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

CAMILLA KARLEMO, MARKUS ENGBLOM, AND ESA K. VAKKILAINEN

ABSTRACT: In this work, the aim was to study the distribution and accumulation of the non-process elements (NPEs) in the recovery cycle of Finnish pulp mills and look at whether the geographical location (North vs. South) correlates with the current Finnish NPE levels. In addition, a comparison to older similar Finnish measurements was made with an attempt to analyze the reasons behind differences in the most typical non-process elements, aluminum (Al), silicon (Si), calcium (Ca), phosphorus (P), magnesium (Mg), manganese (Mn), chlorine (Cl), and potassium (K), taking into account the main elements in the white liquor, sodium (Na) and sulfur (S). The extensive laboratory results gained in this study are from seven sampling points at six pulp mills and present analytical data of metal concentrations.

The data obtained presents an update to previous NPE studies. The levels found did not statistically differ between North and South Finland. The NPE levels, apart from phosphorus, found in Finnish pulp mills today have not changed considerably compared to the levels in earlier investigations in the 1990s. In the newest data, the phosphorus concentration was consistently higher in the as-fired black liquor, electrostatic precipitator (ESP) ash, lime mud, and green liquor than in the previous results. In addition, the levels of Al, Si, Ca, P, and Mg in recovery boiler ESP ash were consistently higher compared to the older results. As the mills start to close their systems more, a stronger accumulation of NPEs can be expected, increasing the likelihood of more operational problems in the process. Further understanding of where the NPEs accumulate and how they can be most effectively removed will be valuable knowledge in the future.

Application: This comprehensive study provides good insight into the levels of NPEs found in the recovery cycle of six Finnish kraft pulp mills.

Non-process elements (NPEs) are defined as those elements that do not actively participate in the pulping process. Some of them, if they accumulate, can cause severe operating problems in pulp mills. The decreased use of fresh water and the increased use of biofuels might raise the levels of NPEs [1].

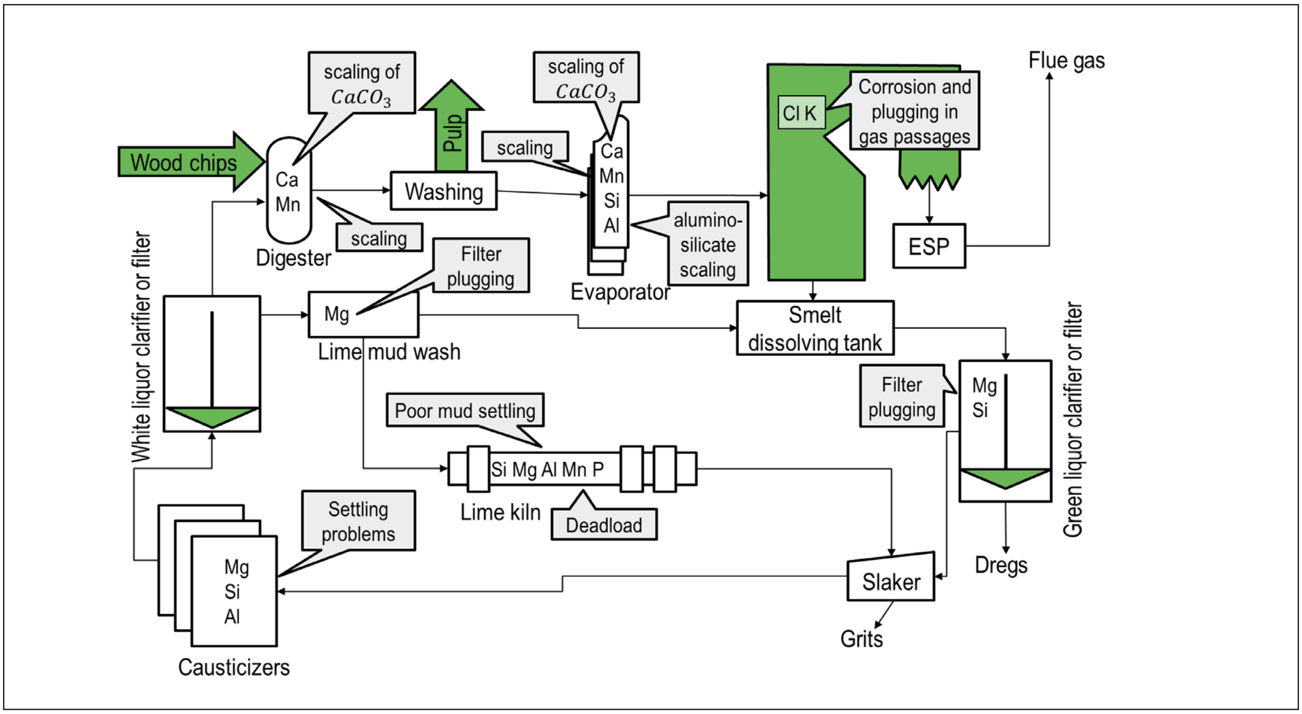
The operational problems caused by NPEs are often expensive to repair. Therefore, better fundamental knowledge is needed to address how, where, and when the NPEs accumulate in the system. The attempt to understand the NPE behavior in the process is important since mills want to remove these elements cost-effectively without affecting the productivity and profitability of pulp production.

Pulp wood is the most significant intake source for NPEs [2]. The wood species substantially impacts the NPE levels found in the recovery cycle [3,4]. Other NPE inputs are, e.g., makeup alkali, makeup limestone, and the burning of biosludge in the recovery boiler. Biosludge is a significant source of sulfur (S), calcium (Ca), phosphorous (P), and magnesium (Mg) [1]. The NPE level can also increase due to the fuel used in the lime kiln. Gasified bark and other biofuels can increase manganese (Mn) and P levels in the recovery cycle [5].

Effective ways to reduce NPEs are needed to avoid the accumulation of these elements in modern pulp mills. There are already some removal points for the NPEs in the recovery cycle. Green liquor dregs removal is one of the most important purging points for the NPEs. Other good purging points are the removal of electrostatic precipitator (ESP) ash from the recovery boiler and lime kiln, purging of lime mud, and removal of grits. One way for the NPE to exit is also with the brownstock pulp [6-9].

Not all NPEs are easily precipitated and removed with green liquor dregs. The NPEs can be divided into three groups according to their solubility in the recovery cycle. The first group contains elements known to form insoluble compounds in the alkali liquor environment, such as Ca, Mn, Mg, and iron (Fe). These elements are effectively removed from the liquor cycle with dregs, grits, and sometimes lime mud. The other group that is more soluble in the liquor cycle contains chlorine (Cl), potassium (K), silicon (Si), and aluminum (Al). Due to their solubility in green and white liquor, they are not as effectively removed through the typical purging points as the insoluble group. The third group includes elements that also accumulate in the lime cycle. For instance, Mg, Al, and P (and smaller amounts of Si and Mn) will accumulate in the lime cycle and cause poor lime mud filterability, filter plugging, and dead load [8-11].

The effects caused by the NPEs are noticeable throughout the recovery cycle. **Figure 1** summarizes some of the problems encountered in pulp mills if the NPEs are left to accumulate. The objective of this work is to study the dis-



1. Summary of some NPE problems encountered in recovery cycle, based on [1,7-11]. (Al = aluminum; Si = silicon; Ca = calcium; P = phosphorus; Mg = magnesium; Mn = manganese; Cl = chlorine; K = potassium; Na = sodium; S = sulfur; $CaCO_3$ = calcium carbonate).

tribution and accumulation of NPEs in the recovery cycle of six Finnish kraft pulp mills. The work reported here was part of Karlemo's M.Sc. thesis project at Åbo Akademi University in Turku, Finland [12].

In this work, the aim was to study the distribution and accumulation of the non-process elements in the recovery cycle of Finnish pulp mills and look at whether the geographical location (North vs. South) correlates with the current Finnish NPE levels. In addition, a comparison to older similar Finnish measurements was made with an attempt to analyze the reasons behind differences in the most typical non-process elements, Al, Si, Ca, P, Mg, Mn, Cl, and K, taking into account the main elements in the white liquor, sodium (Na) and sulfur (S). The extensive laboratory results gained in this study are from seven sampling points at six pulp mills and present analytical data of metal concentrations.

METHODS

Six Finnish kraft pulp mills participated in this project. Three of the mills are located in northern Finland, and three mills are in southern Finland. An outsourced commercial laboratory analyzed the samples.

Mill data

The mills studied in this paper are kraft sulfate pulp mills. The annual capacities of the mills range from 360,000 to 1,300,000 metric tons of air-dried (a.d.) softwood and/or hardwood pulp. The wood is harvested from different locations in Finland, divided into southern and northern Finland. The harvesting location of the raw material affects the NPE concentration, as NPE levels in groundwater are not constant and have an impact on the NPE levels in wood. In this study, the primary raw materials the mills use vary between pine, spruce, and birch, as presented in **Table I**.

Pulp Mill	Location	Raw Material
Mill A	North	Softwood
Mill B	North	Softwood & Hardwood
Mill C	North	Softwood & Hardwood
Mill D	South	Softwood
Mill E	South	Softwood & Hardwood
Mill F	South	Softwood & Hardwood

I. Geographic locations and pulping raw material for the six Finnish mills.

The participating mills differed in several ways, including pulping raw material, production capacity, process units, and the process equipment used. Some of the differences that affect the NPEs are described as follows:

- Notable differences are found in the green liquor handling system between the mills. Three mills use a clarifier, and three have modern crossflow filters.
- Two out of the six mills do not add biosludge to the recovery cycle. The other four mills mix the biosludge from the wastewater treatment plant with black liquor in the black liquor evaporator.

- Due to an unforeseen process disturbance during the measurements, Mill C had an excess amount of Al and Si added to wastewater and subsequently the biosludge. The increased amount of Al and Si created scaling and plugging in the black liquor evaporator. The mill was not in its normal process state during the sampling, and clear Al and Si peaks can thus be seen in the results.
- A wide range of fuels was used in the lime kilns, i.e., natural gas, heavy fuel oil, pitch oil, gasified bark, and hydrogen. Some mills mix biofuels and fossil fuels in their lime kilns. Changing the lime kiln fuel impacts the NPE levels in the lime cycle. The lime kiln fuels are presented in **Table II**.

In addition to the previously mentioned factors, NPE levels in the mill can be affected by the amount of freshwater used, the type of wastewater treatment, lime mud removal rate, and ESP ash removal rate from the recovery boiler and lime kiln.

Only one of the six mills did not purge any recovery boiler ESP ash during the sampling, three mills did not remove lime kiln ESP ash, and two mills did not purge lime mud. The removal of lime mud and ESP ash are the most typical ways to purge P, Al, and Si from the recovery cycle.

Sampling and sample analysis

The sampling for this project was carried out in the fall of 2018. The sampling campaign included, for each mill, seven sampling points (weak black liquor, as-fired black liquor, recovery boiler ESP ash, clarified green liquor, green liquor dregs, white liquor, lime mud) in the recovery cycle. For some of the mills, the process included parallel process lines. For these mills, additional sampling was carried out, and the analysis results are taken into account when presenting the average metal concentrations. Three samples of each sampling point were taken, and from each collected sample, three replicate analyses were carried out by a commercial laboratory. This gives a total of nine analyses per sampling point per mill, or more if the mill had parallel process lines. Sample analysis covered Al, Si, Ca, P, Mg, Mn, Cl, K, Na, and S.

The sample points differed to some extent between the mills, because the mills did not have identical processes or sampling points. For example, some green liquor dregs samples contained lime mud used as dregs filter pre-coat, and some weak black liquor samples did not contain tall soap.

Weak black liquor and as-fired black liquor were both pretreated with the SCAN-N 38:10 “Acid soluble metals” method, and all elements except Cl were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES). The Cl was analyzed with an adsorbable organic halides analyzer (AOX analyzer), where the sample is heated up to 1000°C, and the freed Cl is analyzed with a coulometric titration method.

Lime Kiln Fuel	Fuel
Nr 1	Hydrogen 30% and pitch oil 70%
Nr 2	Pitch oil only
Nr 3	Heavy fuel oil
Nr 4	Gasified bark
Nr 5	Natural gas 66% and pitch oil 33%
Nr 6	Natural gas

II. Lime kiln fuels used in the six mills participating in this study, in random order.

Recovery boiler ESP ash analysis does not have a standardized pretreatment method. The samples were dissolved with hydrogen peroxide and nitric acid in order for the sample to be in liquid form for the analysis. All elements except Cl were then analyzed with ICP-OES. No standardized method for Cl was available. The chlorine sample was handled similarly to the SCAN-N 4:78 “Chloride content” method. The sample was dissolved in water, after which it was potentiometrically titrated with silver nitrate.

Clarified green liquor and white liquor samples were dissolved with hydrogen peroxide, and nitric acid and all elements except Cl were analyzed with ICP-OES. The analysis method for Cl was SCAN-N 4:78.

Green liquor dregs and lime mud have no standardized pretreatment methods. The samples were dissolved with hydrogen peroxide and nitric acid using a microwave digestion system, after which the dissolved samples were analyzed with ICP-OES, except Cl. For Cl, the sample was dissolved in water, and the dissolved chlorine was analyzed with ion chromatography.

The dry solids content for all the samples, except for the liquor samples, was determined after 24 h in a 105°C oven. All data is presented as mg/kg dry weight, except white liquor and green liquor, which are presented as mg/L.

RESULTS AND DISCUSSION

The aim was to obtain an understanding of the non-process element concentrations in the recovery cycle of Finnish pulp mills and look at whether the geographical location (North vs. South) affects these results. In addition, it was studied as to whether the newer data differs significantly from older data in previous studies. **Table III** presents the measurement results obtained from this study, given as the average of three replicate samples.

NPE level comparison between the mills

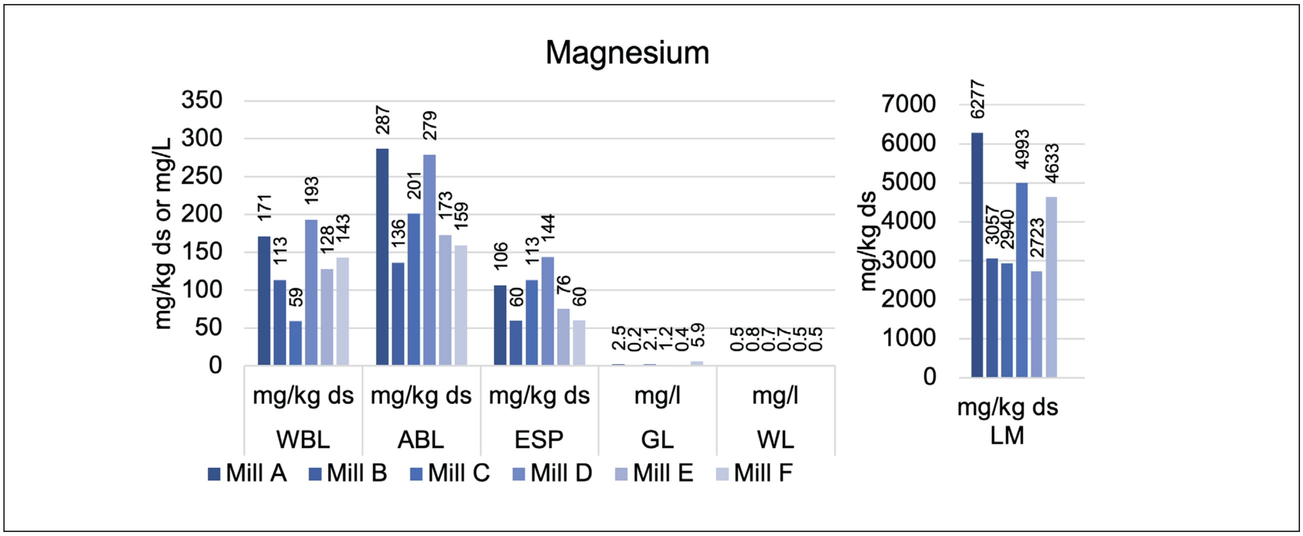
Most of the NPE levels are relatively similar between the six kraft pulp mills. However, some noteworthy differences between the mills were identified.

Mill A stood out from the others because it tends to have low concentrations of elements Ca, Al, Si, and P throughout

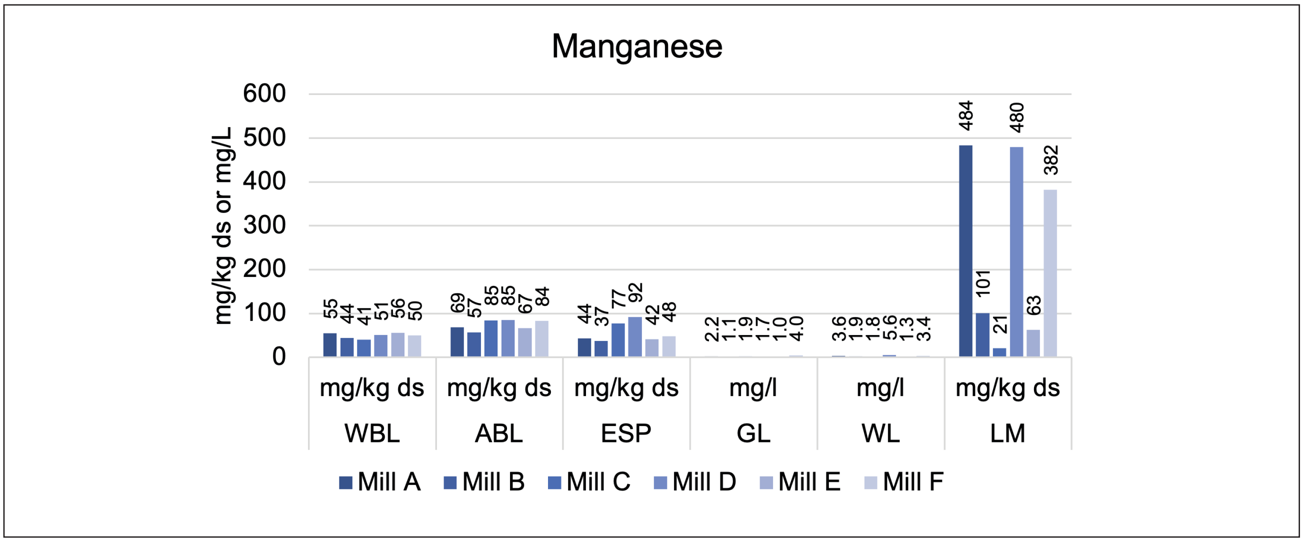
Mill	Sample Point	Unit	Al	Si	Ca	P	Mg	Mn	Cl (×1000)	K (×1000)	Na (×1000)	S (×1000)
Mill A	WBL	mg/kg ds	19.7	128	70.5	52.3	171	54.9	2.1	21.2	200	53.5
Mill B	WBL	mg/kg ds	40.6	279	156	74.1	113	43.7	2.2	24.8	166	59.2
Mill C	WBL	mg/kg ds	235(a)	344	144	83.0	59.3	40.6	0.7	10.6	196	59.5
Mill D(b)	WBL	mg/kg ds	41.1	342	125	64.7	193	51.1	0.8	16.3	191	52.4
Mill E	WBL	mg/kg ds	74.0	775(c)	162	75.4	128	55.5	2.1	17.5	200	50.1
Mill F	WBL	mg/kg ds	20.6	170	134	82.0	143	50.0	1.8	25.7	147	45.5
Mill A	ABL	mg/kg ds	21.1	145	124	79.2	287	68.8	3.2	30.0	193.3	61.4
Mill B	ABL	mg/kg ds	53.1	303	233	73.6	136	56.5	3.2	26.6	194.3	63.5
Mill C	ABL	mg/kg ds	355(a)	550(a)	243	141	201	84.6	0.9	14.5	206.0	85.2
Mill D	ABL	mg/kg ds	52.4	378	329	128	279	85.4	1.1	23.1	201.7	80.0
Mill E	ABL	mg/kg ds	74.0	364	403	124	173	66.6	3.3	25.8	207.0	59.3
Mill F	ABL	mg/kg ds	40.5	201	191	99.8	159	83.5	2.6	28.9	176.2	61.9
Mill A	ESP	mg/kg ds	7.5	64.3	50.7	35.7	106	43.6	11.0	52.5	258.0	174.0
Mill B	ESP	mg/kg ds	14.0	12	104	39.7	59.8	37.1	10.9	54.7	259.0	182.0
Mill C	ESP	mg/kg ds	45.0(a)	316(a)	154	46.7	113	77.4	3.3	34.1	317.3	220.3
Mill D	ESP	mg/kg ds	25.2	269	255	55.7	144	91.8	4.1	58.5	333.0	193.7
Mill E	ESP	mg/kg ds	20.3	142	144	46.7	75.7	41.6	10.9	42.6	279.3	146.3
Mill F	ESP	mg/kg ds	9.3	68.8	66.5	39.0	60.2	48.0	9.8	62.0	263.8	196.5
Mill A	GL	mg/L	5.2	57.7	7.3	30.0	2.5	2.2	0.9	10.9	86.5	28.6
Mill B	GL	mg/L	12.0	130	3.3	42.3	0.2	1.1	0.9	11.5	84.9	27.7
Mill C	GL	mg/L	138(a)	243(a)	13.7	49.3	2.1	1.9	0.3	4.6	73.3	27.6
Mill D	GL	mg/L	9.4	179	5.4	65.0	1.2	1.7	0.4	8.4	80.5	28.2
Mill E	GL	mg/L	17.0	200	6.9	51.7	0.4	1.0	1.0	9.9	101.5	31.2
Mill F	GL	mg/L	7.6	101	19.7	48.0	5.9	4.0	0.8	13.4	87.6	27.4
Mill A	GLD	mg/kg ds	758	492	0.19E5	304	16633	4367	2.72	29.5	285	96.6
Mill B	GLD	mg/kg ds	6517	5910	2.9E5(d)	3650	33400	12367	0.02	0.64	7.3	14.8
Mill C	GLD	mg/kg ds	9850	8360	1.07E5	1070	35167	13500	0.56	8.15	178	68.4
Mill D	GLD	mg/kg ds	14433	27200	1.39E5	425	97400	26967	0.07	6.14	116	32.0
Mill E	GLD	mg/kg ds	7977	7520	1.51E5	468	32033	12167	1.46	13.5	159	52.4
Mill F	GLD	mg/kg ds	173	108	2177	91	988	460	1.00	11.8	72.0	24.9
Mill A	WL	mg/L	6.2	61.3	10.5	21.7	0.5	3.6	0.9	11.1	90.4	29.2
Mill B	WL	mg/L	17.0	136	31.0	11.0	0.8	1.9	1.0	12.3	96.5	29.7
Mill C	WL	mg/L	140(a)	243(a)	24.7	8.5	0.7	1.8	0.3	4.6	76.6	27.9
Mill D	WL	mg/L	23.3	220	12.3	16.0	0.7	5.6	0.4	8.4	79.1	28.5
Mill E	WL	mg/L	22.0	177	12.0	18.0	0.5	1.3	1.0	9.8	99.6	30.6
Mill F	WL	mg/L	8.8	108	11.3	21.7	0.5	3.4	0.9	14.0	92.9	29.3
Mill A	LM	mg/kg ds	434	288	3.58E5	6970	6277	484	0.0067	0.22	8.15	0.27
Mill B	LM	mg/kg ds	533	925	3.96E5	8383	3057	101	0.0110	0.32	7.70	0.21
Mill C	LM	mg/kg ds	1087(a)	1310(a)	3.82E5	7933	2940	21	0.0039	0.11	7.39	0.71
Mill D	LM	mg/kg ds	631	973	3.84E5	8327	4993	480	0.0064	0.22	7.80	0.38
Mill E	LM	mg/kg ds	338	717	3.90E5	2163(e)	2723	63	0.0045	0.16	5.09	0.41
Mill F	LM	mg/kg ds	418	750	3.82E5	10417	4633	382	0.0091	0.36	9.27	0.51

Al = aluminum; Si = silicon; Ca = calcium; P = phosphorus; Mg = magnesium; Mn = manganese; Cl = chlorine; K = potassium; Na = sodium; S = sulfur.
(a) Abnormally high Al and Si concentration in Mill C's sample due to an Al and Si leak in the wastewater treatment plant.
(b) Mill D's sample from weak black liquor did not contain tall soap.
(c) Abnormally high Si concentration. Possibly due to analyzing error.
(d) Mill B's sample from green liquor dregs contained lime mud.
(e) Abnormally low P concentration, possibly due to analyzing error.

III. Elemental analysis results from six Finnish kraft pulp mills. Results include seven sampling points: weak black liquor (WBL); as-fired black liquor (ABL); recovery boiler electrostatic precipitator ash (ESP); clarified green liquor (GL); green liquor dregs (GLD); white liquor (WL); and lime mud (LM). Each result is an average of three or more replicate sample results. All results, except GL and WL, are given as mg/kg dry solids (ds) basis.



2. Magnesium (Mg) concentrations in mg/kg dry solids (ds) or mg/L for six Finnish kraft pulp mills at the following sampling points: weak black liquor (WBL), as-fired black liquor (ABL), recovery boiler ESP ash (ESP), green liquor (GL), white liquor (WL), and lime mud (LM).



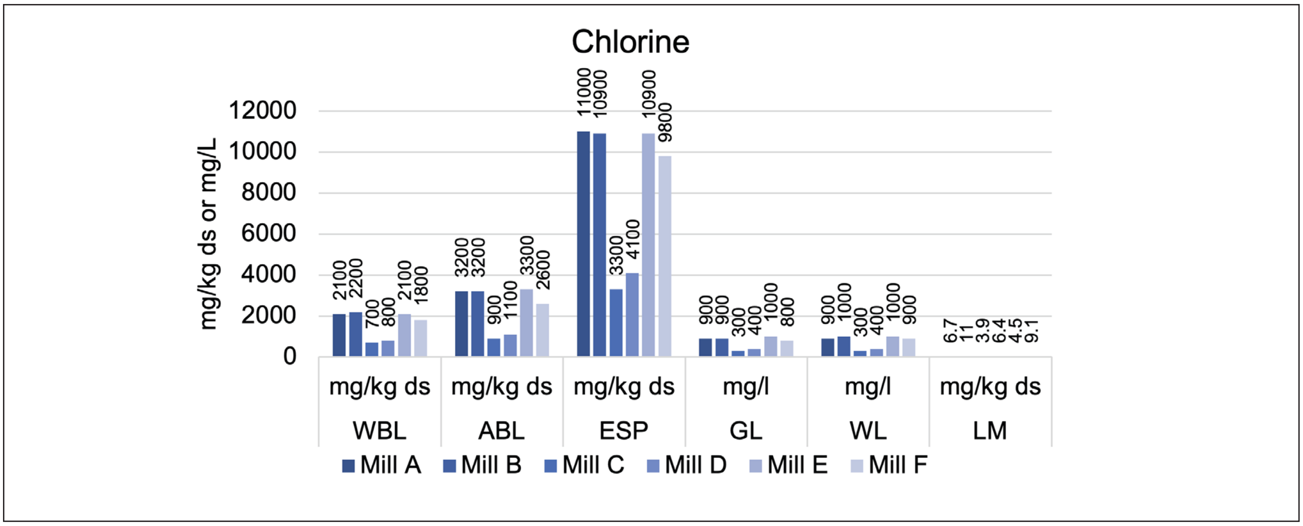
3. Manganese (Mn) concentrations in mg/kg dry solids (ds) or mg/L for six Finnish kraft pulp mills at the following sampling points: weak black liquor (WBL), as-fired black liquor (ABL), recovery boiler ESP ash (ESP), green liquor (GL), white liquor (WL), and lime mud (LM).

the cycle. In most of the sampling points, Mn and Mg are seen 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 input source. **Figure 2** and **Fig. 3** show how much Mg and Mn, respectively, are present in weak black liquor (WBL), as-fired black liquor (ABL), recovery boiler ESP ash (ESP), green liquor (GL), white liquor (WL), and lime mud (LM).

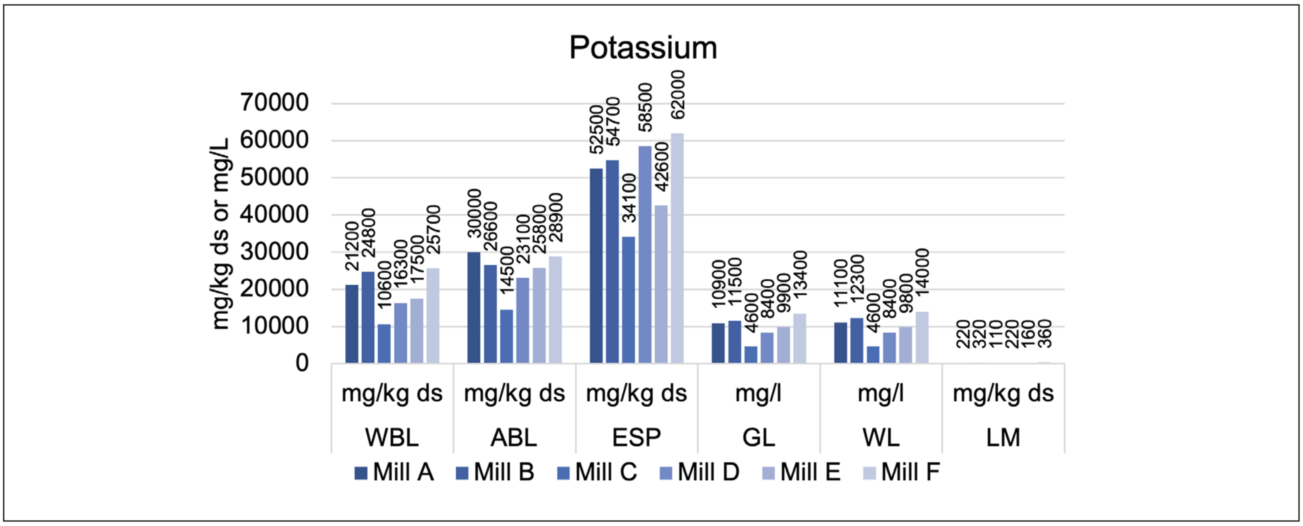
In Fig. 3, considerable differences in Mn levels are seen between the mills. The incoming wood type could be a probable cause of differences, but it cannot be excluded that something else would affect it as well. However, the Mn level of Mill D has increased going from green liquor to white liquor, and this could be due to NPEs entering the system with lime kiln fuel.

Figure 4 and **Fig. 5** show that Cl and K enrich in recovery boiler ESP ash. The K and Cl concentrations in the liquor samples are also high. However, since K and Cl are soluble in liquor, they do not accumulate in lime mud. Mills C and D have the lowest Cl concentrations, and Mill C also has the lowest K concentration of the six mills. No clear correlation between mill equipment and K and Cl levels could be identified, and the most important parameter seems to be the extent of recovery boiler ESP ash purging. However, the K and Cl concentration differences could also be due to other operational parameters and the incoming concentration of the elements in the input streams, as well as how much of the elements are exiting with the possible output streams available.

Burning of biosludge can increase the NPE concentration in the recovery cycle but other factors, such as ESP ash



4. Chlorine (Cl) concentrations in mg/kg dry solids (ds) or mg/L for six Finnish kraft pulp mills at the following sampling points: weak black liquor (WBL), as-fired black liquor (ABL), recovery boiler ESP ash (ESP), green liquor (GL), white liquor (WL), and lime mud (LM).



5. Potassium (K) concentrations in mg/kg dry solids (ds) or mg/L for six Finnish kraft pulp mills at the following sampling points: weak black liquor (WBL), as-fired black liquor (ABL), recovery boiler ESP ash (ESP), green liquor (GL), white liquor (WL), and lime mud (LM).

purging and lime mud removal, can also affect it. In this study, one of the mills burning biosludge also had a process disturbance, and thus its results cannot be used in the analysis of the effect of biosludge.

The differences between the mills depend on many factors, and this study clearly shows that the NPE levels are very mill specific and that there can be many reasons for the NPE concentration variability.

NPE levels based on mill location in Finland

One of the goals of this project was to determine if the geographical location impacts the NPE concentrations found in Finnish mills. Three of the mills are located in the northern part of Finland (Mill A, Mill B, and Mill C), and three are in the southern part of Finland (Mill D, Mill E, and Mill F).

Using a t-test with a p-value of 0.05, only roughly 10% of the data had a p-value below 0.05. If the p-value gained from the t-test is below 0.05, the data has a statistical significance. It can be concluded that the mill location in Finland does not considerably impact the NPE levels, at least concerning these mills.

Change in NPE levels over time in Finland

Similar studies with analytical data from different process streams have been conducted in the past. Older, but very comprehensive Finnish results from nearly two decades ago are presented in the works of Järvinen and Välttilä (1998) [2], Holamo (1999) [13], and Salmenoja et al. (2004) [1]. Each sampling point in the current study was compared to the analysis results available from the earlier studies.

Author	Year	Samples	Sample Point	Unit	Phosphorous (average)	p-value ($p<0.05$ = significant)
Järvinen et al.	1995	37	WBL	mg/kg ds	84	
Holamo	1999	5	WBL	mg/kg ds		
Karlemo	2019	18	WBL	mg/kg ds	72	0.007
Salmenoja et al.	2004	5	ABL	mg/kg ds	71	
Karlemo	2019	18	ABL	mg/kg ds	108	0.002
Salmenoja et al.	2004	5	ESP	mg/kg ds	25	
Karlemo	2019	18	ESP	mg/kg ds	44	0.022
Holamo	1999	9	GL	mg/L	31	
Karlemo	2019	18	GL	mg/L	48	0.000061
Holamo	1999	9	GLD	mg/kg ds	2315	
Karlemo	2019	18	GLD	mg/kg ds	1001	0.314
Järvinen et al.	1995	30	WL	mg/L	13	
Holamo	1999	7	WL	mg/L		
Karlemo	2019	18	WL	mg/L	16	0.028
Holamo	1999	9	LM	mg/kg ds	6959	
Karlemo	2019	18	LM	mg/kg ds	7366	0.784

IV. Presentation of t-test results comparing older Finnish phosphorous references with current values. All comparisons having a $p < 0.05$ are statistically significant. (WBL = weak black liquor; ABL = as-fired black liquor; ESP = recovery boiler ESP ash; GL = green liquor; WL = white liquor; LM = lime mud.)

NPE	Unit	Salmenoja et al. (2004) (average of 5)	Karlemo (2019) (average of 18)	p-value ($p<0.05$ = significant)
Al	mg/kg ds	6	15(a)	0.014
Si	mg/kg ds	105	164	0.037
Ca	mg/kg ds	77	129	0.020
P	mg/kg ds	25	44	0.022
Mg	mg/kg ds	46	93	0.000013
Mn	mg/kg ds	NaN(b)	-	-
Cl	mg/kg ds	8200	8316	0.924
K	mg/kg ds	52863	44731	0.240

Al = aluminum; Si = silicon; Ca = calcium; P = phosphorus; Mg = magnesium; Mn = manganese; Cl = chlorine; K = potassium; ds = dry solids.
(a) Mill C's abnormally high Al values were not included. Average value of 15 samples.
(b) Not a number. Mn was not analyzed.

V. The t-test results comparing older Finnish recovery boiler ESP ash results [1] with present values. All comparisons having a $p < 0.05$ are statistically significant.

The most significant difference was seen in the phosphorous (P) levels. The current values in weak black liquor are lower compared to the values in the past. However, the current values are consistently higher in as-fired black liquor, ESP ash, white liquor, and lime mud. Possible explanations for the rise could be the increased usage of biofuels in the lime kiln and the burning of biosludge in the recovery boiler. However, other reasons cannot be excluded. **Table IV** presents the P comparison between older results and the results from this study. All comparisons having a $p < 0.05$ are statistically significant. Each mill in the current study is represented in the t-test with three samples, although some mills can have more than three samples analyzed from their WBL, ABL, and ESP if they had parallel process streams.

An interesting observation is also the consistently higher NPE levels in the ESP ash in the current results compared to the values presented by Salmenoja et al. in 2004 [1]. All NPEs, except Cl and K (Mn was not analyzed in the older data), were higher in the results from this study. This could indicate that the current mills are running on higher capacities (i.e., hotter furnaces) and therefore accumulating more NPEs in their ESP ash, but other factors may also affect their levels. **Table V** presents the comparison between ESP ash results from older and current data.

When comparing the other sample points, no apparent differences could be found. This indicates that even though there have been significant changes in the recovery cycle, such as increased closure, usage of biofuels in the lime kiln, and burning of biosludge, these mills have found efficient ways to remove NPEs from the recovery cycle. This may also indicate that mills are managing these NPE concentrations well. However, it is important to note that no direct mill-to-mill comparisons between current and older data can be made.

Limitation of results

Since not all input and output streams of the pulp cycle have been analyzed in this study, no solid conclusions can be made about what affects the NPE concentration in the mills. Brownstock pulp is one of the main output streams for NPEs, and wood chips are one of the main input streams for NPEs in the pulping process, but these sample points were not analyzed in this study. Also, no mass balance calculations are shown; therefore, the analysis results do not give representative insight into the actual accumulation of elements. The data needs to be seen as numerical data, and the conclusions are generalized.

ABOUT THIS PAPER

Cite this article as:
Karlemo, C., Engblom, M., and Vakkilainen, E.K., *TAPPI J.* 22(3): 184(2023). https://doi.org/10.32964/TJ22.3.184

DOI: https://doi.org/10.32964/TJ22.3.184

ISSN: 0734-1415

Publisher: TAPPI Press

Copyright: ©TAPPI Press 2023

About this journal

CONCLUSIONS

In this work, typical non-process elements from six Finnish pulp mills were analyzed and compared to literature data. These elements include Al, Si, Ca, P, Mg, Mn, Cl, K, and the elements Na and S forming the alkali charge in white liquor.

The geographical location (North vs. South) of the Finnish mills does not seem to have an impact on the NPE values in the mills participating in this study.

Apart from phosphorus, the NPE levels found in Finnish pulp mills today are not considerably different compared

ABOUT THE AUTHORS

As pulp mills take actions to decrease their environmental impact, the behavior of non-process elements (NPEs) in the recovery cycle has become an interesting topic. Understanding the NPE chemistry has become even more critical, since their unwanted accumulation affects the whole pulp mill.

The most challenging aspect of this research was finding causalities between the mill operation and the NPE levels. No direct parallels could be drawn, and the NPE concentration in a mill seems to be affected by many different parameters.

This study demonstrated that significant changes in pulp mill processes have happened in the last several decades. Increased closure of the water cycle, the usage of biofuels in lime kilns, and burning biosludge in the recovery boiler are all factors that increase the NPE concentration in the recovery cycle. However, mills have found efficient ways to remove NPEs from the recovery cycle, regardless of the more challenging fuels, side streams, or water closure.

Our most interesting finding was that though all the mills had different concentrations of NPEs, all of them could still run their process without any significant operational problems. The NPE levels seem to be very mill specific.

The results presented here offer good insight into where NPEs tend to accumulate and what concentrations can be found in six Finnish kraft pulp mills. The results can be used as an extensive reference for what concentrations of NPEs can be expected in Finnish kraft pulp mills. The next step would be to look further into what parameters affect the NPE accumulation the most and how we can impact the accumulation and improve the removal of NPEs.

Karlemo

Engblom

Vakkilainen

Karlemo is recovery chemistry specialist for Valmet Technologies Oy in Tampere, Finland. Engblom is researcher and docent at Åbo Akademi University in Turku, Finland. Vakkilainen is professor of Sustainable Energy Systems at LUT University in Lappeenranta, Finland. Email Karlemo at camilla.karlemo@valmet.com.

with the NPE levels in Finnish pulp mills in the 1990s. This indicates that the mills remove NPEs more effectively today because the closure of the mills' process cycle has increased compared to the past. Moreover, the increased use of biofuels and the burning of biosludge have increased the need for NPE removal. In the current data, P was consistently higher in as-fired black liquor, ESP ash, lime mud, and green liquor. In addition, recovery boiler ESP ash Al, Si, Ca, P, and Mg were found to be higher compared to older Finnish results.

Several things affect the overall NPE concentration in mills, and based on this study, we can make assumptions on what affects the NPE levels. However, no clear conclusions can be made on what causes a certain NPE to be higher or lower at certain mills. **TJ**

ACKNOWLEDGMENTS

This project was funded by the Finnish Recovery Boiler Committee. This work is part of the activities of the Åbo Akademi University, Johan Gadolin Process Chemistry Centre. This work is also part of the project Clean and Efficient Utilization of Demanding Fuels (CLUE), with support from the industrial partners: Andritz, Fortum, International Paper, UPM-Kymmene Corporation, and Valmet Technologies Oy.

LITERATURE CITED

1. Salmenoja, K., Kivilinna, V.A., Hupa, M., et al., "Chemical balance of non-process elements in five Finnish pulp mills," *Int. Chemical Recovery Conf.*, TAPPI Press, Atlanta, 2004.
2. Järvinen, R., Välttilä, O., and Sirén, K., *Int. Chemical Recovery Conf.*, TAPPI Press, Atlanta, 1998, p. 107.
3. Rabelo, M.S., Morgado, A.F., and Neves, J.M., *Congresso anual de celulose e papel da ABTCP*, ABTCP, São Paulo, 2001, p. 1.
4. Doldán, J., Poukka, O., Salmenoja, K., et al., *O Papel* 72(7): 47(2011).
5. Isaksson, J., "Biomass gasification for lime kiln applications," *7th Colloquium on Black Liquor Combustion and Gasification*, University of Jyväskylä, Jyväskylä, Finland, 2006.
6. Richardson, B., Lownertz, P., Forget, C., et al., *Int. Chemical Recovery Conf.*, TAPPI Press, Atlanta, 1998, p. 1025.
7. Svensson, J., "Non-process elements in the green liquor system," M.Sc. thesis, Lund University, Lund, Sweden, 2012.
8. Ulmgren, P., *Nord. Pulp Pap. Res. J.*, 12(1): 32(1997). *https://doi.org/10.3183/npprj-1997-12-01-p032-041*.
9. Salmenoja, K., Poukka, O., and Battegazorre, M., *Annu. Pulp Pap. Congr. Exhib., 42nd*, ABTCP, São Paulo, 2009.
10. Milanez, A., *O Papel* 68(8): 48(2007).
11. Gu, Y. and Edwards, L., *TAPPI J.* 3(3): 9(2004).
12. Karlemo, C., "Non-process elements in the recovery cycle of six Finnish kraft pulp mills," M.Sc. thesis, Åbo Akademi University, Turku, Finland, 2019.
13. Holamo, S., "The levels of non-process elements in a kraft mill chemical recovery system and the opening of the lime cycle," M.Sc. thesis, LUT University, Lappeenranta, Finland, 1999.