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COMPILATION OF CRITERIA AIR POLLUTANT EMISSIONS DATA FOR SOURCES AT PULP AND PAPER MILLS INCLUDING BOILERS – AN UPDATE TO TECHNICAL BULLETIN NO. 884

TECHNICAL BULLETIN NO. 1020

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detection limits. A web-based program (http://practicalstats.com/nada/downloads.html) was used to calculate the median, mean and standard deviation using the K-M method. The UPL was estimated using either a 95% confidence coefficient (CC) when the data were determined to be normally distributed, or a 85% CC using the Cheybyshev inequality when the data were non-normally distributed (skewed data). For data sets with $n < 3$, only means and medians were estimated.

4.0 KRAFT PULP MILL SOURCES

Due to the nature of the kraft pulping process, some amount of VOCs would be expected to be present in almost every kraft pulp mill source vent. Major kraft pulp mill sources for which VOC emissions are summarized here include tall oil reactor vents, uncontrolled non-condensible gas (NCG) vents, uncontrolled liquor and unbleached pulp storage tank vents, thermal oxidizers, knotters and pre-washer screens, brownstock washers, deckers, bleach plant vents, oxygen delignification system vents, black liquor oxidation tank vents, recovery furnaces, lime kilns, smelt dissolving tanks, and causticizing area sources. VOC emissions from paper machines processing kraft pulp are covered in Section 8.0. Fugitive VOC emissions from wastewater treatment area sources, such as primary clarifiers and secondary treatment systems, surface impoundments, flow-through basins, lagoons, and open sewers are not included in this report.

CO is expected to be present in emissions from O_2 delignification and bleaching system vents, and all vents where some form of combustion, either of spent liquor or fuel, takes place.

Particulate matter is expected to be present in emissions from the main kraft recovery sources (recovery furnaces, lime kilns, smelt dissolving tanks), boilers, and to a lesser extent, thermal oxidizers and wood preparation activities. Fugitive PM emissions and PM emissions from material handling activities (lime, starch, coal, etc.) are also not included in this report. Limited data on particulate matter emissions from paper machines processing kraft and other types of pulp are presented in Section 8.0.

Oxides of nitrogen (or NO_x) are expected to be present in all combustion-related source vents (recovery furnaces, lime kilns, boilers) and thermal oxidizers burning kraft pulp mill non-condensible gases (NCGs) and stripper off-gases (SOGs).

In kraft pulp mills, sulfur dioxide (SO_2) emissions are expected from kraft recovery furnaces, lime kilns and boilers burning sulfur-containing fuels and/or NCGs/SOGs.

4.1 Tall Oil Reactors

Because black liquor skimmings (soap) contain some reduced sulfur compounds (e.g., methyl mercaptan) and other organic compounds (e.g., methanol), these organics may be released during soap acidulation in a tall oil reactor. VOCs are the only criteria-related pollutant emissions expected from tall oil reactors. SO_2 is not expected to be generated by the acidulation reactions. The reactor vent is the primary emission point for VOCs, with only minor emissions coming from subsequent settling and storage tanks. Because of odor concerns, scrubbers are frequently installed on reactor vents for H_2S removal. Table 4.1 presents a summary of VOC emissions measured from five tall oil reactors. Information concerning the specifics of each tall oil reactor system (such as the tons of tall oil processed per hour, vent gas flow rate, scrubber type and make-up liquid) and detailed concentration data for the VOCs in each reactor vent gas stream are provided in electronic format (Excel) in Table A-1 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx. Considering that the typical tall oil yield in kraft mills pulping softwoods is about 1% of the wet wood processed or about 4% of the dry kraft pulp, the

estimates in Table 4.1 should be divided by 25 to convert them to a lb/ADTP basis.

Table 4.1 VOC[1] Emissions from Tall Oil Reactor Vents

No.[3]	Range	Median	Mean[2]	Std. Dev.	UPL[4]
	lb C/ton tall oil				
5	0.11 – 10.02	2.90	4.24	4.24	9.90

[1]As C, measured using EPA Method 25A. [2]See footnote. [3]Number of sources tested.
[4]Upper Prediction Limit with 95% conf. coeff. - normal distribution - UPL = mean + 1.65 x SD.

4.2 Non-Condensible Gases

The collection and treatment of NCGs from kraft pulp mill sources have been practiced for over five decades. Most early systems were designed to only control total reduced sulfur (TRS) emissions from digester and multiple-effect evaporator NCGs. Over the years, vent gases from black liquor concentrators, steam strippers, turpentine decanters, chip steamers, brownstock washer systems, knotters, screens, and liquor storage tanks have also been collected for incineration (NCASI 1985). Incineration may be accomplished in lime kilns, power boilers, thermal oxidizers, or recovery furnaces. The use of flares has largely been phased out. Burning of gases with TRS results in SO_2 formation, and add-on SO_2 control is generally needed on thermal oxidizers. Boilers and lime kilns may require some SO_2 removal if the internal capture of SO_2 is insufficient or when pre-scrubbing of gases to reduce H_2S and methyl mercaptan, prior to introduction to the incineration device, is not practiced. Alternative treatment practices employed include venting with the bleach-plant chlorine or chlorine dioxide-stage washer vent gases for chemical oxidation of the sulfur compounds, and, during process upsets, discharge of selected streams to stacks for improved dispersion, thus minimizing the potential for worker exposure to high concentrations of TRS (NCASI 1985).

The non-condensible gases from the kraft pulping process are handled either as a low-volume, high-concentration (LVHC) stream [“concentrated” NCGs (CNCG)] or a high-volume, low-concentration (HVLC) stream [“dilute” NCGs (DNCG)]. LVHC gases have very little oxygen and are not explosive. Consequently, these gases are maintained above their upper explosive limit (UEL) concentration. HVLC gases can be explosive and are maintained below their lower explosive limit (LEL). CNCGs are usually comprised of gases from the digester area, condensate strippers, evaporators, and so on, while DNCGs include those from brownstock washers, pulp knotters, washer seal tanks, etc. CNCGs are typically burned in lime kilns, boilers, or thermal oxidizers, while DNCGs are burned in boilers or recovery furnaces that can accept large gas volumes. CNCGs are sometimes scrubbed with an alkali solution (usually white liquor) to remove the acidic gases (H_2S and CH_3SH) prior to incineration. The additional sulfur burden from the incineration of CNCGs in lime kilns has been associated with ring formation in the kilns (Ellis 1989).

[2] It should be noted that although the underlying data for the five reactors are the same as that summarized in Table 4.1 of NCASI Technical Bulletin 884, the current mean is significantly lower (4.24 vs. 12.4 lb C/ton tall oil) on account of a correction for the data for one unit [see pgs. 19 and B2 of NCASI Technical Bulletin 677 (NCASI 1994b)]; the durations of the reactor operation (6.4, 13.5 and 6.5 hrs) were not considered correctly in the previous summary.

Occasionally, non-condensible gases (NCGs) that are routed to a collection system for burning may be vented to the atmosphere for a very brief period of time prior to combustion. This venting may either involve bypassing all of the collected gases around the combustion device (due to the momentary loss of burning permissives), or partial venting of gases from an individual piece of equipment, depending on the design and operating characteristics of the collection system and combustion device. Unintended safety-related venting, also for brief periods of time, may occur due to the tripping of control system interlocks, loss of permissives, malfunctions, etc. In all such instances, the composition of vented gases from sources including digesters, evaporators, knotters and screens, brownstock washers, deckers and oxygen delignification systems may be used to estimate atmospheric releases of VOCs. NCGs can also be emitted from batch digester fill exhausts and from continuous digester chip bin exhausts. VOCs are typically the only criteria-related pollutants in these NCGs. Limited data on VOCs in pulp mill and evaporator NCGs, batch digester fill exhausts, and continuous digester chip bin exhausts prior to incineration are summarized in Table 4.2. Information concerning the specifics of each NCG stream (such as source description, pulping capacity, NCG flow rate) and detailed concentration data for the VOCs in each NCG stream are provided in electronic format (Excel) in Table A-2 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.2 VOC[1] Content of Uncontrolled Non-Condensible Gases

NCG Stream Description & Wood Type	No.[2]	Units	Range	Median	Mean
Pulping & Evaporator NCGs (SW/HW)	1	lb C/ADTUBP		0.71	0.71
Batch Digester Fill Exhaust (SW)	1	lb C/ton chips		0.012	0.012
Cont. Digester Chip Bin Exhaust[3] (SW)	3	lb C/ton chips	0.20 – 0.63	0.464	0.432

[1]As C, measured using EPA Method 25A. [2]Number of sources tested; [3]Live or process steam.

4.3 Uncontrolled Liquor and Unbleached Pulp Storage Tank Vents

Vent gases resulting from breathing and working losses in black liquor and unbleached pulp storage tanks may contain small amounts of VOCs. Table 4.3 summarizes the VOC content of vent gases from four weak liquor tanks, four strong liquor tanks, and three high density unbleached pulp tanks. Information concerning the specifics of each tank vent gas (such as source description, vent gas flow rate and pulp type) and detailed concentration data for the VOCs in each vent gas stream are provided in electronic format (Excel) in Table A-3 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx. The tank VOC emission factors shown in Table 4.3 should be used with caution, since the vent gas flow rates on such tanks are generally difficult to measure. These tanks often operate under moderate vacuum conditions, thereby creating the need to induce gas flows during sampling so that an emission rate can be quantified.

Table 4.3 VOC[1] Content of Uncontrolled Liquor and Unbleached Pulp Storage Tanks

Storage Tank Vent	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb C/hr/tank				
Weak Black Liquor	4	0.02 – 1.6	0.54	0.67	0.67	1.77
Strong Liquor	4	0.018 – 0.18	0.11	0.11	0.07	0.22
High Density Unbleached Pulp	3	0.86 – 5.46	4.84	3.72	2.50	7.84

[1]As C, measured using EPA Method 25A. [2]Number of sources tested.
[3]Upper Prediction Limit with 95% conf. coeff. - normal distribution - UPL = mean + 1.65 x SD.

4.4 Thermal Oxidizers

Kraft pulp mills burn their high volume low concentration (HVLC) and low volume high concentration (LVHC) NCGs and stripper off-gases (SOGs) in various thermal oxidation devices including lime kilns, boilers, stand-alone thermal oxidizers, and recovery furnaces. Due to their low TRS and VOC content, the burning of HVLC NCGs in boilers and recovery furnaces is not expected to affect emissions of VOCs from these combustion devices. However, the LVHC NCGs and SOGs can be rich in reduced sulfur compounds and organics such as terpenes and methanol, and the SOGs can also contain significant amounts of ammonia. The sulfur in the reduced sulfur compounds will oxidize to SO_2, yielding two pounds of SO_2 for every pound of S in the NCG stream. Some of the ammonia will oxidize to NO_x, although this conversion is highly dependent on the relationship between temperature, residence time, NH_3, NO, and O_2 in the specific incineration device.

The two most commonly employed types of thermal oxidizers at kraft mills are those with a refractory-lined combustion chamber and those similar to a jet engine. Design residence times for gases in the combustion chamber range from a minimum of 0.5 to 1 second, while the residence time in engines is considerably less due to the extreme turbulence, thus enhancing combustion. Design chamber temperatures normally range between 1200 and 1600°F. In some cases, the gases are scrubbed prior to their introduction into the unit to reduce SO_2 formation. Gases exiting the unit are diluted with ambient air to reduce the temperature to allow the use of less exotic materials of construction. The industry seems to have moved away from jet engine type thermal oxidizers that are known to have high NO_x emissions.

Thermal oxidizers that burn LVHC NCGs and SOGs are generally quite efficient in oxidizing the organics and reduced sulfur compounds contained in these gas streams to CO_2 and SO_2, respectively. Due to the high levels of SO_2 resulting from oxidation of the reduced sulfur compounds, most thermal oxidizers are equipped with a wet scrubber for SO_2 removal.

When ammonia-containing SOGs are burned in a thermal oxidizer, the ammonia partly converts to NO_x. Theoretical considerations suggest the extent of this conversion depends on several factors including temperature and the availability of oxygen for oxidation of the NH_3. Typically, only a small fraction of the SOG-ammonia converts to NO_x. The contribution of ammonia-containing kraft mill steam stripper off-gases to thermal oxidizer NO_x emissions was investigated in an NCASI study (NCASI 2004c). Measurements at nine oxidizers showed conversion rates of NH_3 to NO_x ranging from 5% to 38%. In this study, temperature and oxygen measurements in the post-combustion zone did not relate well to conversion rates. The study results did show that oxidizers using air staging to create both an oxidizing and a reducing zone in the combustion chamber (dual-stage combustion) had approximately 40% lower NH_3 to NO_x conversion rates when compared to single-stage oxidizers.

Introduction of the stripper off-gases with natural gas or LVHC NCGs in single-stage oxidizers resulted in higher conversion rates.

Table 4.4 provides estimates of emissions for VOC, SO_2, NO_x, CO, and total filterable PM (TPM) from thermal oxidizers. NO_x emissions are shown from thermal oxidizers (TO) burning just LVHC NCGs (or CNCGs) and also from those burning SOGs and LVHC NCGs. Information concerning the specifics of each thermal oxidizer (such as source description, pulping capacity, TO vent gas flow rate) and detailed concentration data for the VOCs in each vent gas stream are provided in electronic format (Excel) in Table A-4 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx. No data are currently available for CPM emissions from thermal oxidizers. Since the TOs are invariably followed by a wet scrubber for SO_2 removal, an adequate method for measurement of filterable $PM_{2.5}$ is also not available at the present time.

Table 4.4 VOC, SO_2, NO_x, CO, and TPM Emissions from Thermal Oxidizers

	No.[1]	Units	Range	Median	Mean	Std Dev	UPL[2]
VOC[3]	7	lb C/ADTUBP	1.2E-04 – 0.03	0.003	0.009	0.010	0.026[4]
SO_2	13	lb/ADTUBP[5]	1.5E-04 – 1.05	0.045	0.160	0.291	0.880[6]
NO_x[7]	20	lb/ADTUBP	0.022 – 0.41	0.213	0.214	0.119	0.411[4]
NO_x[8]	9	lb/ADTUBP	0.008 – 0.30	0.047	0.075	0.091	0.303[6]
CO	12	lb/ADTUBP	3.1E-05 – 0.83	0.012	0.134	0.286	0.843[6]
TPM[9]	12	lb/ADTUBP	5.0E-04 – 0.24	0.036	0.062	0.071	0.238[6]

[1]Number of sources tested. [2]Upper Prediction Limit. [3]As C, measured using EPA Method 25A.
[4]UPL with 95% conf. coeff. - normal distribution. [5]The table values represent SO_2 emissions after a scrubber.
[6]UPL with 85% conf. coeff. – non-normal distribution. [7]Thermal oxidizers burning CNCGs & SOGs.
[8]Thermal oxidizers burning only CNCGs. [9]Total (filterable) particulate matter.

4.5 Knotters and Pre-Washer Screens

Pressurized knotters and screens generally have no exhausts to the atmosphere. However, knotters and screens that operate at atmospheric pressure can emit reduced sulfur and volatile organic compounds, including hazardous air pollutants (HAPs) such as methanol and acetaldehyde. Table 4.5 provides a summary of limited data for VOC emissions from knotters and screens. Information concerning the specifics of each knotter and pre-washer screen (such as source description, pulping capacity, vent gas flow rate) and detailed concentration data for the VOCs in each vent gas stream are provided in electronic format (Excel) in Table A-5 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.5 VOC[1] Emissions from Knotters and Washer Screens

Source	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb C/ADTUBP				
Pulp Knotters	3	0.0016 – 0.038	0.005	0.015	0.020	0.048
Pre-Washer Screens[4]	3	0.0028 – 0.077	0.004	0.028	0.043	0.098

[1]As C, measured using EPA Method 25A. [2]Number of sources tested.
[3]UPL with 95% conf. coeff. - normal distribution.
[4]Applies to both pre- and post brownstock washing screening systems.

4.6 Brownstock Washers

Brownstock washing system vent gases contain reduced sulfur compounds and VOCs, including HAPs such as methanol and acetaldehyde. The 1998 MACT rule requires collection and treatment of these vent gases, but a number of mills have been able to use the "Clean Condensate Alternative" which allows emission reductions from other applicable sources in lieu of reductions obtained by controlling the washer emissions. Uncontrolled emissions from washers depend on the vent gas flow rates, quality of shower water, liquor properties, and wood species. Vacuum drum washer systems have the highest flow rates and therefore highest emissions. Emissions from other types of washer systems (diffusion, belt, compaction baffle) are generally much lower, mainly due to the low gas flow rates. Pressurized washing systems emit gases mainly from their filtrate tanks.

Table 4.6 provides estimates of VOC emissions from vacuum drum and other types of washers. Information concerning the specifics of each washer system (such as the washer type, the number of vents included in the test, pulping capacity, and vent gas flow rate) and detailed concentration data for the VOCs in each washer vent gas stream are provided in electronic format (Excel) in Table A-6 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

The VOC emission data in Table 4.6 are also segregated by the type of wood being pulped (i.e., hardwood vs. softwood). Mean VOC emissions from vacuum drum and "low flow" washers washing softwood pulp appear to be somewhat higher than those washing hardwood pulps (73 and 86%), although median VOC emissions do not appear to show such a large difference (34% and -10%).

Table 4.6 VOC[1] Emissions from Brownstock Washers

Type of Washer	No.[2]	Wood Type	Range	Median	Mean	Std Dev	UPL[3]
			lb C/ADTUBP				
Vacuum Drum Washer	5	HW	0.04 to 0.61	0.160	0.289	0.256	0.712[4]
Vacuum Drum Washer	8	SW	0.04 to 2.00	0.215	0.499	0.672	2.197[5]
Vacuum Drum Washer	13	all	0.04 to 2.00	0.209	0.418	0.545	1.765[5]
Low Flow Washer[6]	4	HW	1.8E-04 to 0.20	0.141	0.121	0.089	0.267[4]
Low Flow Washer[6]	5	SW	0.054 to 0.56	0.127	0.225	0.204	0.561[4]
Low Flow Washer[6]	9	all	1.8E-04 to 0.56	0.127	0.179	0.164	0.589[5]

[1]As C, measured using EPA Method 25A. [2]Number of sources tested. [3]Upper Prediction Limit.
[4]UPL with 95% conf. coeff. - normal distribution. [5]UPL with 85% conf. coeff. – non-normal distribution.
[6]Including pressure, diffusion, compaction baffle, or belt washer.

4.7 Pulp Deckers

Pulp washing is complete by the time the pulp slurry reaches the decker. Thus, in most cases, deckers are not significant emission sources, unless additional washing takes place on the decker. If wash water used on a decker is hot and contains high concentrations of volatile organics, it can be a significant source of VOCs and HAPs. Limited data on VOC emissions from deckers are summarized in Table 4.7. Information concerning the specifics of each decker system (such as the vents included in the test, shower water quality, pulping capacity, vent gas flow rate) and detailed concentration data for the VOCs in each decker vent gas stream is provided in electronic format (Excel) in Table A-7 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.7 VOC[1] Emissions from Pulp Deckers

No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
	lb C/ADTUBP				
3	0.051 – 0.09	0.077	0.073	0.020	0.105

[1]As C, measured using EPA Method 25A. [2]Number of sources tested.
[3]Upper Prediction Limit with 95% conf. coeff. - normal distribution.

4.8 Oxygen Delignification System Vents

In mills that practice oxygen delignification, volatile organic compounds present in the incoming pulp slurry, oxidized white liquor, and washer shower water can be released in the blow tank, washer hood, washer filtrate tank, and pulp storage tank vent gases. The amounts of these compounds present in the various process liquids will depend upon the water reuse practices of the mill, particularly if condensates are used on the post-oxygen washers. Releases of volatile organic compounds from

washer systems also are a function of the extent to which exhaust air and process liquids are in contact, which in turn depends upon equipment design and ventilation practices.

Carbon dioxide and smaller amounts of carbon monoxide are formed in the reactor as the delignification proceeds. The majority of these gases will be released from the blow tank vent. In an NCASI study (NCASI 1998), average carbon monoxide emissions from O_2 delignification system vents at eight kraft mills were found to range from 0.01 to 0.28 lb/ODTP, with no readily apparent relationship to either the amount of oxygen applied or to the reduction in kappa number accomplished.

Table 4.8 gives estimates of VOC and CO emissions from oxygen delignification system vents. Information concerning the specifics of each system (such as the vents included in the test, washer type, wood pulp type, pulping capacity, vent gas flow rate) and detailed concentration data for the VOCs in each O_2 delignification system vent gas stream (combined) is provided in electronic format (Excel) in Table A-8 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.8 VOC[1] and CO Emissions from O_2 Delignification System Vents

Pollutant	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb/ADTUBP				
VOC[1]	12	ND – 1.09	0.20	0.35	0.36	1.24
CO	8	0.01 – 0.28	0.05	0.12	0.13	0.45

[1]Measured as C using EPA Method 25A. [2]Number of sources tested.
[3]UPL with 85% conf. coeff. – non-normal distribution.

4.9 Bleach Plant Vents

Trace quantities of VOCs have been measured in bleach plant scrubber vent gases. Carbon monoxide (CO) is generated in bleach plants that use chlorine dioxide. While not regulated specifically from pulp bleaching operations, CO is a criteria pollutant and thus, contributions from pulp bleaching operations may be relevant in accounting for total mill emissions of CO (e.g., for air quality permitting purposes).

In an NCASI study, long-term continuous emission monitoring data collected at six bleach plant scrubber vents showed a range of 0.20 to about 1.65 lb CO/ODTP (NCASI 1998). The major sources of CO emissions from bleach plants were the chlorine dioxide bleaching towers. Contributions from extraction and peroxide stages were typically small. At elemental chlorine-free (ECF) bleach plants, the CO emissions were weakly correlated with total percent ClO_2 applied on pulp. However, for bleaching with less than complete substitution, CO emissions exhibited a poor correlation with percent ClO_2 applied on pulp. The data reviewed during the NCASI investigation suggested that, as long as the total amount of equivalent chlorine applied on pulp remains the same, total bleach plant CO emissions will remain unaffected by increasing the ClO_2 substitution levels in the first stage (NCASI 1998).

Table 4.9 provides estimates of VOC and CO emissions from kraft mill bleach plant vents. Included are bleach plant scrubber vents, extraction-stage vents, and ClO_2 generator scrubber vents.

Information concerning the specifics of each bleach plant (such as the percent ClO_2 substitution, pulp type, bleaching sequence, bleaching capacity) and detailed concentration data for the VOCs in each bleach plant scrubber vent gas stream is provided in electronic format (Excel) in Tables A9a, A9b, A9c, and A9d at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx. The CO emissions from 100% ClO_2 substitution bleach plant vents are presented as equations relating to the amount of ClO_2 applied on pulp (NCASI 1998).

Table 4.9 VOC and CO Emissions from Bleach Plant Vents

Vent(s)		No.[1]	Range	Median	Mean	Std. Dev.	UPL[3]
			lb/ODTUBP[2]				
Bleach Plant Scrubber[4]	VOC[5]	34	0.008 – 0.48	0.054	0.103	0.106	0.360[6]
Bleach Plant Scrubber	CO	[a]	0.20 – 1.65	[a]	[a]	--	--
Extraction Stage Vents	VOC[5]	10	1.1E-04 – 0.231	0.021	0.050	0.071	0.227[6]
Extraction Tower Only	CO	4	0.006 to 0.08	0.037	0.040	0.033	0.095[7]
ClO_2 Generator Scrubber	VOC[8]	2	0.002 to 0.017	0.0094	0.0094	--	--

[1]Number of sources tested. [2]Note that 1 lb/ODTUBP ~1 lb/ADTBP. [3]Upper Prediction Limit.
[4]33 of 34 bleach plant vents passed through a scrubber.
[5]Measured as C using EPA Method 25A, 25, or CARB 100.
[6]UPL with 85% conf. coeff. – non-normal distribution. [7]UPL with 95% conf. coeff. - normal distribution.
[8]Lb C/ton ClO_2 as measured by EPA Method 25A.
[a] For bleaching with 100% ClO_2 substitution, the following correlations may be used (NCASI 1998):

$Y = 0.18 \bullet X + 0.45$ (for softwoods) $n = 9$

$Y = -0.03 \bullet X + 0.69$ (for hardwoods) $n = 7$

where

Y = CO emissions in lb/ODTUBP; and

X = % ClO_2 applied (total) in lb ClO_2 per 100 lb ODTUBP

4.10 Black Liquor Oxidation Systems

Vent gases from black liquor oxidation (BLO) towers and tanks have high moisture contents and large flow rates. Concentrations of reduced sulfur compounds in these gases tend to be low, normally under 50 ppmv. Volatile organic compounds are also present in these gases, having been stripped from the black liquor. Table 4.10 gives estimates of VOC emissions from seven BLO systems. All data correspond to oxidation of strong liquors. Table 4.10 also provides total filterable particulate matter emission data reported on one BLO system (USEPA 1992). Detailed data including descriptions for each BLO system are provided in Table A10 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.10 VOC[1] and TPM Emissions from Black Liquor Oxidation Systems

No.[1]		Units	Range	Median	Mean	Std. Dev.	UPL[3]
7	VOC[2]	lb C/ton BLS	0.00018 – 0.33	0.054	0.124	0.138	0.352[3]
1	TPM	lb/ton BLS	--	0.0049	0.0049		

[1]Number of sources tested. [2]As measured by EPA Method 25A.
[3]Upper Prediction Limit with 95% conf. coeff. - normal distribution.

4.11 Kraft Recovery Furnaces

Major criteria and criteria-related pollutants emitted from kraft recovery furnaces include particulate matter (TPM, PM_{10}, $PM_{2.5}$, CPM), SO_2, NO_x, CO, and VOCs.

4.11.1 *Particulate Emissions*

Recovery furnaces are designed and operated in a manner so as to ensure the presence of high levels of sodium fumes in order to capture the sulfur dioxide which is produced as a result of oxidation of reduced sulfur compounds released from the char bed or the falling liquor droplets. Consequently, recovery furnace flue gases contain high levels of particulate matter. The uncontrolled particulate matter load from recovery furnaces is highly variable and has been reported to range from 100 to 250 lb/ODTP for DCE furnaces and from 200 to 450 lb/ODTP for non-DCE furnaces. The lower particulate loading from DCE furnaces is due to the capture of some particulate matter in the direct contact evaporator.

Particulates generated in the recovery furnace are comprised mainly of sodium sulfate, with lesser amounts of sodium carbonate and sodium chloride. Similar potassium compounds are also generated, but in much lower amounts. Trace amounts of other metal compounds, e.g., magnesium, calcium and zinc, can be present. A significant portion of the particulate material is sub-micron in size, which makes removal with add-on control devices more difficult.

It has been reported that increasing liquor firing density (ton/day/ft^2) increases recovery furnace particulate loading (Nguyen and Rowbottom 1979). Other factors such as bed and furnace temperature, liquor solids, liquor composition, and air distribution also affect uncontrolled particulate emissions from recovery furnaces.

4.11.2 *SO_2 Emissions*

Black liquor contains a significant amount of sulfur, nominally 3 to 5% by weight of the dissolved solids. While the vast majority of this sulfur leaves the furnace via the smelt product, a small fraction (generally under 1%) can escape in gaseous or particulate form. Average SO_2 concentrations in stack gases can range from nearly 0 to 500 ppm, although most furnaces currently operate with <100 ppm SO_2 in stack emissions. Factors which influence SO_2 levels in the stack include liquor sulfidity, liquor solids content, stack oxygen content, furnace load, auxiliary fuel use, and furnace design. None of these factors has exhibited a consistent relationship with SO_2 emissions (NCASI 1991). Liquor quality (such as high Btu, high solids liquors) and liquor firing patterns and furnace operating conditions (air distribution, auxiliary fuel, etc.) that in combination lead to maximizing temperatures in the lower sections of the furnace also generally result in minimizing SO_2 emissions from kraft recovery furnaces. On average, SO_2 emissions from NDCE units tend to be lower than from DCE units.

4.11.3 *NO_x Emissions*

Nitrogen in black liquor ranges from about 0.05 to 0.25% of the liquor solids content, typically averaging about 0.1%. During black liquor combustion, nearly three fourths of the liquor nitrogen is released during pyrolysis or devolatilization, partly as ammonia and partly as N_2. The NH_3 released partly oxidizes to NO and partly reduces to N_2. The remaining liquor nitrogen will be bound in the char residue, mostly as a reduced species in the salt residue or smelt. Forssén et al. (1997) have suggested that the oxidation of the NH_3 released during pyrolysis is perhaps the main contributor to the overall NO formation during normal black liquor combustion.

NCASI (2003c) examined the NH_3-NO-O_2 homogeneous gas phase chemistry in kraft recovery furnaces at various temperatures and residence times. Even though NO_x generation in kraft recovery furnaces is generally agreed to be a "fuel NO_x" phenomenon, furnace temperatures can have a significant effect on the extent of oxidation of the NH_3 released during pyrolysis to NO. Preliminary reports of success in applying staged combustion principles by installing "quaternary" air ports in certain large furnaces, resulting in about a 20 to 40% reduction in baseline NO_x levels, are consistent with the NH_3-NO-O_2 homogeneous gas phase chemistry. Forssén et al. (1997) also suggested that the extent of air staging and the temperatures in the upper furnace region likely affect the fraction of ammonia that will be oxidized to NO and emitted. Overall conversions of black liquor nitrogen to NO are quite low compared with other fuels, ranging from 10 to about 25%. NO_x levels are typically somewhat higher for NDCE furnaces than DCE units. Besides the older ages of the DCE units and perhaps a less robust combustion temperature environment, the reasons for this are unclear.

4.11.4 *CO Emissions*

Carbon monoxide is a product of incomplete combustion. Complete combustion would result in all of the organic carbon in the black liquor being converted to CO_2. CO emissions from recovery furnaces have been known to fluctuate markedly with time, and long-term mean values vary considerably from furnace to furnace. CO levels are affected by swings in liquor firing rates and liquor solids content. Empirical evidence suggests a loose positive correlation between CO and TRS emissions.

4.11.5 *VOC Emissions*

Volatile organic compounds (VOCs) are emitted in small amounts from recovery furnaces. The source of these compounds may be incomplete combustion or the liquor itself when it comes into contact with combustion gases. The most obvious contact between liquor and flue gas is in the DCE furnaces, where methanol and other volatiles can be transferred from the liquor to the flue gas. Less obvious contact occurs in the bottom of electrostatic precipitators where black liquor is used to collect the captured ash, and in furnaces that use liquor to transfer ash removed from the upper furnace areas to the salt cake mix tank. An early NCASI study (NCASI 1981) showed 1) VOC emissions from kraft recovery furnaces could not be correlated to the black liquor firing rate or excess air usage, and 2) VOC emissions from NDCE furnaces correlated with CO emissions, although the significance of this was not well understood.

Table 4.11 provides estimates of emissions for VOC, SO_2, NO_x, CO, total filterable PM (TPM), condensible particulate emissions (CPM), filterable PM_{10}, and filterable $PM_{2.5}$ from DCE kraft recovery furnaces. The average for SO_2 is based on annual average emissions reported by six mills having SO_2 continuous emission monitors (CEMs) in 2010, while the NO_x average is based on reported 2010 emissions for 37 furnaces, largely derived from stack tests (NCASI 2012). The CO emissions data include both DCE and NDCE furnaces since the evaporators on a furnace are not expected to have any impact on its CO emissions. The CPM emission data summarized here were obtained by NCASI using the older (pre-2010) version of EPA Method 202 and thus may be biased high due to the SO_2 artifact (NCASI 2002c). Measurements made with the newer version of Method

202 are not available as of the date of publication of this report. The filterable PM_{10} and $PM_{2.5}$ data are expressed as percentages of total filterable PM, rather than in lb/ton BLS. This allows the percentages to be applied to a particular furnace's total filterable PM emissions to obtain a better estimate of PM_{10} and $PM_{2.5}$ emissions.

Information concerning the specifics of each DCE furnace, such as whether the ESP used to control PM on the furnace had a wet or dry bottom, the black liquor firing rate, etc. are provided in electronic format (Excel) in Tables A11a, A11b, A11c, A11d and A11e at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.11 VOC[1], SO_2, NO_x, CO, TPM, CPM, PM_{10} and $PM_{2.5}$ Emissions from DCE Kraft Recovery Furnaces

	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb/ton BLS				
VOC[1]	12	0.024 – 1.131	0.21	0.39	0.39	1.36[4]
SO_2[5]	6	0.01 – 7.59	0.20	2.53	3.76	12.19[4]
NO_x[6]	37	0.65 – 2.25	1.33	1.38	0.40	2.34[4]
CO[7]	19	0.10 - 6.88	1.21	2.17	1.93	6.89[4]
TPM[8]	23	0.07 – 2.58	0.70	0.74	0.59	2.16[4]
CPM[9,10]	4	0.21 – 0.68	0.33	0.39	0.21	0.73[11]
PM_{10}[12]	4			56.7%		
$PM_{2.5}$[10,12]	6			39.7%		

[1]Measured as C using EPA Method 25A. [2]Number of furnaces tested. [3]Upper Prediction Limit.
[4]UPL with 85% conf. coeff. – non-normal distribution.
[5]Data reported in 2010 NCASI survey for 6 DCE furnaces equipped with SO_2 CEMs.
[6]Data reported in 2010 NCASI survey for 37 DCE furnaces - not CEM data.
[7]CO emissions are the same for DCE and NDCE furnaces. [8]Total (filterable) particulate matter.
[9]Condensible particulate matter – not obtained using the 2010 Revised EPA Method 202 and thus may be biased high due to SO_2 artifact.
[10]Derived from filterable $PM_{2.5}$ data not corrected for blanks, and CPM data with only the allowed blank correction of 2 mg. NCASI will reissue these test results once the issue of blanks has been resolved. Facilities need to discuss the issue of blank correction prior to selecting the $PM_{2.5}$ data appropriate for emissions modeling; see Section 3.1 for details.
[11]UPL with 95% conf. coeff. - normal distribution.
[12]Average (mean) % of TPM – should be applied to specific furnace's TPM emissions.

Table 4.12 provides estimates of emissions for VOC, SO_2, NO_x, CO, total filterable PM (TPM), condensible particulate emissions (CPM), PM_{10}, and $PM_{2.5}$ from NDCE kraft recovery furnaces. The average for SO_2 is based on 2010 annual average emissions reported by 39 mills having SO_2 CEMS, while the NO_x average is based on 2010 emissions reported for 33 units with NO_x CEMS (NCASI 2012). CO emissions data include both DCE and NDCE furnaces. The CPM emission data summarized here for five furnaces were obtained using the current version of EPA Method 202 (issued in December 2010). Measurements for CPM on seven NDCE furnaces using the old M202 were omitted from consideration when determining the averages shown in Table 4.12.

Information concerning the specifics of each NDCE furnace, such as the furnace black liquor firing rate, etc., are provided in electronic format (Excel) in Tables A12a, A12b, A12c, A12d and A11b at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.12 VOC[1], SO_2, NO_x, CO, TPM, CPM, PM_{10} and $PM_{2.5}$ Emissions from NDCE Kraft Recovery Furnaces

	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb/ton BLS				
VOC[1]	25	ND – 0.70	0.07	0.15	0.19	0.53[4]
SO_2[5]	39	0.00 – 7.92	0.07	0.37	1.29	3.47[4]
NO_x[5]	33	0.82 – 2.18	1.44	1.47	0.38	2.09[6]
CO[7]	19	0.10 - 6.88	1.21	2.17	1.93	6.89[4]
TPM[8]	20	0.02 – 3.50	0.37	0.66	0.77	2.54[4]
CPM[9,10]	5	0.03 – 0.33	0.08	0.13	0.12	0.28[6]
PM_{10}[11]	14			49.5%		
$PM_{2.5}$[10,11]	12			33.8%		

[1]Measured as C using EPA Method 25A. [2]Number of furnaces tested. [3]Upper Prediction Limit.
[4]UPL with 85% conf. coeff. – non-normal distribution.
[5]Data reported in 2010 NCASI survey for 39 NDCE furnaces equipped with SO_2 CEMS and 33 NDCEs with NO_x CEMS.
[6]UPL with 95%; conf. coeff. - normal distribution.
[7]CO emissions are the same for DCE and NDCE furnaces. [8]Total (filterable) particulate matter.
[9]Condensible particulate matter obtained using the 2010 Revised EPA Method 202 for CPM.
[10]Derived from filterable $PM_{2.5}$ data not corrected for blanks, and CPM data with only the allowed blank correction of 2 mg. NCASI will reissue these test results once the issue of blanks has been resolved. Facilities need to discuss the issue of blank correction prior to selecting the $PM_{2.5}$ data appropriate for emissions modeling; see Section 3.1 for details.
[11]Average (mean) % of TPM – should be applied to specific furnace's TPM emissions.

4.12 Lime Kilns

Until recent years, because of their readily observable nature (odor and visibility), TRS and particulate matter (PM) emissions from lime kilns received all of the attention. Besides these emissions, other significant emissions from the kiln include SO_2, NO_x, and total hydrocarbons (THCs).

4.12.1 *Particulate Emissions*

Lime kiln combustion gases pick up particulate matter both from lime mud dust formation and from alkali vaporization. This PM must be removed before the gases exit to the atmosphere. Mechanical devices such as dust chambers or cyclones are generally used to remove larger particles that mainly contain calcium. A wet scrubber or electrostatic precipitator follows, for the removal of smaller particulates with aerodynamic diameters less than 10 µm. The following analysis of speciated particulate matter emissions from one lime kiln equipped with a wet scrubber was obtained (USEPA

1990[3]): 34.68% Na, 47.20% SO_4, 1.3% F, 2.63% Cl, 1.28% K, 10.12 % OC (organic C), 0.39% Ca, <0.5% remainder. Although this suggests that a majority of PM emissions exiting the PM control device on a lime kiln, mostly very fine sub-micron sized particulates, are comprised of Na_2SO_4 or Na_2CO_3 and not the equivalent calcium salts, more such characterization data would be needed to confirm this observation.

4.12.2 *SO_2 Emissions*

Sulfur dioxide is formed in lime kilns when fuel oil, petroleum coke, rectified methanol or crude sulfate turpentine is used as fuel. SO_2 will also be formed if NCGs or SOGs containing sulfur are burned in the kiln. Median sulfur contents of CNCGs and SOGs have been reported as 1.22 and 2.83 lb/ADTP, respectively (NCASI 2013). Lime muds also contain a small amount of sulfur that converts to SO_2 during oxidation. Median sulfur contents of 7 lime muds have been reported at 0.2% (NCASI 1999), which translates to about 1.83 lb S/ADTP. [Note: A more recent NCASI study estimates lime mud S to be <0.1% (NCASI 2011)]. Thus, there can be significant inputs of sulfur to a lime kiln.

The regenerated quicklime in the kiln acts as an *in situ* scrubbing agent. Venturi scrubbers used for particulate control can further augment the SO_2 removal process since the scrubbing solution becomes alkaline from the captured lime dust. Efficiencies can be significantly increased when caustic (NaOH) is added to the recirculating scrubber fluid. On average, SO_2 emissions from lime kilns equipped with wet scrubbers are lower than emissions from kilns equipped with only ESPs. Lime kilns with total sulfur inputs under 10 lb/ton CaO have minimal SO_2 emissions (NCASI 2011), with SO_2 emissions tending to increase linearly with sulfur input as input levels increase beyond 10 lb/ton CaO. Thus, one strategy to minimize SO_2 is to limit the sulfur input to the kiln. This can be accomplished by scrubbing the NCGs to remove H_2S and methyl mercaptan prior to introduction to the kiln and/or lowering the fuel sulfur inputs. Installing a wet scrubber after an ESP or adding caustic to an existing scrubber can also lower SO_2 emissions.

There are three potential internal reactions for capture of SO_2 formed in a lime kiln: 1) SO_2 reacting with solid CaO to form solid $CaSO_4$ in the hot end of the kiln; 2) SO_2 reacting in the feed end of the kiln with solid $CaCO_3$ to form solid $CaSO_4$; and 3) reaction of gaseous sodium with SO_2 to form molten Na_2SO_4 in the hot end of the kiln (NCASI 2011). Sodium and sulfur balances around four kilns suggest the reaction with $CaCO_3$ dominates (NCASI 2011). SO_2 capture rates, calculated from kiln sulfur input/output data, indicate the rates are high for sulfur inputs less than 10 lb S/ton CaO but then begin to decline at a linear rate above this amount (NCASI 2010).

4.12.3 *NO_x Emissions*

NO_x emissions from lime kilns result mainly from fossil fuel combustion. A recent NCASI study involving NO_x testing at 15 lime kilns verified that "thermal" NO_x was the sole mechanism operative in gas-fired kilns, while the "fuel" NO_x mechanism was mostly operative in oil-fired kilns (NCASI 2003a). Gas-fired kiln NO_x emissions appeared to be strongly dependent on the dry-end lime temperature. Oxygen availability in the combustion zone was determined to be the key factor in oil-fired kilns. NO_x emissions for gas-fired kilns also exhibited high short-term variability, unlike for oil-fired kilns. Limited test data from two kilns burning petcoke and natural gas showed NO_x emission rates ranging from 0.7 to 4.3 lb/ton CaO, within the range observed for gas-fired kilns (NCASI 2011). It should be noted that in spite of the high N content of petcoke (>1%), only a very small fraction of this N is known to convert to NO_x (NCASI 2010). Analysis of long-term daily average data from two lime kilns showed no difference in NO_x emissions between days with and without LVHC NCG

[3] These emissions are likely for a lime manufacturing kiln since the estimates for F and Cl look suspicious for a kraft mill lime kiln. However, the fact that Na was the predominant alkali element rather than Ca is instructive.

burning. An earlier NCASI study (NCASI 2002b) had shown that when stripper off-gases (SOGs) containing ammonia were burned in lime kilns, a small fraction of the ammonia, from -1 to 23%, converts to NO_x.

The NCASI studies also showed kiln exit O_2 concentrations did not correlate well with gas-fired kiln NO_x emissions. Thus, efforts to reduce kiln exit O_2 levels will likely not affect kiln NO_x emissions. Low NO_x burners (LNB) to reduce NO_x emissions are considered technically infeasible in lime kilns. A 2003 permit review for a new lime kiln states, "Burner flame properties are critical to the quality control and calcining process to convert a high percentage of mud to reburned lime in the lime kiln. The burner flame shape and properties have a dramatic effect on calcining efficiency. Poor efficiency increases energy usage and decreases the calcining capacity of the kiln. Due to these technical complexities, the conversion of a standard lime kiln burner to low NO_x design is not yet technically feasible." However, a recent installation of a new design burner in a kraft pulp mill lime kiln has been claimed to lower NO_x emissions (Hart et al. 2011). In this burner, primary air is added on the inside of the flame to supposedly enhance mixing of the staged air and lower NO_x.

Fossil fuels burned in a kraft pulp mill lime kiln typically account for only about 10% of the total energy expended to make the pulp or paper product. Fossil fuels such as natural gas or residual fuel oil are typically burned in the kiln to generate the bulk of the energy required for calcination of the lime mud. Lime kilns are designed to recover "reburned" lime (CaO) by calcining the $CaCO_3$-containing lime mud with hot combustion gases resulting from fossil fuel combustion. Older kilns practice no heat recovery within the kiln itself. Newer kilns utilize higher efficiency internal components and product coolers to reduce the needed kiln volume and therefore the energy efficiency of the kiln (Hart et al. 2011). In any case, kiln gases typically enter the PM control device (wet scrubber or ESP) at temperatures below about 450°F. As such, the design of the lime kiln precludes the use of post-combustion NO_x reduction techniques such as selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). SNCR reactions require ammonia or urea injection into the flue gas at temperatures between 1,400 and 2,000°F, and ideal SCR reaction temperatures range from 640 to 805°F.

In summary, NO_x control strategies for each kiln have to be evaluated on a case-by-case basis. Techniques to minimize the hot end temperatures in gas-fired kilns, while potentially helpful in reducing NO_x emissions, should be balanced with the simultaneous need to stay within regulated limits for TRS compound emissions and to achieve the required calcining capacity. Controlling kiln exit O_2 concentrations may only have a limited impact in reducing kiln NO_x emissions.

4.12.4 *CO and VOC Emissions*

Emissions of CO and some VOCs (e.g., formaldehyde), mainly products of incomplete fuel combustion, are highly variable among kilns. Some volatile organic compounds that enter the kiln with the liquid component of lime mud are released as the mud is heated and thus have the potential to escape the kiln. VOCs present in scrubber make-up water can be stripped by the hot flue gas exiting the kiln. Methanol has been found to be the dominant organic compound present in lime kiln exhaust gases (NCASI 1994a), mainly a result of volatilization of the methanol in the liquid trapped in the lime mud entering the cold section of the kiln. Methanol and other VOCs entering the hot section of the kiln (where temperatures typically exceed 1800°F) via LVHC NCGs and SOGs are expected to be completely oxidized. An analysis of the emission data for various organic compounds corresponding to three lime kilns, with and without concurrent burning of LVHC NCGs, showed no discernible impact on the emissions due to the NCG burning (NCASI 1993).

Lime kiln CO and VOC emissions are generally quite small. Like all combustion devices, control strategies to minimize CO and VOC emissions involve increasing the residence time, oxygen content, temperature, and level of turbulence in the lime kiln. Use of cleaner water, i.e., water with lower

concentrations of methanol and other volatile organics, in the causticizing area and for scrubber make-up, can reduce VOC emissions.

Table 4.13 provides estimates of emissions for VOCs, SO_2, NO_x, CO, total filterable PM (TPM), condensible particulate emissions (CPM), filterable PM_{10}, and filterable $PM_{2.5}$ from kraft lime kilns. The averages for SO_2 emissions were derived from a combination of CEM data from the 2010 NO_x/SO_x survey (NCASI 2012) (5 kilns with ESPs and 7 with wet scubbers) and data in recent test reports submitted to EPA in response to the 2011 Pulp & Paper Mill Survey. The NO_x emission averages were derived from NCASI studies (NCASI 2003a). Distinct NO_x emission factors are provided for kilns firing oil and kilns firing natural gas.

Table 4.13 VOC[1], SO_2, NO_x, CO, TPM, CPM, PM_{10} and $PM_{2.5}$ Emissions from Lime Kilns

	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb/ton CaO				
VOC[1,4,5,6]	18	ND – 0.20	0.02	0.05	0.06	0.18[7]
SO_2[4]	7	0.006 – 0.93	0.03	0.26	0.42	1.32[12]
SO_2[5,6]	15	ND – 0.36	0.02	0.07	0.12	0.36[12]
NO_x[8]	15	0.30 – 5.90	0.70	1.69	1.72	2.29[12]
NO_x[9]	8	0.30 – 2.70	1.15	1.18	0.78	1.45[12]
CO	14	0.002 – 1.23	0.06	0.18	0.32	0.97[12]
TPM[4,10]	7	0.024 – 0.525	0.09	0.18	0.20	0.60[12]
TPM[5,10]	31	0.35 – 5.34	1.16	1.59	1.16	3.97[12]
TPM[6,10]	2	0.043 – 0.053	0.048	0.048	--	--
CPM[4,11,12]	2	0.022 – 0.151	0.087	0.087	--	--
CPM[5,11,12]	2	0.017 – 0.173	0.095	0.095	--	--
CPM[6,11,12]	2	0.07 – 0.161	0.116	0.116	--	--

[1]Measured as C using EPA Method 25A. [2]Number of kilns tested. [3]Upper Prediction Limit.
[4]Kilns with ESPs. [5]Kilns with wet scrubbers. [6]Kilns with ESP and wet scrubber.
[7]UPL with 95%; conf. coeff. - normal distribution. [8]Gas-fired kilns. [9]Oil-fired kilns.
[10]Total (filterable) particulate matter.
[11]Condensible particulate matter – obtained using the 2010 Revised EPA Method 202.
[12]Derived from filterable $PM_{2.5}$ data not corrected for blanks, and CPM data with only the allowed blank correction of 2 mg. NCASI will reissue these test results once the issue of blanks has been resolved. Facilities need to discuss the issue of blank correction prior to selecting the $PM_{2.5}$ data appropriate for emissions modeling; see Section 3.1 for details.

(continued on next page)

Table 4.13 Continued

	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
		lb/ton CaO				
PM_{10}[4,13]	7	as % of TPM		31.7%		
$PM_{2.5}$[4,12,13]	7	as % of TPM		10.2%		
PM_{10}[5,6,14]		as % of TPM		100%		
$PM_{2.5}$[5,6,14]		as % of TPM		100%		

[13]Average (mean) % of TPM – should be applied to specific kiln's TPM emissions.
[14]In the absence of a valid measurement method for filterable PM_{10} and $PM_{2.5}$ emissions from wet stacks, EPA's recommendation is to use 100% of TPM.

The CPM emission data summarized here for two kilns with ESPs and two kilns with wet scrubbers were obtained using the current version of EPA Method 202 for CPM measurement (issued in December 2010). EPA has developed source measurement methods for PM_{10} (Method 201A) and $PM_{2.5}$ (a modification of Method 201A). However, these methods were designed primarily for stacks following dry PM control devices. A significant fraction of the stacks on combustion sources in the pulp and paper industry are considered to be wet sources. Thus, EPA M201A cannot be used to accurately estimate PM_{10} and $PM_{2.5}$ emissions from these sources. NCASI and others are actively involved in research to develop methods to accurately measure fine PM emissions from wet stacks. In the absence of a valid measurement method for PM_{10} and $PM_{2.5}$ emissions from wet stacks, EPA's recommendation is to use 100% of TPM for both PM_{10} and $PM_{2.5}$ (as indicated in Table 4.13).

Information concerning the specifics of each lime kiln, including the tons of lime recovered per day, etc., are provided in electronic format (Excel) in Tables A13a, A13b, A13c, A13d, A13e and A13f at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

4.13 Causticizing Area Sources

Slakers are generally vented through a stack to discharge the large amounts of steam generated. The steam contains a considerable amount of particulate matter, which largely consists of calcium and sodium carbonates and sulfates. Scrubbers are generally employed to capture this particulate matter. Methanol and other gaseous organics are also present in slaker vent gases.

Numerous other pieces of equipment in the causticizing area are vented to the atmosphere. These sources are associated with the processing of green liquor (clarifiers, storage and surge tanks, dregs filters); white liquor (causticizer tanks, clarifiers, pressure filters, storage tanks); and lime mud (mix tanks, dilution tanks, storage tanks, pressure filters, precoat filters, filter vacuum pump exhausts). These sources typically have small gas flow rates and very low concentrations of gaseous organic compounds, with methanol being the primary one (NCASI 1994a). The amounts of organic compounds in the vent gases will be a function of the process liquid concentrations, temperature of the process, and vent gas flow rates. Total VOC emissions from all of these sources are on the order of 0.3 lb/ton CaO or less. Table 4.14 provides estimates of emissions for VOCs from several causticizing area sources and TPM emissions from six slakers. Detailed data including descriptions for each source are provided in Tables A14a and A14b at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.14 VOC and TPM Emissions from Causticizing Area Vents

Type of Vent(s)		No.[1]	Range	Median	Mean	Std. Dev.	UPL[2]
			lb/ton CaO				
Causticizer & Slaker – Combined	VOC[3]	5	0.011 to 0.27	0.057	0.103	0.103	0.273[2]
Slaker Scrubber Vent	VOC[3]	1		0.041	0.041		
Causticizer Vent	VOC[3]	1		8E-04	8E-04		
Slaker Scrubber Vent	TPM[4]	6	0.004 to 0.156	0.029	0.050	0.058	0.146[2]
Lime Mud Precoat Filter	VOC[3]	3	0.001 – 0.030	0.004	0.012	0.016	0.038[2]
Lime Mud Pressure Filter Vent	VOC[3]	1		0.0038	0.0038		
Lime Mud Dilution Tank	VOC[3]	1		0.085	0.085		
Lime Mud Mix Tank	VOC[3]	1		0.0013	0.0013		
Precoat Filter Vac. Pump Exhaust	VOC[3]	2	2E-04 – 0.035	0.018	0.018		
Green Liquor Clarifier	VOC[3]	1		0.066	0.066		
Green Liquor Surge Tank	VOC[3]	1		0.0014	0.0014		
Pressure Filter – White Liquor & Weak Wash	VOC[3]	1		0.0075	0.0075		
Pressure Filter – White Liquor Tank	VOC[3]	1		0.0056	0.0056		
White Liquor Oxidation Tank	VOC[3]	2	0.011 – 0.014	0.0123	0.0123		

[1]Number of sources tested. [2]Upper Prediction Limit with 95%; conf. coeff. - normal distribution.
[3]As C, measured using EPA Method 25A.
[4]Total (filterable) particulate matter – all TPM was <10μm (PM_{10}) in one slaker vent.

4.14 Smelt Dissolving Tank Vents

A great deal of turbulence occurs in a smelt dissolving tank because of the exothermic reactions between smelt and water. Steam, gases, and entrained particles from the tank are vented through a stack. Particulate matter is removed by a wet scrubbing device, such as a venturi scrubber. This is often followed by a mist eliminator to capture any entrained water droplets. The scrubber make-up water is typically weak wash, and the scrubber water is recycled back to the dissolving tank.

Particulate matter is the only significant criteria pollutant emitted from smelt dissolving tanks, except in cases where process condensates containing significant VOCs are used to either dissolve the smelt or for scrubbing the vent gases.

A relatively new development in control technology is the recirculation of smelt dissolving tank (SDT) vent gases to the recovery furnace. The vent gases are passed through a direct contact condensing scrubber followed by a mist eliminator to remove most of the moisture and particulate matter. The gases are then reheated and introduced as tertiary air in the upper part of the furnace (Medeiros, Kaila, and Simonen 2002). This approach has been used by three US mills that have installed new recovery furnaces within the last five years. The recovery furnace ESP will remove any residual particulate matter and any TRS will be largely oxidized to SO_2 and sulfate. Since the gas flow from the SDT is very small compared to that from the recovery furnace, this practice will have little impact on furnace emissions.

4.14.1 *Particulate Emissions*

As with the recovery furnace, particulates are comprised of mainly sodium compounds with much lesser amounts of potassium compounds and some other trace metal compounds. The dominant compound is sodium carbonate, followed by sodium sulfate. Roughly 90% (by weight) of the particles have equivalent aerodynamic diameters under 10 µm, and 50% have diameters under 1 µm (Pinkerton and Blosser 1981; NCASI 1978).

4.14.2 *VOC Emissions*

Volatile organic compounds such as methanol can be released from the weak wash in both the dissolving tank and the wet scrubber particulate control device.

4.14.3 *NO_x, CO and SO_2 Emissions*

Some mills have made measurements for NO_x, CO and SO_2 in smelt dissolving tank (SDT) vents. However, since no combustion takes place in smelt tanks, and smelt-water explosions are not known to result in NO_x, the low level of NO_x sometimes measured is believed to be an artifact caused by oxidation of a portion of the ammonia (NH_3) emissions from such tanks to NO within the NO_x analyzer (NCASI 2003c). Small amounts of CO and SO_2 at times measured in smelt tank vents could potentially result from oxidation of the carbon and sulfur in the smelt, respectively, during the smelt-water explosions.

Table 4.15 provides estimates of emissions for VOC, SO_2, CO, total filterable PM (TPM), condensible particulate emissions (CPM), PM_{10}, and $PM_{2.5}$ from SDTs that exhaust to the atmosphere. The CPM emission data summarized here for four smelt tanks were obtained using the current version of EPA Method 202 for CPM measurement (issued in December 2010). As discussed earlier, EPA Method 201A for PM_{10} and modified Method 201A for $PM_{2.5}$ cannot be used for sources such as SDTs with wet stacks. Thus, in the absence of a valid measurement method for filterable PM_{10} and $PM_{2.5}$ emissions from wet stacks, EPA's recommendation is to use 100% of TPM for both PM_{10} and $PM_{2.5}$ (as indicated in Table 4.15). Detailed data including descriptions for each smelt tank vent, including the black liquor solids rate, PM control device, etc., are provided in Tables A15a, A15b, A15c, A15d, and A15e at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Table 4.15 VOC, SO_2, NO_x, TPM, PM_{10} and $PM_{2.5}$ Emissions from Smelt Dissolving Tank Vents

	No.[1]	Range	Median	Mean	Std. Dev.	UPL[2]
		lb/ton BLS				
VOC[3]	13	ND – 0.25	0.01	0.066	0.087	0.281[4]
SO_2	20	ND – 0.073	0.006	0.015	0.020	0.062[4]
CO	3	0.006 to 0.025	0.008	0.013	0.010	0.030[5]
TPM[6]	36	0.035 – 0.64	0.15	0.16	0.10	0.41[4]
CPM[7,8]	4	0.008 – 0.026	0.012	0.015	0.008	0.028[5]
PM_{10}[9]		as % of TPM		100%		
$PM_{2.5}$[9]		as % of TPM		100%		

[1]Number of smelt tanks tested. [2]Upper Prediction Limit. [3]Lb C/ton BLS as measured by EPA Method 25A.
[4]UPL with 85% conf. coeff. – non-normal distribution. [5]UPL with 95%; conf. coeff. - normal distribution.
[6]Total (filterable) particulate matter.
[7]Condensible particulate matter - obtained using the 2010 Revised EPA Method 202 for CPM.
[8]Derived from CPM data with only the allowed blank correction of 2 mg. NCASI will reissue these test results once the issue of blanks has been resolved. Facilities need to discuss the issue of blank correction prior to selecting the $PM_{2.5}$ data appropriate for emissions modeling; see Section 3.1 for details.
[9]In the absence of a valid measurement method for filterable PM_{10} and $PM_{2.5}$ emissions from wet stacks, EPA's recommendation is to use 100% of TPM.

4.15 Miscellaneous Kraft Mill Sources

VOCs may be emitted from various other point sources in a kraft pulp mill. Table 4.16 provides estimates of VOC emissions from three salt cake mix tanks, one UNOX system vent, and one "direct contact" cooling tower. It should be noted that "direct contact" cooling tower VOC emissions are expected to be extremely mill-specific, depending mainly on the type of condensate reuse practices at the mill and level of VOCs present in the water sent to the cooling tower. Detailed data including descriptions for each source are provided in Table A16 at http://www.ncasi.org/Programs/Air-Quality/Resources/Air-Emissions-Database---Pulp-and-Paper/2013/Index.aspx.

Several other sources of total VOC emissions, mainly of the area source or fugitive type, potentially exist in a pulp and paper mill. These include wastewater treatment systems, both primary and secondary, open sewers, landfills, etc. No data are available for such sources. However, the total VOC emissions from these sources (except perhaps wastewater treatment systems) are expected to be small compared with those from various process vents and boiler stacks at a mill.

Table 4.16 VOC Emissions from Miscellaneous Kraft Mill Sources

	Units[1]	No.[2]	Range	Median	Mean	Std. Dev.	UPL[3]
Salt Cake Mix Tank Vent	lb/ton bls	3	3.9E-05 – 0.0076	0.0013	0.003	0.0041	0.0097
UNOX System Vent	lb/ADTUBP	1		0.017	0.017		
Cooling Tower[4]	lb/ADTUBP	1		0.79	0.79		

[1]Lb C as measured by EPA Method 25A. [2]Number of sources tested.
[3]Upper Prediction Limit with 95% conf. coeff. – normal distribution.
[4]Mill with steam stripper – tower treats entire mill effluent and discharges to a high rate activated sludge; not applicable for non-contact water cooling tower.

Another potentially large biogenic area source of VOC emissions at pulp mills and wood product mills is the bark and wood chip pile. Although attempts have been made to try and estimate such emissions (Axelsson et al. 1992 – Nordic mill study; Hiltgen and Myers 1996 – theoretical study; FPAC 2003 – Canadian mill study), NCASI is uncomfortable with the sampling methods and estimating methodologies involved in these studies and is currently conducting its own research into arriving at a satisfactory sampling method and emissions estimating methodology to estimate VOC emissions from bark and wood chip piles. Nevertheless, a preliminary methodology for estimating VOC emissions from bark and wood chip piles has been developed by NCASI and is provided in Appendix A. This methodology is based on applying the results of the field work performed by Axelsson et al. (1992) with Nordic spruce wood chips to a typical wood chip/bark pile configuration after adjusting for the turpentine content of a mill's wood species.

5.0 SULFITE PULP MILL SOURCES

In a sulfite pulp mill, VOC and SO_2 emissions can arise from uncontrolled digester and relief gases, pulp washing and bleaching sources, and recovery area sources. Just as for kraft pulp mill sources, fugitive VOC emissions from wastewater treatment area sources, such as primary clarifiers and secondary treatment systems, surface impoundments, flow-through basins, lagoons, and open sewers are not included in this report. CO is expected to be present in emissions from all vents where some form of combustion, either of spent liquor or fuel, takes place. CO is also expected from bleach plant vents (no data available). Particulate matter is expected to be present in emissions from the sulfite recovery furnaces, boilers, wood preparation activities and, to a lesser extent, paper machines. Limited data on particulate matter emissions from paper machines and wood preparation activities are presented in Sections 8.0 and 9.0. Oxides of nitrogen (or NO_x) are expected to be present in all combustion-related source vents.

5.1 Uncontrolled Digester Relief and Blow Gases

Digester vent gases in sulfite pulp mills contain significant concentrations of SO_2. However, because digester relief and blow gases are routed to condensers, absorbers, and scrubbers, and are normally mixed with gases from other sources such as evaporators, data reflecting uncontrolled digester emissions from current sulfite pulping operations are lacking. At many sulfite mills, there is a single SO_2 recovery system that typically treats digester, evaporator, and recovery furnace gases; this system usually has a single vent to the atmosphere. It is also possible to duct digester, evaporator, and washing system vent gases into the recovery furnace combustion chamber for SO_2 control purposes.