Unclassified **ENV/JM/MONO(2006)7**

Organisation de Coopération et de Développement Economiques
Organisation for Economic Co-operation and Development

01-Feb-2006

English - Or. English

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

OECD SERIES ON EMISSION SCENARIO DOCUMENTS
Number 15

EMISSION SCENARIO DOCUMENT ON KRAFT PULP MILLS

JT00200407

ENV/JM/MONO(2006)7
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OECD Environment Health and Safety Publications

Series on Emission Scenario Documents No. 15

EMISSION SCENARIO DOCUMENT ON KRAFT PULP MILLS

Environment Directorate
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris, 2006

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EXPLANATORY NOTES

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used at kraft pulp mills, to assist in the estimation of releases of chemicals into the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, including those from the industry area in countries other than the lead (Canada). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The comments will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD provides information on chemicals used at kraft pulp mills. This ESD was developed along with two sister documents, an ESD on Non-integrated Paper Mills, and an ESD on Recovered Paper Mills. Although they were designed as stand alone documents, by their nature they represent different phases of the life cycle of paper products. This ESD represents the production stage when pulp is first produced. The ESD on Non-integrated Paper Mills is representative of the industrial phase of the life cycle, when the pulp is converted to paper and/or board products. The ESD on Recovered Paper Mills is illustrative of the recovery stage, when paper products are recovered, reworked and recycled back into the community. To cover the entire life cycle of each of these pulp and paper mill types would be quite lengthy and impractical.

Other ESDs relating to the Pulp and Paper Industry have previously been developed in Europe. These include the EU document, "IC-12, Pulp Paper and Board Industry – Assessment of the Environmental Release of Chemicals Used in the Pulp, Paper and Board Industry." Other related documents are specific to the use of biocides in the Pulp and Paper Industry. These include the European Commission "Harmonization of Environmental Emission Scenarios for Slimicides" (Product Type 12; 2003) and "Emission Scenario Document for Biocides Used in Paper Coating and Finishing" by Tissier and Migné (Product Type 6, 7, and 9; 2001). The first-mentioned document covers additives used in printing and writing papers, tissue paper, newsprint, as well as cardboard, carton, packaging and wrapping paper. There is thus some overlapping with the ESDs developed for Non-integrated Mills and Recycle Mills, in terms of material covered. However, none of the European ESDs deal with Kraft pulping, due to the nature of the pulp and paper industry in Europe. Kraft pulping is much more prevalent in North and South America and the Scandinavian countries than in continental Europe.

How this document was developed

This document was produced by Environment Canada and overseen by the OECD Task Force on Environmental Exposure Assessment, along with two sister documents aforementioned. The general information about the processes and chemicals used is derived from literature data and several reports from the European Union and the United States. The emission estimation methods given in this ESD are based on those developed by the OECD with parameter defaults reflecting Canadian operations.

The first draft was circulated to the Task Force in March 2003 and developed through the meetings of the Task Force in 2003 and 2004. The revised draft was circulated to the OECD member countries and posted on the OECD web-site in December 2004, with requests for comments and information by May 2005. Comments were received from the United States, Sweden and Finland. The comments received suggested further improvement of the ESD by recommending additional sections (e.g., sample calculations and data gaps), additional/updated information (e.g., function of each type of listed chemical agents and sources of wastewater), specific industry information (e.g., relationship between different types of mills and wastewater treatment practices adopted by the Canadian industry), editorial changes and points of clarification (e.g., cross-reference to other ESDs; addition to glossary; basis for tonnage values used). All these comments were addressed in this document.

This document is published on the responsibility of the Joint Meeting of the Chemicals Group and Management Committee of the Special Programme on the Control of Chemicals of the OECD.

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1 – INTRODUCTION

1. The purpose of this emission scenario document (ESD) is to provide a realistic worst-case emission scenario for chemicals used at kraft pulp mills. The general information about the processes and chemicals used is derived from literature data and several reports from the European Union and the United States. The emission estimation methods given in this ESD are based on those developed by the Organization for Economic Cooperation and Development with parameter defaults reflecting Canadian operations.

2. This ESD for Kraft Pulp Mills was developed in 2004 along with two sister documents, an ESD on Non-integrated Paper Mills, and an ESD on Recovered Paper Mills. Although they were designed as stand alone documents, by their nature they represent different phases of the life cycle of paper products. This ESD represents the production stage when pulp is first produced. The ESD on Non-integrated Paper Mills is representative of the industrial phase of the life cycle, when the pulp is converted to paper and/or board products. The ESD on Recovered Paper Mills is illustrative of the recovery stage, when paper products are recovered, reworked and recycled back into the community. To cover the entire life cycle of each of these pulp and paper mill types would be quite lengthy and impractical.

3. Other ESDs relating to the Pulp and Paper Industry have previously been developed in Europe. These include the EU document, “IC-12, Pulp Paper and Board Industry – Assessment of the Environmental Release of Chemicals Used in the Pulp, Paper and Board Industry.” Other related documents are specific to the use of biocides in the Pulp and Paper Industry. These include the European Commission “Harmonization of Environmental Emission Scenarios for Slimicides” (Product Type 12; 2003) and “Emission Scenario Document for Biocides Used in Paper Coating and Finishing” by Tissier and Migné (Product Type 6, 7, and 9; 2001). The first-mentioned document covers additives used in printing and writing papers, tissue paper, newsprint, as well as cardboard, carton, packaging and wrapping paper. There is thus some overlapping with the Canadian ESDs developed for Non-integrated Mills and Recycle Mills, in terms of material covered. However, none of the European ESDs deal with Kraft pulping, due to the nature of the pulp and paper industry in Europe. Kraft pulping is much more prevalent in North and South America and the Scandinavian countries than in continental Europe.

2 – CANADIAN KRAFT PULP SECTOR

4. The pulp and paper industry produces commodity grades of wood pulp, primary paper products, and paperboard products. Most pulp is produced for the purpose of subsequent manufacture of paper and board products (European Commission, 1999, p.10). Some is destined for other uses such as thick fibreboard or products manufactured from dissolved cellulose.

5. Pulp and paper mills may be integrated or non-integrated. Integrated mills produce both pulp and primary paper products (USEPA, 1995, p.4). Non-integrated mills include pulp mills and paper mills. Pulp

mills only produce pulp (unbleached to full bleached), which is sold on the open market or shipped via pipe, conveyor, truck, train, or ship to other mills for the production of a final product. In contrast, paper mills only produce paper products from purchased and/or recycled pulp.

6. In Canada, the production of Kraft pulp leads all other types of pulp. Over the years of 1999-2001, Kraft pulp accounted for 51% of the total production that averaged at 25.7 million tonnes/yr, as given in Table 1 (Lockwood-Post Directory, 2002). Out of 151 pulp mills in Canada, there were 37 Kraft pulp mills in 2004 (Pulp & Paper Canada, 2005). Mechanical pulp, representing 45% of the total production, is also a major type of pulp produced in Canada.

Table 1 – Pulp Production in Canada

Type of Pulp	**Annual Production (1000 tonne/yr)**		
	1999	**2000**	**2001**
Kraft, bleached and semibleached	11,793	12,110	11,120
Kraft, unbleached	1,399	1,324	1,320
Sulphite	546	535	412
Semichemical	551	559	533
Mechanical	11,222	12,287	11,457
Total	**25,510**	**26,815**	**24,855**

Source: Lockwood-Post Directory, 2002.

7. The provincial breakdown of the pulp production is not available at the time of preparing this document, but it is believed that Quebec is the province with the highest pulp production in Canada. This is reflected by the production statistics given in Table 2 (Quebec Forest Industry Council, www.cifq.qc.ca). Quebec was ranked first in terms of the total production and followed by British Columbia and Ontario. The other provinces accounted for about 20% of the total.

Table 2 – Production of Pulp, Paper and Paperboard in Canada

Province	Pulp, Paper and Paperboard **(1000 tonne/year)**		Newsprint **(1000 tonne/year)**	
	2000	2002	2000	2002
Quebec	10,206	10,032	3,848	3,726
British Columbia	8,424	7,393	1,428	1,171
Ontario	6,471	5,991	1,924	1,595
Other Provinces	7,098	6,702	2,022	1,973
Total	**32,199**	**30,118**	**9,222**	**8,465**

Source: Quebec Forest Industry Council, www.cifq.qc.ca

3 – KRAFT PULP MANUFACTURING PROCESS

3.1 – Process Description

8. Figure 1 shows a typical process for non-integrated bleached Kraft pulp mills. The process consists of four sections: 1) wood handling; 2) pulping; 3) chemical recovery; and 4) bleaching (USEPA,

1995, p.18-46; European Commission, 1999, p.18). Water and wastewater treatment and recovery and power boilers are commonly integral parts of a Kraft pulp mill. The code used in Figure 1 for chemicals added in various pulp and paper operations is given in Table 3. It should be noted that these chemicals are provided for the pulp and paper industry as a whole and not all of them are necessarily used by Kraft pulp mills.

9. Wastewater streams from the process are generally sent to an on-site wastewater treatment system before being discharged to a receiving water body. These streams primarily include the wastewater from the wood handling, pulping and bleaching operations, and the condensate from the evaporators.

10. As part of the Canadian Fisheries Act, the 1992 Pulp and Paper Effluent Regulations were enacted to set allowable limits on BOD, suspended solids and LC_{50} toxicity values in mill effluents. Today almost all Kraft mills have primary and secondary treatment facilities to meet these targets, as do non-integrated and recycle mills, before discharging to a receiving body of water, be it river, lake, marine or estuary. Only one Kraft mill in Canada is releasing into a town's sewer system (after aerated lagoons). Many board mills (recycle mills) located in large urban centres release to the municipal sewer system following on-site primary treatment.

Table 3 – Pulp and Paper Chemicals

Code Used in Figure 1	Chemical	Function
1	Cooking aids/chip penetrants	Helps increase Kraft cooking yield.
2	Boilouts/cleaners	Removal of organic and inorganic deposition in chests and piping during major cleanups, in combination with an acid or caustic soda.
3	Scale control	Agent to prevent or delay inorganic scale formation.
4	Foam control	Prevention or control of foam in chests, washers and paper machines.
5	Washing/drainage aids	Improves throughput efficiency of brown stock washers.
6	Pitch/stickies control	Control and/or prevention of pitch and pitch-like substances from depositing out in system and/or causing quality problems in the finished pulp or sheet.
7	Clarification aids	An organic or inorganic substance to help in clarification of influent or effluent water.
8	Lime mud dewatering aids	Agent to increase lime mud solids prior to firing at lime kiln.
9	Tall oil separation and acidulation aids	Agent to increase separation yield of tall oil from black liquor at the skim tank in the evaporator train.
10	Turpentine separation aids	Agent to increase separation yield of turpentine from digester relief gases after the separation process.
11	Microbiological control	Substance to control microbiological organisms and the problems they cause (slime, off-odours, corrosion, quality defects).
12	Felt conditioners	Agent to clean felts or condition felt surface to prevent deposition. Applied continuously or in batch fashion.
13	Retention/drainage aids	A flocculant and/or coagulant to aid in the separation of fibre from water at the paper or pulp machine, in save-all and clarifiers, etc.
14	Air pollution control	Agents added to help separation process in wet scrubbers.
15	Condensate treatment	Agents added to prevent return line corrosion in boiler systems.
16	Boiler water treatment	Agents added to prevent water side corrosion problems in boiler systems.
17	Corrosion inhibitors	Filming or sequestering agents to prevent corrosion in various parts of the pulp making process.
18	Settling aids	The use of flocculants in green and white liquor clarifiers.

Code Used in Figure 1	Chemical	Function
19	Nutrients	Sources of nitrogen and phosphate to stimulate microbial action in effluent treatment.
20	Sludge conditioners	Flocculants, coagulants or combinations thereof to increase solids content of sludges in wastewater treatment systems.
21	Odour control	A substance added in wastewater treatment to control off odours caused by microorganisms.
22	Colour control	Usually, an agent added to remove/reduce colour in pulp or paper mill effluent.
23	Starch/sizes	Used to impart water repellency and stiffness to the paper product.
24	Wet strength agents	Agent added to improve wet strength of sheet of paper or board.
25	Dry strength agents	Agent added to impart dry strength of paper or board.
26	Dyes/dye fixatives/fluorescent whites	Agents added to give desired colour and reflectance to a sheet of paper.
27	Charge control	Agent added to help neutralize anionic trash in a paper machine system.
28	Fillers	Inorganic compounds added to paper machine stock to impart desired quality of opacity, printability and/or brightness to sheet.
29	Chelants/sequestrants	Agents used to control undesired metal ions.
30	Emulsifiers	Agent added to improve water solubility or miscibility of a particular component.
31	Antiskid agents	A substance, usually sprayed on at the dry end of a paper/board machine, added to promote stackability of board products, by increasing surface friction.
32	Save-all polymers	Coagulant or flocculant added to improve separation of fibre from white water at save-all.
33	Formation aids	Added at paper machine to improve sheet formation and uniformity.
34	Latex	Part of a specialty paper coating formulation surface treatment.
35	Surfactants/repulping aids	Agents added at the repulper to facilitate pulp slurry formation.
36	Dispersing agents	Agent added to improve water solubility of a hydrophobic constituent, to prevent agglomeration and deposition in a paper machine system.
37	Deinking aids	Agents added to help deinking of printed papers.
38	Soap/fatty acids	Agents used for deinking newsprint and magazines.
39	Barrier chemistry	Agents added at machine to make sheet of paper impervious to various liquids.
40	Bleaching chemicals	Any chemical added alone or in combination with others to improve sheet brightness via oxidative or reductive mechanism.

3.1.1 – Wood Handling

11. Wood handling is the first step of the Kraft process. In this step, wood logs are debarked and cut into manageable sizes (USEPA, 1995, p.19-21; European Commission, 1999, p.18). The bark may be burned for energy production in a boiler. Wood chips are commonly used in chemical pulping. Today, paper is made mostly from chips and sawmill residue (55%), traditional waste products from wood processing (FPAC, www.fpac.ca).

3.1.2 – Pulping

12. Kraft or sulfate pulping is carried out in a digester. Wood chips are mixed with a sodium-based alkaline pulping solution, commonly known as white liquor (USEPA, 1995, p.22; European Commission, 1999, p.17-21). Under the action of the white liquor, lignin is removed from wood matrix and wood fibres are liberated.

13. Cooked wood chips are discharged from the digester under pressure into a blow tank (Grace et al., 1989, p.9). As they are blown from the digester, cooked chips are broken up into individual fibres by the mechanical force of ejection. The discharge from the blow tank consists of separated wood fibres (pulp) and a solution, known as black liquor, of reacted and unreacted pulping chemicals along with dissolved lignin solids (USEPA, 1995, p.22; European Commission, 1999, p.17-21; Grace et al., 1989, p.474).

14. A brownstock washing system is used to remove the black liquor from the resulting pulp (USEPA, 1995, p.22; European Commission, 1999, p.17-21; Grace et al., 1989, p.474). Modern washing systems employ vacuum drum washers, wash presses, diffusers or wire type washers. In the meantime, knots and fibre bundles are removed from the pulp with pressure screens and centrifugal cleaners and then recycled to the digester. The washed pulp is sent to a bleach plant if white pulp is desired or directly to a paper machine if unbleached grades of paper or board are to be produced (Grace et al., 1989, p.9-11).

15. The black liquor upon dilution in the brownstock washing system is known as weak black liquor and is recycled within the process. The majority of the weak black liquor is sent to a chemical recovery section to recover the pulping chemicals, while the remaining small fraction is recycled to the digester directly (USEPA, 1995, p.22; European Commission, 1999, p.17-21).

3.1.3 – Chemical Recovery

16. Cooking chemicals used in pulping are recovered in the chemical recovery section. The majority of the weak black liquor collected from the brownstock washing system is concentrated by evaporation to yield a strong black liquor (USEPA, 1995, p.27; Grace et al., 1989, p.11, 474). The strong black liquor is then sent to a recovery furnace where organic solids are burned for energy generation and the chemicals are recovered in a molten form, known as smelt. A green liquor is formed by dissolving the smelt into a weak liquor. It is then clarified to remove contaminated solids, known as dregs. The dregs are washed prior to disposal and the resulting weak liquor is used for dissolving the smelt.

17. A white liquor is obtained through causticization. The clarified green liquor is first passed through a slaker where lime is slaked into calcium hydroxide (Grace et al., 1989, p.475). It is then causticized in a causticizer where sodium carbonate is converted into sodium hydroxide. The causticized green liquor is clarified to remove precipitated lime mud and a white liquor is generated for use in the digestion.

18. Lime mud is converted into lime through calcination (Grace et al., 1989, p.475). The lime mud filtered out from the white liquor clarifier is washed and the resulting weak liquor is used for dissolving the

smelt. Upon water removal in a thickener, the lime mud is sent to a kiln where it is converted into lime at high temperatures. In the meantime, the lime mud removed from the slaker is recycled to the lime kiln directly.

19. Some other operations are frequently carried out in the chemical recovery section. These include soap skimming and tall oil recovery, black liquor oxidation, and waste gas incineration (Grace et al., 1989, p.475). Fatty and resin acids, known as tall oil, are a minor constituent in black liquor that precipitates as a soap when the liquor is concentrated. The soap can be acidulated with sulphuric acid to form crude tall oil which can be sold as a by-product. The spent acid from the soap acidulation is normally added back to the recovery system. For the majority of Canadian Kraft pulp mills, turpentine and tall oil are used as fuels for energy generation rather than sold as by-products (Whitford, 2002). This is different from European and American mills which have been reported to produce turpentine and tall oil as by-products.

20. Black liquor oxidation is needed if the recovery furnace has a direct contact evaporator (Grace et al., 1989, p.475). Hydrogen sulphide is a very odourous gas produced from residual sodium sulphide in the black liquor in the direct contact evaporator. To minimize odourous emissions, the black liquor can be reacted with air or oxygen to convert the hydrogen sulphide to sodium thiosulphate.

21. Part of the white liquor generated from the chemical recovery section is used in oxygen delignification (European Commission, 1999, p.21). This step is aimed at further removing lignin from the pulp and carried out after brownstock washing in the presence of oxygen. Prior to the oxygen delignification, the white liquor is oxidized to convert sulphide to thiosulphate in order to maintain the sodium balance within the process.

3.1.4 – Bleaching

22. Bleaching is a multistage process. A typical bleaching plant consists of three to five stages with each stage containing pumps, mixers, a washer, and a retention tower (Grace et al., 1989, p.392-410; European Commission, 1999, p.22). These stages form a bleaching sequence which alternates between acid and alkaline conditions. A bleaching sequence can be divided into two operations: delignification and brightening. In the delignification operation, lignin is removed, while in the brightening operation higher brightness is achieved.

23. The bleached pulp is dried before leaving the process. The pulp is first dewatered with a drying machine and then dried with steam (European Commission, 1999, p.25; Grace et al., 1989, p.273). The final pulp product is shipped in the form of bales of sheets or fibre.

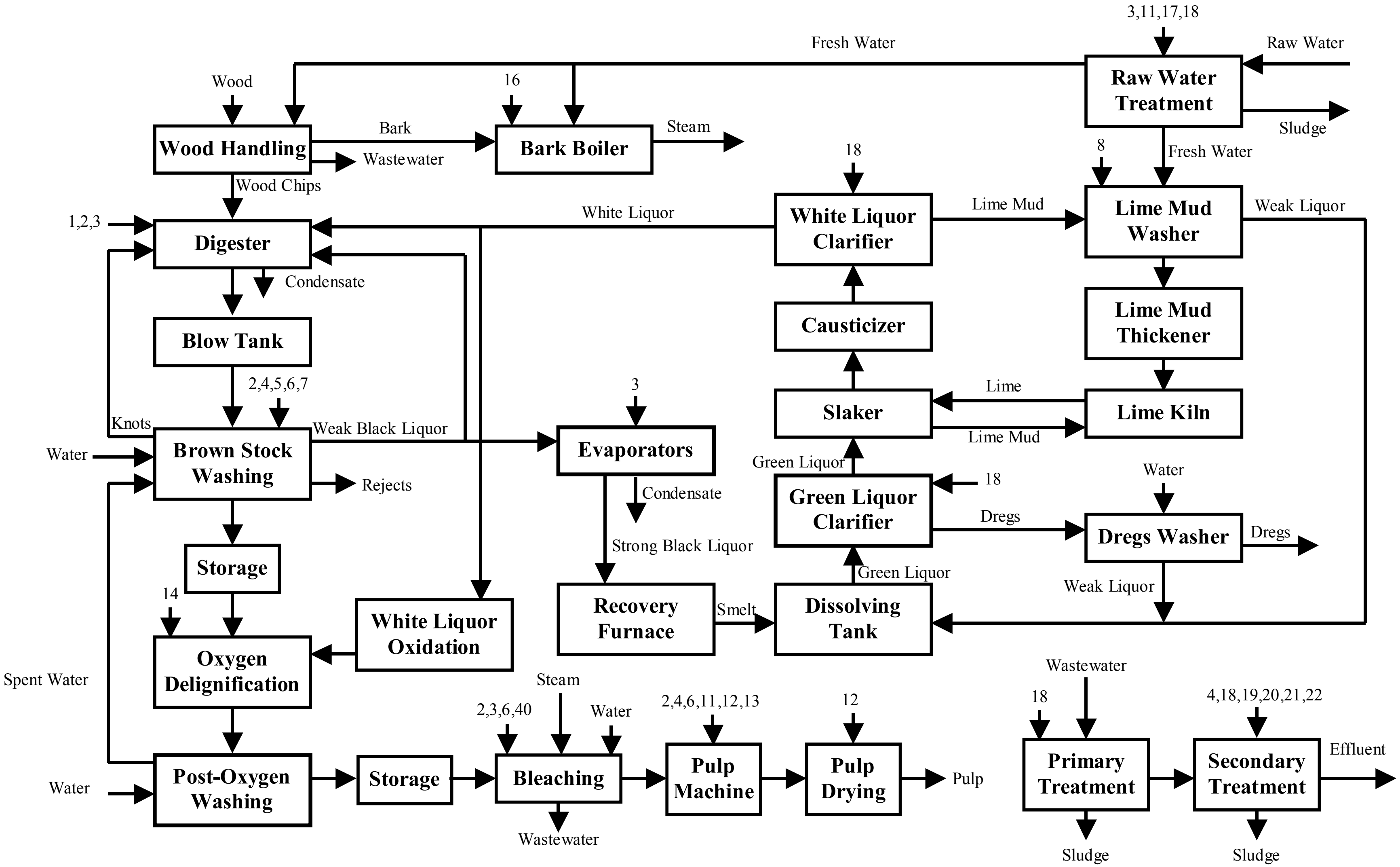

Figure 1 – Typical Process for Non-integrated Bleached Kraft Pulp Mills
(Code for chemicals can be found in Table 3)

3.2 – Chemical Use

24. Chemical products used at non-integrated bleached Kraft pulp mills include specialty and commodity chemicals. Summarized in Table 4 are consumption rates of several major chemicals reported for the European Union (European Commission, 1999, p.50). Most of these chemicals are used for bleaching. Magnesium sulphate ($MgSO_4$) is added to oxygen delignification in order to preserve pulp strength and lime (CaO) is used in liquor causticization.

Table 4 – Some Major Chemicals Used for Production of Bleached Kraft Pulp

Chemical	Consumption (kg/tonne of pulp)
NaOH	25-50
O_2	5-25
$NaClO_3$	20-50
EDTA (chelant)	0-4
SO_2	2-10
H_2O_2	2-30
O_3	0-5
$MgSO_4$	0-3
CaO	5-10

Source: European Commission, 1999, p.50

25. In addition, makeup chemicals for digestion are required. Since digestion chemicals are absorbed on pulp and lost through mechanical problems, a makeup chemical, usually in the form of sodium sulphate (Na_2SO_4), is added to black liquor ahead of a recovery furnace (Grace et al., 1989, p.10-11). A typical quantity of the makeup sulphate is 20-25 kg per tonne of pulp. Part of sodium sulphate may be replaced with caustic soda (NaOH) and soda ash (Na_2CO_3) in order to reduce the sulphur input into the process (Grace et al., 1989, p.139).

26. Quantities of chemicals associated with digestion are dictated by several factors. These factors include type of pulp produced, type of wood used, and type of digester (Green and Hough, 1992, p.124). Summarized in Table 5 are typical values for active alkali charged, lime required, and lime mud produced for various grades of Kraft pulp.

Table 5 – Typical Values for Chemicals Associated with Digestion

Process Parameter	Units	Linerboard	Sack Paper	Bleachable Grades
Pulp yield	%	52-56	48-50	45
White liquor required	m^3/oven-dry tonne	2.4-2.8	2.8-3.2	3.9
Lime required at 85% available	kg/oven-dry tonne	200-230	230-260	320
Lime mud produced	kg/oven-dry tonne	330-385	385-435	525
Green liquor flow (to clarifier)	m^3/oven-dry tonne	3.0-3.5	3.5-4.0	4.8

Source: Green and Hough, 1992, p.125

27. Bleaching chemicals commonly used include chlorine dioxide, oxygen, ozone and peroxide (European Commission, 1999, p.21-27). Chlorine dioxide must be generated on site because it is unstable as a gas and can only be stored as a solution of approximately 1% in water. Ozone (O_3) must also be generated on site because of its instability. Summarized in Table 6 are usage rates of bleaching chemicals in a common C_DE_OHDED bleaching sequence (Grace et al., 1989, p.409). It should be pointed out that elemental chlorine bleaching is no longer common.

Table 6 – Typical Usage Rates of Bleaching Chemicals in a C_DE_OHDED Sequence

Bleaching Chemical	**Use Level (kg/tonne of pulp)**						
	C_D	E_O	H	D_1	E	D_2	Total
Cl_2	60						60
$Ca(OCl)_2$ or NaOCl			10				10
ClO_2	2			8		3	13
NaOH		35		4	5		44
O_2		5					5

Source: Grace et al., 1989, p.409

4 – RELEASE ESTIMATION

4.1 – Wastewater

28. Wastewater generated from Kraft pulp mills originates from pulping and bleaching (USEPA, 1995, p.38; European Commission, 1999, p.32). The wastewater from pulping results from washing operations following the digestion. Bleaching consumes large quantities of water and is a source of chlorinated organic compounds such as dioxins and furans. It should, however, be noted that since 1990, the use of elemental chlorine for bleaching pulp in Canada has decreased by 94% (FPAC, www.fpac.ca). Elemental chlorine-free bleaching (ECF-bleaching) is now the dominant method used in Canada, as well as the U.S., with the use of chlorine dioxide to replace chlorine.

29. Summarized in Table 7 is water consumption data for the pulp and paper industry in Canada, the U.S. and the European Union. In Canada, the water consumption was reduced from 73 m^3/tonne in 1995 to 69 m^3/tonne in 1999 for the industry as a whole (Forest Products Association of Canada, www.fpac.ca, 2004). The data for the province of Quebec was in the range of 57-62 m^3/tonne in 1999 which was lower than the national average (Quebec Forest Industry Council, www.cifg.qc.ca, 2004). The sector of bleached Kraft mills in Canada consumed more water than the industry average at a rate of 97 m^3/tonne in 2002 (personal communications with Environment Canada, 2004).

30. In the U.S., a typical pulp and paper mill consumed 17-50 m^3 of water per tonne of pulp produced (4,000-12,000 gallons/ton) in 2000 (USEPA, 2002, p.36). This data was lower than the Canadian industry average (69 m^3/tonne). In particular, bleached Kraft mills used less water than their counterparts in Canada, ranging from 15 to 45 m^3/tonne in 2003 (personal communications with the U.S. Environmental Protection Agency, 2004).

31. In the European Union, the water consumption varies considerably between different mills, ranging from 15 to 100 m^3 per tonne of pulp (European Commission, 1999, p.32). A consumption volume higher than 50 m^3 per tonne of pulp normally has included clean process cooling water.

32. If the wastewater generation rate is unknown, it can be assumed to be approximately equal to the water consumption rate and vice versa.

Table 7 – Water Consumption by Pulp and Paper Industry

Region	Sector	Water Consumption (m^3/tonne)	Reference
Canada	Pulp and paper industry as a whole	69-73	Forest Products Association of Canada, www.fpac.ca, 2004
Quebec, Canada	Pulp and paper industry as a whole	57-62	Quebec Forest Product Council, www.cifq.qc.ca, 2004
Canada	Bleached Kraft mills	97.4	Personal communications with Environment Canada, 2004
Canada	Non-integrated mills	23.2	Personal communications with Environment Canada, 2004
Canada	Deinking mills	21.4	Personal communications with Environment Canada, 2004
USA	Pulp and paper industry as a whole	17-50	USEPA, 2002, p.36
USA	Bleached Kraft mills	15-45	Personal communications with U.S. Environmental Protection Agency, 2004
European Union	Pulp and paper industry as a whole	15-100	European Commission, 1999, p.32

4.2 – Solid Waste

33. Solid waste is generated in various forms. They include inorganic sludge (dregs and lime mud) from the chemical recovery section, bark and wood residues and rejects (mainly sand) from the wood handling section, sludge from wastewater treatment, ashes from boilers and furnaces (European Commission, 1999, p.48-49). Organic waste such as bark and wood residues can be burned for energy recovery. Table 8 provides quantities of several types of solid waste generated from Kraft pulp mills (European Commission, 1999, p.49).

Table 8 – Solid Waste Generated from Non-integrated Bleached Kraft Pulp Mills

Type of Solid Waste	Generation (kg/tonne of pulp, dry)
Wastewater treatment sludge	10
Ashes from combustion of wood waste	9
Other ashes from energy production	14
Fiber and coating waste	5
Wood waste	6
Hazardous waste	0.2

Source: European Commission, 1999, p.49

34. Wastewater treatment sludge represents a large volume of solid waste. In the U.S., bleached Kraft mills have been reported to generate wastewater treatment sludge in the range of 14 to 140 kg per ton of pulp produced (USEPA, 1995, p.41).

4.3 – Air Emissions

35. Air emissions originate from many process areas. These areas include chip storage, cooking digester, pulp washing, bleaching, chemical recovery, evaporation, bark furnace, recovery boiler, white liquor preparation, lime kiln, and pulp drying (European Commission, 1999, p.27-39). The major environmental concern is sulphur-containing gases including sulphur dioxide and malodorous reduced sulphur compounds such as hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide (CH_3SCH_3) and dimethyl disulphide (CH_3SSCH_3). In addition, nitrogen oxides are emitted from furnaces along with small amounts of particulates. Chlorine compounds may also be released to the atmosphere from the preparation of bleaching chemicals.

36. Volatile organic hazardous air pollutants (HAP's) and volatile organic compounds (VOC's) are also environmental concerns. These emissions were measured in a field test study of 13 Kraft mills in the U.S. and are summarized in Table 9 (NCPI, 1994, No.678). Methanol contributed over 90% of the HAP's emitted.

Table 9 – Emissions of Volatile Organic Hazardous Air Pollutants (HAP's) and Volatile Organic Compounds (VOC's) from Various Process Areas of Kraft Mills

Process Area	Air Emissions (lb/ton of dry pulp)	
	HAP's	VOC's
Brown stock screening and refining	0.60	0.16
Bleaching	0.24	0.068
Oxygen delignification	1.1	0.66
White liquor oxidation	0.019	0.014
Lime kiln	0.036	0.017
Smelt dissolving tank	0.50	0.41
Causticization	0.12	0.064

Source: NCPI, 1994, No.675-679

5 – EMISSION SCENARIOS

5.1 – Fate of Chemical Agents

37. Described in Figure 2 is the fate of a chemical agent used at a facility. The agent is shipped to the facility using one or more types of containers. It is then unloaded or unpackaged and transferred to the production process. The agent leaves the facility via the following routes:

- Container residue that remains in containers after unloading or unpackaging and ends up in wastewater or is disposed of by other means.

- Process residue that remains in process vessels and transfer pipelines and also ends up in wastewater or is disposed of by other means.
- Liquid loss that enters wastewater streams during normal applications.
- Air emission that occurs if the agent contains volatile components.
- Reaction loss that occurs if the agent undergoes chemical reactions during its use.
- Product retention that accounts for a portion of the agent fixed onto finished products.

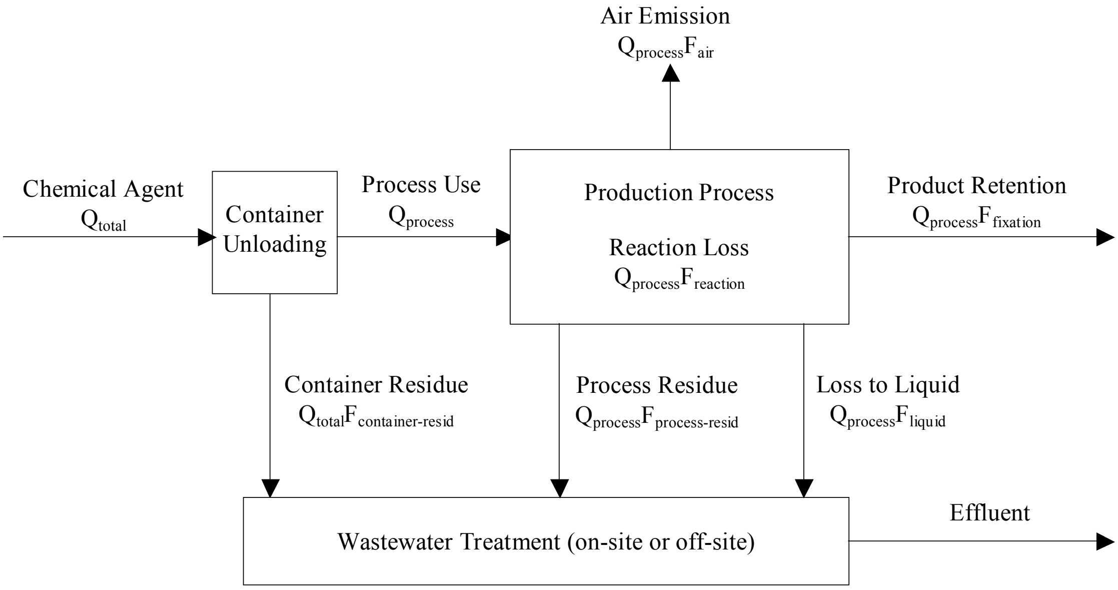

Figure 2 – Fate of a Chemical Agent Used at a Facility

5.2 – General Approach to Aqueous Emission Estimation

38. A general approach to aqueous emission estimation was recommended by the Organization for Economic Cooperation and Development in 2000 in a publication entitled "Guidance Document on Emission Scenario Documents" (OECD, 2000). The approach is based on the fixation of chemical agents onto finished products and can be described by the following equation assuming no air emission and reaction loss:

$$E_{water} = \frac{Q_{product} Q_{agent} C_{substance} (1 - F_{fixation})}{T_{operation}}$$

39. The equation includes a set of input variables on the right and one output variable on the left. The definitions and value types of these variables are provided in Table 10.

Table 10 – Input and Output Variables of Aqueous Emission Estimation Equation

Variable		Symbol	Units	Value Type
Output	Aqueous emission of a substance in chemical agent	E_{water}	kg/d	Calculated
Input	Annual production	$Q_{product}$	tonne/yr	User input without default available
	Chemical agent use rate	Q_{agent}	kg/tonne	Provided with default which can be modified by users
	Substance concentration in chemical agent	$C_{substance}$	%	
	Fixation rate (fraction of chemical agent retained by product)	$F_{fixation}$	%	
	Annual operation days	$T_{operation}$	d/yr	

Source: OECD, 2000.

5.3 – Emission Estimation Calculations

5.3.1 – Emission to Wastewater

40. The emission to wastewater from a Kraft pulp mill can be estimated according to a scheme described in Figure 2. The scheme is based on a spreadsheet formula used by the USEPA for exposure estimation. The emission consists of three portions: 1) liquid loss; 2) container residue; and 3) process residue. Liquid loss is incurred when a fraction of a chemical agent is not retained by finished products and enters wastewater, while container and process residues are common losses resulting from chemical handling and transferring. The following equation can be used for the aqueous emission estimation:

$$E_{water} = liquid\ loss + container\ residue + process\ residue$$

$$= \frac{Q_{total} C_{substance}}{T_{operation}} (1 - F_{container-resid} - F_{process-resid})(1 - F_{air} - F_{reaction} - F_{fixation}) +$$

$$\frac{Q_{total} C_{substance}}{T_{operation}} F_{container-resid} + \frac{Q_{total} C_{substance}}{T_{operation}} F_{process-resid}$$

where

E_{water}: daily aqueous emission of a substance in chemical agent, kg/d
Q_{total}: total chemical agent received by or shipped to a facility, kg/yr
$C_{substance}$: substance concentration in chemical agent, %
$F_{container-resid}$: container residue as percentage of total chemical agent received by or shipped to a facility, %
$F_{process-resid}$: process residue as percentage of total chemical agent received by or shipped to a facility, %
F_{air}: air emission as percentage of chemical agent used in production process, %
$F_{reaction}$: reaction loss as percentage of chemical agent used in production process, %
$F_{fixation}$: fixation rate, i.e., fraction of chemical agent retained by finished products, %
$T_{operation}$: annual operation days, d/yr

41. It should be noted that the liquid loss in the above equation can only be determined with sufficient accuracy if all the three terms for air emission, chemical reaction loss, and product-retained

amount are relatively small. If any one of these terms is close to the amount used in the process, the liquid loss must be determined by other means. This is the case with sulphate mills where the reaction loss is high and is dependent upon such as variables as evaporation and dilution (Fischer, 2005).

5.3.2 – Total Chemical Agent

42. The total amount of a chemical agent received by or shipped to a facility can be estimated from the use rate of the agent if it is not provided directly. The use rate may be expressed on mass of finished products or volume of water or wastewater, depending upon the application of the agent. As a result, one of the equations given below may be used to determine the total amount of a chemical agent.

For use rate based on product mass:

$$Q_{total} = \frac{Q_{product} Q_{agent}}{(1 - F_{container-resid} - F_{process-resid})}$$

For use rate based on water volume (usually water treatment chemicals):

$$Q_{total} = \frac{Q_{product} Q_{water} X_{agent} \times 10^{-3}}{(1 - F_{container-resid} - F_{process-resid})}$$

For use rate based on wastewater volume (usually wastewater treatment chemicals):

$$Q_{total} = \frac{Q_{product} Q_{wwater} X_{agent} \times 10^{-3}}{(1 - F_{container-resid} - F_{process-resid})}$$

where

Q_{total}:	total chemical agent received by or shipped to a facility, kg/yr
$F_{container-resid}$:	container residue as percentage of total chemical agent received by or shipped to a facility, %
$F_{process-resid}$:	process residue as percentage of total chemical agent received by or shipped to a facility, %
$Q_{product}$:	annual pulp production, tonne/yr
Q_{agent}:	chemical agent use rate based on product mass, kg/tonne
Q_{water}:	water consumption rate based on product mass, m^3/tonne
Q_{wwater}:	wastewater generation rate based on product mass, m^3/tonne
X_{agent}:	chemical agent use rate based on volume of water or wastewater, g/m^3 or ppm.

5.3.3 – Air Emission

43. The fraction of a substance in a chemical agent emitted to the atmosphere refers to the release after a pollution control device and is defined as

$$F_{air} = \frac{E_{air}}{Q_{use}} \times 100\%$$

where

F_{air}: fraction of a substance in a chemical agent released to air, %
E_{air}: quantity of a substance in a chemical agent released to air, kg/d
Q_{use}: quantity of a substance in a chemical agent used in production process, kg/d

44. The air emission of a target substance can be estimated from a reference substance based on vapour pressure if the two substances are involved in the same operations (USEPA, 2000).

$$F_{air} = F_{air-ref} \frac{P_{air}}{P_{air-ref}}$$

where

F_{air}: fraction of a target substance released to air, %
$F_{air-ref}$: fraction of a reference substance released to air, %
P_{air}: vapour pressure of a target substance, Pa
$P_{air-ref}$: vapour pressure of a reference substance, Pa

45. A reference substance should be volatile so that its air release reaches a sufficient quantity, while at the same time, it should be found in aqueous discharge to ensure reasonable partition between water and air. To simplify calculations it is necessary to assume that the reference substance is not retained by finished products and is released to air and water only. Under these conditions, the air emission of the reference substance can be estimated by the equation.

$$F_{air-ref} = \frac{E_{air-ref}}{E_{air-ref} + E_{water-ref}}$$

where

$E_{air-ref}$: quantity of reference substance released to air, kg/d
$E_{water-ref}$: quantity of reference substance released to water, kg/d

46. Errors may occur in applying the above equation when the volatilities of the target and reference substances are influenced to different extents by operating conditions such as pH (Stellan Fischer, 2005). Care should, therefore, be taken to select a reference substance that behaves as closely as possible to the target substance with respect to water solubility, partition, stability and ionization.

5.3.4 – Reaction Loss

47. The loss due to chemical reactions is substance specific. In general, it is assumed at zero, i.e., the substance in question does not undergo chemical transformation. Many substances, however, change chemically and need to be evaluated from the data available.

5.4 – Parameter Defaults

5.4.1 – Container Residue

48. Container residue results from chemical unloading and its quantity depends primarily upon the type of containers used. Listed in Table 11 are container residue defaults used by the USEPA for exposure estimation. Semi-bulk and bulk are common container types used by the pulp and paper industry. It is recommended that a value of 3.0% instead of 4.0% be used to estimate liquid drum residue for Canadian

facilities. Recent USEPA OPPT models further suggest 3% as a default for liquid drum residues and 1% for dry solids residues in transport containers.

Table 11 – Container Residue Defaults

Container Type	**Residue as % of Total Quantity Received**	
	Dry	Liquid
Bag	0.1	0.2
Keg	0.3	0.6
Drum	1.0	4.0
Semi-bulk	0.1	0.5
Bulk	0.1	0.2

Source: USEPA spreadsheet exposure estimation, 2004

5.4.2 – Process Residue

49. Process residue results from the use of process vessels and transfer pipelines. Listed in Table 12 are process residue defaults used by the USEPA for exposure estimation.

Table 12 – Process Residue Defaults

Process Hardware	**Residue as % of Total Quantity Received**	
	Dry	Liquid
General	0.1	1.0
Batch vessel	0.2	1.0
Transfer pipeline	0.1	1.0

Source: USEPA Spreadsheet Exposure Estimation, 2004

5.4.3 – Air Emission

50. The fraction of a substance in a chemical agent released to air depends upon its volatility. Its default is zero assuming the substance is a non-volatile compound. This default should be only used when releases to water, land or incineration are estimated. The value for a volatile substance may be estimated using emission factors or engineering calculations.

5.4.4 – Reaction Loss

51. The default for reaction loss is zero assuming no chemical reaction takes place as a chemical agent is used in production processes.

5.4.5 – Water Consumption Rate

52. It was estimated that Canadian Kraft pulp mills consumed 72-120 m^3 of water per tonne of production with an average of 97 m^3/tonne in 2002 (personal communications with Environment Canada, 2004).

5.4.6 – Wastewater Generation Rate

53. It was estimated that Canadian Kraft pulp mills generated 65-110 m^3 of wastewater per tonne of production with an average of 87 m^3/tonne in 2002 (personal communications with Environment Canada, 2004).

5.4.7 – Annual Pulp Production

54. The annual pulp production ($Q_{product}$) for Canadian kraft pulp mills is in the range of 82,000-960,000 tonne/yr per mill with a typical figure at 330,000 tonne/yr. This figure was arrived at by totaling the rated capacity of each Kraft mill (tonnes/yr) as listed in Pulp and Paper Canada (2004) and dividing by the total number of mills to obtain the arithmetical average.

5.4.8 – Annual Operation Days

55. The default for annual operation days ($T_{operation}$) is 350 d/yr. It is based on the assumption that a two-week shutdown period is required for annual maintenance. The actual value may, however, vary from mill to mill.

5.4.9 – Use Rate, Active Substance Concentration and Fixation Rate

56. The use rate, active substance concentration, and fixation rate for chemicals used in various operations were evaluated in a previous study (Crechem Technologies Inc., 2003). Their defaults are reviewed with some revisions in this study and presented in Tables 13-19. It should be noted that pulp bleaching in Canada is now essentially elemental chlorine-free (ECF pulp), with most mills now using chlorine dioxide rather than chlorine and hypochlorites.

57. It has been found that the aqueous releases of some chemical agents are too high when estimated from the use rates given in Tables 13-19. The reason for the overestimation is due to the fact that these chemical agents are only used on an intermittent basis or with variable dosages to treat intermittent problems or continuous problems of varying intensity, while the release calculations are based on continuous operations with conservative assumptions for chemical use. Coagulant polymers, felt wash agents, and chelants are examples of these chemicals.

58. With respect to chemicals that are considered to be totally water soluble in the tables below, a positive fixation rate was still indicated as a range. It is possible that although considered water soluble, a given substance may still be adsorbed onto fibre, and in the absence of specific data to the contrary, a range of 1-20% is used as the fixation rate.

Table 13 – Use Rate, Active Substance Concentration and Fixation Rate for Chemicals Used in Digestion at Kraft Pulp Mills

Chemical Agent	**Use Rate (Q_{agent}, kg/tonne)**		**Concentration ($C_{substance}$, %)**		**Fixation Rate ($F_{fixation}$, %)**	
	Default	Range	Default	Range	Default	Range
Cooking aids/chip penetrants	0.75	0.25-1.25	100	no data	10	1-20
Digester boilouts	no data	no data	100	no data	10	1-20
Scale control	0.09	0.018-0.18	100	no data	10	1-20

Source: Crechem Technologies Inc., 2003

Table 14 – Use Rate, Active Substance Concentration and Fixation Rate for Chemicals Used in Brownstock Washing and Chemical Recovery at Kraft Pulp Mills

Chemical Agent	**Use Rate (Q_{agent}, kg/tonne)**		**Concentration ($C_{substance}$, %)**		**Fixation Rate ($F_{fixation}$, %)**	
	Default	Range	Default	Range	Default	Range
Foam control	1.25	0.25-1.25	100	100	10	1-20
Washing/drainage aids	1.25	0.25-1.25	100	no data	10	1-20
Pitch control (dispersant)	1.0	0.25-2.5	50	10-100	10	1-20
Pitch control (talc)	4.2	0.42-4.2	100	10-100	25	0-50
Boilouts	no data	no data	50	20-50	10	1-20
Clarification aids	0.044	0.0044-0.044	100	20-100	10	1-20
Scale control	0.042	0.0084-0.084	100	no data	10	1-20
Lime mud dewatering aids	0.120	0.081-0.24	100	no data	10	1-20
Tall oil separation & acidulation aids	0.015	0.010-0.015	100	no data	10	1-20
Turpentine separation aids	0.0039	0.00078-0.0039	100	no data	10	1-20

Source: Crechem Technologies Inc., 2003

Table 15 – Use Rate, Active Substance Concentration and Fixation Rate for Chemicals Used in Bleaching at Kraft Pulp Mills

Chemical Agent	**Use Rate (Q_{agent}, kg/tonne)**		**Concentration ($C_{substance}$, %)**		**Fixation Rate ($F_{fixation}$, %)**	
	Default	Range	Default	Range	Default	Range
Chlorine	60	60-80	100	no data	10	1-20
Hypochlorite	10	10-10	100	no data	10	1-20
Chlorine dioxide	40	20-40	100	no data	10	1-20
Sodium hydroxide	40	10-40	100	no data	10	1-20
Oxygen	40	22.5-55	100	no data	10	1-20
Hydrogen or sodium peroxide	30	20-40	100	no data	10	1-20
Peracetic acid	5	5-5	100	no data	10	1-20
Bleaching enzymes	0.2	0.1-0.2	100	no data	10	1-20
Boilouts	no data	no data	100	no data	10	1-20
Pitch control (liquid)	1.0	0.25-2.5	50	10-100	10	1-20
Pitch control (talc)	4.2	0.42-4.2	100	10-100	25	0-50
Scale control	0.1	0.02-0.2	100	no data	10	1-20

Source: Crechem Technologies Inc., 2003

Table 16 – Use Rate, Active Substance Concentration and Fixation Rate for Chemicals Used in Pulp Machines at Kraft Pulp Mills

Chemical Agent	Use Rate (Q_{agent}, kg/tonne)		Concentration ($C_{substance}$, %)		Fixation Rate ($F_{fixation}$, %)	
	Default	Range	Default	Range	Default	Range
Microbiological control	no data	no data	25	10-40	10	1-20
Pitch control (liquid)	1.0	0.25-2.5	50	10-100	10	1-20
Pitch control (talc)	4.2	0.42-4.2	100	10-100	25	0-50
Foam control	1.0	0.25-2	100	10-100	10	1-20
Felt conditioning	1.0[1]	1.0[1]	50	25-100	10	1-20
Boilouts	no data	no data	35	20-50	10	1-20
Retention aids (coagulants)	10	1-20	100	no data	80	70-90
Retention aids (flocculants)	0.2	0.02-1	100	20-100	80	70-90

Source: Crechem Technologies Inc., 2003

[1] The use rate for felt conditioning rarely exceeds 1 kg/tonne for continuous applications.

Table 17 – Use Rate, Active Substance Concentration and Fixation Rate for Chemicals Used in Recovery and Power Boilers at Kraft Pulp Mills

Chemical Agent	Use Rate (Q_{agent}, kg/tonne)		Concentration ($C_{substance}$, %)		Fixation Rate ($F_{fixation}$, %)	
	Default	Range	Default	Range	Default	Range
Air pollution control	0.26	0.17-0.34	100	no data	5	1-10
Condensate treatment	0.026	0.013-0.026	100	no data	5	1-10
Boiler water treatment	0.033	0.0033-0.065	100	no data	5	1-10
Scale control	0.065	0.013-0.13	100	no data	5	1-10
Corrosion inhibitors	0.033	0.0065-0.033	100	no data	5	1-10

Source: Crechem Technologies Inc., 2003

Table 18 – Use Rate and Active Substance Concentration for Chemicals Used in Water Treatment at Kraft Pulp Mills

Chemical Agent	Use Rate (X_{agent}, ppm)		Concentration ($C_{substance}$, %)	
	Default	Range	Default	Range
Corrosion inhibitors	5.0	0.1-5	100	no data
Microbiological control	no data	no data	25	10-40
Scale control	10	2-20	100	no data
Settling aids (coagulants, alum, PAC)	50	5-100	100	no data
Settling aids (flocculants)	2.5	0.1-5	100	20-100

Source: Crechem Technologies Inc., 2003

Table 19 – Use Rate and Active Substance Concentration for Chemicals Used in Wastewater Treatment at Kraft Pulp Mills

Chemical Agent	Use Rate (X_{agent}, ppm)		Concentration ($C_{substance}$, %)	
	Default	Range	Default	Range
Settling aids (coagulants)	50	15-100	100	no data
Settling aids (flocculants)	2.5	0.1-5	100	20-100
Foam control	25	2-25	50	20-100
Nutrients	5	2-5	100	no data
Sludge conditioners (flocculants)	5	0.1-10	100	no data
Odour control	15	5-100	100	no data
Colour control (coagulants)	100	200	100	no data

Source: Crechem Technologies Inc., 2003

6 – EMISSION ESTIMATION EXAMPLE

6.1 – Scenario Description

59. A hindered amine is used as a catalyst in an oxidative pulp bleaching operation at a Kraft pulp mill. The substance is a liquid at ambient temperature and has a low vapour pressure (less than 15 Pa at 20°C). It is shipped in its pure form to the mill in 1,000-litre totes and used in the bleaching operation at a rate of 0.2 kg per tonne of pulp produced.

60. The Kraft pulp mill operates 350 days annually on a continuous basis. The pulp production is 300,000 tonne per year. The bleaching operation is carried out in a closed system. This system consists of storage tanks and transfer pipelines for the amine catalyst, mixing vessels to blend the catalyst with other chemicals, and pulp bleaching towers.

61. The catalyst undergoes degradation reactions during the bleaching operation. The degradation products have similar structures to that of their parent. The overall conversion rate is approximately 50%.

62. The mill is equipped with an on-site wastewater treatment plant. The wastewater generated from the bleaching operation consists of spent bleaching bath and pulp wash water. It contains the spent amine catalyst and other chemicals used. The wastewater is collected together with other mill wastewater streams and sent to the treatment plant before being discharged to a nearby river. It is estimated that the pulp contains 1% of the catalyst used and the rest ends up in the wastewater.

63. Estimate the quantity of the amine catalyst released daily to the on-site wastewater treatment plant.

6.2 – Solution

64. In estimating the aqueous release of the substance in question, degradation reactions should be taken into consideration. In general, if a substance undergoes chemical reactions during a process, its release will be reduced. Derivatives of that substance will, however, form as a result of the reactions. Each of these derivatives as well as their parent must be quantified in order to determine their overall toxic effect

upon releases to a receiving water body. This overall toxic effect is reflective of the risk posted by the use of the substance.

65. The calculation for this example will be limited to the estimation of the aqueous release of the amine catalyst (parent substance) to the on-site wastewater treatment plant to illustrate the use of the emission estimation methods described. The releases for the degradation products of the catalyst can be readily estimated according to the mass balance principle.

6.2.1 – Known Parameters

66. The known parameters given in the example are

- Annual pulp production $Q_{product}$ = 300,000 tonne/yr
- Annual operation days $T_{operation}$ = 350 d/yr
- Substance use rate Q_{agent} = 0.2 kg/tonne
- Substance degradation conversion rate or fractional reaction loss $F_{reaction}$ = 50%.
- Substance fraction retained by pulp or fixation rate $F_{fixation}$ = 1%.

67. The parameters that can be readily estimated are presented below.

- No site-specific data is available for container residue. Considering the substance is a liquid and is shipped in 1,000 L totes (semi-bulk), on-site cleaning is assumed and the default for the fractional loss is $F_{container-resid}$ = 0.5%, as recommended by USEPA (2004).

- Concerning process residue, the storage tanks and transfer pipelines are designated equipment for the substance and operate in a continuous mode. As a result, regular cleaning is not expected for this type of equipment and process residue can be reasonably assumed to be negligible, i.e., $F_{process-resid}$ = 0.

- Since the substance has a low vapour pressure (less than 15 Pa at ambient temperature) and is handled and used in closed systems for storage, transfer, mixing, and bleaching, it is anticipated that the fraction released to air is negligible, i.e., F_{air} = 0.

- Since the substance is supplied in its pure form, the active substance concentration is $C_{substance}$ = 100%.

6.2.2 – Total Chemical Agent

68. The total chemical agent refers to the total amount received in containers and is the same as the total substance received since the substance is supplied in its pure form rather than mixed with other ingredients. This total is determined based on the pulp production and the use rate of the substance and corrected for container and process residues.

$$Q_{total} = \frac{Q_{product} Q_{agent}}{(1 - F_{container-resid} - F_{process-resid})}$$

$$= \frac{300{,}000\ tonne/yr \times 0.2\ kg/tonne}{(1 - 0.5\% - 0)}$$

= 60,302 kg/yr

Total amount received Q_{total} = 60,302 kg/yr

6.2.3 – Container Residue

69. The daily loss from container residue to wastewater prior to on-site wastewater treatment is estimated as

$$Container\ residue = \frac{Q_{total} C_{substance}}{T_{operation}} F_{container-resid}$$

$$= \frac{60{,}302\ kg/yr \times 100\%}{350\ d/yr} \times 0.5\%$$

= 0.86 kg/d

Container residue = 0.86 kg/d

6.2.4 – Process Residue

70. The daily loss from process residue to wastewater prior to on-site wastewater treatment is estimated as

$$Process\ residue = \frac{Q_{total} C_{substance}}{T_{operation}} F_{process-resid}$$

$$= \frac{60302\ kg/yr \times 100\%}{350\ d/yr} \times 0\%$$

= 0 kg/d

Process residue = 0 kg/d

6.2.5 – Liquid Loss

71. The liquid loss refers to the loss from spent bleaching bath and wash water to wastewater prior to on-site wastewater treatment and is estimated as

$$Liquid\ loss = \frac{Q_{total} C_{substance}}{T_{operation}} (1 - F_{container-resid} - F_{process-resid})(1 - F_{air} - F_{reaction} - F_{fixation})$$

$$= \frac{60{,}302\ kg/yr \times 100\%}{350\ d/yr} (1 - 0.5\% - 0\%)(1 - 0\% - 50\% - 1\%)$$

$$= \frac{60{,}302\ kg/yr \times 100\%}{350\ d/yr} \times 99.5\% \times 49\%$$

= 84.00 kg/d

Liquid loss = 84.00 kg/d

6.2.6 – Total Release

72. The total release to wastewater prior to on-site wastewater treatment is the sum of the aqueous releases from container residue, process residue and liquid loss.

Total release to wastewater = Container residue + Process residue + Liquid loss

= 0.86 kg/d + 0 kg/d + 84.00 kg/d

= 84.86 kg/d

Total loss to wastewater = 84.86 kg/d

7 – DATA GAPS AND UNCERTAINTIES

73. Chemical use rate is considered the major area for data gaps and uncertainties. Although a range is provided for each class of chemicals, it is approximate and has not been reviewed by industry. Such a range needs to be confirmed or refined by industry (users and/or suppliers) in order to reflect typical mill operations.

74. The concentration of a substance in a chemical is generally lacking, but is not considered an issue. This is because in assessing the exposure of a given substance in a given scenario, the concentration is provided by the company that is involved with the use of the substance.

75. Data on air emissions originating from each class of chemicals is not readily available. The data depends upon not only the volatility of the ingredients in the chemicals, but also the operating conditions under which the chemicals are applied. Emission factors may be established to provide a realistic approach to the estimation of air emissions.

76. Reaction loss is important to the determination of environmental releases, but little information is available. It is expected that chemicals ending in black liquor will undergo reactions (most likely decomposition) when subjected to high temperature conditions associated with the recovery furnace operations. Hydrolysis, neutralization and ionization may also occur for other chemicals such as biocides that are used in aqueous conditions. All these chemical changes need to be quantified in order to estimate emissions to water on the mass balance basis.

GLOSSARY

White Liquor – Active liquor containing sodium hydroxide and sodium sulfide, for cooking wood chips.

Black Liquor – Spent or residual cooking liquor, containing dissolved organic matter and inorganics.

Green Liquor – Formed when inorganic smelt from the recovery furnace is dissolved in wash water.

Slaking – The conversion of lime, CaO, to slaked lime, $Ca(OH)_2$, prior to recaustizing

Smelt – Inorganic residual from the recovery furnace consisting of sodium carbonate and sodium sulfide.

Tall Oil – A mixture of fatty and resin acids, insoluble in the black liquor evaporator section, is drawn off and acidulated with sulfuric acid to form crude tall oil. Sold to oil processors for recovering different fractions or used for fuel value by the mill.

Caustizing – The reaction of calcium hydroxide with sodium carbonate to form sodium hydroxide, one of the actives in Kraft cooking liquor.

Use Rate – An amount of a chemical agent used in pulp making operations per unit pulp production, usually expressed as kg/tonne of pulp.

Active Substance Concentration – Concentration of an active ingredient, usually a substance of concern, in a chemical agent, usually expressed as wt%.

Fixation Rate – Fraction of an active ingredient in a chemical agent, or a chemical agent, retained by pulp product, usually expressed as wt%.

Boil-out – Recirculation at high temperature over a period of time, usually several hours, of a caustic or acid based dispersant/surfactant solution in a specific part of a pulp or paper mill in order to dissolve or dislodge accumulations or deposits of fibre, fillers, pitch, scale, microbiological slime, or combinations thereof, which are causing throughput or quality problems in the finished product. Chelant boilouts can be performed if the deposition is mainly inorganic scale.

Digester Boil-out – Usually, a recirculation of dispersants and sequestrants to help remove calcium carbonate scale in a specific section of a digester, particularly in the upper cooking zone heat exchanger section of Kamyr digesters.

ABBREVIATIONS

ESD – Emission scenario document

USEPA – United States Environmental Protection Agency

OPPT – USEPA's Office of Pollution Prevention and Toxics

AIFQ – Association Industrielle Forestière du Québec

CIFQ – Conseil Industriel Forestier du Québec

FPAC – Forest Products Association of Canada

C_D - Chlorine bleach stage with partial replacement by chlorine dioxide

E_o – Caustic extraction stage with partial oxygen

H – Hypochlorite bleaching stage

D – Chlorine dioxide bleaching stage

HAP – Hazardous air pollutants

VOC – Volatile organic compounds

ECF – Elemental chlorine free

REFERENCES

Ash, M.; and I. Ash, Handbook of Paper and Pulp Chemicals, Synapse Information Resources, Endicott, NY, USA, 2001.

Austin, G. T., Shreve's Chemical Process Industries, 5th ed., McGraw-Hill, New York, 1984.

Braunschweiler, H., "A reasonable worst-case slimicide PEC-model for paper industry using wastewater treatment in Finland," FEI/Chemicals Division, Tel: +358-9-40300535, Fax: +358-9-40300591, Web: http://www.vyh.fi/eng/fei/fei.html.

Braunschweiler, H., "Spreadsheet calculation model for environmental risk assessment of slimicides released from paper mills," Finnish Environment Institute, 2000.

Brooke, D; M. Crookes; and P. Quarterman, "Review of industry and use categories and emission estimation methods in the EU technical guidance document," prepared for CEFIC-Long Range Research Initiative, 2000.

Crechem Technologies Inc. (2003), "Chemical Releases from Canadian Pulp and Paper Mills," prepared for Environment Canada (Gatineau, Quebec) by Crechem Technologies (Ottawa, Ontario) in association with JANCO (Perth, Ontario), July 7, 2003.

Dence, C. W.; and D. W. Reeve (eds.), Pulp Bleaching: Principles and Practice, TAPPI Press, Atlanta, GA, USA, 1996.

Dingman, D. J.; and C. D. Perry (Buckman Laboratories International, Inc.), "Caustic-free repulping for newsprint production – Part I," presented at the 1999 TAPPI Pulping Conference, available from the web site of Buckman at http://buckman.com/eng/randd/deinking.html.

Drew, J.; J. Russell; and H. W. Bajak (eds.), Sulfate Turpentine Recovery, Pulp Chemicals Association, New York, 1971.

Dykstra, G. M. (Buckman Laboratories International, Inc.), "Coatings additives: the important roles for biocides, dispersants and defoamers," presented at the 1999 TAPPI Coating Materials Short Course, available from the web site of Buckman at http://www.buckman.com/eng/randd/coatings.html.

European Commission, "Integrated pollution prevention and control (IPPC) – draft reference document on best available techniques in the pulp and paper industry," August 1999.

European Commission, "Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substances," Part IV, Office for Official Publications of the European Communities, Luxembourg, 1996.

Fischer, S. (Swedish National Chemicals Inspectorate), comments provided on pulp and paper emission scenario documents, 31st May 2005.

Fitzhenry, J.; P. Hoekstra; and D. Glover (Buckman Laboratories International, Inc.), "New measurement techniques and new technologies for stickies control," presented at PIRA's Wet End Chemistry Conference, June 2000, available from the web site of Buckman at http://www.burckman.com/eng/randd/pira.html.

Forest Products Association of Canada, "Environment Progress Report 2000-2001," (formerly the Canadian Pulp and Paper Association).

Grace, T. M.; E. W. Malcolm; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 5: Alkaline Pulping, Joint Textbook Committee of the Paper Industry, Canada, 1989.

Green, R. P.; and G. Hough, Chemical Recovery in the Alkaline Pulping Process, 3rd ed., TAPPI Press, Atlanta, GA, USA, 1992.

Hagemeyer, R. W.; D. W. Manson; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 6: Stock Preparation, Joint Textbook Committee of the Paper Industry, Canada, 1992.

Hamilton, F.; B. Leopold; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 3: Secondary Fibers and Non-Wood Pulping, Joint Textbook Committee of the Paper Industry, Canada, 1987.

H. A. Simons Ltd., "A technical background information document on pulp and paper mill air emissions," prepared for The Ministry of Environment, Lands and Parks of British Columbia and Environment Canada, Vancouver, BC, Canada, April 1995.

Hoekstra, P. M.; D. E. Glover; and J. W. Fitzhenry (Buckman Laboratories International, Inc.), "Improved productivity with effective stickies control," presented at Tissue World 2001 in Nice, France, march 22, 2001, available from the web site of Buckman at http://www.buckman.com/eng/randd/pmhstickies.htm.

Hoekstra, P. M. (Buckman Laboratories International, Inc.), "Microbiology in the paper industry," presented at the 1990 TAPPI Chemical Processing Aids Short Course, available from the web site of Buckman at http://www.buckman.com/eng/randd/micropap.html.

Huston, J. K., "Manufacture of newsprint using recycled fibers," in Technology of Paper Recycling, R. W. J. McKinney (ed), Blackie Academic & Professional, London, 1995, pp.296-310.

Ingruber, O. V.; M. J. Kocurek; and A. Wong (eds.), Pulp and Paper Manufacture Volume 4: Sulfite Science & Technology, Joint Textbook Committee of the Paper Industry, Canada, 1985.

Kiiskinen, H. T.; and K. E. Edelmann, "Superheated steam drying of paper web," Developments in Chemical Engineering and Mineral Processing 10, 349-365, 2002.

King, V. M.; and M. T. Stoner (Buckman Laboratories International, Inc.), "Novel, environmentally sound methods for paper machine deposit control," presented at the TAPPI Environmental Conference, May 2000, available from the web site of Buckman at http://www.buckman.com/eng/randd/tappi.html.

Kocurek, M. J.; and C. F. B. Stevens (eds.), Pulp and Paper Manufacture Volume 1: Properties of Fibrous Raw Materials and Their Preparation for Pulping, Joint Textbook Committee of the Paper Industry, Canada, 1983.

Leask, R. A.; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 2: Mechanical Pulping, Joint Textbook Committee of the Paper Industry, Canada, 1987.

Marlewski, R. L., "The mill management view," presented at the 3rd Special Recovery Conference Sponsored by the Pulp Chemicals Association, Atlanta, Georgia, USA, January 11, 1984.

McKinney, R. W. J., "Water and waste water treatment in recycling mills," in Technology of Paper Recycling, R. W. J. McKinney (ed), Blackie Academic & Professional, London, 1995, pp.204-243.

Minor, J., "Pulp," in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed, vol.19, M. Grayson; and D. Eckroth (eds.), John Wiley & Sons, New York, 1982, pp.379-419.

NCPI, "Volatile organic emissions from non-chemical pulp and paper mill sources – Part V – Paper machines," Volume 1, U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.740, New York, July 1997.

NCPI, "Volatile organic emissions from non-chemical pulp and paper mill sources – Part IV – Deinking processes," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.739, New York, July 1997.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part I – Oxygen delignification systems," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.675, New York, August 1994.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part II – Lime kilns, smelt dissolving tanks and miscellaneous causticizing area vents," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.676, New York, September 1994.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part III – Miscellaneous sources at Kraft and TMP mills," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.677, New York, September 1994.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part IV – Kraft brownstock washing, screening and rejects refining sources," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.678, New York, October 1994.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part V – Kraft mill bleach plants," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.679, New York, October 1994.

NCPI, "Volatile organic emissions from pulp and paper mill sources – Part VI – Kraft recovery furnaces and black liquor oxidation systems," U.S. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin, No.680, New York, October 1994.

OECD, "Compendium of estimation methods to quantify releases to the environment for use in pollutant release and transfer registries," The Organisation for Economic Co-operation and Development, September 22, 1999.

Oppong, D.; V. M. King; X. Zhou; and J. A. Bowen (Buckman Laboratories International, Inc.), "Cultural and biochemical diversity of pink-pigmented bacteria isolated from paper mill slimes," Journal of Industrial Microbiology and Biotechnology, 25, 74-80 (2000), available from the web site of Buckman at http://www.buckman.com/eng/randd/pinkslime.html.

Shaw, M., "Mills work with clothing suppliers to reduce power use, downtime," Pulp and Paper 76, 51-55, 2002.

Sirkka, S, "Environmental exposure assessment of slimicides – revision of the emission scenario model for Finland," Finnish Environment Institute, Helsinki, January 2001, available at http://www.vyh.fi/eng/orginfo/publica/electro/femim212/femim212.htm.

Thorp, B. A.; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 7: Paper Machine Operations, Joint Textbook Committee of the Paper Industry, Canada, 1991.

USEPA, "Profile of the Pulp and Paper Industry," 2nd edition, EPA/310-R-02-002, U.S. Environmental Protection Agency, Office of Compliance, Washington, DC, November 2002.

USEPA, "Development document for proposed effluent limitations guideline, new source performance standards, and pretreatment standards for the textile mills point source category," US Environmental Protection Agency, Washington, DC, EPA 440/1-79/022b, October 1979.

Whitford, Tim (consultant to Forest Products Association Canada); discussion at a project meeting, Ottawa, February 6, 2002.