



National Pollutant Inventory

# **Emission Estimation Technique Manual**

**for**

## **Pulp and Paper Manufacturing**

First Published in August 1998

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**EMISSION ESTIMATION TECHNIQUES  
FOR  
PULP AND PAPER MANUFACTURING**

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## PULP AND PAPER MANUFACTURING

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## 1.0 Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in pulp and paper product manufacturing.

The pulp and paper product manufacturing activities covered in this Manual apply to facilities primarily engaged in the manufacture of paper pulp, and the conversion of this pulp into paper, cardboard, newsprint, paperboard, and solid fibreboard sheets.

EET MANUAL: Pulp and paper manufacturing

HANDBOOK: Paper and paper product manufacturing  
- Pulp, paper and paperboard manufacturing  
- Solid paperboard container manufacturing  
- Corrugated paperboard container manufacturing  
- Paper bag and sack manufacturing  
- Paper product manufacturing n.e.c.

ANZSIC CODES: 233 (including 2331, 2332, 2333, 2334, and 2339)

This Manual was drafted by the NPI Unit of the Queensland Department of Environment on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

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## 2.0 Process Description

The pulp and paper product manufacturing activities covered by this EET Manual include the production of commodity grades of paper pulp, printing and writing papers, sanitary tissue, industrial-type papers, containerboard, and boxboard. The primary materials used for production are cellulose fibre from timber, and purchased or recycled fibres.

Pulp and paper manufactures can also be categorised by the pulping process used in their production. The pulping process affects the strength, appearance, and intended use of the resultant paper product. Pulping processes are the major source of environmental impacts in this industry, and each pulping process has its own set of process inputs, and subsequent NPI listed substance outputs.

## 3.0 Emission Estimation

Pulp and paper mills generate a range of emissions of listed substances from pulping processes and power generation. Major sources of emissions occur at the pulping and bleaching stages, and in energy generation.

Estimates of emissions of listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility. These are described in *The NPI Guide*. Select the EET, or mix of EETs, which is most appropriate for your purposes. If you estimate your emission by using any of these EET's, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of emission estimation techniques that are not outlined in this Handbook, your data will also be displayed as being of 'acceptable reliability'.

For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

**You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if you already undertake direct measurement, you may use this information for NPI reporting purposes (if you do not undertake direct measurement, the NPI does not require you to do so).**

### 3.1 Emissions To Air

Air emissions may be categorised as :

#### **Fugitive emissions**

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats or open vessels, and material handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions. Emission factor EETs are the usual method for determining losses through fugitive emissions.

#### **Point source emissions**

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. An air emissions control device such as a carbon adsorption unit, scrubber, baghouse, or afterburner may be used prior to the atmospheric release. Table 1 highlights common air emissions from pulp and paper processes.

**Table 1. Common Air Emissions from Pulp and Paper Processes**

Source	Effluent Characteristics
Kraft recovery furnace	Particulate matter (PM <sub>10</sub> )
Fly ash from wood waste and coal fired boilers	Particulate matter (PM <sub>10</sub> )
Sulphite mill operations	Sulphur oxides
Kraft pulping and recovery processes	Reduced sulphur gasses
Chip digester and liquor evaporation	Volatile organic compounds
All combustion processes	Oxides of nitrogen, SO <sub>x</sub> , CO, PM <sub>10</sub>

USEPA 1995, *Pulp and Paper Industry Sector Notebook Project*

### 3.2 Emissions To Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

The discharge of listed substances to a sewer or tailings dam does not require you to report to the NPI (See also Section 3.0 of *The NPI Guide*). The main source of wastewater from this industry is usually from air pollution control equipment such as wet scrubbers.

The most appropriate method for determining emissions to the environment via wastewater is to use direct measurement, however, you may use other EETs for the purposes of reporting to the NPI. Table 2 highlights common water emissions from Pulp and Paper Processes.

**Table 2. Common Water Emissions from Pulp and Paper Processes**

Source	Effluent Characteristics
Water used in wood handling, debarking, and chip washing	Solids, BOD, colour
Chip digester and liquor evaporator condensate	Concentrated BOD, reduced sulphur compounds
'White waters' from pulp screening, thickening, and cleaning	Large volumes of water with suspended solids, can have significant BOD
Bleach plant washer filtrates	BOD, colour, chlorinated organic compounds
Paper machinewater flows	Solids, often precipitated for reuse
Fibre and liquor spills	Solids, BOD, colour

USEPA 1995, *Pulp and Paper Industry Sector Notebook Project*

### 3.3 Emissions To Land

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids, and the use of chemicals to control various elements of the environment where these emissions contain listed substances. These emission sources can be broadly categorised as :

- surface impoundments of liquids and slurries
- unintentional leaks and spills.

### 3.4 Process Inputs And Emission Outputs

Kraft chemical pulping and traditional chlorine-based bleaching are both commonly used, and may generate significant emissions. Emissions from mechanical, semi-chemical, and secondary fibre pulping are small when compared to kraft chemical pulping, which is the most significant source of air pollutant emissions. Pollutant emissions from chlorine bleaching, and chlorinated by-products (ie. chloroform and dioxin), are particular problems due to their persistence, non-biodegradability, and toxicity.

Table 3 shows emission sources for ubiquitous pollutants, and Table 4 illustrates the process inputs and specific emission outputs including micro-pollutants, for a pulp and paper mill using kraft chemical pulping

and traditional chlorine-based bleaching. Currently, extensive chlorine dioxide substitution is practiced in many bleaching processes in place of traditional chlorine bleaching. The process outlined below produces a large portion of Australian pulp.

**Table 3. Emission Sources for the Kraft Process**

Source	Particulate Matter (PM <sub>10</sub> )	SO <sub>2</sub>	Oxides of Nitrogen	Volatile Organic Compounds	CO
Stripping				Y	
Digestion		X <sup>1</sup>		Y	
Washing		X <sup>1</sup>		Y	
Bleaching				Y	
Non-condensable Gases:					
Collected, not Incinerated		X <sup>2</sup>		X	
Incinerated		X <sup>2</sup>	Y		
Turpentine Production				Y	
Tall Oil Recovery				Y	
Chemical Recovery					
Evaporation		Y		Y	
Black Liquor Oxidation				X	
Recovery Furnace	X	X	X	X	Y
Recausticising	X	Y	Y	Y	
Lime Kiln	X	Y	X	X	Y
Pulp Drying				Y	
Boilers (fuel dependent)	Y	X	X	X	
Wastewater Treatment			X		

USEPA 1995, *Pulp and Paper Industry Sector Notebook Project*

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

<sup>1</sup> Depends if the gases are collected.

<sup>2</sup> Depends if the emissions are treated in a scrubber or if incineration takes place in the kiln.

**Table 4. Kraft Chemical Pulped-Chlorine Bleached Paper Production**

Process Step	Material Inputs	Process Outputs	NPI Listed Substance Emissions <sup>a</sup>	Emission Media
Fibre Furnish Preparation	Wood logs Chips Sawdust	Furnish chips	particulate matter (PM <sub>10</sub> )	Air
Chemical Pulping	Furnish chips	Black liquor (to chemical recovery system, pulp (to bleaching & processing))	chlorinated organic compounds (dioxins and furans), VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone)	Water
			chlorinated organic compounds (dioxins and furans), VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone)	Air
	Cooking chemicals: Na <sub>2</sub> S, NaOH, white liquor		reduced sulphur compounds, organo-chlorine compounds	
Bleaching	Chemical pulp	Bleached pulp	chlorinated organic compounds (dioxins and furans), inorganic chlorine compounds (eg chlorate (ClO <sub>3</sub> )) <sup>b</sup>	Water
	Elemental chlorine and chlorine compounds		organo-chlorine compounds (eg dioxins and furans)	
	Hypochlorite and chlorine dioxide		VOCs (acetone, dichloromethane, chloroform, MEK, carbon disulphide, chloromethane, trichloroethane)	Air / Water
Papermaking	Additives, Bleached / Unbleached pulp	Paper / paperboard product	organic compounds	Water
			acetone	
Wastewater Treatment	Process wastewaters	Treated effluent	sludges containing listed substances	Solid

**Table 4. Kraft Chemical Pulped-Chlorine Bleached Paper Production (cont'd)**

Process Step	Material Inputs	Process Outputs	NPI Listed Substance Emissions <sup>a</sup>	Emission Media
			VOCs (terpenes, MEK alcohols, phenols, methanol, acetone, chloroform)	Air
			chlorophenolics	Water
			carbon disulphide	
			VOCs (terpenes, MEK alcohols, phenols, methanol, acetone, chloroform)	
Power Boiler	Natural gas, wood waste, coal	Energy	PM <sub>10</sub> , CO, NO <sub>x</sub> , SO <sub>2</sub>	Air
<b>Chemical Recovery System</b>				
Evaporators	Black liquor	Strong black liquor	evaporator non-condensables (TRS, VOCs, alcohols, phenols, terpenes)	Air
Recovery Furnace	Strong black liquor	Smelt	PM <sub>10</sub> , TRS, SO <sub>2</sub>	Air
		Energy		
Calcining	Lime mud	Lime	PM <sub>10</sub>	Air

Adapted from USEPA 1995, *Pulp and Paper Industry Sector Notebook Project*

<sup>a</sup> Emissions may differ significantly based on mill processes and material inputs.

<sup>b</sup> Chlorate only significantly produced in mills with high rates of chlorine dioxide substitution.

Pulp and paper manufacturing processes in Australia vary significantly, and each reporting facility will handle a different range of substances on the NPI reporting list as a result of the differing processes used. As each facility in Australia is unique, you are encouraged to develop process flow diagrams for your own operations detailing the input of materials and listed substances, and the waste sources and emissions resulting from the operation of each process. The flow diagrams and tables contained in this section are merely a guide to some of the possible emissions that may arise from different processes under different conditions.

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## 4.0 Emission Factor Rating

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in the references section of this document. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived.

The EFR system is as follows :

A	-	Excellent
B	-	Above Average
C	-	Average
D	-	Below Average
E	-	Poor
U	-	Unrated

Estimating your facility's emissions based on emission factors only, and without taking into account any control measures, may have an uncertainty as high as 100%.

Other EETs, such as release calculations based on mass balance of solvent consumption and without taking into account control measures, may have an uncertainty of 50%.

An EET based on an audit or direct measurement, and taking into account control measures, may have an uncertainty of 20% .

## 5.0 Emission Factors

### 5.1 Using Sampling Data

Stack sampling test reports often provide emissions data in terms of kg/hr or grams /dscm (dry standard cubic metre). Annual emissions for NPI reporting can be calculated from this data using Equations (1) or (2) overleaf. Stack tests for NPI reporting should be performed under representative (ie.normal) operating conditions. As stated previously, you may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement.

You should be aware that some tests required for State and Territory license conditions may need to be undertaken when operating under maximum emissions rating. Consequently, emissions are likely to be higher than when operating under normal conditions.

This Section shows how to calculate emissions in kg/hr based on stack sampling data, and how to convert this to an annual emissions figure. Calculations involved in determining PM<sub>10</sub> emissions are used as an example, although the same calculations are applicable for most of the substances listed on the NPI.

**Table 5. List of Variables and Symbols**

Variable	Symbol	Units
Concentration	C	parts per million volume dry
Molecular weight	MW	kg/kg-mole
Molar volume @ STP (standard temperature and pressure)	V	22.4 m <sup>3</sup> /kg-mole @ 0°C and 1 atmosphere
Flow rate	Q <sub>a</sub>	actual cubic metres per minute (acms)
Flow rate	Q <sub>d</sub>	dry standard cubic metres per second (dscms)
Emissions	E <sub>x</sub>	typically kg/hr or pollutant x
Annual emissions	E <sub>tpv,x</sub>	tonnes/year of pollutant x
Filter catch	C <sub>f</sub>	grams (g)
Fuel use	Q <sub>f</sub>	typically, kg/hr
PM <sub>10</sub> concentration	C <sub>PM</sub>	grams/dscm
Metered volume at standard temperature and pressure	V <sub>m, STP</sub>	dscm
Moisture	R	percent
Temperature	T	degrees Celsius
Paper pulp production	A	tonnes/year
Annual operating hours	OpHrs	hours/year

QLD Department of Environment 1998

An example summary of a test method is shown in Table 6. The table shows the results of three different sampling runs conducted during one test event. The source parameters measured as part of the test run include gas velocity and moisture content, which are used to determine exhaust gas flow rates in dscms.

The filter weight gain is determined gravimetrically and divided by the volume of gas sampled (as shown in Equation 1) to determine the PM concentration in grams per dscm. Please note that this example does not present the condensable PM emissions.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation (2) and Example 1.

$$C_{PM} = C_f \div V_{m,STP} \quad (1)$$

where:

- $C_{PM}$  = concentration of PM or gram loading (grams/dscm)
- $C_f$  = filter catch (grams)
- $V_{m,STP}$  = metered volume of sample at STP (dscm)

$$E_{PM} = C_{PM} \times Q_d \times 3\,600 \div 1\,000 \quad (2)$$

where:

- $E_{PM}$  = hourly emissions of PM in kg/hr
- $Q_d$  = stack gas volumetric flow rate (dscms)
- 3 600 = seconds per hour
- 1 000 = grams per kg

**Table 6. Stack Sample Test Results**

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (secs)	sec	7 200	7 200	7 200
Moisture collected (grams)	grams	395.6	372.6	341.4
Filter catch (grams)	$C_f$	0.0851	0.0449	0.0625
Average sampling rate (dscms)	dscms	$1.67 \times 10^{-4}$	$1.67 \times 10^{-4}$	$1.67 \times 10^{-4}$
Standard metered volume (dscm)	$V_{m,STP}$	1.185	1.160	1.163
Volumetric flow rate (acms or dscms)	$Q_a$ or $Q_d$	8.48	8.43	8.45
Concentration of particulate (grams/dscm)	$C_{PM}$	$7.181 \times 10^{-2}$	$3.871 \times 10^{-2}$	$5.374 \times 10^{-2}$
Particulate emission rate (kg/hr)	$E_{PM}$	2.20	1.19	1.65

QLD Department of Environment 1998

**Example 1.**

PM emissions calculated using Equations 1. and 2. and the stack sampling data for Test 1 (presented in Table 6.) are shown below:

$$\begin{aligned}
 C_{PM} &= C_f \div V_{m, STP} \\
 &= 0.085 \div 1.185 \\
 &= 0.072 \text{ grams/dscm} \\
 E_{PM} &= C_{PM} \times Q_d \times 3\,600 \div 1\,000 \\
 &= 0.072 \times 8.48 \times (3\,600 \text{seconds/hr}) \div (1\text{kg}/1\,000\text{grams}) \\
 &= 2.20 \text{ kg/hour}
 \end{aligned}$$

The information from some stack tests may be reported in kilograms of particulate per kilograms of exhaust gas (wet). Use Equation (3) to calculate the dry particulate emissions in kg/hr.

$$E_{PM} = Q_a \div 1\,000 \times 3\,600 \times 1.2 (1 - R) \times [293 \div (273 + T)] \quad (3)$$

where:

$$\begin{aligned}
 E_{PM} &= \text{hourly emissions in kg/hr of PM} \\
 Q_a &= \text{actual cubic metres of exhaust gas per second (acms)} \\
 1\,000 &= 1\,000 \text{ kg exhaust gas per kg of PM} \\
 3\,600 &= \text{seconds per hour} \\
 1.2 &= 1.2 \text{ kg/m}^3 \\
 R &= \text{moisture content (\%)} \\
 293 &= 293\text{K} \\
 273 &= 273\text{K} \\
 T &= \text{stack gas temperature in } ^\circ\text{C}
 \end{aligned}$$

## 5.2 Using Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source to some common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted multiplied by the unit weight, volume, distance, or duration of the activity emitting the substance (eg. kilograms of sulphur dioxide emitted per tonne of air-dried unbleached pulp produced).

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Emission factors are used to estimate a facility's emissions by the general equation:

$$E = A \times T \times EF \times [1 - (ER/100)] \quad (4)$$

where :

- E = emissions;
- A = activity rate;
- T = time (or another variable)
- EF = uncontrolled emission factor; and
- ER = overall emission reduction efficiency, %.

To determine PM<sub>10</sub> emissions from PM, it may be necessary for facility operators to first undertake a sizing analysis of the stack filter catch. The weight PM<sub>10</sub> fraction can then be multiplied by the total PM emission rate to produce a PM<sub>10</sub> number.

Emission factors developed from measurements for a specific mill or process may sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions were measured from one process source, an emission factor could be developed and applied to similar sources. As previously mentioned, it is advisable to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

**Example 2.**

Table 7 shows that 0.55kg of hydrogen sulphide at the multiple effect evaporator are emitted for each tonne of air-dried pulp produced with no venting device in place. It is assumed that the pulp mill operates for 1 500 hours per year.

EF <sub>hydrogen sulphide</sub>	=	0.55kg/tonne
Pulp production rate	=	100 tonnes/hour
H <sub>2</sub> S emissions	=	EF <sub>hydrogen sulphide</sub> x pulp production rate
	=	x operating time
	=	0.55 x 100
	=	55 kg/hr x (1 tonne ÷ 1 000kg)
	=	x 1 500 hr/yr
	=	82.5 tonnes per year

**Table 7. Emission Factors for Kraft Pulping <sup>a</sup>**

Source	Type of Control	Sulphur Dioxide (SO <sub>2</sub> ) kg/t	Carbon Monoxide (CO) kg/t	Hydrogen Sulphide (S <sup>m</sup> ) kg/t	Oxides of Nitrogen (NO <sub>x</sub> ) kg/t	Lead (Pb) kg/t	RSH, RSR, RSSR (S <sup>m</sup> ) kg/t
<b>Digester relief and blow tank</b>	Untreated <sup>b</sup>	ND	ND	0.02	ND	ND	0.6
<b>Brown stock washer</b>	Untreated <sup>b</sup>	ND	ND	0.01	ND	ND	0.2 <sup>c</sup>
<b>Multiple effect evaporator</b>	Untreated <sup>b</sup>	ND	ND	0.55	ND	ND	0.05
<b>Recovery boiler and direct evaporator</b>	Untreated <sup>d</sup>	3.5	5.5	6 <sup>e</sup>	ND	ND	1.5 <sup>e</sup>
	Venturi scrubber <sup>f</sup>	3.5	5.5	6 <sup>e</sup>	ND	ND	1.5 <sup>e</sup>
	ESP	3.5	5.5	6 <sup>e</sup>	ND	ND	1.5 <sup>e</sup>
	Auxiliary scrubber	ND	ND	6 <sup>e</sup>	ND	ND	1.5 <sup>e</sup>
<b>Non-contact recovery boiler without direct contact evaporator</b>	Untreated	ND	5.5	0.05 <sup>g</sup>	ND	ND	ND
	ESP	ND	5.5	0.05 <sup>g</sup>	ND	ND	ND
<b>Smelt dissolving tank</b>	Untreated	0.1	ND	0.1 <sup>h</sup>	ND	ND	0.15 <sup>h</sup>
	Mesh pad	0.1	ND	0.1 <sup>h</sup>	ND	ND	0.15 <sup>h</sup>
	Scrubber	4.02E-04 <sup>m</sup>	3.205E-03 <sup>m</sup>	0.1 <sup>h</sup>	1.045E-01 <sup>m</sup>	ND	0.15 <sup>h</sup>
	ESP	1.495E-03 <sup>m</sup>	0.9505 <sup>m</sup>	ND	0.64 <sup>m</sup>	ND	ND
<b>Lime kiln</b>	Untreated	0.15	0.05	0.25 <sup>j</sup>	ND	0.504E-04 <sup>m</sup>	0.1 <sup>j</sup>
	Scrubber or ESP	ND	0.05	0.25 <sup>j</sup>	ND	ND	0.1 <sup>j</sup>
<b>Turpentine condenser</b>	Untreated	ND	ND	0.005	ND	ND	0.25
<b>Miscellaneous<sup>n</sup></b>	Untreated	ND	ND	ND	ND	ND	0.25

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1:*

<sup>a</sup> Factor units are kg of substance emitted per tonne of air-dried unbleached pulp (ADP) produced. All emission factors have an uncertainty rating of A.

RSH = Methyl mercaptan

RSR = Dimethyl sulphide.

RSSR = Dimethyl disulphide.

ESP = Electrostatic precipitator

ND = No Data

- <sup>b</sup> If non-condensable gasses from these sources are vented to lime kiln, recovery furnace, or equivalent, the reduced sulphur compounds are destroyed.
- <sup>c</sup> Apply within system using condensate as washing medium. When using fresh water, emissions are 0.05 kg/t.
- <sup>d</sup> Apply when cyclonic scrubber or cascade evaporator is used for direct contact evaporation, with no further controls.
- <sup>e</sup> Usually reduced by 50% with black liquor oxidation and can be cut 95 - 99% when oxidation is complete and recovery furnace is operated optimally.
- <sup>f</sup> Apply when venturi scrubber is used for direct contact evaporation, with no further controls.
- <sup>g</sup> Use 7.5 kg/tonne when auxiliary scrubber follows venturi scrubber, and 1.5 kg/tonne when it follows ESP.
- <sup>h</sup> Apply when recovery furnace is operated optimally to control total reduced sulphur (TRS) compounds.
- <sup>j</sup> Usually reduced to 0.01kg/t ADP when water low in sulphides is used in smelt dissolving tank and associated scrubber.
- <sup>m</sup> Usually reduced to 0.015kg/tonne ADP with efficient mud washing, optimal kiln operation and added caustic in scrubbing water. With only efficient mud washing and optimal process control, TRS compounds reduced to 0.04 kg/tonne ADP.
- <sup>n</sup> Includes knotted vents, brownstock seal tanks, etc. When black liquor oxidation is included, emissions are 0.3 kg/t.

**Table 8. Kraft Pulping Emission Factors for Particulate Matter (PM<sub>10</sub>)**

Sources	Emission Factor (kg/t of Air-Dried Pulp)	
	Uncontrolled	Controlled
Recovery boiler with a direct-contact evaporator and an ESP	84	ND
Recovery boiler without a direct-contact evaporator but with an ESP	ND	0.7
Lime kiln with a venturi scrubber	4.7	0.24
Lime kiln with an ESP	4.7	0.22
Smelt dissolving tank with a packed tower	3.1	0.48
Smelt dissolving tank with a venturi scrubber	3.1	0.09

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1*:  
 ND = No data. All emission factors have an uncertainty rating of E.

**Table 9. Emission Factors for VOCs from Kraft Pulping**

Source and Description	Units	Emission Factor	Source and Description	Units	Emission Factor
<b>Digestion</b>	kg/ADt	0.6	<b>Tall Oil Recovery</b>	kg/tonne TO	2.0
<b>Washing</b> - clean condensates used	kg/ADt	0.045	<b>Chemical Recovery</b> - evaporation	kg/ADt	0.05
- foul condensates used	kg/ADt	0.49	- black liquor oxidation	kg/ADt	0.17
<b>Bleaching</b>	kg/ADt	0.05	<b>Recovery Furnace</b> - without direct contact evaporator	kg/ADt	0.14
<b>Non-condensable gases</b> - collected, not incinerated	kg/ADt	0.5	- with direct contact evaporator	kg/ADt	0.53
- incinerated	kg/ADt	ND	<b>Recausticising</b> - with clean condensates	kg/tonne BLS	ND
<b>Turpentine production</b>	kg/tonne turpentine	0.05	- with dirty condensates	kg/tonne BLS	0.031
<b>Oxygen delignification reactors</b>	kg/ADt	0.041		kg/tonne BLS	0.88

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1:*

ADt = air-dried tonnes of pulp. BLS = black liquor solids. TO = tall oil. ND = No data.

All emission factors have an uncertainty rating of U.

The emission factors in Table 9 refer to non-methane VOCs as a group. Inventory reporting also requires characterisation of total VOCs and the reporting of individual substances. Table 10 is to assist in speciating and separately reporting emissions of individual VOCs. Emissions are calculated by multiplying the weight percentage of each individual compound (using Table 10), by the total VOC emission figure (calculated from Table 9).

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**Table 10. VOC Speciation Profile for Kraft Pulping<sup>a</sup>**

CASR Number	Species Name	Composition % by Weight
110-54-3	<i>n</i> -Hexane	3.37
110-82-7	Cyclohexane	0.14
50-00-0	Formaldehyde	15.19
67-64-1	Acetone	4.00
71-43-2	Benzene	1.38
108-88-3	Toluene	1.48
95-47-6	O-Xylene <sup>b</sup>	0.37
	M-Xylene and P-Xylene <sup>b</sup>	1.68

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1:*

<sup>a</sup> The above speciation profile is to be used in conjunction with the total volatile organic carbon emission factors in Table 9. The processes of kraft pulping which are relevant to Table 10 and where VOC emission factors are available are:

- washers/screens
- recovery furnace with direct contact evaporator
- recausticising
- turpentine production
- oxygen delignification reactors
- recovery furnace without contact evaporation

<sup>b</sup> O-Xylene, M-Xylene, and P-Xylene emissions need to be added together and one value reported for total xylene emissions.

**Table 11. Emission Factors for Sulphite Pulping <sup>a</sup>**

Source	Base	Control	Emission Factor <sup>b</sup>		Factor Rating
			PM <sub>10</sub> kg/ADUT	SO <sub>2</sub> kg/ADU T	
Digester / blow pit or dump tank <sup>c</sup>	All	None	Neg	5 to 35	C
	MgO	Process change <sup>d</sup>	Neg	1 to 3	C
	MgO	Scrubber	Neg	0.5	B
	MgO	Process change/scrubber	Neg	0.1	B
	MgO	All exhausts vented	Neg	0	A
	NH <sub>3</sub>	Process change	Neg	12.5	D
	NH <sub>3</sub>	Process change/scrubber	Neg	0.2	B
	Na	Process change/scrubber	Neg	1	C
	Ca	Unknown	Neg	33.5	C
Recovery system <sup>e</sup>	MgO	Multicyclone and venturi scrubbers	1	4.5	A
	NH <sub>3</sub>	Ammonia absorption and mist eliminator	0.35	3.5	B
	Na	Sodium carbonate scrubber	2	1	C
Acid plant <sup>f</sup>	NH <sub>3</sub>	Scrubber	Neg	0.2	C
	Na	Unknown <sup>g</sup>	Neg	0.1	D
	Ca	Jensen scrubber	Neg	4	C
Other <sup>h</sup>	All	None	Neg	6	D

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1:*

ADUT = air-dried unbleached tonne. Neg = negligible.

<sup>a</sup> All factors represent long term average emissions.

<sup>b</sup> Expressed as kg of substance emitted / air dried unbleached tonne of pulp produced.

<sup>c</sup> Factors represent emissions after cook is completed and when digester contents are discharged into blow pit. Some relief gases are vented from digester during cook cycle, but these are usually transferred to pressure accumulators and SO<sub>2</sub> herein reabsorbed for use in cooking liquor. In some mills, actual emissions will be intermittent and for short periods.

<sup>d</sup> May include raising cooking liquor pH (thereby lowering free SO<sub>2</sub>), relieving digester pressure before contents discharge, and pumping out digester contents instead of blowing out.

<sup>e</sup> Recovery system at most mills is closed and includes recovery furnace, direct contact evaporator, multiple effect evaporator, acid fortification tower, and SO<sub>2</sub> absorption scrubbers. Generally only one emission point for entire system. Factors include high SO<sub>2</sub> emissions during periodic purging of recovery systems.

<sup>f</sup> Necessary in mills with insufficient or nonexistent recovery systems.

<sup>g</sup> Control is practiced, but type of system is unknown.

<sup>h</sup> Includes miscellaneous pulping operations such as knotters, washers, screens, et cetera.

**Table 12. Emission Factors for Drying Paper Pulp**

Substance	Emission Factor in kg/tonne <sup>a</sup>	Emission Factor Rating
Carbon monoxide	5 E-05	C
Oxides of nitrogen	2.5 E-04	C
Total VOCs	5 E-06	C

USEPA. October 1996. *Compilation of Air Pollutant Emission Factors, Volume 1:*

<sup>a</sup> Units are kg of substance emitted / tonne of wood waste burned.

The Combustion in Boilers EET Manual is available for mills using this form of combustion in pulp and paper production. This Manual covers emissions from burning wood waste, coal, oil, and natural gas in a variety of boilers and stokers and under different firing configurations. This, and other Manuals should be available from your local environmental authority.

### 5.3 Using Fuel Analysis Data

Fuel analysis can be used to predict SO<sub>2</sub>, metals, and other emissions based on application of conservation laws, if fuel rate (Q<sub>f</sub>) is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulphur which may be converted into other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is the following:

$$E_x = Q_f \times \text{pollutant concentration in fuel} \times (MW_p \div MW_f) \quad (5)$$

where:

E <sub>x</sub>	=	emissions of pollutant x
Q <sub>f</sub>	=	fuel use (kg/hr)
MW <sub>p</sub>	=	molecular weight of pollutant emitted (kg/kg-mole)
MW <sub>f</sub>	=	molecular weight of pollutant in fuel (kg/kg-mole)

For instance, SO<sub>2</sub> emissions from oil combustion can be calculated based on the concentration of sulphur in the oil. This approach assumes complete conversion of sulphur to SO<sub>2</sub>. Therefore, for every kilogram of sulphur (MW = 32) burned, two kilograms of SO<sub>2</sub> (MW = 64) are emitted. The application of this EET is shown in Example 3.

**Example 3.**  
 This example shows how SO<sub>2</sub> emissions can be calculated from oil combustion based on fuel analysis results and the fuel flow information. The pulp mill is assumed to operate 1500 hours per year.

E<sub>SO<sub>2</sub></sub> = may be calculated using Equation (5)

Assume a given Q <sub>f</sub>	=	2 000 kg/hr
Weight percent sulphur in fuel	=	1.17

$$\begin{aligned}
 E_{SO_2} &= Q_f \times \text{pollutant concentration in fuel} \times (MW_p \div MW_f) \\
 &= (2\ 000) \times (1.17 \div 100) \times (64 \div 32) \\
 &= 46.8\text{kg/hr} \times \text{tonne}/1\ 000\text{kg} \times 1\ 500\ \text{hr/yr} \\
 &= 70.2\ \text{tonnes/year}
 \end{aligned}$$

## 5.4 Using CEMS Data

To monitor SO<sub>2</sub>, NO<sub>x</sub>, VOC, and CO emissions using a CEMS, you use a pollutant concentration monitor that measures concentration in parts per million by volume dry air (ppmvd). Flow rates should be measured using a volumetric flow rate monitor. Flow rates estimated based on heat input using fuel factors may be inaccurate because these systems typically run with high excess air to remove the moisture out of the kiln. Emission rates (kg/hr) are then calculated by multiplying the stack gas concentrations by the stack gas flow rates.

Table 13 presents example CEM data output averaged for three periods for a lime kiln. The output includes pollutant concentrations in parts per million dry basis (ppmvd), diluent (O<sub>2</sub> or CO<sub>2</sub>) concentrations in percent by volume dry basis (%v,d), and emission rates in kilograms per hour (kg/hr). This data represents a snapshot of a lime kiln operation at a pulp mill facility. While it is possible to determine total emissions of an individual pollutant over a given time period from this data (assuming the CEM operates properly all year long), an accurate emission estimate can be derived by adding the hourly emission estimates if the CEMS data are representative of typical operating conditions.

Although CEMS can report real-time hourly emissions automatically, it may be necessary to manually estimate annual emissions from hourly concentration data. This Section describes how to calculate emissions for the NPI from CEMS concentration data. The selected CEMS data should be representative of operating conditions. When possible, data collected over longer periods should be used.

It is important to note that prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies the local environmental authority's requirement for NPI emissions estimations.

**Table 13. Example CEM Output Averaged for a Lime Kiln Firing Waste Fuel Oil**

Time	O <sub>2</sub> (%V)	Concentration (C) (ppmvd)				Gas Flow Rate (Q)	Emission Rate (E) (kg/hr)				Pulp Rate (A) (tonnes / hour)
		SO <sub>2</sub>	NO <sub>x</sub>	CO	VOC		SO <sub>2</sub>	NO <sub>x</sub>	CO	VOC	
1	10.3	150.9	142.9	42.9	554.2	8.52	12.34	11.69	1.54	11.33	290
2	10.1	144.0	145.7	41.8	582.9	8.48	11.72	11.86	1.49	11.86	293
3	11.8	123.0	112.7	128.4	515.1	8.85	10.45	9.57	4.77	10.94	270

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Hourly emissions can be based on concentration measurements as shown in Equation (6) and Example 4.

$$E_x = (C \times MW \times Q \times 3\,600) \div (V \times 10^6) \quad (6)$$

where:

$E_x$	=	hourly emissions in kg/hr of pollutant x
$C$	=	pollutant concentration in ppmvd
$MW$	=	molecular weight of the pollutant (kg/kg-mole)
$Q$	=	stack gas volumetric flow rate in dscms
$3\,600$	=	3 600 seconds per hour
$V$	=	volume occupied by one mole of gas at standard temperature and pressure (22.4 m <sup>3</sup> /kg-mole at 20°C and 1 atmosphere)

Actual emissions in tonnes per year can be calculated by multiplying the emission rate in kg/hr by the number of actual operating hours (OpHrs) as shown in Equation (7) and Example 4.

$$E_{tpy,x} = E_x \times OpHrs \div 1\,000 \quad (7)$$

where:

$E_{tpy,x}$	=	annual emissions in tonnes/year of pollutant x
$E_x$	=	hourly emissions in kg/hr of pollutant x
$OpHrs$	=	annual operating hours in hr/yr

Emissions in kilograms of pollutant per tonne of air-dried pulp produced can be calculated by dividing the emission rate in kg/hr by the pulp production rate (tonnes/hr) during the same period (Equation (8)) as shown below. It should be noted that the emission factor calculated below assumes that the selected time period (that is, hourly) is representative of annual operating conditions, and longer time periods should be used for NPI reporting where they are available. Use of the calculation is shown in Example 4.

$$E_{tpy,x} = E_x \div A \quad (8)$$

where:

$E_{tpy,x}$	=	emissions of pollutant x (kg/tonnes) per tonne of air-dried pulp produced
$E_x$	=	hourly emissions in kg/hr of pollutant x
$A$	=	air-dried pulp production (tonnes/hr)

**Example 4.**

This example shows how SO<sub>2</sub> emissions can be calculated using Equation (6) based on the average CEMS data for Time Period 1 shown in Table 13.

$$\begin{aligned} E_{SO_2} &= (C \times MW \times Q \times 3\,600) \div (V \times 10^6) \\ &= (150.9 \times 64 \times 8.52 \times 3\,600) \div (22.4 \times 10^6) \\ &= 296\,217\,907 \div 22\,400\,000 \\ &= 13.22 \text{ kg/hr} \end{aligned}$$

Emissions in tonnes/yr (based on a 1 500 hr/yr operating schedule) can then be calculated using Equation (7); however, based on the above period this estimate should be calculated from the average CEMS data for a year using Equation (6):

$$\begin{aligned} E_{tpy,SO_2} &= E_{SO_2} \times \text{OpHrs} \div 1\,000 \\ &= 13.22 \times (1\,500 \div 1\,000) \\ &= 19.83 \text{ tonnes per year} \end{aligned}$$

Emissions, in terms of kg/tonne of pulp produced, are calculated using Equation (8):

$$\begin{aligned} E_{tpy,SO_2} &= E_{SO_2} \div A \\ &= 13.22 \div 290 \\ &= 4.56 \times 10^{-2} \text{ kg SO}_2 \text{ emitted per tonne of pulp produced} \end{aligned}$$

## 5.5 Using Predictive Emissions Monitoring

Emissions from the pulp and paper manufacturing process depend upon several variables. For example, VOC process emissions for a given mill may vary with several parameters including the type of fuel burned, the relative quantities of various pulp constituents, the type of pulping technique undertaken, the use of bleaching chemicals and processes, and, the fuel combustion rate.

An example of predictive emissions monitoring that could be used to develop a PEM protocol for acceptable NPI reporting would need to account for the variability in these parameters, and consequently, may require a complex testing algorithm.

To develop this algorithm, correlation testing of the process variables could be conducted over a range of potential operating conditions for a suite of listed NPI substances including VOCs and SO<sub>2</sub>. Based on the test data, a mathematical correlation can be developed which predicts emissions using the various parameters. This method may be cost prohibitive for a single source and may need to be undertaken across the Australian pulp and paper industry generally.

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## 6.0 Control Technologies

The chemical recovery systems used in pulping processes are an example of emission control technologies that have evolved alongside process technologies. An efficient chemical recovery system is a crucial component of chemical pulping mill operations. The chemical recovery process regenerates process chemicals, and reduces natural resource usage and associated costs, as well as environmental emissions.

Many recent control technologies in the Australian paper industry have focused on reducing the emissions of toxics, especially chlorinated compounds, by means of source reduction practices and material substitution techniques (eg. defoamers, and bleaching chemical or wood pulp substitution).

### 6.1 Kraft Pulping

Emissions of sulphur compounds are also being reduced by process modifications and improved operating conditions. For example, black liquor oxidation systems that oxidise sulphides into less reactive thiosulphates can considerably reduce sulphur emissions from the direct contact evaporator. In addition, non-condensable gases vented from the digester/blow tank system and multiple effect evaporators can be destroyed by thermal oxidation, usually by passing them through the lime kiln. Efficient operation of the recovery furnace by avoiding overloading, and maintaining sufficient oxygen, residence time, and turbulence, significantly diminishes emissions of reduced sulphur compounds from this source as well.

New mill technology incorporates recovery systems that eliminate the conventional direct-contact evaporators altogether. In these mills, heated combustion air rather than fuel gas provides direct contact evaporation, or the multiple-effect evaporator system is extended to replace the direct-contact evaporator altogether. In both of these systems, sulphur emissions from the recovery furnace/direct-contact evaporator can be reduced by more than 99 percent.

Sulphur dioxide is emitted mainly from the oxidation of reduced sulphur compounds in the recovery furnace. It is reported that the direct contact evaporator absorbs about 75 percent of these emissions, and further scrubbing can provide additional control.

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## 6.2 Acid Sulphite Pulping

Sulphur dioxide is generally considered the major emission from sulphite pulp mills. A major source of SO<sub>2</sub> is the digester and blow pit (dump tank) system. SO<sub>2</sub> is present in the intermittent digester relief gases, as well as in the gases given off at the end of the cook when the digester contents are discharged into the blow pit. The quantity of SO<sub>2</sub> evolved and emitted to the atmosphere in these gas streams depends on the pH of the cooking liquor, the pressure at which the digester contents are discharged, and the effectiveness of the absorption systems employed for SO<sub>2</sub> recovery. Scrubbers can be installed that reduce SO<sub>2</sub> emissions from this source by as much as 99 percent.

Another source of SO<sub>2</sub> emissions is the recovery system. Because magnesium, sodium, and ammonium base recovery systems all use absorption systems to recover SO<sub>2</sub> generated in recovery furnaces, acid fortification towers, and multiple effect evaporators, the magnitude of SO<sub>2</sub> emissions depends on the desired efficiency of these systems. Generally, such absorption systems recover better than 95 percent of the sulphur so that it can be reused (see Table 9).

Abatement equipment and control technologies, such as electrostatic precipitators, scrubbers, and cyclones are often used to reduce emissions in the paper and pulp manufacturing industry. If you have installed these or other abatement equipment at your facility, or you have implemented work practices that reduce emissions, you should multiply the control efficiency of the technology or the practice adopted, by the appropriate emission factors.

Air emission control technologies, such as electrostatic precipitators, fabric filters or baghouses, and wet scrubbers, are commonly installed to reduce the concentration of particulates in process off-gases before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been applied in an emission estimation, the collection efficiency of the abatement equipment needs to be considered. Guidance on applying collection efficiencies to emission factor equations is provided in earlier sections.

In the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 0.9 should be used in the emission factor equation to calculate actual mass emissions.

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## 7.0 References

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