SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Åbo Akademi

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

Master's Thesis

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Outline of this presentation

- Objective and research questions for this Master's Thesis
- Experimental part
- Results
- Conclusions

Objective and research questions

- Objective:
  - Better understanding of non-process element chemistry in Finnish pulp mills

- Research questions:

  - Are there differences in NPE levels between the pulp mills (2018 North vs. 2018 East)
  - How have NPE levels changed in Finland (1995, 1999, 2004 vs. 2018)
  - North American and South American results compared to this projects results
  - Are there NPE level differences due to different process equipment

Non-process elements

- Elements purged via green liquor dregs
  - More insoluble in alkali solutions
  - **Mg, Ca, Mn**
  - More easily removed from green liquor dregs

- Elements accumulated in liquor and lime cycle
  - More soluble in alkali solutions
  - **K, Cl** in liquor cycle
  - **Al, Si, P** in liquor and lime cycle
  - Accumulate significantly before being purged by precipitation

Experimental part

Methods and data treatment

- Methods
  - Sampling
    - 6 Finnish Kraft pulp mills
    - 7 sampling points
    - 10 elements per sampling point (**Na**, **S**, Ca, Mg, Mn, Al, Si, P, Cl, K)
  - Interviews
    - 6 Finnish pulp mills
- Data treatment
  - Comparison with literature data
  - Conversion of concentration data (mg/kg → g/ADt)
  - Hypothesis test: T-tests for statistical analysis

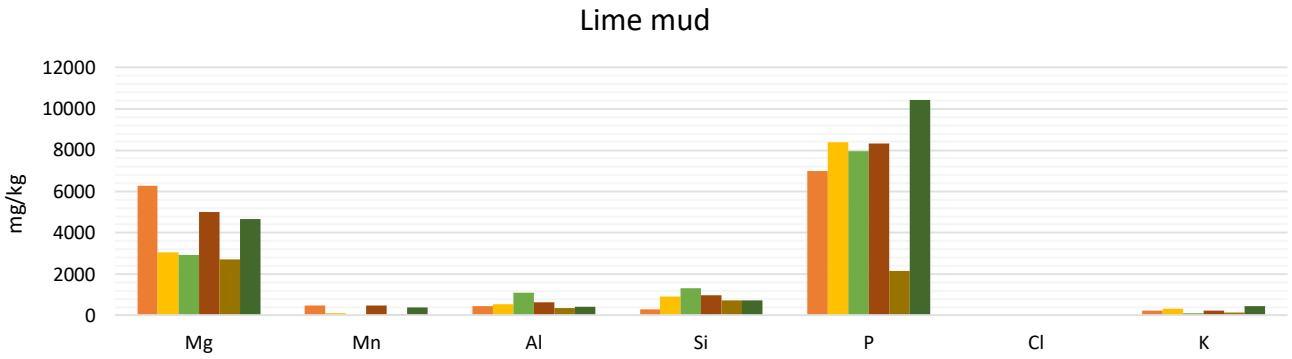
Sample points:

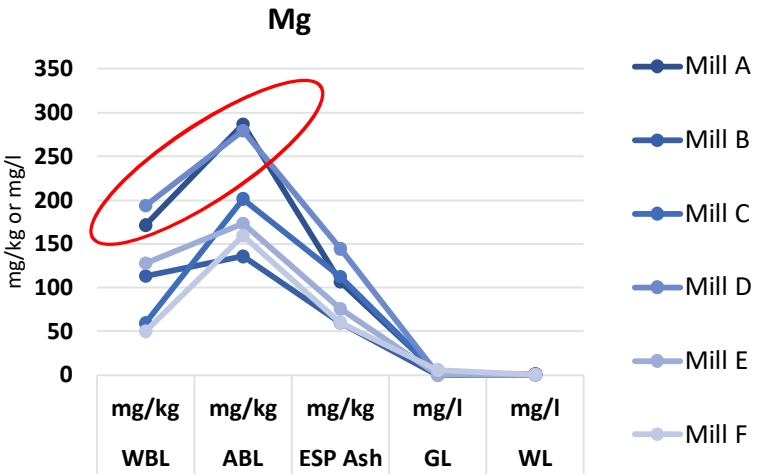
1. Weak black liquor
2. As-fired black liquor
3. ESP ash
4. Clarified green liquor
5. Green liquor dregs
6. White liquor
7. Lime mud

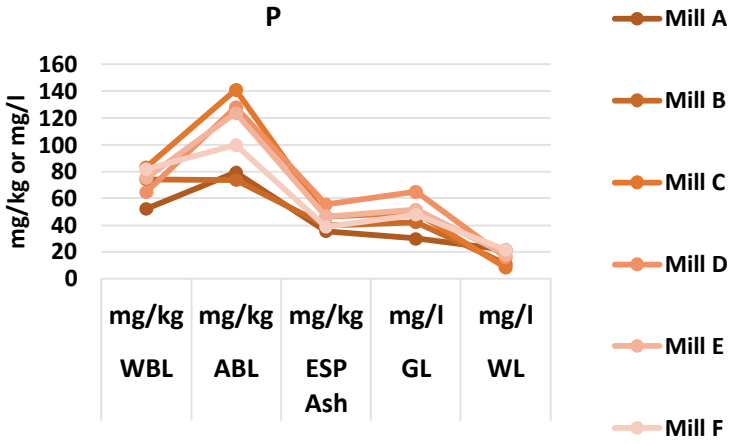
Results

General observations:

- Alkali insoluble elements precipitate in green liquor and are removed with green liquor dregs (**Ca**, **Mg** and **Mn**)
- **Mg** has a tendency to accumulate in lime cycle as well
- Mill A and Mill D use only softwood and their **Mg** conc. is higher in WBL and ABL
- K and Cl accumulate in ESP ash
- Al, Si and P do not get as easily purged with green liquor dregs.
- P Increases in conc. in ABL (addition of side streams) and is high in lime mud





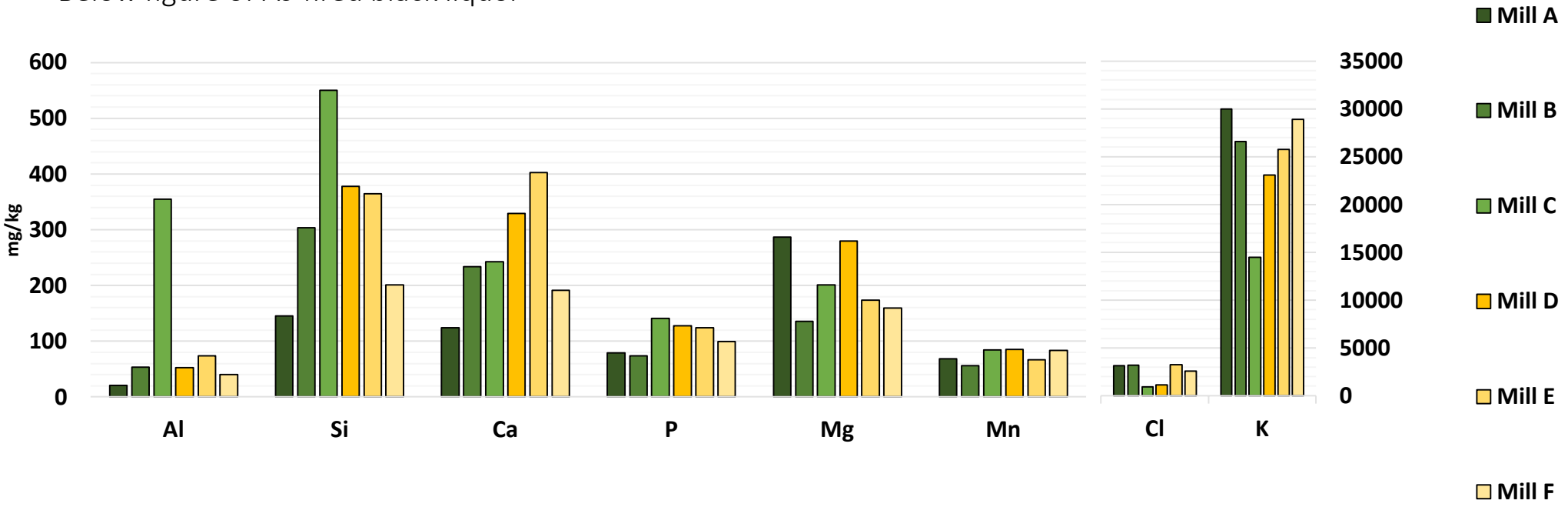


Comparisons

- Are there differences in NPE levels between the pulp mills (2018 North vs. 2018 East)
- How have NPE levels changed in Finland (1995, 1999, 2004 vs. 2018)
- North American and South American results compared to this project's results
- Are there NPE level differences due to different process equipment

FIN North vs. FIN East

- Green = North
- Yellow = East
- Below figure of As-fired black liquor

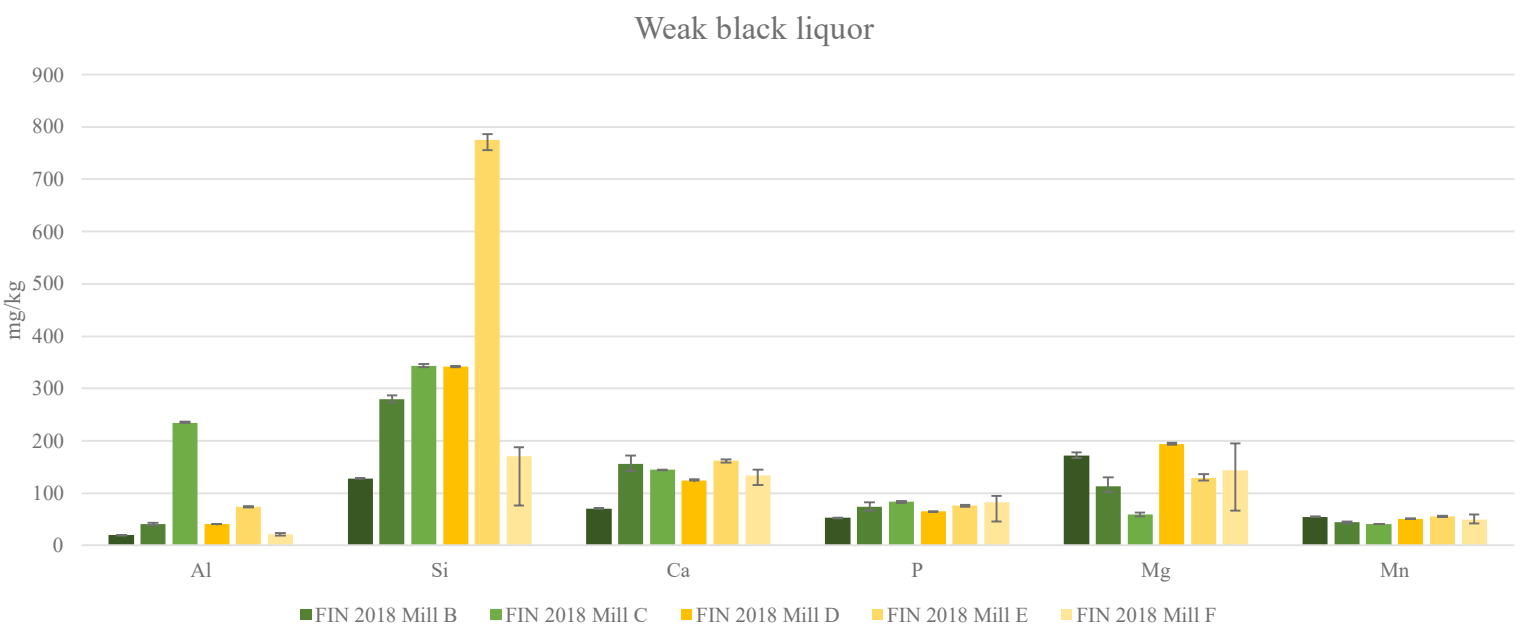


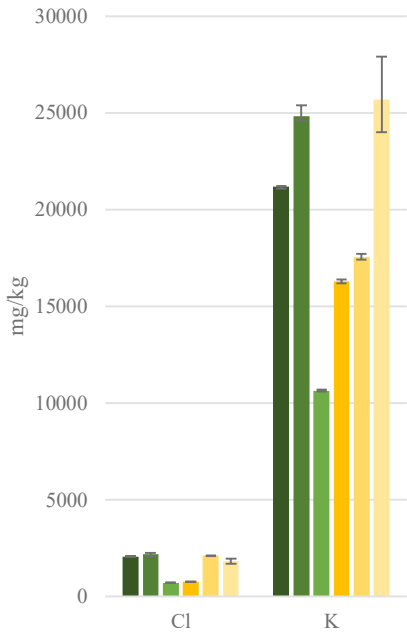
T-test results

- In WBL, Mn is lower in the Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
	North	30	250	124	70	115	46	1645	18878
WBL	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



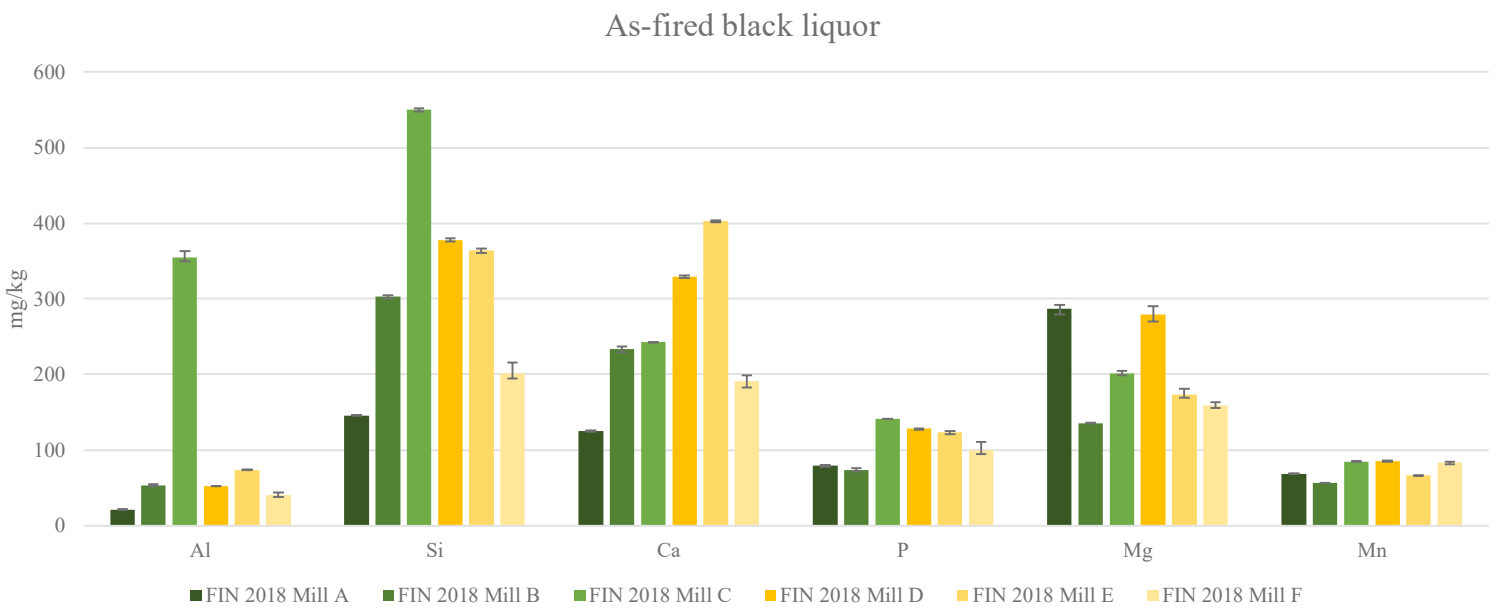


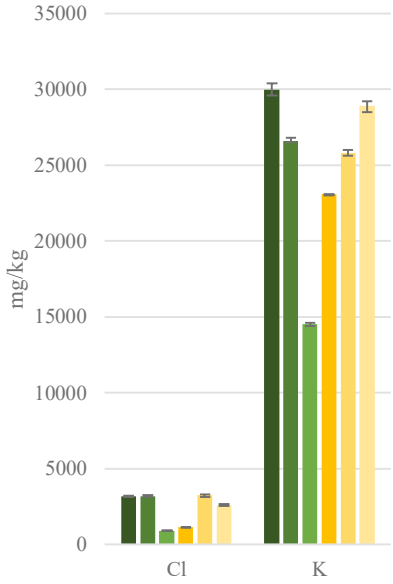
T-test results

- In ABL, Ca is lower in Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
	North	37	333	200	98	208	70	2425	23689
ABL	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



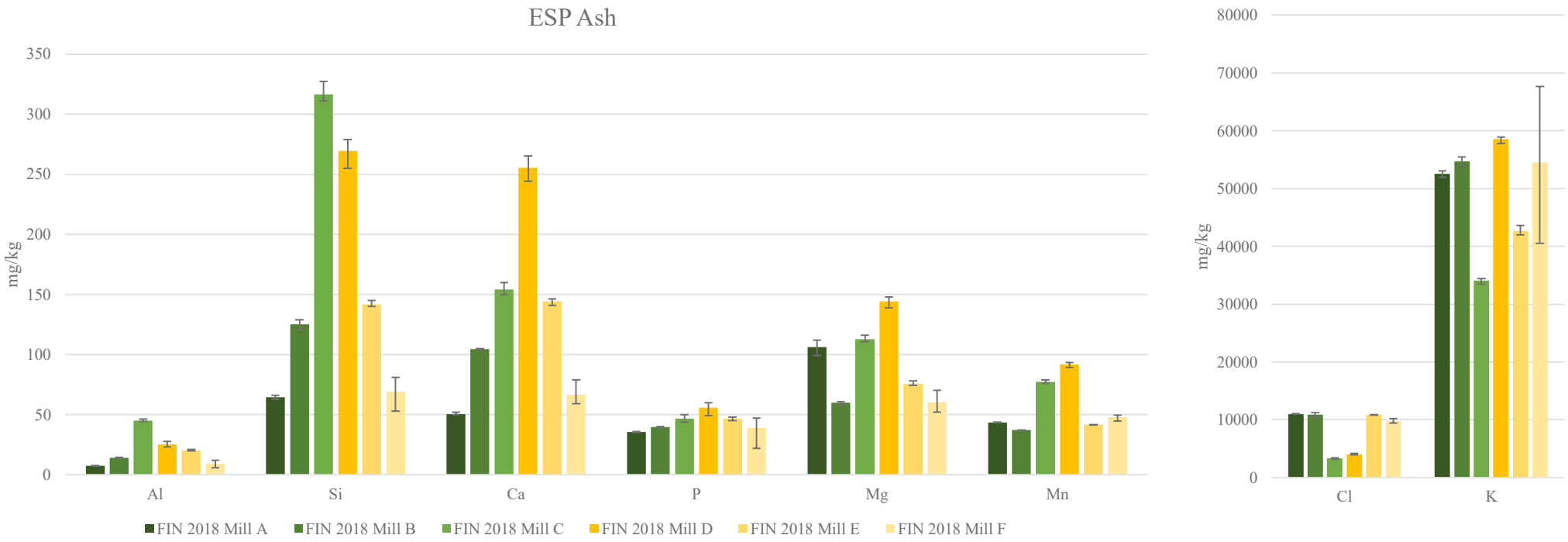


T-test results

- In ESP A, Al is lower in Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
	North	11	169	103	41	93	53	8400	40444
ESP A	East	18	160	155	47	93	60	8233	46500
	p-value	**0.020**	0.858	0.120	0.064	0.975	0.455	0.921	0.344

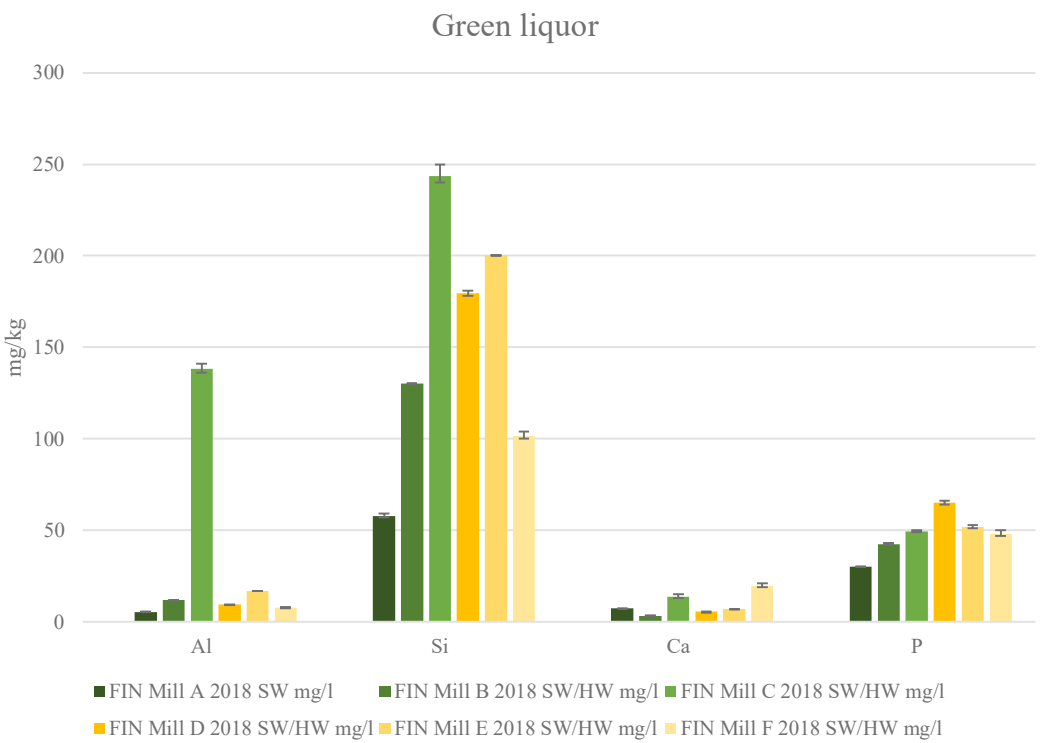


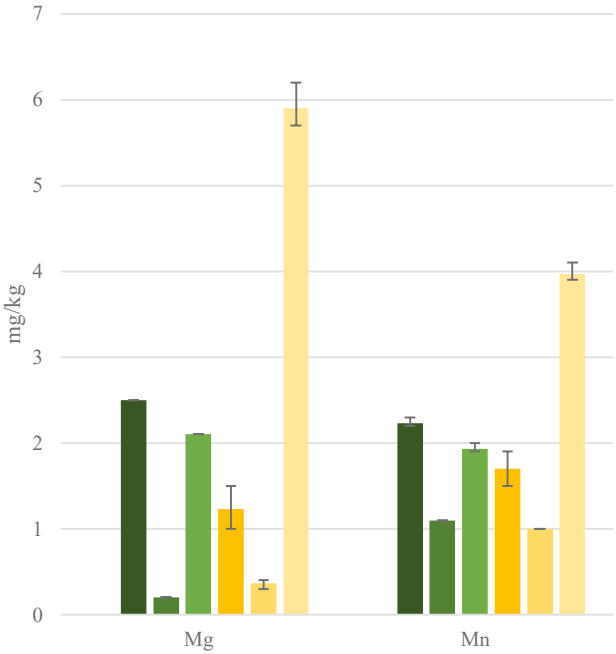
T-test results

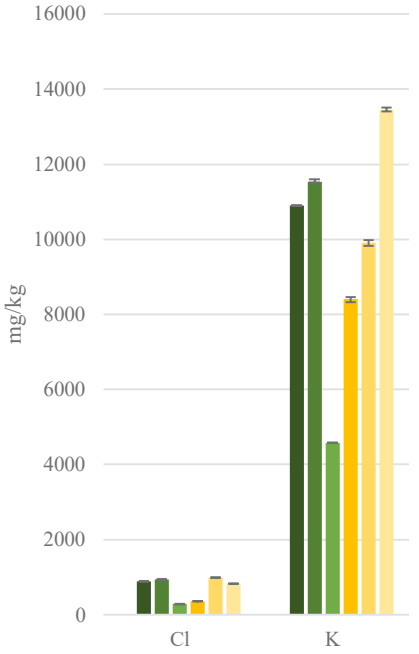
- In GL, P is lower in Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
	North	9	144	8	41	2	2	701	9004
GL	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





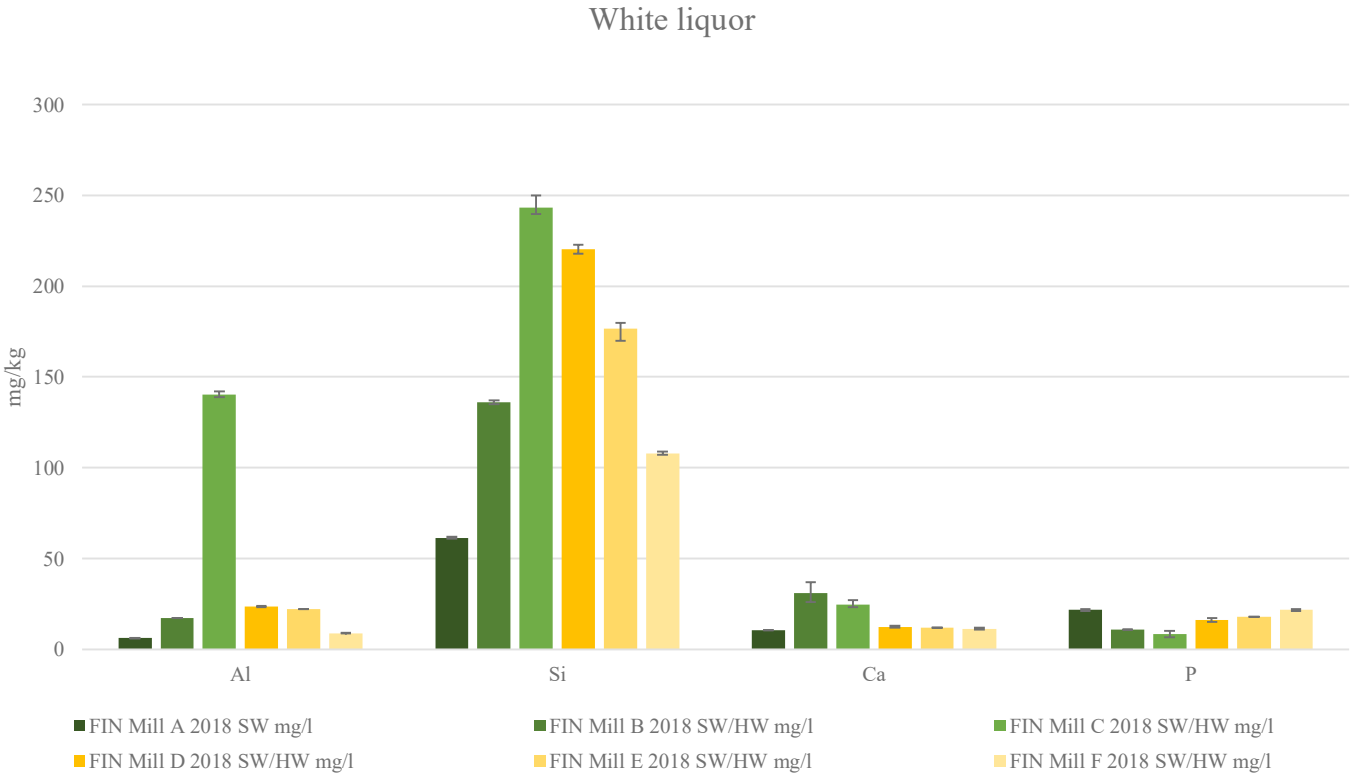


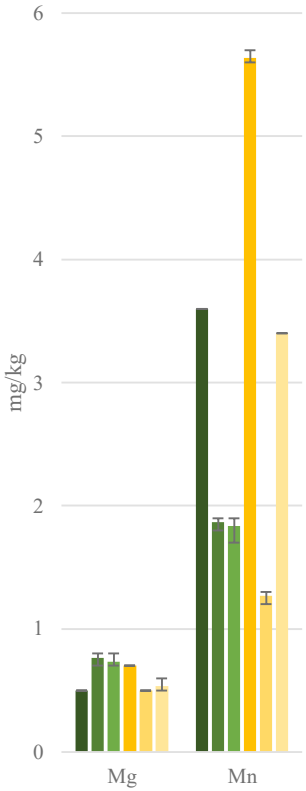
T-test results

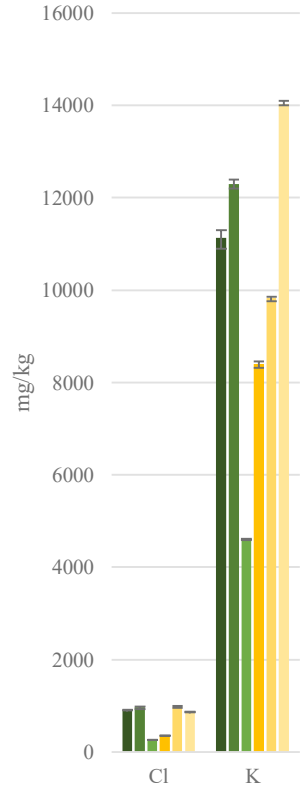
- In WL, Ca is higher in Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
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





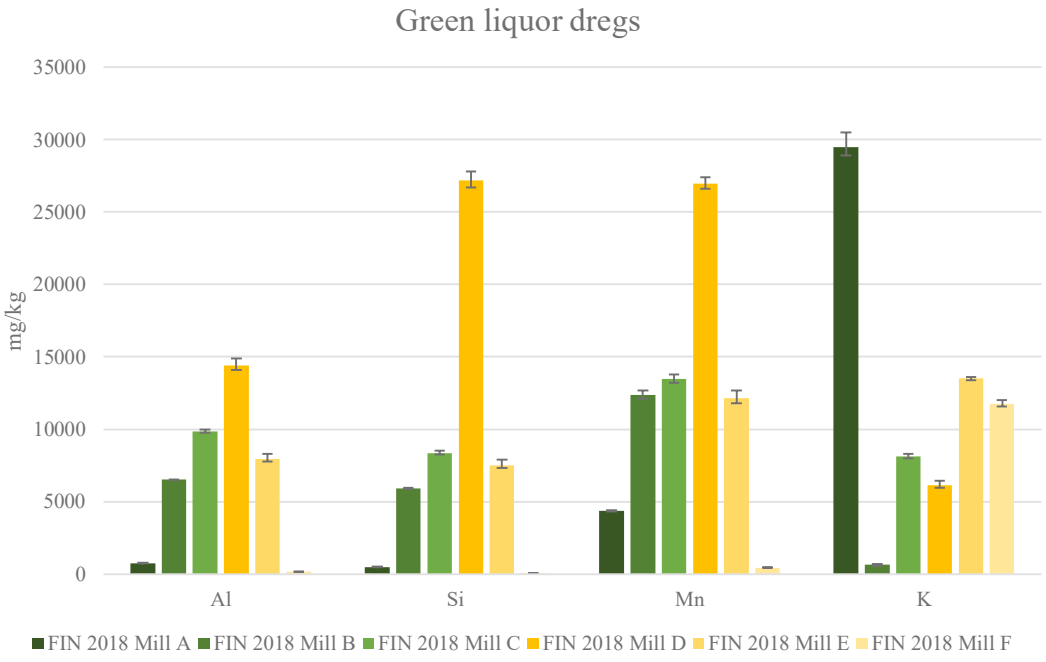


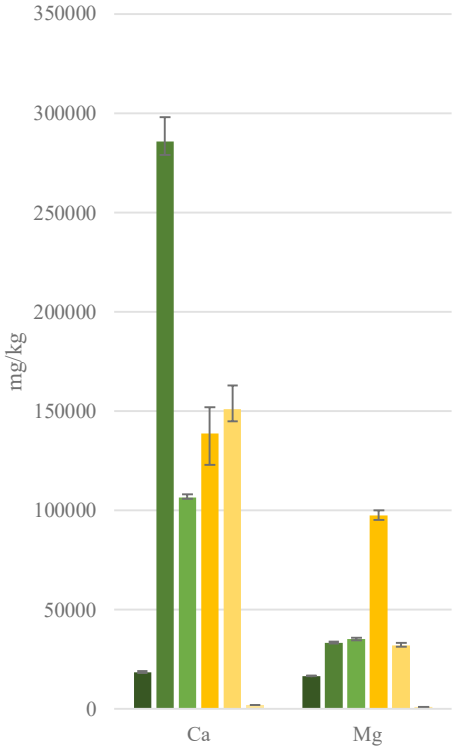
T-test results

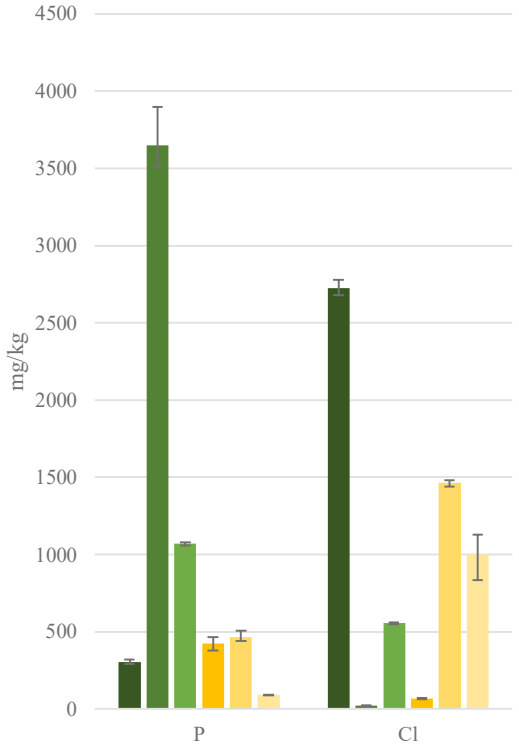
- In GL D P is higher in Northern mills

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
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







T-test results

- In WBL, Mn is lower in the Northern mills
- In ABL, Ca is lower in Northern mills
- In ESP A, Al is lower in Northern mills
- In GL, P is lower in Northern mills
- In WL, Ca is higher in Northern mills
- In GL D P is higher in Northern mills
- **6/56 t-test results significant**

* Mill C's values for Al are not included

		Al *	Si	Ca	P	Mg	Mn	Cl	K
	North	30	250	124	70	115	46	1645	18878
WBL	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
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	p-value	0.077	0.503	**0.013**	0.051	0.125	0.178	0.905	0.352
	North	484	841	378556	7762	4091	202	7	215
LM	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
	North	3638	4921	136955	1675	28400	10078	1100	12754
GL D	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

Comparisons

- Are there differences in NPE levels between the pulp mills (2018 North vs. 2018 East)
- How have NPE levels changed in Finland (1995, 1999, 2004 vs. 2018)
- North American and South American results compared to this project's results
- Are there NPE level differences due to different process equipment

Older Finnish results vs. 2018 results

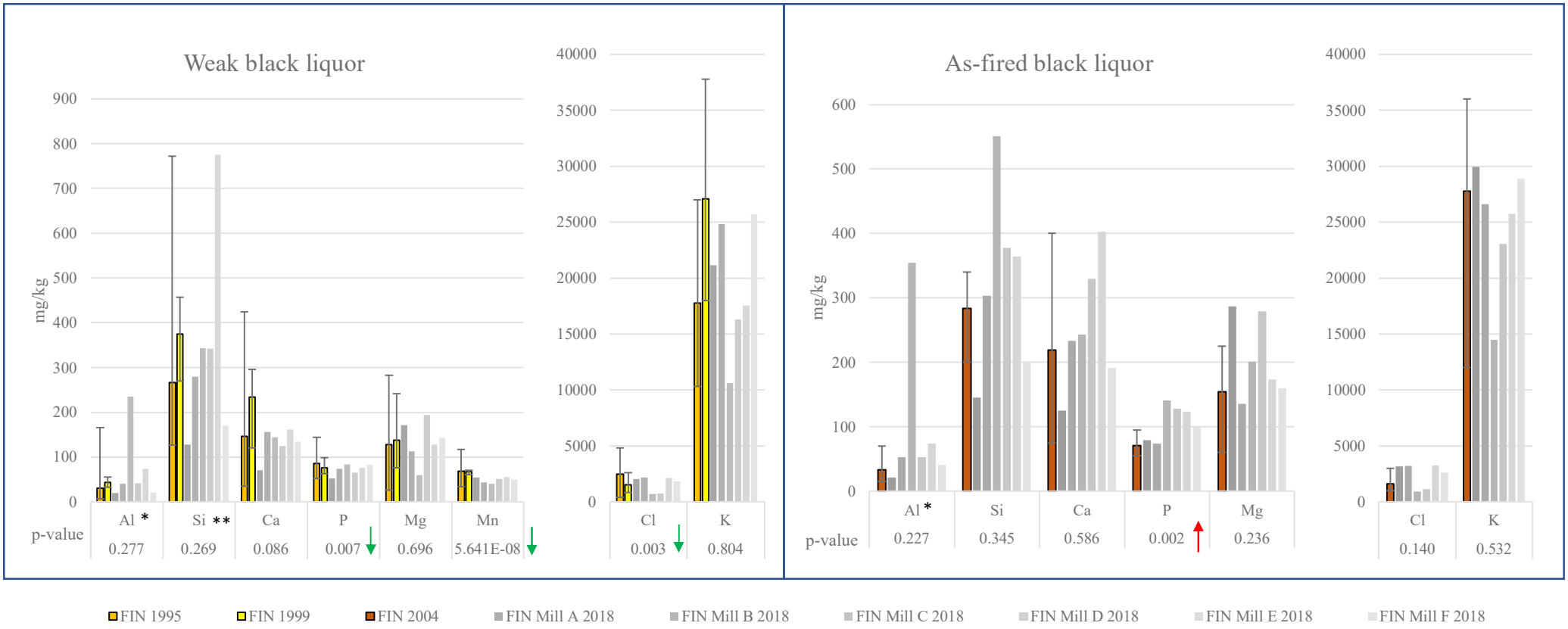


*Figure 39 Weak black liquor and as-fired black liquor comparisons between older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) (Salmenoja, et al., 2004) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values 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 newer values are significantly lower and the red color indicates that the newer 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.*

T-test results

- In WBL, This projects results are lower for P, Mn and Cl compared to older FIN results
- In ESP A, this project's results are higher for Al, Si, Ca, P and Mg
- In WL, Mg, Mn and Cl lower
- In GL D Al is higher in newer results
- P is higher in nearly all sample points in the results from this project!
- 18/51 t-test results significant

* Mill C's values for Al are not included

Comparisons

- Are there differences in NPE levels between the pulp mills (2018 North vs. 2018 East)
- How have NPE levels changed in Finland (1995, 1999, 2004 vs. 2018)
- North American and South American results compared to this project's results
- Are there NPE level differences due to different process equipment

North American results vs. FIN 2018

- WBL and ABL did not have enough good data points in literature to make T-tests

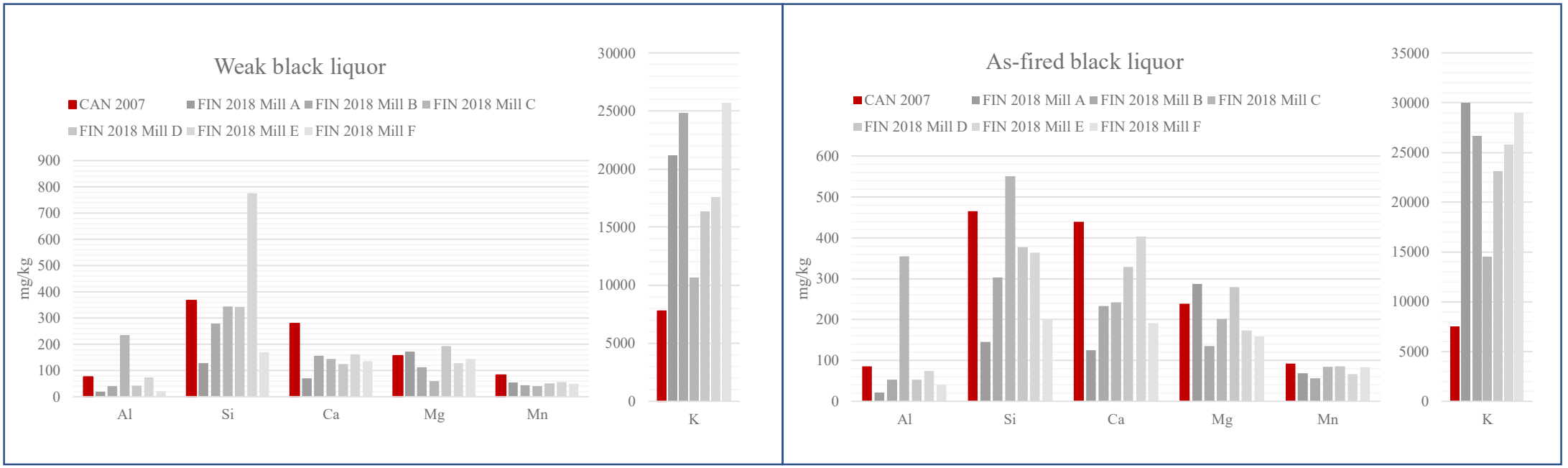


Figure 44 Comparison between North American (Taylor & McGuffie, 2007) (Frederick, et al., 2000) and this project's results in weak black liquor and as-fired black liquor.

Older North American results vs. 2018 FIN results

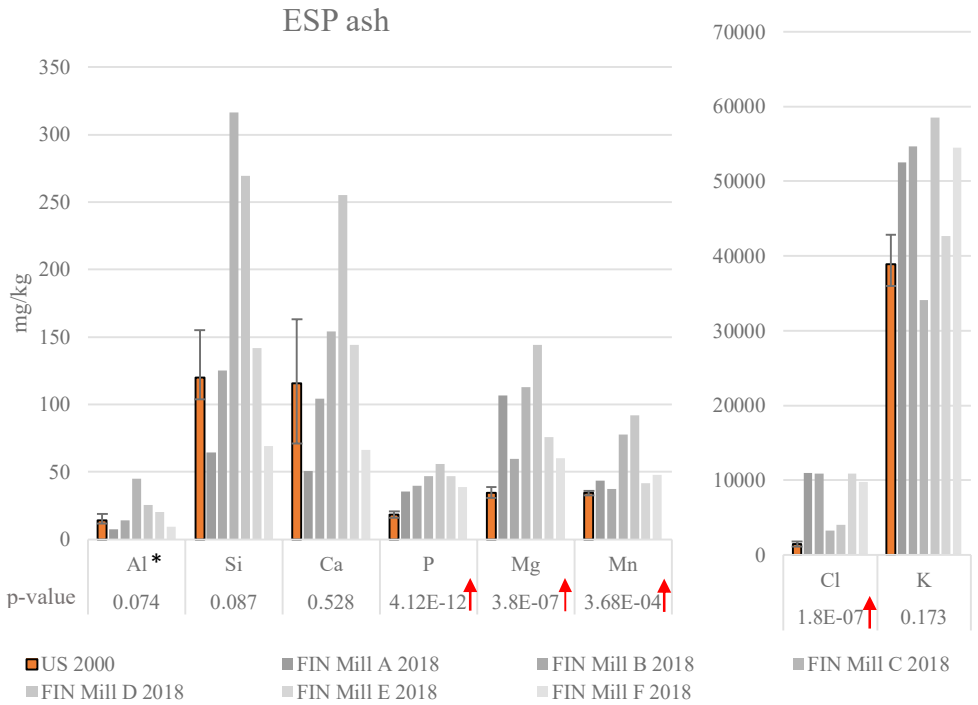


*Figure 45 ESP ash comparison between older North American results (Frederick, et al., 2000)and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower and the red color indicates that the newer values are significantly higher. * The abnormally high Si values from Mill C are included in the t-test.*

- Similar figures made for ESP A, GL, WL, LM, GL D
- Some literature references were in mg/kg unit for GL and WL. They were converted to mg/l for the t-tests.

T-test results

- In ESP A, P, Mg Mn and Cl higher in FIN 2018
- In GL D, Al, Si P and K are higher compared to North American results
- P higher in FIN 2018
- K higher in FIN 2018
- 20/38 t-test results significant

* Mill C's values for Al are not included
** Some literature references converted to mg/l with a density of 1.15 g/l

FIN vs. South America (eucalyptus)

- Not enough literature values were available to make t-tests
- However, one could conclude that Al, Si and Cl are higher in eucalyptus results compared to the results conducted in this project

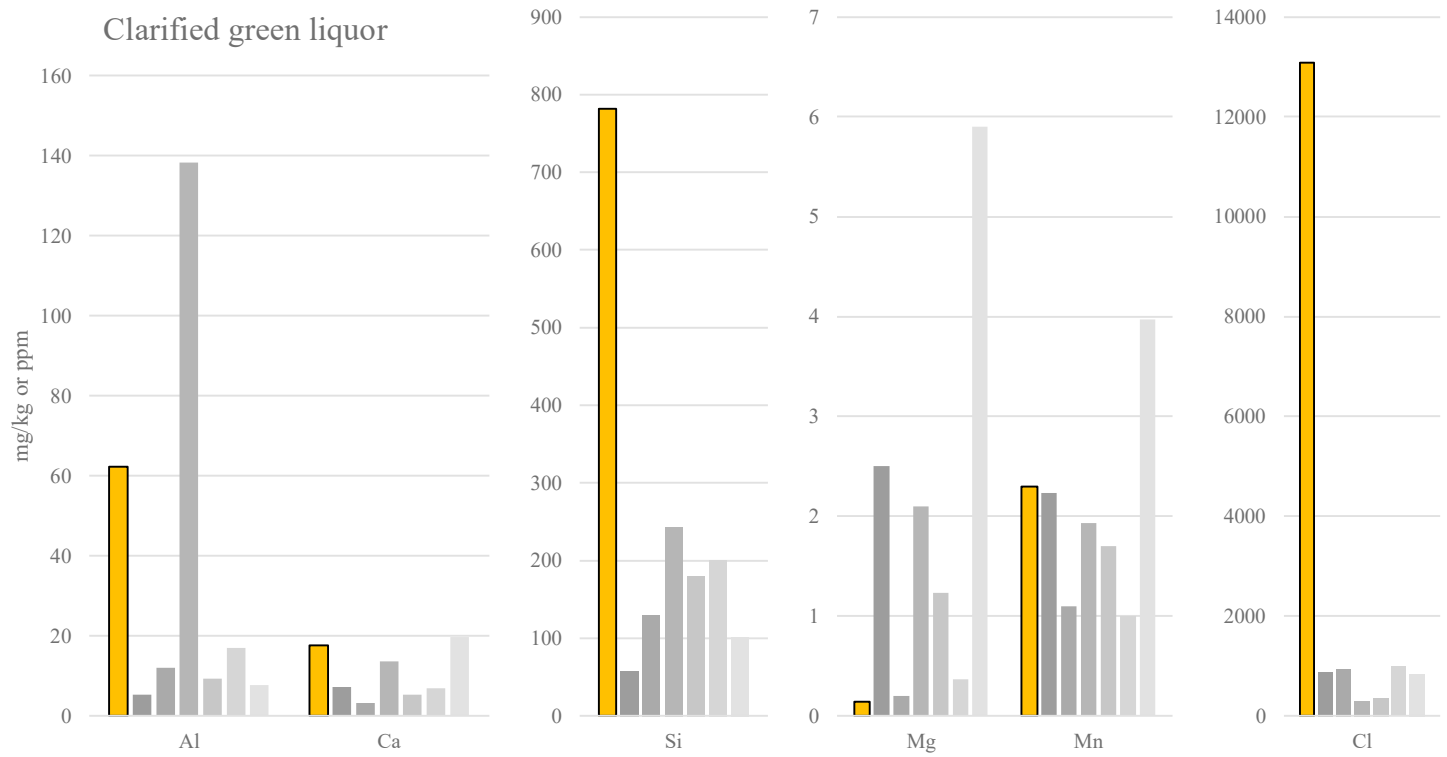


Figure 50 Clarified green liquor and white liquor results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

Comparisons

- Are there differences in NPE levels between the pulp mills (2018 North vs. 2018 East)
- How have NPE levels changed in Finland (1995, 1999, 2004 vs. 2018)
- North American and South American results compared to this projects results
- Are there NPE level differences due to different process equipment

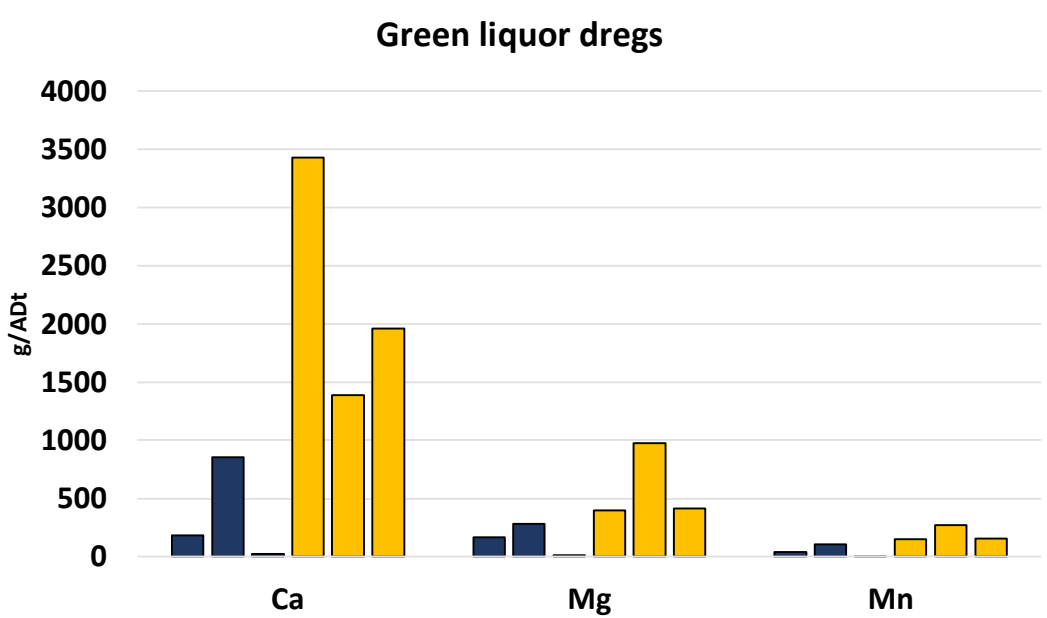
Comparison of green liquor removal techniques

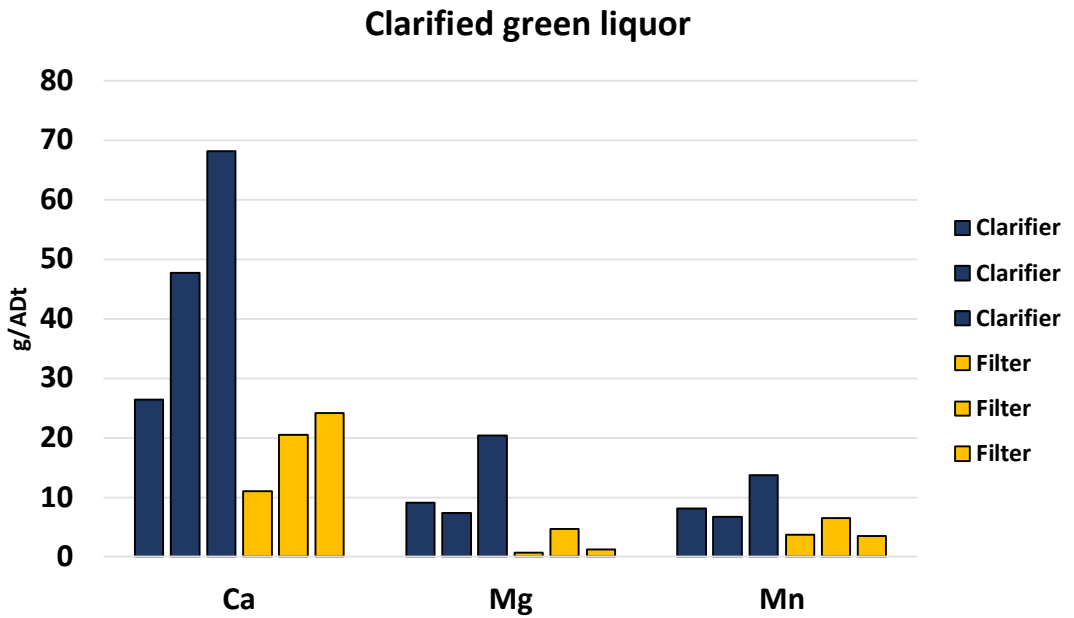
- Two main techniques to remove dregs from green liquor
  - Clarifier (older)
  - Filters (modern option)

- Filters are according to literature more effective in removing dregs
- Clarifiers remove dregs by sedimentation since mid – 1960

- **Three mills use clarifiers**
- **Three mills use cross flow filters to remove dregs**

Comparison of green liquor removal techniques





Conclusions

- Are there differences in NPE levels between the pulp mills (North vs. East)
  - Yes, but minor differences. 10 % of the t-tests were significant. Northern mills had for some NPEs lower values
- How have NPE levels changed in Finland (old vs. up-to-date results)
  - Weak black liquor quality better in the newer results
  - Phosphorous higher in this projects results compared to older Finnish results
  - ESP Ash (Al, Si, Ca, P, Mg) higher in FIN 2018
  - 18/51 t-test results were significant
- Do the results differ compared to North American and South American results
  - ESP Ash (P, Mg, Mn, Cl) values higher in FIN 2018
  - P and K higher in FIN 2018
  - LM P, Mg, Mn higher
  - In GL Ca, Mn lower and in WL Mg lower
  - In GL D Al, Si, P and K are found more in dregs (are removed better)
  - 20/38 t-test results were significant
- Are there NPE level differences due to different process equipment
  - Filters more effective than clarifiers

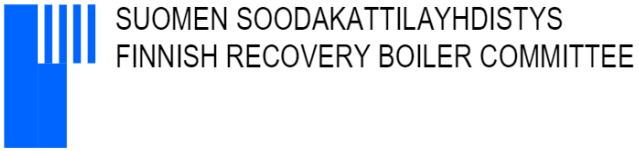
Conclusions

- According to the interviews: Mills have found ways to cope with NPEs
- **BUT** NPEs can create severe damage and fast!
  - During process disturbance or process changes:
    - Unpredictable high NPE levels from side streams e.g. biosludge
    - Using new make up lime and makeup chemicals

- Environmentally friendly solutions and a zero-effluent pulp mills:
  - Even though the waste streams from have decreased around 90 % from 1992 the NPE levels have not increased remarkably!
  - The NPE “symptoms” spotted today in the process might create severe problems in the future

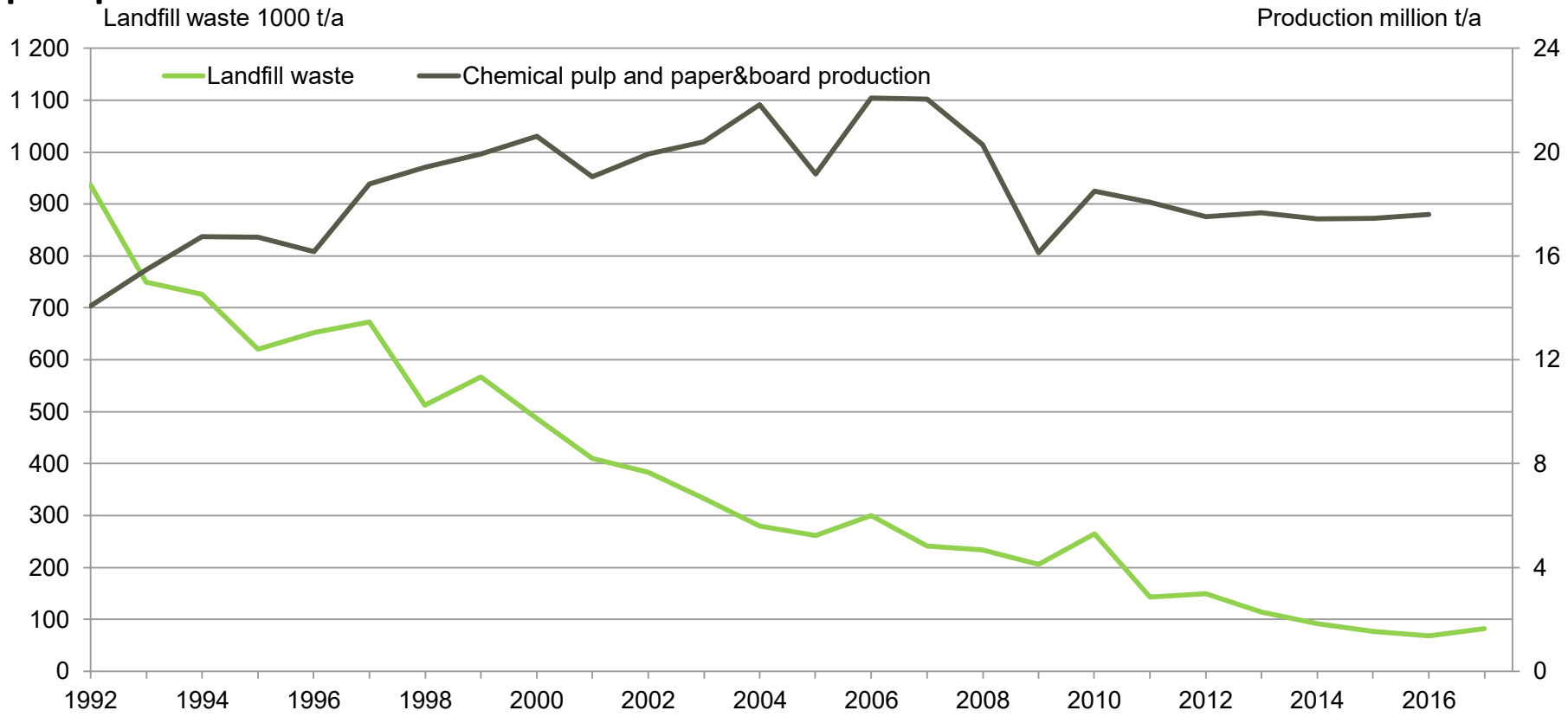
Thank you for listening!

- A special thanks to the Lipeätyöryhmä
- Thank You for your support, your help and giving me the opportunity to do this Master's Thesis!

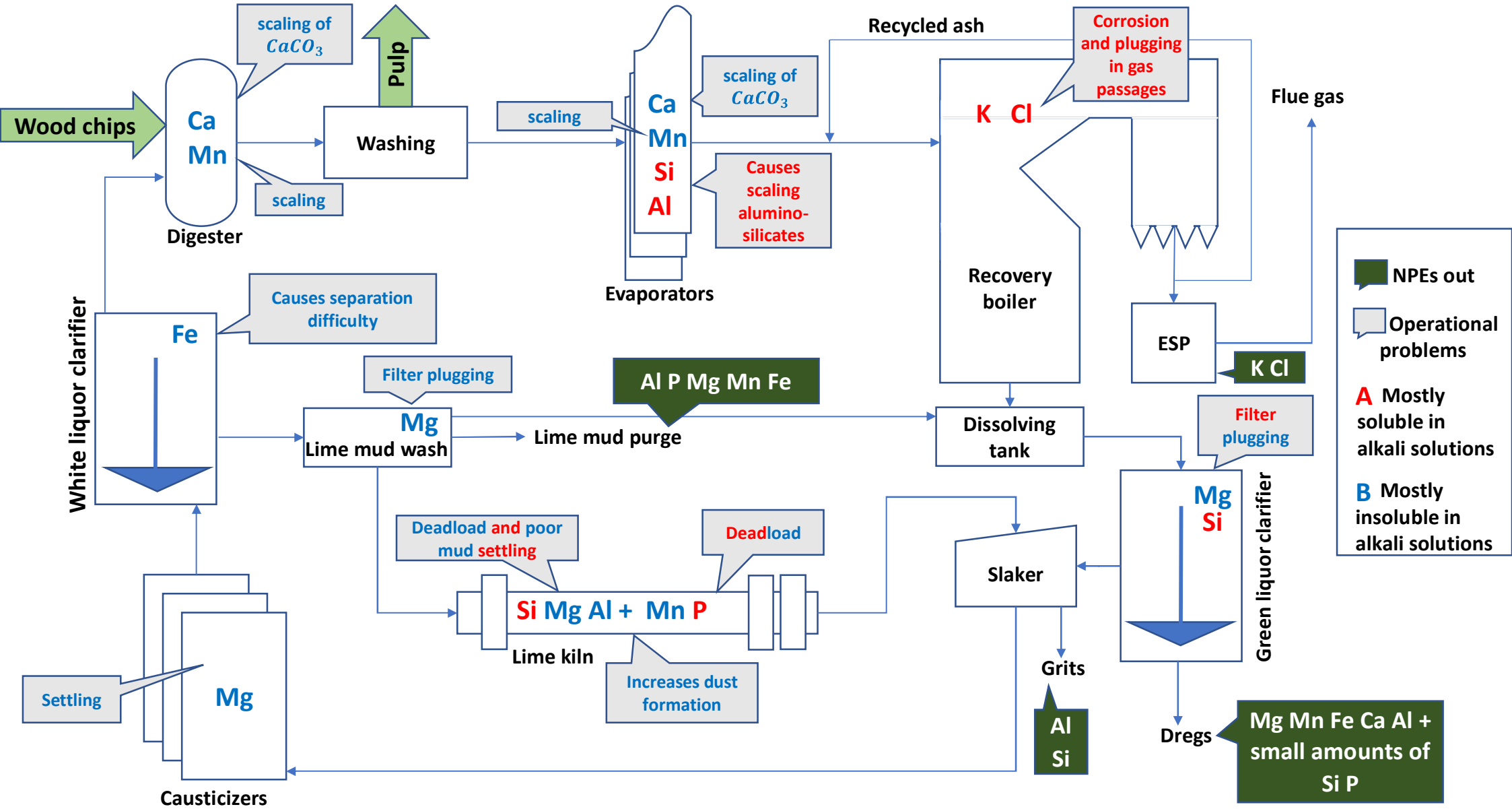


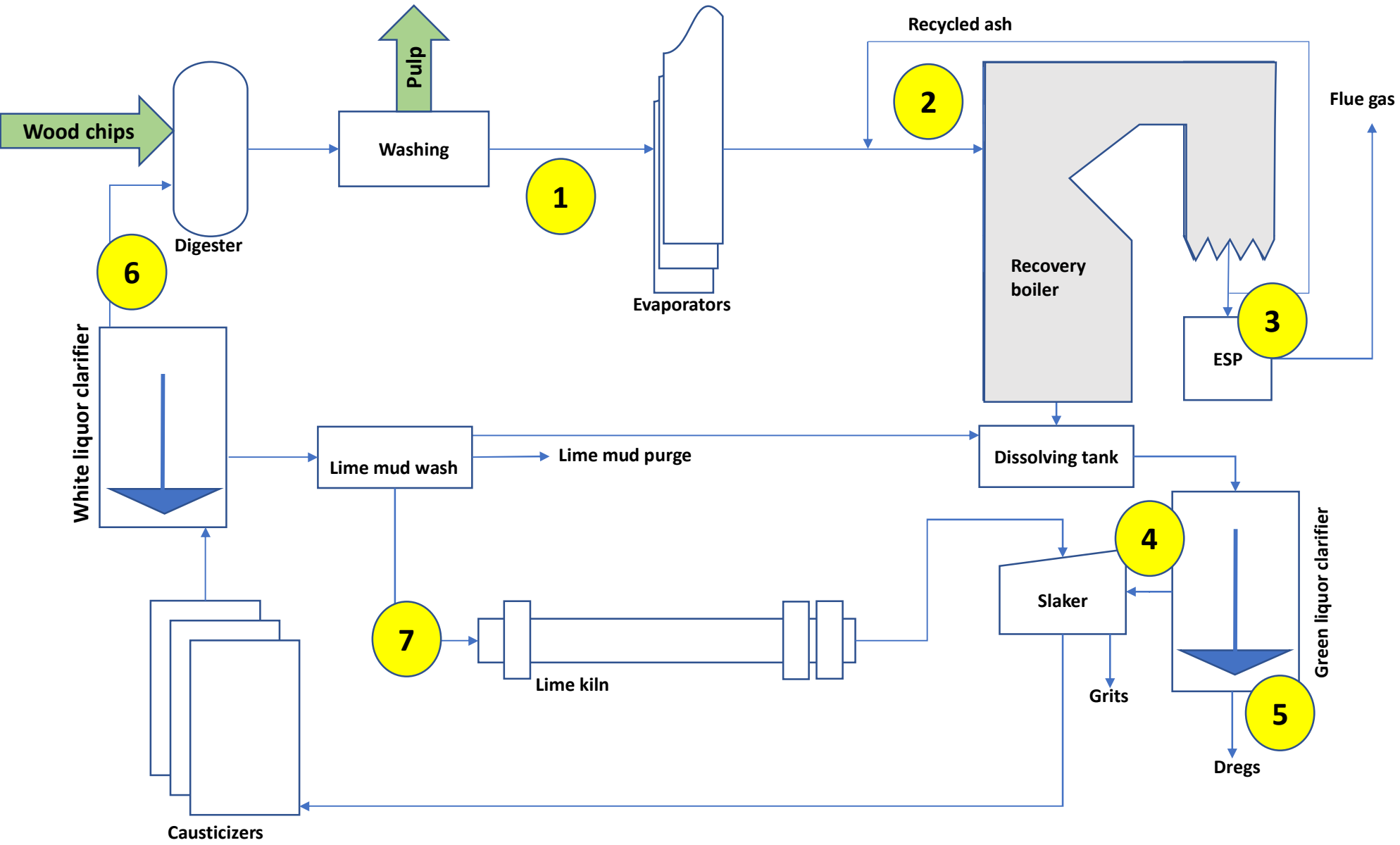
Extra slides

Landfill waste and production and of pulp and paper mills in Finland



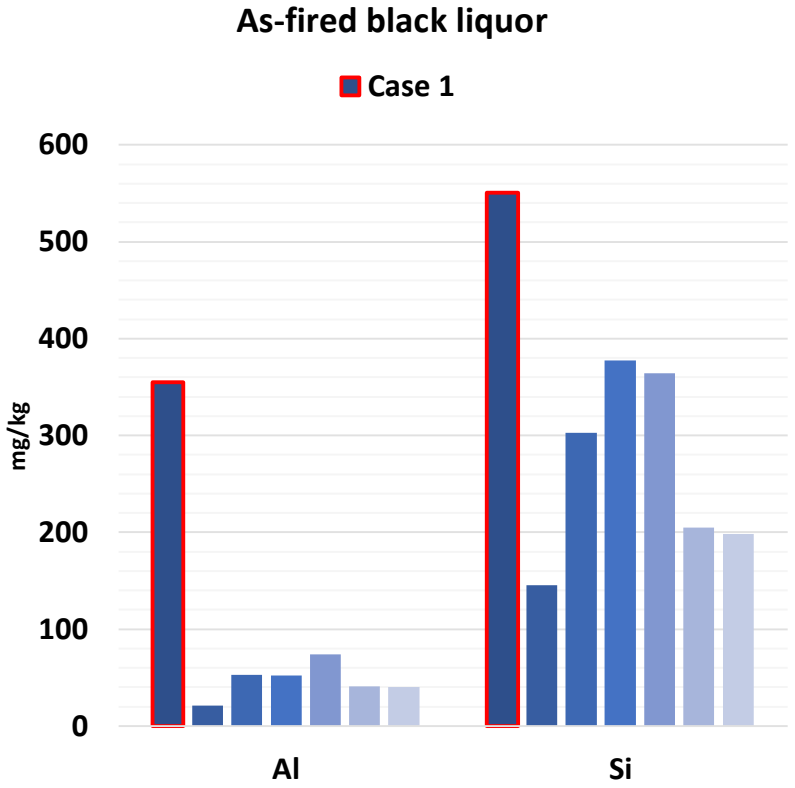
https://www.forestindustries.fi/statistics/environment/


Wood chips
Ca
Mn
Digester
scaling of $CaCO_3$
scaling
Pulp
Washing
scaling
Ca
Mn
Si
Al
Evaporators
scaling of $CaCO_3$
Causes scaling alumino-silicates
Recycled ash
Corrosion and plugging in gas passages
K Cl
Recovery boiler
Flue gas
ESP
K Cl
White liquor clarifier
Fe
Causes separation difficulty
Filter plugging
Mg
Lime mud wash
Al P Mg Mn Fe
Lime mud purge
Dissolving tank
Filter plugging
Mg
Si
Green liquor clarifier
Deadload and poor mud settling
Deadload
Si Mg Al + Mn P
Lime kiln
Increases dust formation
Slaker
Grits
Al
Si
Dregs
Mg Mn Fe Ca Al + small amounts of Si P
Settling
Mg
Causticizers
NPEs out
Operational problems
A Mostly soluble in alkali solutions
B Mostly insoluble in alkali solutions


Wood chips
Digester
Pulp
Washing
1
Evaporators
Recycled ash
2
Recovery boiler
Flue gas
ESP
3
6
White liquor clarifier
Lime mud wash
Lime mud purge
Dissolving tank
4
Slaker
Grits
Green liquor clarifier
5
Dregs
7
Lime kiln
Causticizers

Case studies

- Case 1:
  - One mill had encountered a kaolin contamination
    - Kaolin entered the recovery cycle with biosludge
    - Biosludge was added in the evaporator plant to the cycle
    - The scaling of aluminosilicates turned so bad in the evaporator plant that it had to be temporarily shut down for cleaning
    - During sampling period



Case studies

- Case 2:
  - Ring formation in lime kiln
  - SEM results show that more Al and Si are found in the ring sample.
  - Also TGA indicate that only a small amount of $CaCO_3$ was formed in the ring.
  - Not during sampling period

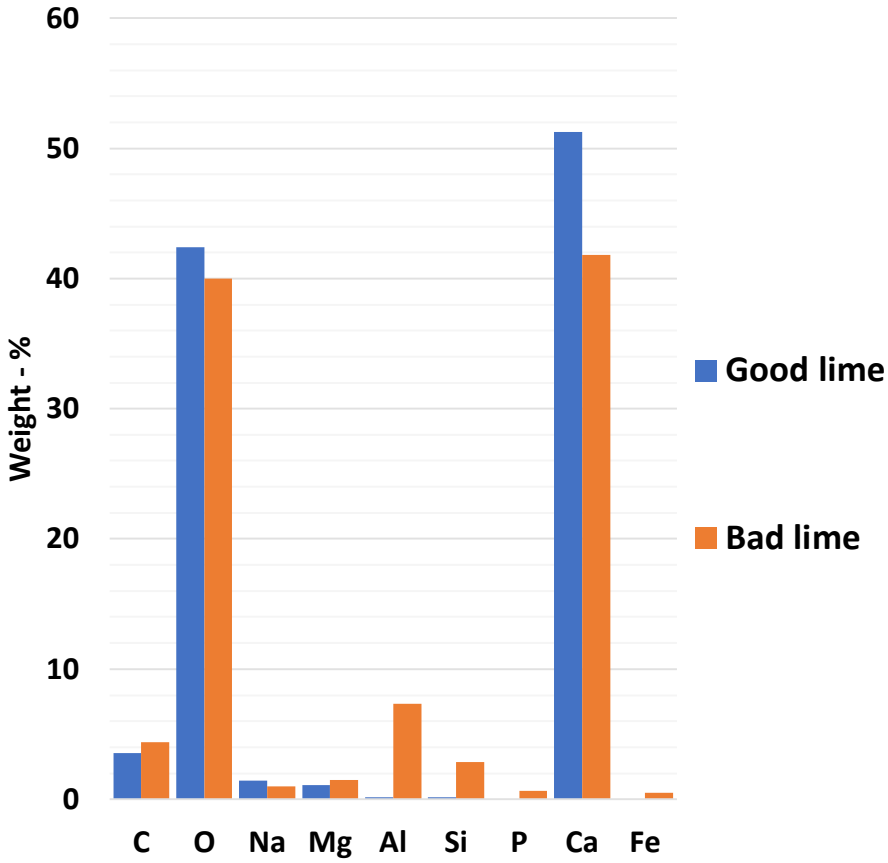
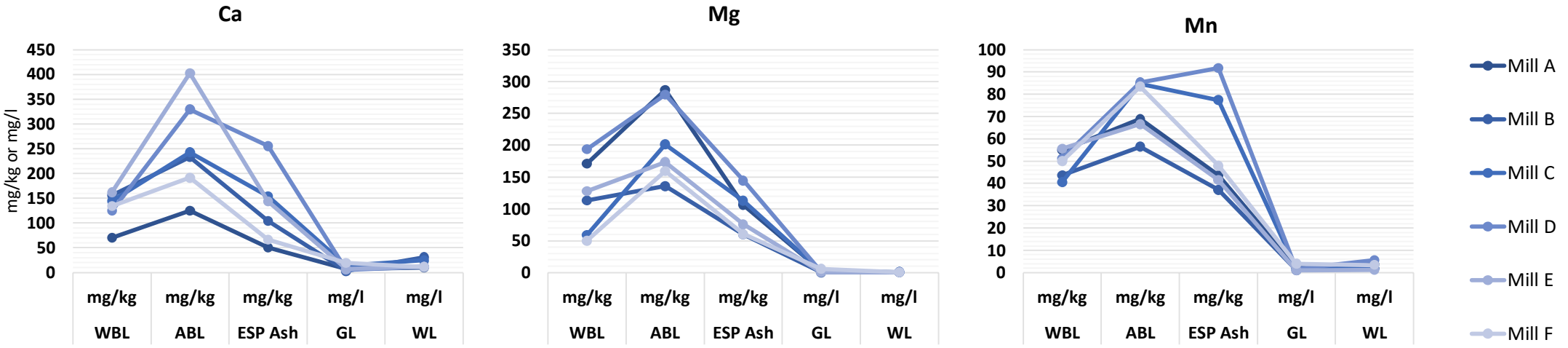


Figure SEM results of good and bad lime.

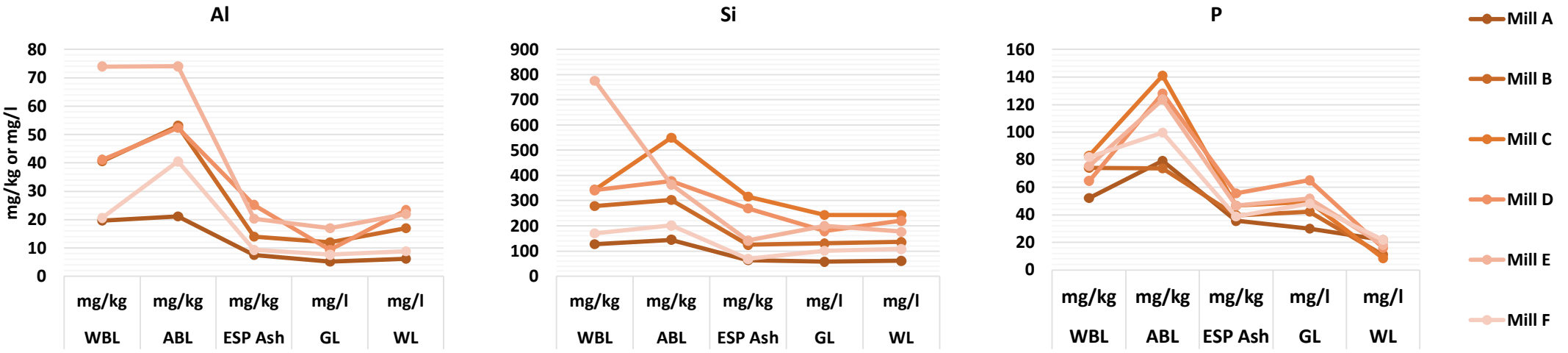
Results

- Alkali insoluble elements precipitate in green liquor and are removed with green liquor dregs
- Mg has a tendency to accumulate in lime cycle if it reaches lime mud



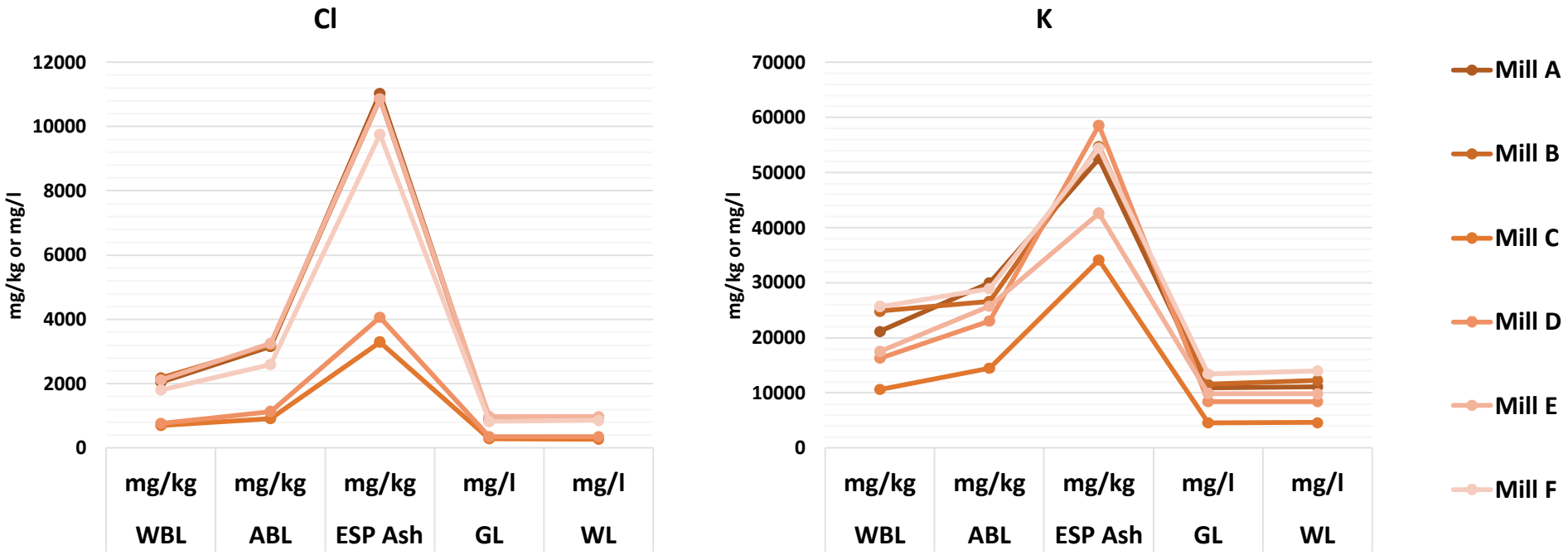
Results

- Al is removed partly with dregs.
- Si level does not seem to change a lot in the sampling points.
- P tends to accumulate in lime mud



Results

- Cl and K tend to accumulate in ESP ash



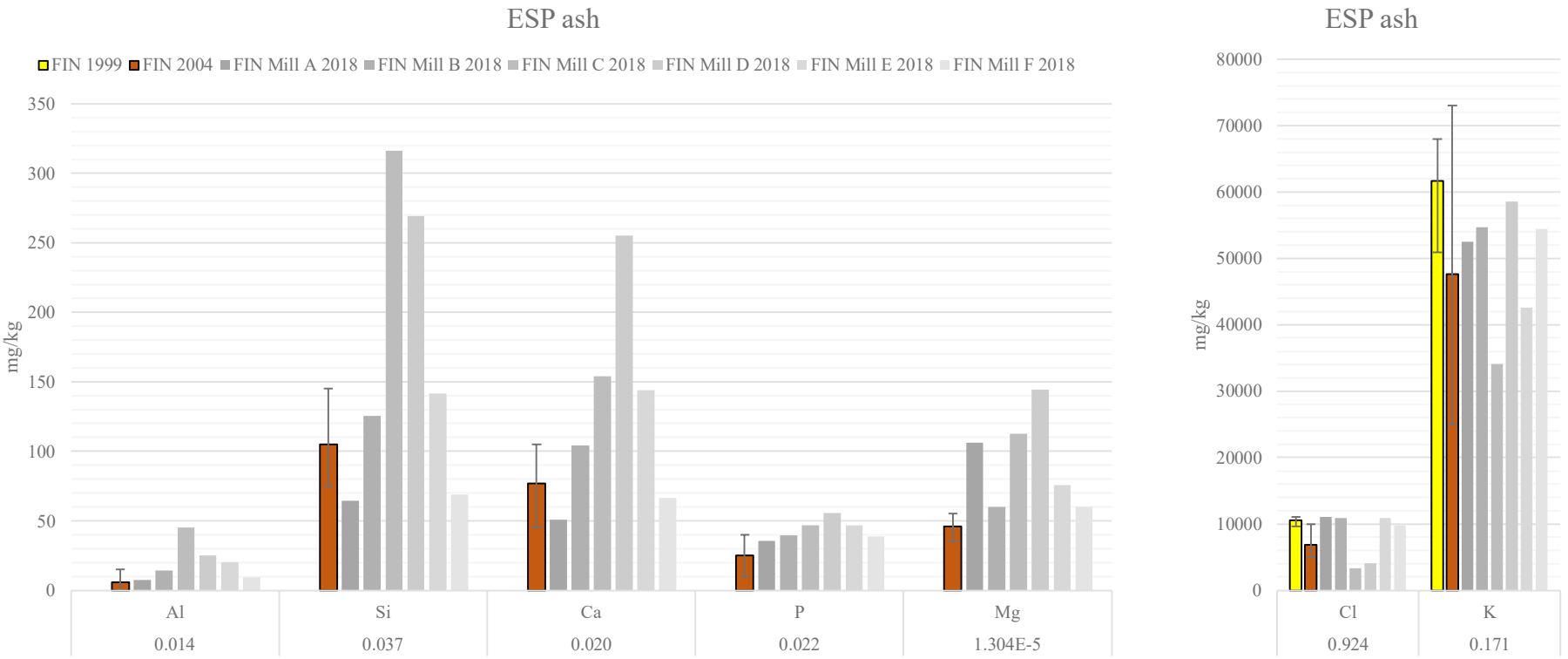


*Figure 40 ESP ash comparison between older Finnish results (Holamo, 2000) (Salmenoja, et al., 2004) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in 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. * Both with or without Mill C's Al value, difference was still significant (Without Mill C, p-value 0.014).*

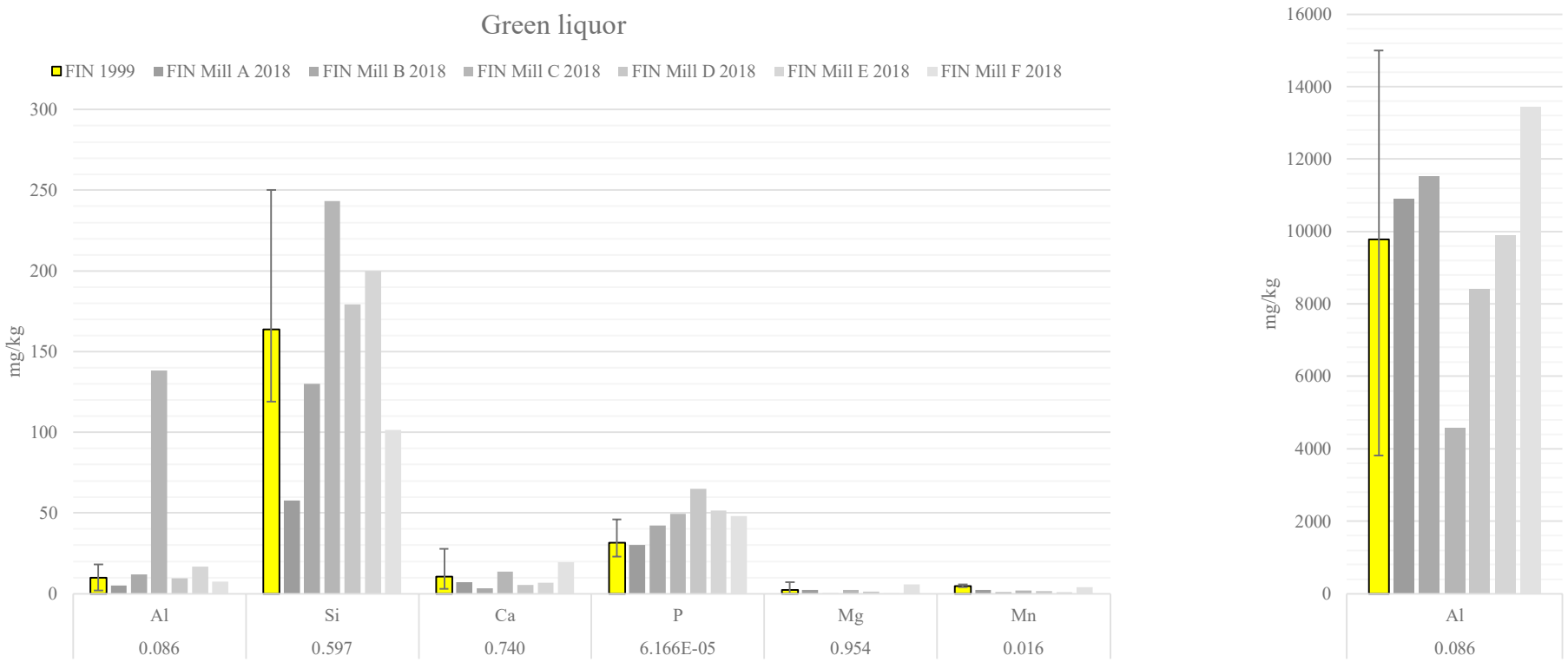


*Figure 41 Green liquor comparison between older Finnish results (Holamo, 2000) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * Both with or without Mill C's Al value, no significant difference (Without Mill C, p-value 0.94 and with Mill C p-value 0.086).*

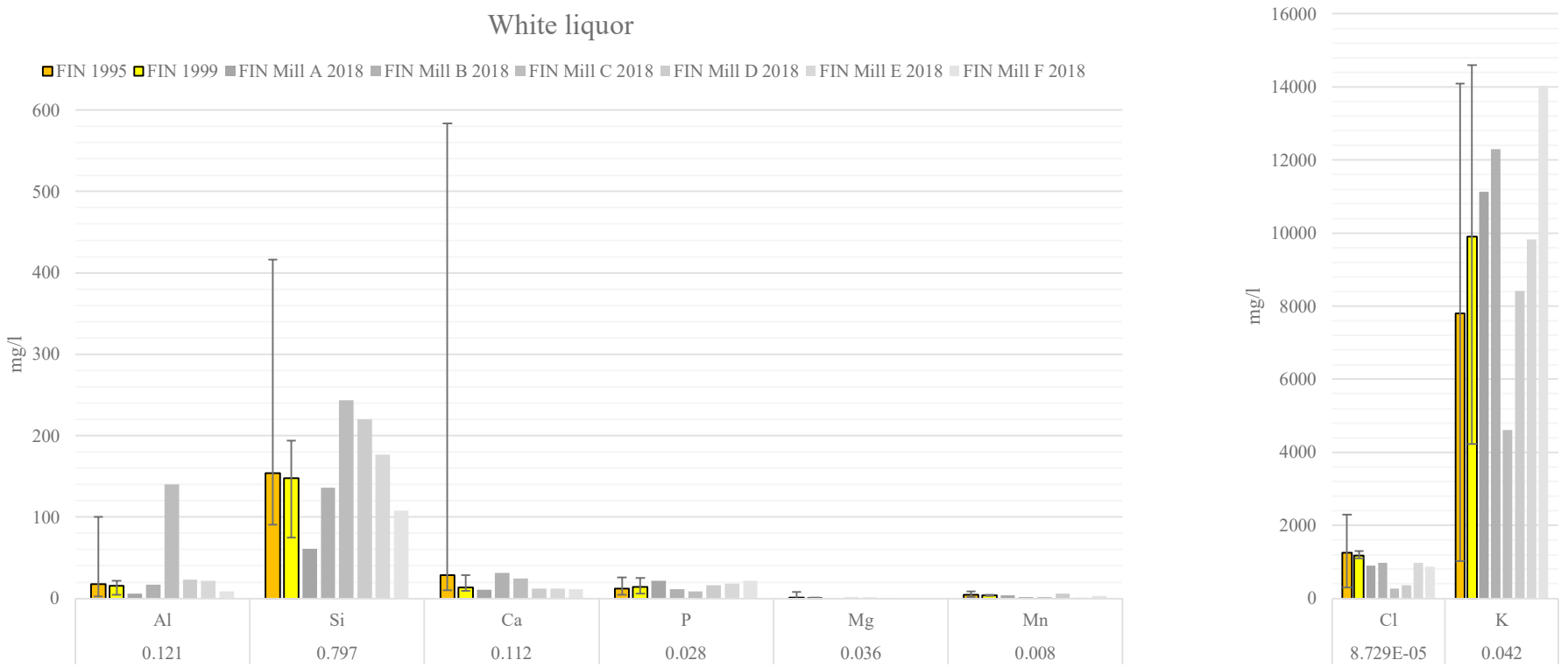


*Figure 42 White liquor comparison between older Finnish results (Järvinen, et al., 1995) (Holamo, 2000) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * Both with or without Mill C's Al value, no significant difference (Without Mill C, p-value 0.64 and with Mill C p-value 0.12).*

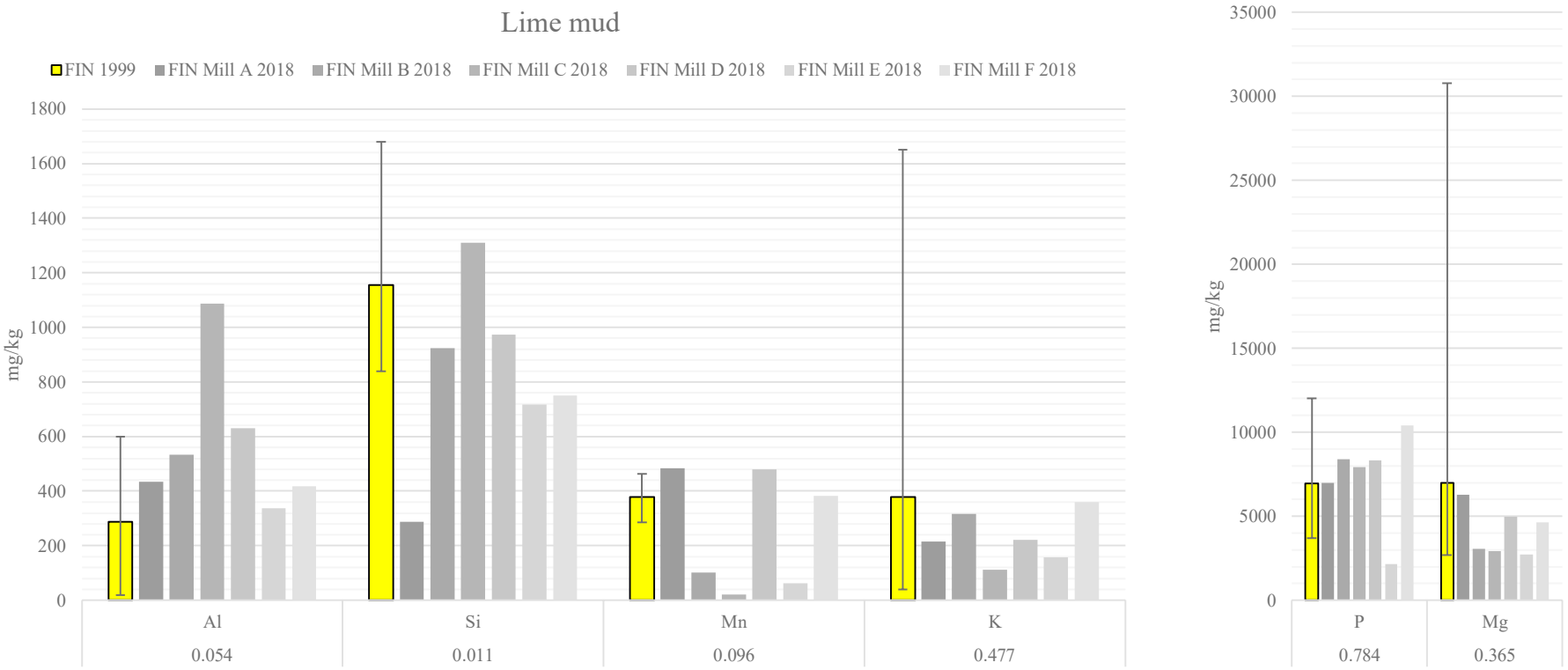


*Figure 43 Lime mud and green liquor dregs comparison between older Finnish results (Holamo, 2000) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * Mill B has lime mud in its green liquor dregs sample.*

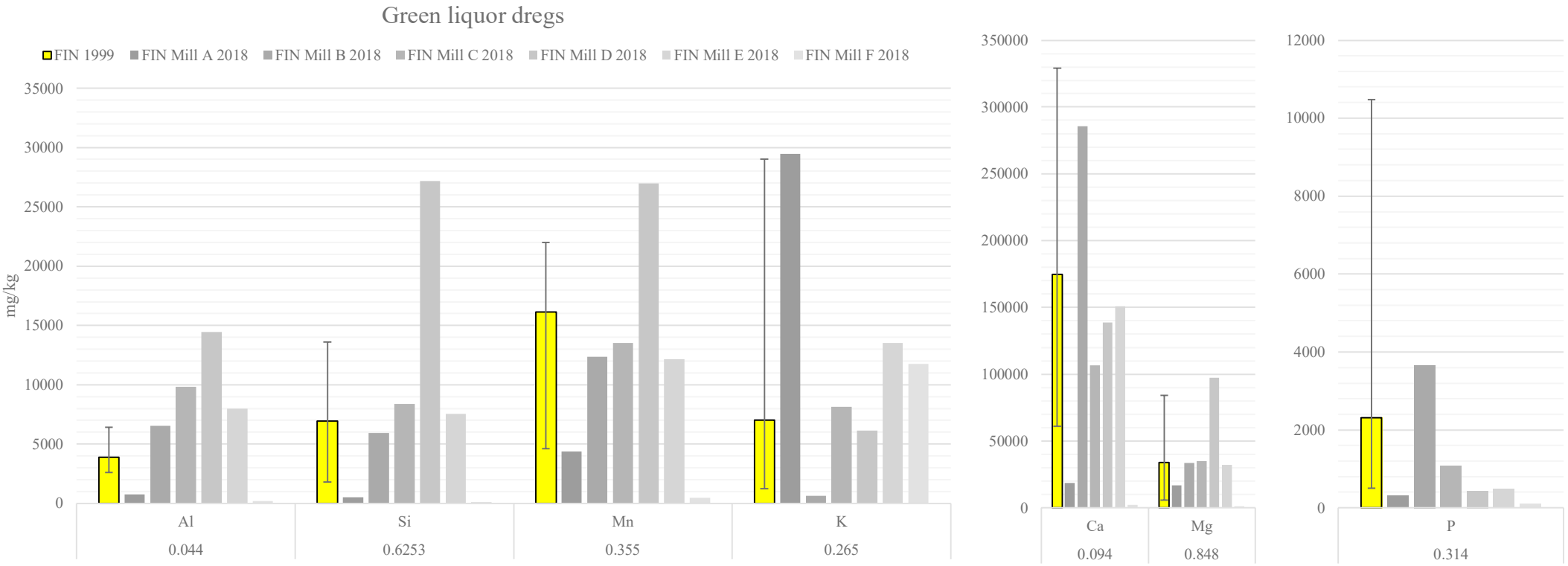


*Figure 43 Lime mud and green liquor dregs comparison between older Finnish results (Holamo, 2000) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * Mill B has lime mud in its green liquor dregs sample.*

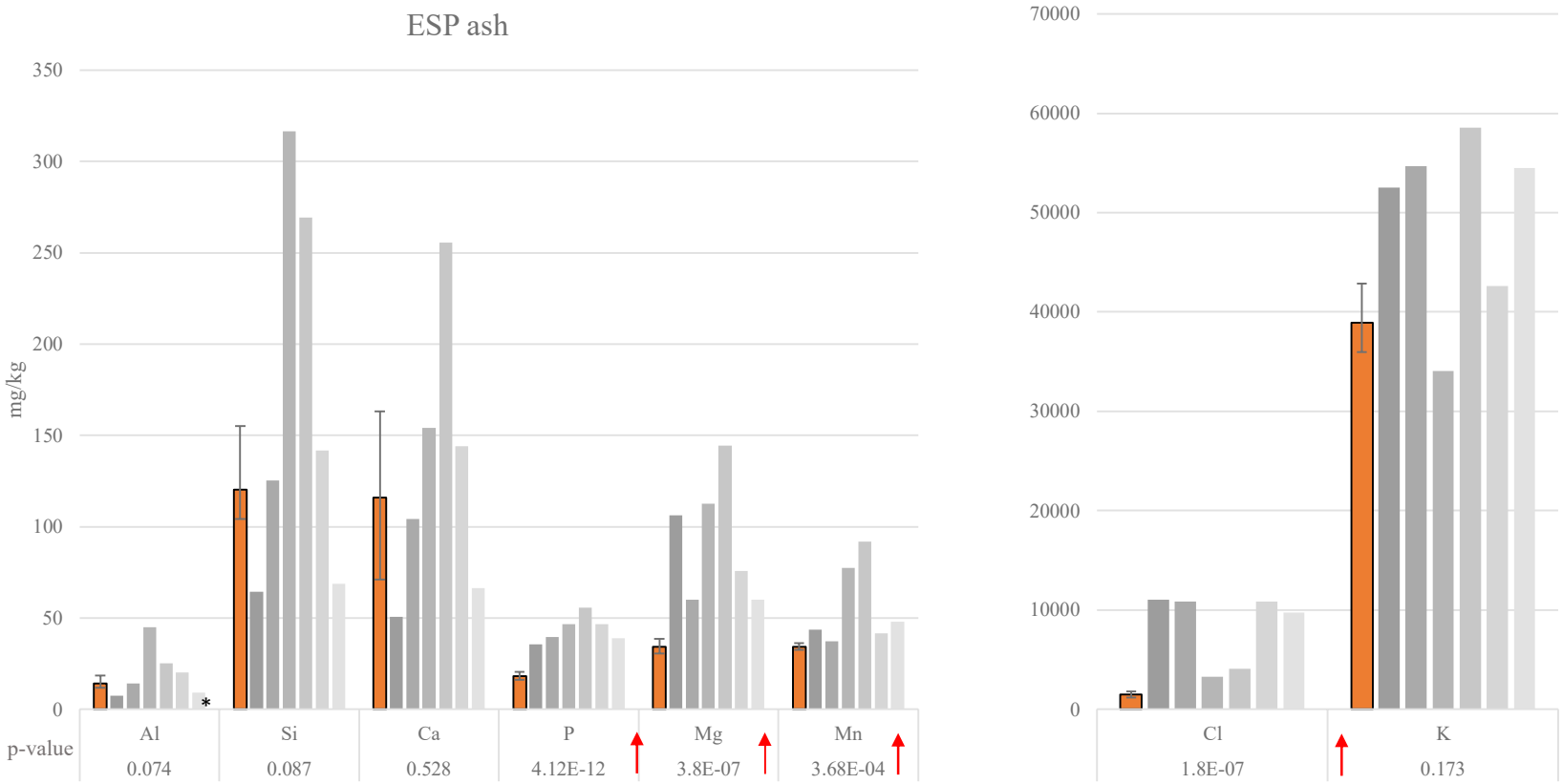


*Figure 45 ESP ash comparison between older North American results (Frederick, et al., 2000)and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values of the literature data. P-value of the t-test is shown in x-axis. Values under 0.05 are considered in this two-tail test significant. The green arrow indicates that the newer values are significantly lower and the red color indicates that the newer values are significantly higher. * The abnormally high Si values from Mill C are included in the t-test.*

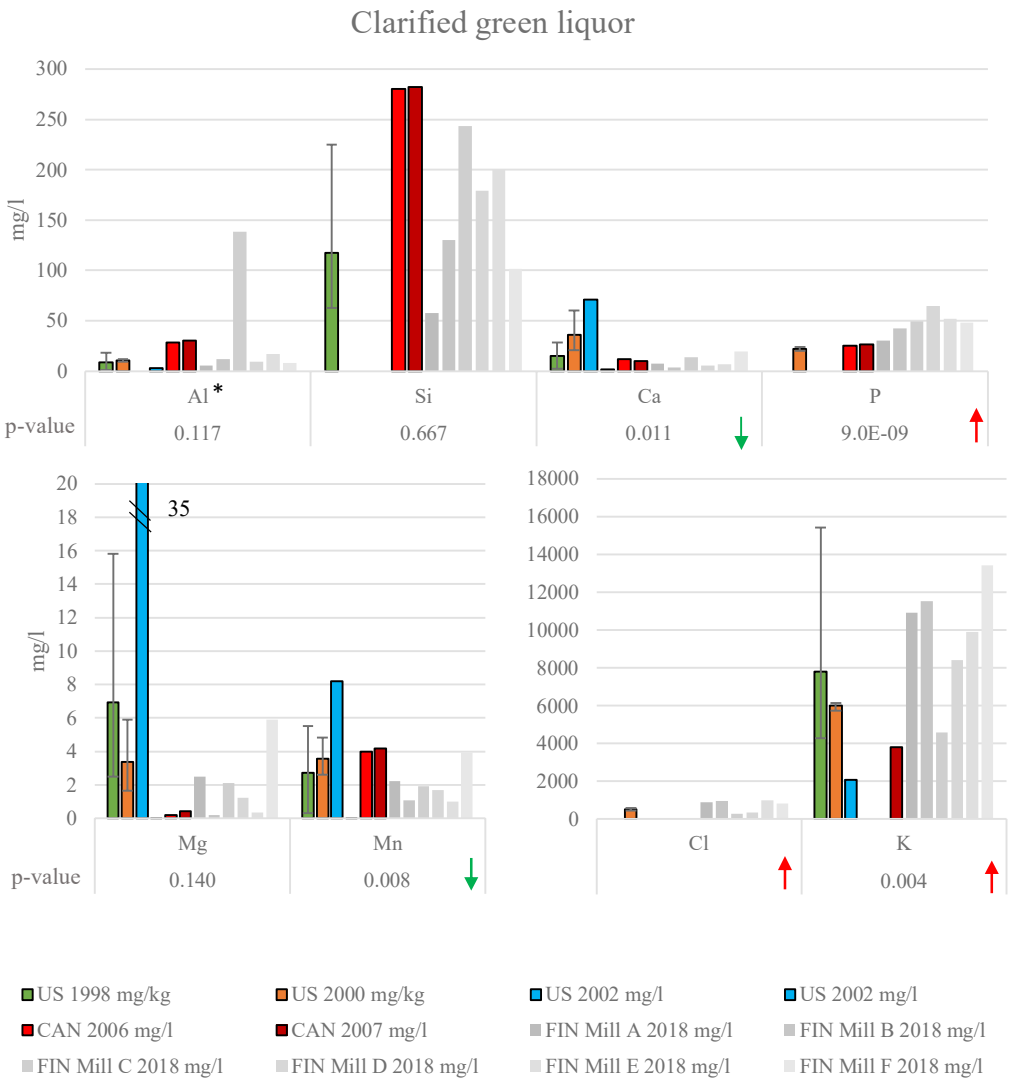


*Figure 46 Clarified green liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results form 2018. The colored column represents the literature results. The error bars 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 newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * The abnormally high Al values from Mill C are included in the t-test. P-value was 0.49 without Mill C.*

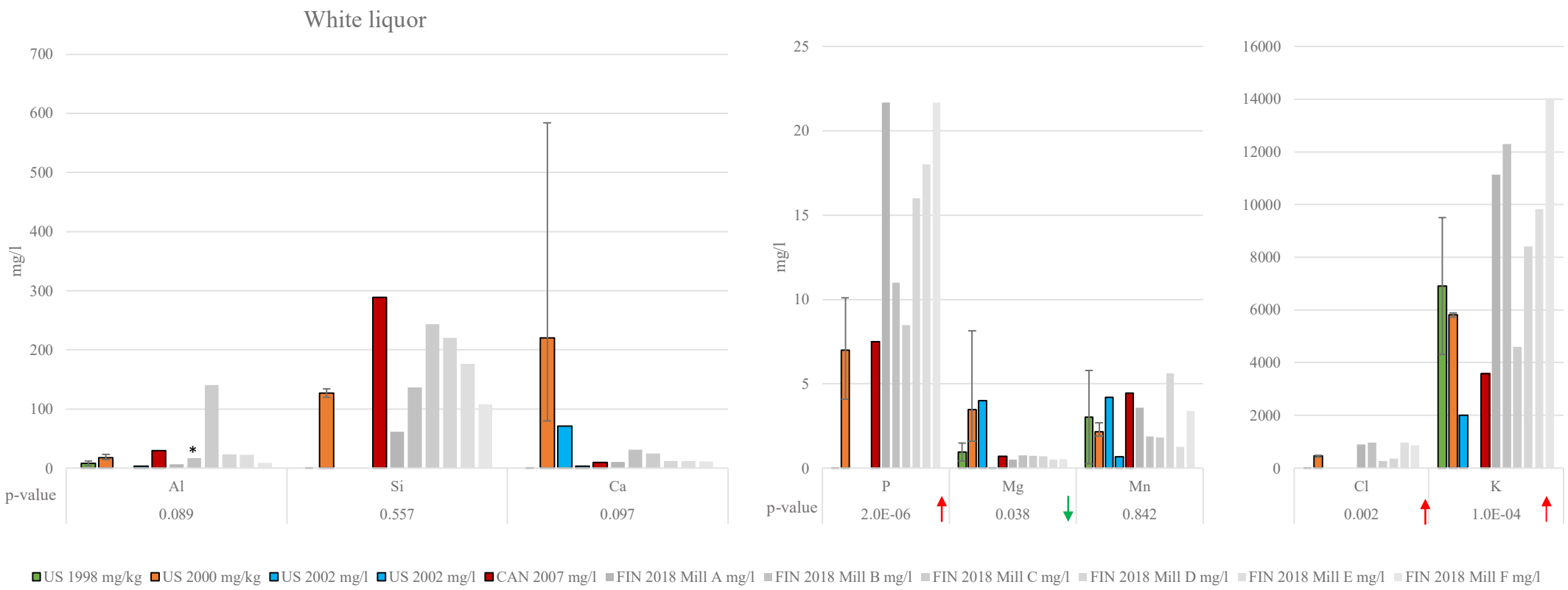


*Figure 47 White liquor comparison between older North American results (Richardson, et al., 1998) (Frederick, et al., 2000) (Gu & Edwards, 2004) (Taylor, 2007) and this project's results form 2018. The colored column represents the literature results. The error bars show the minimum and maximum values 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 newer values are significantly lower, and the red color indicates that the newer values are significantly higher. * The abnormally high Al values from Mill C are included in the t-test. P-value was 0.97 without Mill C.*

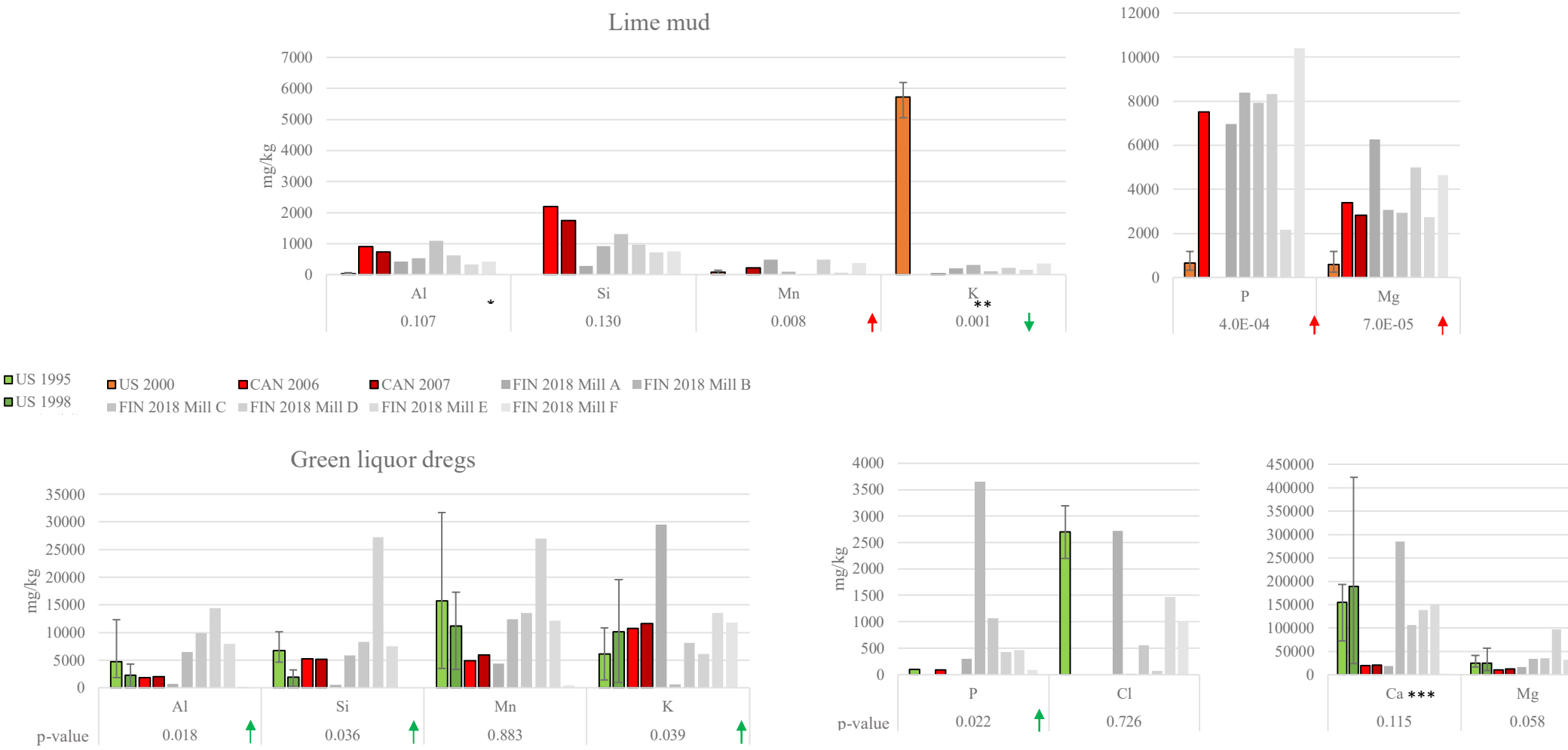
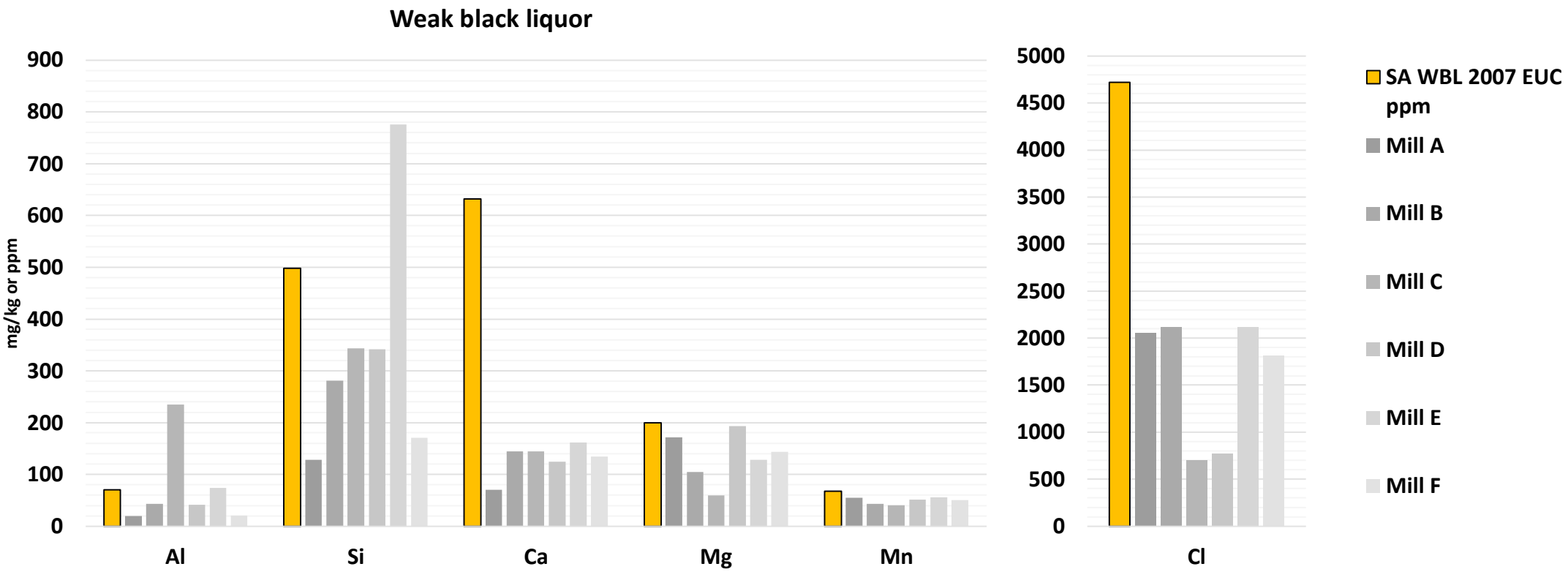


*Figure 48 Lime mud and green liquor dregs comparisons between older North American results (Empie, et al., 1999) (Richardson, et al., 1998) (Frederick, et al., 2000) (Taylor & Bossons, 2006) (Taylor, 2007) and this project's results form 2018. The colored column represents the literature results. The 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 newer values are significantly lower, and the red color indicates that the newer values are significantly higher. In green liquor dregs, the green arrow indicates that the newer value has higher NPE concentration. * The abnormally high Al values from Mill C are not included in the t-test. P-value was 0.037 with Mill C.** 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.*

FIN vs. South America (eucalyptus)



Milanez, A., 2007. Characterization of ions concentration in industrial pulp production and chemical recovery systems. *O Papel,* pp. 48-83.

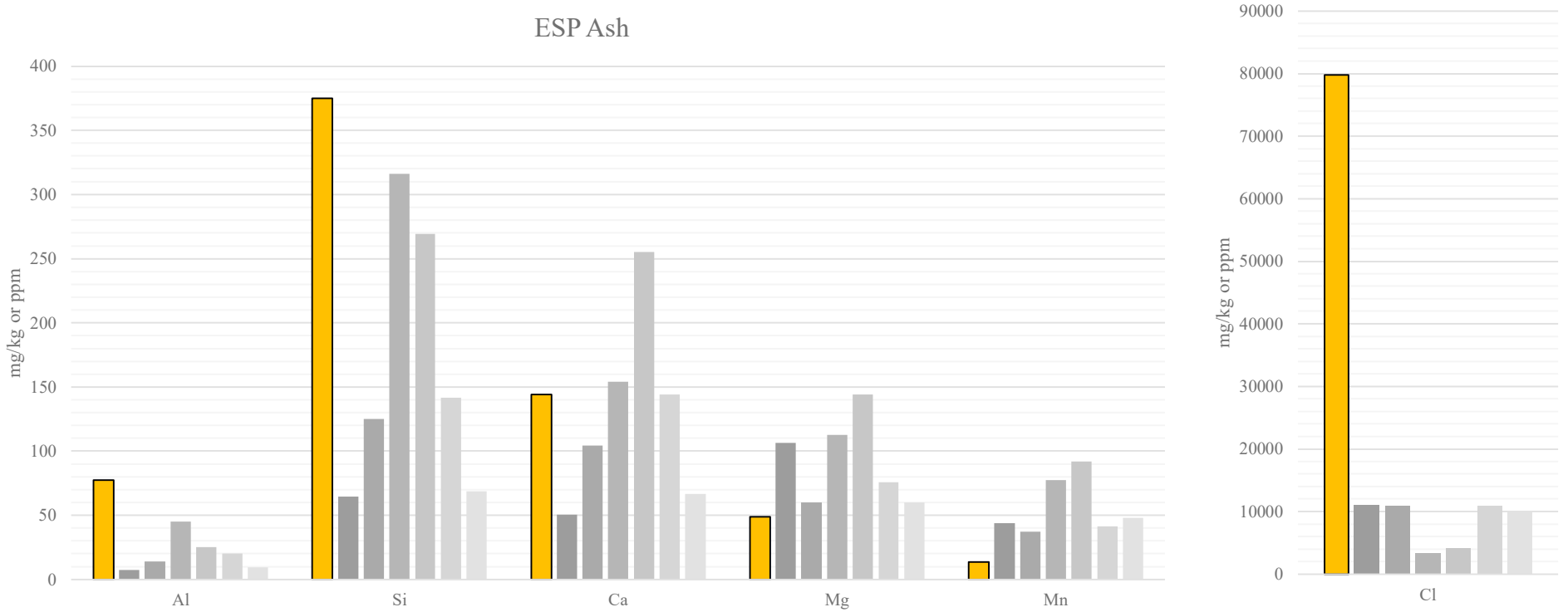


Figure 49 ESP ash results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

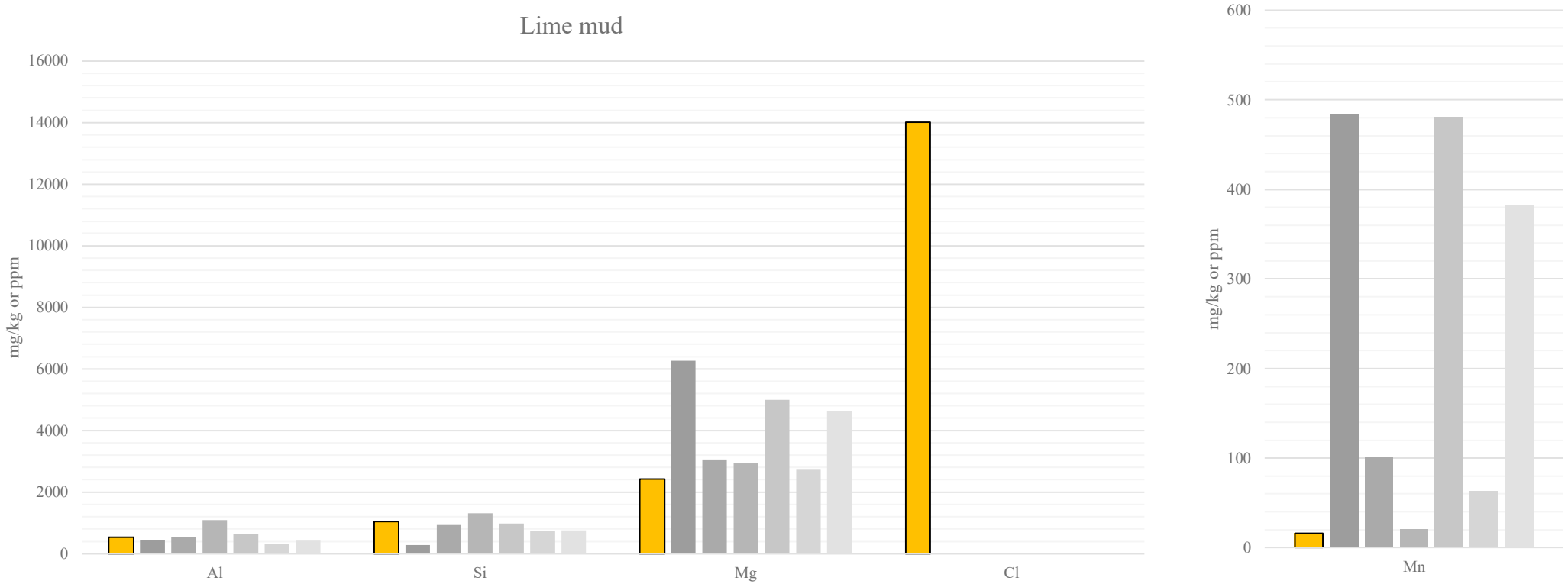


Figure 51 Lime mud results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

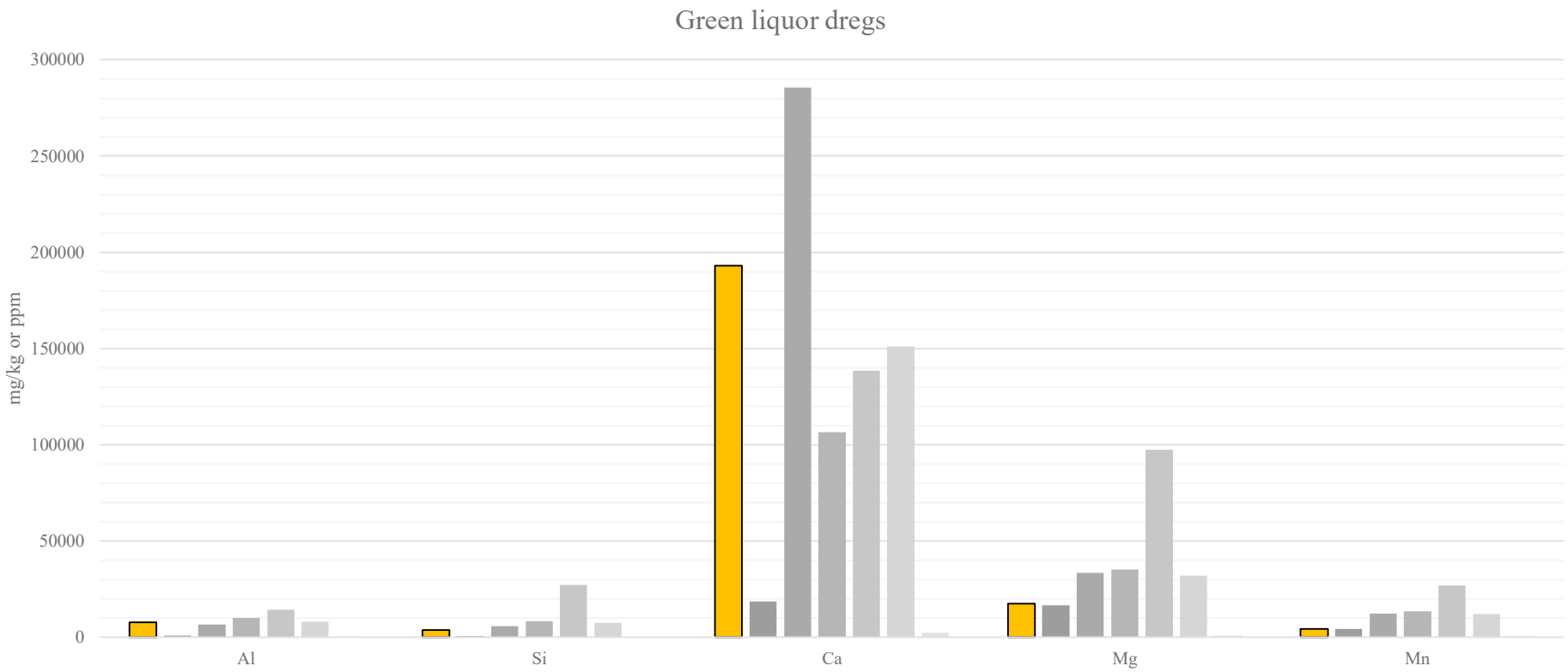


Figure 51 Green liquor dregs results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.

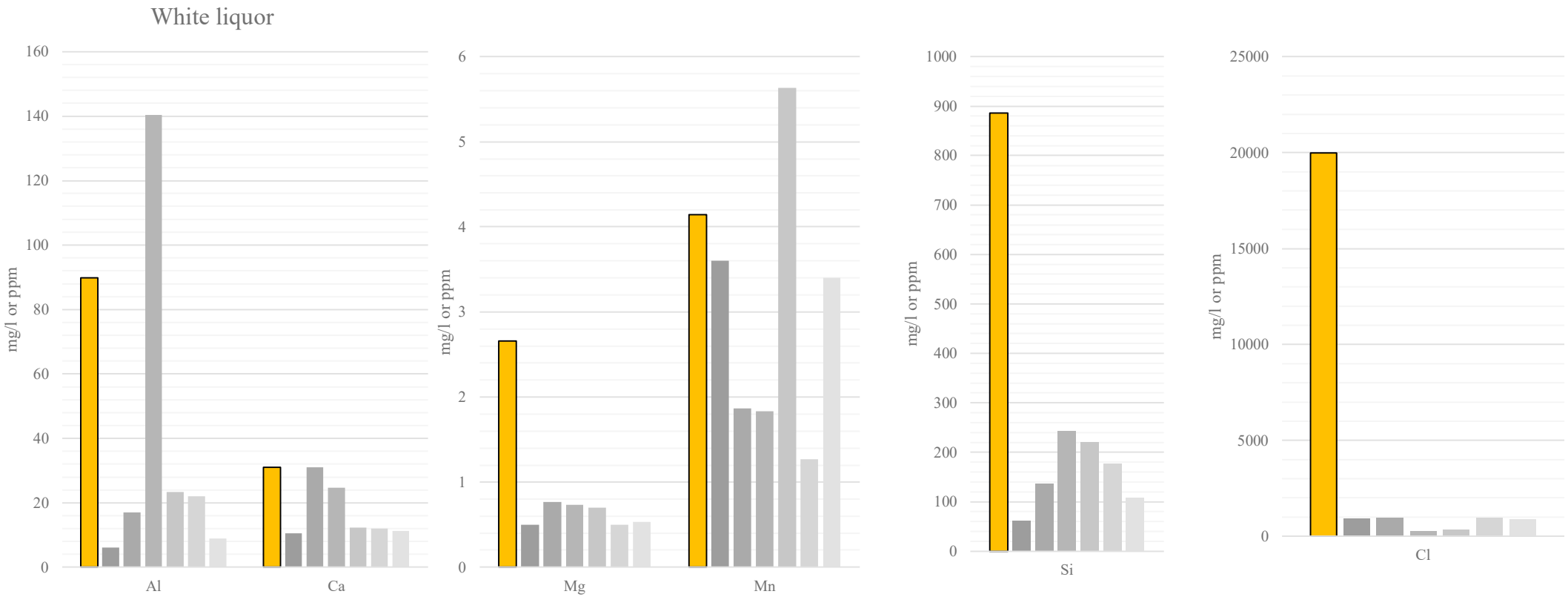


Figure 50 White liquor results from a South American mill (Milanez, 2007) and the six Finnish results from 2018. The colored column is the literature reference and is shown in ppm. The results from 2018 are in mg/kg format.