.2	48.0	9761.7	62016.7	263833.3	196500.0
ESP A	Min	100.0	mg/kg	5.9	53.0	59.0	22.1	51.9	44.4	9390.0	57200.0	235000.0	183000.0
ESP A	Max	100.0	mg/kg	11.8	81.0	79.0	47.0	70.1	49.5	10200.0	67600.0	283000.0	209000.0
GL	Avg		mg/l	7.6	101.3	19.7	48.0	5.9	4.0	826.7	13433.3	87633.3	27433.3
GL	Min		mg/l	7.3	100.0	19.0	47.0	5.7	3.9	820.0	13400.0	85500.0	27200.0
GL	Max		mg/l	8.0	104.0	21.0	50.0	6.2	4.1	830.0	13500.0	90000.0	27700.0
GL D	Avg	39.2	mg/kg	173.0	108.0	2176.7	90.5	988.0	460.0	1001.7	11766.7	72033.3	24933.3
GL D	Min	39.0	mg/kg	169.0	106.0	2120.0	87.9	970.0	439.0	835.0	11600.0	70400.0	24400.0
GL D	Max	39.3	mg/kg	176.0	110.0	2220.0	92.2	1000.0	475.0	1130.0	12000.0	72900.0	25400.0
WL	Avg		mg/l	8.8	108.0	11.3	21.7	0.5	3.4	863.3	14033.3	92900.0	29266.7
WL	Min		mg/l	8.6	107.0	11.0	21.0	0.5	3.4	860.0	14000.0	90500.0	29200.0
WL	Max		mg/l	9.2	109.0	12.0	22.0	0.6	3.4	870.0	14100.0	94800.0	29400.0
LM	Avg	79.4	mg/kg	418.0	750.0	382166.7	10416.7	4633.3	382.0	9.1	360.8	9266.7	507.5
LM	Min	78.3	mg/kg	413.0	739.0	374000.0	10300.0	4530.0	377.0	5.6	227.0	8330.0	<500
LM	Max	80.4	mg/kg	424.0	769.0	389000.0	10600.0	4690.0	386.0	12.8	448.0	10100.0	635.0

Table A 7 Hg and F results for as-fired black liquor, for all six Kraft pulp mills. All values were under the detection limits

Mill	Sample point		Unit	F	Hg
Mill A	ABL	Avg	mg/kg	<20	<0.01
Mill B	ABL	Avg	mg/kg	<20	<0.01
Mill C	ABL	Avg	mg/kg	<20	<0.01
Mill D	ABL	Avg	mg/kg	<20	<0.01
Mill E	ABL	Avg	mg/kg	<20	<0.01
Mill F	ABL	Avg	mg/kg	<20	<0.01

Appendix B

Hypothesis test T-test: Two-Sample Assuming Unequal Variances

Appendix B.1

North Finland results versus east Finland results

Table B 1 Weak black liquor t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

Weak black liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	30.133	250.11	123.544	69.8056	114.6	46.372	1644.67	18877.78
Variance 1	130.740	9224.86	1613.858	188.490	2375.70	42.671	506429.5	40781944
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	45.237	429.07	140.296	74	155.037	52.22	1566.519	19840.74
Variance 2	544.35	73023.2	286.679	58.889	900.929	6.706	374614.4	19537716
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	10	11	13	13	10	16	14
t Stat	-1.665	-1.87207	-1.1528	-0.800	-2.119	-2.498	0.2498	-0.37196
P(T<=t) one-tail	0.060	0.04535	0.13672	0.2190	0.027	0.0158	0.4030	0.35774
t Critical one-tail	1.782	1.81246	1.79588	1.7709	1.771	1.8125	1.746	1.76131
P(T<=t) two-tail	0.122	0.09070	0.27344	0.4381	0.0539	0.0316	0.8060	0.71549
t Critical two-tail	2.179	2.22814	2.20099	2.1604	2.1604	2.228	2.1199	2.14479

Table B 2 As-fired black liquor t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

As-fired black liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	37.117	332.889	200.222	97.944	207.89	69.989	2424.56	23688.89
Variance 1	307.230	31260.1	3231.94	1050.070	4313.6	149.291	1280107	496711
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	55.622	314.44	307.778	117.144	204	78.472	2326.67	25911.1
Variance 2	217.660	7238.84	8638.13	184.833	3266.19	80.614	883000	6411736
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	10	12	13	11	16	15	15	10
t Stat	-2.13131	0.2820	-2.9616	-1.63910	0.1340	-1.67847	0.1997	-0.890
P(T<=t) one-tail	0.02945	0.3914	0.0055	0.06472	0.4475	0.05698	0.422	0.1971
t Critical one-tail	1.81246	1.7823	1.7709	1.79588	1.7459	1.75305	1.753	1.8125
P(T<=t) two-tail	0.05889	0.7827	0.0110	0.12945	0.8951	0.11396	0.844	0.3943
t Critical two-tail	2.22814	2.1788	2.1604	2.20099	2.1199	2.13145	2.131	2.2281

Table B 3 ESP ash t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

ESP Ash	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	10.75	168.667	103	40.667	92.933	52.7	8400	40444.44
Variance 1	13.047	12989.3	2010.5	25.75	637.71	351.77	14670000	115105278
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	18.244	159.944	155.278	47.094	93.422	60.4278	8232.778	49016.67
Variance 2	51.436	7771.22	6790.32	65.2984	1509.5	561.968	9982738	2.88E+08
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	15	12	13	14	15	15	14
t Stat	-2.668	0.1816	-1.67177	-2.02091	-0.0317	-0.76695	0.10104	-1.2812
P(T<=t) one-tail	0.0102	0.429	0.06021	0.03219	0.4876	0.22751	0.46043	0.11047
t Critical one-tail	1.782	1.75305	1.78229	1.77093	1.7613	1.75305	1.75305	1.76131
P(T<=t) two-tail	0.0205	0.85832	0.12042	0.06438	0.9752	0.45501	0.92086	0.22094
t Critical two-tail	2.1788	2.13145	2.17881	2.16037	2.1448	2.13145	2.13145	2.14479

Table B 4 Green liquor t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

Green liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	8.6167	143.667	8.0667	40.556	1.6	1.7556	701.111	9004.44
Variance 1	13.7457	6577	20.9850	72.028	1.1325	0.2603	97236.1	1108745
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	11.3333	160.2222	10.6444	54.889	2.500	2.2222	721.111	10582.2
Variance 2	18.6575	2033	46.6053	61.361	6.6775	1.8169	79136.1	4994194
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	13	14	16	11	10	16	14
t Stat	-1.3005	-0.5353	-0.94064	-3.7231	-0.9661	-0.9714	-0.1429	-1.1803
P(T<=t) one-tail	0.1089	0.3008	0.18142	0.0009	0.1774	0.1771	0.4441	0.1287
t Critical one-tail	1.7823	1.7709	1.76131	1.7459	1.7959	1.8125	1.7459	1.7613
P(T<=t) two-tail	0.2179	0.6015	0.36284	0.0019	0.3547	0.3543	0.8882	0.2575
t Critical two-tail	2.1788	2.1604	2.14479	2.1199	2.20099	2.2281	2.1199	2.1448

Table B 5 White liquor t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

White liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	11.5833	146.8889	22.0556	13.711	0.6667	2.4333	713.33	9346.667
Variance 1	35.2096	6286.1111	91.4653	37.579	0.0175	0.77	111575	12906625
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	18.0556	168.3333	11.8889	18.556	0.5778	3.4333	731.111	10756.67
Variance 2	48.2828	2415.250	0.36111	6.5278	0.0094	3.5775	81286.1	6418800
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	13	8	11	15	11	16	14
t Stat	-1.93110	-0.68967	3.18285	-2.188	1.6246	-1.4388	-0.1214	-0.96222
P(T<=t) one-tail	0.03872	0.25126	0.00647	0.0256	0.0625	0.0890	0.45243	0.17613
t Critical one-tail	1.78229	1.77093	1.85955	1.7959	1.753	1.79588	1.74588	1.76131
P(T<=t) two-tail	0.07743	0.50253	0.01294	0.051	0.1251	0.17805	0.90485	0.35226
t Critical two-tail	2.17881	2.16037	2.30600	2.2009	2.1315	2.20099	2.11991	2.14479

Table B 6 Lime mud t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

Lime mud	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	483.667	840.7778	378555.556	7762.2222	4091.11	202.067	7.201	215.22
Variance 1	3035.47	200187	39302778	448369.44	2733936	46184.9	9.522	8651.9
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	462.111	813.111	385611.11	6968.8889	4116.67	308.178	6.666	246.61
Variance 2	17211.2	14717.7	31423611	13815861	1116981	35746	5.076	9361
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	9	9	9	14	16	15	16
t Stat	0.43834	0.17904	-1.02740	0.63016	-0.0391	-1.112	0.420	-0.7016
P(T<=t) one-tail	0.33446	0.43094	0.16553	0.27213	0.4847	0.141	0.340	0.2465
t Critical one-tail	1.78229	1.83311	1.83311	1.83311	1.7613	1.7459	1.753	1.7459
P(T<=t) two-tail	0.66893	0.86187	0.33105	0.54425	0.9694	0.2825	0.680	0.49299
t Critical two-tail	2.17881	2.26216	2.26216	2.26216	2.1448	2.1199	2.131	2.1199

Table B 7 Green liquor dregs t-test results comparing east Finland and north Finland results from this project. When the two-tail p-value is below 0.05 is the difference significant

Green liquor dregs	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North*	*North*	*North*	*North*	*North*	*North*	*North*	*North*
Mean 1	3637.5	4920.67	136955	1674.77	28400	10077.8	1100.36	12753.8
Variance 1	9.9E+06	1.2E+07	1.4E+10	2.3E+06	7.9E+07	1.9E+07	1.5E+06	1.7E+08
Observations 1	6	9	9	9	9	9	9	9
Variable 2	*East*	*East*	*East*	*East*	*East*	*East*	*East*	*East*
Mean 2	7527.67	11609.3	97281.1	327.722	43473.8	13197.8	844.078	10478.9
Variance 2	3.8E+07	1.5E+08	5.2E+09	3.3E+04	1.8E+09	1.3E+08	3.6E+05	1.1E+07
Observations 2	9	9	9	9	9	9	9	9
Hypothesiz Mean Difference	0	0	0	0	0	0	0	0
df	12	9	13	8	9	10	12	9
t Stat	-1.5996	-1.5899	0.8607	2.6367	-1.0383	-0.7615	0.55466	0.5099
P(T<=t) one-tail	0.0678	0.0732	0.2025	0.0149	0.1631	0.23196	0.29466	0.3112
t Critical one-tail	1.7823	1.8331	1.7709	1.8596	1.8331	1.81246	1.78229	1.8331
P(T<=t) two-tail	0.1357	0.1463	0.40498	0.0299	0.3262	0.46392	0.58932	0.6224
t Critical two-tail	2.1788	2.2622	2.1603	2.3060	2.2622	2.22814	2.17881	2.2622

Appendix B.2

Hypothesis test T-test: Two-Sample Assuming Unequal Variances
Older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) (Salmenoja, et al., 2004) were compared to Finnish results from 2018, conducted during this project. Mill C's high Al values are not included in Table B8 – B14. Mill C's Al values are included in table B15.

Table B 8 Weak black liquor liquor comparisons between older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) and this project's results from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

Weak black liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	31.66	277.39	156.429	84.463	128.98	67.857	2350.67	18969.23
Variance 1	771.40	16021	6003.23	536.45	4692.1	293.39	1283575	33276397
Observations 1	41	41	42	41	42	42	36	39
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	39.196	339.6	131.92	71.90	134.819	49.297	1605.59	19359.26
Variance 2	416.41	47183	968.65	121.07	1974.78	32.295	416225	28631184
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	34	22	58	57	48	56	51	36
t Stat	-1.10	-1.133	1.7473	2.822	-0.3926	6.2638	3.0732	-0.2494
P(T<=t) one-tail	0.139	0.1346	0.0429	0.003	0.3482	2.8E-08	0.0017	0.4022
t Critical one-tail	1.69	1.7171	1.6716	1.672	1.677	1.6725	1.675	1.6883
P(T<=t) two-tail	0.277	0.269	0.0859	0.0066	0.6963	5.6E-08	0.0034	0.8044
t Critical two-tail	2.032	2.074	2.0017	2.002	2.0106	2.0032	2.0076	2.0281

Table B 9 As-fired black liquor t-test results comparing (Salmenoja, et al., 2004) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

As-fired black liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Cl**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	33	284	219	71	154	1600	27800
Variance 1	532.5	3293	15705	242.5	6442.5	800000	9.2E+07
Observations 1	5	5	5	5	5	5	5
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	48.22	323.67	254	107.54	205.94	2375.6	24800
Variance 2	322.16	18207	8648	678.71	3571	1020469	2.8E+07
Observations 2	15	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0
df	6	17	5	11	5	7	5
t Stat	-1.345	-0.9707	-0.58	-3.94	-1.35	-1.666	0.671
P(T<=t) one-tail	0.114	0.1727	0.293	0.001	0.118	0.070	0.2659
t Critical one-tail	1.943	1.7396	2.015	1.796	2.015	1.895	2.0150
P(T<=t) two-tail	0.227	0.3453	0.586	0.002	0.236	0.1396	0.5319
t Critical two-tail	2.447	2.1098	2.571	2.201	2.571	2.365	2.5706

Table B 10 ESP ash t-test results comparing (Salmenoja, et al., 2004) and this project's results from 2018. this projects data from 2018 for Al, Si, Ca, P, Mg, Cl and K. (Holamo, 2000) data was also available for Cl and K. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

ESP Ash	**Al**	**Si**	**Ca**	**P**	**Mg**	**Cl**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	6	105	77	25	46	8200	52862.5
Variance 1	30	837.5	732.5	150	67.5	6320000	2.5E+08
Observations 1	5	5	5	5	5	8	8
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.2467	164.3056	129.1389	43.8806	93.178	8316.39	44730.56
Variance 2	48.494	9789.769	4864.994	53.783	1010.5	11608690	2.09E+08
Observations 2	15	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0
df	9	21	18	5	21	18	12
t Stat	-3.043	-2.2235	-2.554	-3.288	-5.6534	-0.09716	1.237
P(T<=t) one-tail	0.00697	0.01864	0.009967	0.0109	6.52E-06	0.46184	0.1199
t Critical one-tail	1.8331	1.7207	1.734	2.015	1.7207	1.7340636	1.7823
P(T<=t) two-tail	0.0139	0.0373	0.01994	0.0218	1.3E-05	0.9236714	0.2397
t Critical two-tail	2.2622	2.0796	2.1009	2.57058	2.0796	2.100922	2.179

Table B 11 Clarified green liquor t-test results comparing (Holamo, 2000) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

Green liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	10.0556	163.778	10.55	31.444	2.1133	4.6667	9787.778
Variance 1	48.22278	2316.694	82.90571	43.028	8.353	0.6933	11462944
Observations 1	9	9	8	9	9	3	9
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	10.2467	151.9444	9.3556	47.722	2.05	1.9889	9793.333
Variance 2	17.468381	4124.29	33.566	117.154	3.89	1.035	8226788
Observations 2	15	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0
df	12	21	10	24	12	3	14
t Stat	-0.07483	0.53647	0.3415767	-4.8446	0.0592	4.984	-0.0042
P(T<=t) one-tail	0.470792	0.29863	0.369869	3.08E-05	0.4769	0.0076	0.498345
t Critical one-tail	1.78229	1.7207429	1.812461	1.71088	1.7823	2.3534	1.76131
P(T<=t) two-tail	0.94158	0.597269	0.739739	6.17E-05	0.954	0.0155	0.9967
t Critical two-tail	2.17881	2.07961	2.228139	2.0639	2.179	3.1824	2.144787

Table B 12 White liquor t-test results comparing (Järvinen, et al., 1995) (Holamo, 2000) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

White liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	17.1333	152.8333	26.07838	12.6417	0.885	4.15	1250	8194
Variance 1	332.50	3793.06	1022.261	29.1140	0.51354	1.875	323871	8891930
Observations 1	36	36	37	36	37	34	32	37
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.4667	157.611	16.9722	16.133	0.6222	2.9333	722.2	10052
Variance 2	50.9367	4216.49	70.5727	26.968	0.01477	2.31059	90842	9620579
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	49	33	45	35	40	32	48	33
t Stat	0.46894	-0.259	1.621211	-2.299	2.16846	2.8399	4.285	-2.110
P(T<=t) one-tail	0.32060	0.3985	0.05598	0.0138	0.01806	0.0039	4.3E-05	0.0212
t Critical one-tail	1.67656	1.69236	1.679428	1.6896	1.68385	1.69389	1.677	1.692
P(T<=t) two-tail	0.6412	0.7970	0.11196	0.0276	0.0361	0.0078	8.7E-05	0.04249
t Critical two-tail	2.00958	2.0345	2.014103	2.0301	2.021	2.03693	2.0106	2.03451

Table B 13 Lime mud t-test results comparing (Holamo, 2000) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

Lime mud	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	286.88	1155	381888.89	6958.8	6986.667	379	378.25
Variance 1	48978.1	60857.1	1686611111	13685984	80191725	8968.67	303630
Observations 1	8	8	9	8	9	4	8
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	470.733	826.944	382083.333	7365.56	4103.89	255.122	230.91
Variance 2	11038.5	101334	212919118	6879180	1812369.3	41536.2	8737.5
Observations 2	15	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0
df	9	17	9	10	8	10	7
t Stat	-2.2201	2.8514	-0.013776	-0.281197	0.9603	1.83654	0.7515
P(T<=t) one-tail	0.02678	0.00552	0.49465	0.3921461	0.1825	0.04807	0.2384
t Critical one-tail	1.83311	1.73961	1.83311	1.812461	1.8595	1.81246	1.8946
P(T<=t) two-tail	0.05355	0.01104	0.9893	0.784292	0.3650	0.09614	0.4769
t Critical two-tail	2.26216	2.109816	2.262158	2.2281389	2.3060	2.2281	2.3646

Table B 14 Green liquor dregs t-test results comparing (Holamo, 2000) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

Green liquor dregs	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**K**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	3881.25	6913.75	174666.7	2315	33812.22	16150	7012.5
Variance 1	1289527	21093913	5.0E+09	11268229	599488844	619566667	87008993
Observations 1	8	8	9	8	9	4	8
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	6618	8265	117118	1001.25	35936.889	11637.778	11616.333
Variance 2	26371545	86805554	9.4E+09	1585801.9	952757602	73667248	85666732
Observations 2	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0
df	20	24	21	8	20	5	13
t Stat	-2.146	-0.4948	1.7519	1.0738799	-0.19432	1.01968	-1.16430
P(T<=t) one-tail	0.0221	0.3126	0.0472	0.1570983	0.4239401	0.1773277	0.132612
t Critical one-tail	1.7247	1.71088	1.7207	1.8595480	1.7247182	2.015048	1.77094
P(T<=t) two-tail	0.0443	0.62527	0.0944	0.314197	0.847880	0.354655	0.265225
t Critical two-tail	2.0860	2.063899	2.0796	2.306004	2.085963	2.570582	2.160369

Table B 15 T-test results of older Finnish data (Holamo, 2000) compared with this projects data from 2018 with the Mill C high Al values included. When the two-tail p-value is below 0.05 is the difference significant

Al with Mill C	**WBL**	**ABL**	**ESP A**	**GL**	**WL**	**LM**
Variable 1	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*	*Older Finnish results*
Mean 1	31.65854	33	6	10.0556	17.1333333	286.875
Variance 1	771.3805	532.5	30	48.22	332.502286	48978.125
Observations 1	41	5	5	9	36	8
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	71.774	99.2944	20.2111111	31.594	36.2777778	573.388889
Variance 2	5962.05	14081.7	170.578987	2427.81	2335.11712	64908.281
Observations 2	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0
df	19	20	17	18	19	15
t Stat	-2.1441	-2.2237	-3.6123524	-1.8189	-1.6240156	-2.9048761
P(T<=t) one-tail	0.02258	0.018927	0.00107523	0.0428	0.06042337	0.00544324
t Critical one-tail	1.72913	1.72472	1.73960673	1.7341	1.72913281	1.75305036
P(T<=t) two-tail	0.04517	0.037854	0.00215047	0.0856	0.12084674	0.01088649
t Critical two-tail	2.09302	2.08596	2.10981558	2.101	2.09302405	2.13144955

Appendix B.3

Hypothesis test T-test: Two-Sample Assuming Unequal Variances

Older North American results (Empie, et al., 1999) (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004)(Taylor & Bossons, 2006) (Taylor, 2007) were compared to this project's results from 2018. Weak black liquor and as-fired black liquor could not be tested with the t-test because literature references did not have enough good data points. Richardson 1998 and Frederick 2000 use mg/kg to present green and white liquor results. The reference values are converted to mg/l by using three possible green liquor densities 1.1 kg/l, 1.15 kg/l and 1.20 kg/l. Mill C's high Al values are not included in the t-tests except in Table B 25, Table B 26 and Table B 27.

Table B 16 ESP ash t-test results comparing (Frederick, et al., 2000) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

ESP Ash	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	14.1	120.2	115.8	18.3	34.367	34.42	1525.2	38902
Variance 1	6.18	333.77	974.09	3.698	8.255	1.454	39756	5.7E+06
Observations 1	6	6	6	6	6	6	6	6
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.247	164.306	129.14	43.88	93.178	56.6	8316.4	44730.6
Variance 2	48.49	9789.8	4865.0	53.783	1010.52	445.8	1.2E+07	2.1E+08
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	19	20	20	22	18	17	17	19
t Stat	-0.5554	-1.8027	-0.6429	-13.47	-7.7547	-4.429	-8.413	-1.644
P(T<=t) one-tail	0.2926	0.0433	0.2638	2.1E-12	1.90E-07	1.8E-04	9.1E-08	0.0583
t Critical one-tail	1.7291	1.7247	1.7247	1.7171	1.7341	1.740	1.7396	1.7291
P(T<=t) two-tail	0.5851	0.0865	0.5276	4.2E-12	3.81E-07	3.7E-04	1.8E-07	0.1166
t Critical two-tail	2.0930	2.0860	2.0860	2.07	2.1009	2.11	2.1098	2.0930

Table B 17 Clarified green liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results from 2018.. The density 1.1 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

Green liquor Density 1.1 kg/l	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	12.85	179.98	28.46	24.39	6.33	3.72	550.37	6655.53
Variance 1	72.25	10337.29	508.55	1.99	86.99	4.49	3065.49	1.30E+07
Observations 1	13	6	14	8	14	14	6	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	10.25	151.94	9.36	47.72	2.05	1.99	711.11	9793.33
Variance 2	17.47	4124.29	33.57	117.15	3.89	1.04	83104.58	8.23E+06
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	17	6	14	18	14	18	20	20
t Stat	1.0025	0.6346	3.0907	-8.9767	1.6884	2.8169	-2.2448	-2.5313
P(T<=t) one-tail	0.1651	0.2746	0.0040	2.29E-08	0.0567	0.0057	0.0181	0.0099
t Critical one-tail	1.7396	1.9432	1.7613	1.7341	1.7613	1.7341	1.7247	1.7247
P(T<=t) two-tail	0.3301	0.5491	0.0080	4.58E-08	0.1135	0.0114	0.0363	0.0199
t Critical two-tail	2.1098	2.4469	2.1448	2.1009	2.1448	2.1009	2.0860	2.0860

Table B 18 Clarified green liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results from 2018.. The density 1.15 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

Green liquor Density 1.15 kg/l	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	13.22	183.90	29.44	25.21	6.50	3.84	575.38	6935.84
Variance 1	71.99	10262.71	537.64	1.69	87.96	4.63	3350.51	1.43E+07
Observations 1	13	6	14	8	14	14	6	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	10.25	151.94	9.36	47.72	2.05	1.99	711.11	9793.33
Variance 2	17.47	4124.29	33.57	117.15	3.89	1.04	8.31E+04	8.23E+06
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	17	6	14	18	14	18	20	19
t Stat	1.1477	0.7257	3.1652	-8.6862	1.7470	2.9664	-1.8867	-2.2233
P(T<=t) one-tail	0.1335	0.2477	0.0034	3.72E-08	0.0513	0.0041	0.0369	0.0193
t Critical one-tail	1.7396	1.9432	1.7613	1.7341	1.7613	1.7341	1.7247	1.7291
P(T<=t) two-tail	0.2670	0.4954	0.0069	7.45E-08	0.1025	0.0083	0.0738	0.0385
t Critical two-tail	2.1098	2.4469	2.1448	2.1009	2.1448	2.1009	2.0860	2.0930

Table B 19 Clarified green liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results from 2018.. The density 1.2 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

Green liquor	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	13.59	187.83	30.43	26.03	6.68	3.95	600.40	7216.15
Variance 1	71.88	10224.01	568.66	1.90	89.00	4.79	3648.19	1.58E+07
Observations 1	13	6	14	8	14	14	6	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	10.25	151.94	9.42	47.72	2.05	1.99	711.11	9793.33
Variance 2	17.47	4124.29	31.77	117.15	3.89	1.04	8.31E+04	8.23E+06
Observations 2	15	18	19	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	17	6	14	18	14	17	21	19
t Stat	1.2921	0.8161	3.2308	-8.3538	1.8041	3.1072	-1.5316	-1.9353
P(T<=t) one-tail	0.1068	0.2228	0.0030	6.58E-08	0.0464	0.0032	0.0703	0.0340
t Critical one-tail	1.7396	1.9432	1.7613	1.7341	1.7613	1.7396	1.7207	1.7291
P(T<=t) two-tail	0.2136	0.4456	0.0060	1.32E-07	0.0928	0.0064	0.1405	0.0680
t Critical two-tail	2.1098	2.4469	2.1448	2.1009	2.1448	2.1098	2.0796	2.0930

Table B 20 White liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor, 2007) and this project's results from 2018. The density 1.1 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

White liquor Density 1.1 kg/l	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	16.36	189.12	144.85	7.65	2.21	3.00	509.85	5963.04
Variance 1	85.74	5951.19	41316.49	4.05	5.74	2.63	1187.82	7206845.36
Observations 1	12	6	9	7.00	13.00	13.00	4.00	12.00
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.47	157.61	16.97	16.13	0.62	2.93	722.22	10051.67
Variance 2	50.94	4216.49	70.57	26.97	0.01	2.31	90841.83	9.62E+06
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	20	8	8	23	12	25	19	26
t Stat	0.2754	0.8997	1.8866	-5.8870	2.3843	0.1095	-2.9052	-3.8377
P(T<=t) one-tail	0.3929	0.1973	0.0480	2.66E-06	0.0172	0.4568	0.0045	0.0004
t Critical one-tail	1.7247	1.8595	1.8595	1.7139	1.7823	1.7081	1.7291	1.7056
P(T<=t) two-tail	0.7858	0.3945	0.0959	5.32E-06	0.0345	0.9137	0.0091	0.0007
t Critical two-tail	2.0860	2.3060	2.3060	2.0687	2.1788	2.0595	2.0930	2.0555

Table B 21 White liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor, 2007) and this project's results from 2018. The density 1.15 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

White liquor Density 1.15 kg/l	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	16.87	193.34	150.96	7.90	2.29	3.08	533.03	6199.35
Variance 1	87.63	5460.34	45258.60	4.48	6.24	2.75	1298.25	8.10E+06
Observations 1	12	6	9	7	13	13	4	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.47	157.61	16.97	16.13	0.62	2.93	722.22	10051.67
Variance 2	50.94	4216.49	70.57	26.97	0.01	2.31	90841.83	9.62E+06
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	20	8	8	23	12	25	19	25
t Stat	0.4282	1.0563	1.8888	-5.6302	2.4050	0.2590	-2.5815	-3.5032
P(T<=t) one-tail	0.3365	0.1609	0.0478	4.95E-06	0.0166	0.3989	0.0091	0.0009
t Critical one-tail	1.7247	1.8595	1.8595	1.7139	1.7823	1.7081	1.7291	1.7081
P(T<=t) two-tail	0.6731	0.3217	0.0956	9.91E-06	0.0332	0.7978	0.0183	0.0018
t Critical two-tail	2.0860	2.3060	2.3060	2.0687	2.1788	2.0595	2.0930	2.0595

Table B 22 White liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor, 2007) and this project's results from 2018. The density 1.2 kg/l is used for Richardson and Fredericks results. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are not included

White liquor Density 1.2 kg/l	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	18.36	216.80	157.52	8.58	2.39	3.31	556.20	6555.17
Variance 1	121.33	10076.35	49236.01	4.91	6.69	3.38	1413.60	8.38E+06
Observations 1	12	6	9	7	13	13	4	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	15.47	157.61	16.97	16.13	0.62	2.93	722.22	10051.67
Variance 2	50.94	4216.49	70.57	26.97	0.01	2.31	90841.83	9.62E+06
Observations 2	15	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	18	6	8	23	12	23	19	25
t Stat	0.7869	1.3530	1.8995	-5.0936	2.4671	0.6034	-2.2592	-3.1492
P(T<=t) one-tail	0.2208	0.1124	0.0470	1.85E-05	0.0148	0.2761	0.0179	0.0021
t Critical one-tail	1.7341	1.9432	1.8595	1.7139	1.7823	1.7139	1.7291	1.7081
P(T<=t) two-tail	0.4416	0.2248	0.0940	3.70E-05	0.0296	0.5522	0.0358	0.0042
t Critical two-tail	2.1009	2.4469	2.3060	2.0687	2.1788	2.0687	2.0930	2.0595

Table B 23 Lime mud t-test results comparing (Frederick, et al., 2000) (Taylor & Bossons, 2006) (Taylor, 2007) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are not included

Lime mud	**Al**	**Si**	**P**	**Mg**	**Mn**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	230.83	1975.00	1639.14	1226.25	96.97	4904.71
Variance 1	133763.63	101250.00	6760384.48	1460206.50	4306.20	4791047.24
Observations 1	8	2	7	8	7	7
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	470.73	826.94	7365.56	4103.89	255.12	230.92
Variance 2	11038.53	101334.20	6879179.08	1812369.28	41536.21	8737.48
Observations 2	15	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0
df	8	1	11	15	23	6
t Stat	-1.8158	4.8404	-4.9323	-5.4073	-2.9253	5.6474
P(T<=t) one-tail	0.0535	0.0648	0.0002	3.63E-05	0.0038	0.0007
t Critical one-tail	1.8595	6.3138	1.7959	1.7531	1.7139	1.9432
P(T<=t) two-tail	0.1069	0.1297	0.0004	7.27E-05	0.0076	0.0013
t Critical two-tail	2.3060	12.7062	2.2010	2.1314	2.0687	2.4469

Table B 24 Green liquor dregs t-test results comparing results (Empie, et al., 1999) (Richardson, et al., 1998) (Taylor & Bossons, 2006) (Taylor, 2007) data to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are included

Green liquor dregs	**Al**	**Si**	**Ca**	**P**	**Mg**	**Mn**	**Cl**	**K**
Variable 1	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*	*North American results*
Mean 1	3164.9	3114	1.8E+05	233.0	20278	11248.6	799.00	5861.2
Variance 1	6.8E+06	7.2E+06	1.5E+10	66057	2E+08	5E+07	1.5E+06	3.9E+07
Observations 1	18	16	18	8	18	18	8	17
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	6618.0	8265	1.2E+05	1001.3	35937	11637.8	972.22	11616
Variance 2	2.6E+07	8.7E+07	9.4E+09	1.6E+06	10E+08	7.4E+07	9.2E+05	8.6E+07
Observations 2	18	18	18	18	18	18	18	18
Hypothesized Mean Difference	0	0	0	0	0	0	0	0
df	25	20	33	20	22	33	11	30
t Stat	-2.5438	-2.24	1.6211	-2.475	-2.005	-0.149	-0.3590	-2.1643
P(T<=t) one-tail	0.0088	0.018	0.0573	0.011	0.029	0.441	0.3632	0.0193
t Critical one-tail	1.7081	1.725	1.6924	1.725	1.717	1.692	1.7959	1.6973
P(T<=t) two-tail	0.0175	0.036	0.1145	0.022	0.058	0.883	0.7264	0.0385
t Critical two-tail	2.0595	2.086	2.0345	2.086	2.074	2.035	2.2010	2.0423

Table B 25 T-test results for ESP ash and lime mud comparing older North American results to this projects data from 2018. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high Al values are included

Sample points with Mill C's Al values	**ESP A**	**LM**
Variable 1	*North American results*	*North American results*
Mean 1	14.10	230.83
Variance 1	6.18	133763.63
Observations 1	6	8
Variable 2	*FIN 2018*	*FIN 2018*
Mean 2	20.21	573.39
Variance 2	170.58	64908.28
Observations 2	18	18
Hypothesized Mean Difference	0	0
df	20	10
t Stat	-1.8853	-2.4028
P(T<=t) one-tail	0.0370	0.0186
t Critical one-tail	1.7247	1.8125
P(T<=t) two-tail	0.0740	0.0371
t Critical two-tail	2.0860	2.2281

Table B 26 T-test results for green liquor comparing older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) to this projects data from 2018. The density values 1.1 kg/l, 1.15 kg/l and 1.2 kg/l. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are included

Mill C's Al values included in green liquor	**Density 1.1 kg/l**	**Density 1.15 kg/l**	**Density 1.2 kg/l**
Variable 1	*North American results*	*North American results*	*North American results*
Mean 1	12.846	13.217846	13.589692
Variance 1	72.250387	71.987869	71.880739
Observations 1	13	13	13
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	31.594444	31.594444	31.594444
Variance 2	2427.8064	2427.8064	2427.8064
Observations 2	18	18	18
Hypothesized Mean Difference	0	0	0
df	18	18	18
t Stat	-1.582072	-1.5508055	-1.5194699
P(T<=t) one-tail	0.0655225	0.0691762	0.0730073
t Critical one-tail	1.7340636	1.7340636	1.7340636
P(T<=t) two-tail	0.1310449	0.1383523	0.1460145
t Critical two-tail	2.100922	2.100922	2.100922

Table B 27 T-test results for green liquor comparing older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor, 2007) to this projects data from 2018. The density values 1.1 kg/l, 1.15 kg/l and 1.2 kg/l. When the two-tail p-value is below 0.05 is the difference significant. Mill C's abnormally high al values are included

Mill C's Al values included in white liquor	**Density 1.1 kg/l**	**Density 1.15 kg/l**	**Density 1.2 kg/l**
Variable 1	*North American results*	*North American results*	*North American results*
Mean 1	16.360833	16.867292	18.35875
Variance 1	85.736623	87.633067	121.3303
Observations 1	12	12	12
Variable 2	*FIN 2018*	*FIN 2018*	*FIN 2018*
Mean 2	36.277778	36.277778	36.277778
Variance 2	2335.1171	2335.1171	2335.1171
Observations 2	18	18	18
Hypothesized Mean Difference	0	0	0
df	19	19	20
t Stat	-1.7024059	-1.6581592	-1.5153026
P(T<=t) one-tail	0.0524922	0.0568519	0.0726708
t Critical one-tail	1.7291328	1.7291328	1.7247182
P(T<=t) two-tail	0.1049843	0.1137038	0.1453415
t Critical two-tail	2.0930241	2.0930241	2.0859634

Appendix C

T distribution table from (Tiemann, 2012)

Table C 1 T distribution table (Tiemann, 2012)

Degrees of Freedom	**Significance level** **0.2**	**0.1**	**0.05**	**0.025**	**0.01**	**0.005**
1	1.376	3.078	6.314	12.706	31.821	63.657
2	1.061	1.886	2.92	4.303	6.965	9.925
3	0.978	1.638	2.353	3.182	4.541	5.841
4	0.941	1.533	2.132	2.776	3.747	4.604
5	0.92	1.476	2.015	2.571	3.365	4.032
6	0.906	1.44	1.943	2.447	3.143	3.707
7	0.896	1.415	1.895	2.365	2.998	3.499
8	0.889	1.397	1.86	2.306	2.896	3.355
9	0.883	1.383	1.833	2.262	2.821	3.25
10	0.879	1.372	1.812	2.228	2.764	3.169
11	0.876	1.363	1.796	2.201	2.718	3.106
12	0.873	1.356	1.782	2.179	2.681	3.055
13	0.87	1.35	1.771	2.16	2.65	3.012
14	0.868	1.345	1.761	2.145	2.624	2.977
15	0.866	1.341	1.753	2.131	2.602	2.947
16	0.865	1.337	1.746	2.12	2.583	2.921
17	0.863	1.333	1.74	2.11	2.567	2.898
18	0.862	1.33	1.734	2.101	2.552	2.878
19	0.861	1.328	1.729	2.093	2.539	2.861
20	0.86	1.325	1.725	2.086	2.528	2.845
21	0.859	1.323	1.721	2.08	2.518	2.831
22	0.858	1.321	1.717	2.074	2.508	2.819
23	0.858	1.319	1.714	2.069	2.5	2.807
24	0.857	1.318	1.711	2.064	2.492	2.797
25	0.856	1.316	1.708	2.06	2.485	2.787
26	0.856	1.315	1.706	2.056	2.479	2.779
27	0.855	1.314	1.703	2.052	2.473	2.771
28	0.855	1.313	1.701	2.048	2.467	2.763
29	0.854	1.311	1.699	2.045	2.462	2.756
30	0.854	1.31	1.697	2.042	2.457	2.75
31	0.853	1.309	1.696	2.04	2.453	2.744
32	0.853	1.309	1.694	2.037	2.449	2.738
33	0.853	1.308	1.692	2.035	2.445	2.733
34	0.852	1.307	1.691	2.032	2.441	2.728
35	0.852	1.306	1.69	2.03	2.438	2.724
36	0.852	1.306	1.688	2.028	2.434	2.719

Degrees of Freedom	**Significance level** **0.2**	**0.1**	**0.05**	**0.025**	**0.01**	**0.005**
37	0.851	1.305	1.687	2.026	2.431	2.715
38	0.851	1.304	1.686	2.024	2.429	2.712
39	0.851	1.304	1.685	2.023	2.426	2.708
40	0.851	1.303	1.684	2.021	2.423	2.704
41	0.85	1.303	1.683	2.02	2.421	2.701
42	0.85	1.302	1.682	2.018	2.418	2.698
43	0.85	1.302	1.681	2.017	2.416	2.695
44	0.85	1.301	1.68	2.015	2.414	2.692
45	0.85	1.301	1.679	2.014	2.412	2.69
46	0.85	1.3	1.679	2.013	2.41	2.687
47	0.849	1.3	1.678	2.012	2.408	2.685
48	0.849	1.299	1.677	2.011	2.407	2.682
49	0.849	1.299	1.677	2.01	2.405	2.68
50	0.849	1.299	1.676	2.009	2.403	2.678
51	0.849	1.298	1.675	2.008	2.402	2.676
52	0.849	1.298	1.675	2.007	2.4	2.674
53	0.848	1.298	1.674	2.006	2.399	2.672
54	0.848	1.297	1.674	2.005	2.397	2.67
55	0.848	1.297	1.673	2.004	2.396	2.668
56	0.848	1.297	1.673	2.003	2.395	2.667
57	0.848	1.297	1.672	2.002	2.394	2.665
58	0.848	1.296	1.672	2.002	2.392	2.663
59	0.848	1.296	1.671	2.001	2.391	2.662
60	0.848	1.296	1.671	2.000	2.39	2.66
61	0.848	1.296	1.67	2.000	2.389	2.659
62	0.847	1.295	1.67	1.999	2.388	2.657
63	0.847	1.295	1.669	1.998	2.387	2.656
64	0.847	1.295	1.669	1.998	2.386	2.655
65	0.847	1.295	1.669	1.997	2.385	2.654
66	0.847	1.295	1.668	1.997	2.384	2.652
67	0.847	1.294	1.668	1.996	2.383	2.651
68	0.847	1.294	1.668	1.995	2.382	2.65
69	0.847	1.294	1.667	1.995	2.382	2.649
70	0.847	1.294	1.667	1.994	2.381	2.648
71	0.847	1.294	1.667	1.994	2.38	2.647
72	0.847	1.293	1.666	1.993	2.379	2.646

Degrees of Freedom	Significance level 0.2	0.1	0.05	0.025	0.01	0.005
73	0.847	1.293	1.666	1.993	2.379	2.645
74	0.847	1.293	1.666	1.993	2.378	2.644
75	0.846	1.293	1.665	1.992	2.377	2.643
76	0.846	1.293	1.665	1.992	2.376	2.642
77	0.846	1.293	1.665	1.991	2.376	2.641
78	0.846	1.292	1.665	1.991	2.375	2.64
79	0.846	1.292	1.664	1.99	2.374	2.64
80	0.846	1.292	1.664	1.99	2.374	2.639
81	0.846	1.292	1.664	1.99	2.373	2.638
82	0.846	1.292	1.664	1.989	2.373	2.637
83	0.846	1.292	1.663	1.989	2.372	2.636
84	0.846	1.292	1.663	1.989	2.372	2.636
85	0.846	1.292	1.663	1.988	2.371	2.635
86	0.846	1.291	1.663	1.988	2.37	2.634
87	0.846	1.291	1.663	1.988	2.37	2.634
88	0.846	1.291	1.662	1.987	2.369	2.633
89	0.846	1.291	1.662	1.987	2.369	2.632
90	0.846	1.291	1.662	1.987	2.368	2.632
91	0.846	1.291	1.662	1.986	2.368	2.631
92	0.846	1.291	1.662	1.986	2.368	2.63
93	0.846	1.291	1.661	1.986	2.367	2.63
94	0.845	1.291	1.661	1.986	2.367	2.629
95	0.845	1.291	1.661	1.985	2.366	2.629
96	0.845	1.29	1.661	1.985	2.366	2.628
97	0.845	1.29	1.661	1.985	2.365	2.627
98	0.845	1.29	1.661	1.984	2.365	2.627
99	0.845	1.29	1.66	1.984	2.365	2.626
100	0.845	1.29	1.66	1.984	2.364	2.626
100000	0.842	1.282	1.645	1.96	2.326	2.576

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