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Fate of Biosludge Nitrogen in Black Liquor Evaporation and Combustion

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Ammonia Formation and Recovery in a Kraft Pulp Mill and Fate of Biosludge Nitrogen

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1. Introduction

The nitrogen in black liquor originates mainly from the wood and the white liquor used in kraft pulping [Veverka, 1993; Kymäläinen, 2001b; DeMartini, 2004]. The main pulp wood species contains roughly 0.05-0.10 wt-% nitrogen [Ververka, 1993]. The nitrogen in wood is primarily associated with amino acids and proteins [Sudachkova, 2000; Dietrichs, 1967; Dill, 1984] and vegetative storage proteins [Stepien, 1992a; 1992b; Langheinrich, 1991]. After cooking, the nitrogen exits the digester primarily with the weak black liquor and blow gases with a small amount leaving with the pulp and carryover [DeMartini, 2004]. Volatile nitrogen species such as NH_3, pyrrole and other volatile organic nitrogen species are released from the black liquor in the early effects of black liquor evaporation [DeMartini, 2004; Niemelä, 2004]. This volatilized nitrogen is eventually found mostly in methanol and non-condensable gases (NGC) [Kymäläinen, 1999; DeMartini, 2004; Niemelä, 2004].

The nitrogen in as-fired black liquor is the primary source of NO in a Kraft recovery furnace. During devolatilization, about 60% of the black liquor nitrogen is released, primarily as an NH_3 intermediate with some NO and N_2 also formed, Figure 1 [Aho, 1994a; Aho, 1994b; Forssén, 1997]. The remaining 30-40% is in the char. A part of this char nitrogen is released as NO and N_2 during char conversion with 20-35% of the original black liquor nitrogen exiting the recovery boiler with the smelt as the cyanate ion (OCN^-) [DeMartini, 2001; Kymäläinen, 1999; 2001a; 2001b; 2001c; 2002´; Vähä-Savo, 2011]. Cyanate dissolves with the smelt in the smelt dissolving tank and reacts to form ammonia in the recausticizing process [DeMartini, 2001]. The reaction of cyanate to ammonia is slow in alkaline solutions and reacts throughout the chemical recovery cycle [Kymäläinen, 1999]. This ammonia is released in the vent gases of recausticizing and is ultimately vented in the digester blow gases and in the early effects of black liquor evaporation [Kymäläinen, 1999].

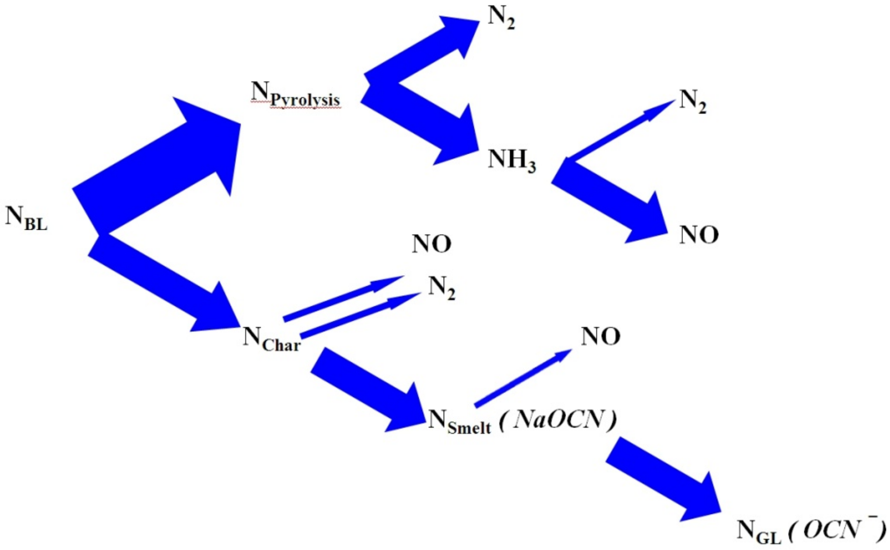

Figure 1. Path of nitrogen in black liquor combustion.

Prior to this study, six full mill balances have been made for nitrogen in the Kraft recovery cycle, four of them in Finland [Kymäläinen, 1999; 2001a; 2001b; 2001c; 2002; DeMartini, 2004], with the other two being European mills [DeMartini, 2004]. These studies found the same general conclusions:

- The flow of nitrogen with the black liquor is equivalent to the flow of nitrogen with the wood

- 15-30% of the black liquor nitrogen is released in the early effects of evaporation
- 25-35% of the as fired black liquor nitrogen exits the recovery boiler as NO
- 25-35% of the as fired black liquor nitrogen exits the recovery boiler with the smelt as cyanate
- Cyanate then reacts to form NH_3, part of which is released with the vent gases; part ends up in the weak wash from dregs and lime mud washing; and, part of which enters the digester with the white liquor
- This white liquor nitrogen is equivalent to about 15-20% of the nitrogen entering with the wood.
- About 15% of the wood nitrogen is released as ammonia during pulping
- About half of the ammonia in pulping is released with the digester blow gases and the other half exits with the weak black liquor

A separate detailed study of nitrogen distribution in a Kraft recovery boiler showed that both NO and cyanate could be minimized at the same time [Saviharju, 2006].

In addition to the 6 balances mentioned above, 8 mill balances were made around recovery boilers in Finland as part of a SKY project. In those studies, analysis was made of: black liquor before and after biosludge addition; N with methanol and weak gases; NO in the stack gases; cyanate in the smelt and nitrogen in the weak wash to the smelt dissolving tank, and nitrogen out of the smelt dissolving tank with the green liquor.

One unique feature of the balance at Kymi was the ability to get some information about the fate of biosludge nitrogen as there were some measurements made in periods with and without biosludge addition.

2. Analysis

Wood and black liquor samples were analyzed by a modified Kjeldahl method and weak black liquor and other liquid streams were analyzed for NH_3. Two different laboratories were used for the NH_3 and total N analysis results used in the May 2011 nitrogen balance. At both laboratories, ammonia was stripped using steam followed by analysis according to either the modified method SFS 5505:1988 or SFS5664:1988. Total nitrogen was analyzed by both laboratories using the modified Kjeldahl method SFS 5505:1988. Cyanate in green liquor samples was analyzed by ion chromatography [DeMartini, 2001].

Ammonia in the dissolving tank vent gases was captured by bubbling vent gases through two impinger bottles with an acidic solution (pH~2). For analysis the pH of the samples was raised and they were analyzed for ammonia.

Combustion and cyanate formation experiments were conducted for the collected as-fired black liquor samples at Åbo Akademi University (ÅAU) in a quartz glass reactor. Six 10 ±0.5 mg droplets of each liquor were burned at 1100 °C and 3% O_2 in N_2. The formed NO was measured with an on-line chemiluminescence analyzed (Teledyne Model 200EM). Cyanate formation in the collected as-fired black liquors was determined by pyrolysing six droplets (14 ±1 mg) of each as-fired black liquor at 800 °C in 100% N_2 for 10 seconds to form chars. The chars were then gasified at 800 °C in 13% CO_2 / 87% N_2 to obtain the smelt. The smelts were dissolved in ultrapure water and analyzed for cyanate.

3. Mill Sampling Campaign

The first sampling campaign was made on December 1, 2010 at the UPM Kymi Mill. There were problems with the analysis of nitrogen in the condensates and the samples were disposed of before the samples could be reanalyzed. There were other questionable analytical results and it was decided to have another sampling campaign in May, 2011. The black liquor nitrogen results, however, were considered accurate and those results are presented in this report in addition to the sampling campaign results from May 2011.

Biosludge addition was started on May 23, 2011. Black liquor and green liquor samples were pulled on the 19th and 20th before biosludge addition and then on the 30th and 31st after biosludge addition to determine the fate of biosludge nitrogen, Figure 2. Samples for the full mill balance were pulled on May 31 to obtain a full mill balance when the mill was adding biosludge. Samples for a full mill balance were also pulled on May 30th as back-up, but were not used in this work. Appendix I lists the samples pulled along with dates pulled. Analysis results are given in Appendix II. Mill data was obtained for the full 15 day period which allowed for following NO formation both before and after biosludge addition.

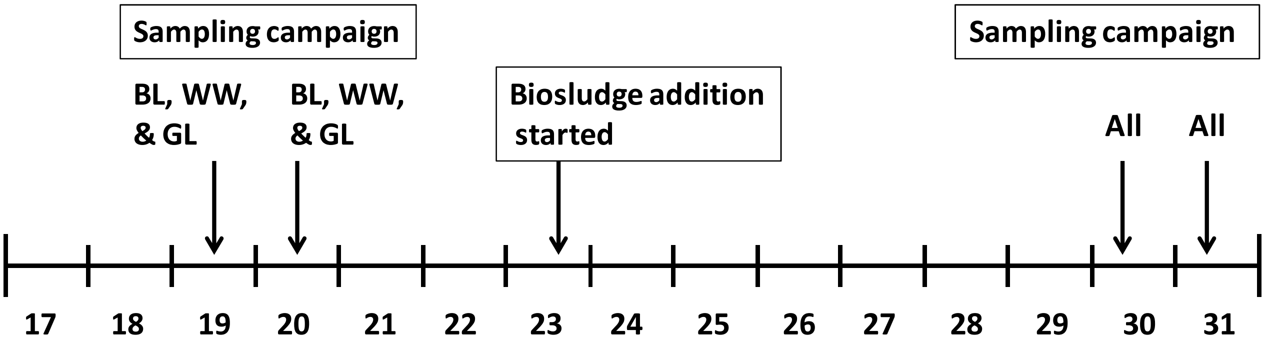

Figure 2. Sampling days.

Pulp production and black liquor solids firing during the 15 days in May as shown in Figure 3. The drops in pulp production were due to drops in hardwood pulp production. Softwood pulp production was nearly constant throughout the course of the trial. The operation was reasonably stable during both of the sampling periods.

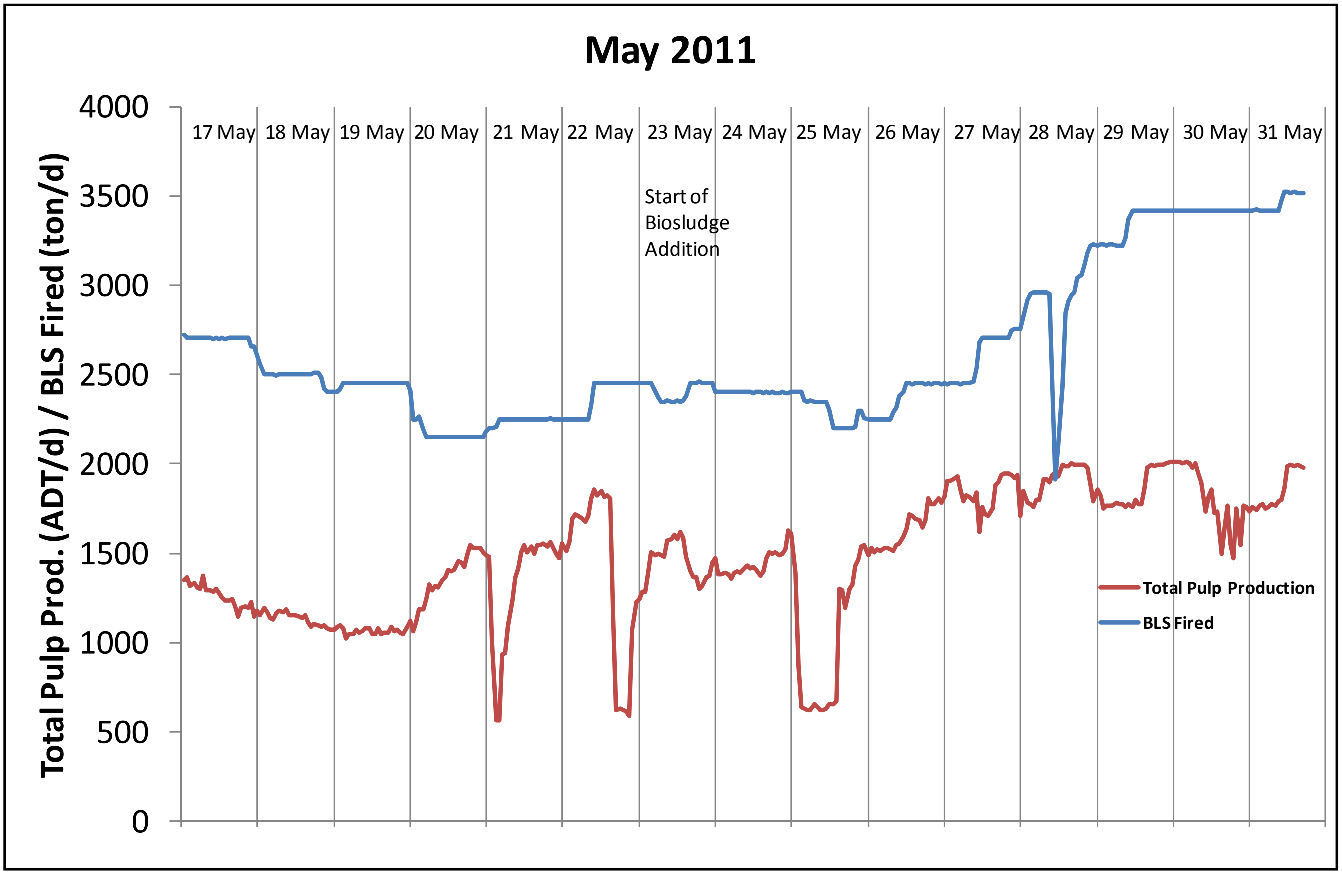

Figure 3. Pulp production (red) and black liquor solids firing rate (blue) during the 15 day period followed in this work.

3.1. *Pulping*

The wood is fed on a volumetric basis and we have not obtained a good correlation to convert this to a mass flow rate of wood. However, it is possible to draw the main conclusions from the results. The total N concentration of the softwood, hardwood and sawdust are 0.057, 0.096 and 0.123 wt% N respectively. The concentrations and flows of nitrogen with white liquor, condensates for pulp washing, carryover, pulp and black liquor from the three lines are given in Table I. The flows for the individual lines are also shown in Figure 4 on a gN/s basis. Figure 5 shows the combined nitrogen flows for the 3 pulp lines on an ADt/d basis. The average total pulp production was 1915 ADt/d during the 8 hour period of sampling on May 31.

Table I. Concentrations of N for the three wood sources and white liquor, pulp, carry-over and black liquor concentrations and flows.

	Wood	White Liquor		Pulp*		Carry-over		Black Liquor	
Pulp Line	(wt-% N)	(mg N/l)	gN/s	(wt-% N)	**(gN/s)**	(wt-% N)	**(gN/s)**	(wt % N)	**(gN/s)**
SW	0.06 %	41	1.15	0.006 %	**0.47**	0.07 %	**0.09**	0.10 %	**15.8**
HW	0.10 %		2.05	0.007 %	**0.97**	1.3 %	**0.32**	0.09 %	**21.4**
Sawdust	0.12 %		0.13	0.007 %	**0.04**	0.12 %	**0.01**	0.07 %	**0.83**

*The detection limit for pulp was 0.006 wt-% N.

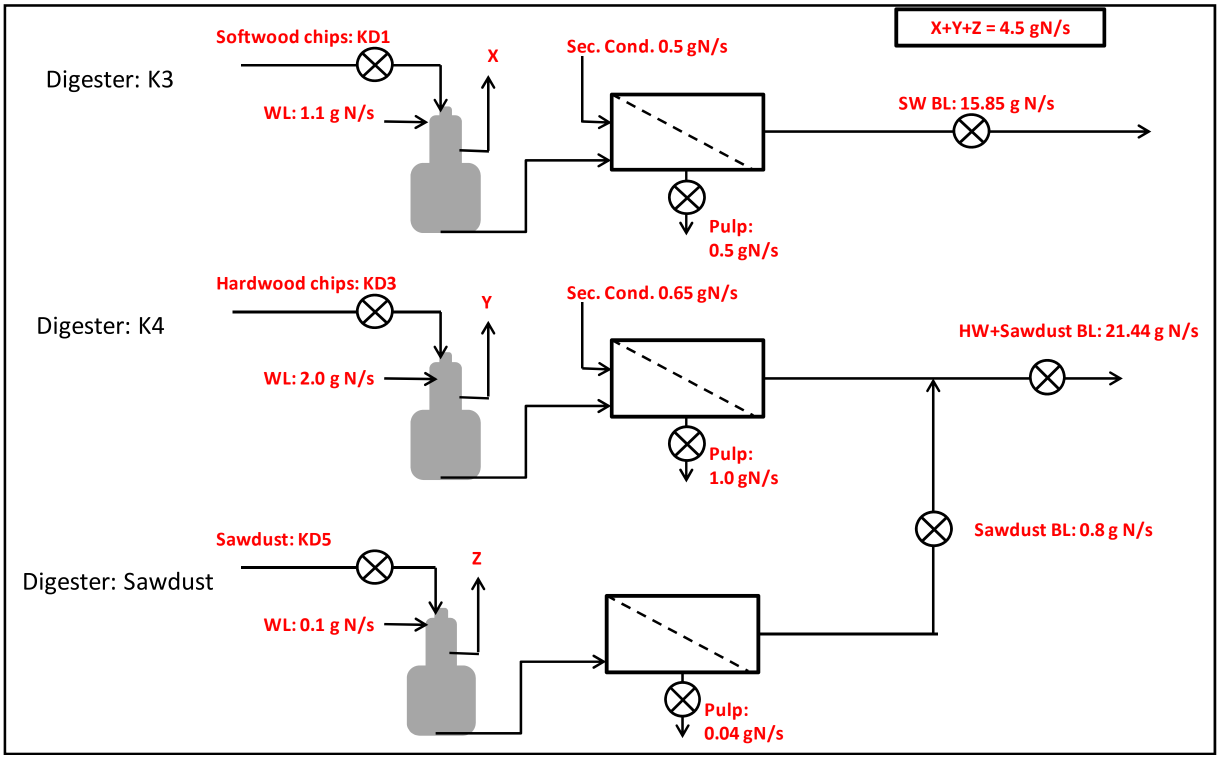

Figure 4. Nitrogen flows around the three digesters.

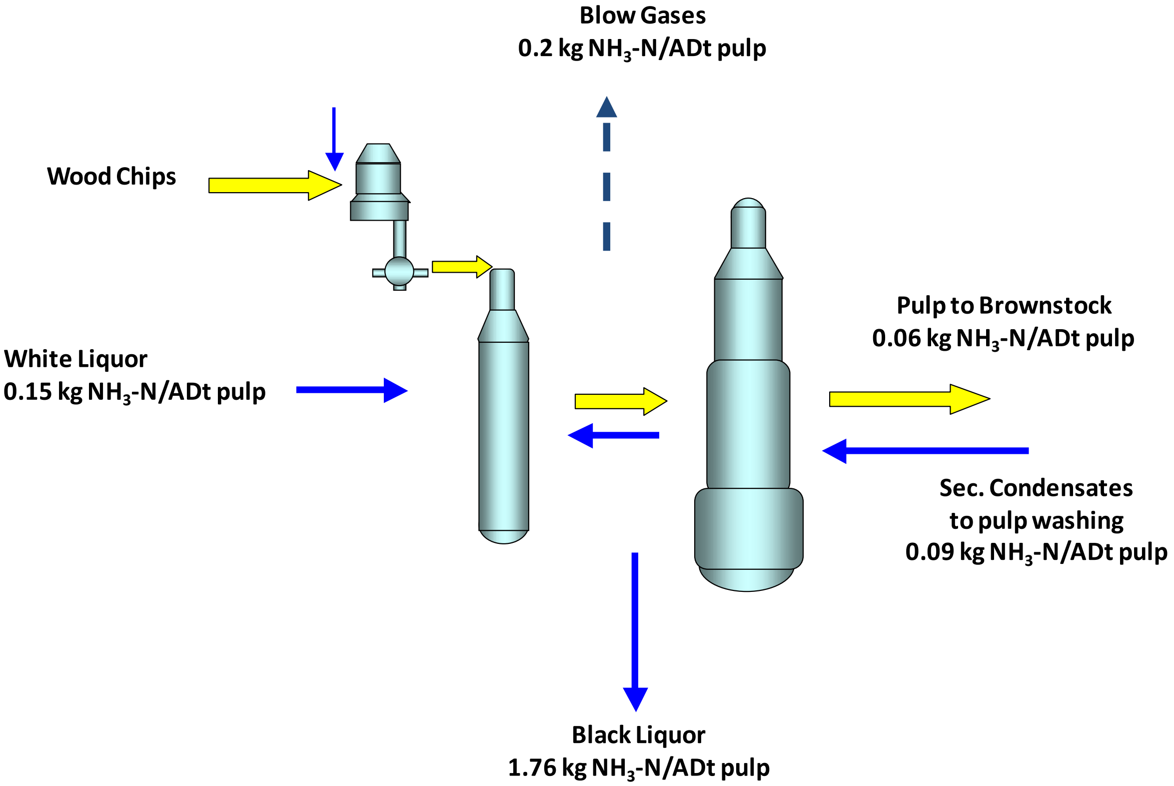

Figure 5. Combined nitrogen flows for 3 pulping lines.

3.2. *Black Liquor Evaporators*

To ensure that measured flows were accurate, the flow of dry solids at different points were calculated using: black liquor solids; the recorded volumetric flow data; recorded black liquor temperatures; and, calculated densities based on Frederick [1997]. As can be seen in Figure 6, the flows of black liquor solids was similar at each measurement point which was expected as the measured tank levels were almost constant during sampling.

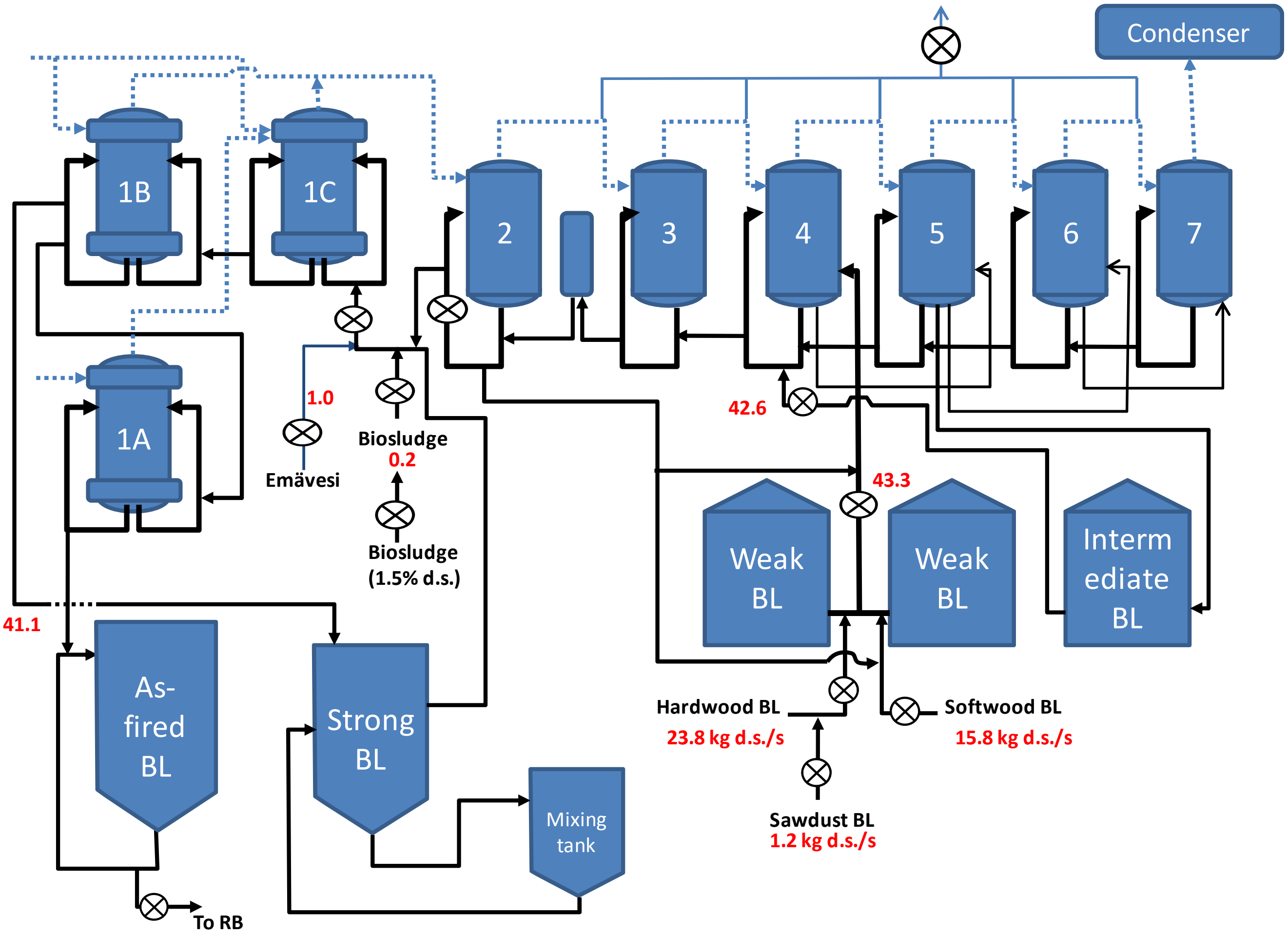

Figure 6. Dry solids flows of black liquor, biosludge and emä vesi based on dry solids analysis and mill flow data. All flows given as kg d.s./s.

Figure 7 shows the concentration of black liquor nitrogen from different sampling points for three different sampling days, 1 Dec 2010; and 30 and 31 May 2011. In December 2010 there was no biosludge added to the black liquor and the concentration of total nitrogen did not change between the intermediate black liquor and the as-fired black liquor. In the 30 of May sample, the nitrogen concentration was nearly constant until after biosludge addition. The addition of biosludge increased the nitrogen content by about 30%. The total nitrogen content of the biosludge was 5.0 wt% d.s. and the NH_3-N concentration was 0.3 wt% d.s. The small drop in total nitrogen between the IC and the as-fired black liquor can only be partially explained by the volatilization of NH_3. On 31 May the concentration of 2nd effect nitrogen was higher than the intermediate black liquor nitrogen. There is no clear explanation for this higher nitrogen concentration in the 2nd effect black liquor unless as-fired black liquor was brought back to before the 2nd effect in a significant quantity between the 30th and 31st. Two different labs obtained similar results for that sample. As with the sample on the 30th, the addition of biosludge resulted in a significant increase in total nitrogen, with a larger decrease seen across the concentrators. When no biosludge is added, the picture looks as it has in earlier studies, the black liquor nitrogen concentration decreases as the liquor is concentrated to 30% dry solids and the ammonia and some low molecular weight organic nitrogen species are volatilized. The concentration of nitrogen then remains essentially constant across the rest of the evaporation set. When biosludge is added, the concentration of total nitrogen increases about 20-30% and is mostly stable across the concentrators. Thus, it can be concluded that the addition of biosludge results in a substantial increase in nitrogen to the recovery boiler compared to what it would be if no biosludge is added.

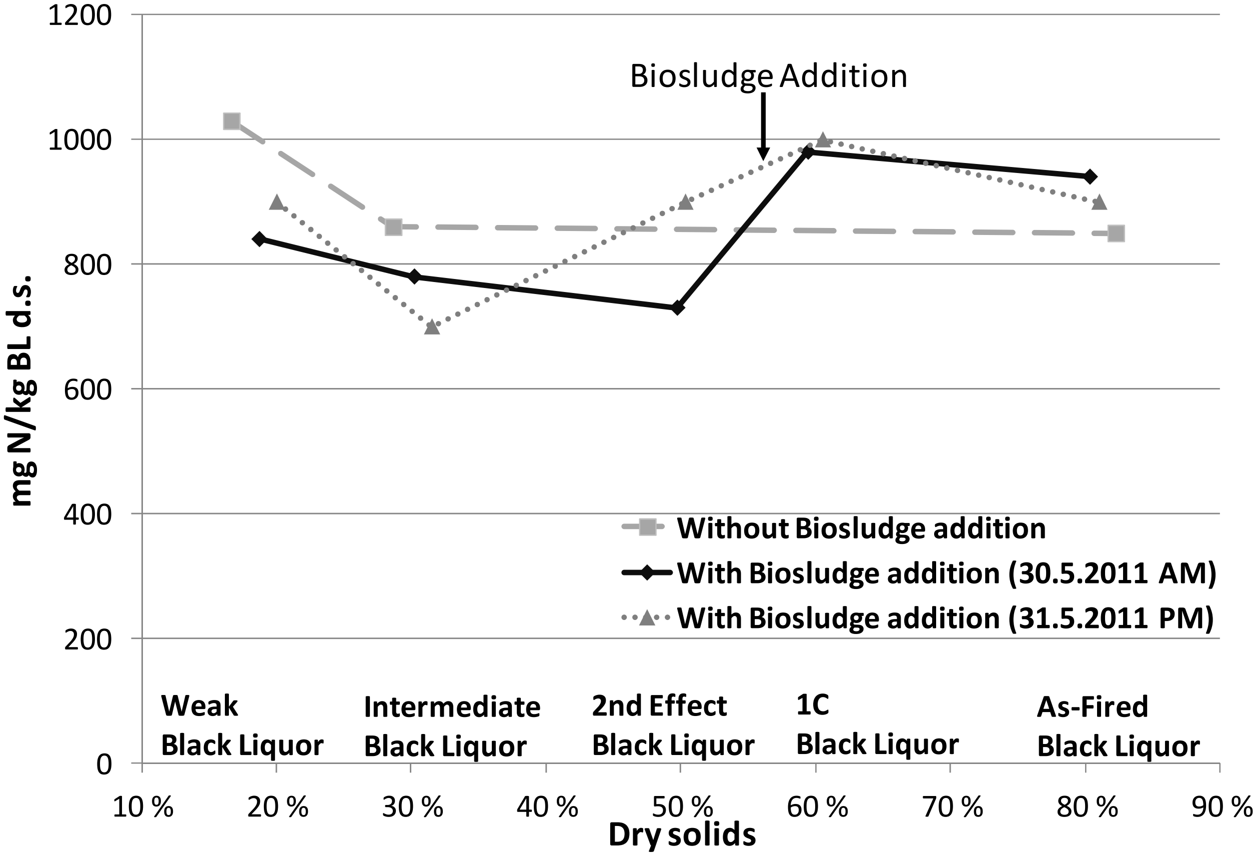

Figure 7. Concentration of total Kjeldahl nitrogen vs. dry solids during the two campaigns. Biosludge was added to the black liquor during the 30 and 31 May 2011, but not the Dec 2010 campaign.

The detailed analytical results for the different samples on the different sampling days can be found in Appendix III. The analyzed total nitrogen content of the HW black liquor is lower than for the SW and the analyzed nitrogen content of the sawdust black liquor is the lowest. Previous experience would indicate that the order in N content should be sawdust BL > hardwood BL > softwood BL. Based on the wood analysis we would also expect sawdust BL> hardwood BL> softwood BL. The flows of nitrogen in black liquor evaporators based on the 31 May analytical results are given in Figure 8.

Ammonia was analyzed in the sample of the mixed feed black liquor and in the biosludge samples. The concentration in the feed black liquor was 0.01 wt%-N which is equivalent to a flow of 4.2 gN/s. This translates to 11% of the N flow in the feed liquor. This compares well to the measured 5.3 g N/s measured in the dirty condensates from evaporators 2 to 7 and the surface condensers. The biosludge nitrogen from water treatment is 1.5 wt% d.s. It is concentrated to 13 wt% d.s. in the centrifuge. There is no loss of ammonia or total nitrogen in the centrifuge step.

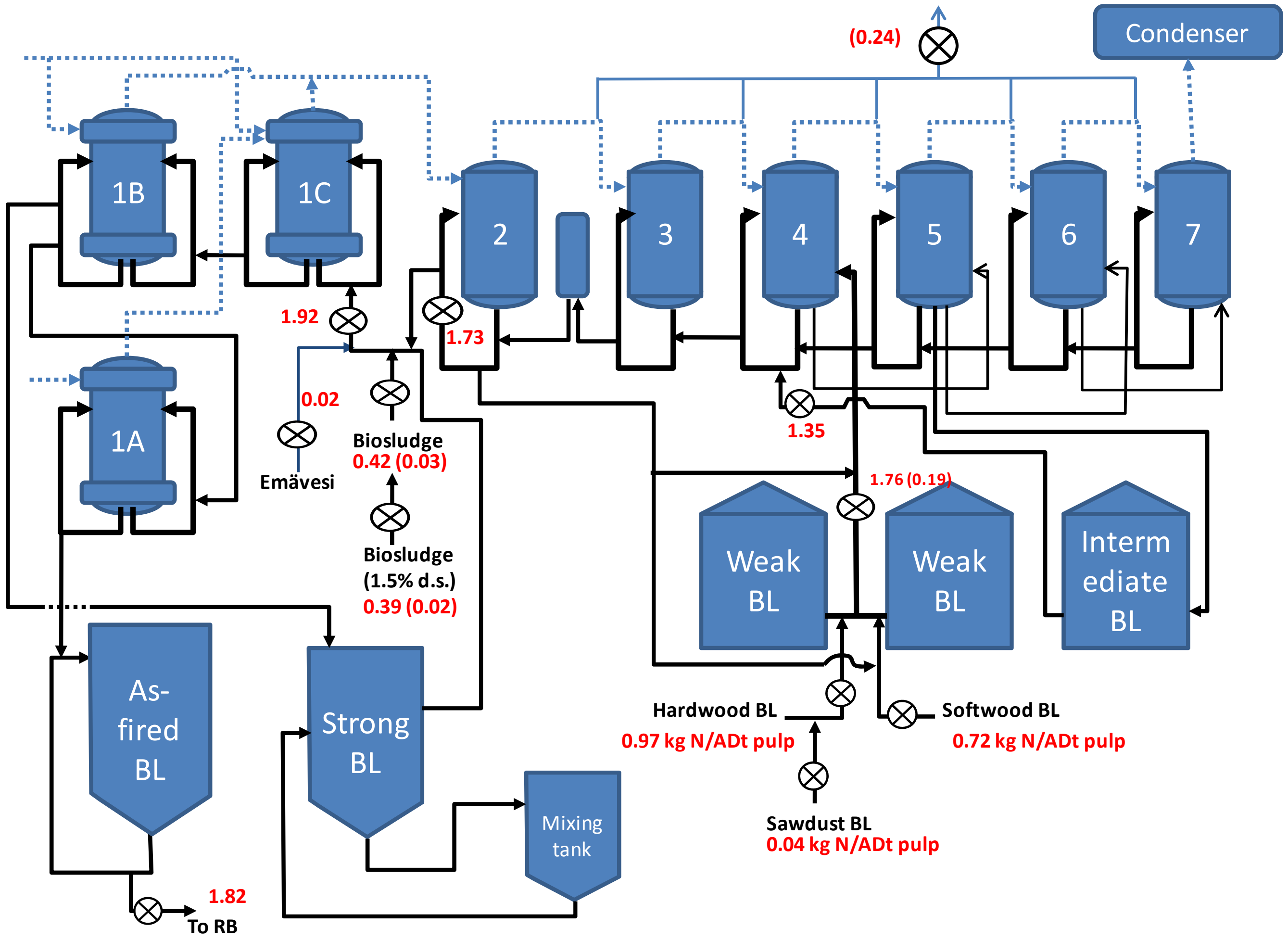

Figure 8. Nitrogen flows for 31 May 2011. Values given are total N on a kg N/ADt pulp basis, the values given in parenthesis are for NH_3-N.

3.3. *Condensate and Methanol*

Figure 9 shows the nitrogen flows in the condensate and stripper systems. Condensate segregation in evaporation also results in successful segregation of ammonia into the dirty condensates. The dirty condensates represent 87% of the NH_3 in all of the condensates combined which is equivalent to 12% of the total black liquor nitrogen to evaporation. The ammonia flow with the dirty condensates from pulping can be estimated by subtracting the flow of ammonia with the dirty condensates from the evaporators from the flow of dirty condensates to the stripper. This gives a flow of NH_3 with the dirty condensates from pulping of 0.2 kg NH_3-N/ADt which is similar to the flow of ammonia with dirty condensates from the evaporators 0.24 kg NH_3-N/ADt. The similar NH_3 flows with blow gases from pulping and weak black liquor is consistent with earlier findings at three European pulp mills [DeMartini, 2004]. The flow of ammonia with the weak black liquor is 0.19 kg NH_3-N/ADt. This is lower than the ammonia flow with the dirty condensates from the evaporators, but of a similar value.

One of the interesting questions is the fate of biosludge nitrogen in the concentrators. Ammonia in biosludge is expected to be volatilized in the concentrators. The flow of NH_3 with the biosludge was 0.03 kg NH_3-N/ADt. A tenth of this (0.003 kg NH_3-N/ADt) is seen in the condensates from the IC condensate. The rest of this is likely to be found in the condensates in the 2nd effect which would be ammonia released in the IC concentrator. This explains part, but not all of, the discrepancy between the NH_3 flow with the dirty condensates and the ammonia flow with the feed black liquor.

The flow of NH_3 with the methanol is 3.8 gN/s. This is about half of the nitrogen released in the stripper based on the flow with dirty condensate to the stripper and the flow with the stripped condensate. The methanol is normally burned in a separate incinerator with the high concentration non-condensable gases (NCG). The rest of the NH_3 released in the stripper goes to the incinerator with the strong NCG.

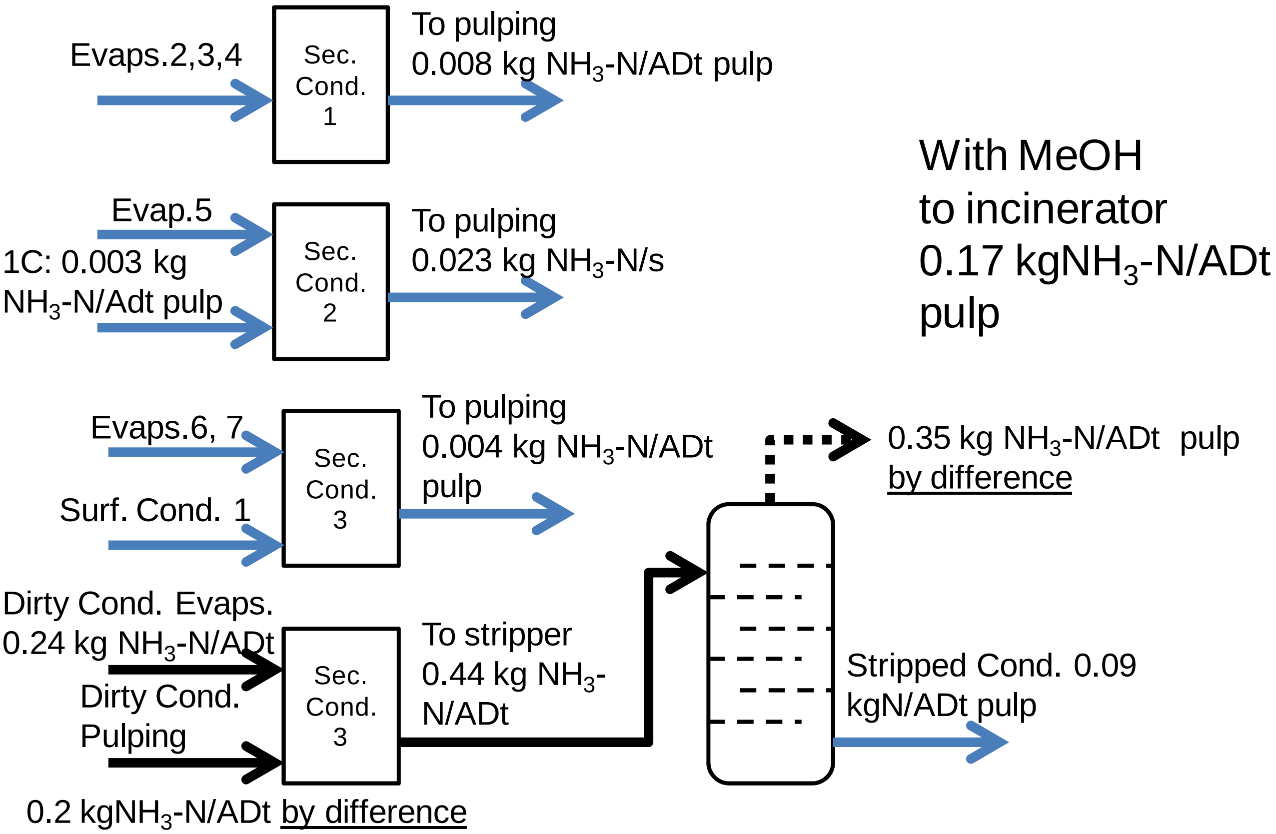

Figure 9. Condensate flows.

3.4. *Recovery Boiler*

The nitrogen flows around the recovery boiler and smelt dissolver are shown in Figure 10. The measured flow of nitrogen to the recovery boiler with the as-fired black liquor was 1.8 kg N/ADt. The mill was not burning MeOH or strong NCG in the recovery boiler at any time during the sampling campaign. The mill did add weak NCG from the pulp and black liquor tanks to the recovery boiler. The nitrogen flow with the weak NCGs was not measured, but has been found to be equivalent to about 5% of the black liquor nitrogen flow [Salmenoja, 2007]. The flow of nitrogen as NOx was 0.44 kg N/ADt or 24% of the incoming black liquor nitrogen. The nitrogen flow of the smelt was determined by the difference in the NH_3-N flow with the weak wash and the NH_3-N + OCN-N flow with the green liquor + the NH_3 flow with the vent gases. This gives a nitrogen flow of 0.32 kg N/ADt or 18% of the black liquor nitrogen. While the cyanate flow with the green liquor from the dissolving tank is lower than this; this is presumably because part of the cyanate already reacts to form ammonia in the dissolving tank. It has been shown that a mill can obtain both low cyanate and low NO at the same time with proper operating conditions [Saviharju, 2006], which Kymi achieves.

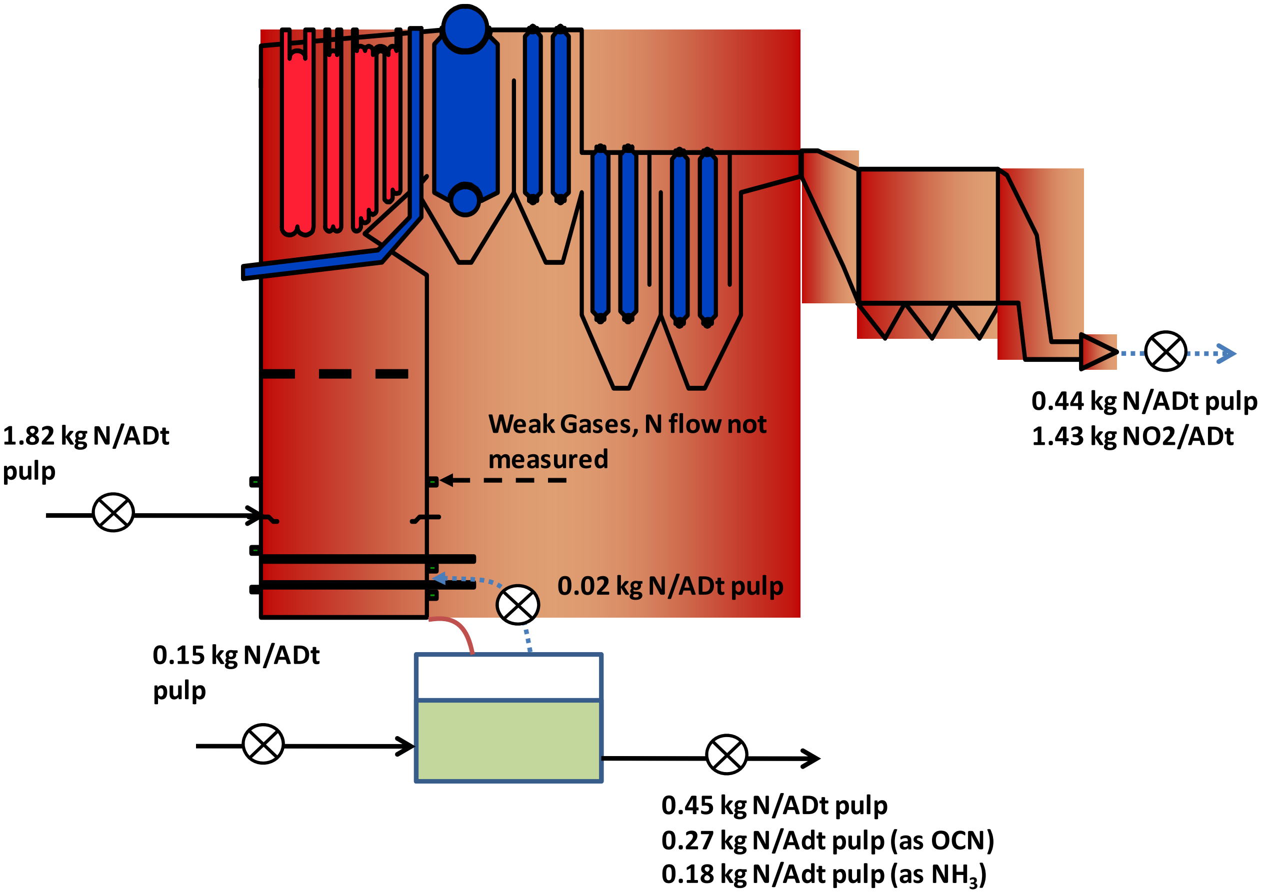

Figure 10. Nitrogen flows around the recovery boiler at Kymi.

3.5. *Recausticizing*

During the recausticizing process, the cyanate will react to form ammonia. The kinetics of this reaction has been studied and reported elsewhere [DeMartini, 2004b; 2004c; Vogels, 1970] and the relevant kinetics in green liquor can be described by the equation:

$$\frac{d[NH_3]}{dt} = -\frac{d[OCN^-]}{dt} = \left(k_3 + k_{HCO_3^-}[HCO_3^-]\right)[OCN^-] = \left(k_3 + k_{HCO_3^-}\frac{K_{H_2O}}{K_{HCO_3^-}}\frac{[CO_3^{2-}]}{[OH^-]}\frac{f_{CO_3^{2-}}}{f_{OH^-}f_{HCO_3^-}}\right)[OCN^-]$$

Where k_3 and k_{HCO3}- are the rate constants for the uncatalyzed and bicarbonate catalyzed formation of ammonia from cyanate. Their temperature dependence is given by an Arrhenius expression [DeMartini, 2004b]:

$$k_3 = 7.96\times10^{10}e^{\frac{-11600}{T}} \quad (\text{min}^{-1})$$

$$k_{HCO_3^-} = 4.55\times10^{9}e^{\frac{-8625}{T}} \quad (\text{l min-1 mol}^{-1})$$

A part of the ammonia will be vented. At Kymi, the flow of nitrogen to the recausticizing process was 0.45 kg N/ADt and the amount of nitrogen exiting with the white liquor was 0.15 kg N/ADt, Figure 11. Cyanate was found in the green liquor from the dissolving tank and green liquor to the slaker, but not the liquor from the slaker. The NH_3 in the weak wash comes from white liquor and green liquor washed out of dregs and lime mud. Based on the flows in Figure 10, much of the NH_3 in the weak wash may come from washing of dregs, but no detailed balance done around the dregs or lime mud washers. Using the flow of nitrogen with the weak wash, the nitrogen flow with the green liquor and the nitrogen flow with the white liquor, a flow of 0.15 kg NH_3-N/ADt is vented in recausticizing.

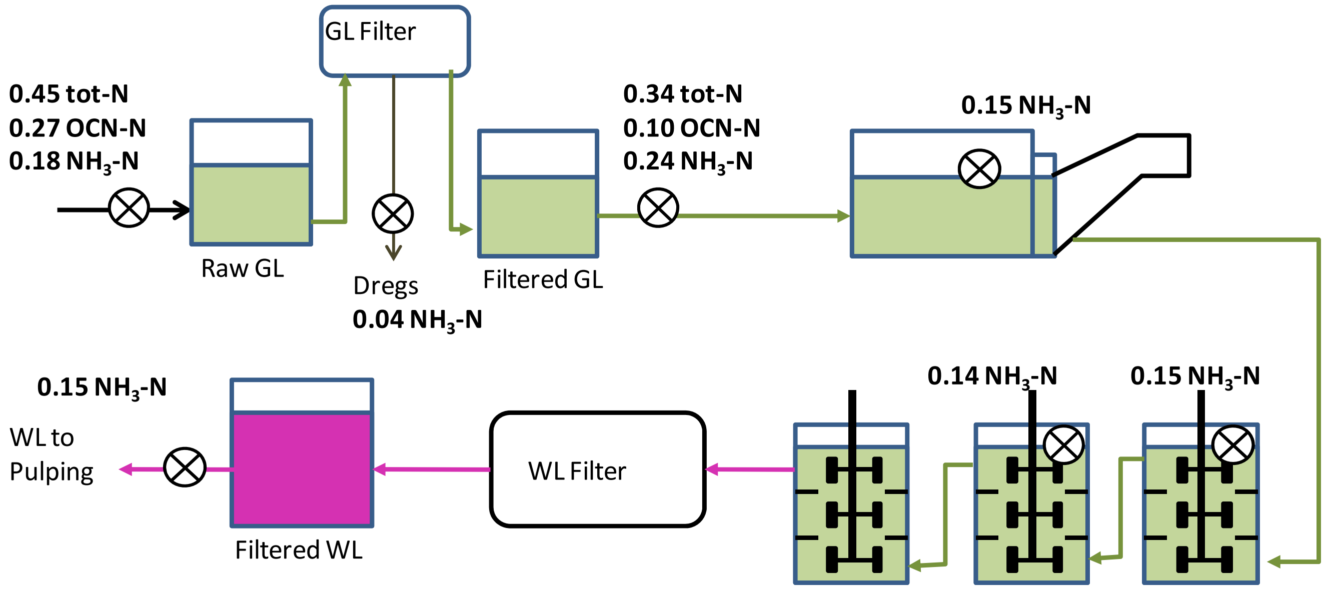

Figure 11. Nitrogen flows in the recausticizing process. Values given as kg N/ADt pulp

3.6. *Impact of Biosludge on Recovery Boiler NO$_x$ formation*

The recovery boiler NOx formation; black liquor firing rate; and biosludge flow rate are given in Figure 12 for 15 days in May 2011. The mill began adding biosludge to the black liquor on Day 7. As can be seen, there is no clear increase in NO (solid grey line) with biosludge addition (dashed black line). We collected black liquor samples both before and after biosludge addition. We burned those samples in a single particle reactor and did see an increase in NO for the black liquors with biosludge added, Figure 13. This indicates that either the nitrogen with the biosludge is effectively reduced in the recovery boiler, or it exits the recovery boiler as cyanate in the smelt, or both.

In addition to pulling black liquor samples before and after biosludge addition, we pulled green liquor samples from the dissolving tank before and after biosludge addition. As can be seen in Figure 14, the concentration of OCN-N was higher with biosludge addition. This was supported by cyanate formation tests in the single particle reactor where the cyanate formation, Figure 15.

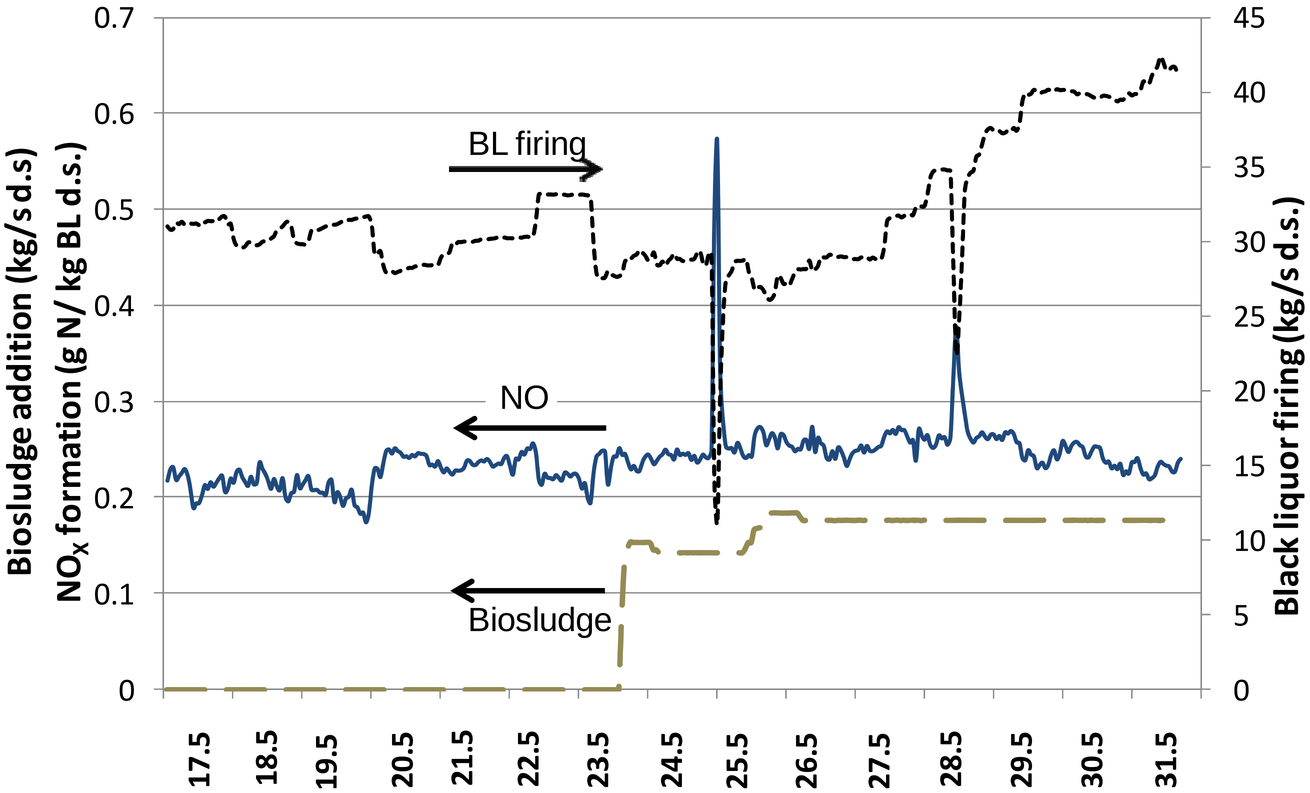

Figure 12. NOx formation as gN/s; biosludge addition rate (kg d.s./s) and black liquor firing rate (kg d.s./s) during the days 17-31 of May 2011.

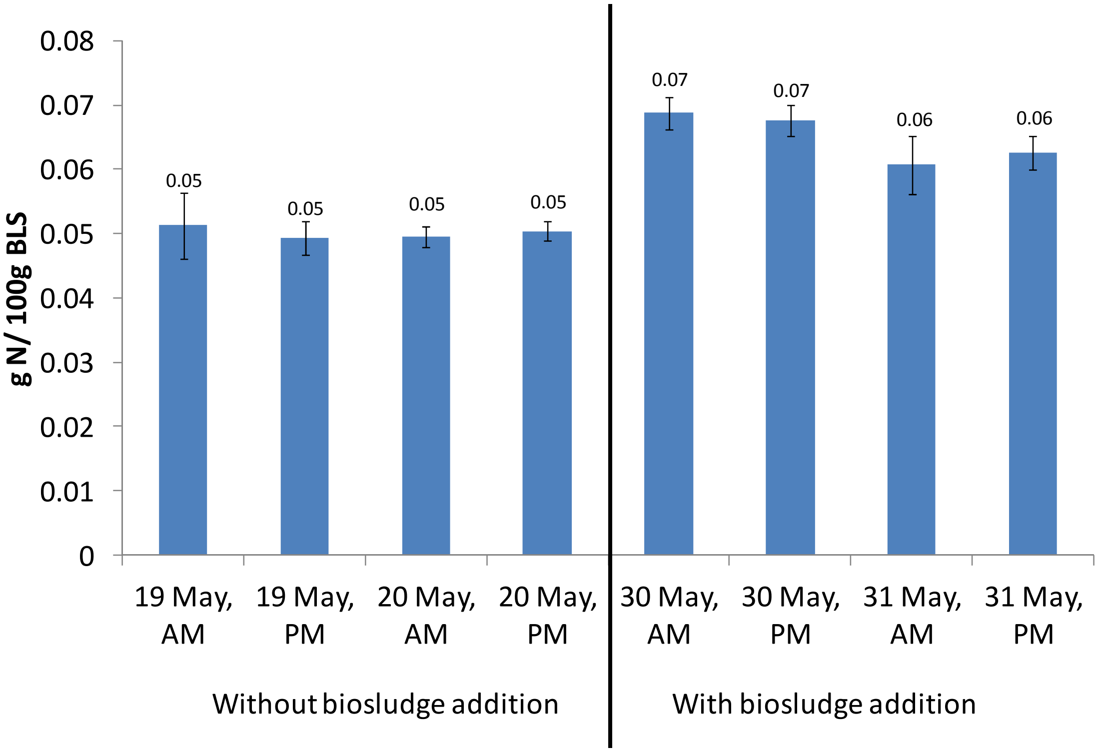

Figure 13. Average NO formation for 8 as-fired black samples from UPM-Kymi (4 without biosludge added and 4 with biosludge) burned in a single particle reactor at 1100 C with 3.3% O_2/bal. N_2. Error bars represent 1 standard deviation of 6 separate droplets.

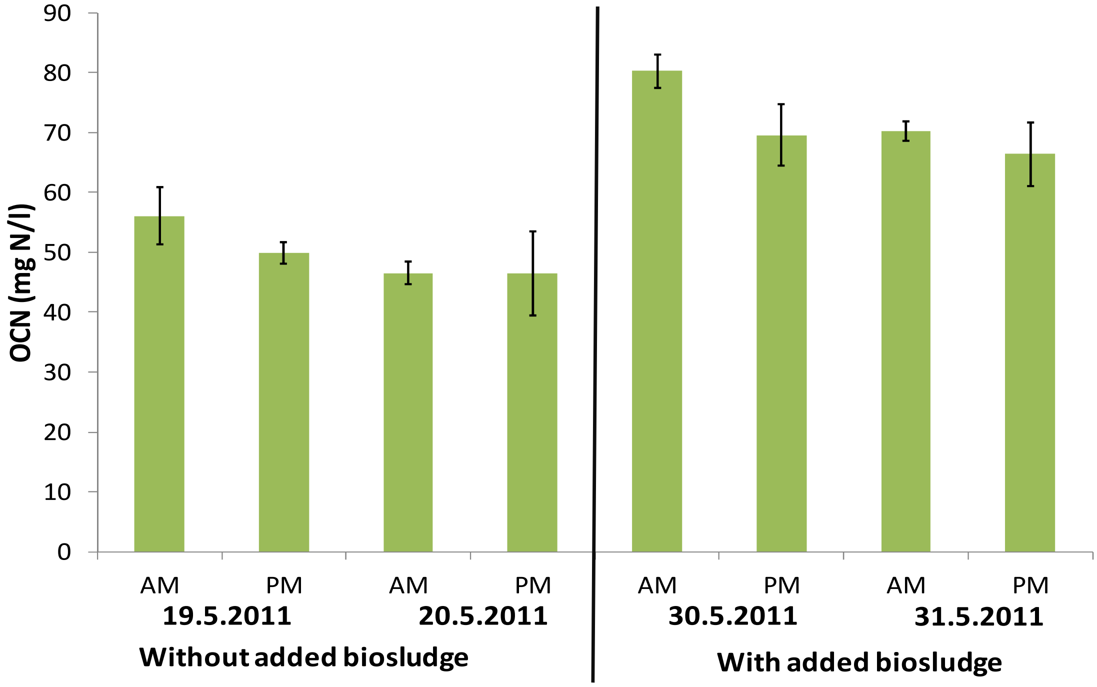

Figure 14. OCN-N concentration in green liquor samples taken before biosludge addition and after biosludge addition. Six replicate analysis were made for each sample and the error bars represent 1 standard deviation.

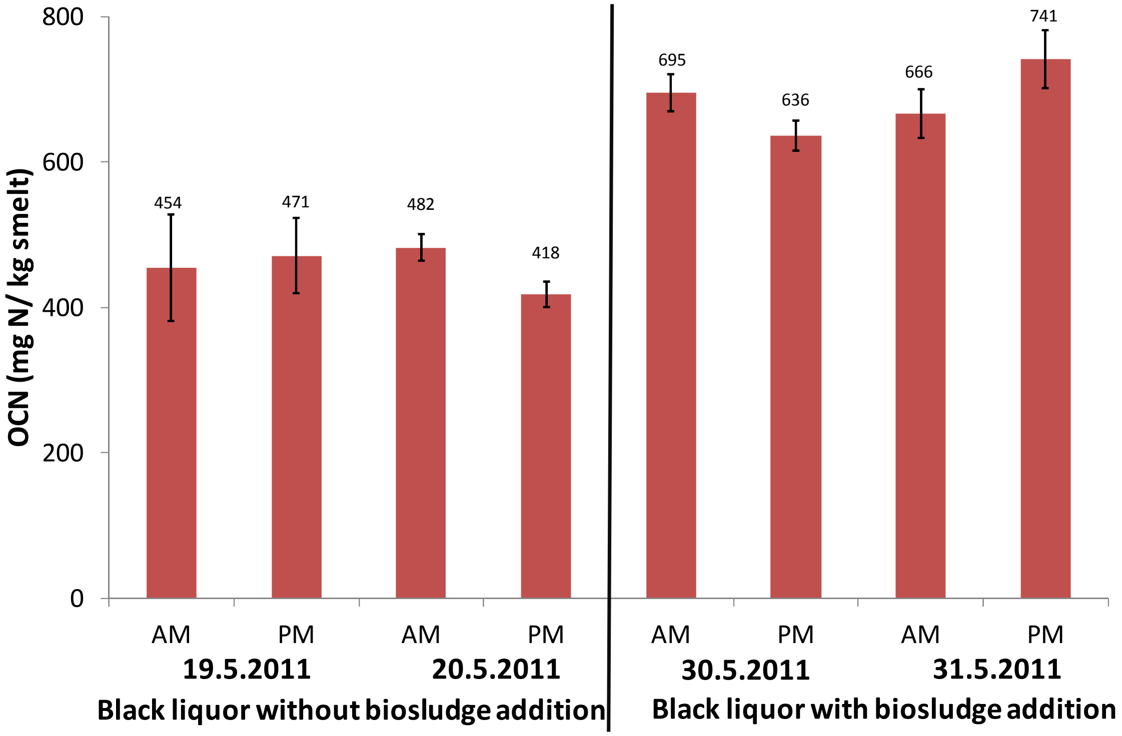

Figure 15. Cyanate formation after pyrolysis and gasification to 100% smelt for the black liquor samples.

3.7. *Impact of Biosludge on Lime Kiln and NCG-boiler NO_x formation*

The lime kiln burns natural gas so any NOx formed from burning natural gas is due to thermal NOx formation. The weak NCG from the recausticizing plant go to the lime kiln and these gases do contain ammonia that originates from the cyanate in the smelt from the recovery boiler. Since this cyanate nitrogen concentration increased in the green liquor after biosludge addition, it is reasonable to assume that the ammonia flow with the weak NCG might have increased by a small amount, but no measurements were taken of the weak NCG, so this cannot be confirmed. Regardless, no clear increase in lime kiln NOx was noticeable when comparing the NOx from the lime kiln for the 3 weeks before biosludge addition and the 3 weeks after biosludge additions (Figure 16). In the case of the NCG boiler, there was 21% increase in the concentration of NOx in the flue gases for the period after biosludge addition compared to the period before biosludge addition. This can be explained again by the higher cyanate concentration in the green liquor after biosludge addition. The higher green liquor nitrogen content can result in a higher white liquor nitrogen content which in turn results in more ammonia in the dirty condensates from the digesters and evaporators. This nitrogen in turn is found in the stripper off gases and MeOH which are burned in the NCG boiler and which are the source of NOx from the NCG boiler. Since a full balance was not performed before and after biosludge addition, this explanation is not confirmed in this work.

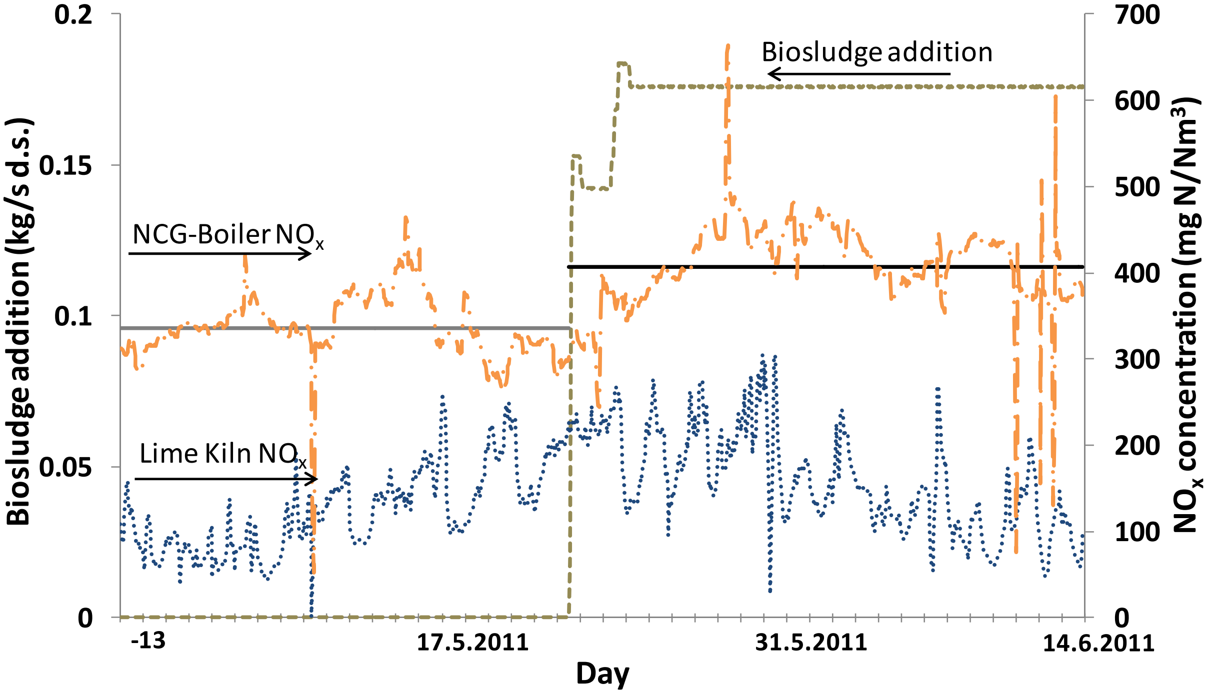

Figure 16. NOx from the NCG boiler (orange line); lime kiln (blue line) and the biosludge flow rate (brown line).

3.8. *White liquor oxidation*

White liquor oxidation was very effective at removing NH_3. The NH_3 concentration in the white liquor was 41.2 mg N/l and the NH_3 concentration in the oxidized white liquor is 2.4 mg N/l.

4. Stripping experiments with white liquor and air

The equilibrium for ammonia between water and air can be described by Henry’s law.

$$y_e = \frac{k_H}{p} \cdot C$$

k_H: Henry´s constant
p: pressure
C: concentration of ammonia (mol/l)

The temperature dependence of the Henry’s constant (atm) for ammonia can be described by the equation below and is shown in Figure 17.

$$log k_H = \frac{-A}{T} + B$$

A = 1887.12
B = 6.315
T: temperature in K

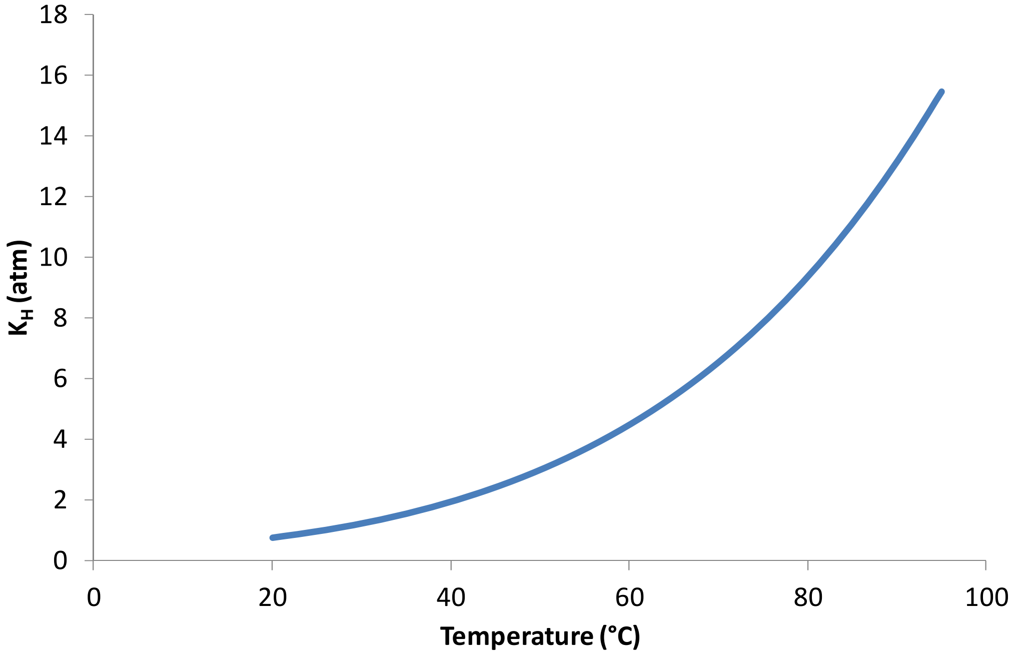

Figure 17. Temperature dependence of the Henry's law constant for NH_3.

The minimum amount of air needed to strip a certain amount of ammonia from water can be calculated assuming that the concentration of NH_3 in the air is at equilibrium with the NH_3 remaining in the solution during stripping. To determine how close to the theoretical minimum the ammonia stripping system might be, ammonia was stripped from a batch solution of white liquor at different temperatures. The volume of white liquor for each run was between 150 and 225 ml and the volumetric flow rate of air through the impinger bottle was 760 ml/min. Separate experiments were run for different lengths of time at three different white liquor temperatures (70, 80 and 90 °C). The white liquor was placed into an impinger bottle that was sealed. It was heated to the desired temperature and then air was bubbled through the bottle for a fixed time corresponding to steps equivalent to approximately 33% of the theoretical minimum required air. At the completion of the fixed time the impinger bottle was sealed and cooled before collecting the liquid solution for analysis. Figure 18 shows the ammonia concentration as a function of the theoretical minimum air required to reduce the NH_3 concentration in the white liquor from the initial 33 mg N/l to 2 mg N/l. Table II gives the data shown in Figure 18.

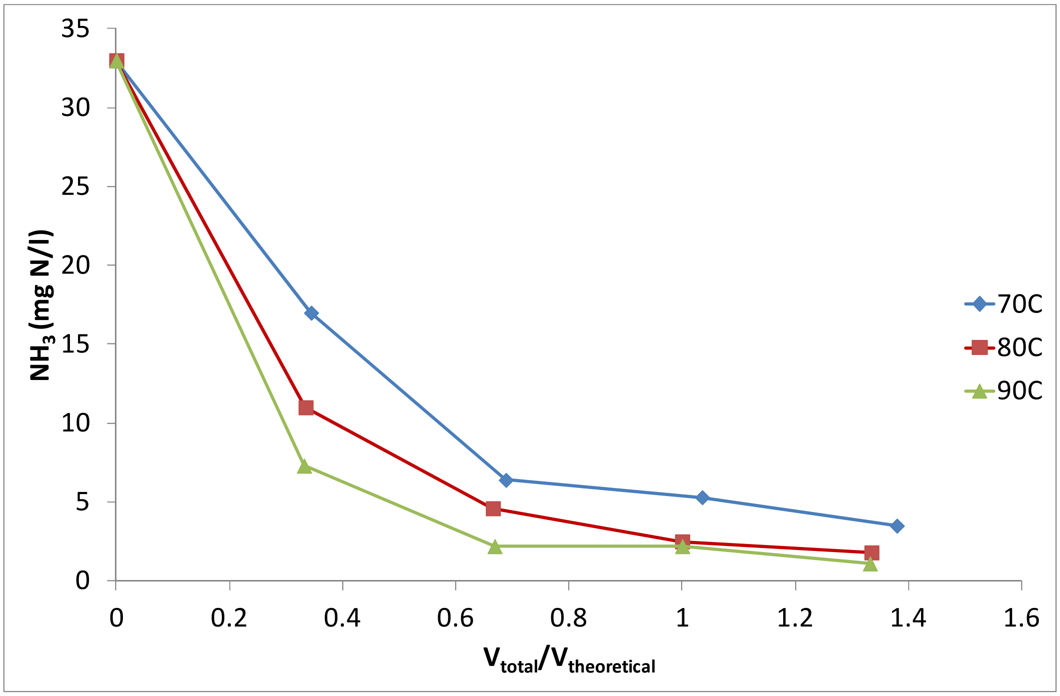

Figure 18. Concentration of NH_3 vs. fraction of theoretical minimum air required to reduce the ammonia concentration from 33 to 2 mg N/l in a alkaline solution.

Table II. Concentration of NH_3 (mg N/l) in white liquor after stripping with air as a function of the theoretical minimum.

Temp (°C)	$V_{tot}/V_{theoretical}$	NH_3 (mg N/l)
70	0 %	33
	34 %	17
	69 %	6.4
	104 %	5.3
	138 %	3.5
80	0 %	33
	35 %	11
	69 %	4.6
	104 %	2.5
	139 %	1.8
90	0 %	33
	34 %	7.3
	69 %	2.2
	104 %	2.2
	138 %	1.1

5. Conclusions

The total amount of ammonia that is theoretically recoverable based on the balance made on 31 May 2011 at UPM Kymi is about ~0.6 kgNH_3-N/ADt pulp. The ammonia found in the dirty condensates would represent 75% of this ammonia while the other 25% of this would be found in the vent gases from recausticizing. Since the ammonia in white liquor is ultimately found in the dirty condensates from pulping and evaporation, its flow from recausticizing is not included in the potential nitrogen recoverable from recausticizing. One challenge of recovering the NH_3 from the dirty condensates would be to separate it apart from the MeOH.

The flow of NOx from the recovery boiler, lime kiln and NCG boiler at Kymi for the 31 May campaign are given in Table III. The NCG boiler's NOx originates from the ammonia in the MeOH and NCG and therefore removal of ammonia from the dirty condensates would have a positive effect on the total mill NOx emissions.

Table III. Average NOx emissions at UPM during the 31 May 2011 sampling campaign based on the stack gas analyzers at the mill.

Unit	NOx as NO_2	Source of NO
Recovery boiler	1.43 kg NO_2/ADt	Fuel-N
Lime kiln	0.30 kg NO_2/ADt	Thermal-NO
NCG boiler	0.23 kg NO_2/ADt	Fuel-N
Total	1.95 kg NO_2/ADt	

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Appendix I. Sample List

Pulping and White Liquor Oxidation		Dates Sampled (2011)
Name	**Position**	
UPM-KD1	SW Chips to K3	30.5, 31.5
UPM-KD2	Washed Pulp from K3	30.5, 31.5
UPM-KD2-b	Carry-over with Pulp from K3	31.5
UPM-KD3	HW Chips to K4	30.5, 31.5
UPM-KD4	Washed Pulp from K4	30.5, 31.5
UPM-KD4-b	Carry-over with Pulp from K4	31.5
UPM-KD5	Sawdust to Sawdust digester	30.5, 31.5
UPM-KD6	Pulp from washer	30.5, 31.5
UPM-KD6-b	Carry-over with Pulp from sawdust digester	31.5
UPM-KD7	Black liquor from washer	19,20,30,31.5
UPM-KD8	Oxidized WL	30.5, 31.5
Evaporation and Stripper		
Name	**Position**	
UPM-KEV1	Weak Black Liquor from K3	19,20,30,31.5
UPM-KEV2	Weak Black Liquor from K4	19,20,30,31.5
UPM-KEV3	Weak Black Liquor to Evaporators	19,20,30,31.5
UPM-KEV4	Intermediate black liquor	19,20,30,31.5
UPM-KEV5	Black Liquor from 2nd Effect	19,20,30,31.5
UPM-KEV6	As-fired black liquor	19,20,30,31.5
UPM-KEV7	Secondary Condensate 1	30.5, 31.5
UPM-KEV8	Secondary Condensate 2	30.5, 31.5
UPM-KEV9	Secondary Condensate 3	30.5, 31.5
UPM-KEV10	Condensate from 1C	30.5, 31.5
UPM-KEV11	Dirty Condensate from evaporators	30.5, 31.5
UPM-KEV12	Dirty condensate to stripper	30.5, 31.5
UPM-KEV13	Stripped Condensate	30.5, 31.5
UPM-KEV14	MeOH	30.5, 31.5
UPM-KEV15	Biosludge (wet)	30.5, 31.5
UPM-KEV16	Biosludge (mechanically dried)	30.5, 31.5
UPM-KEV17	Emävesi	30.5, 31.5
UPM-KEV18	IC Black Liquor	19,20,30,31.5
UPM-KEV19	Cond. From Stripper Cond.	
UPM-KEV20	Cond. From 2nd Effect Dirty	

Recovery Boiler		
Name	**Position**	
UPM-KRB1	NOx stack gases	Data from
UPM-KRB2	Gas from Dissolving Tank	30.5, 31.5
UPM-KRB3	Mechanically cleaned hot water from RB	30.5, 31.5
Recausticizing		
Name	**Position**	
UPM-KCW1	Weak Wash to disolving tank	19,20,30,31.5
UPM-KCW2	GL from Dissolving tank 1	19,20,30,31.5
UPM-KCW3	GL from Equilizing tank to x-filter	30.5, 31.5
UPM-KCW5	WL from slaker	30.5, 31.5
UPM-KCW6	WL from cuasticizer 1	30.5, 31.5
UPM-KCW7	WL from cuasticizer 2	30.5, 31.5
UPM-KCW9	WL to digester & WL oxidation	30.5, 31.5
UPM-KCW10	Lime Mud from CD filter	30.5, 31.5
UPM-KCW11	Lime Mud from disc filter	30.5, 31.5
UPM-KCW12	Filtrate from lime mud washer	30.5, 31.5
UPM-KCW13	Dregs to Dregs Washer	30.5, 31.5
UPM-KCW15	Filtrate from dregs washer	30.5, 31.5
UPM-KCW16	Mechanically Cleaned Hot Water from lime kiln	30.5, 31.5

Appendix II. Analytical Results

Pulping and White Liquor Oxidation		Total N	NH3-N	OCN-N	Dry Solids
Name	**Position**	wt% d.s.	mg N/l	mg N/l	wt% d.s.
UPM-KD1	SW Chips to K3	0.057 %			
UPM-KD2	Washed Pulp from K3	0.006 %			
UPM-KD2-b	Carry-over with Pulp from K3	0.070 %			1.9 %
UPM-KD3	HW Chips to K4	0.096 %			
UPM-KD4	Washed Pulp from K4	0.007 %			
UPM-KD4-b	Carry-over with Pulp from K4	1.300 %			0.1 %
UPM-KD5	Sawdust to Sawdust digester	0.123 %			
UPM-KD6	Pulp from washer	0.007 %			
UPM-KD6-b	Carry-over with Pulp from sawdust digester	0.120 %			1.2 %
UPM-KD7	Black liquor from washer	0.070 %			10.6 %
UPM-KD8	Oxidized WL		2.4		
Evaporation and Stripper					
Name	**Position**				
UPM-KEV1	Weak Black Liquor from K3	0.10 %			19.8 %
UPM-KEV2	Weak Black Liquor from K4	0.09 %			19.4 %
UPM-KEV3	Weak Black Liquor to Evaporators	0.09 %			20.0 %
UPM-KEV4	Intermediate black liquor	0.07 %			31.5 %
UPM-KEV5	Black Liquor from 2nd Effect	0.09 %			51.4 %
UPM-KEV6	As-fired black liquor	0.10 %			82.9 %
UPM-KEV7	Secondary Condensate 1		4.1		
UPM-KEV8	Secondary Condensate 2		26		
UPM-KEV9	Secondary Condensate 3		2.2		
UPM-KEV10	Condensate from 1C		75		
UPM-KEV11	Dirty Condensate from evaporators		124		
UPM-KEV12	Dirty condensate to stripper		173		
UPM-KEV13	Stripped Condensate		35		
UPM-KEV14	MeOH		16328		
UPM-KEV15	Biosludge (wet)	5.00 %	40.8		1.5 %
UPM-KEV16	Biosludge (mechanically dried)	5.30 %			13.3 %
UPM-KEV17	Emävesi	0.05 %			48.6 %
UPM-KEV18	IC Black Liquor	0.11 %			60.5 %
UPM-KEV19	Cond. From Stripper Cond.		1700		
UPM-KEV20	Cond. From 2nd Effect Dirty		620		

Recovery Boiler		Total N wt% d.s.	NH3-N mg N/l	OCN-N mg N/l	Dry Solids wt% d.s.
Name	**Position**				
UPM-KRB1	NOx stack gases				
UPM-KRB2	Gas from Dissolving Tank				
UPM-KRB3	Mechanically cleaned hot water from RB				
Recausticizing					
Name	**Position**				
UPM-KCW1	Weak Wash to disolving tank		42		
UPM-KCW2	GL from Dissolving tank 1		47.2	205	
UPM-KCW3	GL from Equilizing tank to x-filter		68	119	
UPM-KCW5	WL from slaker		42.5		
UPM-KCW6	WL from cuasticizer 1		41		
UPM-KCW7	WL from cuasticizer 2		39.8		
UPM-KCW9	WL to digester & WL oxidation		41.2		
UPM-KCW10	Lime Mud from CD filter				
UPM-KCW11	Lime Mud from disc filter				
UPM-KCW12	Filtrate from lime mud washer				
UPM-KCW13	Dregs to Dregs Washer				
UPM-KCW15	Filtrate from dregs washer				
UPM-KCW16	Mechanically Cleaned Hot Water from lime kiln				

Appendix III. Black liquor analysis for 1 Dec 2011 samples and all samples analyzed for May 2011 campaign.

Sampling Date	Time	Biosludge added	mg N/kg d.s.							
			WBL (SW)	WBL (HW)	WBL (Puru)	Feed WBL	Intermediate BL	2nd effect BL	IC BL	As-fired BL
1.12.2010	Composite	No	960	1100	890	1040	860			850
19.5.2011	AM	No								690
	PM	No								690
20.5.2011	AM	No								660
	PM	No								680
30.5.2011	AM	Yes				840	780	830	980	940
	PM	Yes						860		880
31.5.2011	AM	Yes						920		920
	PM	Yes	700	1000	900	900	700	900	1100	1000/900*

LIITE II

Effect of timescale on emission levels from pulp mills

LUT

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Tutkimusraportti

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Research report

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Effect of timescale on emission levels from pulp mills

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Abstract

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Effect of timescale on emission levels from pulp mills

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The aim of this study is to examine the air emissions from Finnish recovery boilers. The recovery boiler is largest source of air emissions in a pulp mill. In this study, the data used is emission from the stack of several pulp mills in Finland. The studied pulp mill emission data were all from at least a calendar year and was recorded as hourly averages.

The scope of the study was to: analyse of the data by using different time point views; study the emissions by the load and other operating factors of the recovery boiler; study whether regulation by maximum concentration (ppm) equals to regulation by maximum emission as weight flow per time unit and study the instability periods in the behaviour of the emissions.

It has been discovered that the time point of view is of key importance. It is common to see the measurement of emission with some irregularities, such as some short term peaks with no apparent reason. Often these peaks can be locally observed. Mostly the pulp mill emission regulations are based on yearly or monthly averages instead of hourly data.

Recovery boiler operates normally with a high load close to its MCR, but sometimes the load is reduced because of production problems. Recovery boilers are shut down and started up, often several times during one calendar year.

Another point of interest was the excessive fluctuations in some emission data with no obvious explanation. Those phenomena could be caused for various factors, such as problems in the measurement devices. But there is also the possibility that they occur for other factors.

Keywords: emissions, recovery boiler, renewable energy generation

Tiivistelmä

Marcelo Hamaguchi, Esa Vakkilainen

Päästötason riippuvuus tarkasteluajanjaksosta

Lappeenranta 2011
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Tämän tutkimuksen tavoitteena on tarkastella ilmapäästöjä Suomen soodakattiloista. Soodakattila on suurin ilmapäästöjen lähde sellutehtaalla. Tässä tutkimuksessa käytetyt tiedot ovat useiden sellutehtaitten piippupäästöjä. Tutkittujen sellutehtaitten päästötiedot olivat kaikki vähintään kalenterivuoden tuntikeskiarvoja.

Tarkoitus oli: analysoida kerättyjä tietoja; käyttäen erilaisia analyysiajan näkemyksiä; tutkia päästöjä kuormituksen ja muiden soodakattilan toiminta-arvojen avulla, tutkimaan onko suurin raja-arvopitoisuus (ppm) yhtä suuri kuin maksimi-päästö painotettuna virtauksella aikayksikköä kohden ja tutkia epävakauksien käyttäytymistä ja päästöjä.

On havaittu, että käytetty ajan näkökulma on erittäin tärkeää. On yleistä nähdä mittauksissa päästöjen joitakin sääntöjenvastaisuuksia, kuten lyhyen aikavälin huippuja ilman näkyvää syytä. Usein nämä huiput voidaan havaita vain paikallisesti. Enimmäkseen sellutehtaan päästömääräykset perustuvat vuosi- tai kuukausikeskiarvoihin tunnin mittaustuloksien sijaan.

Soodakattila toimii normaalisti suurella kuormituksella lähellä huippukuormaa, mutta joskus kuormaa on vähennettävä, koska tuotannossa on ongelmia. Soodakattiloita on suljettu ja käynnistetty uudelleen, usein monta kertaa kalenterivuoden aikana.

Lisäksi tutkittiin, oli liikaa vaihtelua joissain päästötiedoissa ilman selvää selitystä. Nämä ilmiöt voisivat johtua eri tekijöistä, kuten ongelmista mittauslaitteista. Mutta on olemassa myös mahdollisuus, että ne syntyvät muista tekijöistä.

Keywords: energy taxes, electricity price, renewable energy generation

Contents

Abbreviations

CO	Carbon monoxide
NOx	Nitrogen oxide emissions
SD	Standard deviation
TRS	Total reduced sulfur
VOC	Volatile organic carbohydrates

1 Introduction

The pulp and paper industry has in the recent past significantly reduced emissions from recovery boilers [Bruuce and van der Vooren, 2003]. Despite recent progress in reducing emissions, the pulp industry generates emissions to air similar to many other industries. Currently the emission limits are based on long time periods; yearly or monthly averages. Therefore examining them through hourly data brings a new perspective on used data.

It is important to know where the main sources of emissions are in the pulp mill. Figure 1 shows an overview of all process steps within a pulp mill detailing where the emissions are released. These sources can be divided into two groups. Firstly the stages in the process which emit small amounts of VOC, malodorous gases or chlorine compounds. They are chip storage, digester, pulp washing, bleaching, bleaching chemical preparation, various tanks and evaporation. Secondly there is another group which emits particulates, SO_2 NOx, TRS and other minor emissions through combustion. These are lime kiln, bark boiler, recovery boiler, odorous gas combustion and sometimes other auxiliary boilers. The trend has been that gas flows from the first group are collected and sent to combustion devices in the second group for destruction.

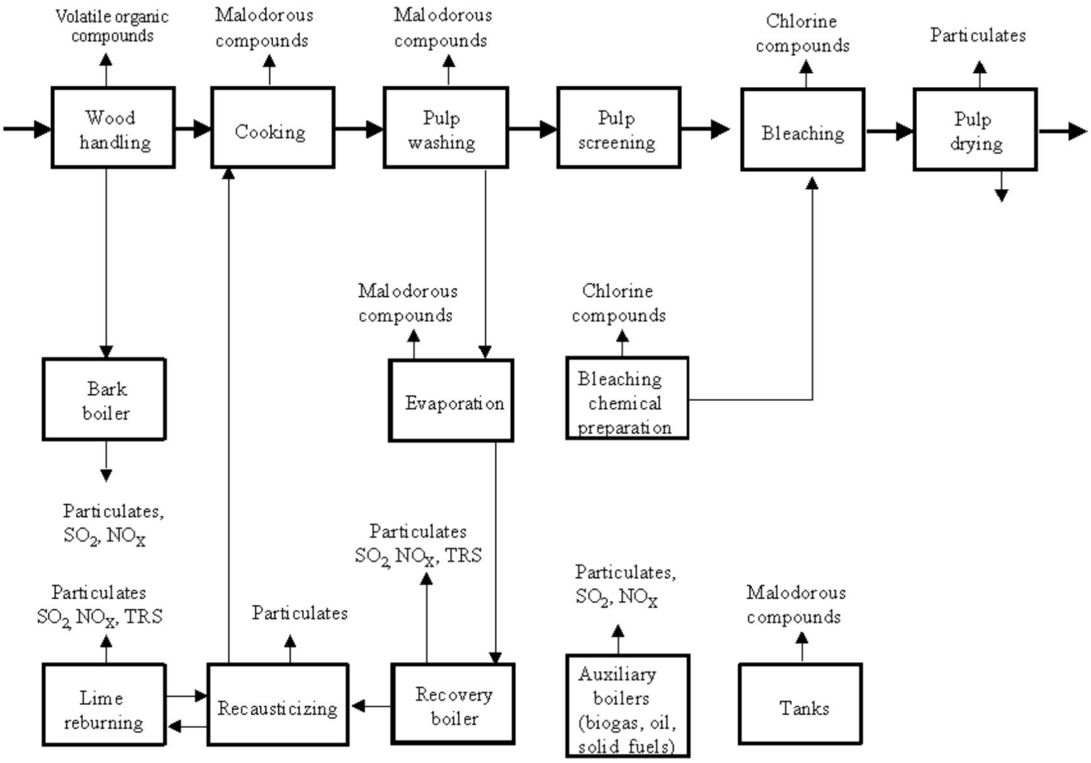

Figure 1. Emissions to the atmosphere from kraft pulp mills [EU IPPC, 2001].

The aim of this paper is to study the emissions from the recovery boilers. Recovery boiler carries out several functions, it burns the organic material that is contained in the black liquor to generate high pressure steam; it regenerates the used chemicals in black liquor, and reduces some waste streams in an environmentally friendly way [Vakkilainen, 2000]. The recovery boiler is the major source of atmospheric emissions in a kraft pulp mill, with sulphur dioxide, nitrogen oxide and particulate as the largest emissions. The recovery boiler is fired with evaporated black liquor. The current average black liquor dry solids content in Finland is around 80% dry solids. One benefit of this level of black liquor dry solids is the reduction of sulphur emissions as a result of the increase in the furnace temperature[Wallen et al., 2004]. On the other hand with a higher temperature and introduction of malodorous gases to furnace the emission of NOx has not decreased[Brink et al., 2009]. An electrostatic precipitator removes a large amount of particulates from the flue gases[EU IPPC, 2001]. Another problematic emission is total reduced sulfur (TRS)[Adams et al., 1997]. Typical emissions to the air from the modern recovery boiler are shown in table 1 for 3% excess oxygen and dry flue gas.

Table 1. Typical emission (dry, 3% O_2) to air from recovery boilers [Vakkilainen, 2005].

Emission	ppm	mg/ m^3n	mg/MJ	kg/ADt
SO_2	35-275	100-800	60-250	1-4
TRS	<7	<10	<5	<0,05
NOx	50-125	100-260	50-80	0,8-1,8
Dust		10-200		0,1-1,8

The modern view is to look at the total amount of the air emissions from kraft pulping. Typical emissions from the modern pulp mill are shown in table 2.

Table 2. BAT emission levels from kraft pulping process and recovery boiler [EU IPPC, 2001].

Emission	Unit	Kraft pulping	Recovery boiler
SO_2	kg(S)/ADt	0,2…0,4	<0,1
TRS	kg(S)/ADt	0,1…0,2	<0,1
NOx	kg(NO_2)/ADt	1,0…1,5	0,7…1,1
Dust	kg/ADt	0,2…0,5	0,2…0,5

Effect of operation values to emissions has been studied [Costa et al., 2004 and Alameida et al., 2000]. Monthly variability of NOx and SO_2 emissions from modern recovery boilers was noted by Salmenoja[2009]. Expressing the statistical variability of recovery boiler emissions is still lacking, which this study tries to address.

2 Study of emissions from recovery boiler

Figure 2. View of the recovery emissions from one pulp mill [Tikka, 2008].

The aim of this paper is to study the statistical variability of emissions from recovery boilers. Recovery boiler is largest source of air emission in a pulp mill. Data used in this study are the emissions from the stack of pulp mills in Finland, Table 3.

Table 3. Data on studied mills

Mill	Study period, hours (days)	Boiler up, hours	Steam MCR, kg/s	Analyzed emissions[1)]
Mill A	11688 (487)	11104	128.7	SO_2, NOx, CO, TRS
Mill B	10926 (455)	10634	152.5	SO_2, NOx, CO, TRS, Dust
Mill C	10416 (434)	10159	122.6	SO_2, NOx, CO, TRS, Dust

[1)] For all emissions reliable online measurements were not available

2.1 Determination of recovery boiler load

The maximum continuous rate (MCR) can be defined as the flow value that corresponds to the ten per cent of the uptime in the recovery boiler main steam flow duration graphic, Figure 3. Steam flow duration graphic is formed by arranging all hourly steam flows from largest to smallest. In the case in Figure 3 the value of MCR is 128,7 kg/s.

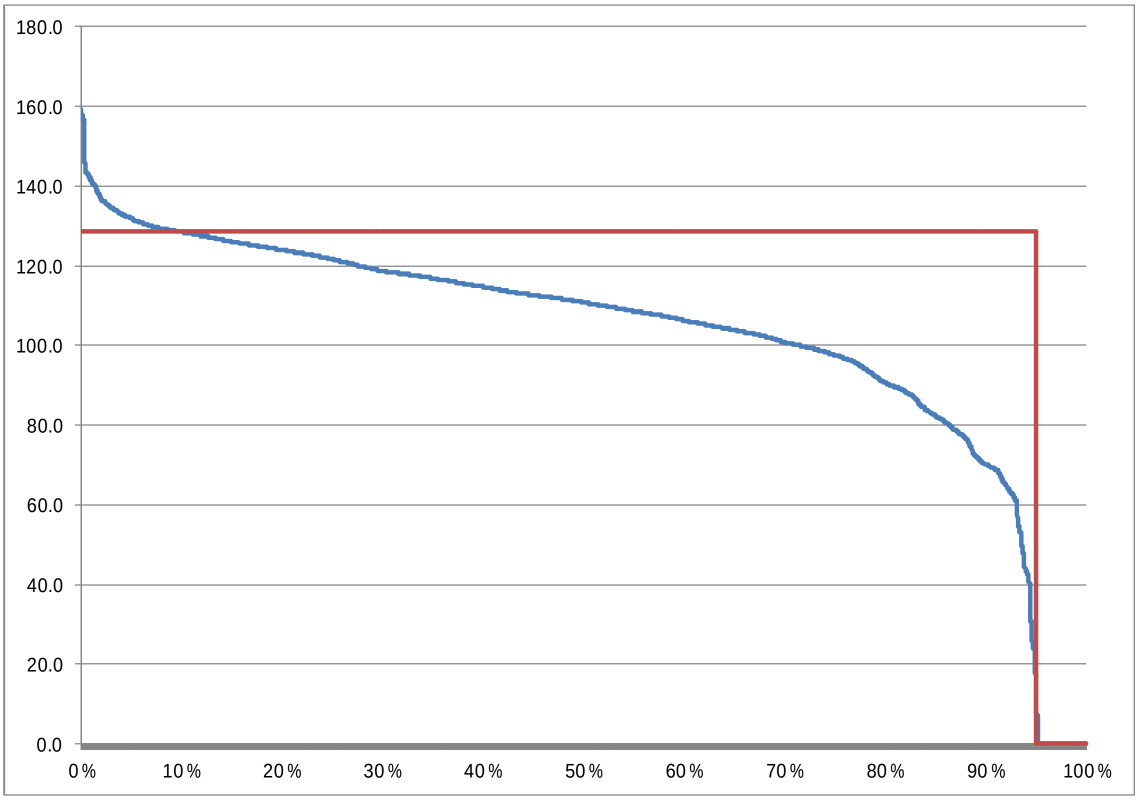

Figure 3. MCR of the recovery boiler from main steam flow duration curve.

Uptime can be defined as those hours where the main steam flow of a recovery boiler has been higher than 10 % of the MCR flow. The definition of MCR and uptime as presented here are standard industry practices.

2.2 Data collection

Recovery boiler emissions were recorded on each mills control system as hourly averages and retrieved to excel form. Stack emission data and some operating parameters such as flow of flue gas (Nm^3/s(dry)), temperature in the stack (ºC), O_2%, SO_2, NOx, CO, TRS and dust (mg/Nm^3) were retrieved for study periods. Emission data were retrieved as actual i.e. not corrected to 3 % O_2. There are also unwanted deviations; devices can malfunction or will record zero as well maximum during calibration or maintenance for several hours with the recovery boiler in operation. For some of the boilers, various boiler operating parameters such as steam flows, black liquor dry solids, black liquor flows etc. were recorded. This data was also stored and retrieved as hourly averages.

2.3 Analysing of the emission data

In Figure 2 the recovery boiler emissions to air are presented as hourly averages for the whole fourteen month period. The emissions are expressed as mg/Nm^3 (dry) and are not corrected to fixed % of O_2. It can be seen that SO_2 is very unsteady. There is no overall trend. Large peaks seem to appear almost randomly. The NOx emissions are clearly making a trend and are ranging between maximum and minimum. CO behaves similar to SO_2. It has some peaks, but mostly CO emission keeps stably in the lower part of the graphic. TRS is not as high as others. Nevertheless some peaks of TRS are visible covering the whole range of the measurement device. The last measured emission is dust. It seems that there are some problems with this emission measurement. Dust emission seems to behave irrationally and it is an clear example of why several dust measurements have not been further considered in this study

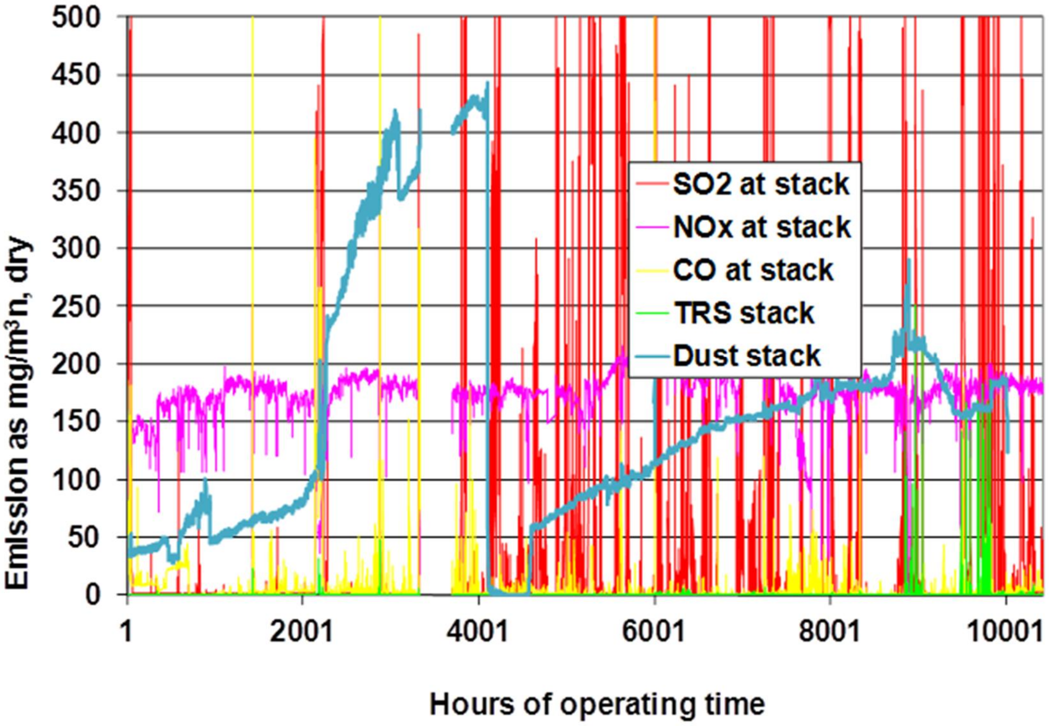

Figure 4. Example emission data of the recovery boiler.

Typically emissions are discussed as averages of long time periods. Even if it is common to see the emission display short time irregularities, such as, large peaks. With different time point of views we can look at emissions from fresh perspectives. Also we can find out how the emission indicators differ if we review them on a daily or on a monthly basis. For this study the emissions have been measured for at least a whole calendar year operating period. Thus, the emissions can be studied from different time scales up to one year.

In addition to retrieved hourly data also daily (calendar day from 0:00 to 24:00) and monthly average data were calculated. For those days that contained hours when the recovery boiler was up an average was calculated. So in theory average calendar day can contain data from one to twenty four hours, but in practice they contain at least fourteen hours. The monthly data contained all the days of that month when the boiler was up. In theory a calendar month can contain data from one to thirty one days, but in practice they all contain at least twenty five days.

2.4 Study of the emissions as a function of the load of the recovery boiler

The emission data are usually presented chronologically. This is not the only way to present emission data. Recovery boiler emissions are a function of many process variables such as temperatures (in many different points of the combustion process), where and how much air is inserted, composition of the black liquor and other operating parameters [Salmenoja, 2009]. Another way to examine the data is to review it as a function of the load of the recovery boiler. The load can be expressed as either steam flow or what was used the flue gas flow, Figure 5.

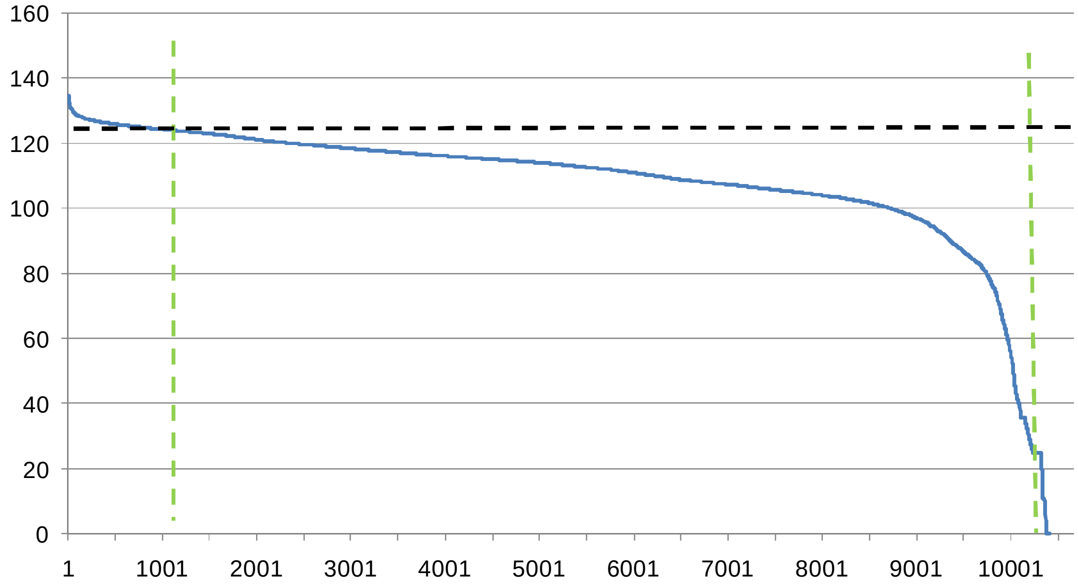

Figure 5. MCR of the recovery boiler from flue gas flow duration curve

2.5 Study of the emissions as durability curves

In emission duration graphics the emission data from boiler uptime is ordered in descending order of magnitude, rather than chronologically. Example of this is shown Figure 6. Black line represents the hourly emissions. More jagged blue line represents daily average emissions. Green line with flat parts represents monthly emissions. It can be seen that different time scales change average hourly emission duration graphs. Higher averaging time means that peaks are reduced and emission values concentrate more around average value. Yearly average would be a straight line.

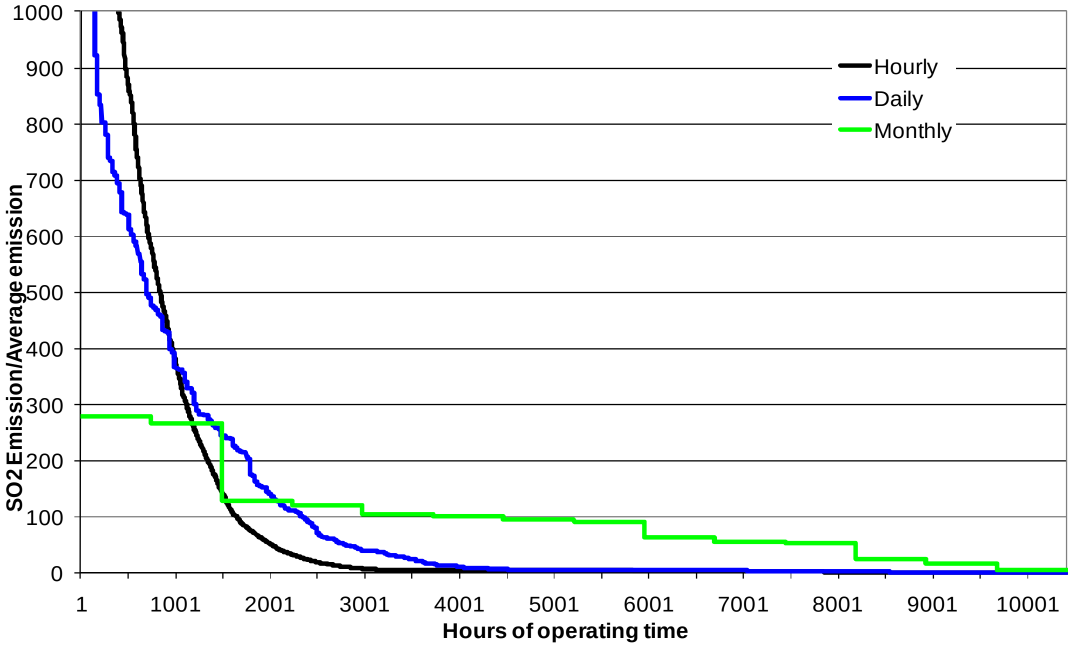

Figure 6. Example recovery boiler SO_2 emission durability distribution by hourly, daily and monthly averages, concentration.

The similar treatment has been given to emissions by flow. Emissions by flow have been calculated by multiplying the hourly average concentration by hourly average flow.

3 Mill A: Recovery boiler

The recovery boiler in question is a large new recovery boiler. The emission data were retrieved from 1.9.2009 to 31.12.2011. The period was sixteen months or 11688 hours. Of that time the recovery boiler was up 11104 hours or 95.0 %

The retrieved emission data were SO_2, NOx, CO, TRS and dust. Of these, based on mills own opinion, the dust data were left out as the mill had had continuous problems with dust measuring device.

3.1 Operation during measuring time

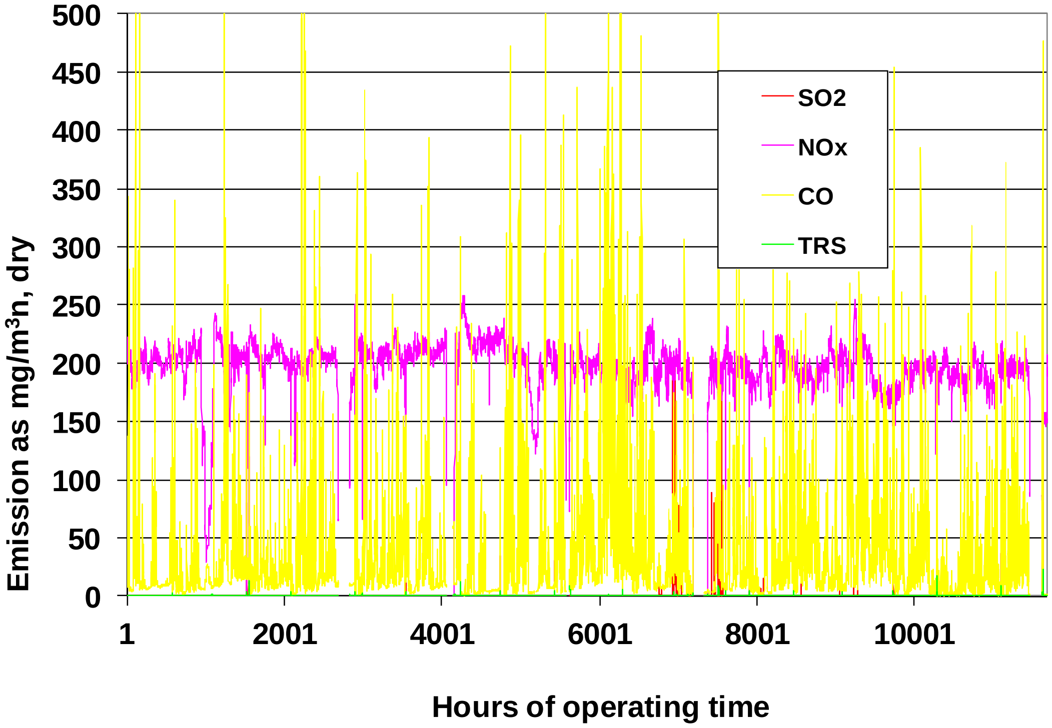

Figure 7. Recovery boiler A emissions by concentration (hourly averages).

As can be seen from Figure 7 the TRS emissions are typically very low, SO_2, peaks very seldom, NOx varies around rather fixed value and CO keeps peaking regularly. It should be pointed out that typically O_2 is lowered to increase boiler efficiency until the CO starts peaking.

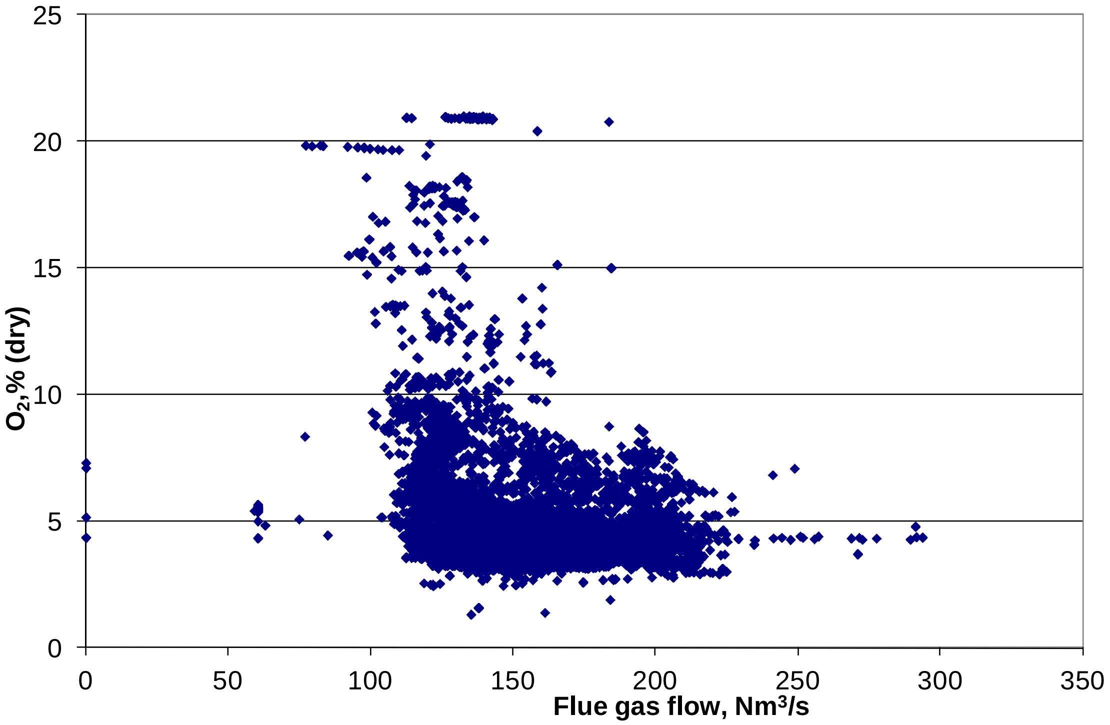

Figure 8. Recovery boiler A O_2-concentration in flue gas versus flue gas flow (hourly averages).

As seen in the Figure 8 the O_2 content in the flue gases is mainly below 5 %. One can observe large number of values around 21 %. Theoretically this would mean that no fuel is fired and recovery boiler produces steam by blowing air through the boiler which is not possible. More relevant explanation is calibration or malfunction of the O_2 measurement device.

It can be observed that keeping the air ratio (=flue gas oxygen content) low all the time has not succeeded. From pure optimum operation point of view it should be preferable to keep O_2 close to 3. In actual operation this does not seem to succeed.

There are very few flue gas flow values below 100 Nm^3/s. In practice it is very difficult to operate at much lower than 60 % of recovery boiler MCR load. Smaller loads are mostly during recovery boiler shut-downs or start-ups.

3.2 Stability of operation during measuring time

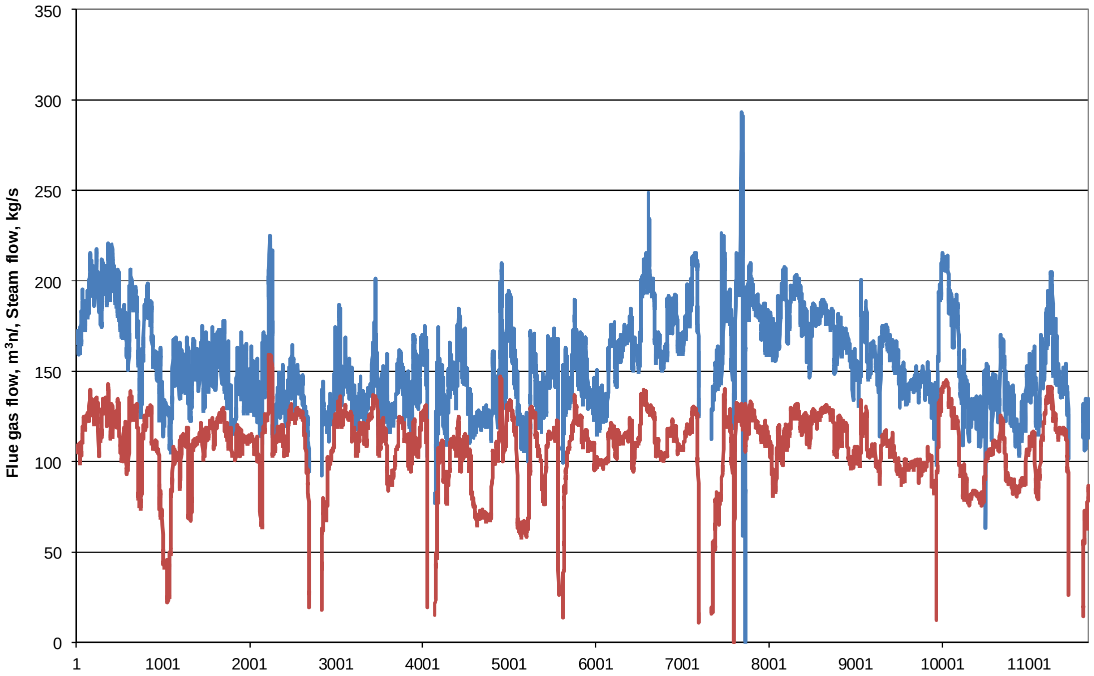

Figure 9. Recovery boiler A main steam and flue gas flow (hourly averages).

Recovery boiler a main steam flow (lower line) can be seen to correspond to flue gas flow (upper line), Figure 9. As seen the Mill A has had to make four large stoppages and roughly the same amount of load decreases to accommodate operating and maintenance demands. But overall the load of the recovery boiler has been stable.

One should note the abrupt swings in flue gas flow around 7700 hours first up to close of 300 m^3n/s and then to almost zero during two days while e.g. steam flow, NOx and O_2 remain fairly stable. This incident was classified as flue gas flow measurement malfunction.

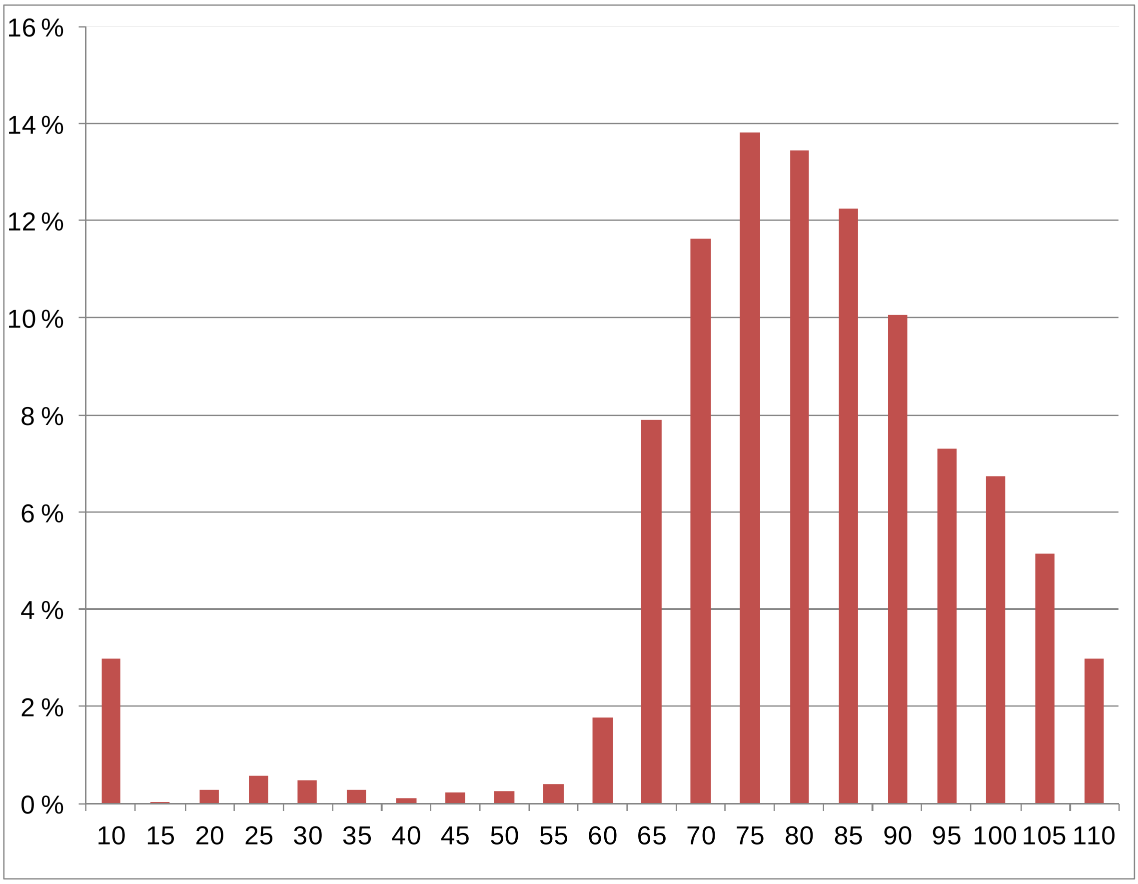

Figure 10. Recovery boiler A flue gas flow frequency curve (hourly averages).

As seen in Figure 9 practically all operation is done above 60 % of MCR flue gas flow. The flue gas flow data is a bit skewed but otherwise it corresponds to a bell curve with some randomly distributed flows during start-up and shutdown. The peak in <10 % data (~3 %) is the boiler operating with fossil fuel during start-up and shut-down.

3.3 Emission durability curves

The retrieved hourly averages emission values as concentration from boiler uptime were arranged as durability curves. These durability curves were done based on hourly, daily and monthly data. The curves are shown not as absolute values but as differences to averages for uptime hours for the whole period. Following each durability curve there is an emission frequency chart.

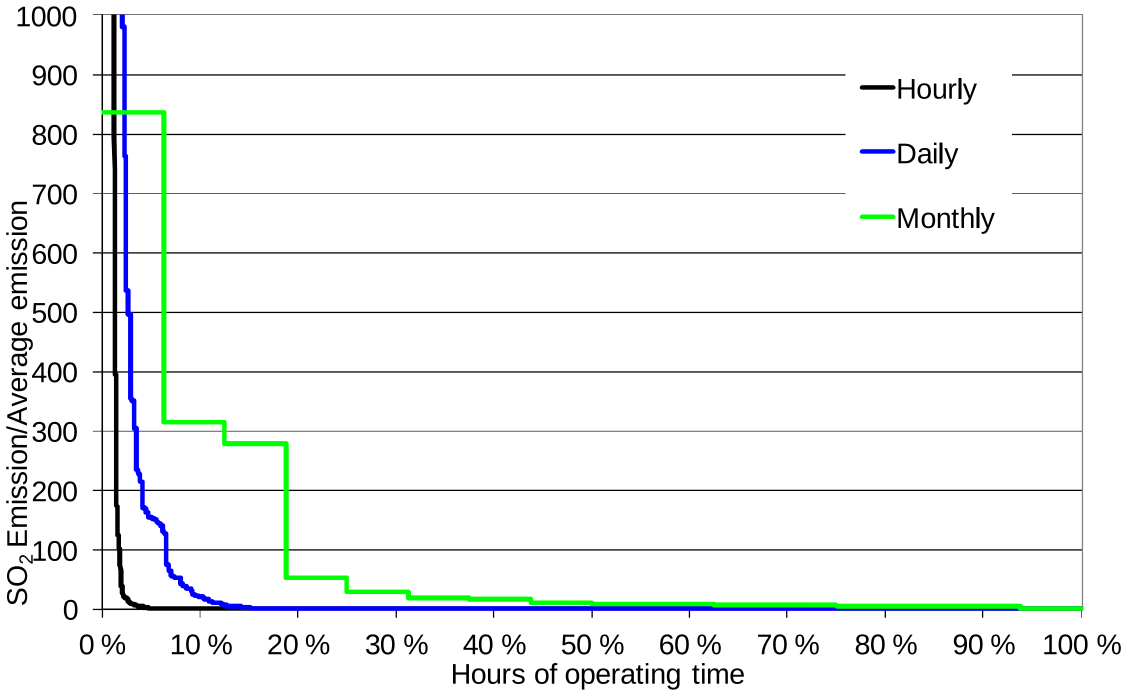

Figure 11. Recovery boiler A SO_2-durability curve, concentration.

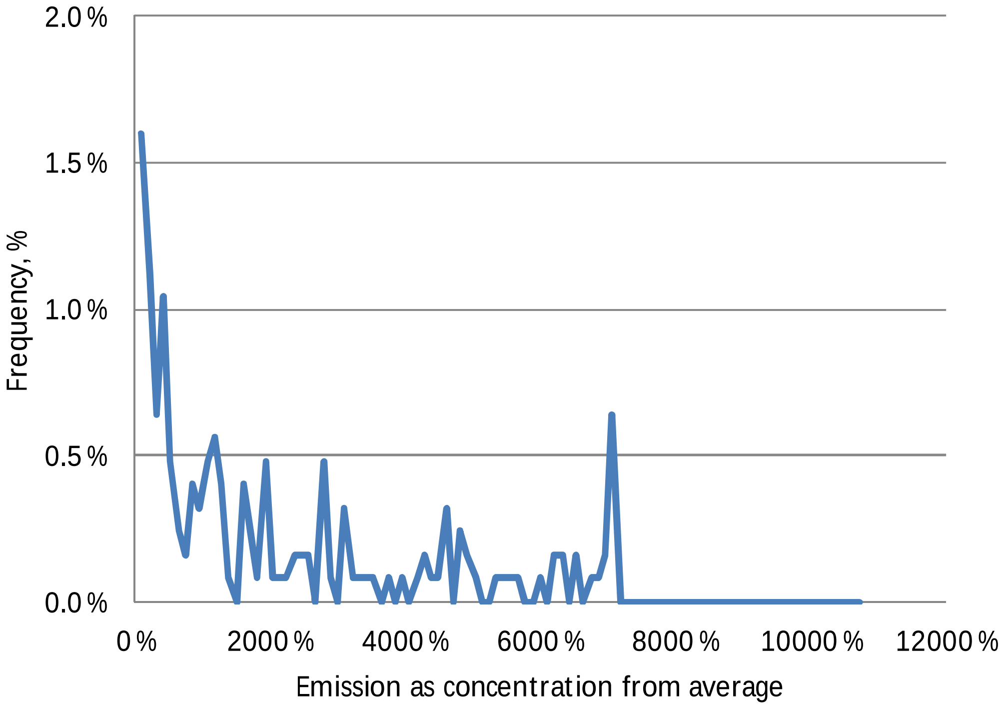

Figure 12. Recovery boiler A SO_2-emission frequency curve, concentration.

One notices on SO_2 curve that it has only a few months (three) higher than average. It has 6.6 % days and 1.8 % hours higher than average. One can see from the frequency curve that apart from high frequency below 200 % there is a peak close to 7000 %. This is because the maximum measured (recorded) value is 7000 %. It is difficult to have measurements that accurately reflect small typical values and record extreme peaks.

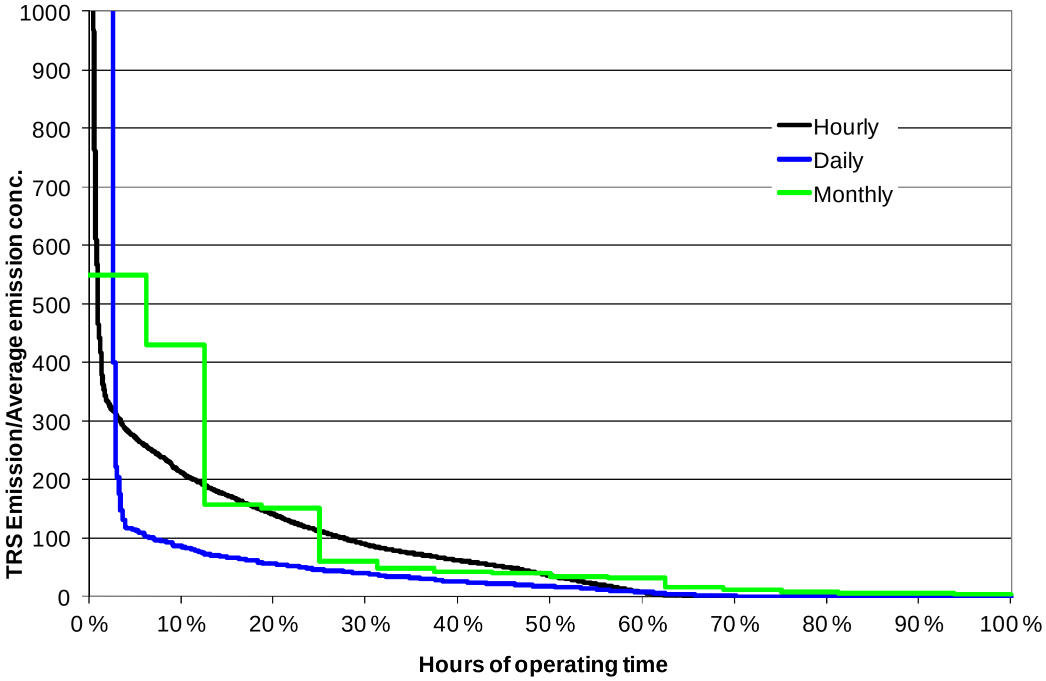

Figure 13. Recovery boiler A TRS-durability curve, concentration.

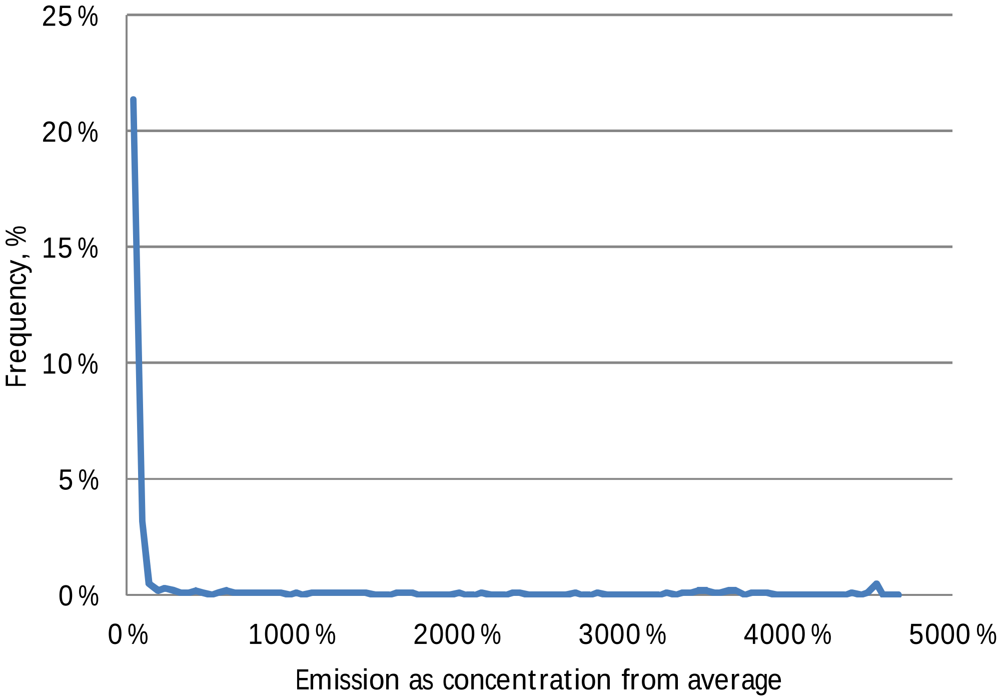

Figure 14. Recovery boiler A TRS- emission frequency curve, concentration.

The TRS behaves similarly to SO_2. The upper range of TRS measurement is ~4700 %. But practically all the measurements are at lower edge of range with average value below the measurement error. There are four months above average, 7 % of hours and 27 % of days above average.

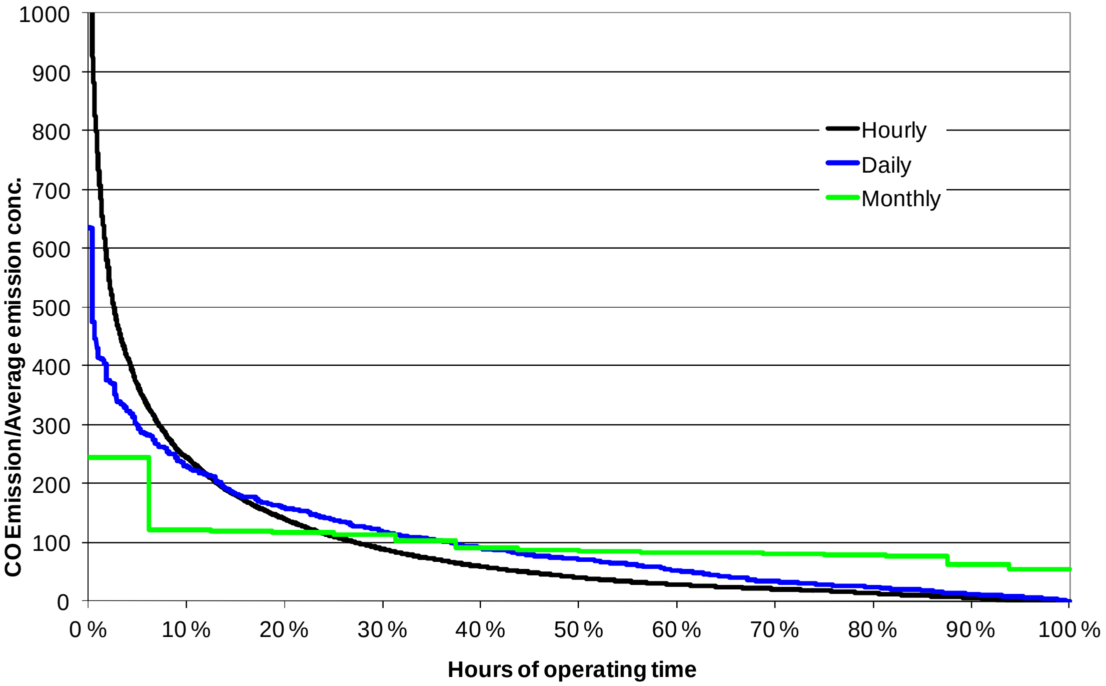

Figure 15. Recovery boiler A CO-durability curve, concentration.

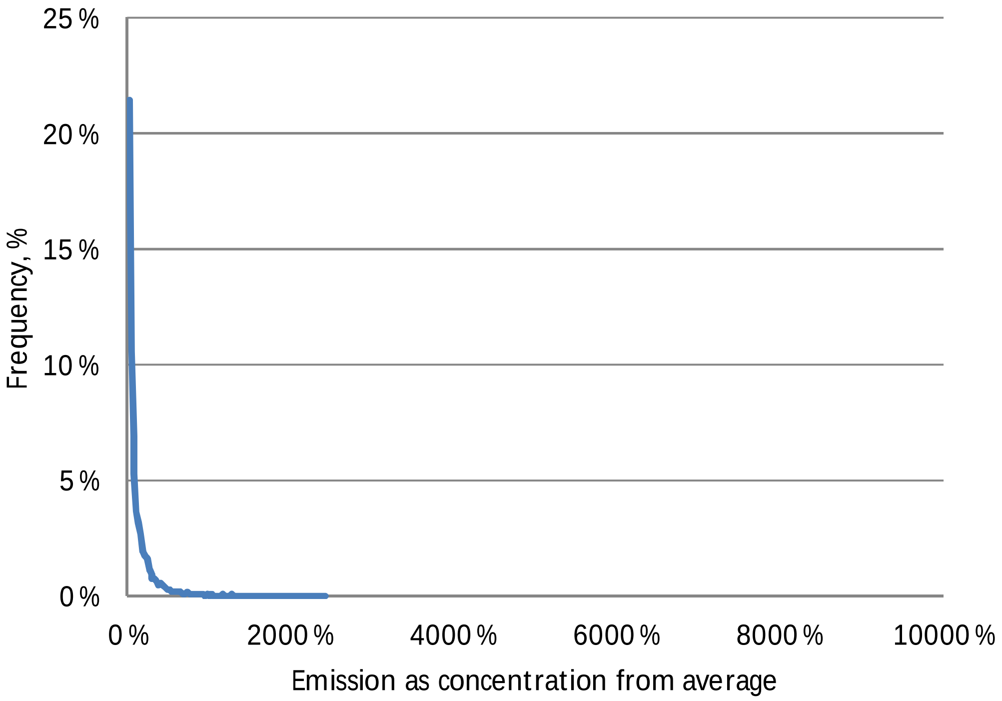

Figure 16. Recovery boiler A CO- emission frequency curve, concentration.

CO shows much more regular peaking behaviour with most of the values below 200 %. There is practically only one month above average. Days and hours are roughly equal.

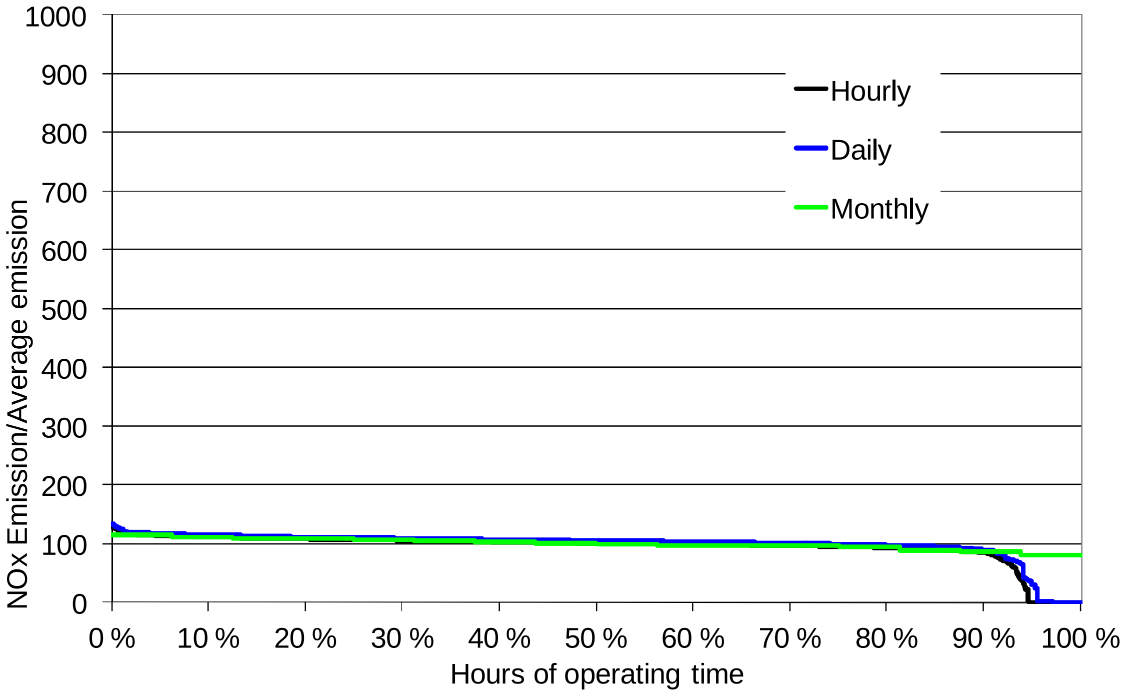

Figure 17. Recovery boiler A NO_x-durability curve, concentration.

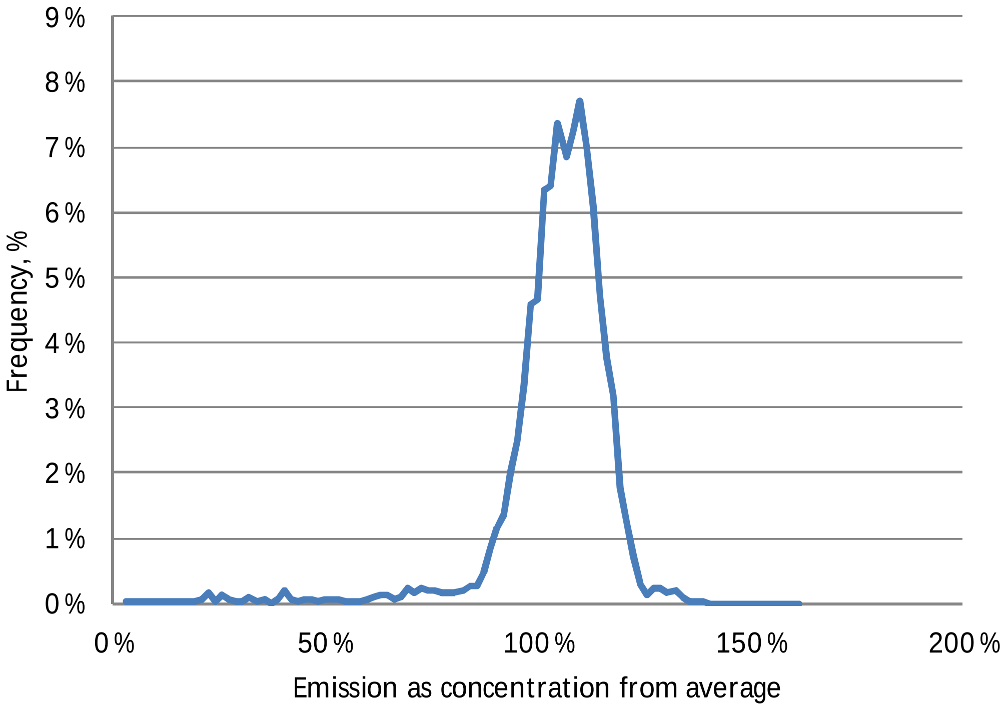

Figure 18. Recovery boiler A NO_x - emission frequency curve, concentration.

NOx behaves close to a bell curve with values distributed around average. The distribution of hourly, daily and monthly values does not differ much. NOx is the only emission which varies with bell shape around one average value.

3.4 Emission as function of load

The recovery boiler emission values were organized to classes based on the flue gas flow and emission averages for each of these classes were calculated. The results are shown in Figure 19.

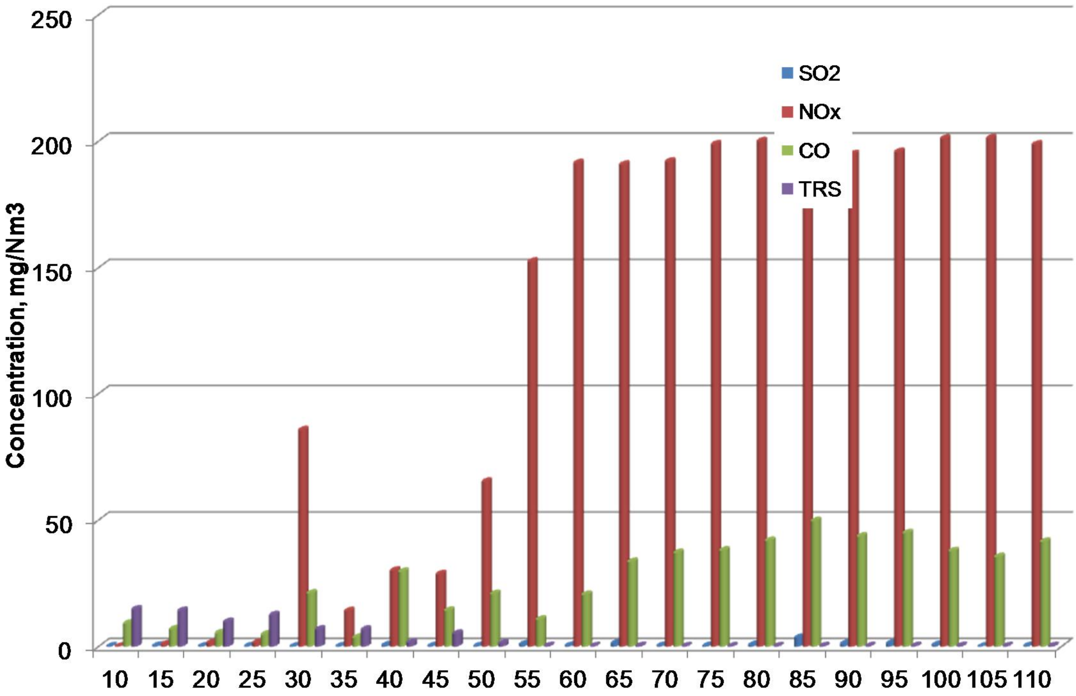

Figure 19. Emission data as class averages (mg/m^{3}n) organized by recovery boiler load to classes based on flue gas flow.

The emissions do change when we dilute them with air. So based on retrieved oxygen content the emission data were corrected for changes in flue gas oxygen content. The resulting data are shown in Figure 19. It should be pointed out that for low loads not as many data points are used for averages as for higher loads. So validity of emission versus load is weak below 60 % with only about 7 % of data points.

It should be pointed out that the emissions in Figure 19 are corrected to 3 % O_2. In Figure 20 the same emissions are shown as not corrected to 3 % O_2.

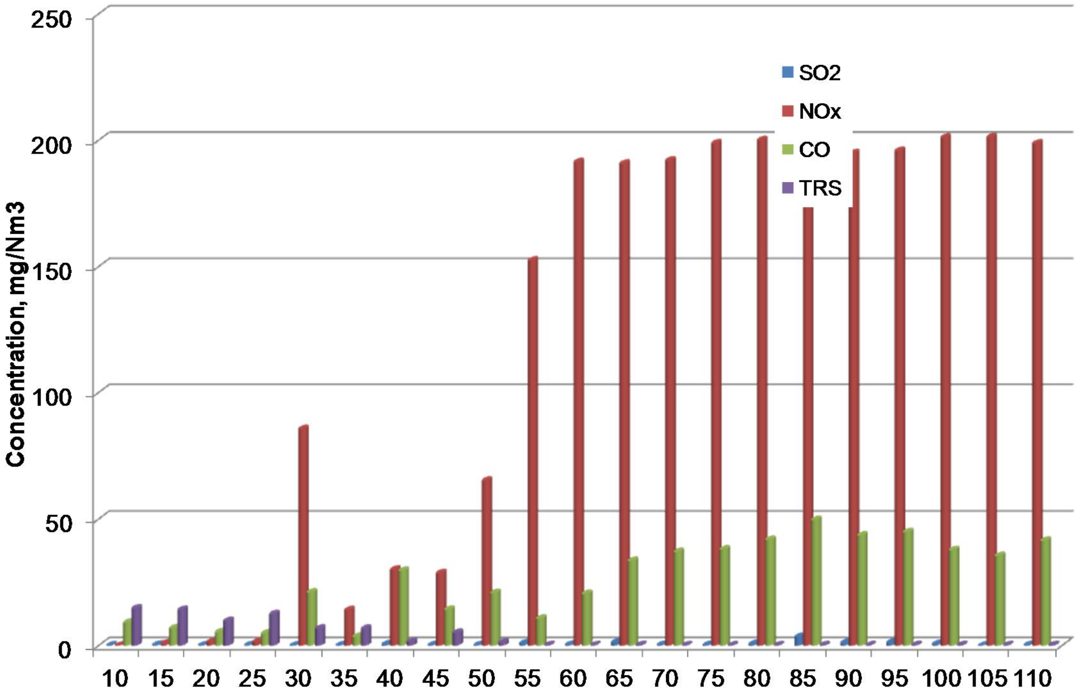

Figure 20. Emission data as class averages (mg/m^{3}n, uncorrected to 3 % O_2) organized by recovery boiler load.

We notice from both sets of data that there are two operating regimes. Above 60 % the boiler is run almost all the time with black liquor firing only. Below 60 % the natural gas firing dominates as seen from NOx values.

Whether we correct the emissions or not they seem approximately equal. The reason for it is that the needed correction is below 10 % as long as the O_2 level is between 1.2 and 4.8 % in dry gases. From Figure 8 we note that O_2 is not dependent on the load.

4 Mill B: Recovery boiler

The recovery boiler in question is a large recovery boiler. The emission data were retrieved from 2.1.2007 to 1.4.2008. The period was fifteen months or 10926 hours. Of that time the recovery boiler was up 10634 hours or 97.4 %

The retrieved emission data were SO_2, NOx, CO, TRS and dust. Of these the dust data were left out as the dust emission clearly didn't follow any known trends. Obviously the mill had problems with the dust measuring device.

4.1 Operation during measuring time

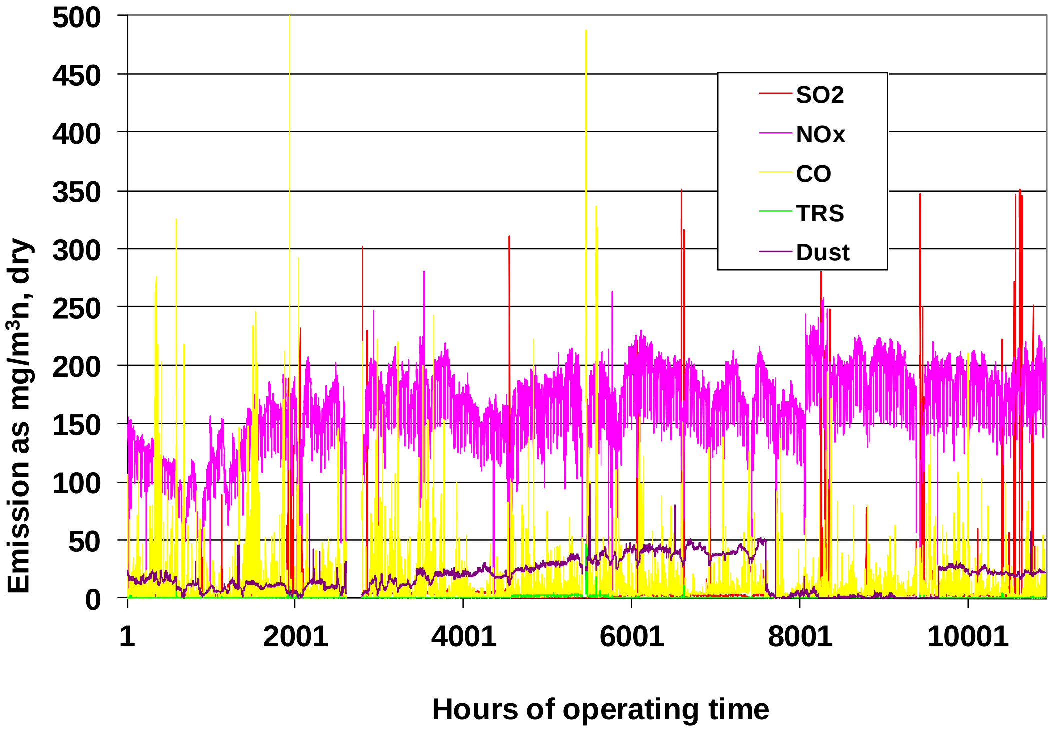

Figure 21. Recovery boiler B emissions by concentration (hourly averages).

As can be seen from Figure 21 the TRS emissions are typically very low, SO_2, peaks seldom, NOx varies around rather fixed value and CO keeps peaking regularly. It should be pointed out that typically O_2 is lowered to increase boiler efficiency until the CO starts peaking.

As can be seen the dust is low the first about 4000 hours, then starts climbing. It reaches double the value at about 7000 hours. Then it is practically zero for more than 2000 hours after which it again starts to behave normally. The dust emission data was deemed not to be fit for processing.

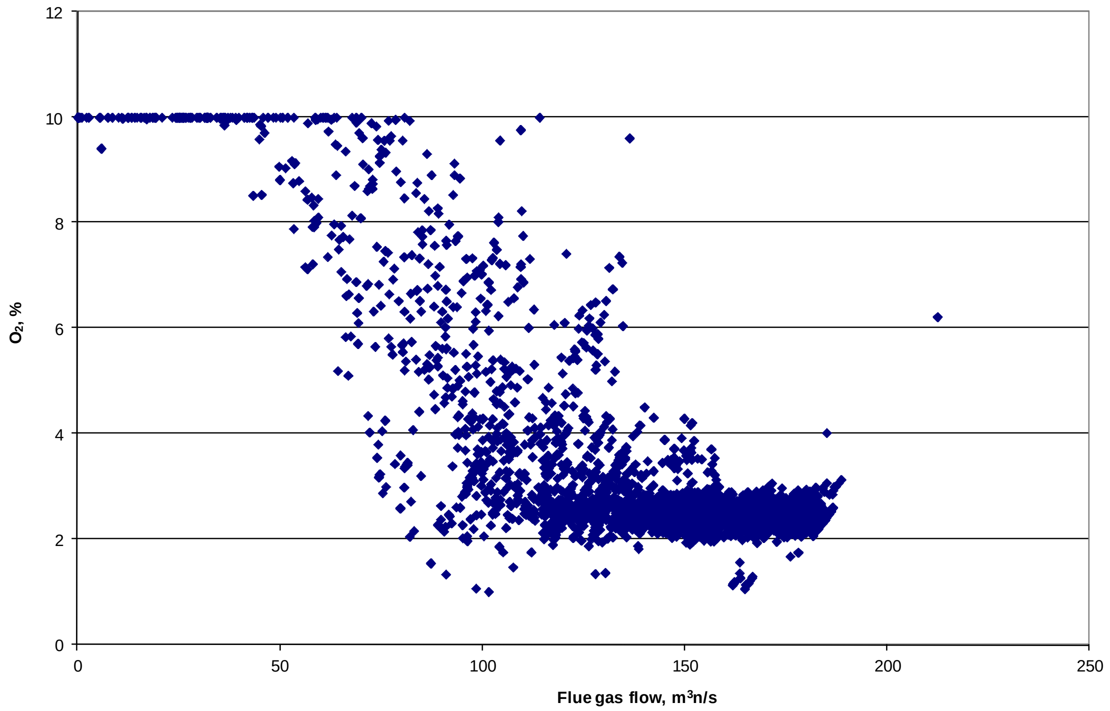

Figure 22. Recovery boiler B O_2-concentration in flue gas versus flue gas flow (hourly averages).

As seen in Figure 22 the flue gas oxygen concentration tends to increase when the flow is less than about 130 m^3n/s. Below about 70 m^3n/s the oxygen content hits the recording maximum 10 %.

4.2 Stability of operation during measuring time

Recovery boiler main steam flow (lower line) can be seen to correspond to flue gas flow (upper line) in Figure 23. As seen the Mill B has had to make two large stoppages and roughly a dozen load decreases to accommodate operating and maintenance demands. But overall the load of the recovery boiler has been fairly stable except a decline at the end of the period.

One should note the abrupt downward swings in steam and flue gas flow. Even though during several of more than 24 hour incidents the steam generation stays above 20 kg/s but the flue gas flow hits long periods of zero. This kind of behaviour can be considered as malfunction of the flue gas flow measurement.

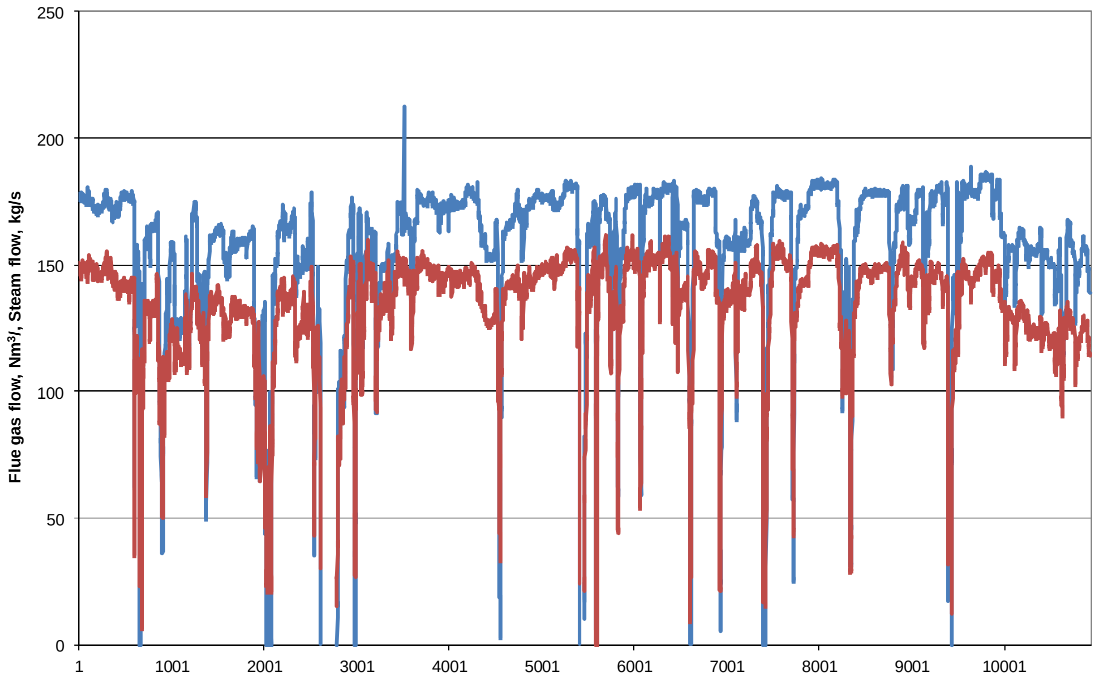

Figure 23. Recovery boiler B steam and flue gas flow (hourly averages).

As seen most of the time the recovery boiler has been operating between 100 to 160 kg/s and 100 to 180 m^{3}n/s.

4.3 Emission durability curves

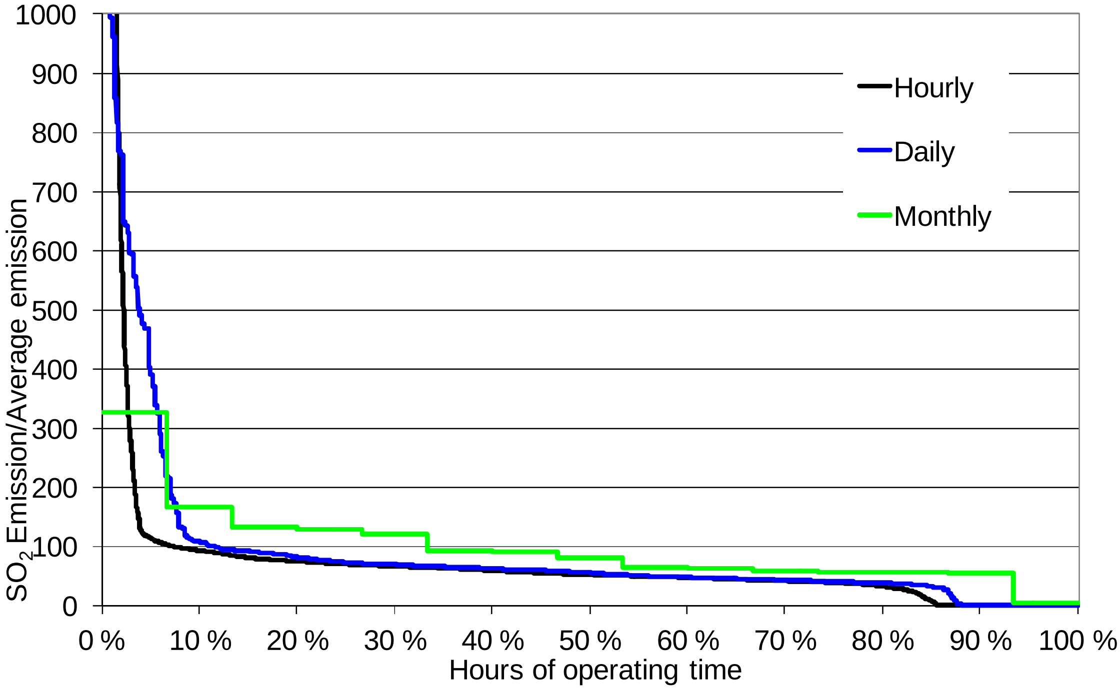

Figure 24. Recovery boiler B SO_2-durability concentration, curve.

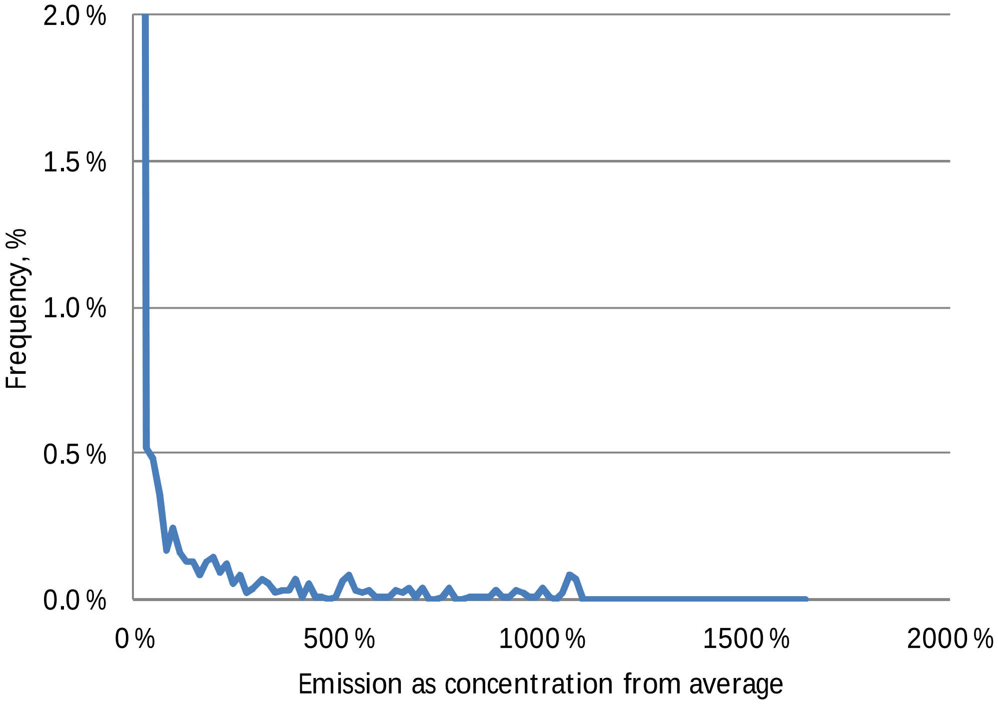

Figure 25. Recovery boiler B SO_2 - emission frequency curve, concentration.

The SO_2 peaks around 5 % of time and maintains few mg/m^{3}n concentration the rest of the time. The 100 % concentration is still within the error margin of the measuring device. The peak around 1000 % represents the upper range of measurements.

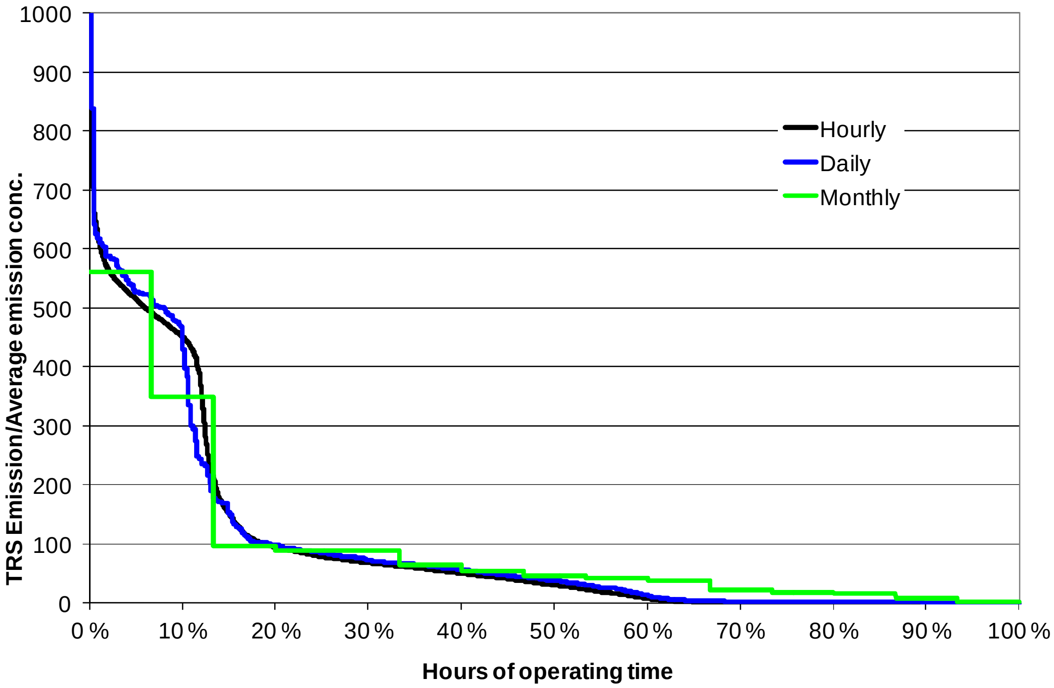

Figure 26. Recovery boiler B TRS-durability concentration, curve.

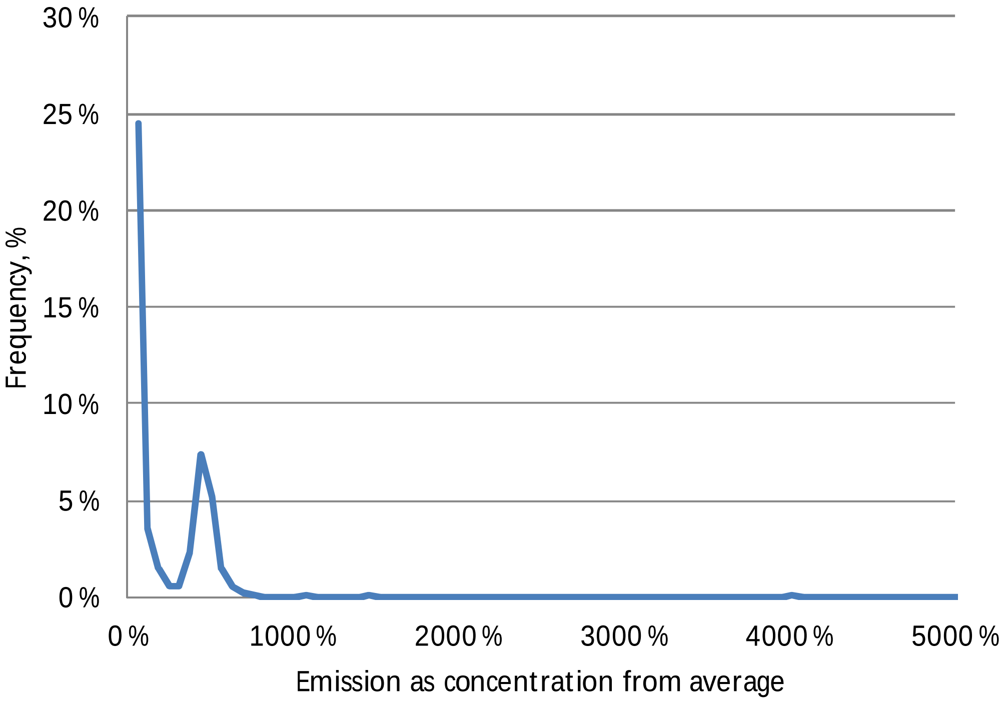

Figure 27. Recovery boiler B TRS - emission frequency curve, concentration.

TRS shows similar behaviour to SO_2. The average is below one mg/m^{3}n concentration. The second peak can be explained by this. The second peak shows as a bump around 500 % in the frequency curve, Figure 27. The data shows again the problems associated with operation around the lowest measuring range during most of the operation.

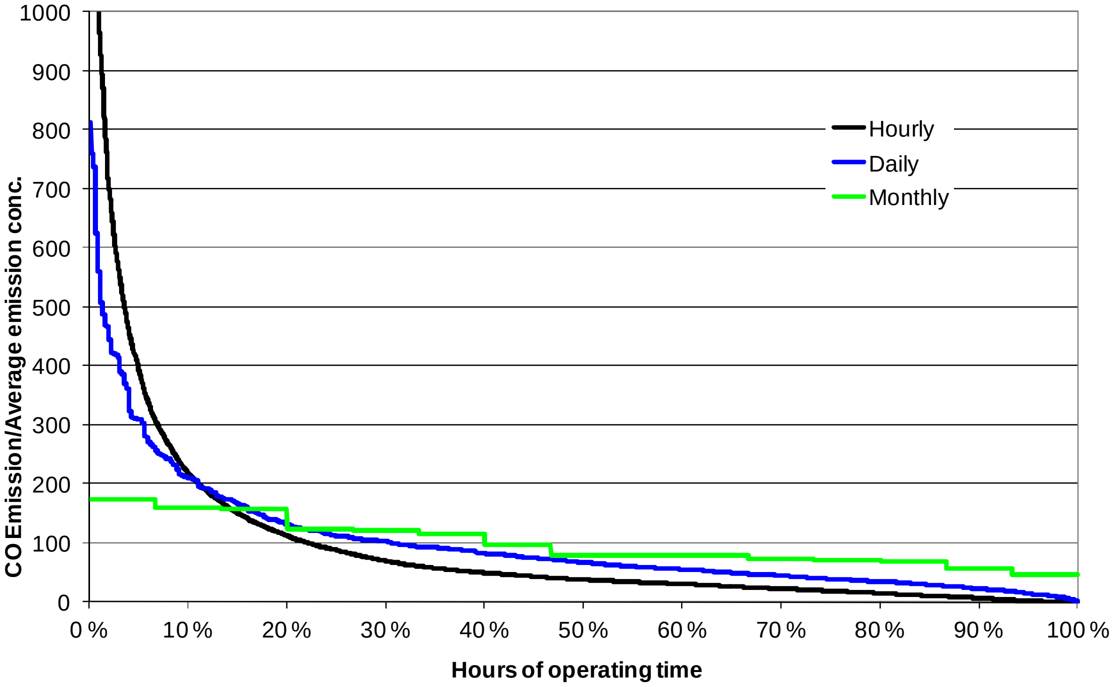

Figure 28. Recovery boiler B CO-durability concentration, curve.

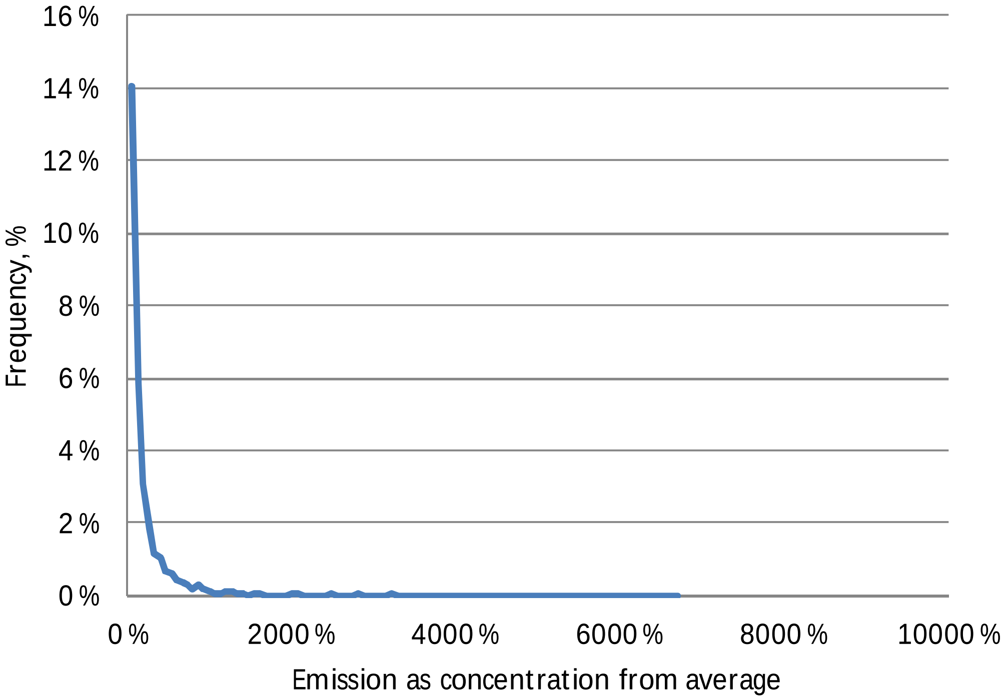

Figure 29. Recovery boiler B CO - emission frequency curve, concentration.

CO exhibits similar behaviour to SO_2 and TRS.

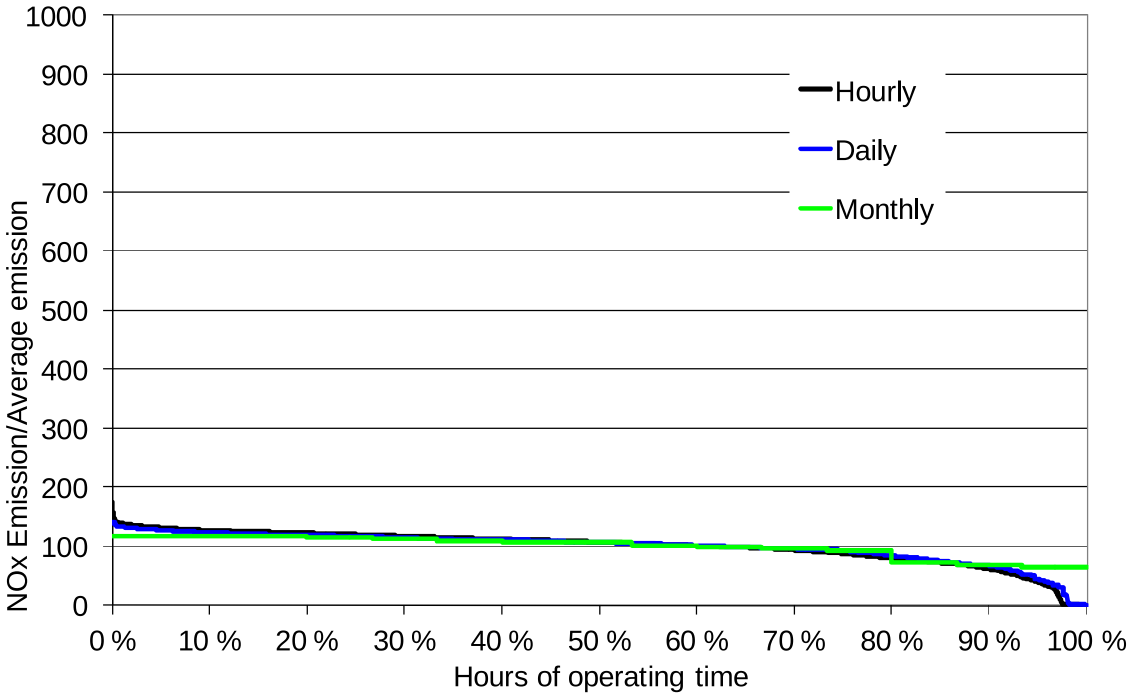

Figure 30. Recovery boiler B NO_x-durability concentration, curve.

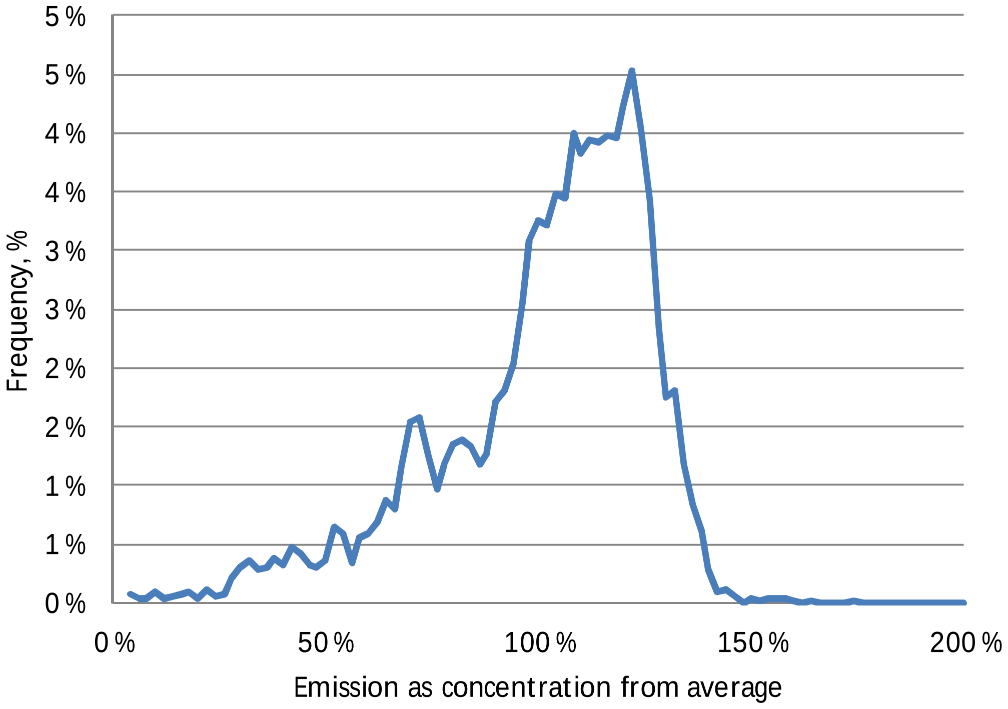

Figure 31. Recovery boiler B NO_x - emission frequency curve, concentration.

NOx emission is showing bell shape behaviour. It is slanted towards higher values because at the beginning of measuring period the NOx was lower for bit more than 1000 hours.

4.4 Emission as function of load

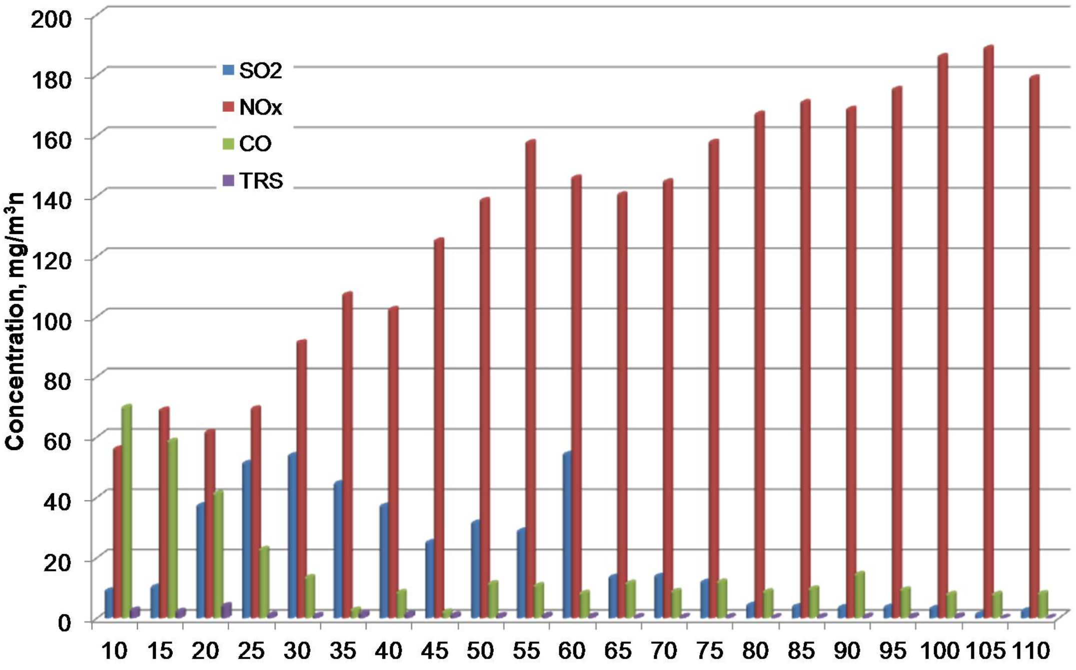

Figure 32. Emission data as class averages (mg/m^{3}n) organized by recovery boiler flue gas load.

One can clearly see that the lower the load the higher is SO_2. Decrease in NOx is not real but is caused by the higher O_2 at loads below 85 %. Note that in the largest two categories >110 % and 110%-105% there are only a few datapoints.

5 Mill C: Recovery boiler

The recovery boiler in question is a large recovery boiler. The emission data were retrieved from 1.1.2007 to 10.3.2008. The period was fourteen months or 10416 hours. Of that time the recovery boiler was up 10159 hours or 97.5 %

The retrieved emission data were SO_2, NOx, CO, TRS and dust. Of these the dust data were left out as the dust emission clearly didn't follow any known trends. Obviously the mill had problems with the dust measuring device.

5.1 Operation during measuring time

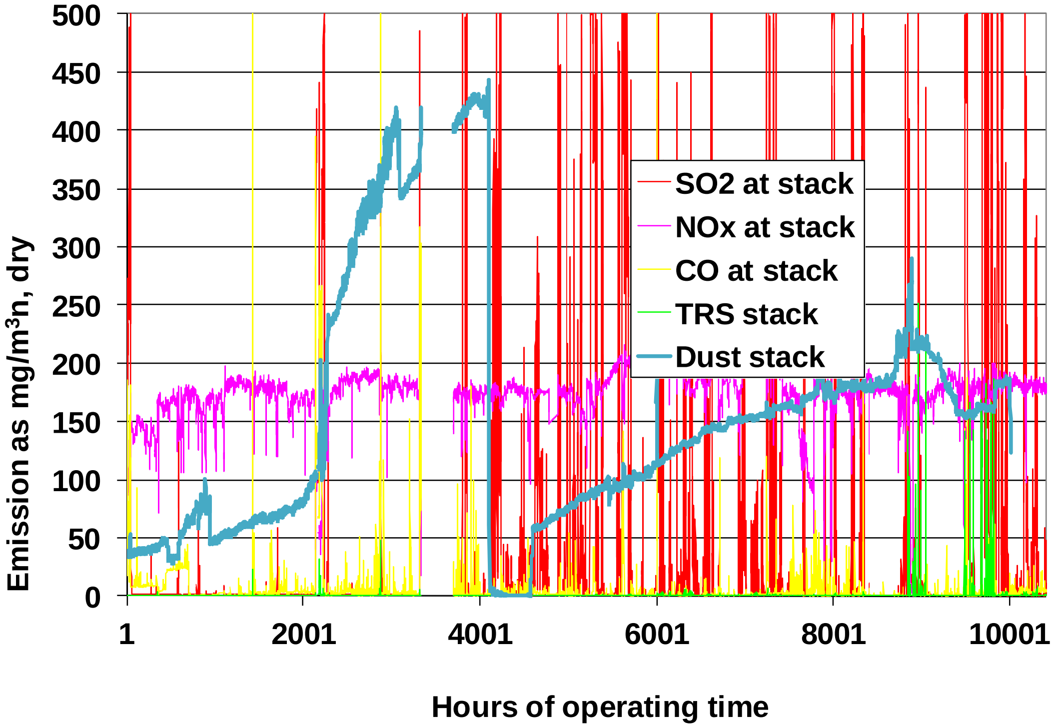

Figure 33. Recovery boiler C emissions by concentration (hourly averages).

As can be seen from Figure 33 the TRS emissions are live and exhibit regular peaking. Similarly SO_2, peaks especially during the latter two thirds of the recorded period, NOx varies around rather fixed value between 150 and 200 mg/m^3n. CO keeps peaking regularly. It should be pointed out that typically O_2 is lowered to increase boiler efficiency until the CO starts peaking.

As can be seen the dust is low the first about 2000 hours, then starts climbing. It reaches very high value at about 400 hours. Then it is practically zero for about 500 hours after which it claims again and starts to behave normally. The dust emission data was deemed not to be fit for processing.

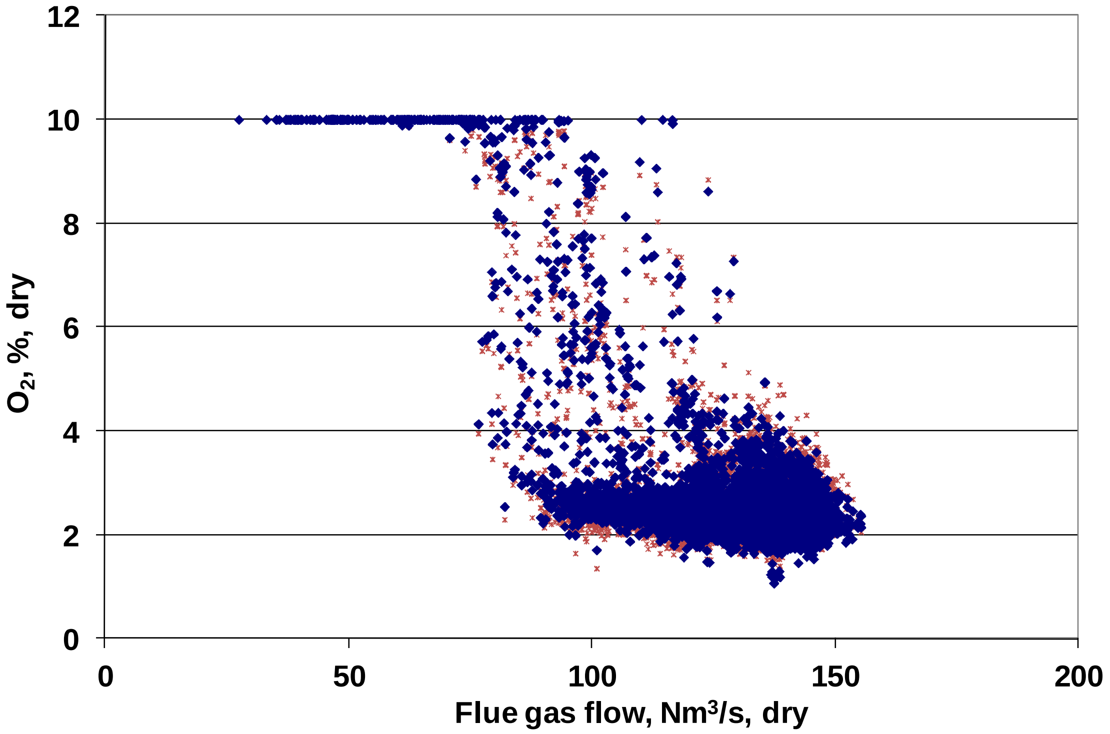

Figure 34. Recovery boiler C O_2-concentration in flue gas versus flue gas flow (hourly averages).

As seen in Figure 34 the flue gas oxygen concentration tends to increase when the flow is less than about 130 m^{3}n/s. Below about 80 m^{3}n/s the oxygen content hits the recording maximum 10 %.

5.2 Stability of operation during measuring time

Recovery boiler a main steam flow (Figure 35, lower line) can be seen to correspond to flue gas flow (upper line). As seen the Mill C has had to make one short and one large stoppage and roughly twenty large load decreases to accommodate operating and maintenance demands. But overall the load of the recovery boiler has been fairly stable except a decline at the end of the period.

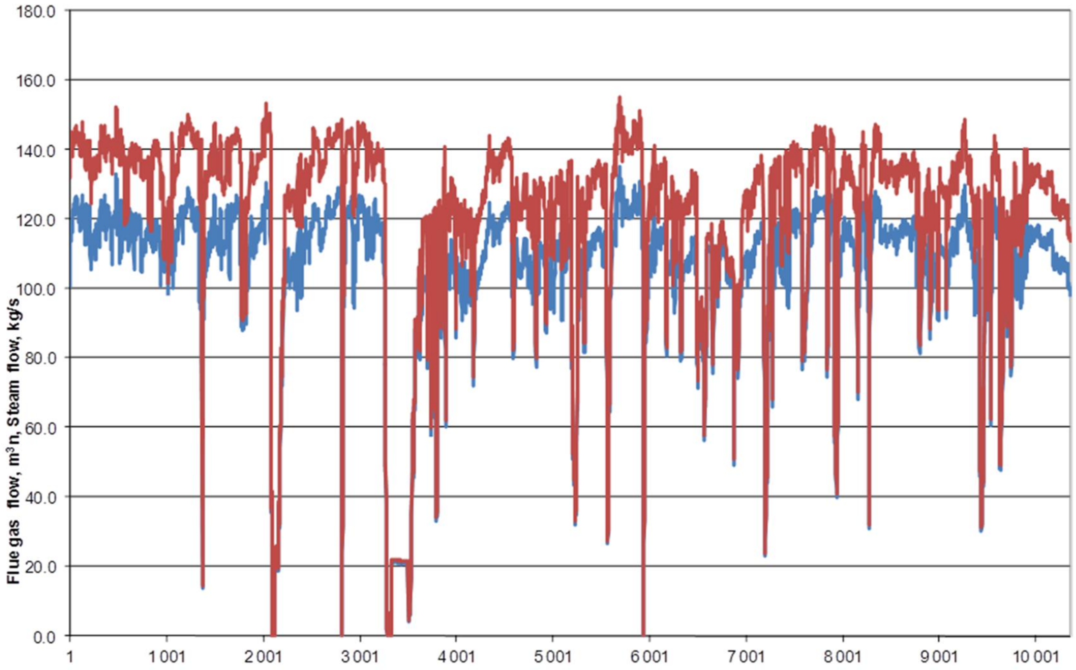

Figure 35. Recovery boiler C steam and flue gas flow (hourly averages).

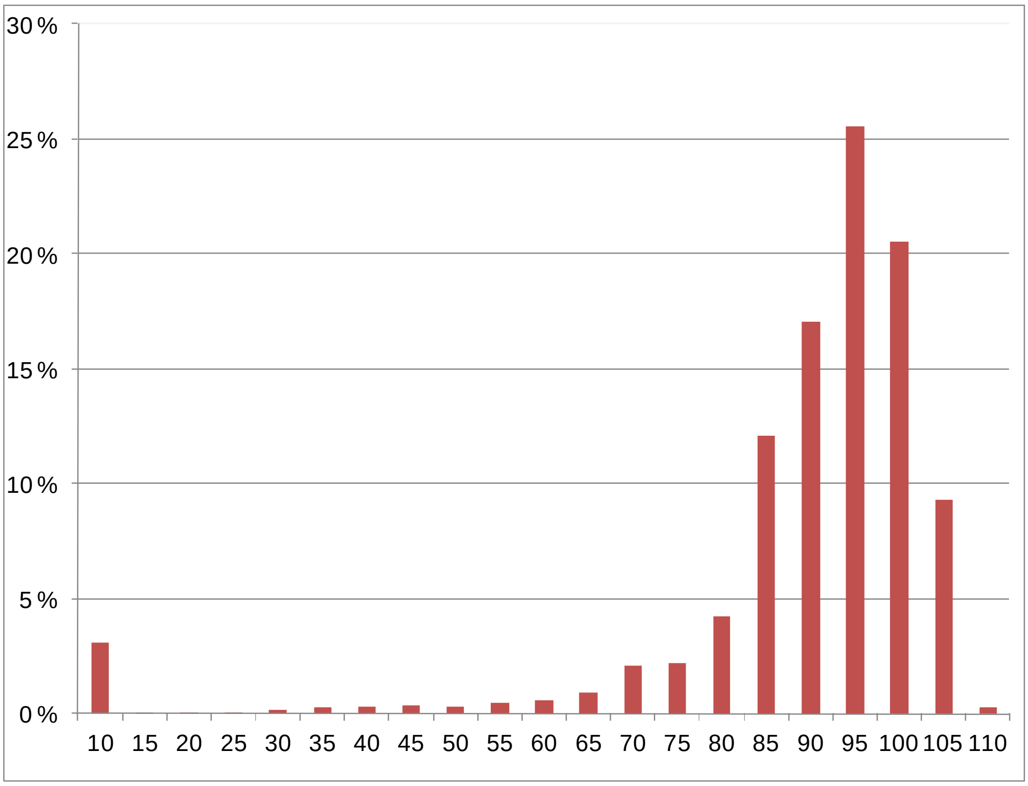

Figure 36. Recovery boiler C frequency of flue gas flow (hourly averages).

In Figure 36 we can see that boiler C operates very steadily. The flue gas flow frequency curve is almost a bell shaped curve.

5.3 Emission durability curves

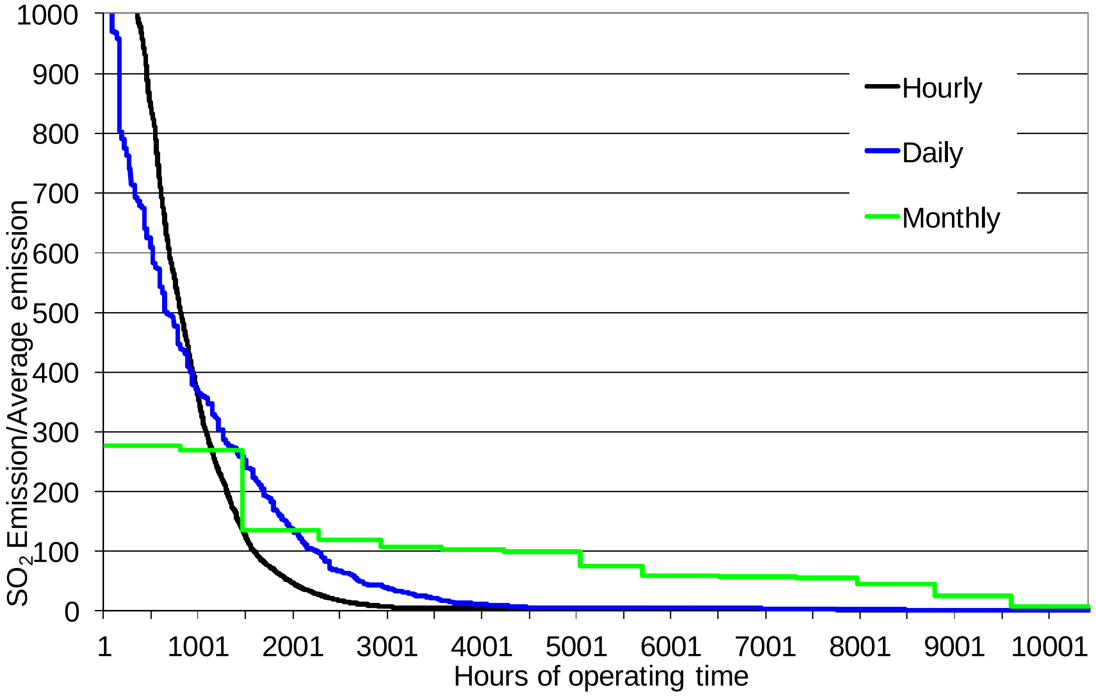

Figure 37. Recovery boiler C SO_2-durability concentration, curve.

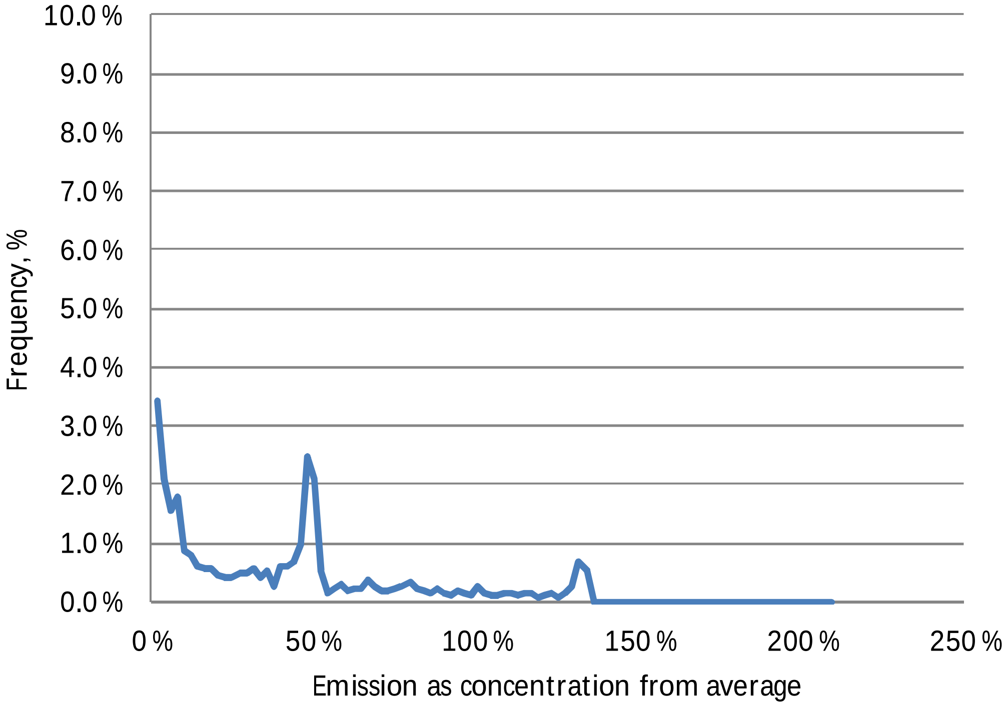

Figure 38. Recovery boiler C SO_2 - emission frequency curve, concentration.

The SO_2 peaks around 20 % of time and is below five mg/m^{3}n concentration the rest of the time. The 100 % concentration is still within the error margin of measuring device.

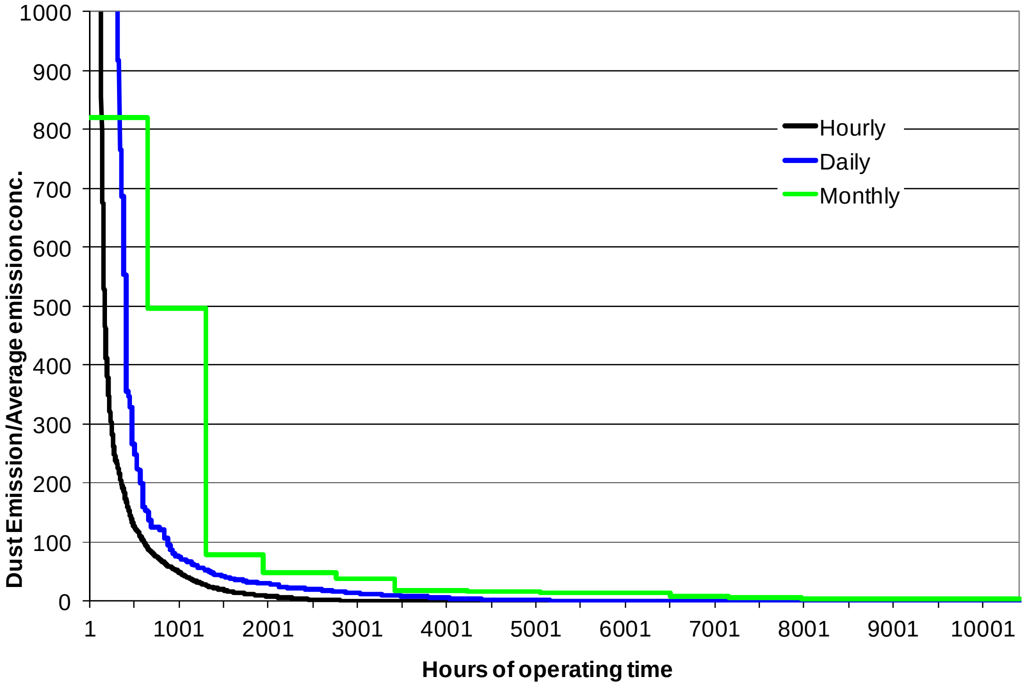

Figure 39. Recovery boiler C TRS-durability concentration,curve.

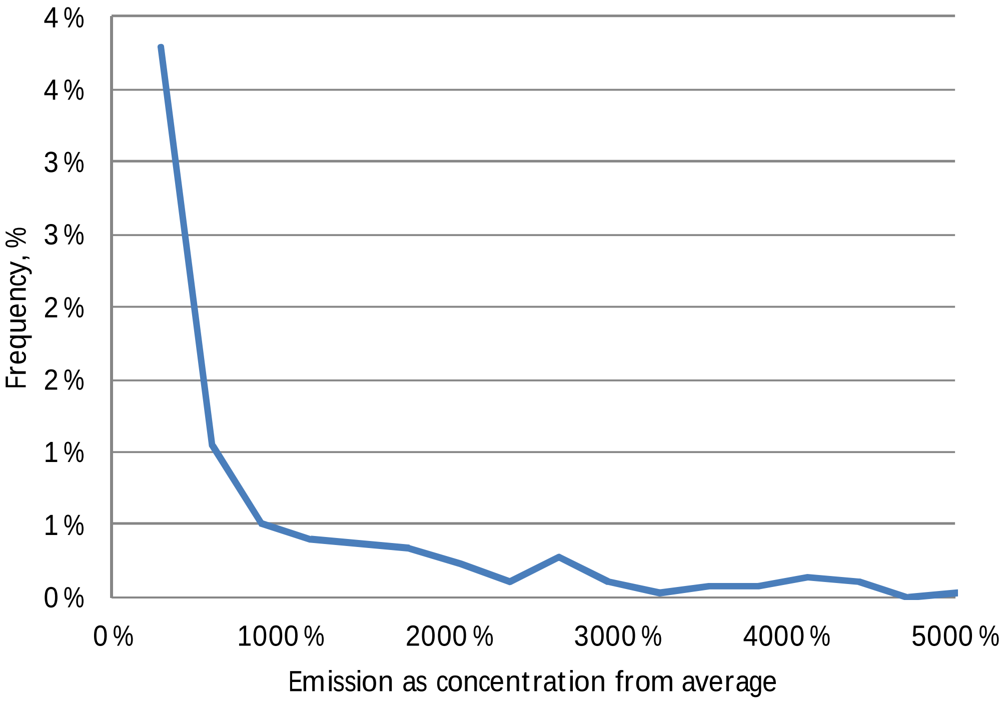

Figure 40. Recovery boiler C TRS - emission frequency curve, concentration.

TRS shows similar behaviour to SO_2. The average is below one mg/m^{3}n concentration.

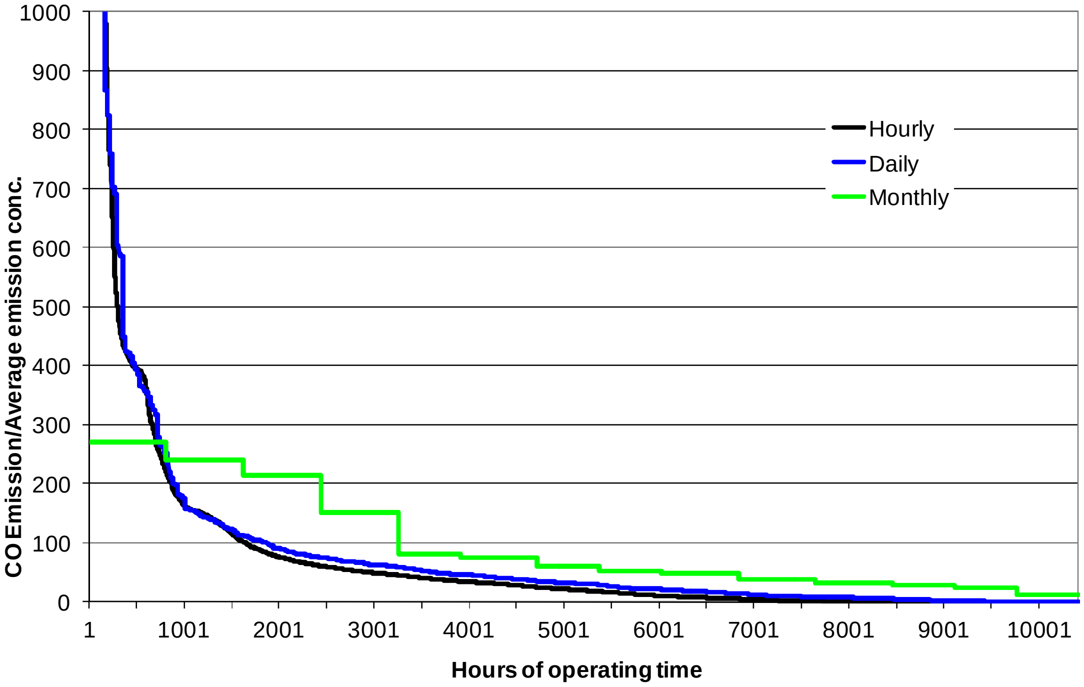

Figure 41. Recovery boiler C CO-durability concentration,curve.

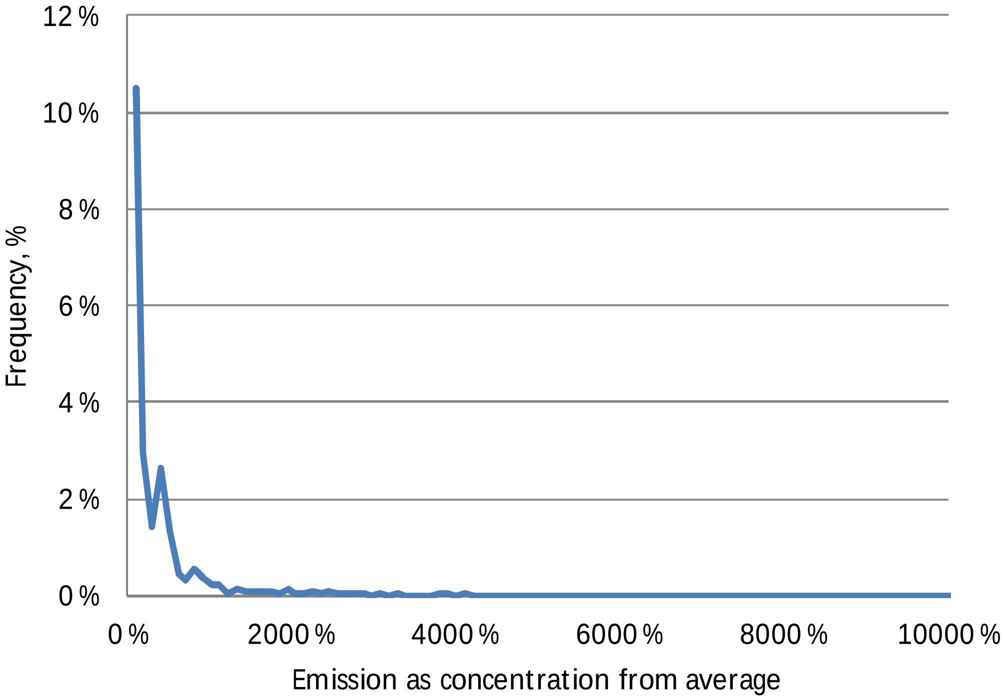

Figure 42. Recovery boiler C CO - emission frequency curve, concentration.

CO exhibits similar behaviour to SO_2 and TRS.

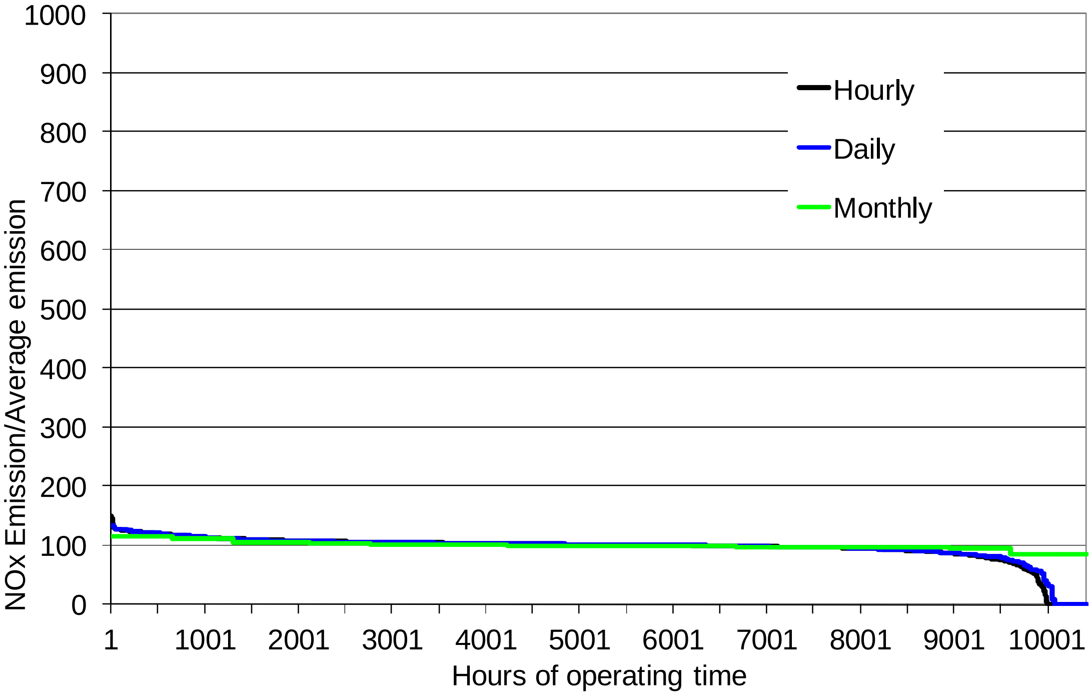

Figure 43. Recovery boiler C NO_x-durability concentration,curve.

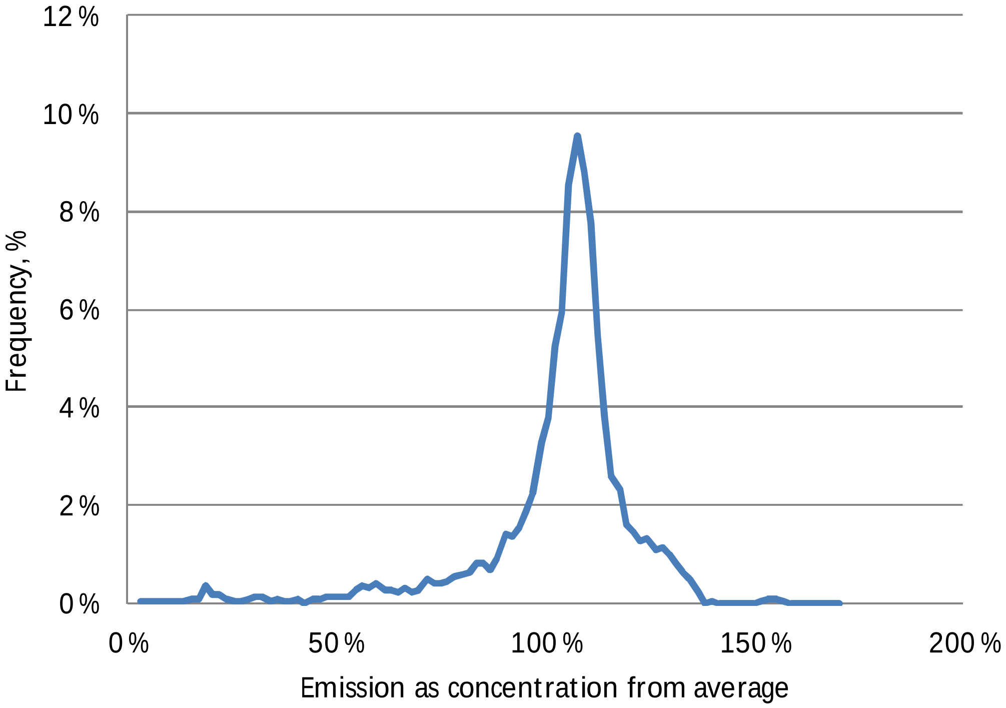

Figure 44. Recovery boiler C NO_x - emission frequency curve, concentration.

NOx emission is showing bell shape behaviour.

5.4 Emission as function of load

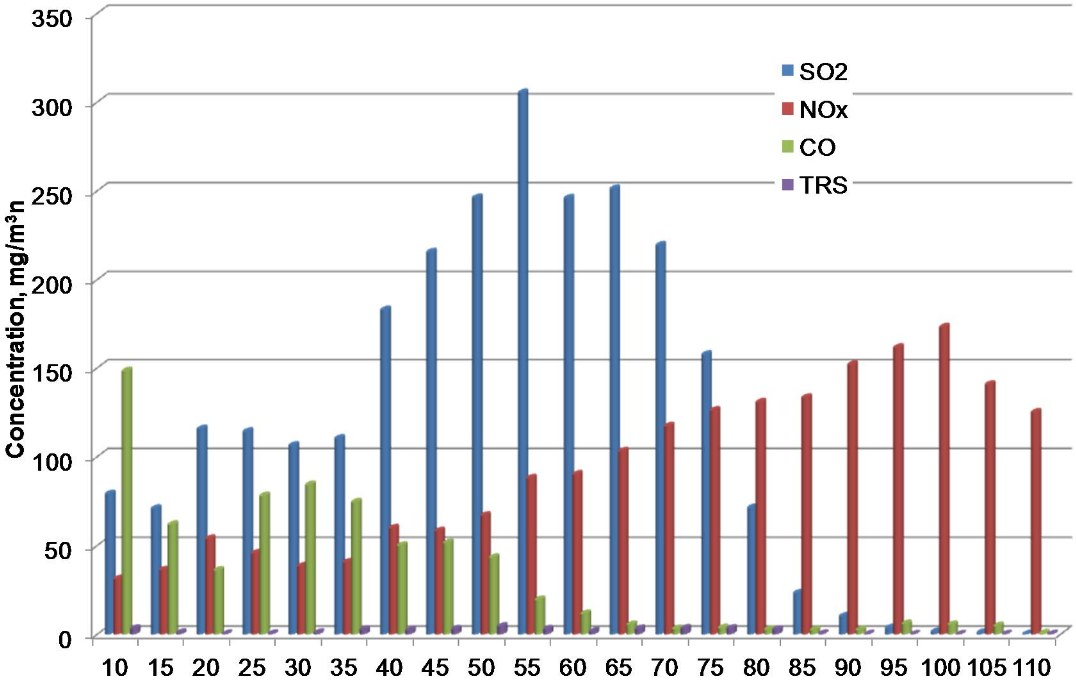

Figure 45. Emission data as class averages (mg/m^{3}n) organized by recovery boiler flue gas load.

Contrary to boilers A and B, boiler C operates with higher sulphur emission. One can clearly see that the lower the load the higher is SO_2. NOx is fairly stable. TRS starts to come apparent at lower than 45% loads.

6 Emission durability distributions

The emission curves change if we organize the data by hour, day or month. Even the maximum is reduced strongly when we look at the monthly averages. The averages and standard deviations for each time scale of representing the SO_2 emission data are shown for each boiler in Appendices I to III. Differences in averages are caused by the time periods omitted from averaging i.e. not all months have the same number of hours, but still they are treated equally when we average months. All collected hourly operating data above 10 % steam flow was used but only operating days and months without any data were left off.

Recovery boilers are regulated based on emission concentrations in the flue gas flow at the stack. The ground concentrations depend on the mass flow of each emission from the stack. The mass flow of each emission as calculated simply by multiplying the concentration (mg/m^3n) by flue gas flow (m^3n/s) and expressing the result as g/s.

Table 4: Average and standard deviation of SO_2 data hourly/daily/monthly.

		A	**B**	**C**
Average		100 %	100 %	100 %
Hourly SD		1124 %	392 %	256 %
Daily SD		720 %	242 %	207 %
Monthly SD		212 %	72 %	78 %
Hourly average		100 %	100 %	100 %
	99 %	3446 %	2174 %	1109 %
	95 %	2 %	116 %	846 %
	90 %	0 %	94 %	343 %
	80 %	0 %	75 %	40 %
	70 %	0 %	67 %	5 %
	60 %	0 %	59 %	4 %
Daily Average		100 %	100 %	100 %
	99 %	4649 %	1499 %	1025 %
	95 %	155 %	468 %	624 %
	90 %	22 %	109 %	364 %
	80 %	0 %	83 %	126 %
	70 %	0 %	70 %	33 %
	60 %	0 %	62 %	8 %
Monthly Average		100 %	100 %	100 %
	99 %	835 %	326 %	276 %
	95 %	835 %	326 %	276 %
	90 %	315 %	166 %	268 %
	80 %	53 %	133 %	134 %
	70 %	28 %	120 %	106 %
	60 %	17 %	93 %	102 %

Durability curves based on flow for SO_2, TRS, CO and NOx can be seen as Figures 46 – 50 respectively.

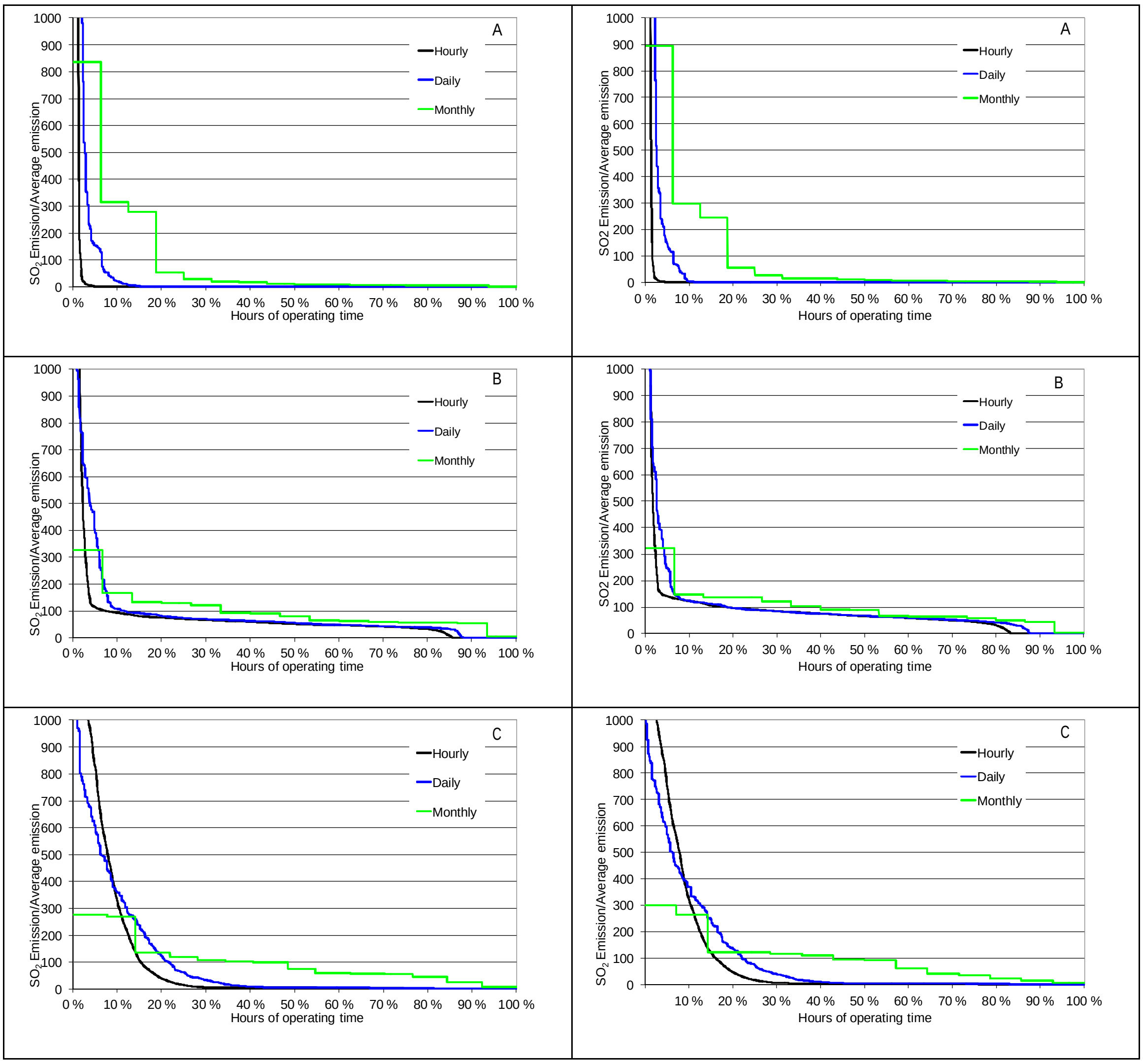

Figure 46. Recovery boiler SO_2-durability, concentration left flow right, curves.

There seems to be no difference between SO_2 emission distributions expressed as mass flow of emission or as concentration from recovery boiler stack. This is mainly because the boilers mostly operate around the MCR load.

If we look at emissions we note that they look alike. In practice boiler A has lowest SO_2 emission followed by the boiler B and then C. This can be seen in Table 4 where the durabilities follow the same respective trend. Low SO_2 is also signified by high standard deviation (SD).

We note, for example, that hourly SO_2 emissions exceeded the average emission about 2, 10 or 15 % of time respectively for boilers A, B and C. Daily averages exceeded the average emission by about 7, 10 and 25 % of time and in each case 3, 5 and 5 monthly averages exceeded the average emission. So the consequence of analyzing emission data with these different time scales is that depending on the used averaging time scale we get a different answer to question; How often does the SO_2 emissions exceeded the yearly average emission. The larger time averaging results in smaller standard deviation. This means that if some value is used as e.g. not to be exceeded 5 % of time the resulting maximum average yearly emission depends on the averaging time scale.

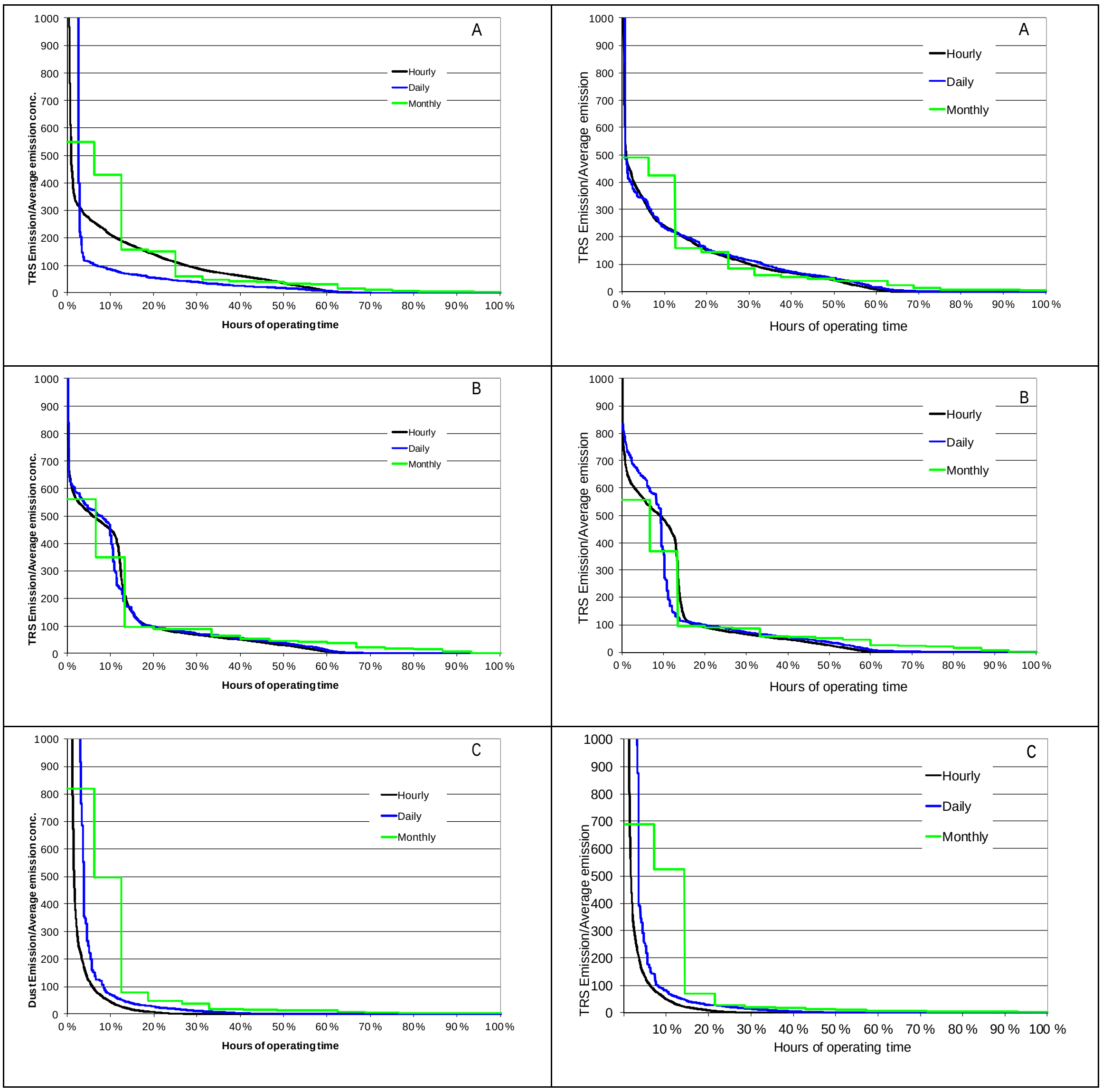

Figure 47. Recovery boiler TRS-durability, concentration left flow right, curves.

There is much more shape variation in the TRS emissions than in the SO_2 emissions. This was because in all cases the level of TRS emissions was very low and practically all the time at the limit of measuring accuracy.

If we look at the Standard deviations of TRS, Table 5, we note that TRS varies more than SO_2. Statistically the TRS is then signified by abrupt spikes followed by long periods of practically zero.

Table 5: Average and standard deviation of TRS data hourly/daily/monthly.

		A	**B**	**C**
Average		100 %	100 %	100 %
Hourly SD		434 %	255 %	980 %
Daily SD		494 %	192 %	457 %
Monthly SD		156 %	148 %	219 %
Hourly average		100 %	100 %	100 %
	99 %	622 %	637 %	2404 %
	95 %	276 %	519 %	128 %
	90 %	215 %	455 %	47 %
	80 %	142 %	96 %	8 %
	70 %	91 %	68 %	0 %
	60 %	63 %	51 %	0 %
Daily Average		100 %	100 %	100 %
	99 %	3918 %	627 %	3158 %
	95 %	115 %	532 %	267 %
	90 %	87 %	473 %	75 %
	80 %	56 %	99 %	28 %
	70 %	40 %	73 %	13 %
	60 %	26 %	57 %	5 %
Monthly Average		100 %	100 %	100 %
	99 %	549 %	561 %	820 %
	95 %	549 %	561 %	820 %
	90 %	430 %	350 %	496 %
	80 %	152 %	97 %	49 %
	70 %	60 %	89 %	38 %
	60 %	42 %	65 %	18 %

Allowable recovery boiler TRS emission is often unlike the other emissions regulated based on “time over limit”. Average TRS emission for all recovery boilers is very low, Table 5. The standard deviation of TRS is however very high. TRS is known to “peak every now and then”. If we look at the requirement “95 per cent of the time below limit”, then the hourly data shows that average for boiler C almost fulfils this requirement. For boilers A and B the average is close to 80 per cent of the time. If we look at the daily value, then the limit is from close to five times the average value.

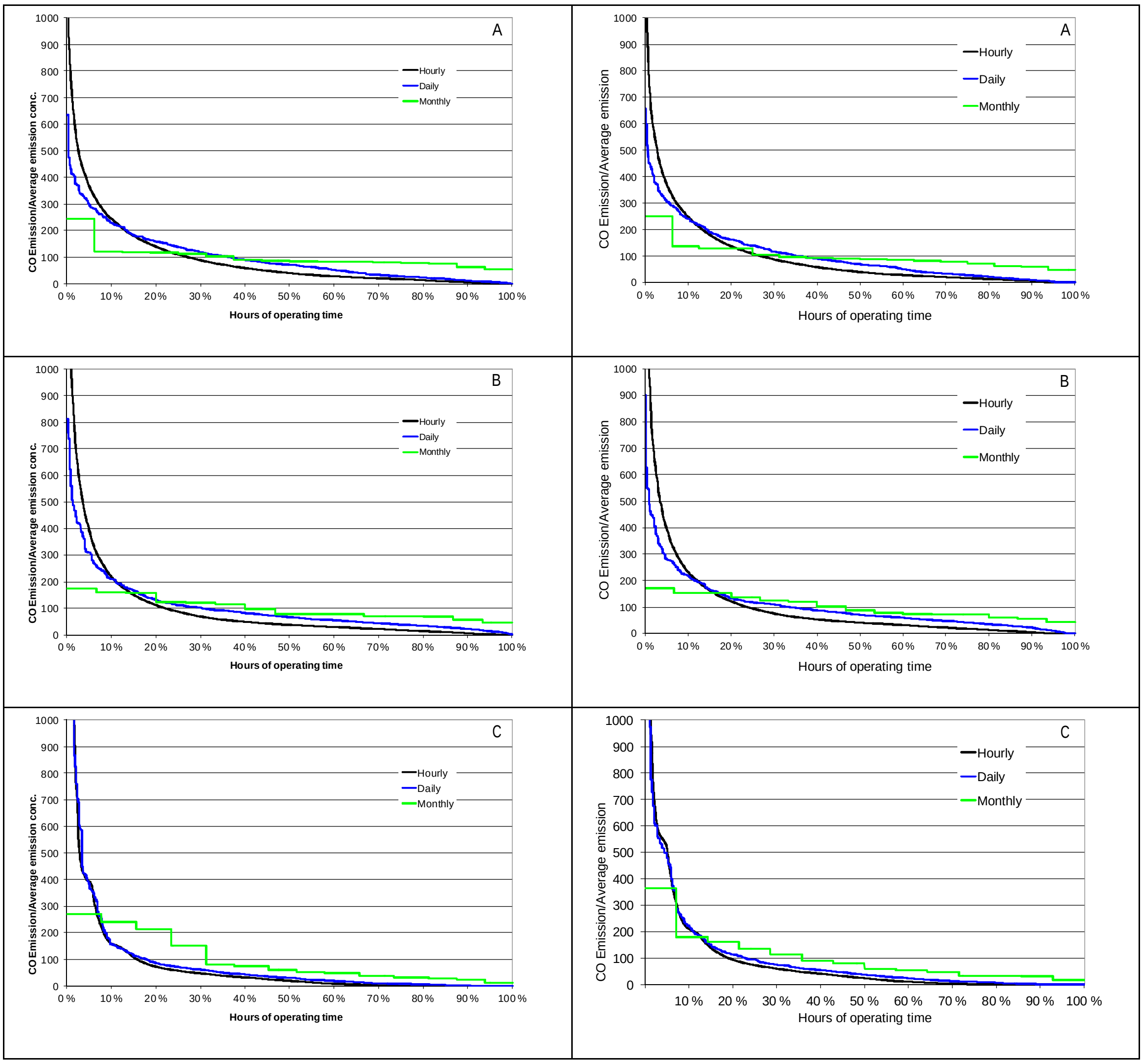

Figure 48. Recovery boiler CO-durability, concentration left flow right, curves.

The emission of CO has a shape like the TRS and SO_2 emissions. It is influenced by the excess air factor shown as O_2 in the flue gases. It can be seen that the difference between the hourly and daily data is rather small. The monthly data tends again to cut the maximum and flatten the peaks.

Table 6 shows standard deviations and durability distributions for carbon monoxide emission from the tree recovery boilers A, B and C. It can be seen that 95 per cent of time means about 400 % for hourly data. The variability does not decrease much even if we look at daily or monthly variation. This is because CO is fairly high all the time and the swings tend to happen fairly regularly.

Table 6: Average and standard deviation of COx data hourly/daily/monthly.

		A	**B**	**C**
Average		100 %	100 %	100 %
Hourly SD		151 %	236 %	376 %
Daily SD		97 %	107 %	278 %
Monthly SD		42 %	38 %	86 %
Hourly average		100 %	100 %	100 %
	99 %	806 %	1165 %	2060 %
	95 %	376 %	411 %	396 %
	90 %	247 %	224 %	161 %
	80 %	142 %	113 %	74 %
	70 %	89 %	70 %	48 %
	60 %	60 %	50 %	33 %
Daily Average		100 %	100 %	100 %
	99 %	447 %	623 %	2008 %
	95 %	303 %	310 %	394 %
	90 %	231 %	211 %	158 %
	80 %	159 %	134 %	89 %
	70 %	120 %	102 %	62 %
	60 %	92 %	83 %	44 %
Monthly Average		100 %	100 %	100 %
	99 %	244 %	173 %	270 %
	95 %	244 %	173 %	270 %
	90 %	122 %	159 %	240 %
	80 %	116 %	158 %	215 %
	70 %	112 %	121 %	152 %
	60 %	90 %	114 %	75 %

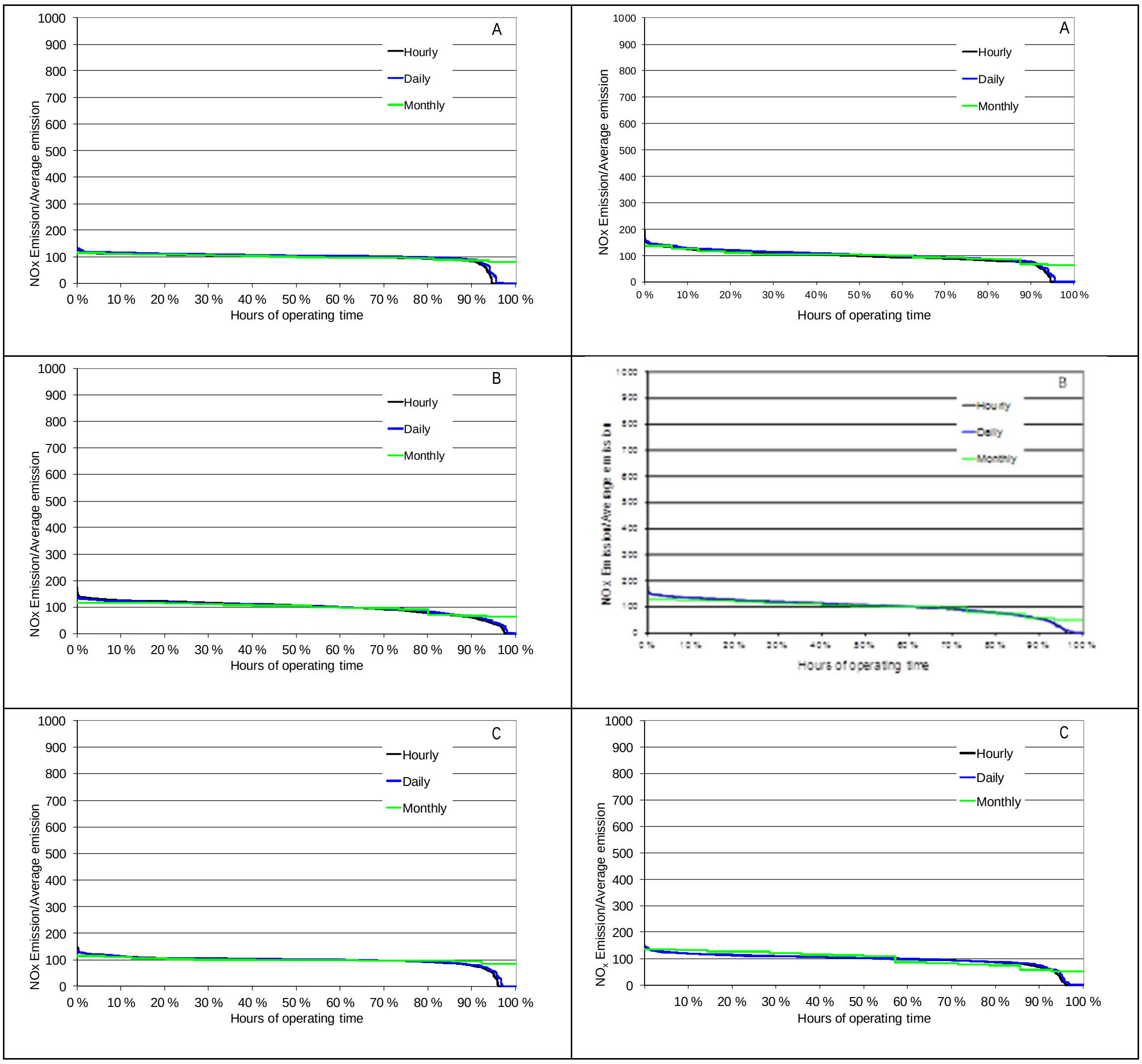

Figure 49. Recovery boiler NO_x-durability, concentration left flow right, curves.

The stability of NOx emission is a model of how all the emissions are often though to behave. The formation of NOx in a recovery boiler is influenced mainly by the nitrogen content in the black liquor, excess O_2 during combustion and amount of additional nitrogen containing flows. We could guess that these variables were also behaving rather steadily as well as the way of how the boiler was run.

Table 7: Average and standard deviation of NOx data hourly/daily/monthly.

		A	**B**	**C**
Average		100 %	100 %	100 %
Hourly SD		15 %	29 %	15 %
Daily SD		24 %	25 %	14 %
Monthly SD		9 %	17 %	7 %
Hourly average		100 %	100 %	100 %
	99 %	123 %	140 %	127 %
	95 %	114 %	132 %	120 %
	90 %	112 %	128 %	114 %
	80 %	108 %	123 %	107 %
	70 %	106 %	118 %	105 %
	60 %	104 %	113 %	103 %
Daily Average		100 %	100 %	100 %
	99 %	127 %	133 %	127 %
	95 %	117 %	128 %	121 %
	90 %	115 %	124 %	114 %
	80 %	112 %	119 %	107 %
	70 %	110 %	116 %	105 %
	60 %	108 %	111 %	103 %
Monthly Average		100 %	100 %	100 %
	99 %	115 %	118 %	114 %
	95 %	115 %	118 %	114 %
	90 %	111 %	118 %	112 %
	80 %	108 %	117 %	106 %
	70 %	108 %	112 %	101 %
	60 %	102 %	109 %	100 %

The emission durability curves as concentration and as flow look remarkably the same. This is based on the fact that most of the time the recovery boiler seems to operate around some mean target value, with variations. If we assume that emissions are independent of flow then the curves would be exactly alike. Looking at the emission data as classes arranged with load we can conclude that for practical purposes the gaseous emissions do not differ much in during typical operation.

It can also be concluded that limiting recovery boiler emissions by concentration at the stack leads to the same end result as limiting the recovery boiler emissions by mass flow of the same emission at the stack. Concentration variations, therefore, can be used to model the distribution of recovery boiler emissions when we are interested on the total mass flow of some emission.

7 Emission instabilities

Emission instabilities were studied with respect of various recovery boiler parameters.

7.1 Emissions by the load of the recovery boiler

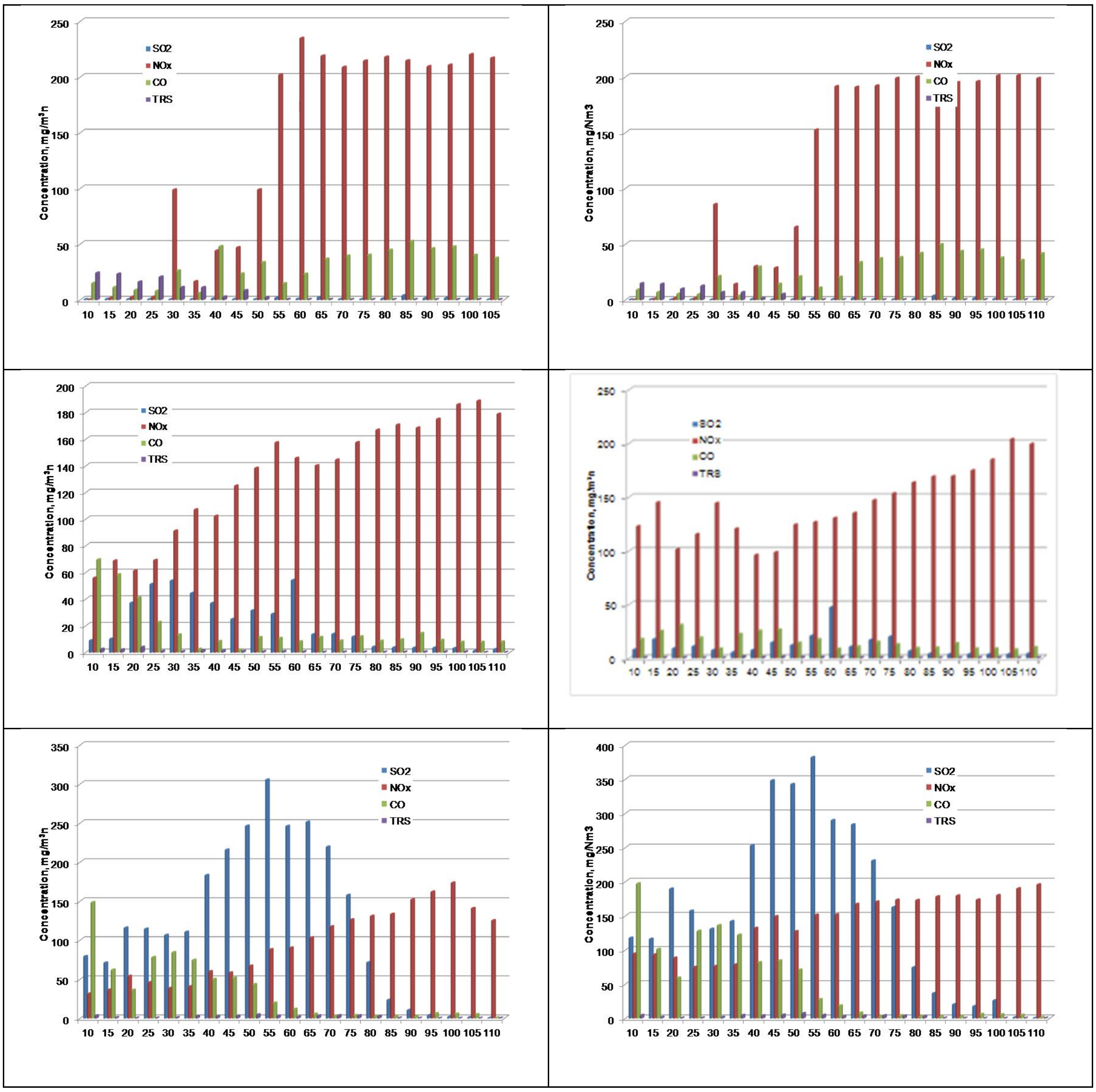

Figure 50. Data organized by recovery boiler load, top A, then B bottom C; left emissions at 3 % O_2, right emissions uncorrected.

The data of emissions normally are presented chronologically, though there are many other ways to study the emissions depending in what we are interested. Analyzing the emission from the recovery boiler we can find out that they are function of many variables as temperature (in many different points of the combustion process), how is (air pattern) and how much air is supplied, composition of the black liquor, and others.

We can assume that MCR is how the RB should work at optimum load; this means that we can calculate how the emissions are according with the recovery boiler load. That is represented in the following figure where the emissions are ordered by the load, and the load is split 5% by 5%, Figure 50. This figure is not useful to evaluate the quantities of the emissions, but it is useful to see how they behave with the load, and to observe how emissions follow a trend.

Looking all the emission together, it is possible to realize that around 60 - 70 % there is a change in the behaviour of the emissions. It is also possible to appreciate how fairly steady the emissions NOx are down to the 60 - 70 % range. NOx seems to slightly increase with the load. TRS and SO_2 seem to be very low at full load in all the boilers. Looking at the boilers we notice that lowering the load increases TRS and SO_2 at same manner no matter what the final emission seems to be. CO is low and steady when the RB is run over 70% load.

7.2 Operation by the stack temperature of the recovery boiler

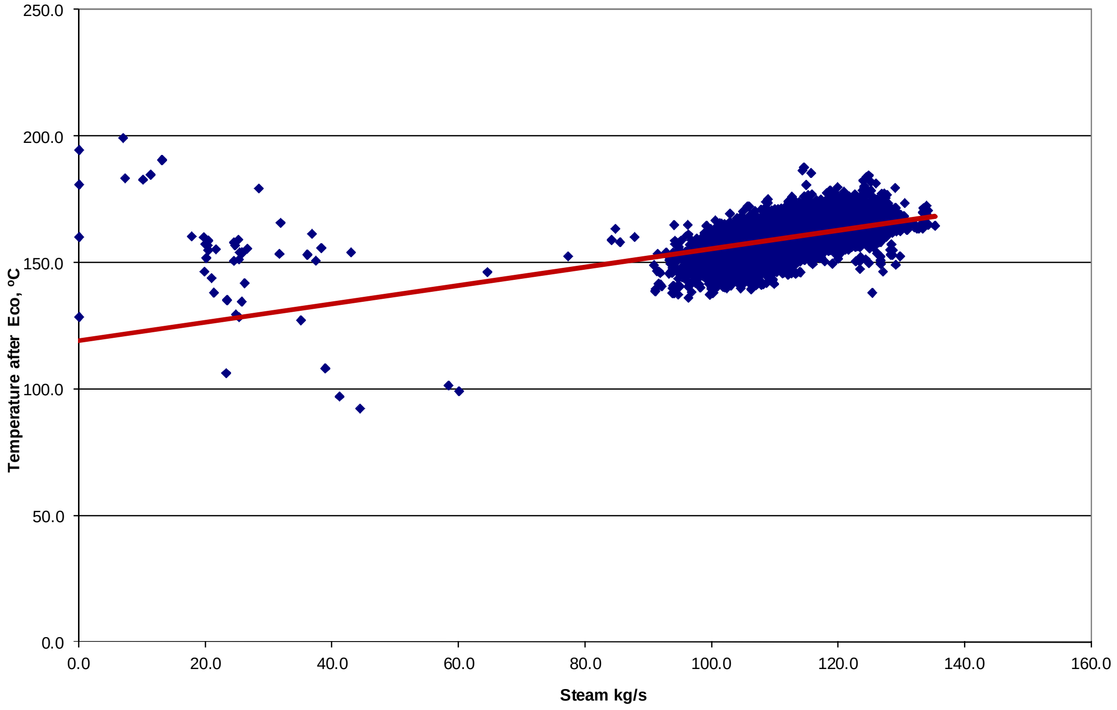

Figure 51. Stack flue gas temperature versus load in the recovery boiler C.

We have also studied how the load in a recovery boiler affects stack temperature. The temperature is a variable that is easy to measure and it can give us some information about how the recovery boiler is working. We can observe in the figure that when the recovery boiler is working over rate 60 % load, there is a correlation (in this case clearly lineal) between the load and the temperature, below this value it is difficult to find out correlation. This is because the air ratio (flue gas O_2) varies. We can observe that the range of temperature is large. There is a 30 °C of difference between the lowest temperature (~150 °C) and highest temperature (~180 °C) when the recovery boiler is working at 100% load. The temperature differences are caused by differing flue gas flows. High load means higher flue gas flow which is more difficult to cool down.

We reach the same conclusion again from this point of view. The recovery boiler follows somehow a trend from the 60% of its load. In the case of stack temperature and load it was easy to suppose that they should have a lineal correlation.

7.3 Operation by the stack oxygen of the recovery boiler

The measured oxygen indicates us how close to the full oxidation the combustion has been done. The Figure 52 is showing us again two different regimes, one until 60% and other from 60% until over 100% of MCR. Between 0% and up to almost 60% the level of oxygen is the maximum measured, after 60 % the oxygen has a clear trend, but some of the measurements are out of this trend. It seems that the recovery boiler when is working at full load, the stack is emitting an average of 3% of oxygen.

Oxygen is typically regulated though CO. One lowers the oxygen content until CO starts to spike. It is possible to look the NOx as function of carbon monoxide, Figure 52. In all three boilers one sees a clear trend of lower NOx with higher CO. It should be noted that A has the highest CO, then B and boiler C runs the lowest carbon monoxide.

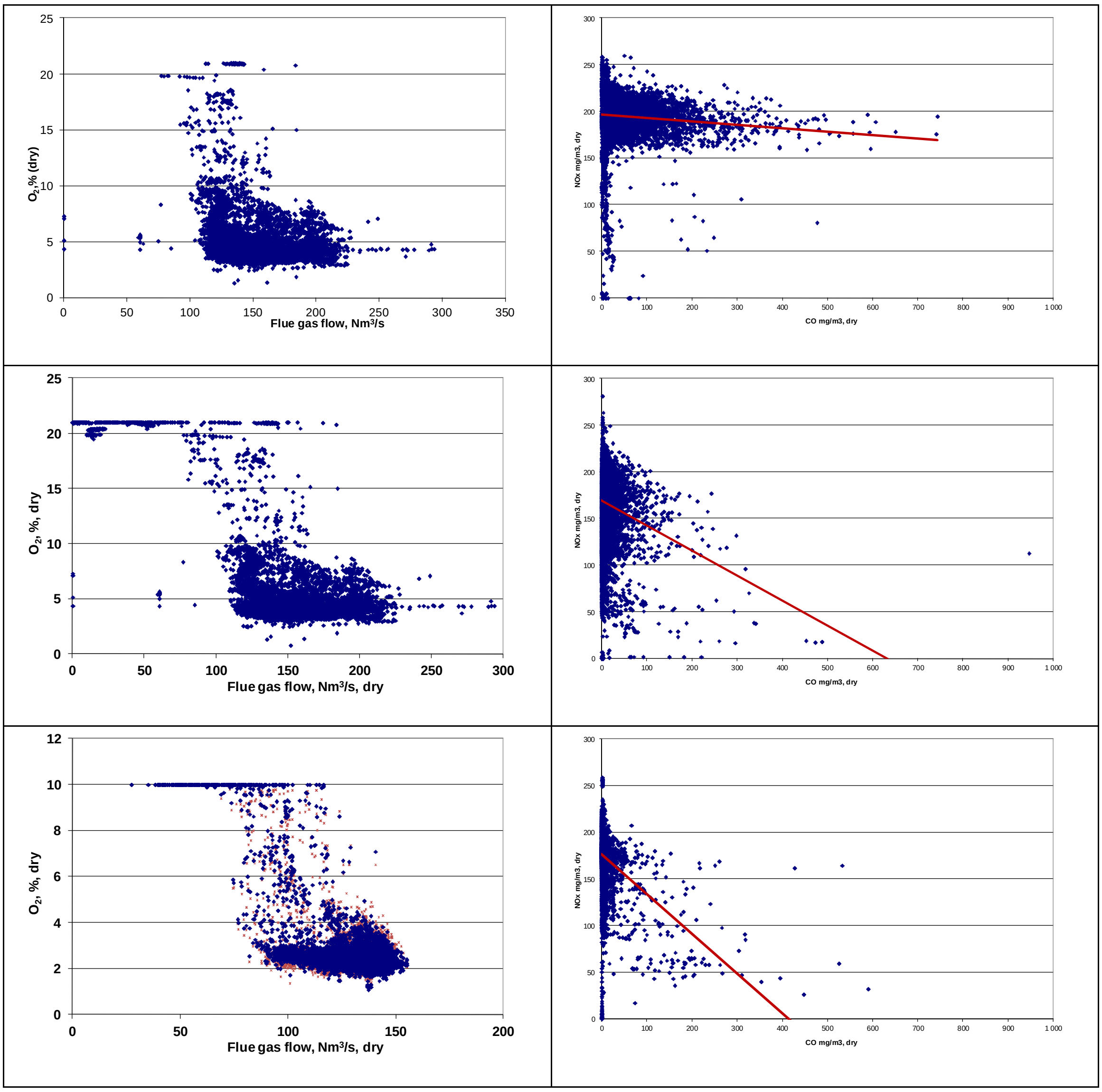

Figure 52. Left O_2 versus load in the recovery boiler, top A, then B bottom C. Right NOx versus O_2 in the recovery boiler, top A, then B bottom C.

7.4 Instabilities in the behaviour of the emission

The idea is to find an explanation with the moments when the recovery boiler C is working below the 60% of the load. Actually, time that the recovery boiler is working with this load is considerable. This time is over the 7% of the all time, as we can see in the figure “time versus recovery boiler load” in the previous point of the paper. If we plot the load of the data we get the following graphic, Figure 53.

In the figure we can see that the recovery boiler has been running below 60 % MCR loads many times. The “low loads” have been organized into three groups. They are distinguished by colour. The organisation is based on dividing load decreases into three groups. The first group is indicated with red circle, (circles one, three and five starting from the left). The drops of load in red circles are strong and last long. The second kind is indicated with green circle (circles two six and eight). The load decrease at these points is not to as low as at the red ones. The third group is indicated with purple (four and seven). The load drop in purple circles is quicker than at the red ones.

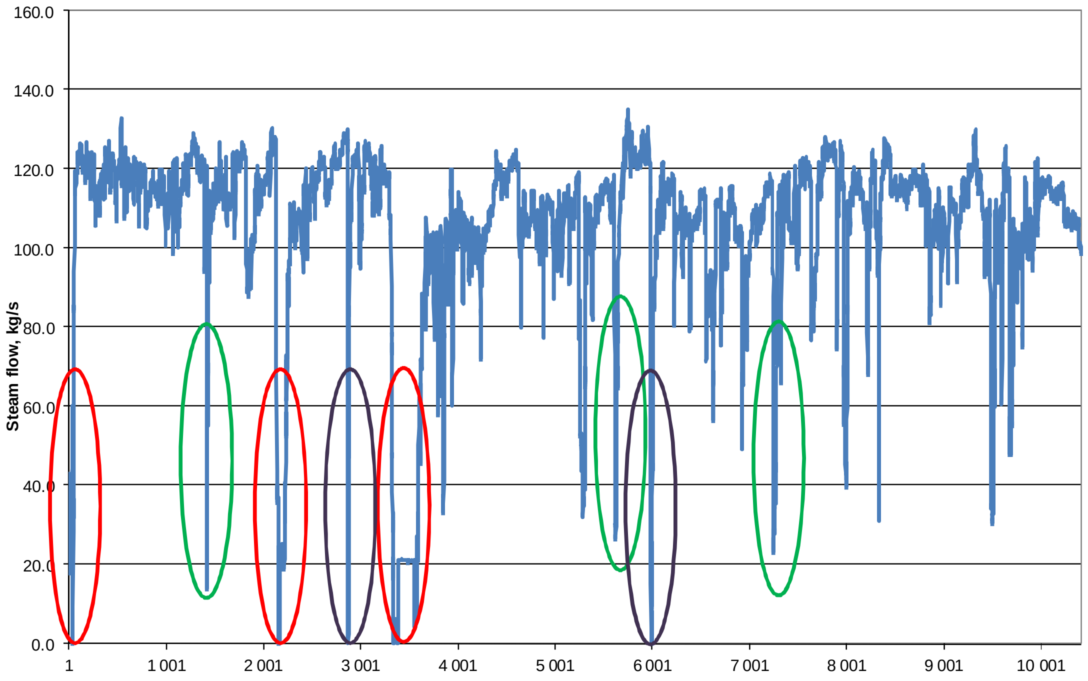

Figure 53. Steam flow versus hours.

It is not simple to make conclusions from these kinds of graphics, but analysis can give some hints to further research. So

Looking into the load change 1, Figure 54, we can see four different changes. They have been numbered as 1 2 3 and 4. The number 1 (around the second hour) starts with SO_2 increase, NOx decrease, CO increase and TRS decrease. The number 2 (around thirteenth hour) is triggered by decrease of load; it means in this case, SO_2 decreases, NOx decreases, CO decreases and TRS spikes. Before any comment on what happens at the point number 3, it is interesting to note that SO_2 presents a strong increase, NOx also increases a bit, CO does not seem to follow any trend. Event number 3 is also triggered by a decrease of the liquor firing load; this is the strongest decrease in this first event. With the drop in load, we can see in there is a decrease of SO_2, also in NOx, but on the other hand CO and TRS increase. Particularly, the increase of CO is very strong. The event number 4 is the increase in load: It takes around ten hours to reach over 60% MCR. The reactions of the emissions are; the SO_2 increases similarly with NOx, and TRS. CO is reduced.

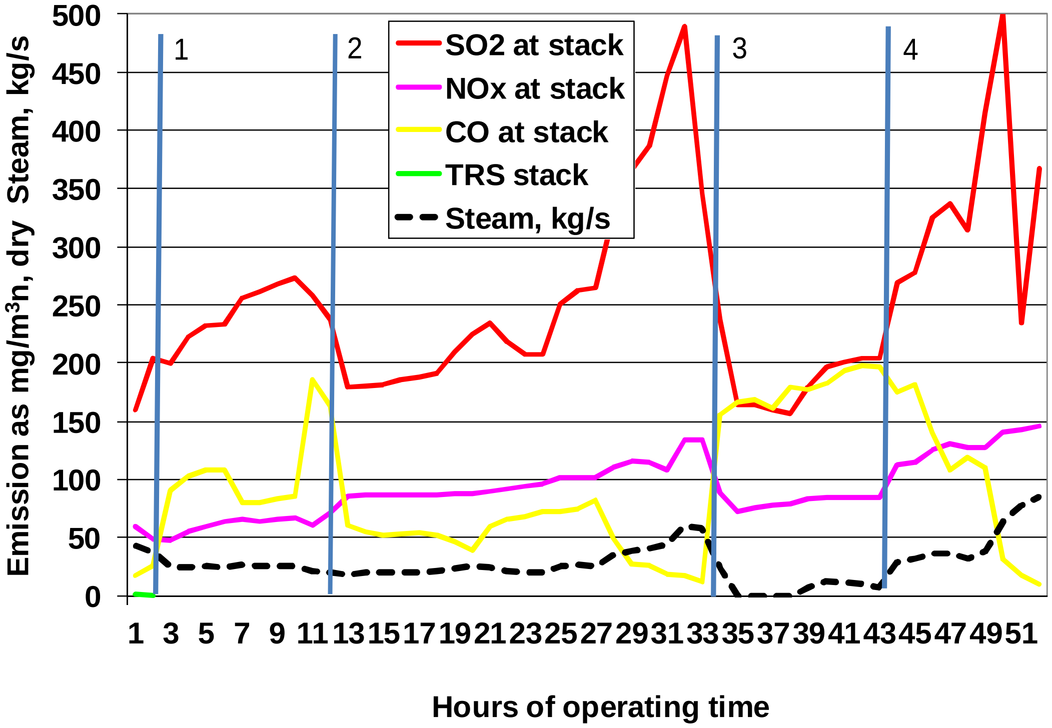

Figure 54. Load event number 1 (start of the boiler).

The start-up after shut down is represented in the figure 55. Low load operation is quite long, with a total of 96 hours below 60 % MCR. Four events are commented.

The load is decreased quickly in eight hours from 100% to below 40% (event 1). We see an increase of SO_2, first decrease and then increase of NOx and a very strong increase of CO with some TRS. Then at event number 2 the liquor firing is stopped. The emissions answer with a somewhat steady behaviour. We can observe that the O_2% was all the time over the maximum level that the device can record, or over 10% O_2. Looking at the event number 3, where the steam load keeps constant, but the gaseous emissions have a jump upwards and later start unstable downward trend with the exception of NOx, that keeps flat. The change during event number four coincides with an increase of the load. The instability finishes with the load being constant. The emissions react with SO_2 spiking strongly and then decreasing, when the recovery boiler is reaching 70% of the load. NOx also increases but at the end it keeps up. CO starts a strong descent until levels very low. TRS, as it has done during the whole shut down, maintains unsteady spiking.

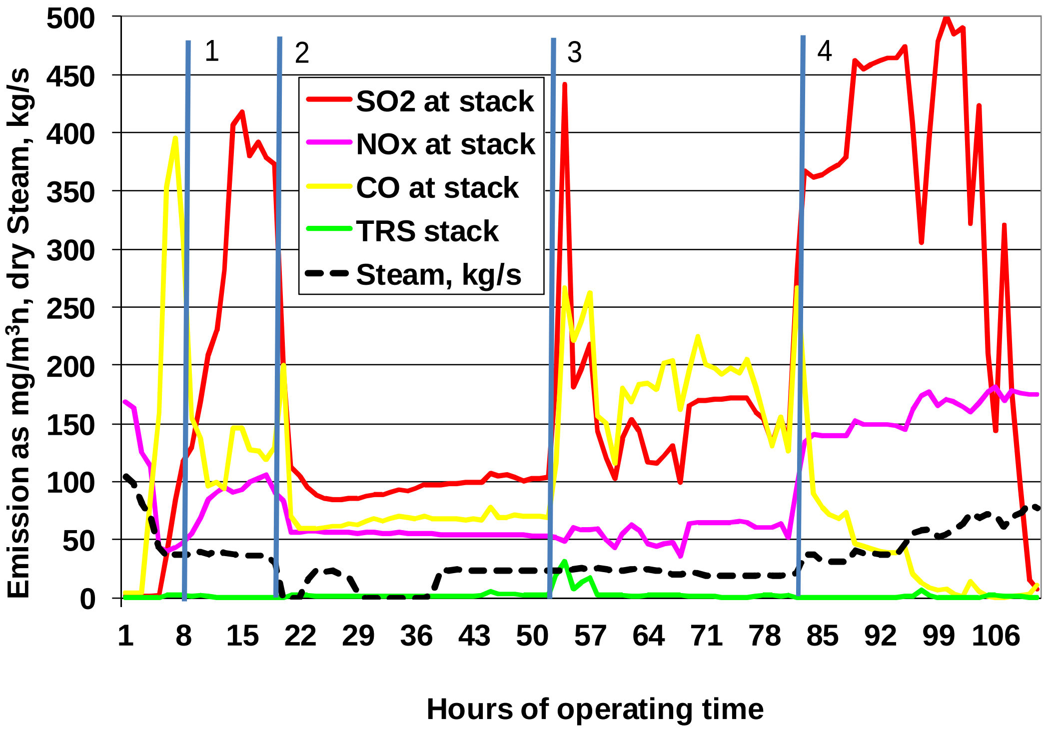

Figure 55. Load event number 3.

In the following tables the previous paragraphs are put as arrows. The arrows mean the trend of the emission during each event. The number in the load means the range where it is situated versus the MCR load of the recovery boiler C.

Table 8: Trends of emission and loads during load event number one.

	Line1	**Line2**	**Line3**	**Line4**
%load	50-100 ↓	0-50 ↓	0-50 ↓	0-50 ↑
SO_2	↑	↓	↓	↑
NOx	↓	↓	↓	↑
CO	↑	↓	↑↑	↓
TRS	↓	↑	↑	↓

The other load event three looks similar

Table 9: Trends of emission and load event number three.

	Line1	**Line2**	**Line3**	**Line4**
%load	50-100 ↓	0-50 ↓	0-50→	50-100 ↑
SO_2	↑	↓	↑	↑
NOx	↓	↓	→	↑
CO	↓↓	↑↑	↑↑	↓
TRS	↓↓	↑↑	↑	↑↓

The conclusion is that the emissions exhibit large changes when there is a strong change of load. SO_2 is really sensible to load changes. The reason is the lower furnace temperature which affects to sodium volatilization when load changes happen. NOx seems to be more insensible to these changes. NOx seems to depend mainly on the amount of nitrogen put in to the furnace with the fuels. TRS is all the time low. CO exhibits large spikes.

8 Conclusions

Recovery boiler operation in a pulp mill is a complex process with several interrelated parameters and almost infinite variables. To better understand these phenomena, the present study gathered emission and operation data on more than 10 000 continuous hours. Recovery boiler average emissions can be expressed with different time scales. Hourly averages can be compiled to daily, monthly and yearly average emissions. The hourly average emission as mass flow (g/s) is the hourly average concentration multiplied with the hourly average flue gas flow. This emission flow data can similarly be expressed also as daily, monthly and yearly average.

The averages change only slightly if we organize the data by hour, day or month. This is due to the fact that there are hours in the year when no reliable emission measurement exist. It was noted that the larger the averaging time period the smaller the variation for every emission. The maximum emission is reduced strongly for the monthly averages. There seems to be no difference between emission duration distributions expressed as mass flow of emission or as concentration from recovery boiler stack. It can be concluded that during at least most of the recovery boiler operating time the flue gas flow is independent from the emission concentration.

It can also be concluded that limiting recovery boiler emissions by concentration at the stack leads closely to the same end result than limiting the recovery boiler emissions by mass flow of the same emission at the stack. One can also conclude that concentration variations can be used to model the distribution of recovery boiler emissions when one is interested in the total mass flow of some emission. It should be noted that emissions are strongly related the load of the recovery boiler. It seems that for this boiler the emissions are rather stable from the 60 to 70 per cent load.

Of special interest is the start-up and the shut-down of the recovery boilers. To understand the effect of these on boiler emission, more data is required. Also it is beneficial to make a comparative study of the recovery boiler with other boiler types, to obtain a better understanding of how the emissions from boilers in general behave.

9 Acknowledgements

We especially want to extend our gratitude to the mill personnel who helped to gather this data.

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Appendix I Boiler A, Data by concentration and by flow

Variation, concentration mg/m^3n, dry

	SO_2	NOx	CO	TRS
Average	1	195	38	0
Hrly SD	11	28	57	1
Daily SD	8	45	36	3
Mthly SD	2	17	15	1

Variation, concentration from average 100%

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
Hrly SD	1124%	15 %	151 %	434 %
Daily SD	720 %	24 %	97 %	494 %
MthlySD	212 %	9 %	42 %	156 %

Time below average concentration, hourly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	3446%	123 %	806 %	622 %
95 %	2 %	114 %	376 %	276 %
90 %	0 %	112 %	247 %	215 %
80 %	0 %	108 %	142 %	142 %
70 %	0 %	106 %	89 %	91 %
60 %	0 %	104 %	60 %	63 %

Time below average concentration, daily

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	4649%	127 %	447 %	3918%
95 %	155 %	117 %	303 %	115 %
90 %	22 %	115 %	231 %	87 %
80 %	0 %	112 %	159 %	56 %
70 %	0 %	110 %	120 %	40 %
60 %	0 %	108 %	92 %	26 %

Time below average concentration, monthly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	835 %	115 %	244 %	549 %
95 %	835 %	115 %	244 %	549 %
90 %	315 %	111 %	122 %	430 %
80 %	53 %	108 %	116 %	152 %
70 %	28 %	108 %	112 %	60 %
60 %	17 %	102 %	90 %	42 %

Variation, flow g/s

	SO_2	NOx	CO	TRS
Average	4	15	0	0
Hrly SD	10	7	1	1
Daily SD	8	6	1	0
Mthly SD	3	4	0	0

Variation, flow from average 100%

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
Hrly SD	257 %	44 %	274 %	1005%
Daily SD	202 %	42 %	176 %	455 %
Mthly SD	84 %	27 %	88 %	210 %

Time below average flow, hourly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	1245%	160 %	1354%	2372%
95 %	825 %	152 %	548 %	143 %
90 %	347 %	147 %	221 %	55 %
80 %	53 %	139 %	100 %	10 %
70 %	7 %	134 %	63 %	0 %
60 %	6 %	125 %	43 %	0 %

Time below average flow, daily

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	995 %	158 %	1116%	3089%
95 %	575 %	150 %	488 %	282 %
90 %	355 %	146 %	243 %	81 %
80 %	141 %	138 %	129 %	30 %
70 %	45 %	133 %	87 %	14 %
60 %	10 %	125 %	63 %	5 %

Time below average flow, monthly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	299 %	134 %	364 %	688 %
95 %	299 %	134 %	364 %	688 %
90 %	264 %	132 %	180 %	525 %
80 %	123 %	126 %	160 %	70 %
70 %	116 %	120 %	115 %	18 %
60 %	110 %	115 %	90 %	16 %

Appendix II Boiler B, Data by concentration and by flow

Variation, concentration mg/m^{3}n, dry

	SO_2	NOx	CO	TRS
Average	6	160	10	0
Hrly SD	24	46	25	1
Daily SD	15	41	11	1
Mthly SD	5	28	4	1

Variation, concentration from average 100%

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
Hrly SD	392 %	29 %	236 %	255 %
Daily SD	242 %	25 %	107 %	192 %
Mthly SD	72 %	17 %	38 %	148 %

Time below average concentration, hourly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	2174%	140 %	1165%	637 %
95 %	116 %	132 %	411 %	519 %
90 %	94 %	128 %	224 %	455 %
80 %	75 %	123 %	113 %	96 %
70 %	67 %	118 %	70 %	68 %
60 %	59 %	113 %	50 %	51 %

Time below average concentration, daily

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	1499%	133 %	623 %	627 %
95 %	468 %	128 %	310 %	532 %
90 %	109 %	124 %	211 %	473 %
80 %	83 %	119 %	134 %	99 %
70 %	70 %	116 %	102 %	73 %
60 %	62 %	111 %	83 %	57 %

Time below average concentration, monthly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	326 %	118 %	173 %	561 %
95 %	326 %	118 %	173 %	561 %
90 %	166 %	118 %	159 %	350 %
80 %	133 %	117 %	158 %	97 %
70 %	120 %	112 %	121 %	89 %
60 %	93 %	109 %	114 %	65 %

Variation, flow g/s

	SO_2	NOx	CO	TRS
Average	4	15	0	0
Hrly SD	10	7	1	1
Daily SD	8	6	1	0
Mthly SD	3	4	0	0

Variation, flow from average 100%

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
Hrly SD	257 %	44 %	274 %	1005%
Daily SD	202 %	42 %	176 %	455 %
Mthly SD	84 %	27 %	88 %	210 %

Time below average flow, hourly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	1245%	160 %	1354%	2372%
95 %	825 %	152 %	548 %	143 %
90 %	347 %	147 %	221 %	55 %
80 %	53 %	139 %	100 %	10 %
70 %	7 %	134 %	63 %	0 %
60 %	6 %	125 %	43 %	0 %

Time below average flow, daily

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	995 %	158 %	1116%	3089%
95 %	575 %	150 %	488 %	282 %
90 %	355 %	146 %	243 %	81 %
80 %	141 %	138 %	129 %	30 %
70 %	45 %	133 %	87 %	14 %
60 %	10 %	125 %	63 %	5 %

Time below average flow, monthly

	SO_2	NOx	CO	TRS
Average	100 %	100 %	100 %	100 %
99 %	299 %	134 %	364 %	688 %
95 %	299 %	134 %	364 %	688 %
90 %	264 %	132 %	180 %	525 %
80 %	123 %	126 %	160 %	70 %
70 %	116 %	120 %	115 %	18 %
60 %	110 %	115 %	90 %	16 %

Appendix III Boiler C, Data by concentration and by flow

Variation, concentration mg/m^3n, dry

	SO_2	NOx	CO	TRS	Dust
Average	45	174	6	1	166
Hrly SD	116	25	22	8	114
Daily SD	94	24	18	4	103
Mhly SD	35	12	6	1	105

Variation, concentration from average 100%

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
Hrly SD	256 %	15 %	376 %	980 %	69 %
Daily SD	207 %	14 %	278 %	457 %	68 %
Mthly SD	78 %	7 %	86 %	219 %	65 %

Time below average concentration, hourly

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	1109%	127 %	2060%	2404%	297 %
95 %	846 %	120 %	396 %	128 %	252 %
90 %	343 %	114 %	161 %	47 %	220 %
80 %	40 %	107 %	74 %	8 %	130 %
70 %	5 %	105 %	48 %	0 %	109 %
60 %	4 %	103 %	33 %	0 %	98 %

Time below average concentration, daily

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	1025%	127 %	2008%	3158%	284 %
95 %	624 %	121 %	394 %	267 %	265 %
90 %	364 %	114 %	158 %	75 %	225 %
80 %	126 %	107 %	89 %	28 %	126 %
70 %	33 %	105 %	62 %	13 %	117 %
60 %	8 %	103 %	44 %	5 %	105 %

Time below average concentration, monthly

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	276 %	114 %	270 %	820 %	254 %
95 %	276 %	114 %	270 %	820 %	254 %
90 %	268 %	112 %	240 %	496 %	176 %
80 %	134 %	106 %	215 %	49 %	166 %
70 %	106 %	101 %	152 %	38 %	114 %
60 %	102 %	100 %	75 %	18 %	105 %

Variation, flow g/s

	SO_2	NOx	CO	TRS	Dust
Average	4	15	0	0	17
Hrly SD	10	7	1	1	12
Daily SD	8	6	1	0	12
Mthly SD	3	4	0	0	9

Variation, flow from average 100%

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
Hrly SD	257 %	44 %	274 %	1005%	71 %
Daily SD	202 %	42 %	176 %	455 %	70 %
Mthly SD	84 %	27 %	88 %	210 %	53 %

Time below average flow, hourly

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	1245%	160 %	1354%	2372%	299 %
95 %	825 %	152 %	548 %	143 %	261 %
90 %	347 %	147 %	221 %	55 %	231 %
80 %	53 %	139 %	100 %	10 %	137 %
70 %	7 %	134 %	63 %	0 %	120 %
60 %	6 %	125 %	43 %	0 %	101 %

Time below average flow, daily

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	995 %	158 %	1116%	3089%	295 %
95 %	575 %	150 %	488 %	282 %	260 %
90 %	355 %	146 %	243 %	81 %	233 %
80 %	141 %	138 %	129 %	30 %	137 %
70 %	45 %	133 %	87 %	14 %	119 %
60 %	10 %	125 %	63 %	5 %	100 %

Time below average flow, monthly

	SO_2	NOx	CO	TRS	Dust
Average	100 %	100 %	100 %	100 %	100 %
99 %	299 %	134 %	364 %	688 %	193 %
95 %	299 %	134 %	364 %	688 %	193 %
90 %	264 %	132 %	180 %	525 %	181 %
80 %	123 %	126 %	160 %	70 %	169 %
70 %	116 %	120 %	115 %	18 %	126 %
60 %	110 %	115 %	90 %	16 %	113 %

LIITE III

Best Available Techniques (BAT) Reference Document for in the Production of Pulp,
Paper and Board
Draft May 2012
Review of Kraft Pulping, 13.5.2012. E. Vakkilainen

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Best Available Techniques (BAT)Reference Document for in the Production of Pulp, Paper and Board - Draft May 2012

Review of Kraft Pulping, 13.5.2012
E. Vakkilainen

Problem with BAT BREF values

- Determining BAT emission values does not correspond to The Directive 2008/1/EC concerning integrated pollution prevention and control where it has been stated; that BAT implies an integrated approach (balance across different environmental impacts) and considers cross media effects.
- Article 9(4) of the Directive 2008/1/EC states that one must take into account
  - The technical characteristics of the plant
  - Its geographical location and
  - The local environmental conditions
- However the method has been to take every and all parameters and determine BAT statistically by 10 % and 50 % of values given.

Redetermining BAT BREF values

- BAT BREF reference values should be based on
  1. New mills started after 2000
  2. Achievable results of best mills in integrated fashion.
  3. Vendor emission guarantees
  4. Not to tighten emissions that do not pose risk to the environment and human health
- No study how the values reflect on most modern installations has been done.
- No study whether the equipment vendors are willing to guarantee BAT BREF values has been done.
- No study whether mills are technically able to modify processes to BAT BREF values given has been done.
- No study done what emission levels actually pose risk to the environment and human health

Are BAT BREF values economically and technically viable

Article 2(11) states that adopting the proposed levels should be both **technically** and **economically** viable

- No study whether the equipment vendors are willing to guarantee BAT BREF values has been done.
- No study whether mills are technically able to modify processes to BAT BREF values given has been done.
- No study how much the implementation will cost

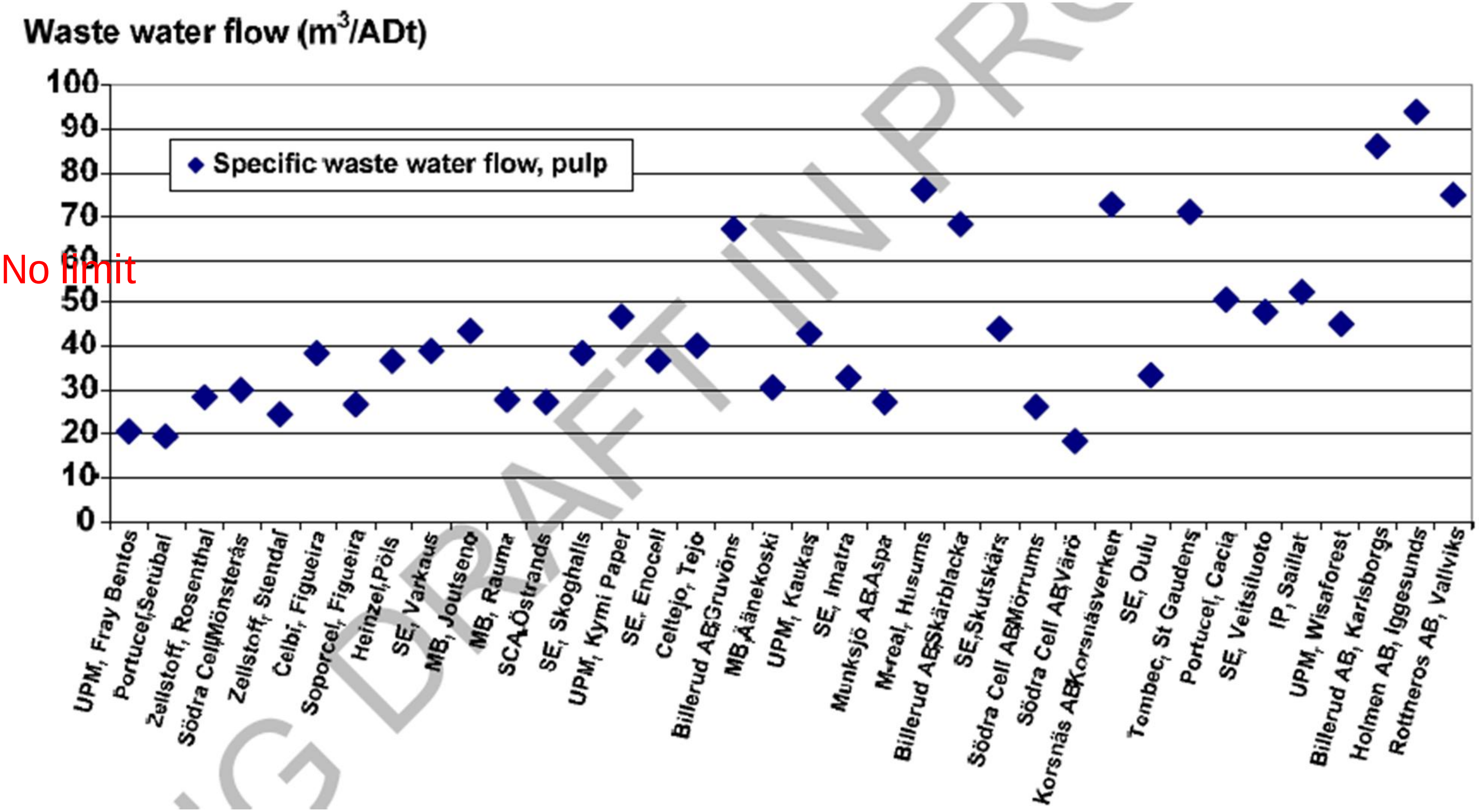
- Only basis is that if some mills report the value it then it must be technically and economically viable for ALL mills. This without taking into account process characteristics (raw material and end product). Which is clearly untrue.

Is error range in the measurement taken account in BAT BREF values

- Mills report continuous measurements with mill's own measurement system
- The environmental authorities demand that e.g. high sulfur emission occurences must be measured accurately
- Therefore e.g. measurement range 0 – 500 mg/Nm^3 has often been selected for sulfur emissions
- This means that total measurement error in lower range (close to zero) is easily 100 mg/Nm^3
- If mill reports ~ 10 mg/Nm^3 then can one assume that this is what emission really is (error 100 mg/Nm^3)?
- Can one enforce e.g. <50 mg/Nm^3 if error is 100 mg/Nm^3 ?
- No attempt has been to separate mills that report the whole year's emissions based on one or two, short, few hour measurement periods.
- If 70 – 90 % of sulfur emissions are created during 5 – 10 % of yearly hours then what do two, short, few hour measurement periods imply of yearly average?

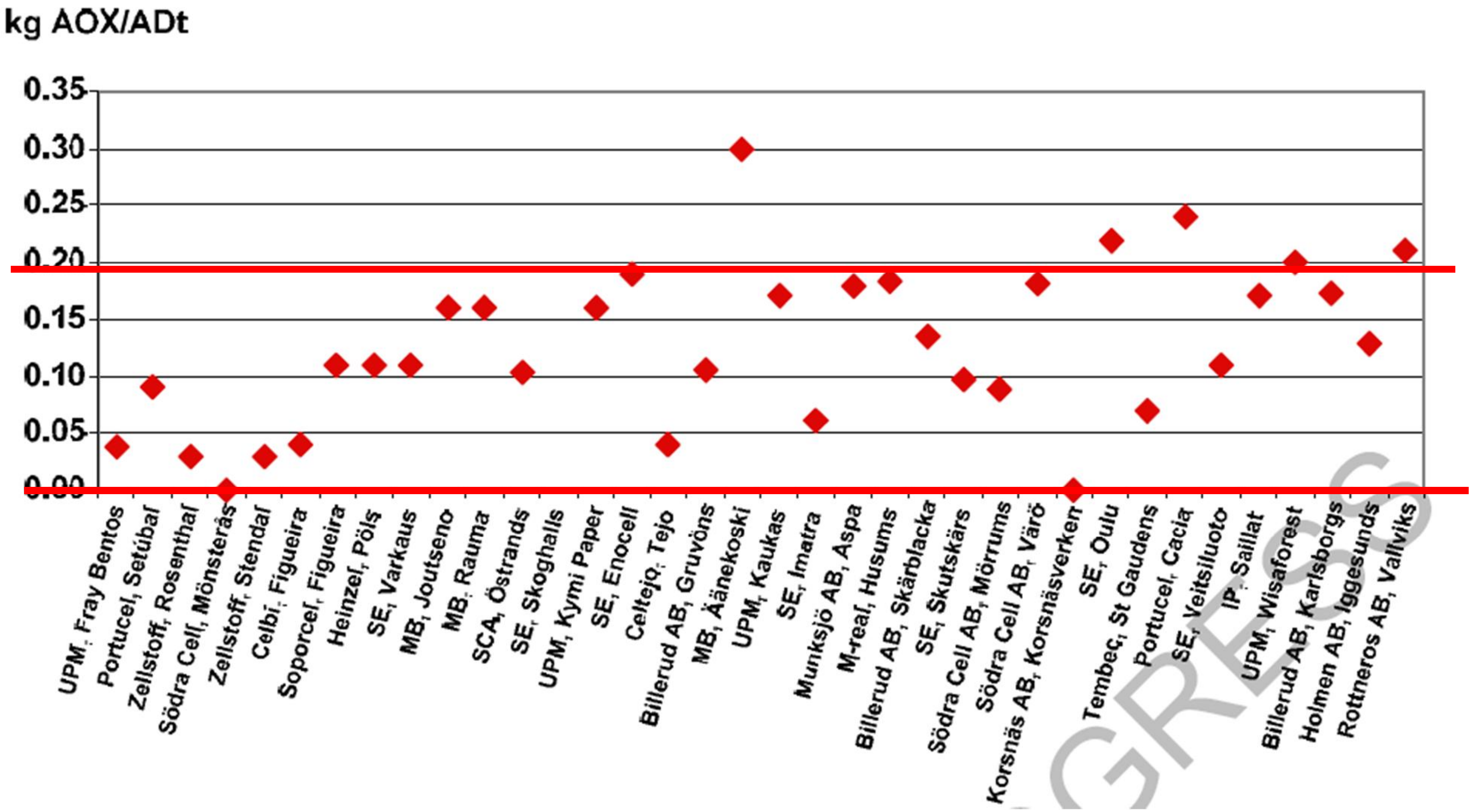
Emissions to water

Specific waste water flow of bleached kraft pulp mills

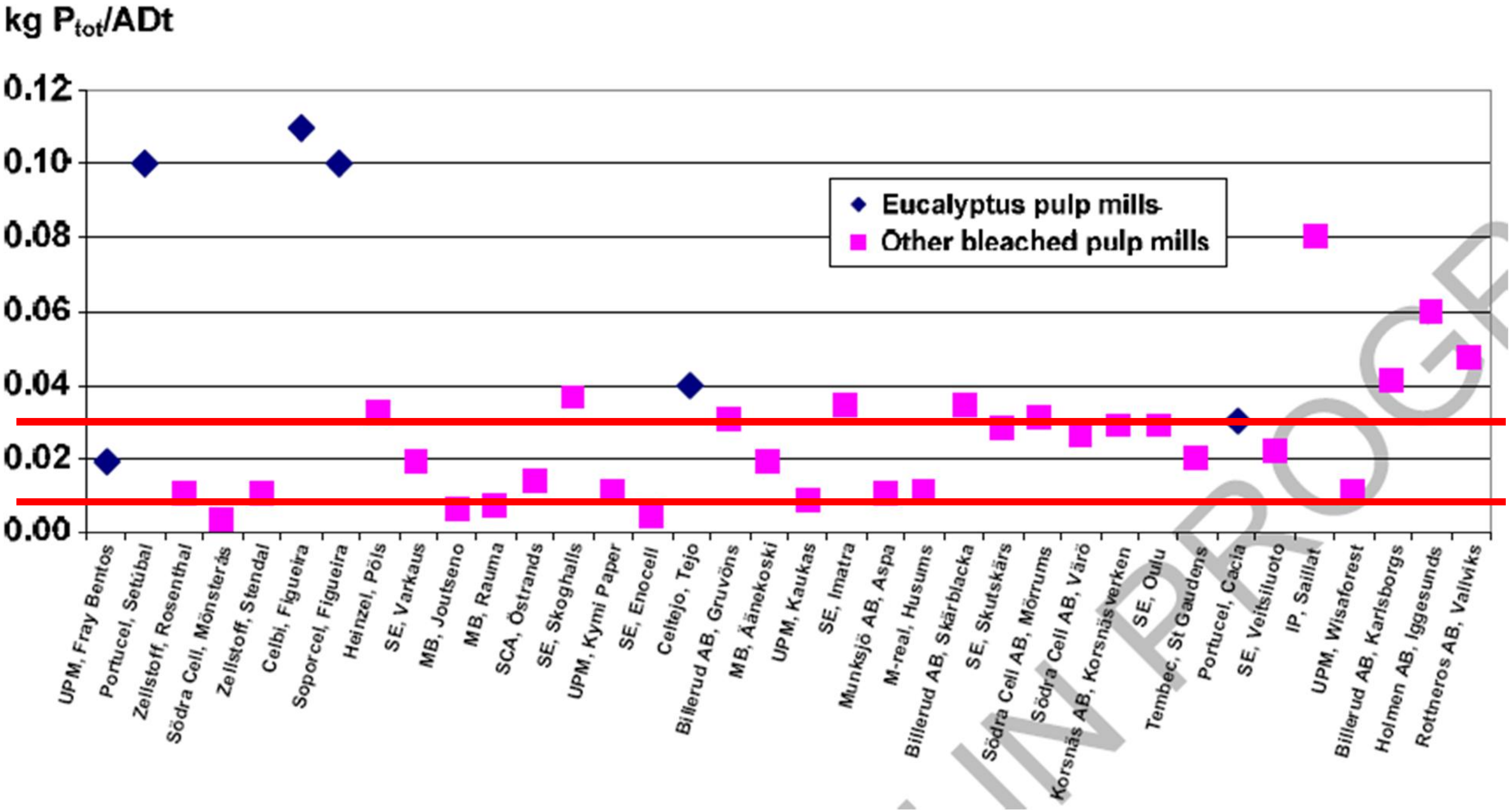


No limit

Specific AOX emissions of bleached kraft pulp mills 0 – 0,2 kg/ADt



Specific emissions of total phosphorus from BKPM 0.01 – 0.03 kg/ADt



Specific emissions of total nitrogen from BKPM 0.02 – 0.25 kg/ADt

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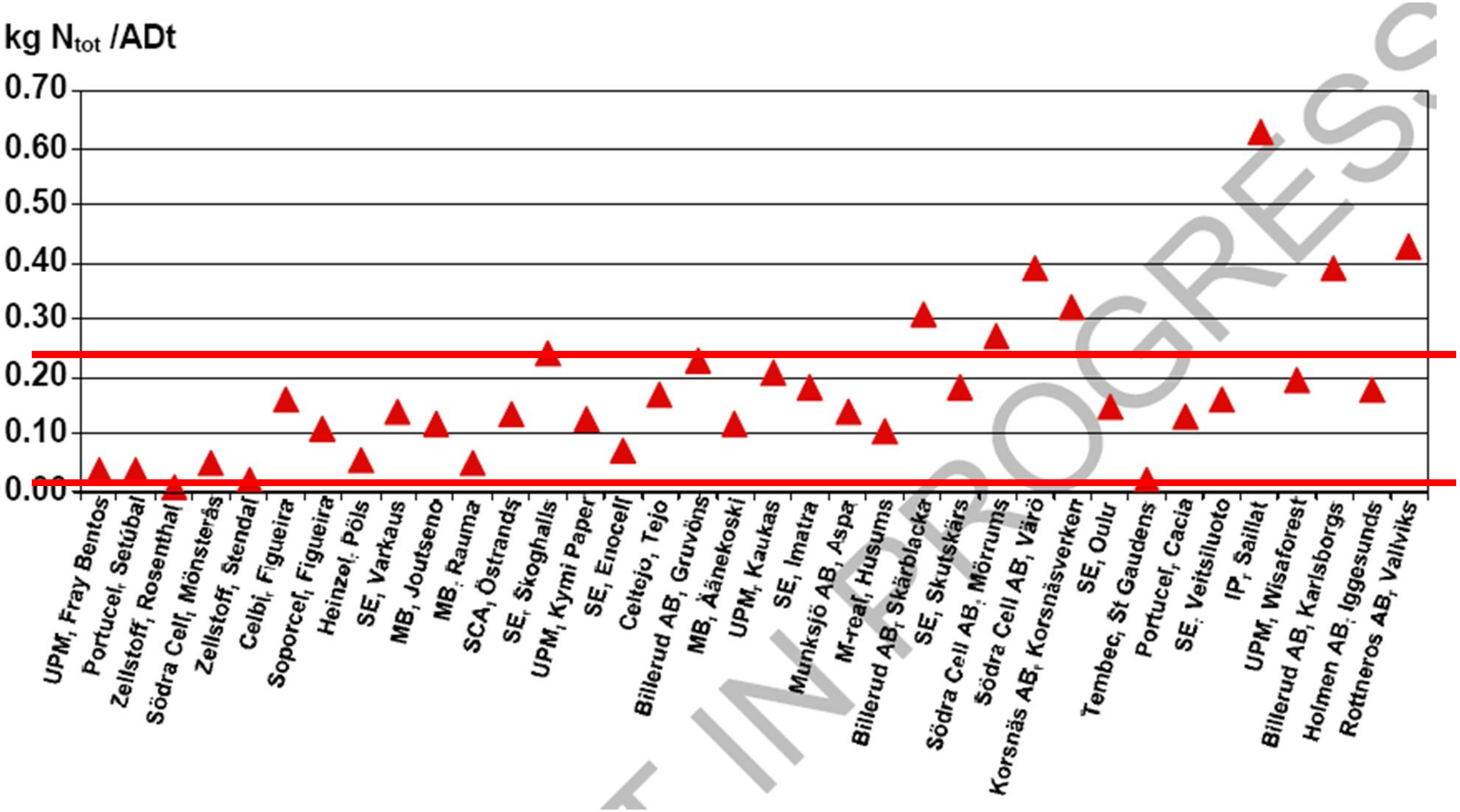
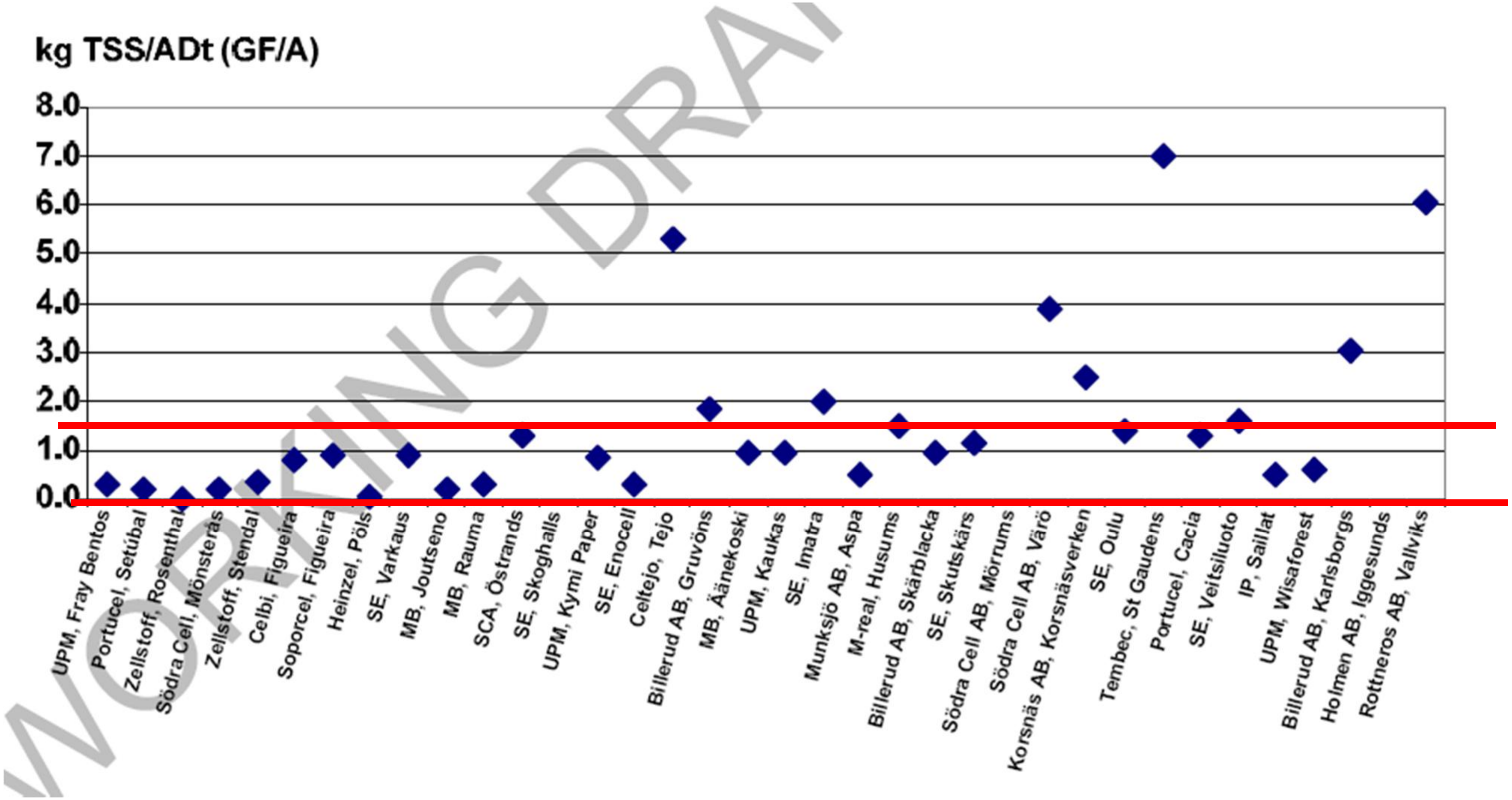
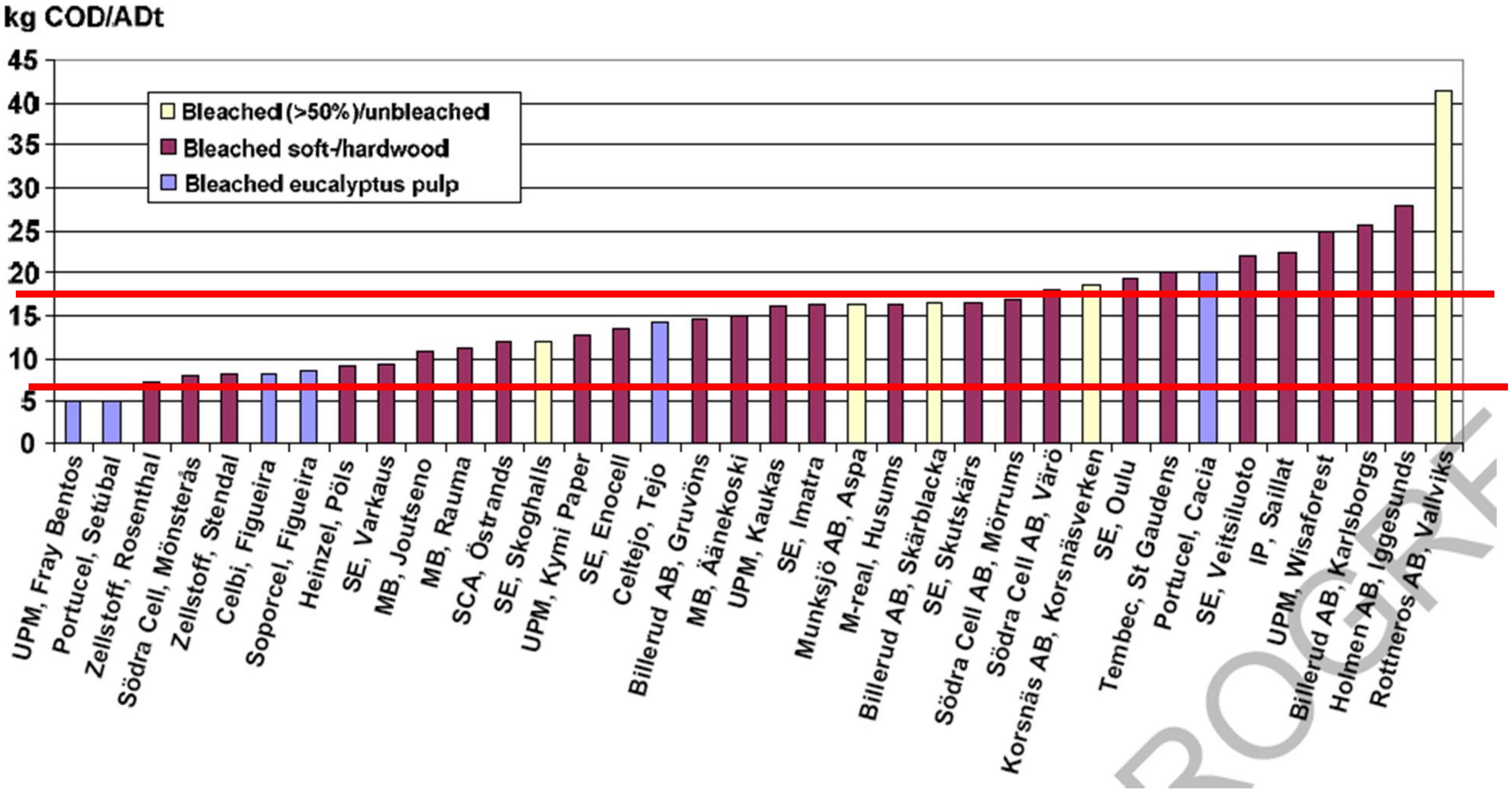


Specific emissions of total suspended solids from BKPM 0.02 – 1.5 kg/ADt



Specific COD emissions after bleaching from BKPM 7 – 17 kg/ADt

5-14 for Euca



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Emissions to air recovery boiler

General questions

- How to interpret the daily and yearly concentrations
- Why no flue gas flow data available even if that was collected?
- Why no explanation on differences in national emissions?
- No crosscorrelation of NOx vs sulfur emissions
- No crosscorrelation of NOx kgNOs/ADt vs as concentration

Measurements

- How can we say anything about the SO_2 and TRS as reported values are significantly lower than the measurement error
- There are several problems in the EIPPC collected mill data. No attempt has been given to resolve them. i.e. concentration * average flow **is not** average emission
- The data does not separate mills that report single measurement as yearly average and mills with continuous measurement and reporting
- The data does not separate mills that collect NCGs (which contain nitrous compounds and so increase NOx)

National Averages RB

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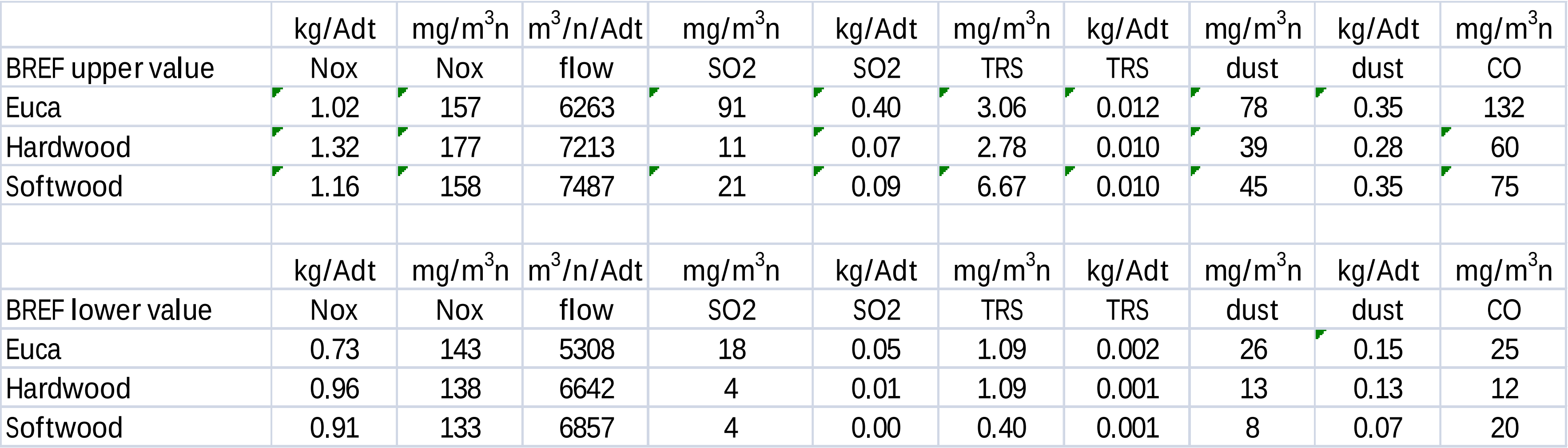
	kg/Adt	mg/m^3n	m^3/n/Adt	mg/m^3n	kg/Adt	mg/m^3n	kg/Adt	mg/m^3n	kg/Adt
Averages	NOx	NOx	flow	SO_2	SO_2	TRS	TRS	dust	dust
Austria	1.46	200	7289	8	0.08	1.5	0.04	16	0.14
Finland	1.47	187	7299	14	0.06	2.5	0.01	37	0.30
France	1.20	155	7696	12	0.08	0.4	0.00	39	0.31
Germany	1.22	161	7574	2	0.02	-	0.00	8	0.07
Portugal	0.93	165	6055	41	0.09	3.9	0.02	38	0.22
Spain	0.99	127	7121	156	0.63	2.7	0.02	126	0.43
Sweden	1.06	149	7236	21	0.08	12.1	0.01	57	0.40

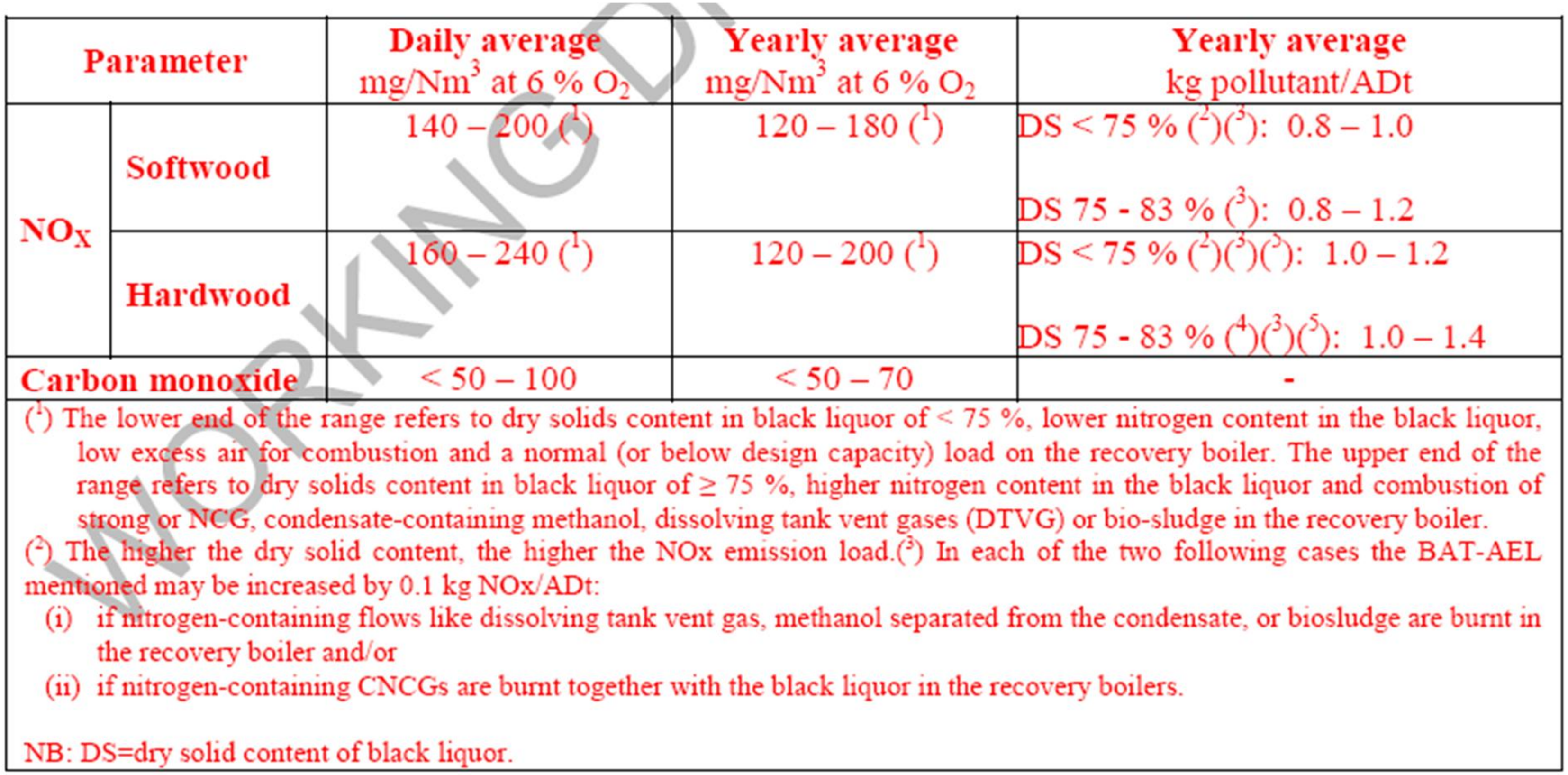
Wood species averages and lower values



	kg/Adt	mg/m^{3}n	m^3/n/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n
BREF upper value	Nox	Nox	flow	SO2	SO2	TRS	TRS	dust	dust	CO
Euca	1.02	157	6263	91	0.40	3.06	0.012	78	0.35	132
Hardwood	1.32	177	7213	11	0.07	2.78	0.010	39	0.28	60
Softwood	1.16	158	7487	21	0.09	6.67	0.010	45	0.35	75
	kg/Adt	mg/m^{3}n	m^3/n/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n	kg/Adt	mg/m^{3}n
BREF lower value	Nox	Nox	flow	SO2	SO2	TRS	TRS	dust	dust	CO
Euca	0.73	143	5308	18	0.05	1.09	0.002	26	0.15	25
Hardwood	0.96	138	6642	4	0.01	1.09	0.001	13	0.13	12
Softwood	0.91	133	6857	4	0.00	0.40	0.001	8	0.07	20

Note hardwood is actually mixture of Hard- and softwood. No euca values why?

NOx and CO from RB, Table 8.8 p. 784



Parameter		Daily average mg/Nm^3 at 6 % O_2	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg pollutant/ADt
NOx	**Softwood**	140 – 200 (1)	120 – 180 (1)	DS < 75 % (2)(3): 0.8 – 1.0 DS 75 - 83 % (3): 0.8 – 1.2
	Hardwood	160 – 240 (1)	120 – 200 (1)	DS < 75 % (2)(3)(5): 1.0 – 1.2 DS 75 - 83 % (4)(3)(5): 1.0 – 1.4
Carbon monoxide		< 50 – 100	< 50 – 70	-

(1) The lower end of the range refers to dry solids content in black liquor of < 75 %, lower nitrogen content in the black liquor, low excess air for combustion and a normal (or below design capacity) load on the recovery boiler. The upper end of the range refers to dry solids content in black liquor of ≥ 75 %, higher nitrogen content in the black liquor and combustion of strong or NCG, condensate-containing methanol, dissolving tank vent gases (DTVG) or bio-sludge in the recovery boiler.

(2) The higher the dry solid content, the higher the NOx emission load.(3) In each of the two following cases the BAT-AEL mentioned may be increased by 0.1 kg NOx/ADt:

(i) if nitrogen-containing flows like dissolving tank vent gas, methanol separated from the condensate, or biosludge are burnt in the recovery boiler and/or

(ii) if nitrogen-containing CNCGs are burnt together with the black liquor in the recovery boilers.

NB: DS=dry solid content of black liquor.

Why lower NOx limits for softwood

- The lowest values from each category are
  - Lowest value for softwood <75 % is 0.75
  - Lowest value for softwood >75 % is 0.89
- If we take away two lowest values from each category then
  - Lower value for softwood <75 % is 0.91
  - Lower value for softwood >75 % is 1.17
- Proposed lower values for softwood are
  - Lower value for softwood <75 % is 0.8
  - Lower value for softwood >75 % is 0.8
- The BAT value **can not** be ”Best of the best”
- The BAT value **can not** be lower than ”Best of the best”

Why upper NOx limits for softwood

- Proposed upper values for softwood are
  - upper value for softwood <75 % is 1.0
  - upper value for softwood >75 % is 1.2
- The average values from each category are
  - Average value for softwood <75 % is 0.96
  - Average value for softwood >75 % is 1.33
- If we take value higher than lowest 25 % from each category then
  - upper value for softwood <75 % is 1.0
  - upper value for softwood >75 % is 1.23
- Softwood BAT values lower than 25 %
- The BAT value **can not** be ”Best of the best”

Does Nox limit treat all RB similarly

- For eucalyptus mills >75 % 100 % (1/1) needs to reduce av. 0.28 kgNO_2/Adt
- For eucalyptus mills <75 % 0 % (0/10) needs to reduce av. 0 kgNO_2/Adt
  - So only 1 eucalyptus mills out of 11 needs to reduce (9 %)
- For hardwood mills >75 % 43 % (3/7) needs to reduce av. 0.36 kgNO_2/ADt
- For hardwood mills <75 % 43 % (3/7) needs to reduce av. 0.07 kgNO_2/ADt
  - So 6 hardwood mills out of 14 needs to reduce (43 %)
- For softwood mills >75 % 70 % (7/10) needs to reduce av. 0.22 kgNO_2/ADt
- For softwood mills <75 % 47 % (8/17) needs to reduce av. 0.13 kgNO_2/ADt
  - So 15 softwood mills out of 27 needs to reduce (56 %)

If the wood species i.e. mill process would have been taken into account properly the percentages for each pulped species would be the same! In addition 11/18 (60 %) mills with DS >75 % (better newer mills) need to reduce compared to 11/34 (32 %) mills with DS <75 % ~+0.25 kg/ADt for mills > 75 %.

~+0.25 kg/ADt for mills > 75 % would help 4 Finnish mills.

Does Nox limit treat all RB similarly

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- For hardwood mills >75 % 44 % (4/9) needs to reduce av. 0.32 kgNO_2/ADt
- For hardwood mills <75 % 18 % (3/17) needs to reduce av. 0.07 kgNO_2/ADt
  - So 7 hardwood mills out of 26 needs to reduce (27 %)
- For softwood mills >75 % 70 % (7/10) needs to reduce av. 0.22 kgNO_2/ADt
- For softwood mills <75 % 47 % (8/17) needs to reduce av. 0.13 kgNO_2/ADt
  - So 15 softwood mills out of 27 needs to reduce (56 %)

If the wood species i.e. mill process would have been taken into account properly the percentages for each pulped species would be the same! Similarity means at least +0.1 kgNO_2/Adt more for softwood

In addition 10/18 (56 %) mills with DS >75 % (better newer mills) need to reduce compared to 11/34 (32 %) mills with DS <75 %. Also reductions for DS>75 % higher not lower!

Hardwood and eucalyptus mills grouped together, 0.1 kg/Adt does not help Finnish mills

Is increasing allowable NOx 0.2 kg/Adt enough? Figure 3.44 p. 311

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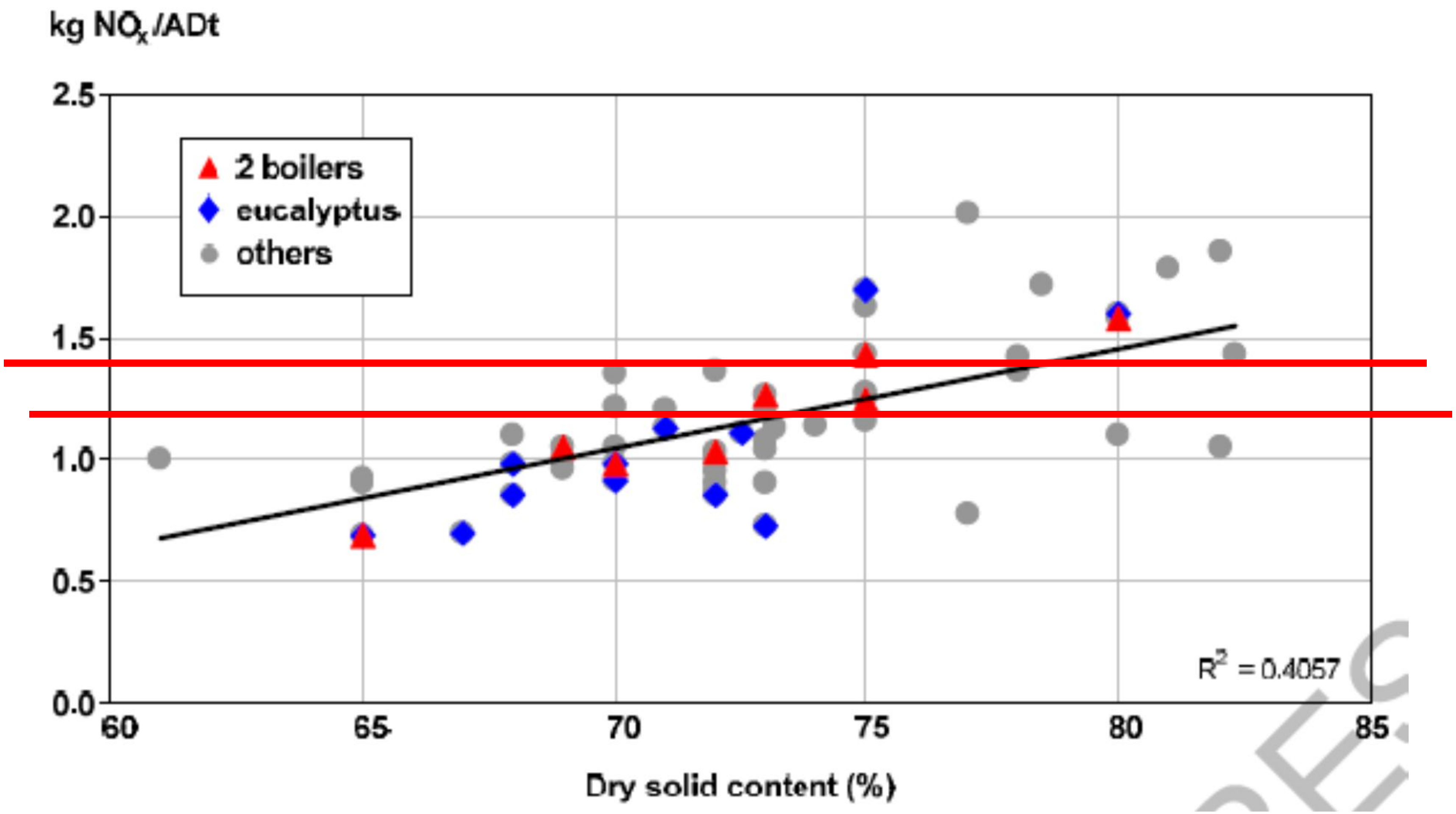

Because of yield there is a range of values for each concentration

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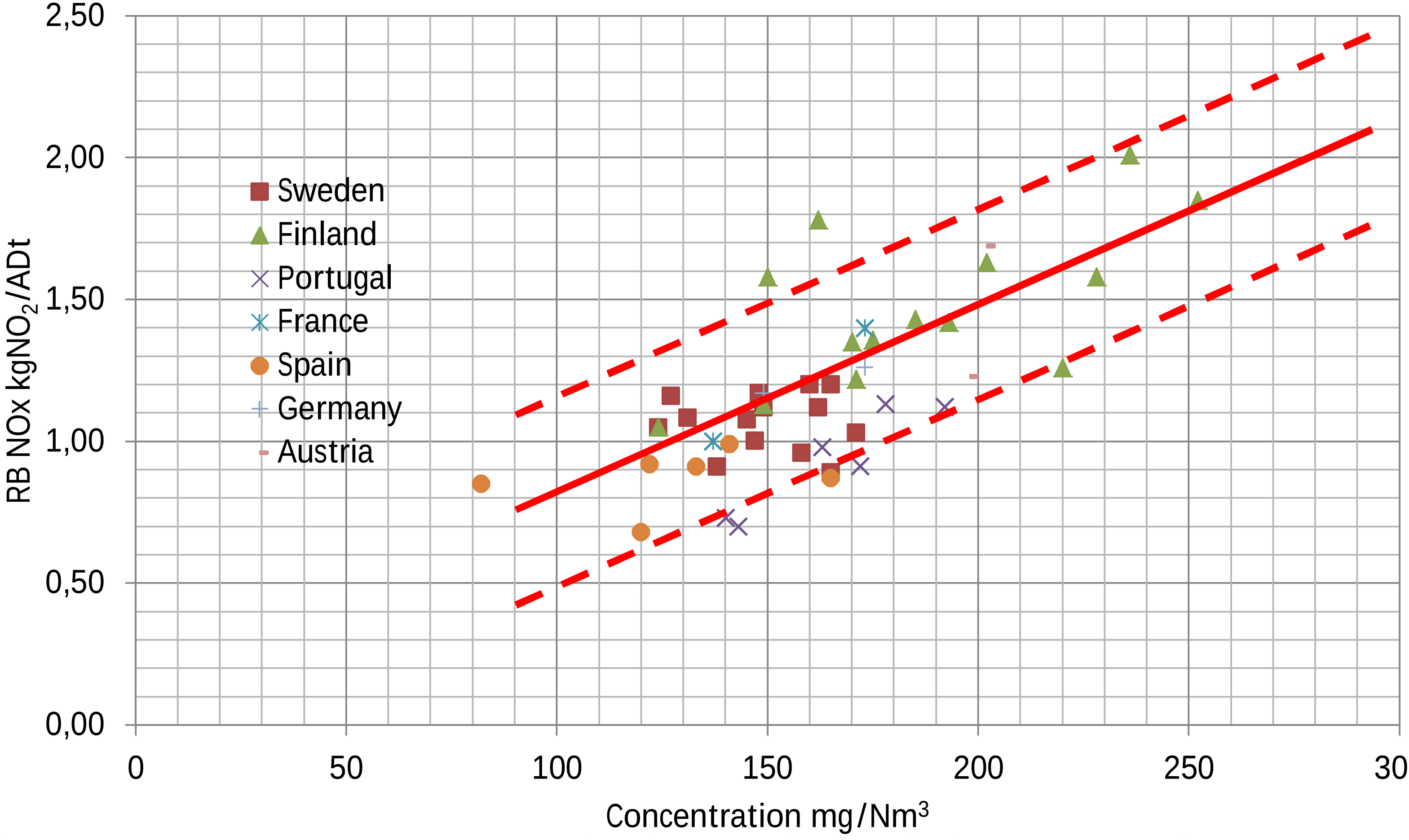
200 mg/Nm3 = 1.1 ... 1.75 kg/ADt



The operator can affect concentration but not kgNO$_2$/Adt corresponding to concentration

Because of yield there is a range of values for each concentration

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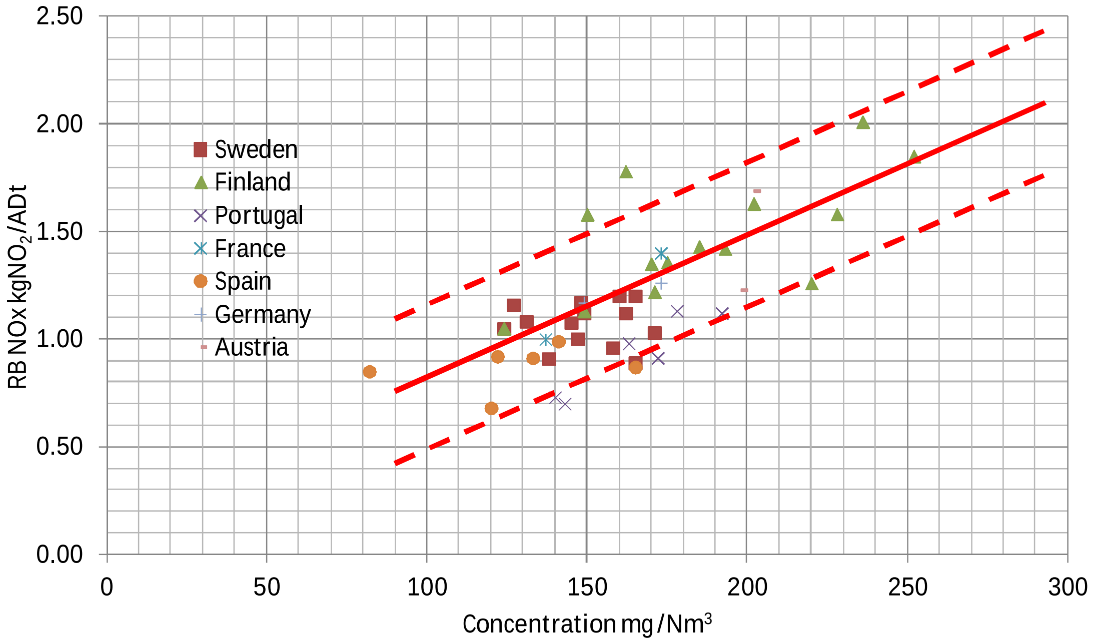
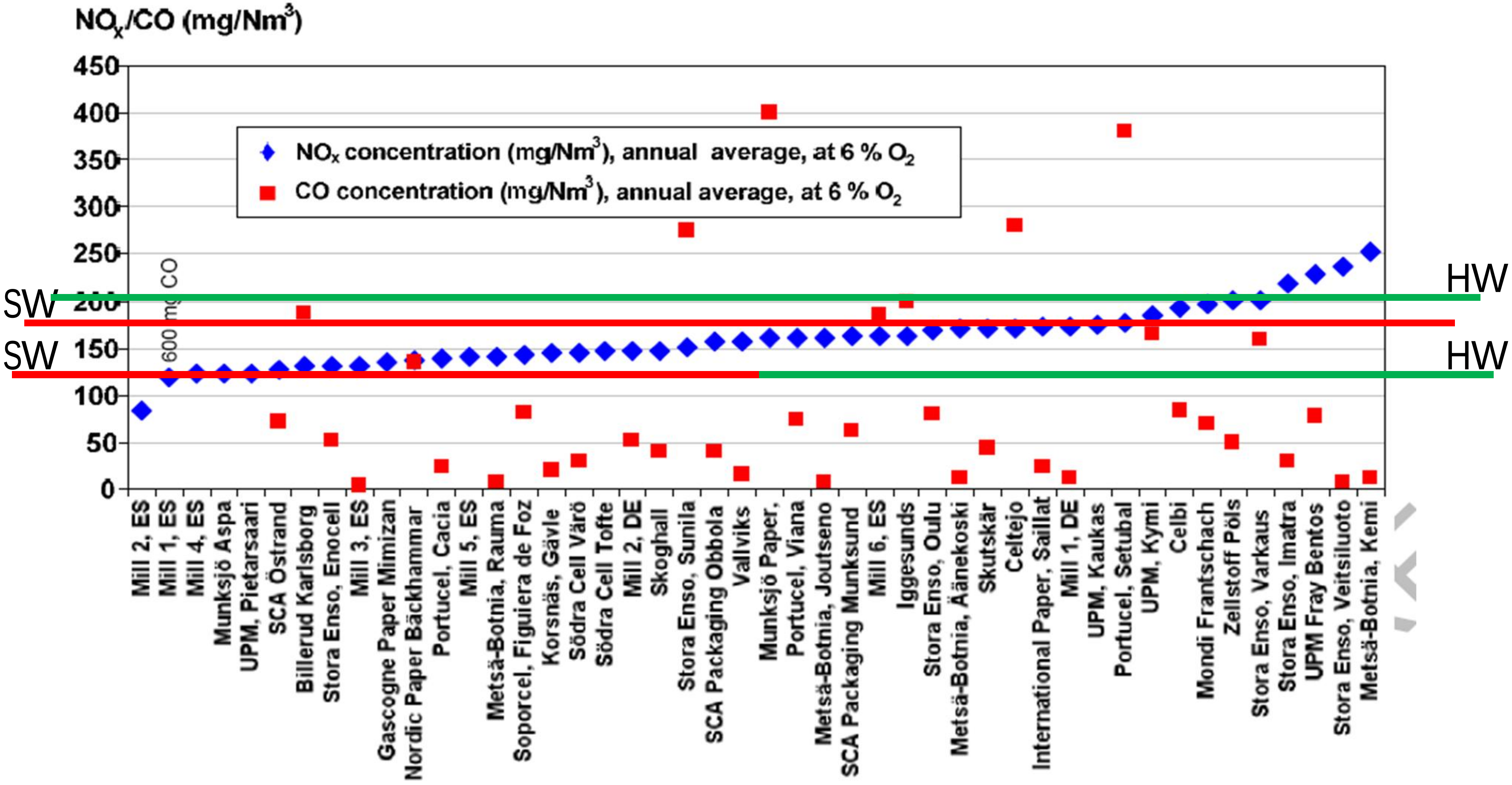


200 mg/Nm3 = 1.1 … 1.75 kg/ADt
180 mg/Nm3 = 1.0 … 1.6 kg/ADt
140 mg/Nm3 = 0.75 … 1.3 kg/ADt
120 mg/Nm3 = 0.6 … 1.2 kg/ADt

The operator can affect concentration but not kgNO$_2$/ADt corresponding to concentration. Emission as kgNO$_2$/Adt is determined by flue gas flow times concentration. Flue gas flow depends on the pulping species and can not be affected by the operator.

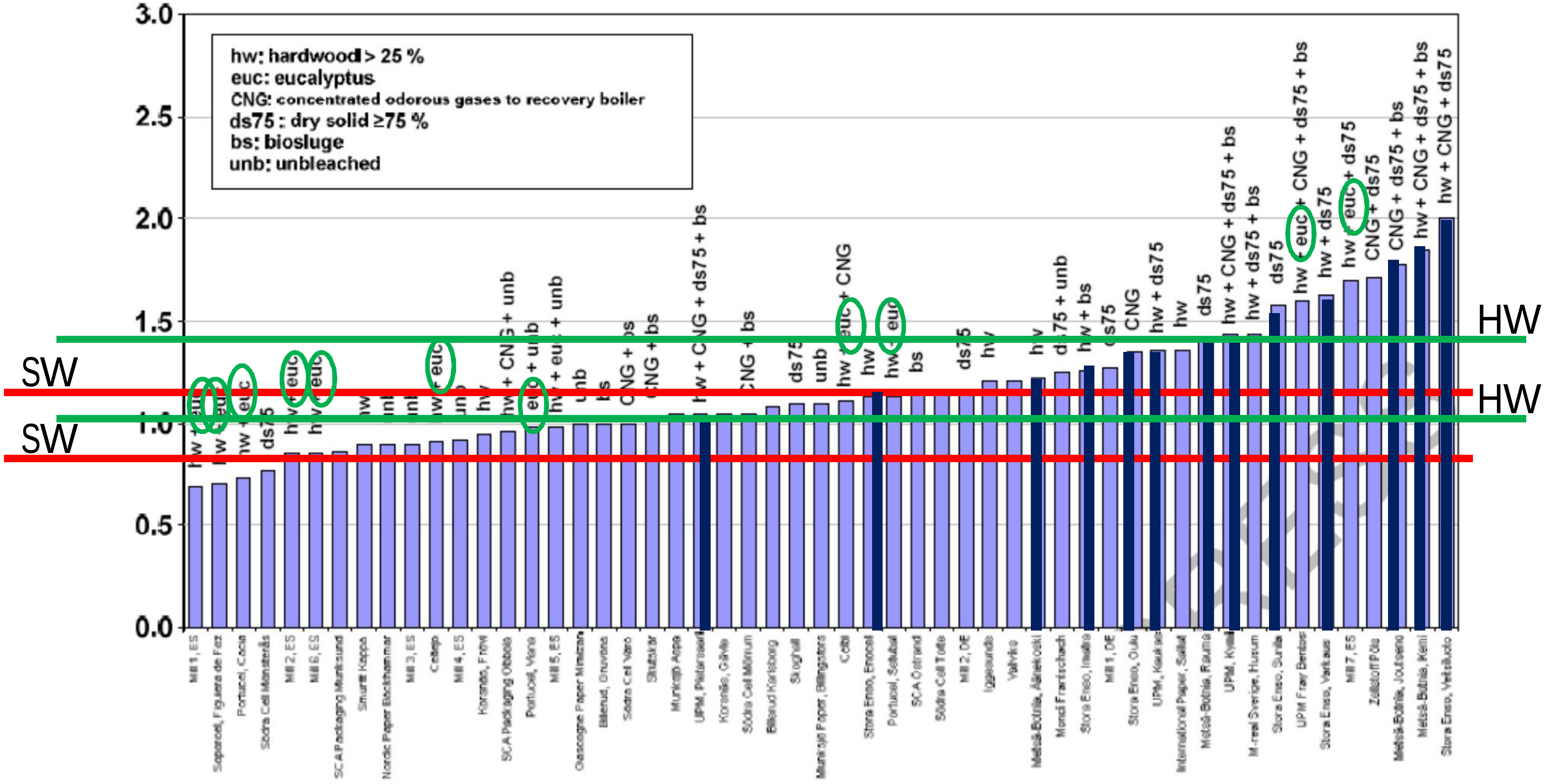
NOx emission from recovery boilers SW 120 – 180, HW 120 – 200 mg/Nm^3



NOx emission from recovery boilers SW 0.8 – 1.2, HW 1.0 – 1.4 kg/ADt

fired with different black liquors, dry solids and NCG, kg/ADt (EU IPPC, 2011)

Effect of euca = -0.27*



*Effect calculated as difference of mill averages between euca and not

Eight of fifteen Finnish Boilers need to invest to reduce NOx

	Emission		Reported	Fit	Limit		Limit	
	mg /Nm^3	kg NO$_2$/ADt	Nm^3/Adt	Nm^3/Adt	kg NO$_2$/ADt	diff.	mg /Nm^3	diff.
Mill A	171	1.22	7128	7135	1.20	**-0.02**	200	29
Mill B	162	1.78	8250	10988	1.40	**-0.38**	180	18
Mill C	252	1.85	7356	7341	1.60	**-0.25**	200	**-52**
Mill D	193	1.42	7630	7377	1.20	**-0.22**	180	**-13**
Mill E	149	1.13	7600	7567	1.20	0.07	200	51
Mill F1	220	1.26	3480	3436	1.30	0.04	200	**-20**
Mill F2	220		2320	2291	1.30		200	**-20**
Mill G	170	1.35	7250	7941	1.10	**-0.25**	180	10
Mill H1	137	1.58	4235	4086	1.20	**-0.38**	180	43
Mill H2	169		6256	6036	1.20		180	11
Mill I	202	1.63	8000	8069	1.40	**-0.23**	200	**-2**
Mill J	236	2.01	7600	8517	1.50	**-0.51**	200	**-36**
Mill K	175	1.36	6800	7782	1.40	0.04	200	26
Mill L	185	1.43	6642	7730	1.60	0.17	200	15
Mill M	124	1.05	7400	8468	1.60	0.55	200	76

Average 1.27 kg/ADt
Four mills can invest to higher ds for 0.2 kg/ADt

Five of fifteen Finnish Boilers need to invest to reduce CO

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	Emission		Limit		Limit	
	mg /Nm^3	kg CO/ADt	kg COADt	diff.	mg /Nm^3	diff.
Mill A	11.6	0.08	XX		70	58
Mill B	7	0.06	XX		70	63
Mill C	11	0.08	XX		70	59
Mill D	12	0.09	XX		70	58
Mill E	59	0.45	XX		70	11
Mill F1	50		XX		70	20
Mill F2	10		XX		70	60
Mill G	80	0.58	XX		70	**-10**
Mill H1	464	2.51	XX		70	**-394**
Mill H2	87	0.00	XX		70	**-17**
Mill I	160	1.30	XX		70	**-90**
Mill J	7	0.05	XX		70	63
Mill K	-		XX		70	
Mill L	165	1.10	XX		70	**-95**
Mill M	-		XX		70	

Especially NOx conversions not realistic

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		mg/Nm^3	Nm^3/ ADt	Nm^3/ ADt	kg NO$_2$/ADt	kg NO$_2$/ADt
Recovery boiler		Emission	Softwood	Hardwood	Softwood	Hardwood
SO2	lower	5	7500	6200	0.04	0.03
SO2	upper	25	7500	6200	0.19	0.15
TRS	lower	1	7500	6200	0.01	0.01
TRS	upper	5	7500	6200	0.04	0.03
NOx	lower	120	7500		0.90	
NOx	upper	180	7500		1.35	
NOx	lower	120		6200		0.74
NOx	upper	200		6200		1.24
CO	lower	50	7500	6200	0.38	0.31
CO	upper	70	7500	6200	0.53	0.43
Dust	lower	10	7500	6200	0.08	0.06
Dust	upper	30	7500	6200	0.23	0.19

<-120 does not correspond to 0.8

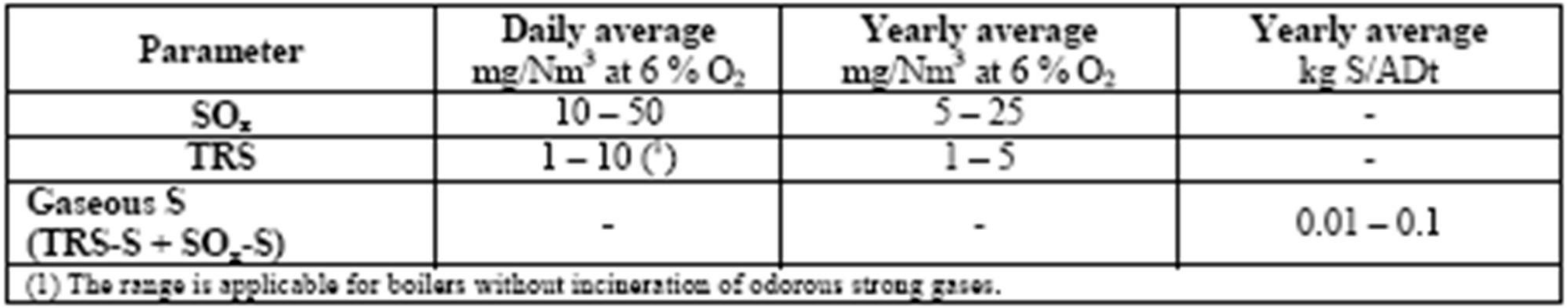
<-180 does not correspond to 1.2

<-120 does not correspond to 1.0

<-200 does not correspond to 1.4

What is the average flow of flue gas per ton of pulp?
This information was collected but is not shown in BAT BREF!

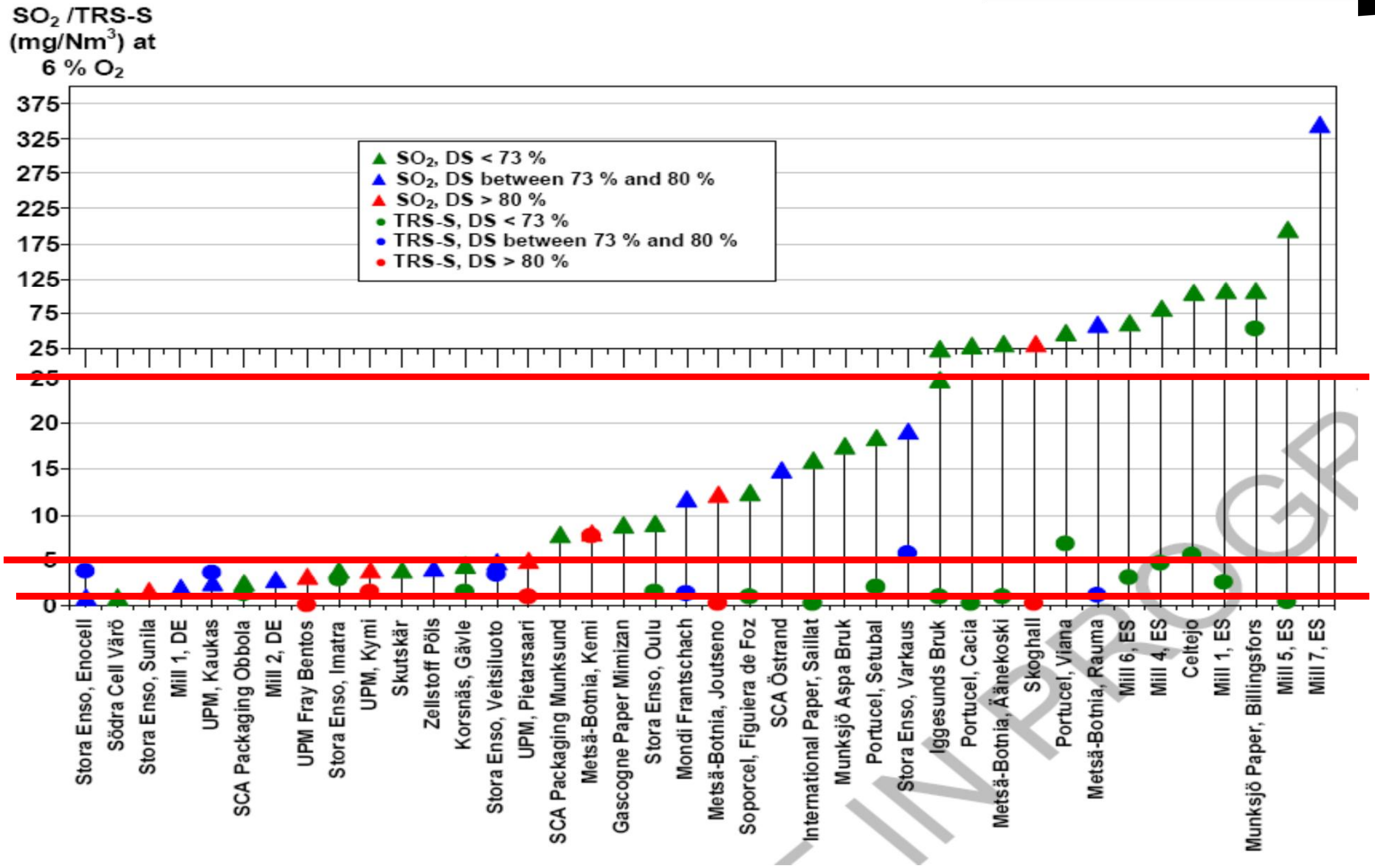
SO2 and TRS emission recovery boiler, Table 8.8 p. 784



Parameter	Daily average mg/Nm^3 at 6 % O_2	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg S/ADt
SO_x	10 – 50	5 – 25	-
TRS	1 – 10 (1)	1 – 5	-
Gaseous S (TRS-S + SO_x-S)	-	-	0.01 – 0.1

(1) The range is applicable for boilers without incineration of odorous strong gases.

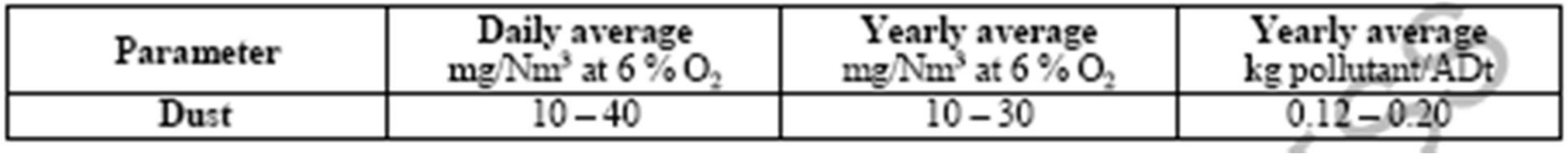
SO2 and TRS-S emission from RB
SO2 5 – 25, TRS 1 – 5 mg/Nm^3



Four out of fifteen boilers need to reduce SO_2 and TRS

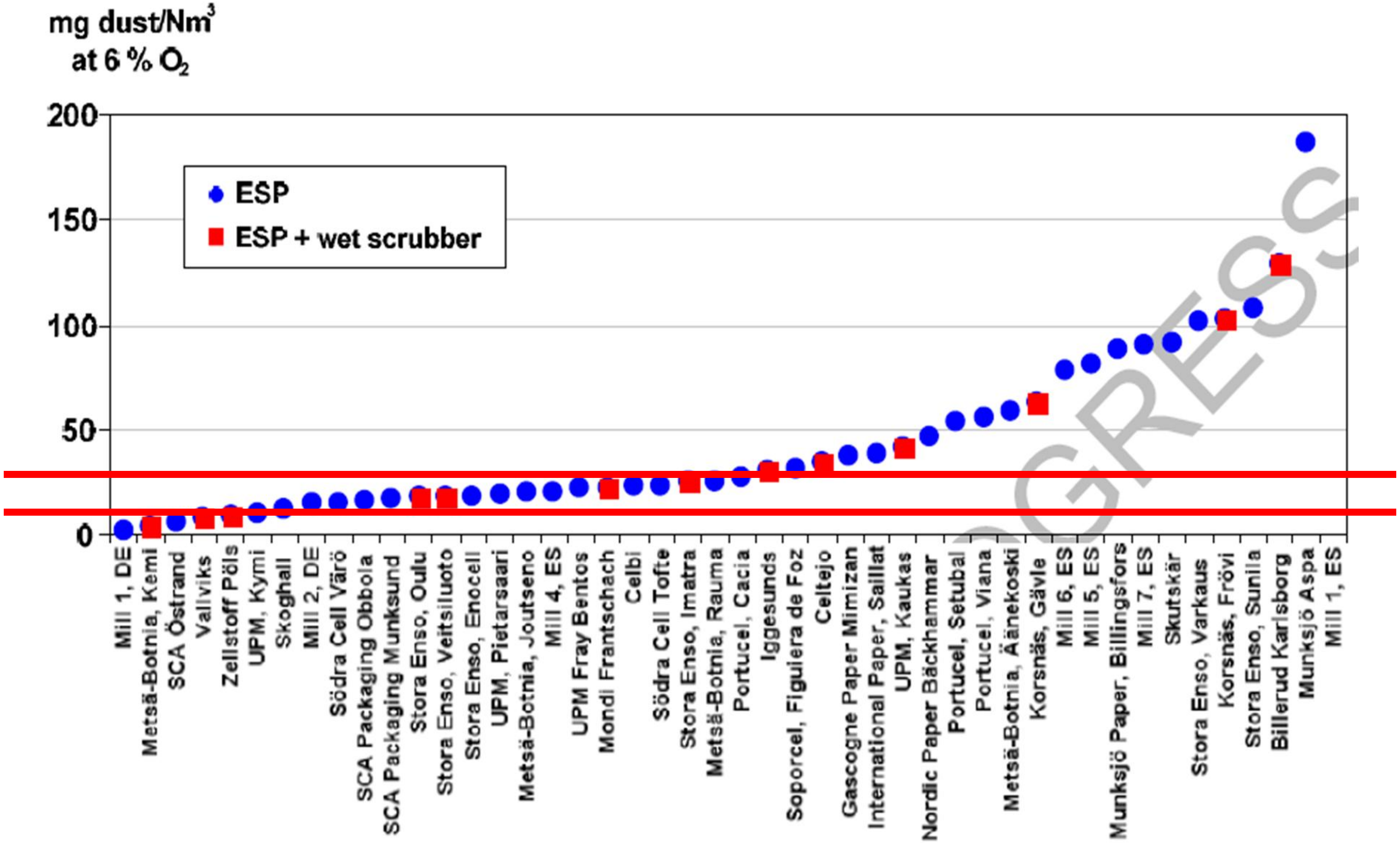
	Emission		Emission		Limit		Limit		Limit	
	mg /Nm^3	kg SO_2/ADt	Nm^3/Adt	kg TRS/ADt	kg SO_2+TRS/ ADt	diff.	mg /Nm^3	diff.	mg /Nm^3	diff.
Mill A	31.3	0.22	1	0.007	0.10	**-0.13**	25	**-6**	5	4.0
Mill B	12.3	0.09	0.32	0.002	0.10	0.01	25	13	5	4.7
Mill C	8	0.03	7.7	0.017	0.10	0.05	25	17	5	**-2.7**
Mill D	82	0.29	2	0.01	0.10	**-0.20**	25	**-57**	5	3.5
Mill E	1	0.01	4	0.006	0.10	0.08	25	24	5	0.7
Mill F1	4	0.02	3	0.01	0.10	0.07	25	21	5	2.0
Mill F2	4	0.02	3	0.01	0.10	0.07	25	21	5	2.0
Mill G	9.1	0.03	1.6	0.012	0.10	0.06	25	16	5	3.4
Mill H1	1.6	0.01	0.5	0.003	0.10	0.09	25	23	5	4.5
Mill H2	1.8	0.01	0	0.003	0.10	0.09	25	23	5	4.7
Mill I	19.3	0.06	6	0.02	0.10	0.02	25	6	5	**-0.7**
Mill J	4.8	0.03	3.5	0.003	0.10	0.07	25	20	5	1.5
Mill K	3	0.01	4	0.029	0.10	0.06	25	23	5	1.3
Mill L	4	0.01	2	0.001	0.10	0.09	25	21	5	3.5
Mill M	5	0.02	1	0.001	0.10	0.08	25	20	5	4.0

Dust emission recovery boiler, Table 8.9 p. 785

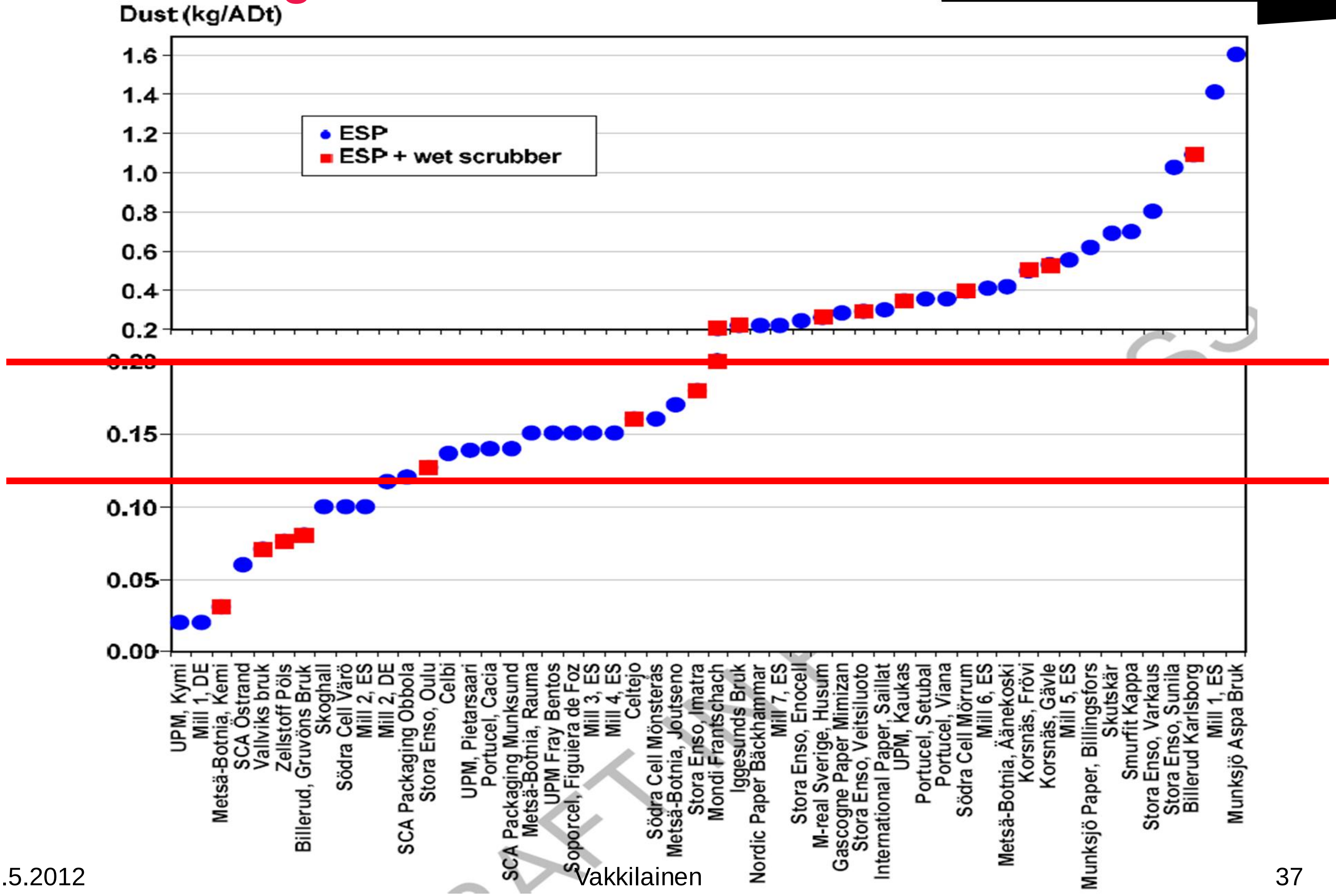


Parameter	Daily average mg/Nm^3 at 6 % O_2	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg pollutant/ADt
Dust	10 – 40	10 – 30	0.12 – 0.20

Dust emission from recovery boilers
10 – 30 mg/Nm^3 at 6 % O$_2$



Dust emission from recovery boilers 0.12 – 0.2 kg/ADt



Eight of fifteen Finnish Boilers need to invest to reduce dust

	Emission		Limit		Limit	
	mg /Nm^3	kg dust/ADt	kg dustADt	diff.	mg /Nm^3	diff.
Mill A	58.5	0.42	0.20	**-0.22**	30	**-29**
Mill B	20	0.17	0.20	0.03	30	10
Mill C	4	0.03	0.20	0.17	30	26
Mill D	35	0.15	0.20	0.05	30	**-5**
Mill E	21	0.24	0.20	**-0.04**	30	9
Mill F1	25	0.18	0.20	0.02	30	5
Mill F2	25	0.18	0.20	0.02	30	5
Mill G	18	0.13	0.20	0.07	30	12
Mill H1	131	1.03	0.20	**-0.83**	30	**-101**
Mill H2	84	1.03	0.20	**-0.83**	30	**-54**
Mill I	102	0.80	0.20	**-0.60**	30	**-72**
Mill J	18	0.29	0.20	**-0.09**	30	12
Mill K	42	0.35	0.20	**-0.15**	30	**-12**
Mill L	10	0.02	0.20	0.18	30	20
Mill M	19	0.14	0.20	0.06	30	11

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Emissions to air lime kiln

Comments on LK emisisons

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- Why are the lime kiln flue gas flows per ton of pulp not listed although they were collected.
-

National averages LK

		kg/Ad	g/m3	kg/Adt	mg/m3n	kg/Ad	ng/m3	kg/Adt	mg/r
Averages		Nox	Nox	SO2	SO2	TRS	TRS	Dust	Dust
Austria		0.36	540	0.006	12.0	0.003	1.00	0.051	28
Finland		0.23	262	0.016	32.6	0.005	8.40	0.019	23
France		0.23	243	0.130	150.5	-	1.00	0.010	7
Germany		0.23	311	0.017	9.5	0.001	1.00	0.020	23
Portugal		0.16	280	0.071	342.0	0.014	25.33	0.035	55
Spain		0.20	287	0.028	272.4	0.031	2.80	0.048	76
Sweden		0.20	233	0.044	98.6	0.030	26.00	0.073	61

Effect of wood species on LK BREF upper and lower value

	kg/Adt	ng/m^3	kg/Adt	mg/m^3	kg/Adt	ng/m^3	kg/Adt	ng/m^3
BREF up	Nox	Nox	SO2	SO2	TRS	TRS	dust	dust
Euca	0.17	255	0.055	309	0.02	14.8	0.039	60
Hardwo	0.23	273	0.022	33	0.01	15.7	0.021	13
Softwo	0.22	282	0.040	81	0.02	11.9	0.064	51
	kg/Adt	ng/m^3	kg/Adt	mg/m^3	kg/Adt	ng/m^3	kg/Adt	ng/m^3
BREF lo	Nox	Nox	SO2	SO2	TRS	TRS	dust	dust
Euca	0.18	210	0.024	50	0.005	4.0	0.011	17
Hardwo	0.18	280	0.020	8	0.009	8.2	0.010	10
Softwo	0.19	225	0.007	6	0.003	1.0	0.020	16

Does Lime kiln BREF take into effect process differences

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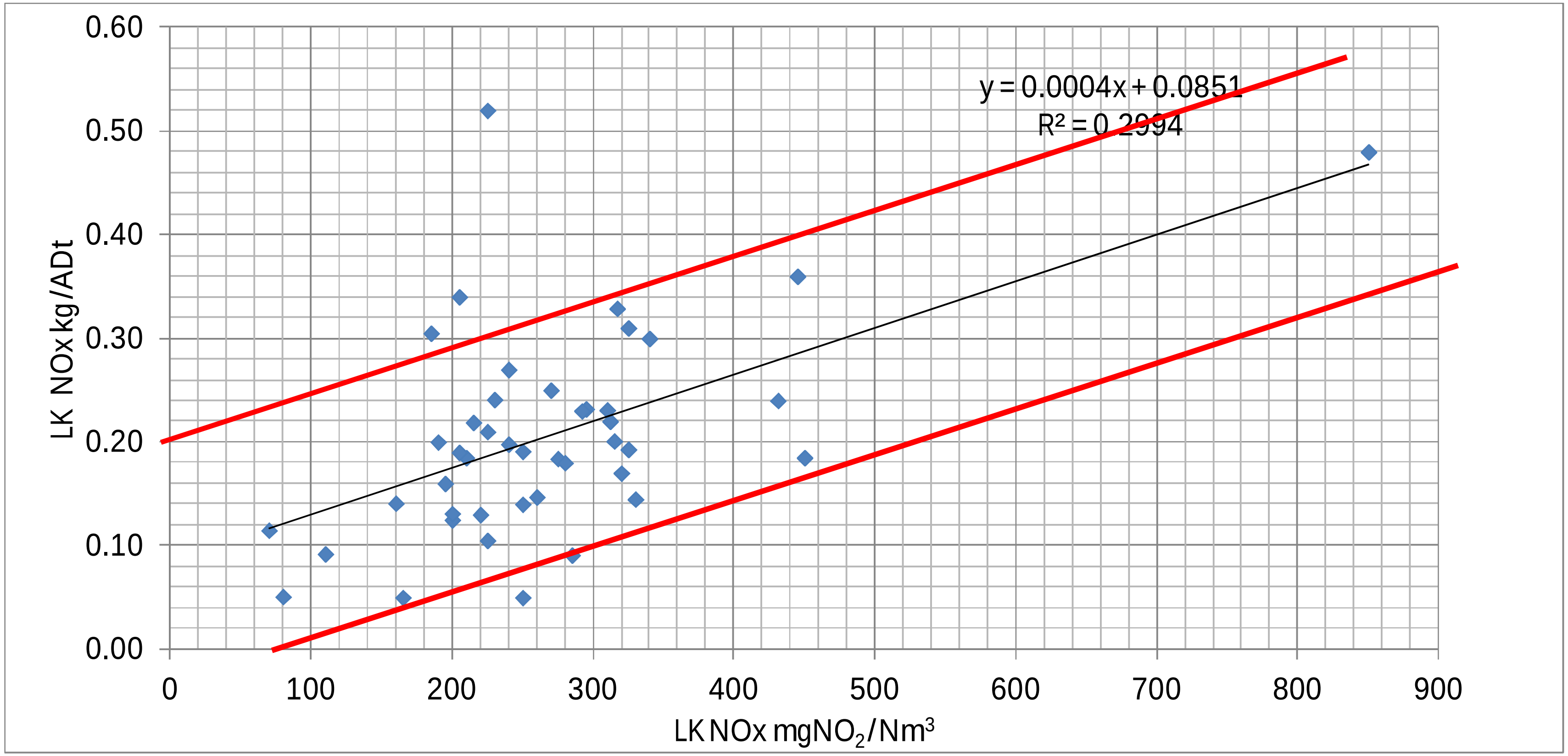
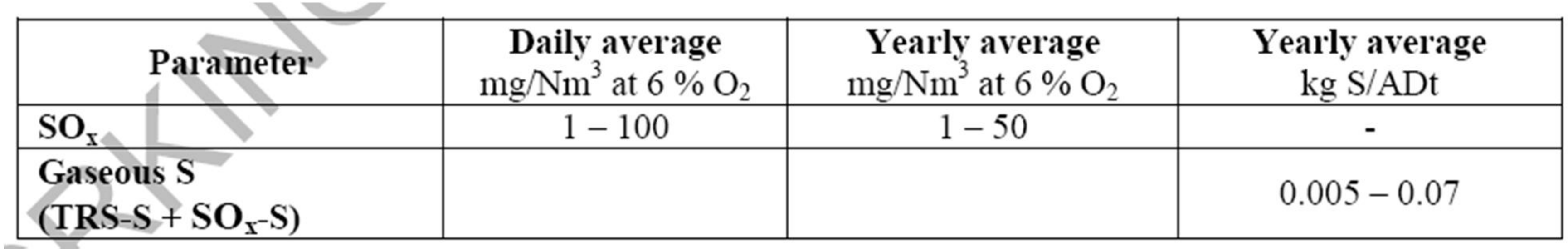
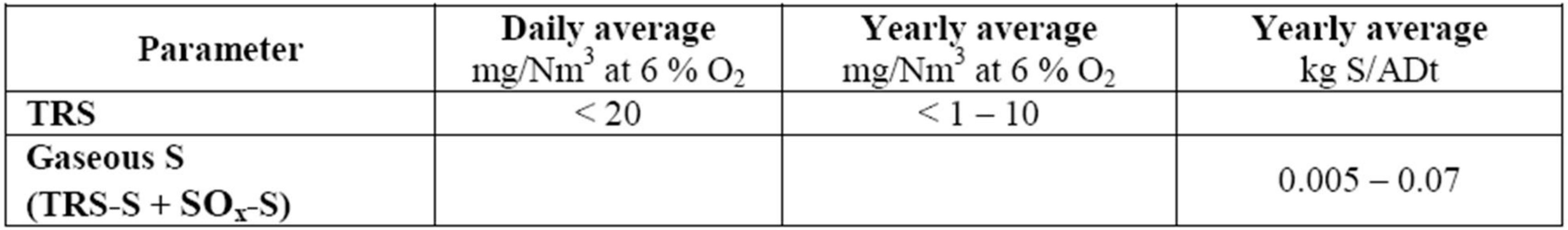


The operator can affect emission as $mgNO_2/Nm^3$ but not as $kgNO_2/ADt$. $kgNO_2/ADt$ is simply the flue gas flow times concentration. Flue gas flow depends on wood species, yield and sulfidity.

SO_2 and TRS Lime kiln

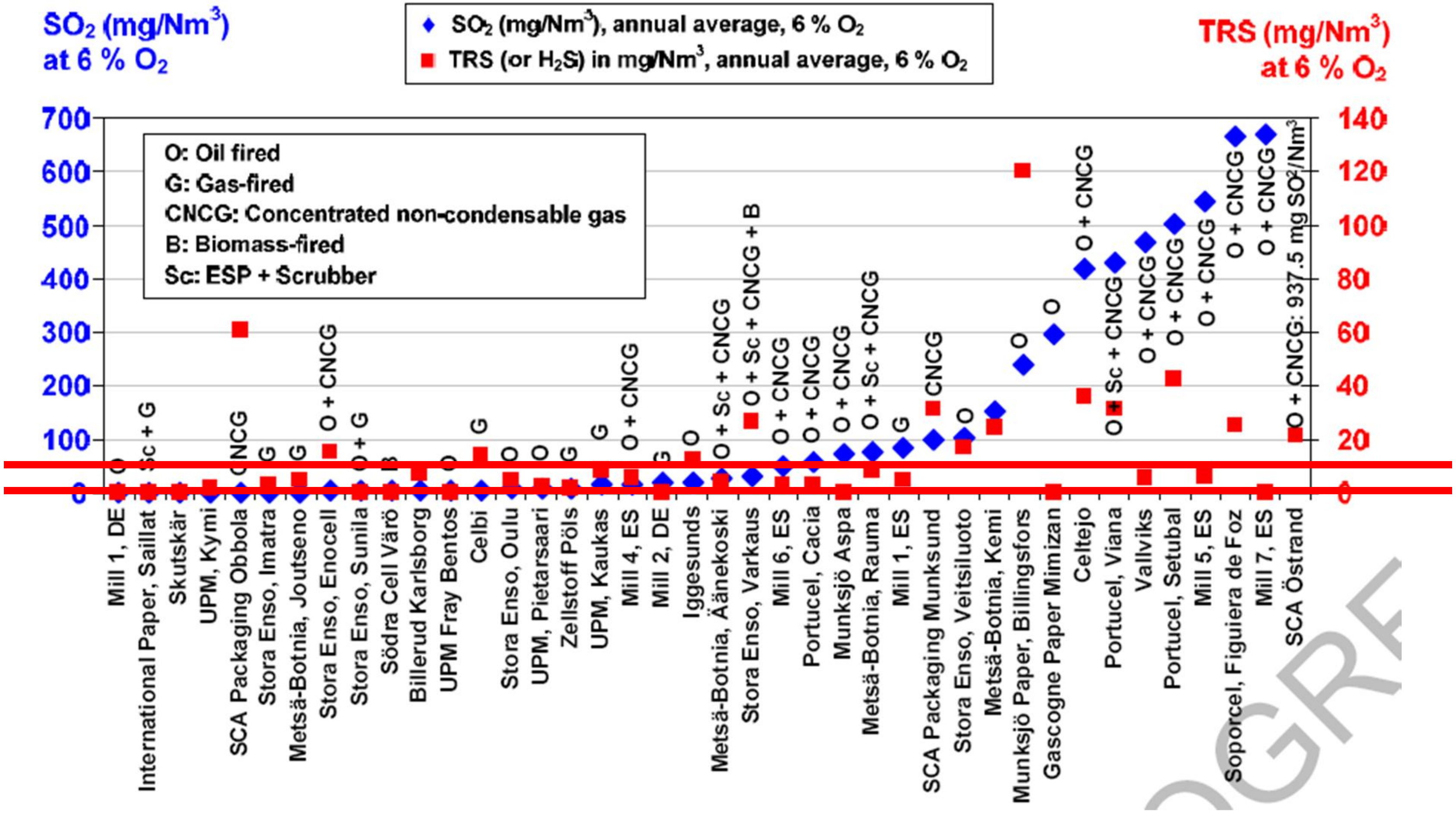


Parameter	Daily average mg/Nm^3 at 6 % O_2	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg S/ADt
SO_x	1 – 100	1 – 50	-
Gaseous S ($TRS\text{-}S + SO_x\text{-}S$)			0.005 – 0.07

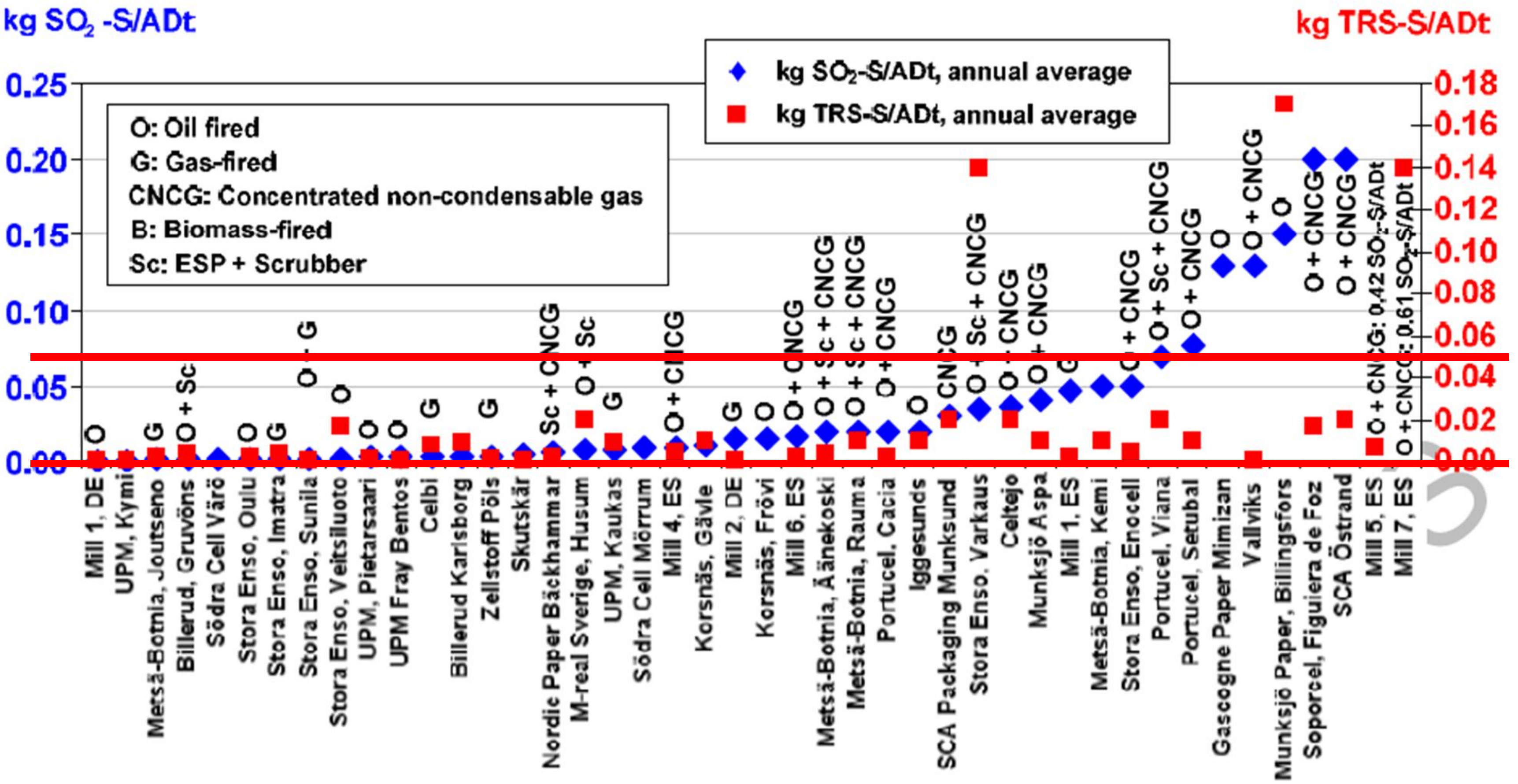


Parameter	Daily average mg/Nm^3 at 6 % O_2	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg S/ADt
TRS	< 20	< 1 – 10	
Gaseous S ($TRS\text{-}S + SO_x\text{-}S$)			0.005 – 0.07

TRS and SO_2 emission from lime kiln
TRS 1 – 10 SO_2 1 – 50 mg/Nm^3 at 6 % O_2



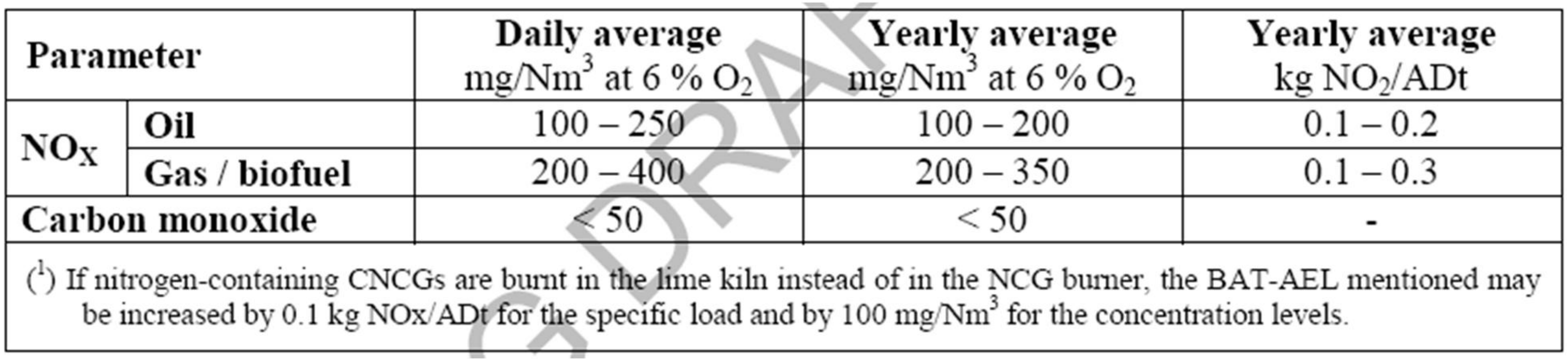
TRS and SO$_2$ emission from lime kiln, TRS + SO$_2$ 0.005 – 0.07 kg/ADt



Five out of fourteen lime kilns need to invest to reduce SO_2 and TRS

	Emission		Emission		Limit		Limit		Limit	
	mg /Nm^3	kg SO_2/ADt	Nm^3/Adt	kg TRS/ADt	kg SO_2+TRS/ ADt	diff.	mg /Nm^3	diff.	mg /Nm^3	diff.
Mill A	25	0.02	3.5	0.003	0.10	0.08	50	25	10	6.5
Mill B	1.7	0.00	4.8	0.002	0.10	0.10	50	48	10	5.2
Mill C	152	0.05	24	0.01	0.10	0.04	50	-102	10	-14.0
Mill D	67	0.02	7	0.01	0.10	0.07	50	-17	10	3.0
Mill E	2	0.05	15	0.004	0.10	0.05	50	48	10	-5.0
Mill F1	1.4	0.002	3	0.003	0.10	0.10	50	49	10	7.0
Mill F2	1.4	0.002	3	0.003	0.10	0.10	50	49	10	7.0
Mill G	6.2	0.00	4.3	0.0027	0.10	0.10	50	44	10	5.7
Mill H	2.16	0.00	0.32	0.0003	0.10	0.10	50	48	10	9.7
Mill I	38	0.04	12	0.01	0.10	0.05	50	12	10	-2.0
Mill J	102	0.002	17	0.016	0.10	0.08	50	-52	10	-7.0
Mill K	15	0.01	8	0.009	0.10	0.08	50	35	10	1.8
Mill L	1	0.00	2	0.0005	0.10	0.10	50	49	10	8.5
Mill M	8	0.00	2	0.001	0.10	0.10	50	42	10	8.0

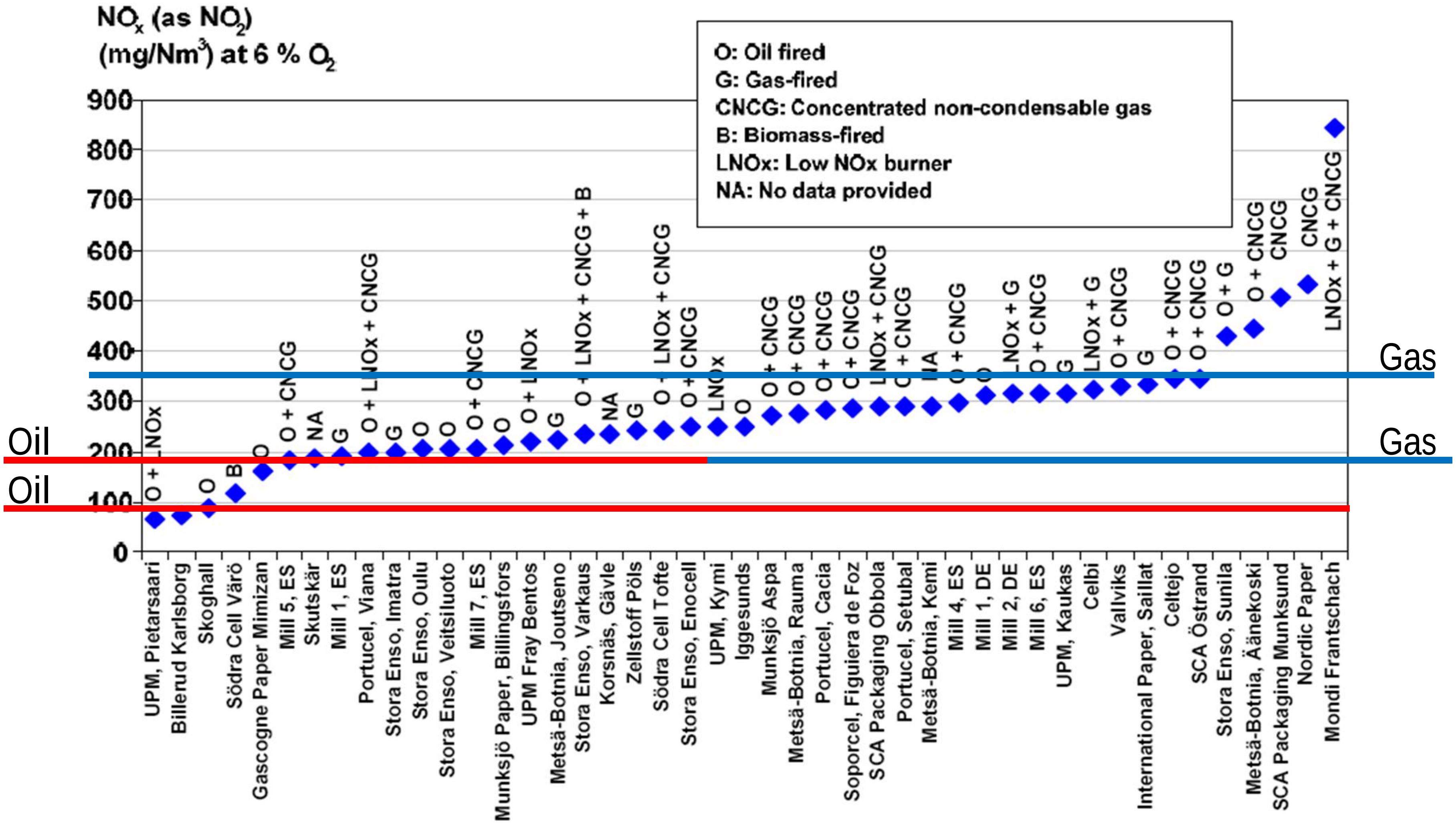
NOx and CO from Lime kiln
Table 8.12 p. 786



Parameter		**Daily average** mg/Nm^3 at 6 % O_2	**Yearly average** mg/Nm^3 at 6 % O_2	**Yearly average** kg NO_2/ADt
NO_X	**Oil**	100 – 250	100 – 200	0.1 – 0.2
	Gas / biofuel	200 – 400	200 – 350	0.1 – 0.3
Carbon monoxide		< 50	< 50	-

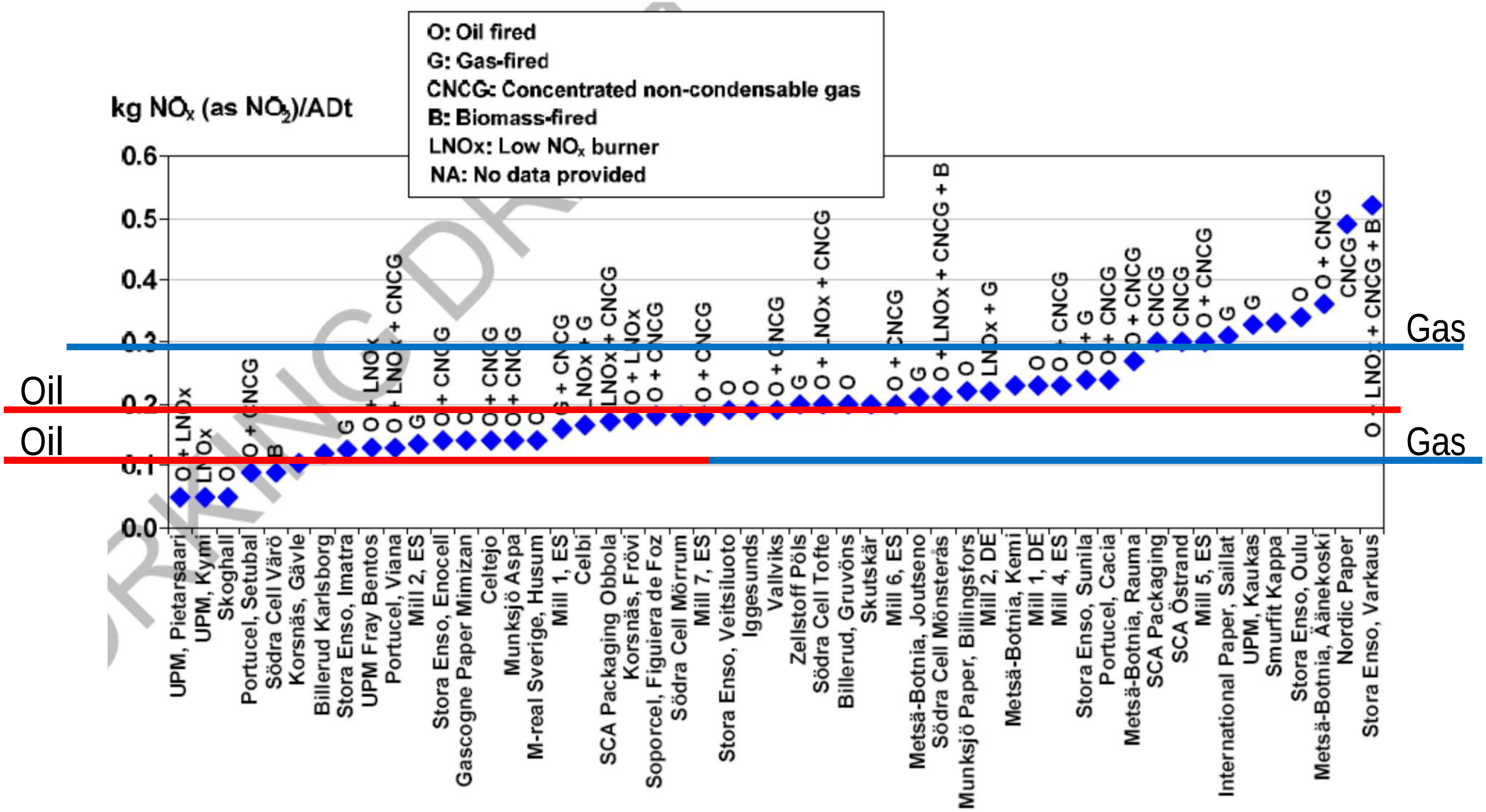
(^{1}) If nitrogen-containing CNCGs are burnt in the lime kiln instead of in the NCG burner, the BAT-AEL mentioned may be increased by 0.1 kg NOx/ADt for the specific load and by 100 mg/Nm^3 for the concentration levels.

NOx emission from lime kiln
Oil 100 – 200 Gas/BF 200 – 350 mg/Nm^3



NOx emission from lime kilns

fired with different fuels, CNCG, kg/ADt (EU IPPC, 2011)



Ten out of fourteen lime kilns need to invest to reduce NOx

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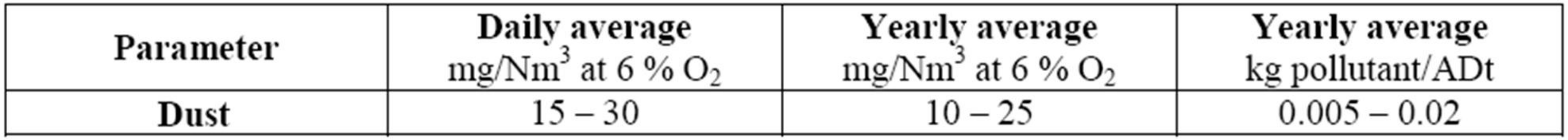
	Emission		Reported	Fit	Limit		Limit	
	mg /Nm^3	kg NO$_2$/ADt	Nm^3/Adt	Nm^3/Adt	kg NO$_2$/ADt	diff.	mg /Nm^3	diff.
Mill A	445	0.36	819	809	0.30	**-0.06**	300	**-145**
Mill B	225	0.21	1000	933	0.30	0.09	350	125
Mill C	292	0.23	767	788	0.30	0.07	350	**58**
Mill D	240	0.27	572	1125	0.30	0.03	300	**60**
Mill E	250	0.14	1000	560	0.30	0.16	300	50
Mill F1	200	0.125	300	313	0.30	0.18	350	**150**
Mill F2	200	0.125	300	313	0.30	0.18	350	**150**
Mill G	205	0.34	636	1659	0.20	**-0.14**	200	**-5**
Mill H	431	0.24	528	557	0.20	**-0.04**	200	**-231**
Mill I	445	0.52	1000	1169	0.30	**-0.22**	300	**-145**
Mill J	205	0.19	250	927	0.20	0.01	200	**-5**
Mill K	317	0.33	760	1038	0.30	**-0.03**	350	33
Mill L	250	0.05	303	200	0.30	0.25	350	100
Mill M	65	0.05	750	765	0.20	0.15	200	135

None out of fourteen lime kilns need to invest to reduce CO

	Emission		Limit		Limit	
	mg /Nm^3	kg CO/ADt	kg COADt	diff.	mg /Nm^3	diff.
Mill A	34		XX		50	16
Mill B	7		XX		50	43
Mill C	10		XX		50	40
Mill D	34		XX		50	16
Mill E	15		XX		50	35
Mill F1	4		XX		50	46
Mill F2	21		XX		50	29
Mill G	5		XX		50	45
Mill H	9		XX		50	41
Mill I	45		XX		50	5
Mill J	6		XX		50	44
Mill K	-		XX		50	
Mill L	-		XX		50	
Mill M	-		XX		50	

Dust from Lime kiln
Table 8.13 p. 786



Parameter	**Daily average** mg/Nm^3 at 6 % O_2	**Yearly average** mg/Nm^3 at 6 % O_2	**Yearly average** kg pollutant/ADt
Dust	15 – 30	10 – 25	0.005 – 0.02

Dust emission from lime kiln, 10 – 25 mg/Nm^3

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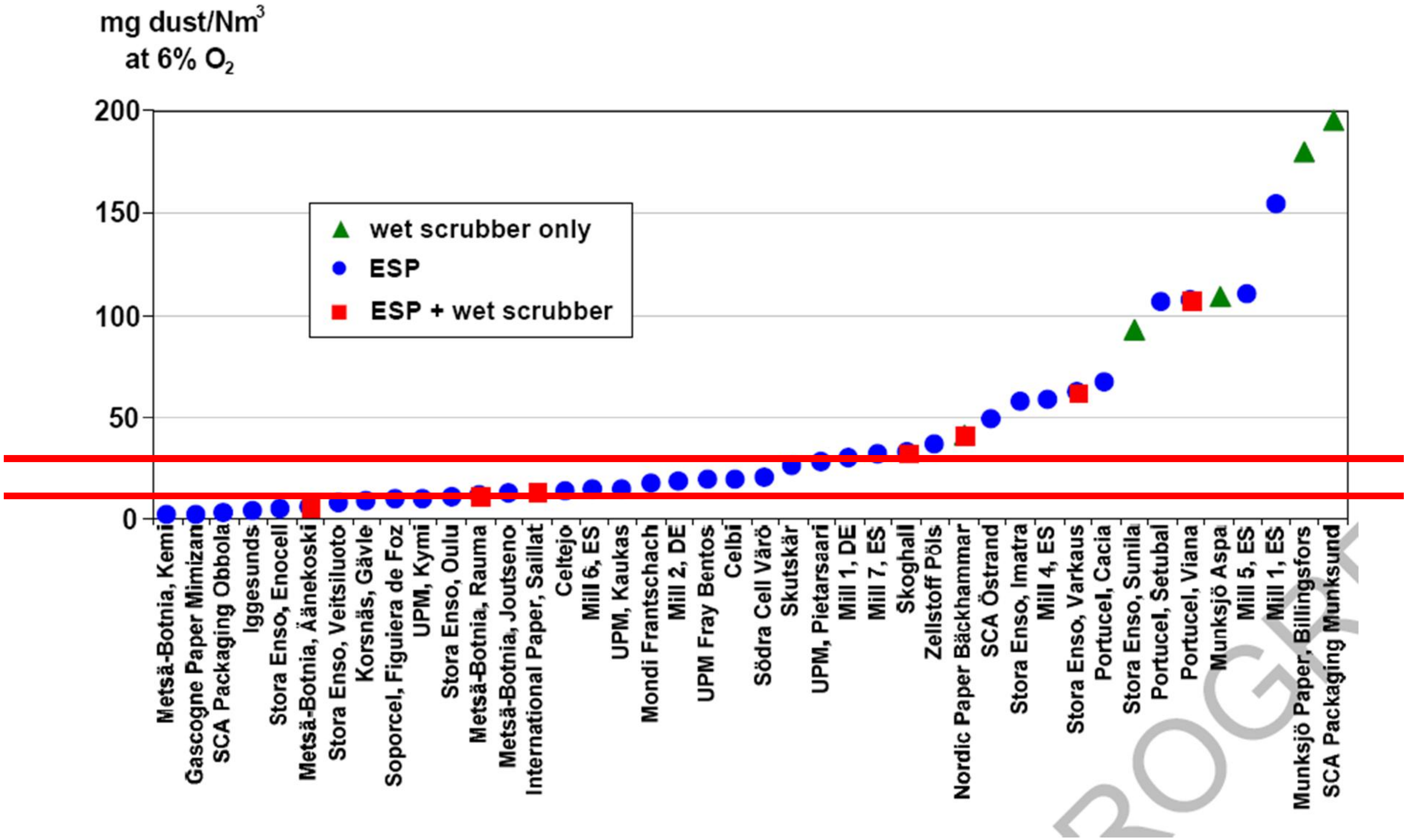
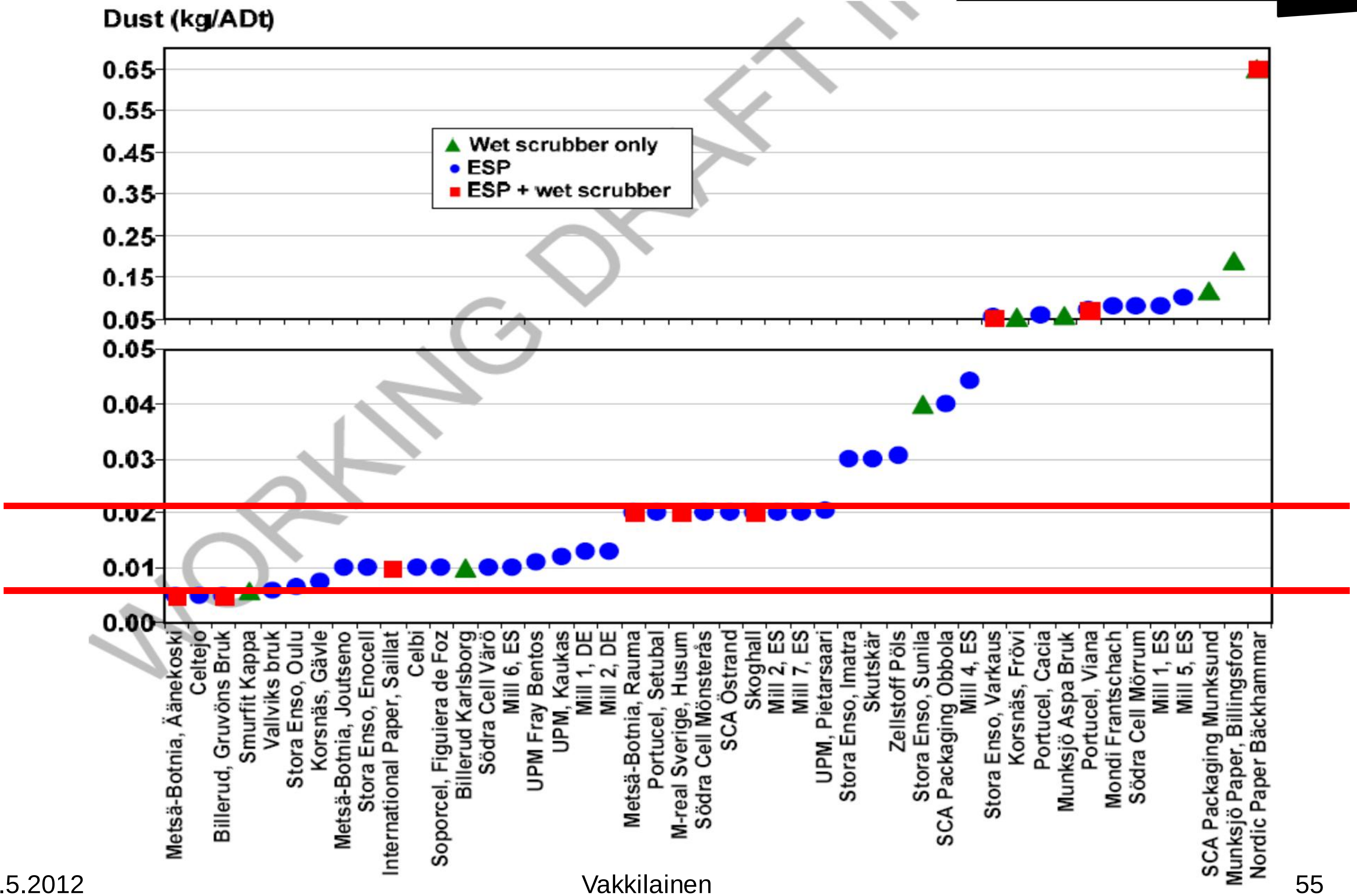


Dust emission from lime kiln, 0.005 – 0.02 kg/ADt



Five out of fourteen lime kilns need to invest to reduce dust

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	Emission	Limit			Limit	
	mg /Nm^3	kg dust/ADt	kg dustADt	diff.	mg /Nm^3	diff.
Mill A	6	0.01	0.02	0.02	25	19
Mill B	12	0.01	0.02	0.01	25	13
Mill C	2	0.00	0.02	0.02	25	23
Mill D	10	0.02	0.02	0.00	25	15
Mill E	5	0.01	0.02	0.01	25	20
Mill F1	57	0.03	0.02	**-0.01**	25	**-32**
Mill F2	57	0.03	0.02	**-0.01**	25	**-32**
Mill G	11	0.01	0.02	0.01	25	14
Mill H	93	0.04	0.02	**-0.02**	25	**-68**
Mill I	50	0.05	0.02	**-0.03**	25	**-25**
Mill J	8	0.003	0.02	0.02	25	17
Mill K	14	0.01	0.02	0.01	25	11
Mill L	10	0.00	0.02	0.02	25	15
Mill M	28	0.02	0.02	0.00	25	**-3**

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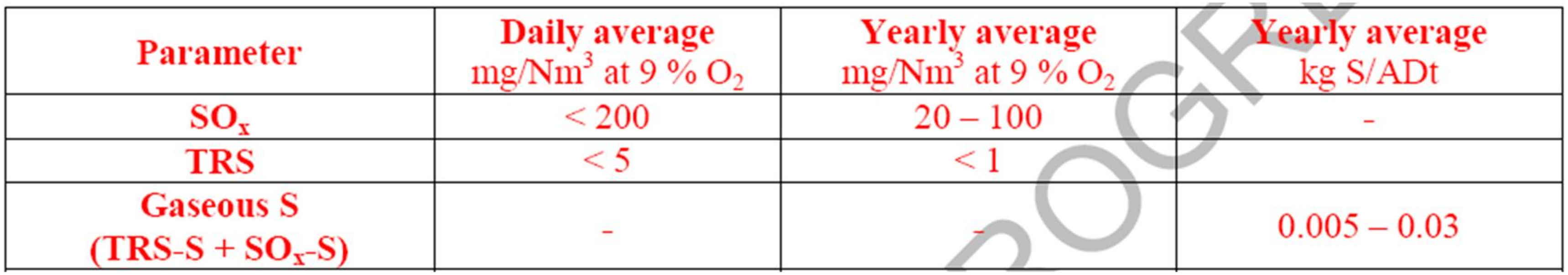
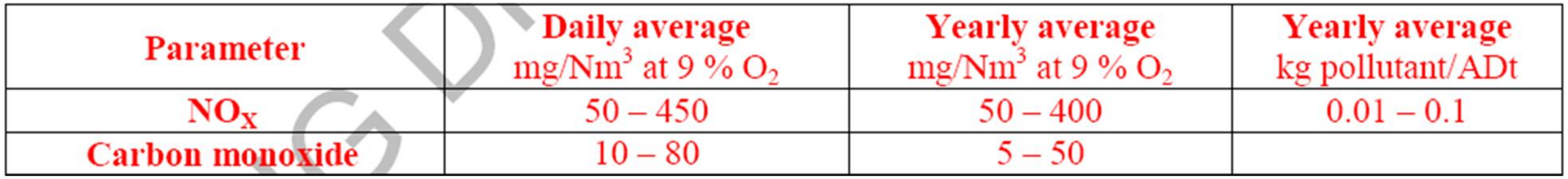
Emissions to air NCG

TRS burner



Parameter	Daily average mg/Nm^3 at 9 % O_2	Yearly average mg/Nm^3 at 9 % O_2	Yearly average kg S/ADt
SO_x	< 200	20 – 100	-
TRS	< 5	< 1	
Gaseous S (TRS-S + SO_x-S)	-	-	0.005 – 0.03



Parameter	Daily average mg/Nm^3 at 9 % O_2	Yearly average mg/Nm^3 at 9 % O_2	Yearly average kg pollutant/ADt
NO_X	50 – 450	50 – 400	0.01 – 0.1
Carbon monoxide	10 – 80	5 – 50	

TRS below 1 mg/Nm^3 seems extremely tight

NOx below 400 mg/Nm^3 seems extremely tight

Almost all NCG burners need to reduce SO_2 and TRS

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	Emission		Emission		Limit		Limit		Limit	
	mg /Nm^3	kg SO_2/ADt	Nm^3/Adt	kg TRS/ADt	kg SO_2+TRS/ ADt	diff.	mg /Nm^3	diff.	mg /Nm^3	diff.
Mill A	53000	1.02	280	0.005	0.03	**-1.00**	100	**-52900**	1	**-279.0**
Mill B										
Mill C										
Mill D										
Mill E	15	0.03	3	0.0002	0.03	0.00	100	85	1	**-2.0**
Mill F	18	0.00	0.96	0.0005	0.03	0.03	100	82	1	0.0
Mill G										
Mill H	129.6	0.01	129.6	0.0002	0.03	0.02	100	100	1	**-128.6**
Mill I										
Mill J										
Mill K		0.32	6	0.003	0.03	**-0.29**	100	100	1	**-5.4**
Mill L		0.00	3.6	0.001	0.03	0.03	100	100	1	**-2.6**
Mill M										

Two NCG burners need to reduce CO

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	Emission		Limit		Limit	
	mg /Nm^3	kg CO/ADt	kg COADt	diff.	mg /Nm^3	diff.
Mill A	152		XX		50	**-102**
Mill B						
Mill C						
Mill D						
Mill E	350		XX		50	**-300**
Mill F	15		XX		50	35
Mill G						
Mill H	5		XX		50	45
Mill I						
Mill J						
Mill K						
Mill L	30		XX		50	20
Mill M						

Four NCG-burners need to reduce NOx

	Emission		Reported	Fit	Limit		Limit	
	mg /Nm^3	kg NO$_2$/ADt	Nm^3/Adt	Nm^3/Adt	kg NO$_2$/ADt	diff.	mg /Nm^3	diff.
Mill A	1411	0.05	36	35	0.10	**0.05**	400	**-1011**
Mill B								
Mill C								
Mill D								
Mill E	400	0.20	180	500	0.10	-0.10	400	0
Mill F	1700	0	216	59	0.10	0.00	400	**-1300**
Mill G								
Mill H	309	0.04	142.8	129	0.10	**0.06**	400	91
Mill I								
Mill J								
Mill K	1256	0.22		175	0.10	**-0.12**	400	**-856**
Mill L	1500	0.18	204	120	0.10	-0.08	400	**-1100**
Mill M	400	0.00	247	3	0.10	0.10	400	0

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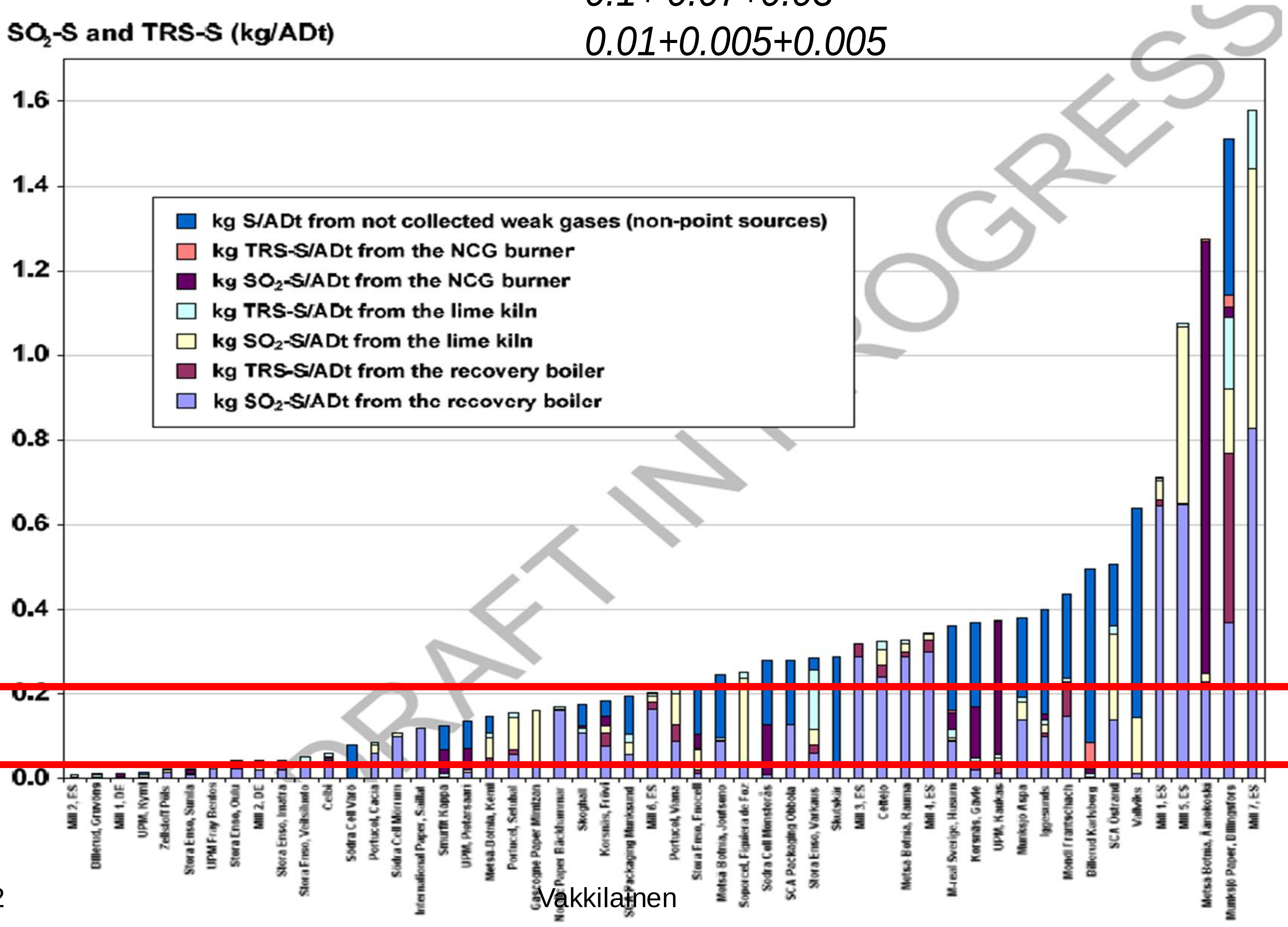
Emissions to air process

Total S emission from process

RB+LK+NCG, kg/ADt (EU IPPC, 2011)

0.1+ 0.07+0.03

0.01+0.005+0.005

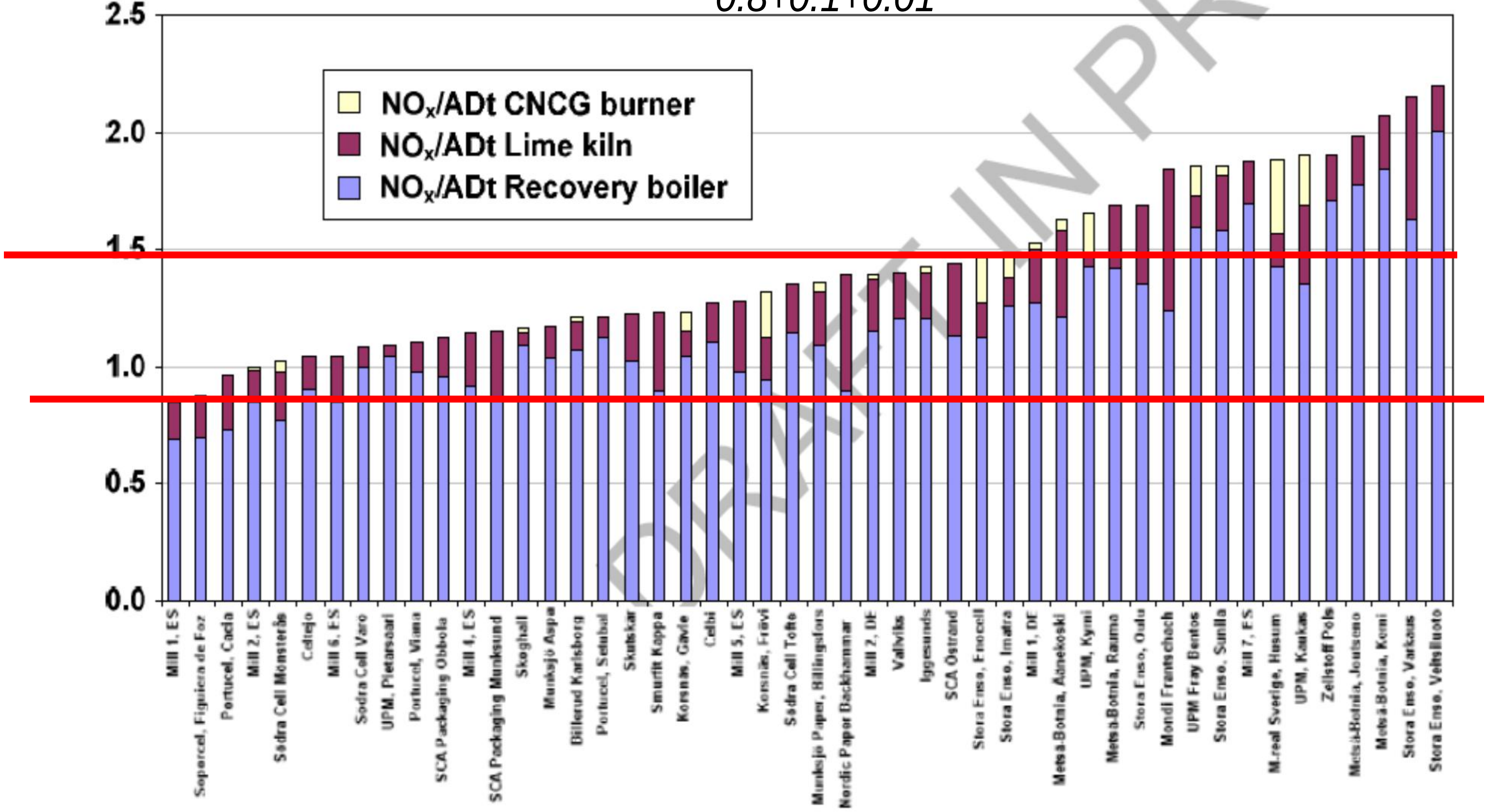


NOx emission from process

RB+LK+NCG, kg/ADt (EU IPPC, 2011)

1.2+ 0.2+0.1

0.8+0.1+0.01



Suggested vs. real BAT table NOx kg/Adt is stricter than mg/Nm^3

	Emission	Pine, 46%	Birch, 53%	Euca, 56%	Emission
	mg/Nm^3	Nm^3/ ADt	Nm^3/ ADt	Nm^3/ ADt	kg NO$_2$/ADt
Recovery boiler	200	7500	6200	4800	1.50, 1.24, 0.96
Lime kiln	250	780	650	600	0.20, 0.16, 0.15
CNCG boiler	400	100	100	100	0.04
Total	N.A.				1.74, 1.44, 1.15

	Suggested	Pine, 46%	Birch, 53%	Euca, 56%	Emission
	mg/Nm^3	mg/Nm^3	mg/Nm^3	mg/Nm^3	kg NO$_2$/ADt
Recovery boiler	200	160	220	290	**1.2**, 1.4, 1.4
Lime kiln	200	250	300	330	0.2, 0.2, 0.2
CNCG boiler	400	1000	1000	1000	0.1
Total					**1.5,** 1.7, 1.7

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Energy consumption

BAT energy consumption

Electricity

- market pulp mill 660 – 750 kWh/ADt
- +100 kWh/ADt if making of own chemicals
- market pulp mill 500 – 550 kWh/ADt if new eucalyptus
-

In the next BAT BREF more data is asked and then BAT is done based on 10 % and 50 %.

Bat Energy consumption

- Should be states that energy consumption is for 100 % MCR load.
- For partial loads energy use is less but specific energy use is larger.
- For few tons production specific energy use is hunderds of times the 100 % MCR load use.

Minor errors still in the document

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- P.212 At the Zellstoff Stendal mill in Germany about 13 450 t tall oil are produced **each year** by decantation of tall oil soap from the black liquor before evaporation.
- P.212 methanol and red oil not mentioned
- P.213 reference of the figure
- P.213 There are half a dozen mills than concentrate eucalyptus to 80 % or higher.
- P. 225 Figure 3.5 contains Gruvön and Skärblacka where also NSSC p.369, they also contain numerous sites where also mechanical pulp, many have integrated paper or board manufacture and even sawmills, and board manufacture. This also applies to P. 226 Figure 3.6, P. 231 Figure 3.8, P. 232 Figure 3.9, P. 234 Figure 3.13, P. 236 Figure 3.15, P. 249 Table 3.16
- P. 226 3.2.2.5 E**m**issions to water

Minor errors still in the document

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- P.228 About 8 – 10 m^3/**AD**t of total condensates are formed with an organic load of about 20 – 30 kg COD/**AD**t or 7 – 10 kg BOD_5/**AD**t. The COD is mainly methanol (5 – 10 kg/**AD**t) with some ethanol and a number of organic sulphuric compounds (1 – 2 kg TRS/**AD**t), 1 – 2 kg turpentine and inorganic nitrous compounds. … About 7 – 9 m^3 of weaker condensates are formed with an organic load that ranges from 0.5 to 2 kg COD/m^3 containing a total of about 8 – 12 kg of COD/**AD**t of pulp.
- P.238 “Table 3.13 should have a range of black liquor properties, not collected from once source and two special cases” has not been reacted on. Data has been sent.

LIITE IV

POPE
Itä-Suomen Yliopisto
kokouspöytäkirja 4.4.2012

4.4.2012

Polttoperäisten päästöjen ja nanohiukkasten haitallisuuden määrittäminen uudella tutkimusmenetelmällä, POPE

Johtoryhmän 3. Kokous
Melania 220, Kuopion Kampus 4.4.2012

1. Kokouksen avaus 9.32
2. Läsnäolijat
   a. Maija Riitta Hirvonen, UEF
   b. Pekka Matilainen, Ecocat Oy
   c. Timo-Pekka Veijonen Stora Enso/ Soodakattilayhdistys
   d. Juha Timonen, Tulikivi Oyj
   e. Tarmo Hatunen, MW Power Oy
   f. Mikko Happo, UEF
   g. Kari Lehtinen, FMI
   h. Heidi Niskanen, FMI
   i. Stefanie Kasurinen, UEF
   j. Ari Leskinen, FMI
   k. Terhi Kaivosoja, UEF
   l. Kari Kuuspalo, UEF
   m. Jorma Jokiniemi, UEF
   n. Pasi Jalava, UEF
3. Puheenjohtajan ja sihteerin valinta:
   Puheenjohtajaksi ehdotettiin Maija-Riitta Hirvosta ja sihteeriksi Pasi Jalavaa. Hyväksyttiin puheenjohtajan ja sihteerin valinta.
4. Esityslistan hyväksyminen:
   Muutetaan vuosiluku 2012
   Lisätään edellisen kokouksen pöytäkirjan hyväksyminen
5. Edellisen kokouksen pöytäkirjan hyväksyminen: Ei muutoksia, hyväksytään pöytäkirja.
6. Projektin tilannekatsaus:
   -Kari Kuuspalo esitti projektin tilanteen Vitrocell-altistuslaitteistoon tehtyjen muutosten osalta. Nämä periaatteessa valmiiseen kaupalliseen laitteistoon tehtävät muutokset ovat vaatineet runsaasti työtä projektin tässä vaiheessa. Muutoksilla saatiin kuitenkin tehtyä Vitrocellistä parempi hiukkasdepositioiden osalta. Aerosoli-inletin lyhentäminen sai aikaan paremman deposition ja pienemmän hiukkasten häviön linjastoon. Ikääntymiskammio ja siitä solualtistukseen johtava näytelinja ovat valmiit.

   - Jorma Jokiniemi kävi läpi projektin projektisuunnitelman ja tavoitteet. Käytiin läpi eri päästötilanteet, joita projektissa on tarkoitus tutkia. Myös tuleva aikataulu käytiin läpi tähän saakka on tehty pääosin Laitteiston testausta ja validointia. Seuraavaksi projektissa tutkitaan dieselmoottorista peräisin olevia päästöjä ja niiden käyttäytymistä muutuntakammiossa ja solualtistuksissa. Kattiloiden osalta tehtiin tarkennuksia, hakekattilakokeet tehdään Siilinjärven Vuorelassa sijaitsevassa lämpölaitoksessa (Savon Voima). Jorma Jokiniemi esitteli myös lyhyesti vitrocellin rakennetta ja käyttöä soualtistuksiin.Sovittiin, että aikataulu soodakattiloiden osalta käsitellään erikseen ja yliopisto tekee tarjouksen lisäkattiloista Soodakattilayhdistyksen toiveiden mukaan. esim soodakattiloiden osalta. Todettiin myös, että tutkimussopimus on hyväksytty ja kaikki osapuolet ovat allekirjoittaneet

- StefanieKasurinen esitteli hopeanaohiukkasilla tehtyjen solualtistuskokeiden tuloksia. Hopeahiukkaset aiheuttavat etenkin IL-8 tuotantoa, mutta myös proinflammatorista tulehdusvastetta Menetelmäkehitys etenee, ja luvassa on kiinnostavia toksikologisia tuloksia pienemmällä hajonnalla, kun laitteisto on saatu paranneltua.
- Seuraavaksi Heidi Niskanen esitteli mallinnustuloksia, joita on tehty Vitrocellin altistusosan putkesta. Myös laitteiston geometria esiteltiin, sekä ongelmat, joita on havaittu jakaumassa. Jakauma on epätasainen, koska imuilma otetaan vain altistuskannen toisesta reunasta. Laitteistoa on muokattu laittamalla suodatin imuilman ja poistoreikien väliin, joka tasaa virtausta aukoissa.

Suunnitelman muutoksia kattiloista kerättävän aerosolin pölytyksen osalta. Pölytytys ei todennäköisesti onnistu alkuperäisen suunnitelman mukaan aerosolien huonon dispergoitumisen yms. osalta. Ehdotus on, että kerätään DGI impactorilla ja uutetaan perinteisellä menetelmällä. Vertailuna näihin voidaan käyttää aikaisempia tuloksia. Pölytystä varten joutuisi keräämään huomattavan pitkään ja riski olisi että ei saada edustavaa näytettä.

Terhi Kaivosoja esitteli tuloksia Bioher projektista päästöjen osalta. Päästöt olivat erilaisia eri polttotilanteiden välillä. Sähkösuodattimella saatiin päästöjä vähennettyä huomattavasti. Pasi Jalava esitteli vastaavia tuloksia toksikologisista vasteista. Tuloksissa havaittiin mielenkiintoinen piirre, jossa sähkösuodattimen jälkeen kerätty näyte oli huomattavasti aktiivisempi kuin enne sitä kerätty. Tuloksissa erilaisista hyvän polton komponenteista näytti siltä, että sinkkioksidi voisi olla näiden havaittujen korkeiden vasteiden taustalla.

-
- Tutkimusaikataulu soodakattiloiden osalta: Sovitaan yhteyshenkilöiden kanssa tarkemmin
- UPM Kymmene Kymi, Kouvola (Kuusankoski); Teija Ahola

  - uusi soodakattila, sekalipeä, pesurilla varustettu savukaasujen puhdistus, meesauuni vain tästä tehtaasta

- Metsä Fibre Joutseno, Lappeenranta (Joutseno); Hilkka Hännikäinen
-
-
  - suhteellisen hyväkuntoinen ylikuormainen kattila, havulipeä.
-
- Stora Enso Sunila, Kotka; Terttu Heinonen
  - kaksi vanhaa ylikuormaista kattilaa, havulipeä
  - tehdas haluaa molempien kattiloidensa pienhiukkasmäärät mitattaviksi
- Mitattavia parametreja esim. hiukkaspäästön pitoisuus, lentotuhka (K, Cd, Ca)
- Perus päästömittaukset ja DGI keräykset, toksikologia ja kemialliset analyysit.
- Selvitetään mittauspaikoilla yhteet yms. ja tehdään kustannusarvio ja lähetetään soodakattilayhdistykselle. Symo Oy toteuttaa osan keräyksistä ja Itä-Suomen yliopisto

vastaa suodatinkeräyksistä toksikologiaa varten. Tulosten julkaisemisesta neuvotellaan tehtaiden ja soodakattilayhdistyksen kanssa.Tehtaiden seisokit yms. otetaan huomioon.

- Hakelaitoksen keräykset jätetään ensi talveen, jotta kuormat vastaavat todellista tilannetta lämmityskaudella. Keräykset toteutetaan Savon Voiman Tiprusniemen tai Vuorelan lämpölaitoksessa Siilinjärvellä.
-

7. Muita esille tulevia asioita
   -Abstrakteja lähetetään EAC ja AAAR tieteellisiin kokouksiin.
   - Avajaistilaisuus 12.6 klo 10-13 Ilmansaasteiden haitallisuuden tutkimuslaitteisto -hanke, Rehtori avaa tilaisuuden, johtoryhmälle ja yhteistyökumppaneille lähetetään kutsut
   - Soodakattilayhdistyksen sihteerille Markus Nieminen (@poyry.com) tiedot hankkeesta, pöytäkirjat yms.
   - Ecocat osalta vaihdetaan johtoryhmän jäsen Toni Kinnunen ->Pekka Matilainen

8. Seuraava kokous
   - vko 40 ke 3.10.2012, 13.00-16.00
9. Puheenjohtaja päätti kokouksen klo. 11.22

Kuopiossa 24.4.2012

Maija-Riitta Hirvonen	Pasi Jalava

LIITE V

Soodakattilan päästöhiukkasten fysikaalis-kemialliset ja toksikologiset ominaisuudet (SOTOX)
Itä-Suomen Yliopisto
tarjous 23.5.2012

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Kuopion kampus
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FAKSI 017 162 131

Savonlinnan kampus
Kuninkaankartanonk. 5
PL 86, 57101 Savonlinna
FAKSI 015 531 060

Puhelinvaihde:
0294 45 1111

www.uef.fi

Tarjous

TUTKIMUSSUUNNITELMA

Soodakattilan päästöhiukkasten fysikaalis-kemialliset ja toksikologiset ominaisuudet (SOTOX)

Osallistujat:

Itä-Suomen Yliopisto

Maija-Riitta Hirvonen, Ph.D., professori
- Pasi Jalava, Ph.D, Mikko Happo, Ph.D, Oskari Uski, Ph.D. student

Jorma Jokiniemi, Ph.D., professori
- Kari Kuusapalo, Development Manager, N.N, MSc student, Ilpo Nuutinen, MSc student

1 LÄHTÖKOHTA JA TAVOITTEET

Hankkeen tavoitteena on:

- Selvittää soodakattilan hiukkaspäästöjen kemiallisen koostumuksen ja toksikologisten ominaisuuksien välistä yhteyttä
- Lisäksi verrataan laitosten soodakattilan hiukkaspäästöjen välisiä eroja niiden toksissa ja kemiallisissa ominaisuuksissa

2 TOIMENPITEET

2.1 NÄYTTEEN KERÄYKSET (Prof. Jorma Jokiniemi)

Kokeissa mitataan/kerätään kaasumaiset päästöt, hiukkaspäästöt (TSP, PM2.5) ja näiden hiukkasten fysikaalis-kemialliset ominaisuudet. Lisäksi kerätään näytteet toksisuuskokeita varten.

Päästöistä mitataan SFS standardien mukaan hiukkasten kokonaispitoisuudet, NOx, CO, CO2, SO2 ja O2 pitoisuudet sekä savukaasun tila ja virtaama Lisäksi kerätään toksisuusnäytteet UEF:n FINE laboratoriossa kehitetyllä sykloni-impaktori-menetelmällä sekä analysoidaan näistä näytteistä PAH ja epäorgaanisten koostumus.

Pienhiukkasnäytteet kerätään teflonsuodattimille, jotka on eivät aiheuta käytettävissä toksikologisissa analyyseissä vasteita. Ennen keräyksiä suodattimet pestään metanolilla, kuivataan ja punnitaan.

Keräysten jälkeen suodattimet punnitaan ja suodattimelle kerätyt pienhiukkaset uutetaan metanolilla ja kuivataan kemiallisia ja toksikologisia analyysejä varten.

2.2 PÄÄSTÖJEN KEMIALLINEN KARAKTERISOINTI

(Prof. Jorma Jokiniemi)

Kerättyjen näytteiden epäorgaanisen aineksen koostumus analysoidaan IC:llä (ionikromatograafi) (K, Na, Cl, SO_4), karbonaatit määritetään termis-optisella menetelmällä. Metallit analysoidaan ICP-MS:llä (inductive coupled mass spectrometer). Lisäksi analysoidaan 30 PAH yhdistettä GS-MS menetelmällä.

2.3 TOKSIKOLOGINEN KARAKTERISOINTI

(Prof. Maija-Riitta Hirvonen)

Kerättyjen näytteiden toksikologiseen karakterisointiin käytetään nisäkässolumallia, jossa elistön puolustusjärjestelmän soluja altistetaan pienhiukkasille ja mitaan hengitys–ja sydänsairauksien riskiä kuvastavia tulehduksen ja solukuoleman biokemiallisia merkkiaineita. Lisäksi mitataan syöpäriskistä kertovaa genotoksisuutta (perimämyrkyllisyyttä).– Hiukkasten kemian (PAH-yhdisteet, alkuaineet ja, ionit) ja toksisuuden yhteydet mallinnetaan. (Taulukko 1)

Taulukko 1 : Analysoitavat näytteet, solualtistukset ja toksikologiset analyysit

	Kattila 1 POPE	**Kattila 2**	**Kattila 3**	**Kattila 4**	**Blankit**	**Yhteensä**
Nättteet						
PM 1	**1 + Blank**	**1**	**1**	**1**	**3**	**6**
Solualtistukset						
Altistukset tulehduksen ja solukuoleman markkereiden määrityksiin						
4 annosta /näyte	4	4	4	4	12	**24**
3 altistuskertaa /näyte	12	12	12	12	36	**72**
Altistukset genotoksisuuden määrityksiin						
4 annosta /näyte	4	4	4	4	12	**24**
2 altistuskertaa/ näyte	8	8	8	8	24	**48**
Analyysit						
Tulehdus						
• Sytokiinit	72	72	72	72	48	**264**
Solukuolema						
• Nekroosi	24	24	24	24	12	**84**
• Apoptoosi	24	24	24	24	12	**84**
• Solusykli analyysit	24	24	24	24	12	**84**
Genotoksisuus						
• Comet assay	24	24	24	24	12	**84**
Analyysien kokonaismäärä	**284 POPE (ei kuluja)**					**852**

2.3.1 Solualtistus

Hiiren RAW264.7 makrofageja (ATCC, American Type Culture Collection) kasvatetaan hiilidioksidi-inkubaattorissa (+37 °C, CO_2 5 %) RPMI1640 soluviljelymediumissa (10 % FBS-seerumi, 2 mM l-glutamiini ja 100 U/ml penisilliini-streptomysiini). Soluja altistetaan annosvasteisesti (37°C, 5 % CO_2) vuorokauden ajan, jonka jälkeen näyte sentrifugoidaan (380 g, 10min) ja supernatantti pakastetaan sytokiinimäärityksiä varten (-70°C). Altistetut solut käytetään solujen elävyyden ja solukuoleman selvittämiseen.

2.3.2 Mitattavat terveyshaittoja indikoivat biokemialliset vasteet

Tulehdus

- **Typpioksidimääritys (NO): Solujen** typpioksidituotanto mitataan määrittämällä stabiilia metaboliittia nitriittiä spektrofotometrisesti Griess:n menetelmällä.
- **Sytokiinimääritykset:** Altistetuista näytteistä määritetään seuraavat käynnistyneestä tulehdusreaktiosta kertovat sytokiinit solujen tuottamina proteiineina. (IL-1, IL-6, MIP-2 TNFα) ELISA (enzyme-linked immunosorbent assay)–kitin avulla (R&D systems, MN, USA). Tulokset mitataan spektrofotometrisesti ja niitä verrataan altistamattomien kontrollisolujen tuottamiin tulehdusvälittäjäaineisiin.

Solukuolema

- ***MTT-testi.*** Solujen elävyys mitataan spektrofotometrisesti määrittämällä toimivien mitokondrioiden määrää altistetuissa soluissa.
- ***Solusyklianalyysi.*** DNA:n määrä soluissa analysoidaan propidiumjodidi (PI) värjätyistä permeabilisoiduista soluista virtaussytometrin (Beckman Coulter) avulla. Analyysistä saadaan selville makrofagien solusyklin vaiheet.
- ***Ohjelmoitu solukuolema (Apoptoosi).*** Solusyklianalyysistä saadaan selville myös apoptoottisten solujen osuus kokonaissolumäärästä
- ***Hallitsematon solukuolema (Nekroosi).*** Nekroottisten solujen osuus määritetään PI-värjätyistä tuoresolunäytteistä virtaussytometrilla (Beckman Coulter). Tuorevärjäyksessä PI-väriaine värjää nekroottisten solujen sisältämän DNA:n, mutta ei läpäise muiden solujen solukalvoa.

Genotoksisuus

- Altistetuista soluista analysoidaan perimävaurioita ns. komeettatestillä. Tämä genotoksisuustesti mittaa DNA-vauriota juostekatkoksina.

2.4. RAPORTOINNIT

Tuloksista raportoidaan projektin seurantakokouksissa ja väliraporteissa. Tutkimustuloksista laaditaan tieteellisiä julkaisuja ja kansantajuisia lehtiartikkeleja. Tuloksia esitellään kansallisissa ja kansainvälisissä seminaareissa. Julkaisujen sisällöstä sovitaan hankkeeseen osallistuvien kanssa.

3 AIKATAULU

Tutkimus toteutetaan 2012-2013, Osakokonaisuuksien ajoitus on esitetty Taulukossa 2.

Taulukko 2. Tutkimusaikataulu.

	2012							2013				
Kuukausi	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*1*	*2*	*3*	*4*	*5*
Näytteiden keräykset	🟫	🟫										
Näytteiden uutto analyyseihin		🟩	🟩									
Kemialliset analyysit			🟩	🟩	🟩	🟩						
Solualtistukset			🟩	🟩	🟩							
Solukuoleman määritykset			🟩	🟩	🟩	🟩	🟩					
Tulehdus markkereiden analyysit				🟩	🟩	🟩	🟩	🟩				
Genotoksisuuden määritykset					🟩	🟩	🟩					
Data-analyysit						🟩	🟩	🟩	🟩	🟩		
Raportointi								🟩	🟩	🟩	🟩	🟩

4 KUSTANNUSARVIO

Hankkeen kokonaiskustannukset ovat 135 671 EUR. sisältäen arvonlisäveron.

VÄLITTÖMÄT KUSTANNUKSET		**68 500**
Henkilöstökustannukset		***46 050***
Välittömät palkka- ja palkkiokustannukset		30 700
Henkilösivukustannukset kokonaiskustannusmallin mukaan	50 %	15 350
Muut kustannukset		***22 450***
Aineet ja tarvikkeet		5 600
Matkakustannukset		4 000
Palvelujen ostot		22 877
Muut kustannukset (sis. <10 000 € laitteet)		
VÄLILLISET KUSTANNUKSET		**31 775**
Yleiskustannukset	69 %	31 775
KOKONAISKUSTANNUKSET		**110 302**
Arvonlisävero*		25 369
ARVONLISÄVEROLLINEN ULKOINEN HINTA		**135 671**

Kuopiossa 23.5. 2012

Maija-Riitta Hirvonen, Professori, varadekaani

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p.050-3525160
email. Maija-Riitta.Hirvonen@uef.fi

LIITE VI

Muiden työryhmien kuulumiset

KTR kokous

14.6.2012

Työryhmien toiminta

Valmistuneet projektit

Työryhmien toiminta

Käynnissä olevat projektit

ATR projektit

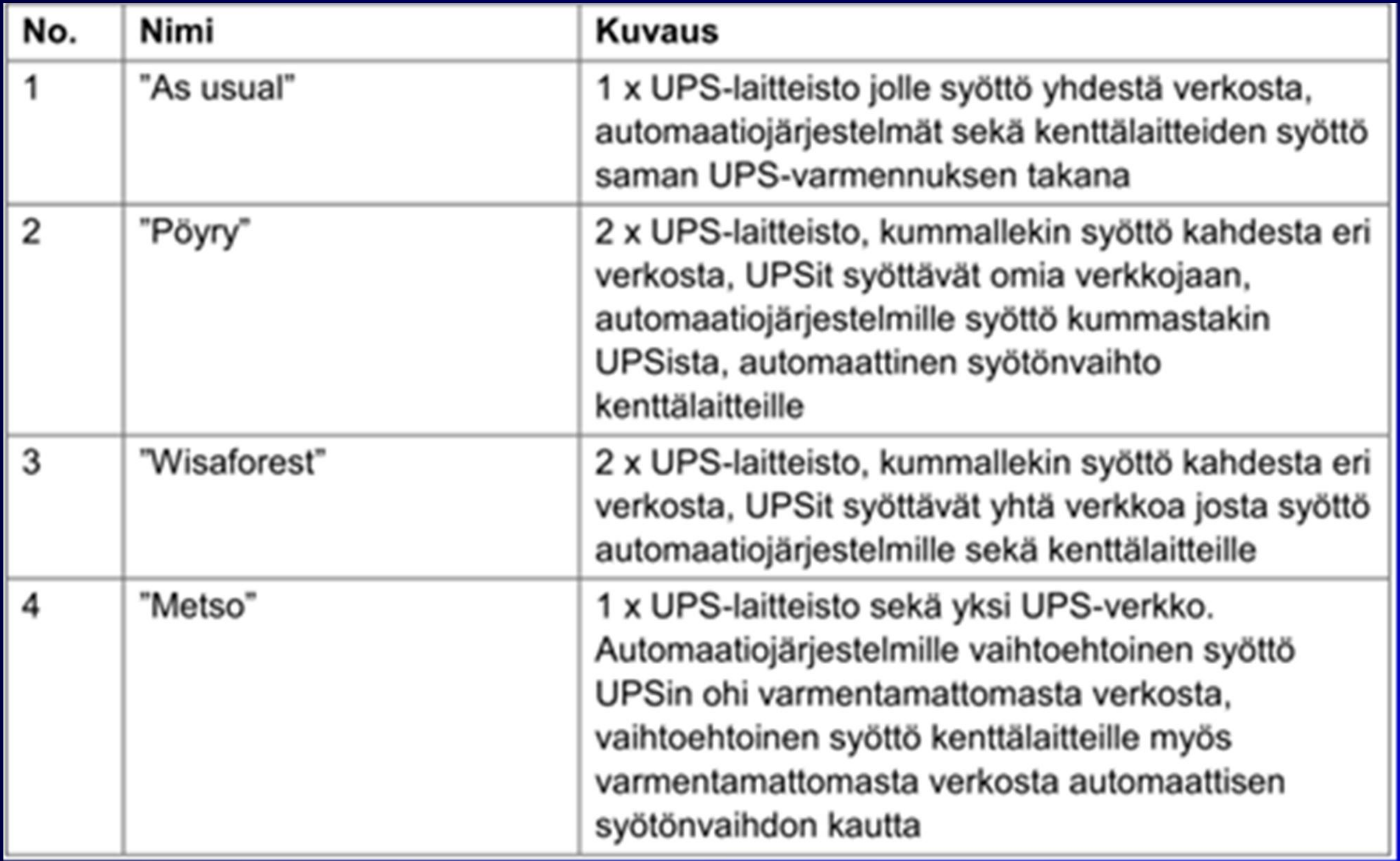
ATR: Ohje UPS-järjestelmän periaatteeksi

- Vertaillaan vikapuuanalyysin avulla neljää eri UPS-kytkentävaihtoehtoa,
  - Vikapuuanalyysien laadinnan työkaluna käytettiin OpenFTA-nimistä freeware-ohjelmaa
  - Analyysissä käytetty vikadata (vikataajuudet) ovat peräisin kirjasta Tboken (data kerätty ydinvoimaloista)
  - Saadut luotettavuus arvot eivät ole absoluuttisia, tuloksista nähdään eri vaihtoehtojen luotettavuus toisiinsa nähden.

Johtopäätökset

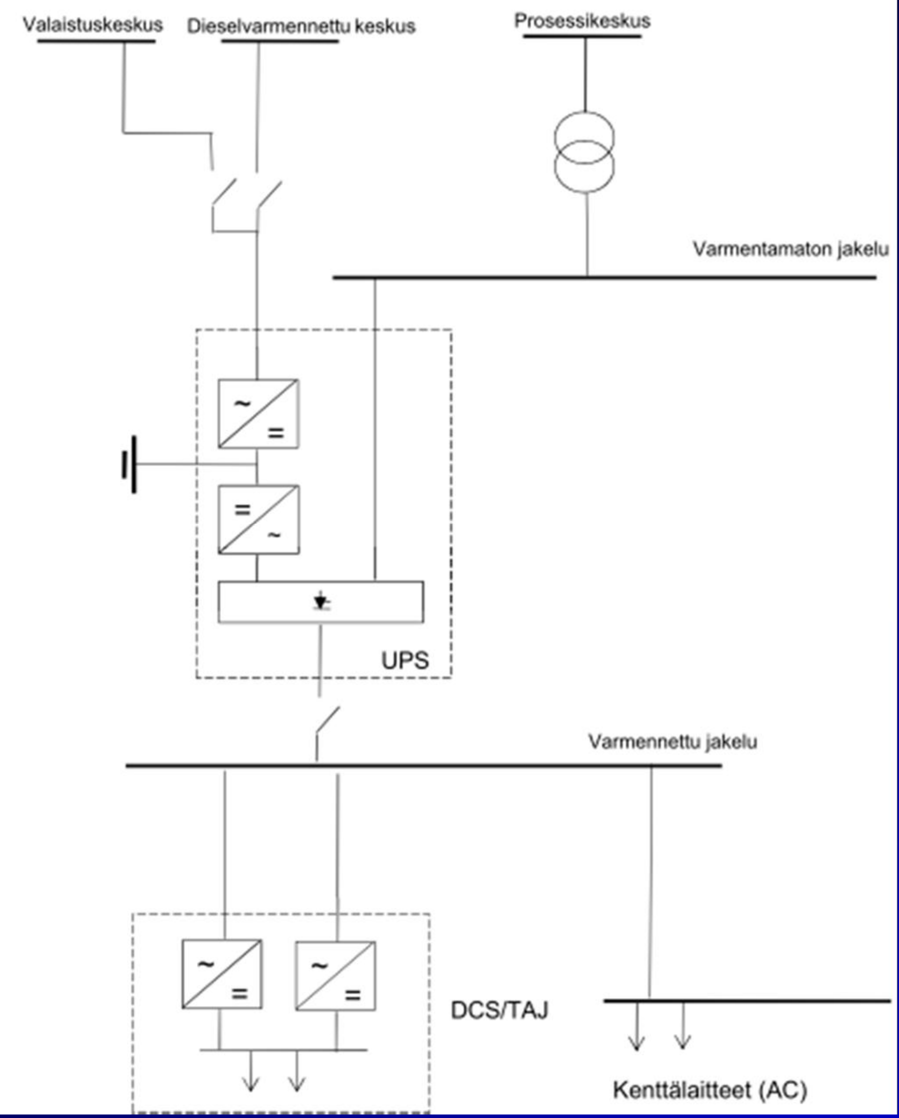
- Sähkön syötölle tulisi mahdollisuuksien mukaan tarjota useampi toisistaan täysin riippumaton kulkutie. Yksittäisiä yhteisiä osia tulisi välttää (automaattinen syötönvaihto, yhteinen UPS kisko)
- UPS-laitteiden lisääminen parantaa lähinnä sähkönsyötön toimintavarmuutta katkostilanteessa. Varsinkin kun huomioidaan UPS laitteiden taipumus vikaantua juurikin tarvetilanteessa
- Oleellista on kiinnittää huomiota myös normaalitilanteen sähkönsyötön varmuuteen kriittisten laitteiden ja järjestelmien osalta. Automaationjärjestelmien sähkönsyöttö tulisi ottaa aina kahdesta eri verkosta.

Tutkitut verkkovaihtoehdot

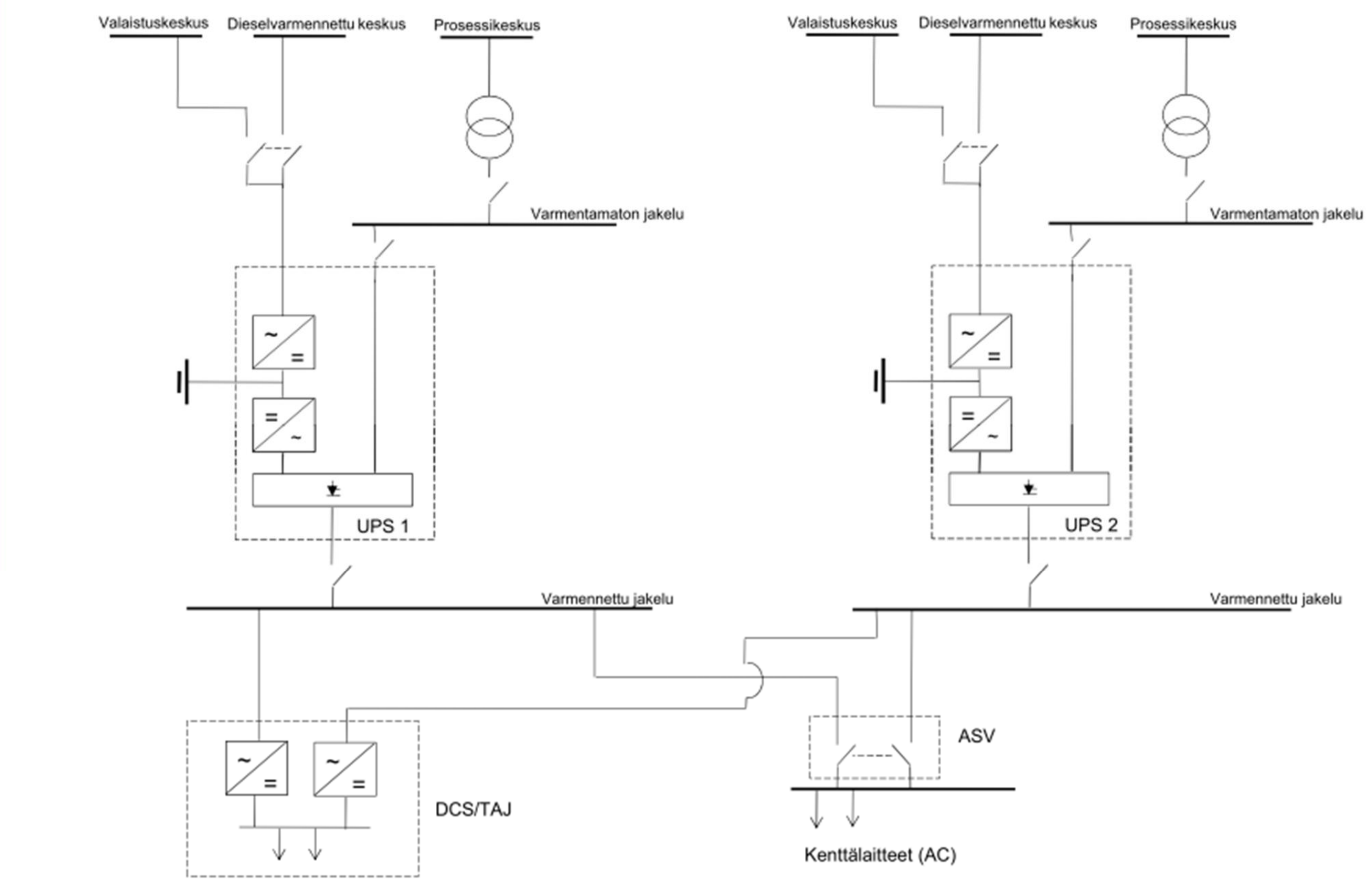


No.	Nimi	Kuvaus
1	"As usual"	1 x UPS-laitteisto jolle syöttö yhdestä verkosta, automaatiojärjestelmät sekä kenttälaitteiden syöttö saman UPS-varmennuksen takana
2	"Pöyry"	2 x UPS-laitteisto, kummallekin syöttö kahdesta eri verkosta, UPSit syöttävät omia verkkojaan, automaatiojärjestelmille syöttö kummastakin UPSista, automaattinen syötönvaihto kenttälaitteille
3	"Wisaforest"	2 x UPS-laitteisto, kummallekin syöttö kahdesta eri verkosta, UPSit syöttävät yhtä verkkoa josta syöttö automaatiojärjestelmille sekä kenttälaitteille
4	"Metso"	1 x UPS-laitteisto sekä yksi UPS-verkko. Automaatiojärjestelmille vaihtoehtoinen syöttö UPSin ohi varmentamattomasta verkosta, vaihtoehtoinen syöttö kenttälaitteille myös varmentamattomasta verkosta automaattisen syötönvaihdon kautta

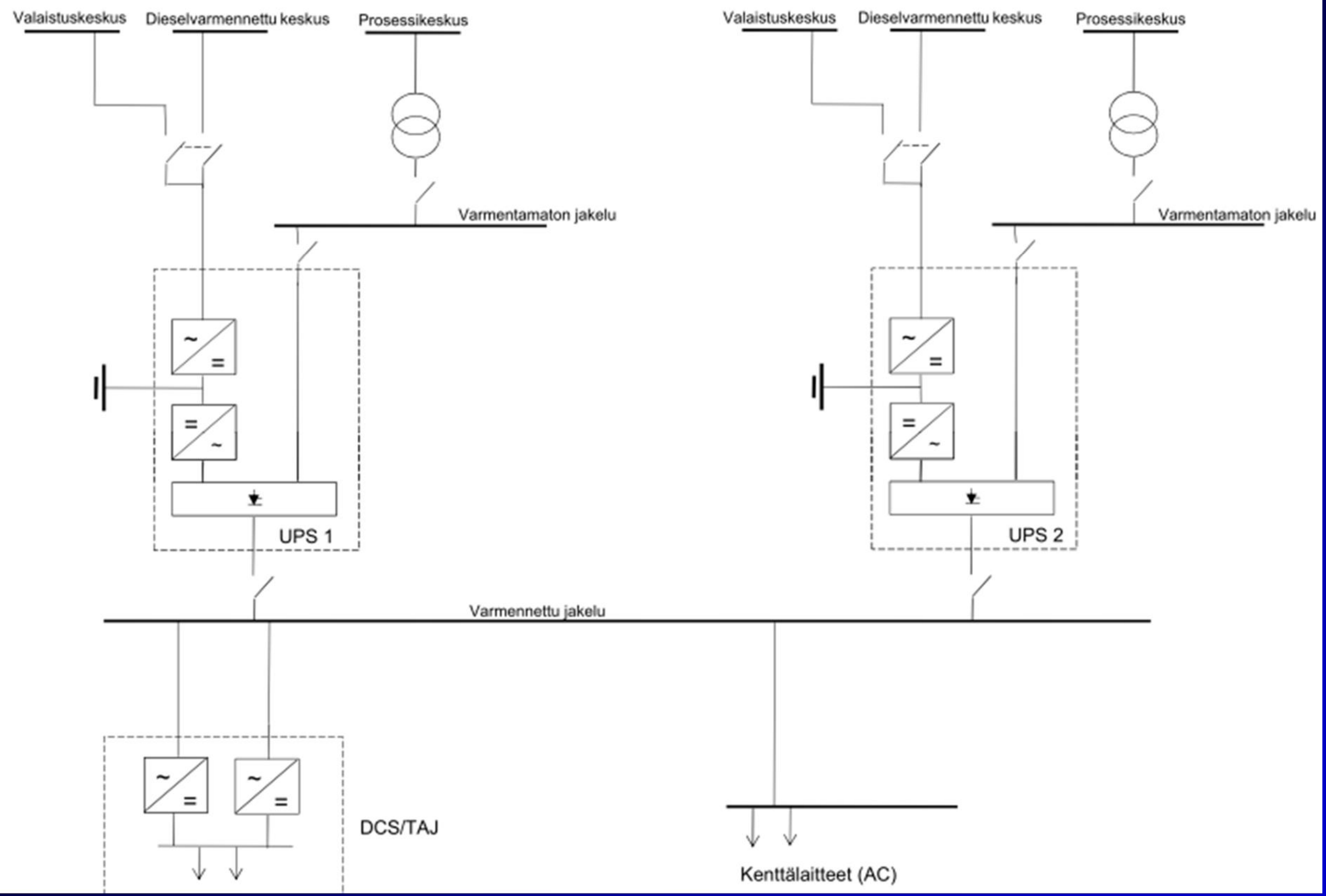
Vaihtoehto 1: "As usual"



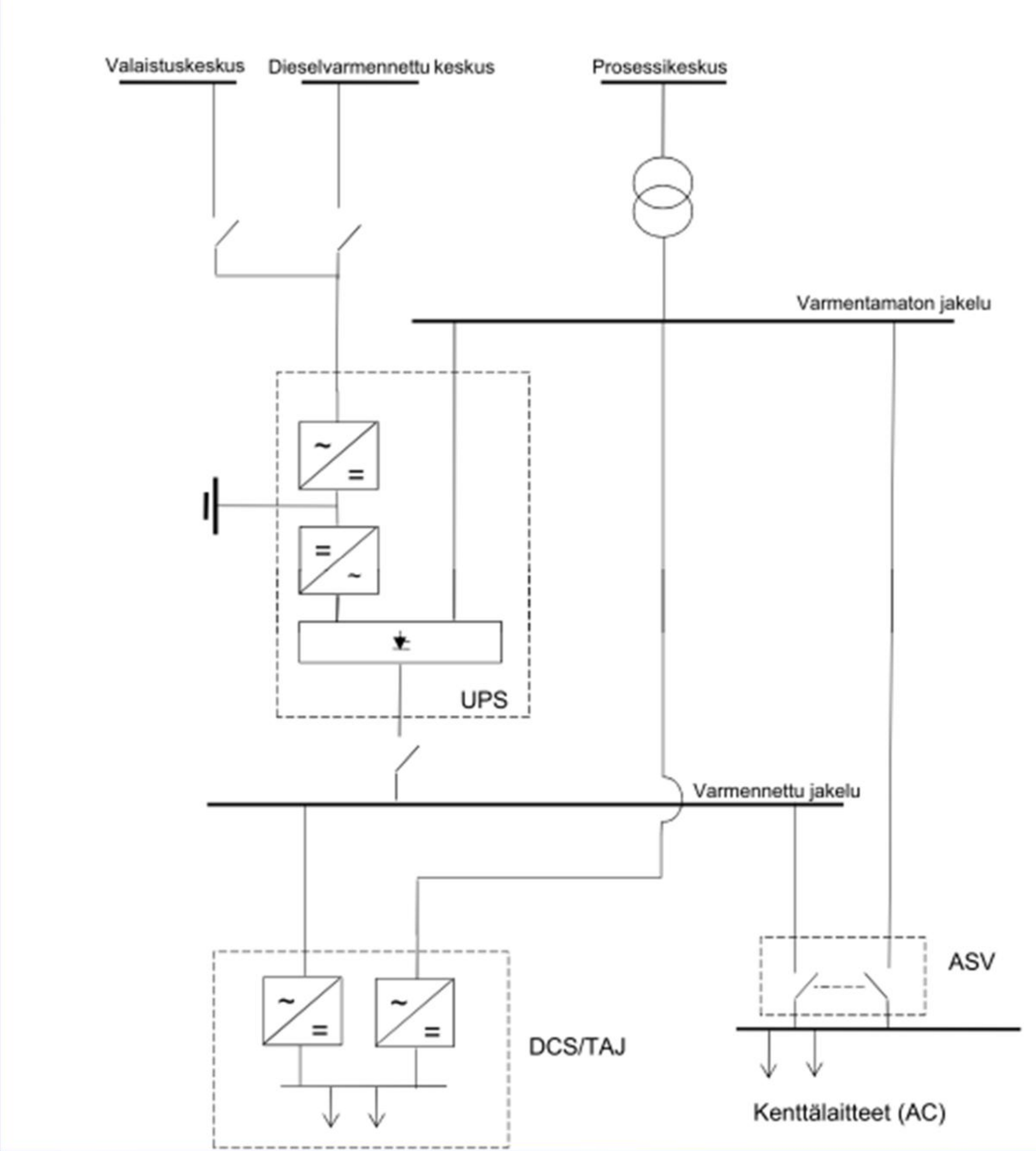
Vaihtoehto 2: "Pöyry"



Vaihtoehto 3: "Wisa"



Vaihtoehto 4: "Metso"



ATR/YTR: Hajukaasujen polttosuosituksen päivitys

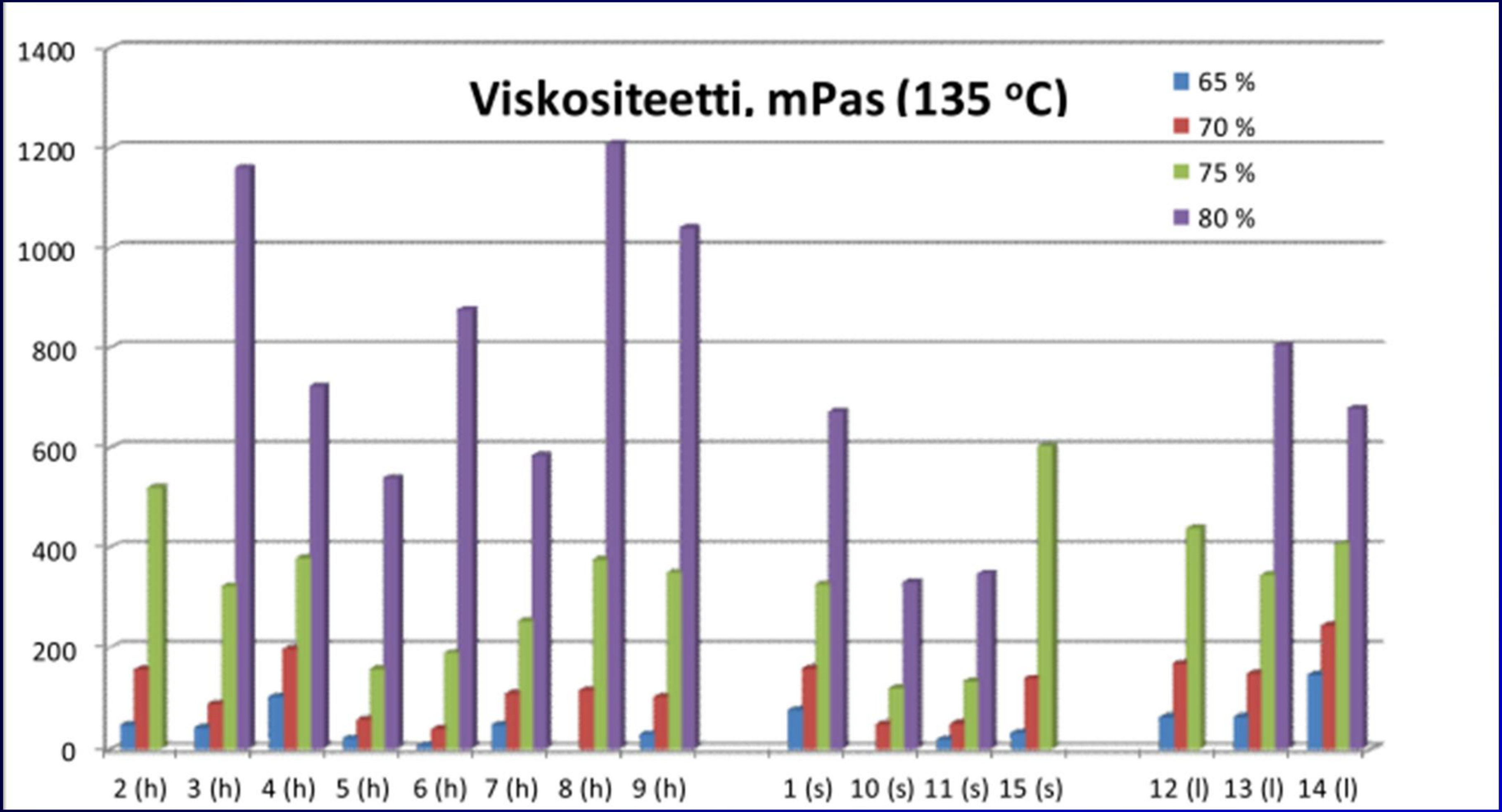
- Päivitystyöryhmä kokoontui edellisen kerran 16.3.2012 Kymillä
- Seuraava työryhmän kokous syksyllä 2012
  - Suositustekstin läpikäynti kokonaisuudessaan

- Väkevien polton aloitus:
  - Tuliteho > 0,7 MW/m2 ≈30 % MCR
- Tukiliekin sammuttamisesta:
  - Tukiliekin voi sammuttaa 50%- 60% MCR-kuorman jälkeen

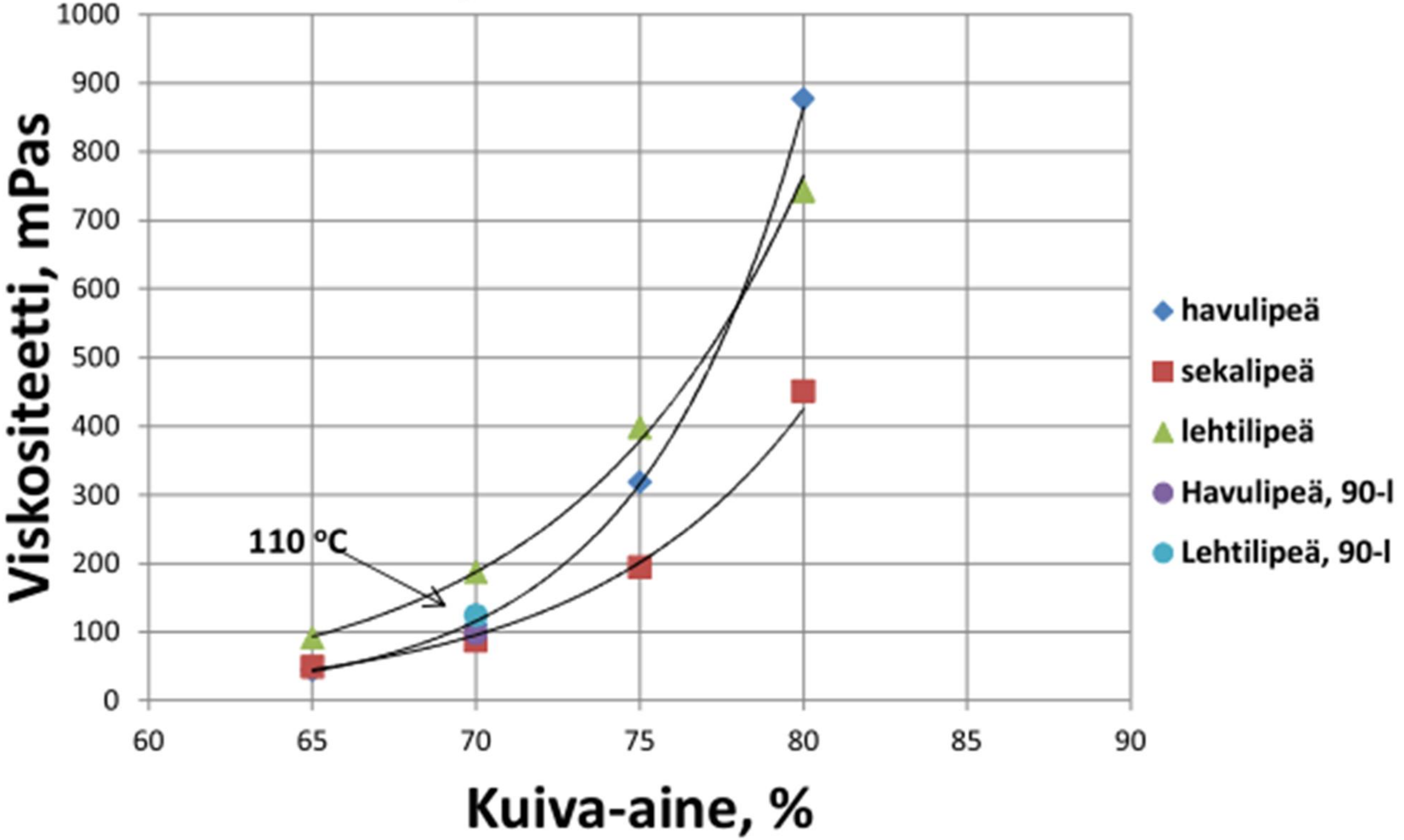
LTR projektit

LTR: Mustalipeän viskositeetti, VTT

- Yksi näyte, 2 viskositeettia per tehdas:
- hinta 1000 euroa, 15 tehdasta
- polttolipeä
- yksi yhteinen lämpötila 135 °C
- toinen lämpötila tehtaan valitsema, jos ei sama 1.näyte
- mielenkiintoisista näytteistä voidaan tehdä jatkotutkimusta
- Kaikilta tehtailta ole saatu näytettä, jäljelle jäävät analyysit käytetty laitetoimittajien lähettämiin lipeänäytteisiin.
- Tuloksia esitetty Soodakattilapäivillä 2011 ja LTR:n kokouksessa 9.12.2011
- Loppuraportti tekeillä


Viskositeetti, mPas (135 °C)
65 %
70 %
75 %
80 %
1400
1200
1000
800
600
400
200
0
2 (h)
3 (h)
4 (h)
5 (h)
6 (h)
7 (h)
8 (h)
9 (h)
1 (s)
10 (s)
11 (s)
15 (s)
12 (l)
13 (l)
14 (l)

Mustalipeiden viskositeetti 135 °C



Syöttövesipumppujen säätö, LUT

- Sellutehdasprojekteissa tulee aika ajoin vastaan kysymys, montako syöttövesipumppua ja miten säädettynä tulisi kattilassa olla
- Työssä tehdään esiselvitys kolmen soodakattilan syöttövesipumppauksen mahdollisuuksista säästää sähköä toteuttamalla pumppauksen säätö uudella tavalla.
- Mietitään miten suurella syöttövesisäiliöllä kukin soodakattila pärjäisi
- Mietitään monellako syöttövesipumpulla pitäisi soodakattilaprojekti toteuttaa

YTR projektit

- Ammonia formation and recovery in a kraft pulp mill + biosludge, ÅA
- Päästötason riippuvuus ajanjaksosta, LUT
- BAT/BREF-DOKUMENTIN KOMMENTOINTI
- HAJUKAASUSUOSITUKSEN PÄIVITYS
- POLTTOPERÄISTEN PÄÄSTÖJEN JA NANOHIUKKASTEN HAITALLISUUDEN MÄÄRITTÄMINEN UUDELLA TUTKIMUSMENETELMÄLLÄ (POPE)

OTR projektit

OTR: 50-vuotisjuhla ja ICRC 2014

- Tampere-talosta varattu ma 9.6.2014 - to 12.6.2014
- ICRC Ma, Ti, To
- Ke 11.6 SKY 50v-juhla.
- Pe 13.6 jää mahdollisuus järjestää excursioita

- Seuraavaksi perustetaan 50v-juhlatoimikunta miettimään juhlapäivän ohjelmaa/luennoitsijoita, ICRCn-toimikunnat vastaavat muiden päivien ohjelmasta. Yhteistyö ICRC kanssa?

OTR: Soodakattilapäivä 2012

- 25.10.2012 Tampereella, Scandic Tampere City
- Samaan aikaan Tampereella, Energiamessut 23-25.10.2012
- Alustava ohjelma

OTR: Painelaitepäivä 19.9.2012

- Painelaiteturvallisuuden hallintaan yrityksissä liittyy monenlaisia haasteita ja ongelmia.
- Painelaitteen omistajan ja haltijan koulutuspäivän tarkoituksena on kerätä yhteen painelaitteiden omistajia, haltijoita ja käytönvalvojia jakamaan kokemuksiaan ja kuuntelemaan asiantuntijaluentoja aiheesta.
- Luennot käsittelevät mm. painelaiteturvallisuutta, riskienhallintaa sekä kunnossapitoa.
- Ohjelma

Projektiehdotuksia

ATR: projektiehdotukset

- Ilmakanavan venturimittaukset
  - korvaavat mittaustavat (hyväksyttävät)

OTR: Energiapäivä, LUT

- Esa Vakkilainen ehdotti että järjestettäisiin energiapäivä esimerkiksi Lappeenrannan Teknillisessä Yliopistossa. Järjestelytapa ja kustannukset voisivat olla samanlaiset kuin päästömittauspäivässä Aalto yliopistolla
- Energiapäivän aiheita voisivat olla:
  - LUT tutkimus optimaalisista paineista
  - Tehtaiden energia-analyysit (Energiansäästö) Pöyry
  - Tehtaiden energiankäyttö ja niiden raportointi (uusi IPPC BAT BREF)
  - Uusien energiatehokkaampien tehtaiden käytännöt
  - Lisäsähkö soodakattiloilla
  - LUT tutkimus soodakattilan paineista ja lämpötiloista sekä välitulistuksesta
  - Haihdutusasiaa
  - Sekundäärilämpöasiaa
  - Soodakattilan hyötysuhde
- Vierailu Joutsenoon, meesauunikaasutin

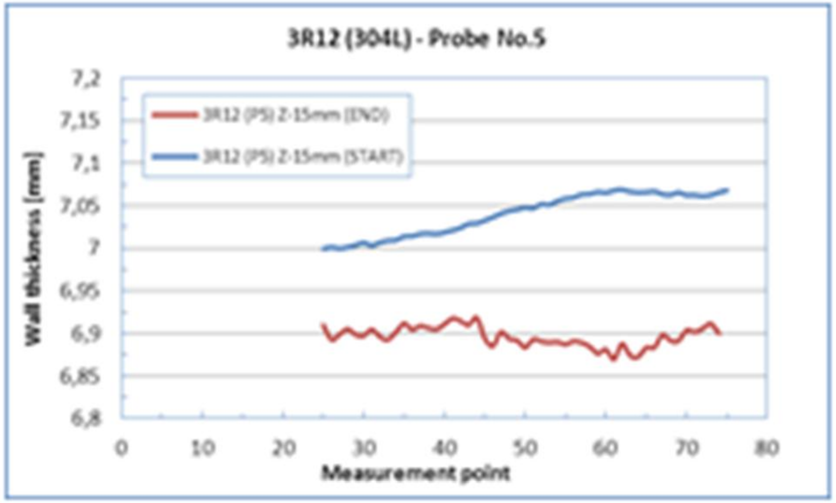
SKYREC

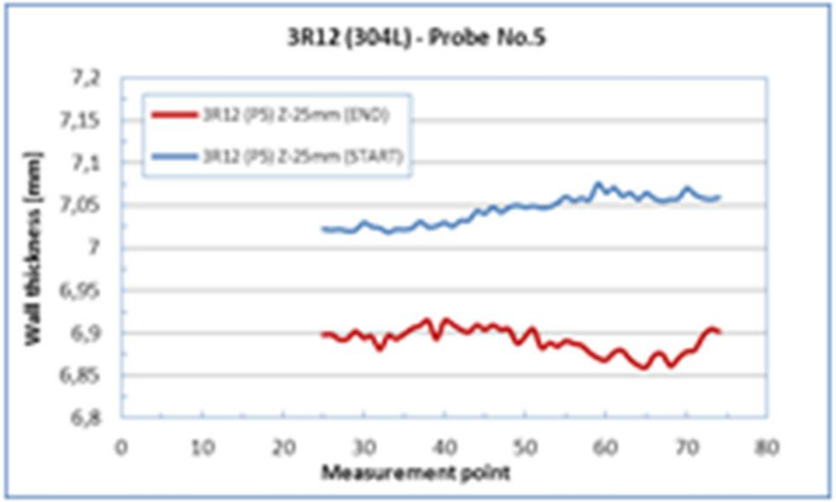
SKYREC
Tulipesän sondikokeiden analysointi ja korroosionopeuksien määritys, VTT

- Conclusions:
  - Carbon steel corrodes at extremely high rate (4 mm/a) at the temperature of 440 °C.
  - The 3R12 (AISI 304L) composite tube material corrodes in such high rate (average ca. 0.5-0.6 mm/a and maximum ca. 0.8 mm/a) that it can’t be safely used in the lower furnace
  - Sanicro 38 (mod. UNS N08825) and HR11N are ca. 3-4 times better than the 3R12 (AISI 304L). HR11N long term sample needs to be reanalysed (Probe No. 5)
  - Sanicro 28? - Long term sample needs to be re-analysed (Probe No. 5)

Probe No.5 after the test

3R12 (AISI 304L) – Examples of WT profiles





SKYREC
Dew point project, Phase 2

- The aim is to understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler.
- The dewpoint study would indicate that corrosion should not occur to any significant extent in the economizers under normal operating conditions due to acid dew point corrosion.
- One hypothesis is that the corrosion is caused acidic condensates during shutdowns and water washes. In the project probe tests are carried out during normal operation and shutdown.