SNAP CODE: **040602**

SOURCE ACTIVITY TITLE: **PROCESSES IN WOOD, PAPER PULP, FOOD, DRINK & OTHER INDUSTRIES**
Paper Pulp (Kraft Process)

NOSE CODE: **105.07.01**

NFR CODE: **2 D 1**

1 ACTIVITIES INCLUDED

Pulp and paper production has three major processing steps: pulping, bleaching, and paper production. The type of pulping and the amount of bleaching used depends on the nature of the feedstock and the desired qualities of the end product. Kraft (sulphate) pulping is one of the chemical pulping processes that can be used. It is the most widely used pulping process and is typically used to produce strong paper products. The Kraft pulping process includes wood digestion in a water solution of sodium sulphide and sodium hydroxide, pulp washing, bleaching, chemical recovery, and by-product recovery.

Not all Kraft pulping and related processes that could result in the emission of significant amounts of NMVOC, SO_x, particulates, NO_x and CO are included under SNAP code 040602. Other significant sources are listed in Table 1.

Table 1.1 Other Relevant SNAP Codes for Paper Pulping - Kraft Process

Source	**SNAP CODE**
Combustion in boilers	03 01 xx
Lime kilns	03 03 12
Paper-mill industry (drying processes)(paper machines)	03 03 21
Waste water treatment	09 01 xx

In addition to more conventional fuels such as wood/bark, coal, oil and natural gas, boilers at pulp and paper mills may combust non-condensable gases, wastewater treatment sludge (from both virgin pulp and recycle operations), non-recyclable recovered paper, tire-derived fuel, old corrugated container materials etc (NCASI 1993).

It is assumed that these non-conventional fuels that are combusted in boilers will be covered in SNAP group 03.

2 CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions inventoried from Kraft pulp and paper processes are summarized in Table 2.1 and 2.2 below.

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

Table 2.1 Contribution to Total Emissions of the CORINAIR90 Inventory *(28 countries)*

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Paper Pulp	040602	0.1	0.1	0.1	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
= no emissions are reported

Table 2.2 1990 Emissions from Paper Pulping Kraft Process

Country	**Particulate**		**PM 10**		**PM 2.5**		**Hg**		**Pb**		**Cd**	
	Emissions (Mg)	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**
Canada[2] 1995	17901	1.5	12059	1.7	10013	2.3		0.01				
United States (1985)	112480						1.62[3]	1.1[4]				

Country	**SO_x**		**NO_x**		**CO**		**NMVOC**		**PAH**	
	Emissions (Mg)	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**	**Emissions (Mg)**	**%[1]**
Canada[2] 1995	5473	0.2	11092	0.5	24726	0.3	2757	0.1		
United States (1985)	112480	0.2			557867	0.6				

[1] As a percentage of total anthropogenic emissions for given country.

[2] Percentage Excludes Open Sources: Road Dust, Forest Fires, Wind Erosion, Construction, Prescribed Burning.

[3] 1994 - 5: US EPA 1997, Locating and Estimating

[4] 1995: US EPA 1997, Report to Congress.

Sources contributing to Kraft pulping emissions of VOCs in Canada in 1990 are summarised in Table 2.3.

Table 2.3 Sources of VOCs in Paper Pulping in Canada (CPPA n.d.)

Source	**Percent of Total Kraft Emissions**	**Percent Total Pulp and Paper**
Recovery boiler stack	42	16
Digester relief and blow tank	31	12
Lime kiln stack	8	3
Multiple effect evaporators	6	2
Black liquor oxidation system	5	2
Washers and screen	4	2
Smelt dissolving tank vent	3	1
Fluid bed calciner	0.3	0.1

3 GENERAL

3.1 Description

In Kraft pulping, white liquor, a water solution of sodium sulphide and sodium hydroxide, is used under high temperature and pressure to chemically dissolve the lignin that binds the cellulose fibres of the wood together. After the wood chips are subjected to this digestion, the wood pulp is washed, screened and dried to unbleached pulp or further delignified in an oxygen stage and bleached in a bleach plant. The inclusion of a bleaching step depends upon the intended use of the product. The remainder of the Kraft processes are designed to recover chemicals and heat. The spent cooking liquor, containing process chemicals and water and spent chemicals from the wood, is combined with pulp wash water to form what is called black liquor. This black liquor is concentrated through evaporation and then combusted in a recovery furnace, where heat from the combustion of organics is recovered for process use and for the generation of electrical power; inorganic chemicals are recovered as molten smelt. Water and quicklime are used to convert this smelt back to white liquor in a causticizing tank. The lime mud which precipitates from the tank is calcined in a lime kiln to regenerate quicklime. Kraft recovery systems may also receive spent liquor from neutral sulphite semi-chemical pulping mills.

3.2 Definitions and 3.3 Techniques

The main process steps involved in Kraft pulping are briefly described below. It is important to note that some of the main air emission sources for Kraft pulping are inventoried under separate SNAP codes (see section 1 above).

3.2.1 Stripping

Wet or dry barking techniques may be used.

3.2.2 Digestion

Wood chips are cooked in a digester with white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). There are two types of digester systems: batch and continuous. Once cooking is complete in either a batch or continuous process, the chemical mixture (black liquor) and pulp are discharged into a blow tank - a low pressure vessel. Vapours from the blow tank may be vented to an accumulator or a vapour sphere for collection. The vapours may be incinerated, stripped, or recovered for resale as turpentine or tall oil.

3.2.3 Washing

The pulp from the blow tank is washed to remove the black liquor from the pulp. There are several types of washers, including counter-current vacuum, diffusion, rotary pressure, horizontal belt filters, chemiwashers, wash press, and dilution/extraction. The black liquor extracted from this process is diluted with wash water, and so is called weak black liquor.

3.2.4 Delignification

In many mills, delignification is done in the digester. However additional reductions in lignin may be achieved through oxygen delignification and/or ozone bleaching.

3.2.5 Bleaching

The pulp is produced as a slurry after removal of spent cooking chemicals and dissolved wood organics. Bleaching chemical pulps is generally complex and uses several chlorine-based chemicals. Not all pulp is bleached.

3.2.6 Turpentine Production

The vapours discharged from the digester contain up to about 6 kg turpentine per tonne of pulp, depending upon wood species and cooking conditions. These vapours are normally condensed as part of the odour control system. Turpentine has a different specific gravity than water, and so can be decanted or recovered by other processes based on the density differences. The recovered turpentine is purchased by refining companies, or is used as fuel in the mill, most commonly in the lime kiln (see SNAP Code 03 03 12) (Environment Canada 1983).

3.2.7 Tall Oil Recovery

Tall oil precursors can be recovered from black liquor cooling and evaporation. The black liquor can have soap and other tall oil precursors skimmed from the surface of weak, intermediate, or strong black liquor storage tanks and from the black liquor oxidation process. The soap can then be sold or processed into tall oil by acidification (U.S. EPA 1991).

3.2.8 Chemical Recovery

The primary functions of the Kraft recovery system are: converting sulfur compounds in the black liquor to Na_2S; regenerating NaOH; generating large quantities of steam from combustion of organic by-products; and reducing or eliminating a potential pollution source by destroying the organic substances (mostly lignin) dissolved during the cooking. The key steps in the black liquor recovery are: evaporation or concentration; black liquor oxidation (optional); combustion/oxidation in a recovery furnace; recausticizing; and calcining in a lime kiln (the latter is described in SNAP Code 030312) (U.S.EPA 1991).

3.2.9 Evaporation

The majority of water removal from the weak black liquor, to about 55 percent solids, is usually carried out in multiple effect evaporators. This is a series of evaporators operated at different pressures so that the vapour from one evaporator body becomes the steam supply to the next evaporator. The vapour from the final evaporator is condensed in either a large heat exchanger (surface condenser) or by direct contact with water in a barometric condenser. A surface condenser requires a small vacuum system to remove non-condensable gases from the system.

Direct contact evaporators may then be used to further concentrate the black liquor to about 65 percent solids by bringing the liquor into direct contact with the flue gases from the recovery furnace. Alternatively, a forced circulation indirectly heated steam-heated evaporator, generally known as a concentrator, may be used.

3.2.10 Black Liquor Oxidation

Generation of H_2S results in the direct contact evaporator when sodium sulphide in black liquor comes in contact with carbon dioxide in the recovery furnace gases. This can largely be eliminated by oxidising the sodium sulphide with air, or oxygen, to sodium thiosulphite. Black liquor oxidation is not required if indirect evaporator concentrators are used (U.S. EPA 1991).

3.2.11 Recovery Furnace

The black liquor recovery furnace further concentrates the liquor solids. The heavy black liquor from the evaporators is heated and sprayed into the furnace. Water is evaporated from the liquor solids and the organics are burned to reduce oxidised sulphur components to sulfide. The inorganic black liquor chemicals form a molten smelt.

3.2.12 Recausticizing

In recausticizing, sodium carbonate (Na_2CO_3) in the smelt is converted into NaOH, an active cooking chemical. The smelt from the recovery furnace is dissolved in a tank with weak wash to form green liquor. After clarification, the green liquor is mixed with reburned lime to form a slurry and agitated at high temperatures to form lime mud. White liquor is clarified from the lime mud by decantation. The lime mud then goes to the lime kiln for calcination (SNAP CODE 030312).

Currently, research in new pulping processes based on organic solvents is directed to reduce the environmental effects and to reduce operating and investment costs. These organosolve processes result in lower gaseous emissions of sulphur dioxide and odorous compounds. However, these processes are generally characterised by high reaction temperatures and pressures, complicated pulp washing and recovery systems, and inferior pulp strength.

3.4 Emissions

Emission sources at Kraft pulp and paper mills are summarised in Table 3.1 (NCASI 1993, U.S. EPA 1985). Sources that are inventoried under separate SNAP Codes (marked *) have been included to provide an overall picture of these operations.

The term non-condensable gases is applied to the gases emitted from the pulping and black liquor evaporation processes, including digester relief gases, digester blow gases, evaporator gases and condensate stripper gases. These gases, which are stored in a tank, consist of a mixture of terpenes, total reduced sulphur (TRS) compounds and methanol along with a variety of less significant organics. Strictly speaking, these gases are all condensable, but the term is used to distinguish them from the vapours which do condense in the relief vent, blow heat recovery vent and evaporator non-condensable extraction system under normal conditions of operation. (Environment Canada 1983) In some cases these non-condensable gases are not collected, and so are considered as emission sources at the point of creation (i.e. digester, evaporator). However, they are, in North America and Scandinavia, typically collected and incinerated in the lime kiln or a dedicated boiler. In certain circumstances, however, about 2% of the time, these gases may be vented to the atmosphere, although in Scandinavia there is usually a second or back-up system for collection and destruction of non-condensable gases, which means that these gases are directly vented to the atmosphere less than 0.5% of the time. The non-condensable gases, collected but not incinerated, must be considered a potential source of VOCs. (NCASI 1993) Thus in Table 3.1 the digestion and evaporators will not be sources of VOCs if non-condensable gases are collected.

Table 3.1 Emission Sources in Paper Pulping - Kraft Process

Source							
	TPM	**PM 10**	**PM 2.5**	**SO_2**	**NO_x**	**VOC_s**	**CO**
Stripping						x	
Digestion				X[1]		x	
Washing				X[1]		x	
Bleaching						x	
Non-condensable gases:							
-- Collected, not incinerated				X[2]		X	
-- Incinerated				X[2]	x		
Turpentine Production						x	
Tall Oil Recovery						x	
Chemical Recovery							
-- Evaporation				x		x	
-- Black Liquor Oxidation						X	
-- Recovery Furnace			X	X	X	X	x
-- Recausticizing			X	x	x	x	
-- Lime Kiln[3]			X	x	X	X	x
Pulp Drying[3] (this will have to be confirmed based on SNAP code 03 03 21)						x	
Boilers (fuel-dependent)[3]			X	X	X	X	
Wastewater Treatment[3] (this will have to be confirmed based on SNAP code 09 01 xx)					X		

Major sources are marked with an X, minor sources are marked with an x.

1. Depending on if the gases are collected.
2. Depending on if the emissions are treated in a scrubber or if the incineration takes place in the lime kiln.
3. Recorded under separate SNAP codes.

Although these contaminants are emitted in varying quantities, the major problem for this industry is odour related due to TRS emissions.

3.5 Controls

This summary only refers to those Kraft pulp and paper processes that are included under SNAP Code 040602.

Emissions control at these mills is a major consideration in the design of a Kraft pulping mill and will, to a large extent, depend on the methods used to control odours. Control may include process modifications and improved operating conditions, as well as add-on emissions control.

For example, particulate control on recovery furnaces is achieved in a number of ways. In mills with either a cyclonic scrubber or cascade evaporator as a direct contact evaporator, particulate control efficiencies of 20 to 50% are achieved for the recovery furnace if gases from the recovery furnace are routed to these processes. An electrostatic precipitator or venturi scrubber and possibly auxiliary scrubbers may then be added to achieve the desired reduction of 85 to 99% (U.S. EPA 1985).

Since the particulate material that is released is largely sodium sulphate and sodium carbonate, the recovery through the use of ESPs or scrubbers is normally practised for economic reasons on all recovery furnaces (Environment Canada 1983).

Sulphur dioxide is emitted mainly from oxidation of reduced sulphur compounds in the recovery furnace, The U.S. EPA (1985) reports that the direct contact evaporator absorbs about 75% of these emissions, and that further scrubbing can provide additional control. Other methods may also be used to decrease the SO_2 emissions from the recovery boiler (SEPA 1992):

- changed combustion conditions;
- increased dry solids content of the strong liquor;
- decreased sulphur-to-sodium ratio in the furnace;
- decreased load of inert compounds;
- improved process control.

The major cause of carbon monoxide emissions from the recovery furnace is furnace operation well above rated capacity, which results in failing to maintain oxidising conditions.
Non-condensable gases are usually incinerated. In some cases the non-condensable gases are incinerated in a dedicated incinerator, which is effective but usually requires auxiliary fuel to maintain combustion. More recent installations incinerate the gases in the lime kiln, the power boiler or the recovery furnace. Incineration of these gases does result in the emission of SO_2. Scrubbers may be used to recover sulphur for the pulping process prior to incineration (Environment Canada 1983).

The reader is referred to European Commission 2001, Environment Canada 1983, and Swedish Environmental Protection Agency 1992 for more details.

4 SIMPLER METHODOLOGY

Emissions from Kraft pulping, tall oil and turpentine may be inventoried using the default emission factors provided in Table 8.1. These emission factors represent the high end of typical emission factors, and assume limited control technology is in place.

As an alternative method one can make use of emission calculation programmes which usually are based on average emission factors of typical mill configurations. In annex I there is a short description of a programme which can be used to calculate SO_2, TRS and NO_x emissions of Scandinavian or Iberian Kraft pulp mills.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

5 DETAILED METHODOLOGY

The preferred methodology is the use of continuous measurement data, which, in some countries, is available for major sources of SO_2, TRS and NO_x. This is particularly the case for modern Kraft mills, where there is collection of strong and dilute gases and as such there are a limited number of emission points to be monitored.

In older Kraft mills there are usually numerous emission sources and it is not economically possible to measure them all continuously. In these cases, the facilities are inventoried as point sources using total production statistics for each plant in combination with the most appropriate emission factors from Table 8.2. The selection of these factors will involve: a basic knowledge of the technology used at that facility (direct or indirect contact evaporator, the use of black liquor oxidation towers); some knowledge of the air pollution control techniques where choices are available for emission factors (primarily for the recovery furnace); a knowledge of by-product recovery facilities (turpentine and/or tall oil); and information on the occurrence of releases of non-condensable gases.

To facilitate the estimation of the fine particulate fraction of Total Particulate matter released the US EPA has developed software which will apply the effects of control devices on the fine fractions. Portions of the information contained in the software have been put into tables in this document for ease of use. This software is available on the Internet at: http://www.epa.gov/ttn/chief/index.html

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

Most emission factors are based on the production of air dried tonnes of pulp. Production of tall oil and/or turpentine in tonnes and tonnes of black liquor solids recausticized may also be relevant statistics.

7 POINT SOURCE CRITERIA

All Kraft pulping facilities could be inventoried as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

A summary of default emission factors for use with a simpler methodology for estimating emissions are provided in Table 8.1. The emission factors are extracted from the Integrated

Pollution Prevention and Control Reference Document on Best Available Techniques [IPPC, BREF] (European Commission, 2001) and are relative to existing plants as shown in Table 8.4. Emissions reported here are average values. Value for Carbon Monoxide is from EPA (EPA, 1985).

Care should be taken not to double-count emissions reported in 0301 Combustion in boilers, gas turbines and stationary engines, and 040602.

Table 8.1 Emission Factors for Kraft Pulping

Pollutant	kg/ADt pulp *
Total suspended particulate	1
NOx	1
SO_2	2,5
VOC	2
CO	5.5

* ADt = air dried tonnes of pulp

8.2 Detailed Methodology

Table 8.2 is a summary of reference emission factors for the detailed methodology for inventorying emissions from Kraft pulping processes. The values in this table are based mainly on the NCASI up-date of factors (NCASI 1993). For some processes, the most recently available data are from AP-42 (US EPA 1985 or Stanley 1991). Where data ranges are available, these are provided in the table immediately below the mean value. For particulate emissions, both controlled and uncontrolled emission factors are provided. The type of particulate control device used is provided in the table and applies only to the TSP emissions; the emissions of the other species are provided without specification of any control method. NO_x, SO_2 and CO emissions are expressed as NO_2, SO_2 and CO respectively.

Care must be exercised when using the VOC emission factors; the VOCs in the table are defined as the total gaseous non-methane organics (TGNMO). The NCASI factors are expressed in terms of kilograms of carbon per tonne air dry pulp and include both hydrocarbons such as turpentine (turpenes) and methanol as well as reduced sulphur compounds such as methyl mercaptan, dimethyl sulphide and dimethyl disulphide. The VOC emission factors in the table from AP-42 represent reduced sulphur compounds only, expressed in terms of sulphur. In either case, the average molecular weight of the gaseous mixture is required in order to permit a mass based emission factor to be calculated.

Table 8.2 Kraft Pulping Processes - Emission Factors

		TSP (Note 2)							
Source and Description	**Units (Note 1)**	**Uncontrolled**	**Controlled**	**Control Device**	**Ref**	**NOx (Ref) (Note 4)**	**SO2 (Ref) (Note 5)**	**VOC (Ref) (Note 3)**	**CO (Ref)**
Digestion	kg/Adt							0.6 (b) 0 (c)	
Washing									
- clean condensates used	kg/Adt					0 (a)	0 (a)	0.045 (a) (0.001-0.085) (a) 0.025 (b)	
- foul condensates used	kg/Adt					0 (a)	0 (a)	0.49 (a) (0.45-0.52) (a) 0.2 (b)	
Bleaching	kg/Adt					0 (a)	0 (a)	0.05 (a) (0.004-0.2) (a)	
Non-condensible gases									
- collected, not incinerated	kg/Adt							0.5 (a)	
- incinerated	kg/Adt						3 (a) (1.0-10.0) (a)		
Turpentine Production	kg/tonne turpentine							0.25 (b) 0.05 (c)	
Oxygen delignification reactors	kg/Adt					0 (a)	0 (a)	0.041 (a) (0.016-0.075) (a)	
Tall Oil Recovery	kg/tonne TO					0 (a)	0 (a)	2.0 (a) (0.1-4.9) (a)	
Chemical Recovery:									
Evaporation								0.05 (b)	
Black Liquor Oxidation	kg/Adt					0 (a)	0 (a)	0.17 (a) (0.12-0.22) (a)	
Recovery Furnace									

		TSP (Note 2)							
Source and Description	**Units (Note 1)**	**Uncontrolled**	**Controlled**	**Control Device**	**Ref**	**NOx (Ref) (Note 4)**	**SO2 (Ref) (Note 5)**	**VOC (Ref) (Note 3)**	**CO (Ref)**
- Without Direct Contact Evaporator	kg/Adt	115	1	ESP	b	1.16 (a) (0.85-2.0) (a)	2.1 (a) (0.005-43) (a)	0.14 (a) (0-0.8) (a)	5.5 (b)
- With Direct Contact Evaporator	kg/Adt	90	24 1 7.5 1.5	VS ESP VS/AXS ESP/AXS	b b b b	0.9 (a) (0.45-1.7) (a)	1.7 (a) (0.02-8.6) (a) 3.5(b)	0.53 (a) (0.005-1.13) (a) 1.5 (b)	5.5 (b)
Recausticizing	kg/tonne BLS	3.5	0.5 0.1	MP S	b b	0.017 (a) (<4E-4-0.075) (a)	0.008 (a) (0.0-0.038) (a) 0.1 (b)		
- With clean condensates	kg/tonne BLS							0.031 (a) (1.E-5-0.107) (a) 0.01 (b)	
- With dirty condensates	kg/tonne BLS							0.88 (a) (0.72-1.2) (a) 0.15 (b)	

Note 1: ADt = air dried tonnes of pulp. BLS = black liquor solids. TO = tall oil.

Note 2: Control device applies only to TSP emissions; no control devices specified for other species; ESP = electrostatic precipitator, VS = venturi scrubber, AXS = auxiliary scrubber, MP= mesh pad, S = packed tower scrubber.

Note 3: Units for Reference (a) are expressed as carbon; Units for Reference (b) are expressed as sulphur; VOC is defined as total gaseous non-methane organics (TGNMO) which includes reduced sulphur compounds.

Note 4: Ranges given in brackets apply to the value immediately above: emissions expressed as NO_2.

Note 5: Ranges given in brackets apply to the value immediately above: emissions expressed as SO_2.
REFERENCES: (a) NCASI, 1993; (b) US EPA, 1985; (c) Stanley, 1991

Quality Rating:

AP-42 factors are reported to have an A class quality rating at the time they were published in 1986; this rating may need to be reviewed in the light of process changes and particularly in terms of more recent control requirements. The NCASI emission factors would likely warrant an A quality rating.

The table below lists the US EPA FIRE 6.22 Emission factors from the processes in Kraft mills. These emission rates are for different control devices so care must be taken to use the appropriate emission rate.

Table 8.3 Emission Rates for Criteria and Toxic Pollutants (US EPA 1999)

Process	Pollutant	Control	Emission Rate	Units	Material	Quality
Digester Relief and Blow Tank						
	Methyl alcohol	None	8.50E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	7.00E-03	kg/Mg	ADt	D
Washer/Screens						
	Sulfur oxides (SOx)	None	5.00E-03	kg/Mg	ADt	A
	Volatile organic compounds (VOC)	None	1.00E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	1.35E-02	kg/Mg	ADt	D
Multi-effect Evaporator						
	Methyl ethyl ketone	None	1.35E-02	kg/Mg	ADt	D
Recovery Furnace/Direct Contact Evaporator						
	PM, filterable	None	9.00E+01	kg/Mg	ADt	U
	PM10, filterable	None	8.40E+01	kg/Mg	ADt	U
	PM 2.5 (AP-42, EPA 95)	None	7.5E+01	kg/Mg	ADt	C
	Carbon monoxide	None	5.50E+00	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	3.50E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	9.75E-01	kg/Mg	ADt	U
	Hexachlorodibenzo-p-dioxins, total	ESP	1.10E-03	mg/Mg	ADt	U
	Methyl ethyl ketone	None	7.50E-03	kg/Mg	ADt	D
	Nitrogen oxides (NOx)	None	1.00E+00	kg/Mg	ADt	U
	Pentachlorodibenzo-p-dioxins, total	Misc.	3.80E-04	mg/Mg	ADt	U
	Tetrachlorodibenzo-p-dioxins, total	Misc.	2.90E-04	mg/Mg	ADt	U
	2,3,7,8-Tetrachlorodibenzofuran	ESP	3.40E-05	mg/Mg	ADt	U
Smelt Dissolving Tank						
	PM, filterable	None	3.50E+00	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.00E-01	kg/Mg	ADt	U
	PM10, filterable	None	3.10E+00	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	5.00E-01	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	8.00E-02	kg/Mg	ADt	U
Lime Kiln						
	PM10, filterable	None	4.70E+00	kg/Mg	ADt	U
	PM, filterable	None	2.80E+01	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.50E-01	kg/Mg	ADt	A
	Carbon monoxide	None	5.00E-02	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	1.40E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	1.25E-01	kg/Mg	ADt	U
	Nickel	None	6.45E-05	kg/Mg	ADt	U
	Mercury	None	1.45E-07	kg/Mg	ADt	U
	Lead	None	5.44E-05	kg/Mg	ADt	U
	Copper	None	1.40E-05	kg/Mg	ADt	U
	Chromium	None	2.33E-04	kg/Mg	ADt	U
	Cadmium	None	1.01E-06	kg/Mg	ADt	U
	Arsenic	None	2.34E-07	kg/Mg	ADt	U
	Selenium	None	2.02E-07	kg/Mg	ADt	U

Process	Pollutant	Control	Emission Rate	Units	Material	Quality
	Manganese	None	1.75E-05	kg/Mg	ADt	U
	Beryllium	None	3.90E-06	kg/Mg	ADt	U
	Fluoranthene	None	<1.74E-6	kg/Mg	ADt	U
	Acetaldehyde	None	3.70E-05	kg/Mg	ADt	U
	2,3,7,8-Tetrachlorodibenzofuran	None	0.00E+00	kg/Mg	ADt	U
	Polychlorinated dibenzofurans, total	None	4.23E-10	kg/Mg	ADt	U
	Polychlorinated dibenzo-p-dioxins, total	None	1.42E-09	kg/Mg	ADt	U
	Pentachlorodibenzofurans, total	None	5.37E-11	kg/Mg	ADt	U
	Octachlorodibenzo-p-dioxins, total	None	8.76E-10	kg/Mg	ADt	U
	Tetrachlorodibenzofurans, total	None	1.27E-10	kg/Mg	ADt	U
	Hexachlorodibenzofurans, total	None	4.20E-11	kg/Mg	ADt	U
	Heptachlorodibenzofurans, total	None	8.31E-11	kg/Mg	ADt	U
	Hydrogen chloride	None	1.10E-06	kg/Mg	ADt	U
Turpentine Condenser						
	Methyl ethyl ketone	None	4.50E-03	kg/Mg	ADt	D
	Volatile organic compounds (VOC)	None	3.50E-02	kg/Mg	ADt	U
Fluid Bed Calciner						
	PM10, filterable	None	2.52E+01	kg/Mg	ADt	U
	Sulfur oxides (SOx)	None	1.50E-01	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	1.40E+00	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	1.25E-01	kg/Mg	ADt	U
Liquor Oxidation Tower						
	Sulfur oxides (SOx)	None	1.00E-02	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	2.25E-01	kg/Mg	ADt	U
	Methyl ethyl ketone	None	5.00E-03	kg/Mg	ADt	D
Recovery Furnace/Indirect Contact Evaporator						
	PM, filterable	None	1.15E+02	kg/Mg	ADt	U
	PM10, filterable	None	1.15E+02	kg/Mg	ADt	U
	Carbon monoxide	None	5.50E+00	kg/Mg	ADt	U
	Nitrogen oxides (NOx)	None	9.50E-01	kg/Mg	ADt	U
	Volatile organic compounds (VOC)	None	4.00E-01	kg/Mg	ADt	U
Other Not Classified						
	Chloroform	None	9.25E-03	kg/Mg	ADBt	U
	Formaldehyde	None	3.23E-03	kg/Mg	ADBt	U
	Ethylene dibromide	None	< 2.01E-4	kg/Mg	ADBt	U
	Dichloromethane	None	6.91E-05	kg/Mg	ADBt	U
	Methyl alcohol	None	2.68E-03	kg/Mg	ADBt	U
	Chlorine	None	1.07E-06	kg/Mg	ADBt	U
	Carbon tetrachloride	None	4.07E-04	kg/Mg	ADBt	U
	Benzene	None	9.12E-05	kg/Mg	ADBt	U
	Acetaldehyde	None	5.47E-06	kg/Mg	ADBt	U
	Methyl alcohol	None	3.91E+00	kg/Mg	ADBt	U
	Methyl alcohol	None	8.44E-04	kg/Mg	ADBt	U
	Methyl ethyl ketone	None	1.50E-03	kg/Mg	ADBt	D
	1,1,1-Trichloroethane	None	1.57E-04	kg/Mg	ADBt	U
	Trichloroethylene	None	3.32E-05	kg/Mg	ADBt	U
	Acetaldehyde	None	7.01E-06	kg/Mg	ADBt	U
	Acetaldehyde	None	3.61E-04	kg/Mg	ADBt	U

ADt - tonnes Air Dried Unbleached Pulp; ADBt - tonnes Air Dried Bleached Pulp

The emission factors, for recovery furnaces, extracted from the IPPC BREF (European Commission, 2001) are reported in Table 8.4. Typical emissions are the emissions from existing plants. best available techniques (BAT) for reducing emissions to air included in BREF are:

- SO_2 emissions are controlled by firing high dry solids concentration black liquor in the recovery boiler and/or by using a flue gas scrubber;
- NO_x emissions ensuring proper mixing and division of air in the boiler, and for new or altered installations also by appropriate design;
- flue gases are cleaned with efficient electrostatic precipitators to mitigate dust emissions.

In the table the BAT emission levels to air from the process that are associated with a combination of these techniques are shown. The emission levels refer to yearly averages and standard conditions.

Table 8.4 IPPC BREF Emission Factors for Kraft Pulping (recovery furnaces)

Source	**Units***	**TSP**	**NO_x**	**SO_2**	**VOC**
Typical	kg/ADt	0.1-1.8 (1)	0.6-1.8	1-4 (2) 0.1-0.4 (3) 0.2-0.5 (4)	0.1 (5) 0.4 (6)
BAT	kg/ADt	0.2-0.5	1-1.5	0.2-0.4	
Chips store	kg/m^3 of wood				0.2-0.3 (7)

* ADt = air dried tonnes of pulp
(1) after electrostatic precipitator
(2) without scrubber and 63-65% dry solids of black liquor
(3) with scrubber and 63-65% dry solids of black liquor
(4) without scrubber and 72-80% dry solids of black liquor
(5) softwood kraft
(6) hardwood kraft
(7) mainly turpenes, emitted to the atmosphere from wood chips stored in heaps outdoors the process

Table 8.5 below lists the latest US EPA emission percentages for the fine particulate fraction of Total Suspended Particulate (TSP) from the PMCALC software for estimating PM 10 and PM 2.5 emissions.

Table 8.5 Fine Particulate Fractions of Total Suspended Particulate. (US EPA 1997)

	Fine Particulate Fraction [%]		
Process	**PM10**	**PM6**	**PM2.5**
Digester Relief and Blow Tank	94.0	91.0	78.0
Washer/Screens	94.0	91.0	78.0
Multi-effect Evaporator	94.0	91.0	78.0
Recovery Furnace/Direct Contact Evaporator	93.3	92.2	83.3
Smelt Dissolving Tank	88.6	85.7	74.3
Lime Kiln	16.8	13.6	10.4
Turpentine Condenser	85.0	62.0	30.0
Fluid Bed Calciner	70.0	60.0	40.0
Liquor Oxidation Tower	94.0	91.0	78.0
Recovery Furnace/Indirect Contact Evaporator	100.0	80.5	78.3

Process	Fine Particulate Fraction [%]		
	PM10	PM6	PM2.5
Liquor Clarifiers	94.0	91.0	78.0
Other Not Classified	94.0	91.0	78.0

Control Devices:

The US EPA PMCALC program for calculating PM 10, PM 6, and PM 2.5 emissions based on TPM emissions lists the following control percentages for control devices:

Table 8.6 Fine Particulate Control Efficiencies (US EPA 1997)

Control Device	Control Efficiencies [%]		
	PM 10	PM 6	PM 2.5
None	0.0	0.0	0.0
None	0.0	0.0	0.0
Wet scrubber - hi-efficiency	99.0	95.0	90.0
Wet scrubber - med-efficiency	95.0	85.0	25.0
Wet scrubber - low-efficiency	90.0	80.0	20.0
Gravity collector - hi-efficiency	6.0	5.0	3.6
Gravity collector - med-efficiency	4.8	4.0	2.9
Gravity collector - low-efficiency	3.7	3.2	1.5
Centrifugal collector - hi-efficiency	95.0	95.0	80.0
Centrifugal collector - med-efficiency	85.0	75.0	50.0
Centrifugal collector - low-efficiency	50.0	35.0	10.0
Electrostatic precipitator (high efficiency)	99.5	99.0	95.0
Electrostatic precipitator - med-efficiency	97.0	90.0	80.0
Electrostatic precipitator - low-efficiency	90.0	80.0	70.0
Mist eliminator - high velocity >250 FPM	90.0	75.0	10.0
Mist eliminator - low velocity <250 FPM	75.0	40.0	5.0
Fabric filter - high temperature	99.5	99.5	99.0
Fabric filter - med temperature	99.5	99.5	99.0
Fabric filter - low temperature	99.5	99.5	99.0
Liquid filtration system	85.0	75.0	50.0
Packed-gas absorption column	99.0	95.0	90.0
Tray-type gas absorption column	95.0	85.0	25.0
Spray tower	90.0	80.0	20.0
Venturi scrubber	99.0	95.0	90.0
Process enclosed	3.7	3.2	1.5
Impingement plate scrubber	99.0	95.0	25.0
Dynamic separator (dry)	99.0	95.0	90.0
Dynamic separator (wet)	85.0	75.0	50.0
Mat or panel filter - mist collector	97.0	94.0	92.0
Multiple cyclone w/fly ash reinjection	20.0	15.0	10.0
Metal fabric filter screen	90.0	65.0	40.0
Dust suppression by water sprays	90.0	65.0	40.0
Dust suppression by chemical stabilizer or wetting	80.0	5.0	0.0
Wet cyclonic separator	97.0	90.0	80.0
Gravel bed filter	90.0	20.0	10.0
Annular ring filter	50.0	35.0	10.0

Control Device	**Control Efficiencies [%]**		
	PM 10	**PM 6**	**PM 2.5**
Fluid bed dry scrubber	85.0	75.0	50.0
Single cyclone	95.0	95.0	80.0
Multiple cyclone w/o fly ash reinjection	85.0	75.0	50.0
Water curtain	90.0	45.0	10.0

9 SPECIES PROFILES

The U.S. EPA (1994) generic VOC speciation profile for the Kraft Pulping classification under the Pulp and Paper Source Category (Profile 9001, External Combustion Boilers - Industrial - Average) is presented in Table 9.1.

Table 9.1 U.S. EPA VOC Speciation Profile for Kraft Pulping (U.S. EPA 1994)

Species Name	**Mol. Wt.**	**% Wt.**
Isomers of hexane	86.17	0.89
Isomers of heptane	100.2	0.37
Isomers of octane	114.23	0.67
Isomers of pentane	72.05	2.07
C7-C16 paraffins	156.31	5.62
Methane	16.04	23.35
Ethane	30.07	11.41
Ethylene	28.05	1.67
Propane	44.09	4.19
Propene	42.08	2.65
Acetylene	26.04	2.32
n-Butane	58.12	9.24
Butene	56.1	0.87

This profile is applied to washers/screens, recovery furnaces (with or without direct contact), recausticizing, turpentine condensers and black liquor oxidation. A quality rating of E is provided with this profile.

It is important to note that the definition of VOCs used by the U.S. EPA excludes reduced sulphur compounds and halogenated organics. The National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI) (1993) VOC definition is based on TGNMO and includes organo-sulphur compounds such as methyl mercaptan, dimethyl sulphide and dimethyl disulphide. A typical VOC content of non-condensable gas emissions provided by NCASI (1993) is summarised in Table 9.2.

Table 9.2 NCASI VOC Speciation Profile for Kraft Pulping (NCASI 1993)

Species	Composition % by volume
Methyl mercaptan	2.1
Dimethyl sulphide	2.1
Dimethyl disulphide	1.7
Turpentine	0.1
Methanol	0.2

If these sulphur compounds are incinerated and the combustion vented without scrubbing, then the sulphur dioxide produced by combustion should be added to the SO_2 emissions.

The U.S. EPA has published a particulate matter speciation profile for Kraft recovery furnaces (available through the CHIEF bulletin board system). Part of this particulate profile number 23103 is presented in Table 9.3.

Table 9.3 U.S. EPA Partial Profile for Particulate Emissions from Kraft Recovery Furnaces with ESP and Wet Scrubber - (Profile 23103 - Data Quality D)

Species	% weight	Uncertainty
Arsenic	0.004	0.003
Cadmium	0.018	0.013
Chromium	0.016	0.010
Copper	0.004	0.004
Mercury	0.002	0.003
Nickel	0.026	0.042
Lead	0.026	0.017
Selenium	0.005	0.004
Zinc	0.017	0.014

Emissions from stripping and chip storage operations consist of terpenes.

The Swedish Environmental Protection Agency (SEPA 1992) reports that over sixty compounds have been identified in Kraft condensates, at concentrations between trace levels and 1% by weight. The impurities include:

Bivalent sulphur compounds	- hydrogen sulphide
	- methyl mercaptan
	- dimethyl sulphide
	- dimethyl disulphide
Alcohols	- methanol
	- ethanol
Ketones	- acetone
Terpenes	- pinene
	- terpineol
Phenolics	- phenol
	- guaiacols
	- cresols

Methanol is the main impurity, with a total emission of about 5 to 10 kg/ADt.

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simpler methodology relies on emission factors that may not be representative of the process. The detailed methodology is more detailed but still relies on typical emission factors, and may still not result in accurate estimates. The preferred methodology would involve the measurement of emissions from each plant to develop site-specific emission factors for all potentially significant sources. These emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, new site-specific emission factors should be derived based on testing. However, this program is costly and time consuming. Continuous measurements are required in some countries (see section 5).

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emissions estimate can be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Kraft pulping facilities normally run year-round. It may be assumed that emissions occur uniformly over diurnal and annual cycles, barring unusual operational disruptions.

14 ADDITIONAL COMMENTS

While organo-sulphur compounds have, in some cases, been included under the VOC classification, in some circumstances these compounds should be classed as sulphur dioxide emissions depending on the application of the inventory data. Reduced sulphur compound are a source of odour and toxic effects and where considerations are focused on the impacts of emissions on local to urban scales, it is appropriate to consider these compounds separately and not to group them in the VOC class. Where impacts on regional, continental or global scales are of concern, the reduced sulphur compounds should probably be classed with sulphur dioxide emissions since they are fairly rapidly oxidised in the atmosphere yielding SO_2, which participates in other chemical reactions in the atmosphere to produce acidification.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

17 REFERENCES

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19 RELEASE VERSION, DATE AND SOURCE

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