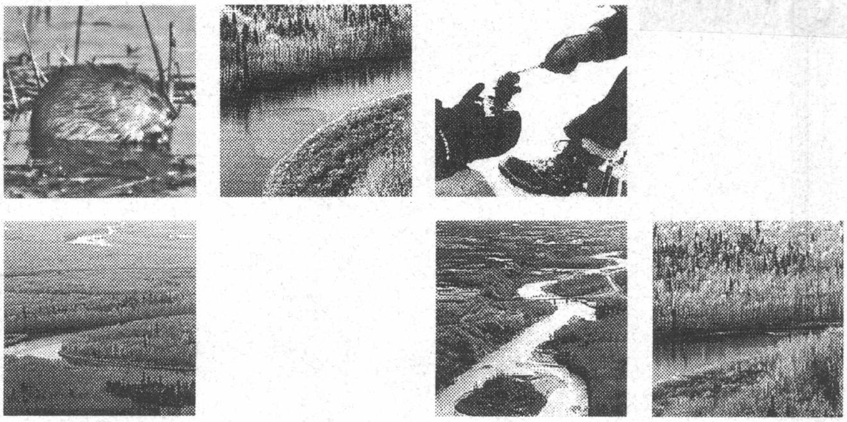
Canada Alberta Northwest Territories

Northern River Basins Study



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by
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NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 15

A REVIEW OF LITERATURE ON PULP AND PAPER MILL EFFLUENT CHARACTERISTICS IN THE PEACE AND ATHABASCA RIVER BASINS

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

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NORTHERN RIVER BASINS STUDY
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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
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Wrona
(Dr. F.J. Wrona, Ph.D., Science Director)

26 August 1993
(Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
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SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [✓] No

Larkin
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(Bev Burns, Co-chair)

93/09/20
(Date)

A REVIEW OF LITERATURE ON PULP AND PAPER MILL EFFLUENT CHARACTERISTICS IN THE PEACE AND ATHABASCA RIVER BASINS

STUDY PERSPECTIVE

Industrial activity within the Northern River Basins Study area has generally been restricted to exploitation of natural resources namely, fossil fuels and forestry resources. There are other industries related to the agriculture sector and the mining of mineral resources, but these are less extensive and of less concern in the context of "point source pollution." The forestry industry is associated with significant economic growth for this region of Alberta and for the Province as a whole. Also associated with this industry is the impact of forestry management and pulp and paper mill solid and liquid wastes on the health of terrestrial and aquatic ecosystems. With continuing growth in the forestry industry and the expansion and development of existing and new pulp and paper mills, there is increasing public concern over cumulative impacts of these and other developments on the health of northern ecosystems.

Related Study Questions

1b) *How can the ecosystem be protected from the effects of these compounds?*

2) *What is the current status of water quality in the Peace, Athabasca and Slave river basins, including the Peace-Athabasca Delta?*

4a) *Describe the contents and nature of the contaminants entering the system and describe their distribution and toxicity in the aquatic ecosystems with particular reference to water, sediment and biota.*

5) *Are the substances added to the rivers by natural and man-made discharges likely to cause deterioration of water quality?*

This report is intended to provide the reader with a generalized working knowledge about the pulp and paper mill treatment processes and about contaminants generally associated with their effluents. The report discusses the technological differences between bleached kraft pulp mills, bleached chemi-thermomechanical pulp mills and newsprint operations. It draws upon information from plants elsewhere in the country and from experiences gained from around the world. Topical contaminants discussed include general wastewater variables (eg. chemical oxygen demand, biochemical oxygen demand, dissolved organic carbon, nutrients, suspended solids, sulphur, colour and turbidity) and several more exotic variables (eg. toxicity, resin acids, steroids, chelating substances, adsorbable organic halogens, chlorophenols, dioxins and furans, chlorates and metals). A useful glossary is included with this report which explains many of the terms which are often used by regulators and scientists.

To supplement the report, a dBASEIV database, "NORTHDAT", has been assembled from 1990, 1991 and 1992 information and contains summary statistics on the quality of licensed effluents.

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1 SUMMARY

1.1 Background and Purpose

This report is brief review of the literature on the characteristics of pulp and paper mill effluents which are relevant to the Northern River Basins in Alberta. It is a part of a broad study of the aquatic conditions and environmental needs of the area currently being undertaken by the governments of Alberta, British Columbia, Canada and the North-West Territories.

1.1.1 Contract

This report was prepared under Agreement No 920704 issued March 13, 1992 by the Northern River Basins study.

1.1.2 The Northern River Basins

The Northern River Basins include the Athabasca, Wapiti, Smoky and Peace rivers, as well as other rivers which do not receive wastewaters from any pulp and paper mills.

1.2 Pulp and Paper Industry in the Northern River Basins

There are six pulp and paper mills in Alberta that discharge into the Northern River Basins, and three in British Columbia, as indicated in Table 1.

Table 1 Pulp and paper mills in Northern River Basins

Company	Location	Recipient	Product
Alberta Mills			
Weldwood of Canada Ltd.	Hinton	Athabasca	Bleached kraft pulp
Procter and Gamble Cellulose Ltd.*	Grande Prairie	Wapiti	Bleached kraft pulp
Diashowa Canada Ltd.	Peace River	Peace	Bleached kraft pulp
Millar Western Pulp Ltd.	Whitecourt	Athabasca	Bleached CTMP
Slave Lake Pulp Corporation	Slave Lake	Pembina	Bleached CTMP
Alberta Newsprint Co. Ltd.	Whitecourt	Athabasca	Newsprint
BC Mills			
Fletcher Challenge Canada Ltd.	Mackenzie	Peace	Bleached kraft pulp
Fiberco Pulp Inc.	Taylor	Peace	Bleached CTMP
Finlay Forest Industries Ltd.	Mackenzie	Peace	Newsprint

* At the time of writing it appeared that the Procter and Gamble Cellulose Ltd mill would be sold to Weyerhaeuser Co.

The bleached kraft mills use quite similar processes, and discharge generally similar effluents. The principal difference between the kraft mill processes that effect effluent characteristics is that mills at Peace River and Hinton have extended cooking oxygen delignification systems while the other kraft mills use traditional pulping and bleaching technology.

The bleached chemi-thermomechanical pulp (CTMP) mills manufacture mechanical pulps and bleach them with a hydrogen peroxide based process. They do not use any chlorine compounds.

The two newsprint mills manufacture mechanical pulp without using any chemicals, except perhaps small quantities of chlorine-free bleaching agents. It is common to refer to such processes as brightening rather than bleaching.

The CTMP and newsprint mills are generally referred to by the generic term "mechanical pulp mills".

1.3 Effluent Characteristics

There is no simple single number that can characterize an effluent. Although the pulp and paper industry is often considered as a single source of effluents, the pulp and paper industry must be considered as several sub-sectors which discharge effluents with widely differing characteristics. The effluents discharged from the mechanical and bleached kraft type of mill[1] are complex, particularly the latter. There are hundreds of known compounds in pulp mill effluents, and perhaps thousands of unknown ones. Only a small proportion are environmentally important, and although considerable progress has been made in identifying and reducing discharges of these, today's scientific knowledge is not yet complete.

Some generic group parameters are commonly used to simplify analysis of effluent data and assessment of probable environmental effects. Those which are most relevant to the pulp and paper industry are Biochemical Oxygen Demand (BOD), Total Suspended solids (TSS), Chemical Oxygen Demand (COD) and Adsorbable Organic Halogen (AOX). While these have been useful in the past, they are relatively simplistic tools for controlling water pollution, and their limitations must be understood. In the past, it was always environmentally desirable to reduce these parameters in pulp and paper mill effluent, but in many locations current discharges have been reduced to the point that careful analysis is required to determine whether further reduction would be environmentally beneficial.

As effluent control technology advances, and measures to eliminate the gross pollution by pulp mills that was common in the 1960s are implemented, it is necessary to utilize more advanced techniques for assessing environmental effects. It is becoming steadily more important to consider more specific effluent parameters than those mentioned above. This is particularly true in the case of the pulp and paper industry in the Northern River Basins of Alberta and British Columbia, where, by international standards, the mill effluent quality ranges from very good to equaling the best in the world.

AOX was a useful measure of the pollutants discharged from bleached kraft mills when discharges were normally in the range of 4 to 10 kg/tonne pulp. However, in the more advanced of today's mills, where the discharges are generally under 2 kg/tonne, many experts now believe AOX is a poor predictor of environmental effects. AOX discharges

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[1] *All mills in the Northern River Basins are in either the mechanical or bleached kraft sub-sectors.*

from the Alberta mills are now under 2 kg/tonne pulp, and recently some have been under 1 kg/t. It has been suggested by several authors that it would be more appropriate to regulate the highly chlorinated phenols which are a small but environmentally important fraction of AOX.

Tables 2 to 5 list the effluent parameters which are generally of most interest in the kinds of pulp and paper mills that operate in the Northern River Basins.

Table 2 Pulp mill effluent parameters (general variables)

Variable	Comments	Mill Type
General wastewater variables		
BOD_5	BOD is a measure of the oxygen consumed in a sample over a 5 day period by the action of microorganisms. Reduced in biological treatment plants. Can be of importance for discharges to receiving waters that are vulnerable to oxygen depletion.	K M
COD	Biological treatment removes up to approx. 40%. Internal measures are generally more efficient in reducing COD.	K M
Dissolved Organic Carbon (DOC)	As for COD.	K M
Total Suspended Solids (TSS)	Depends strongly on biological treatment system performance.	K M
Volatile Suspended Solids (VSS)	Closely related to TSS for pulp mills.	K M
Specific Conductance	Should generally be high for pulp mill effluents. Low conductivity relative to mills with similar processes indicates potential for a successful water conservation program.	K M
Total Kjeldahl Nitrogen (TKN)	Reduced by biological treatment. Normally about 8% of it is very persistent and not available to algae.	K M
Ammonia plus Ammonium ion	Must often be added to biological treatment plants in the pulp and paper industry for maximum BOD removal efficiency. Excess controlled by treatment plant operation. Free ammonia is very toxic to fish. Generally, ammonia is of no concern below pH 8.	K M
Nitrate + Nitrite	Probably a non-issue for pulp mill effluents, because the effluent treatment plants are nitrogen limited. Can be reduced to atmospheric nitrogen in the anoxic zones of a biological treatment plant.	K M
Phosphorus	Must be added to biological treatment plants to achieve maximum BOD removal efficiency. Excessive concentrations can cause eutrophication of receiving waters.	K M
Sulphide	Very toxic to aerobic life such as fish and crustaceans. Efficiently oxidized to sulphate in aerobic treatment. Precipitates many heavy metals.	K
Adsorbable Organic Halogen (AOX)	A measure of chlorinated organic substances formed by use of chlorine chemicals in bleaching of pulp. A major fraction of AOX consists of chemically unstable or readily biodegradable materials, which are easily mineralized in any biological treatment plant. Materials which are not mineralized during biological treatment are more persistent in the environment. Approx. 0.1% of AOX is bioaccumulative.	K

In Mill Sub-sector column, K= Kraft, , M=CTMP or newsprint

Of the traditional effluent group parameters, COD is probably the most useful in today's context, since it provides a measure of the content of organic substances that are relatively difficult to degrade. COD restrictions encourage inplant control measures, and are becoming common in Scandinavia and Japan. The difference between BOD and COD in an effluent sample provides an indication of the presence of persistent materials.

The data available on metals discharged from the NRBS mills are summarised in Table 3. It is apparent that the effluents would mostly comply with receiving water quality objectives, without any dilution.

Table 3 Pulp mill effluent parameters (metals)

Variable	Comments	WQ*	Mill Type
Metals			
Aluminum	Routinely used to reduce COD, AOX and toxicity of effluents. Precipitates with phosphate or sulphide.		K M
Cadmium	Found up to 10 µg/L.	10	M
Chromium	Found up to 120 µg/L., average 0.33 µg/L.	50	K M
Cobalt	Found up to 30 µg/L., average 0.13 µg/L.		M
Copper	Copper salts are generally used in wood preservatives, fungicides and toxic pigments in anti fouling agents. Common in raw water. Very toxic to fish. Found up to 300 µg/L, average 0.44 µg/L.	20	K M
Lead	Found up to 70 µg/L, average < 0.4 µg/L.	50	M
Molybdenum	Found up to 10 µg/L, average 0.04 µg/L. .		K M
Nickel	Found up to 50 µg/L, average < 0.24 µg/L..		K M
Zinc	Not used in NRBS mills. Toxic in higher concentrations. Essential for synthesizing certain co-enzymes. Human uses as a nutrient and in creams. Precipitates with phosphates or sulphide. Found up to 1270 µg/L, but average was under 11 µg/L in the three mills tested.	50	K M
Mercury	Not found in Alberta mill effluents Not used in NRBS mills. Prior to 1970 mercury compounds were used as slimicides in white water systems in the industry.,	0.1	K

In Mill Sub-sector column, K= Kraft, , M=CTMP or newsprint
WQ = Alberta Water Quality Objectives expressed in µg/L.

Table 4 Pulp mill effluent parameters (Chlorinated methanes and phenolics)

Variable	Comments	Mill Type
Chlorinated methanes		
Dichloromethane (Methylene Chloride)	Formed by a similar mechanisms as chloroform . Any dichloromethane formed would be purged to the air during aeration in biological treatment plants.	K
Trichloromethane (Chloroform)	Formed in kraft bleach plant chlorination and, principally, in hypochlorination stages. Purged to the air during aeration in biological treatment plants.	K M
Bromodichloromethane	Formed by the same mechanisms as chloroform when trace amount of bromine is present in the chlorine gas, or by bromide chloride substitution of chloroform if aqueous bromide is present.	K
Phenolics		
Phenol, guaiacol, syringol and others	Common constituents in black liquor. Phenol is readily degradabl and is digested in biological treatment plants. The more substituted phenolics are more difficult to degrade.	K M
2,4-dichlorophenol	Originate from C-stages. Washed out at the E-stage. Eliminated by oxygen delignification and low chlorine multiples.	K
2,4,6-trichlorophenol	Originate from C-stages. Washed out at the E-stage. Eliminated by oxygen delignification and low chlorine multiples.	K
2,3,4,6-tetrachlorophenol	Originate from C-stages. Washed out at the E-stage. Eliminated by oxygen delignification and low chlorine multiples.	K
2,5-DCG, 3,4-DCG 4,6-DCG, 4,5-DCG	Dichloroguaiacols are formed mainly in softwood BKME.when th chlorine multiple is above about 0.05.	K
3,4,6,-TCG 3,4,5-TCG, 4,5,6-TCG	Trichloroguaiacols mainly in softwood BKME.when the chlorine multiple is beyond about 0.13.	K
TeCG	Tetrachloroguaiacol mainly in softwood BKME.when the chlorine multiple is beyond about 0.17.	K
Chlorinated catechols	As for guaiacols. They are more difficult to analyze due their water solubility.	
Chlorinated syringols	As for guaiacols, but they originates from hardwood pulping.	
Chlorinated vanillins	As for guaiacols.	
Dioxins and furans		
2,3,7,8 TCDD	The most toxic and best known of the PCDD/PCDFs, formed in CD stage of bleach plant. Controlled by various ways of reducin or eliminating chlorine usage in bleaching	K
2,3,7,8 TCDF	The most toxic of the polychlorinated furans. Formed in same unit operations as 2,3,7,8 TCDD, and controlled by same proces modifications.	K
Octachlorodibenzo-p-dioxin	A ubiquitous and relatively benign member of the PCDD/PCDF family. Found in Ontario mills that have no bleach plant operatio but which use waste paper and board furnish. No data on Alberta mills.	K M

In Mill Sub-sector column, K= Kraft, M=CTMP or newsprint

It is becoming apparent that the substances that are responsible for the sub-lethal effects of effluent from bleached kraft mills with AOX discharges below about 2 kg/tonne are non-chlorinated compounds. Some of these effects have been found to be approximately independent of whether the mill bleaches with chlorine or not, or whether it has biological treatment or not. There are some indications that steroids from wood extractives play a significant role in this regard.

Table 5 Pulp mill effluent parameters (resin & fatty acids and miscellaneous)

Variable	Comments	Mill Type
Resin and fatty acids		
Abietic Acid	Resin acids are naturally occurring compounds in wood resins, particularly in pine and spruce. Released during mechanical and kraft pulping. Very toxic to fish and a frequent reason for a pulp and paper mill effluent sample failing toxicity testing. Substantial amounts in kraft mill effluents indicate soap spills or black liquor carry-over from the evaporators. Reduced by spill control and biological treatment All resin acids released in the mechanical pulping are discharged to the effluent treatment system.	K M
Chlorodehydroabietic Acid		K
Dehydroabietic Acid		K M
Isopimaric Acid		K M
Levopimaric Acid		K M
Neoabietic Acid		K M
Pimaric Acid		K M
Oleic Acid	This is a fatty acid. However, the discussion on resin acids applies.	K M
Dichlorodehydroabietic Acid	Controlled by either reducing black liquor carry-over to the bleach plant and/or reducing the chlorine multiple at the C-stage. Refer to resin acid discussion. More persistent in biological treatment.	K
Miscellaneous, non-traditional parameters		
Steroids	Found in wood extractives. Suspected to be responsible for growth inhibition and maturing of certain species of fish. Can be reduced by internal water recirculation, extended cooking, oxygen delignification.	K M
Chelating substances	New bleach sequences involving extensive use hydrogen peroxide use chelating agents such as EDTA to shield hydrogen peroxide from metal ions. EDTA resists biological treatment, but is normally bound so tightly to ferro ions that no exchange of ions occur in the receiving waters. EDTA is abiotically degradable.	M
Chlorate	Formed during chlorine dioxide generation from chlorate. Extremely toxic to higher algae when nitrogen limited. Can be removed during anoxic wastewater treatment.	K

In Mill Sub-sector column, K= Kraft, M=CTMP or newsprint

2 PULP MANUFACTURING PROCESSES

Wood Preparation

Logs must be converted to chips to feed kraft digesters or the refiners of a mechanical pulp mill. Prior to this, the outer bark and dirt contamination must be removed. The process for carrying out this operation is termed debarking and may be a wet or a dry process. The wet process causes resin acids and other (mostly non-persistent) toxic and highly colored substances to leach out of the bark and be discharged with the effluent.

There are few data available on the effluents from the wood preparation areas of the mills in the Northern River Basins. A high proportion is debarked dry.

Dry debarking is always more desirable environmentally than wet debarking, and has been almost universally adopted in new mills and modernization projects for wood preparation systems built since the mid 1970s. Effectively, many mills with wet debarking operations are moving steadily towards dry debarking, by increasing the proportion of wood that is being purchased in the form of chips from sawmills, which are invariably dry debarked.

2.1 Kraft Pulp

Bleached kraft pulp is manufactured by almost 50 Canadian mills, including five mills in the Northern River Basins. It is sold on the international market to paper mills where it is used for manufacture of tissues and fine papers, including grades used for books, photocopy paper, and office papers.

All five mills have to comply with customer specifications to sell their pulp. Current market demands in many parts of the world require very high brightnness for market pulps, typically over 88 ISO. This is an impediment to adopting the emerging low- and no- chlorine bleaching technologies, since these are most cost effective and environmentally efficient when applied to the slightly lower brightness pulps (81 to 85 ISO) that are almost universally considered acceptable in integrated mills[2].

The process has been described in many texts, of which the most comprehensive and up to date is (Kocurek 1986), with simpler descriptions being provided by Smook (1990, 1988). McCubbin (1991) discussed the kraft process from the point of view of formation of pollutants and inplant measures available for their control.

The following brief description of the manufacturing and inplant pollution prevention technology is provided for the convenience of readers.

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[2] *"Integrated" implies that the pulp manufactured is used on site to manufacture paper. Most US mills and many Scandinavian ones are integrated.*

2.1.1 Traditional kraft pulping process

The kraft process is the dominant chemical pulping process worldwide. It is frequently sub-categorized as follows, when discussing environmental aspects:

Unbleached, including brown pulp for sale, liner board, and sack	Pulp is not bleached. May be sold or converted to paper on-site. *
Bleached market kraft	Bleached kraft pulp is dried and shipped to remote paper mills.
Integrated kraft	Implies that a paper mill is adjacent to the pulp mill, which uses some or all of the pulp produced*.
Dissolving kraft pulp	Processes similar to bleaching are used to remove hemicellulose, leaving quite pure cellulose *.

* No such mills in the Northern River Basins

All the kraft mills in the Northern River basins are in the bleached market kraft sub-category. They are frequently described simply as "market kraft" mills.

2.1.2 Kraft process description

Kraft pulping utilizes an alkaline solution referred to as white liquor, typically about 10% concentration of Na_2S and NaOH, to delignify the wood for fiber separation. The series of cycles characteristic of this process is schematically illustrated in Figure 1.

The spent cooking liquors (known universally as black liquor) are separated from the pulp by washers following cooking in the digester, and are then treated in the chemical recovery system. The recovery system regenerates the cooking chemicals of Na_2S and NaOH while utilizing the heat value of the organic residue to generate steam for the process. The chemical recovery system is described on page 23.

In the cooking process, the extent to which the lignin is separated from the pulp is expressed as the Kappa number. Typical current Kappa numbers are shown in Table 6 on page 11. The Kappa number is approximately proportional to the quantity of lignin which remains attached to the pulp fibers, either because it was not dissolved in the cooking process, or because it was so closely bound to the fibers as to be difficult to wash out. Low lignin content is desirable for pulps which will subsequently be bleached in the interests of reducing bleach chemical consumption and, where chlorine is used, the consequent discharges of organochlorines.

The **Kappa number** is a widely used test (TAPPI 1988) which has been used as the measure of the content of ligneous and related organic material for most mill operations and research work in this field. The permanganate number (or "K Number") is commonly used in mill operations as a control test because the analytical procedure is simpler. Although it is related to the lignin content, it does not have a linear relationship with the Kappa number. When extended delignification is being practiced by differing processes, the Kappa number provides a better representation of the pulp characteristics for the purpose of predicting effects of process modifications than the permanganate number. For this reason, only the Kappa number is used in this report.

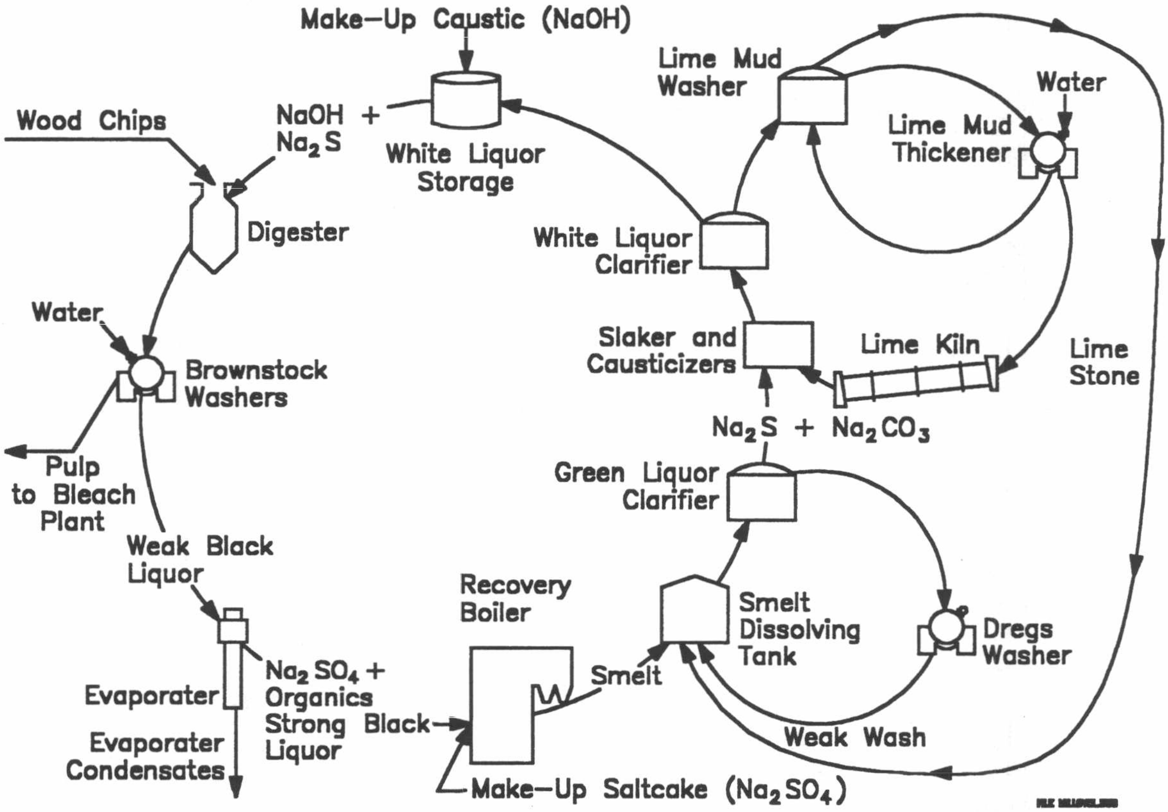

Figure 1 Kraft process concept

In general, lowering the Kappa number of a pulp prior to bleaching leads to lower discharges of pollutants, particularly soluble organics (COD, colour, resin acids and others), and, indirectly, chlorinated organics (AOX). The optimum Kappa number for the pulp leaving the digester(s) depends on many factors, including the existence or absence of downstream processes for the reduction of Kappa number. The ability of the mill's recovery boiler(s) to burn the additional quantities of lignin removed from the fibers where cooking is extended to lower Kappa numbers, must also be considered. Several processes, including oxygen delignification and extended cooking, are available for reducing the Kappa number. These are discussed below.

If the process operated perfectly as shown in Figure 1, there would be no effluent from the pulping operation. However, the brown stock washing operation can never be perfect, since it is a separation process. This causes lignin and sodium salts to leave the pulping process along with the pulp. These may be lost from subsequent equipment where the pulp is screened to remove improperly cooked wood, or chlorinated in the bleach plant and discharged to the mill sewer from there.

The evaporator condensates shown on Figure 1 contain methanol, sulphides, turpentine and many volatile organics in small quantities. These substances are been mentioned in many older publications as significant contrubutors to kraft mill effluent toxicity. However, in the Northern River basin mills they do not contribute to water pollution since such substances are treated very effectively in biological treatment systems. The sulphides and malodorous compounds must be stripped from the condensates before biological treatment if air pollution in the form of unpleasant but medically harmless odours is to be avoided.

2.1.3 Processing cooked pulps

The processes of cooking, washing and screening the pulp remove most of the lignin from the wood, and the material is recycled to the recovery boiler. In a traditional mill, the pulp would then be bleached with chlorine and alkali to remove the remaining lignin. The essential difference between bleaching and delignification, with respect to effluent characteristics is that the lignin removed from the pulp in bleaching, is NOT recycled, but is discharged from the system to the mill effluent stream, along with the bleaching chemicals.

However, an increasing number of mills now practice some form of extended delignification to remove a greater proportion of the lignin from the fibers prior to bleaching and recycle it to the recovery boiler for incineration and recovery of heat and chemicals.

2.1.4 Extended delignification

Since the early 1970s, several processes have been developed to extend delignification of the kraft pulps beyond the conventional levels, all of which are environmentally desirable in most circumstances where the pulp will be bleached in subsequent processes.

These are summarized in Table 6 and are discussed in detail later in this report. The process described as "extended cooking" is also known as "extended delignification" or more often by one of the following trade names:

For continuous digesters		
Modified Continuous Cooking	MCC	Kamyr Inc
Extended Modified Continuous Cooking	EMCC	Kamyr Inc
For batch digesters		
Rapid Displacement Heating	RDH	Beloit Corporation
Super Batch	------	Sunds Defibrator Inc

The only two of those relevant in the Northern River basins are MCC and EMCC, since all mills use continuous digesters.

Table 6 Extended delignification processes

Process name	Process concept	Attainable Kappa number	
		Softwood	Hardwood
Traditional **	Traditional batch or continuous cooking.	30	18
Extended cooking **	Modification to digester equipment and operating procedures to add white liquor progressively to the wood, permitting lower Kappa numbers without loss of strength.	12	8
Hot alkali extraction	Soak unwashed pulp at 150 deg C for about 30 minutes with white liquor to liberate dissolved lignin within fibers so that it can be washed out in subsequent washing stages.	Up to 50% drop, still under laboratory investigation	
Medium consistency oxygen delignification **	Application of gaseous oxygen to dissolve lignin at approximately 12% to 15% consistency.	45% drop	35% drop
High consistency oxygen delignification **	Application of gaseous oxygen to dissolve lignin at approximately 25% to 30% consistency.	50% drop	35% drop
Enzyme bleaching *	Solubilize lignin by addition of enzymes with xylenese activity, for subsequent washing with water.	Full scale trials indicate effect similar to 20% drop	
Ozone delignification *	Application of ozone to dissolve lignin.	Drop 5-10 Kappa points	

* Used in a few mills in full scale commercial production
** Used widely in commercial installations

2.2 Bleaching of Kraft Pulp

SUMMARY In Alberta and BC kraft mills, the pulp is bleached immediately after the washing/screening operation in a continuous bleach plant installed adjacent to the pulp mill. The conventional bleaching process is the source of about half the BOD, all the organochlorines, most of the colour and much of the toxicity in the effluent from a typical bleached kraft mill. In bleach plants, the lignin is first converted to compounds which are soluble in alkali by treatment with chlorine and chlorine dioxide, and then washed out with sodium hydroxide (caustic). The process is repeated two or three times with sodium hypochlorite and/or chlorine dioxide as the bleaching agent. There is a trend toward extending delignification in the prebleaching stages to reduce the quantities of chlorine based chemicals used for bleaching, effectively replacing as much as possible of the chlorine with other bleaching agents, such as oxygen, or hydrogen peroxide. In some cases, chlorine dioxide is used to substitute for all of the molecular chlorine.

The basic technology of the various bleaching processes were described by Kocurek (1986-89), McCubbin (1983b), Bonsor (1988) and many other authors, and it is assumed that the reader is familiar with them.

2.2.1 Bleaching terminology

Table 7 shows the abbreviations widely used in discussing bleaching sequences, and which have been adopted in this report[3]. A single washing stage is assumed between each unit operation unless otherwise indicated.

Table 7 Abbreviations for bleaching unit operations

Abbreviation	Unit operation
C	Chlorination stage, where pulp is treated with gaseous, molecular chlorine, primarily to chlorinate the residual lignin, so that it can later be solubilized.
E	Caustic Extraction. Dissolution of reaction products with sodium hydroxide.
E_o	As "E" above, with the addition of about 5 kg/tonne elemental oxygen. Relatively new (1980s) technology which has rapidly become universal in Canada and popular elsewhere.
O	Treatment of pulp with elemental oxygen, in alkaline conditions.
Z	Treatment of pulp with ozone, under acid conditions.
D	Reaction with chlorine dioxide, applied as an aqueous solution.
C/D or CD	Chlorination stage with chlorine dioxide.
C_d	Chlorination stage with chlorine dioxide addition after Cl_2.
D_c	Sequential addition of chlorine dioxide followed by chlorine.
H	Reaction with hypochlorite (normally sodium).
P	Reaction with hydrogen peroxide.
Q	Chelating agents such as EDTA.
Y	Reaction with dithionite (also known as hydrosulphite).
W	Wash stage. (Indicated only where a washer would not normally be expected, e.g. WW where two stage washing is installed).
n or N	No-wash (Indicated only where a washer would normally be expected).

Subscripts frequently used to indicate percentage substitution of molecular chlorine where relevant for example CD_{70} would imply 70% substitution of molecular chlorine with chlorine dioxide.
Most mills use chlorine dioxide in the C stage, and the abbreviation "C" is often loosely used to refer to a C/D stage.

The term **oxygen bleaching** is widely used to refer to extended delignification by oxygen, but this is considered to be a **pre-bleaching technology**, or **delignification**, and it has been discussed separately.

Washed softwood pulp arriving at the bleach plant in the older mills in the Northern River Basins (Grande Prairie and Mackenzie) can be expected to contain about 8% by weight of lignin and related material which gives it a brown colour, similar to that of the familiar paper grocery bag. The other mills use oxygen delignification and extended cooking to lower the lignin content to in the order of 4%. In any mill, this residual lignin must be removed without excessive degradation of the fibers if the pulp is to be suitable for production of printing papers, either white or lightly coloured.

To bleach kraft pulp, the unwanted lignin is first converted to compounds which are soluble in alkali, by treatment with molecular chlorine or chlorine dioxide, and then washed out with sodium hydroxide (caustic). The pulp is then further bleached with hydrogen peroxide, sodium hypochlorite or chlorine dioxide, and washed again in alkali conditions. Subsequent

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[3] *Subscripts 1,2 etc. are used to indicate first, second .... stages using the same bleaching agent* *(E_1, E_2.....).*

treatment is usually by chlorine dioxide, and where there are two dioxide stages, an intermediate alkali extraction stage with a washer is usually employed. The kraft mill flowsheet in Figure 4 includes a typical bleach plant. There are many bleaching sequences used in kraft pulp mills, but those in the Northern River Basins are quite conventional and are similar to the classic textbook sequences.

Each washing stage generates an effluent stream, the washer filtrate, which contains the soluble matter washed out of the pulp. In the past, the filtrate from each washer flowed directly to the sewer, but today, mills practice an increasingly intensive recycle of filtrates. Generally the low pH effluents from the chlorination, and chlorine dioxide stage washers are categorized as the "acid sewer", while the others are considered as the "alkali sewer" in the technical literature.

The quantities of chemicals required to bleach the pulp depend on wood species, quality of unbleached pulp, product quality targets and the bleaching equipment installed. Typically about 100 kg of molecular chlorine/tonne pulp or equivalent oxidizing power in some form, is required to bleach softwoods to market quality, while hardwoods require substantially less.

2.2.2 Chlorine-based bleaching sequences

All kraft pulp bleached in the Northern River Basin is processed by conventional processes, but with relatively high chlorine dioxide substitution. The mills at Hinton and Peace River use oxygen delignification, while the others do not.

Many North American kraft pulp mills, including those in the Northern River Basins, have modified their bleaching equipment to be able to operate with 100% substitution of chlorine with chlorine dioxide. It is increasingly common for those mills to operate for periods as long as several days to produce pulp grades based on 100% substitution, thus avoiding using any molecular chlorine, and some mills operate continuously in this mode. Operating costs are several dollars per tonne pulp higher than conventional bleaching operations. The reports of actual cost differences vary, and much of the relevant data is considered as being proprietary.

The efficiency of the pulp delignification and washing stages which precede the bleach plant can have as much impact on the bleach plant effluent characteristics as the bleaching process itself. Residual lignin that is not removed from the pulp by the washing system, will be discharged with the bleach plant effluent, usually in a chlorinated form which is normally even less environmentally desirable than the lignin and associated substances themselves. Effective brown stock washing is therefore a prerequisite to action in the bleach plant itself to minimize effluent discharges. Any analysis of data concerning such effluents must take account of the lignin content of the unbleached pulp.

Any process which reduces the lignin content of the pulp entering the bleach plant, as summarized in Table 6 on page 11, will reduce the consumption of molecular chlorine and chlorine based chemicals, with consequent reduction of organochlorine discharges. However, dioxin discharges will not necessarily be reduced by such processes (Berry 1991).

2.2.3 Extended cooking

SUMMARY Since 1986, extended cooking has been installed in many mills, and it is estimated that about 25% of the world bleached kraft pulp will be produced by mills using the technology by 1993. The additional organic material extracted from the pulp in an extended cook is recycled to the chemical recovery system, removing a proportion of the non-biodegradable substances from the mill effluent. The implementation of extended cooking will allow most bleached kraft mills to reduce bleach plant BOD discharges by 30% to 60%. Discharges of AOX and colour will be reduced by approximately 35% to 60%.

In conventional kraft cooking, the complete charge of chemicals (sodium hydroxide and sodium sulphide) is added to chips simultaneously, leading to high concentrations in the early stages of the cook, which gradually fall off as the process proceeds. The wide range in chemical concentration leads to aggressive chemical action at the beginning of a cook and relatively gentle pulping at the end. The Swedish Forest Products Laboratory (STFI) developed the concept of "modified" cooking (Hartler 1978, Teder and Olm 1980). The approach was to level off the alkali concentration throughout the cook so that the initial action would be less aggressive, and additional lignin could be removed in the latter stages of the process. This has become more popularly known as "extended cooking", and the late 1980s, vendors of both batch and continuous digester systems developed practical, commercial kraft pulp cooking systems based on Hartler's modified cooking concept. Macleod (1992) and Whitley (1990) have presented recent updates on extended cooking technology.

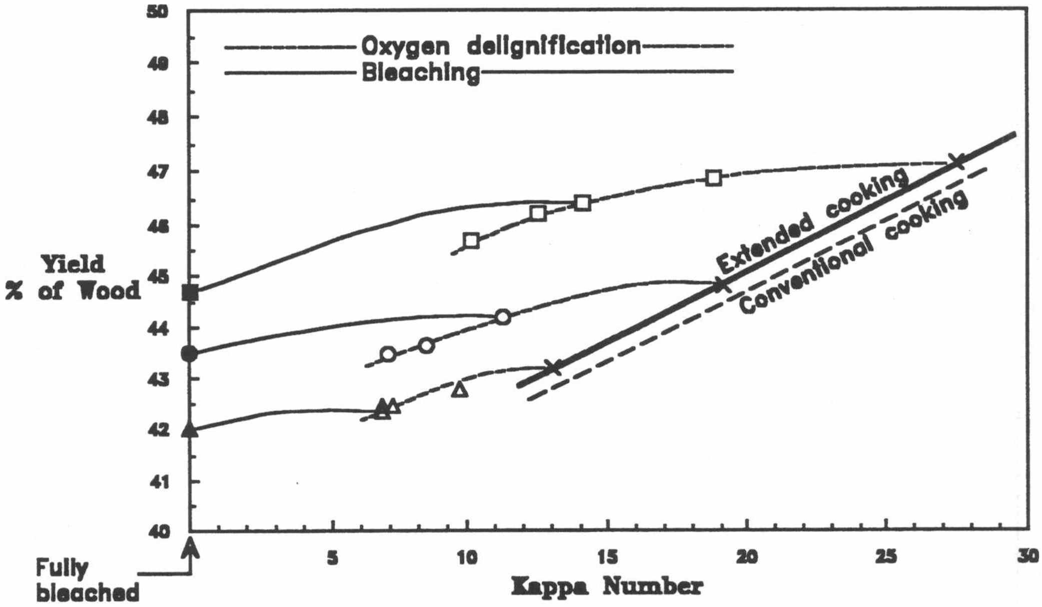
The implementation of extended cooking is quite different in continuous and batch digesters. Only the former is of interest in this report, since all kraft mills in the Northern River Basins, including the one being built at Athabasca, have continuous digesters.

In the Modified Continuous Cooking (MCC®) process the cooking liquor is added at several points, instead of only in the chip feed to the digester as is indicated in the conventional continuous digester shown in Figure 4.

In the modern continuous digesters, including all mills in the Northern River Basins, the pulp is washed with hot black liquor in the lower "wash zone" of the digester. Several mills have added white liquor to this wash circuit, and installed heat exchangers to raise the temperature to levels normal for cooking pulp. This is known as the Extended MCC (EMCC®) process, and is the variation of most interest for retrofitting to existing digesters.

Current extended continuous cooking technology will allow pulps to be produced at Kappa numbers of under 10 for hardwood and 10 to 13 for softwood (Haas 1992). This corresponds to lignin contents of about 1.5% and 2.3% respectively. Full scale mill experience has demonstrated that these low Kappa pulps have strengths equal to those of the 25 to 35 Kappa pulps produced by conventional cooking methods (Elliott 1989, Whitley 1990). The Longview Fiber mill pulped to very low Kappa with only modest loss in strength (Haas 1990). The pulp viscosity was low, but under extended cooking conditions the viscosity is not a valid indicator of pulp strength.

There is some loss in cooking yield when cooking to very low Kappa numbers, as indicated in Figure 2. For example if a mill is cooking to 38 Kappa, the yield would be 47%. If the process is modified to operate with a Kappa number leaving the digester of 20, the yield would be 45%. If the Kappa were lowered to 15, then the yield would be 43.5%. However, this is partially or completely offset by the substantial reduction in screen rejects from the cooked pulp. The pulp from conventional cooks contains 2% to 3% of knots, and poorly cooked fiber, which must be removed from the pulp by the brown stock screening system. In principle these screen rejects can be recovered by re-processing, but few mills accomplish this due to practical operating difficulties of the reject recovery process, so the rejects are landfilled. Pulp from extended cooking is almost free of rejects.



Source: Gullichsen 1991

Figure 2 Yield vs Kappa for extended delignification and bleaching softwood kraft

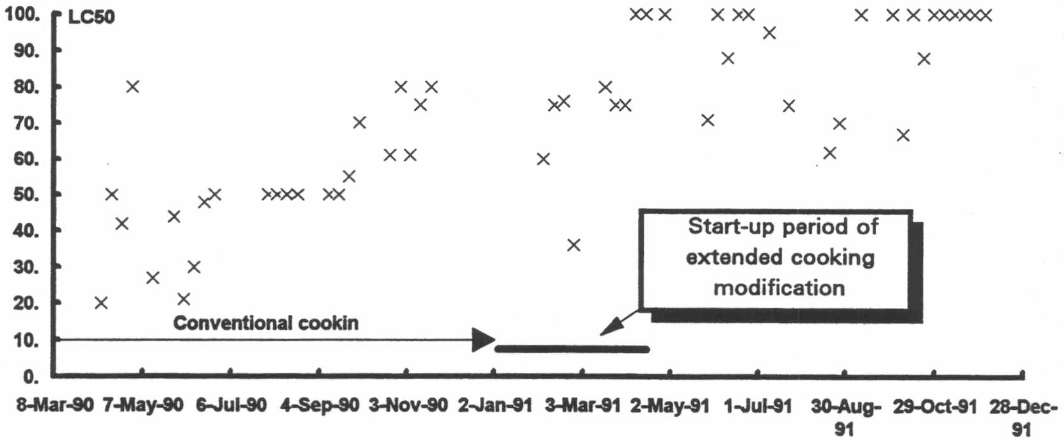
Many mills have reported reducing the Kappa number steadily in the years following the installation of extended cooking (Haas 1992). This experience suggests that extended delignification within the digester has not yet been exploited to its maximum potential, and that further developments can be expected over the next few years. The limiting factor could well be yield loss. If the operating techniques or equipment modifications can be developed so that post-bleaching yield is acceptable, or the loss minor, then it appears that very low lignin content pulps will be produced in future by extended cooking technologies.

Effects on effluent characteristics

There are few direct references in the literature to the improvement in effluent quality attained by the implementation of extended cooking technology. Consideration of the reduction in the Kappa number of the unbleached pulp indicate that discharges of organic matter from the bleach plants of up to 65% can be achieved, with 35% being more normal. This will reduce BOD, COD, colour and AOX proportionately. Where a mill exploits the reduced demand for bleaching chemicals by raising the degree of chlorine dioxide substitution in the first chlorination stage of the bleach plant, colour and AOX reduction would be greater.

When extended cooking was retrofitted to the Eddy mill at Espanola, Ontario, the LC50 of the untreated mill effluent increased as indicated in Figure 3. There is considerable scatter in the data, as is normal for untreated effluents, but the improvement after the installation and optimization is clear. This mill has oxygen delignification on both their hardwood and softwood pulping lines, but extended cooking on the softwood line only. The biologically treated effluent from the mill invariably has an LC50 > 100%.

Consideration of the process fundamentals leads the present authors to conclude that the effect of extended cooking on the mill effluent will be approximately equal to the effect of oxygen delignification.



Source: Private Communication, F. Munro, E B Eddy Forest Products Ltd.

Figure 3 Effect of extended cooking on toxicity of untreated whole mill effluent

Retrofitting modified continuous cooking

Existing installations of some conventional digesters may be retrofitted to use the Modified Continuous Cooking technology. Technical feasibility depends upon several factors including space availability, age of the installation, capacity limitations of the existing equipment, and other site specific requirements. (Personal communication, B. Greenwood, Kamyr Inc)

In some cases a relatively new digester that is operating at or below design capacity can be modified to take advantage of MCC mode to some extent by installing cooking liquor addition points to the washing section and other appropriate points. Performance may approach that of a new MCC system, and local conditions will dictate how close it will be. This approach is relatively inexpensive and easily carried out.

Where the existing installation is old and/or overloaded, it is usually technically feasible to convert the existing digester into the penetration vessel, and install a new digester for cooking. This is a major capital cost, normally less expensive than a completely new system, but providing all the benefits of the current technical developments.

2.2.4 Enzyme assisted delignification

Since late 1991, there has been a rapid upsurge in interest in using enzymes to treat pulp prior to bleaching, in order to reduce the demand for chlorine based chemicals. Research has been active since the mid 1980s, and several mills have conducted trials on a production scale in the past two years. Enzymes are manufactured from micro biological cultures grown under controlled conditions in closed tanks. After digestion the culture is isolated, the cells are broken and the enzyme of interest is isolated. Proteolytic enzymes have been used in washing powder for decades to remove protein spots from cloth.

The mill scale trials and commercial operations are all based on adding some commercial variation of xylanase, and sulphuric acid, to the pulp just upstream of the brown stock high density storage tank (this is not shown on Figure 4, but would be located immediately upstream of the first, "C" bleaching stage). The enzyme has no readily discernible effect on the pulp in storage, but the amount of chlorine (or bleaching agent with equivalent oxidizing power) required in the subsequent bleaching stages is reduced by up to about 25%. Quantities of enzyme used are typically under 1 kg/tonne pulp, and several kg of sulphuric acid per tonne are normally required to lower the pH to the range 4 to 6 which is required for the enzyme to react as desired. The reaction temperature has to be under about 60 degrees Celsius.

The organochlorine content of the mill effluent will be reduced in proportion to the reduction in chlorine based bleaching chemicals.

Enzyme technology must be considered as "developing" rather than "proven", but it appears probable that it will be a routine part of pollution prevention measures in the future.

2.2.5 Oxygen delignification

SUMMARY Since the early 1970s, oxygen delignification has been installed in many European and Japanese mills, as well as a growing number of mills in the US and in Canada. The filtrate from an oxygen delignification stage is invariably recycled to the chemical recovery system. The installation of an oxygen stage will allow most bleached kraft mills to reduce bleach plant BOD discharges by approximately 50% and colour by 60%. Discharges of organochlorines will be reduced by approximately 35% to 50%. A reduction of the TER by about 50% can be expected.

The terms "**oxygen delignification**" and "**oxygen bleaching**" are often used interchangeably to refer to the process discussed in this section. The term "Oxygen Bleaching" is also sometimes used to refer to the addition of elemental oxygen to the caustic extraction stage, which is almost universal practices in Canadian bleached kraft mills. Of the mills in the Northern River Basins, Hinton and Peace River use oxygen delignification, while the others do not. A typical installation is shown in Figure 4.

The raw effluent from an oxygen delignification system is generally highly coloured and has somewhat higher BOD than chlorination bleaching effluent, so the maximum environmental benefits are realized only if the filtrate from the oxygen stage is recycled to the chemical recovery system, which is the universal practice. However, the efficacy of oxygen delignification in reducing the discharge of chlorinated organic materials is not dependent on such a recycle. The installation of oxygen delignification will allow most bleached kraft mills to reduce bleach plant BOD discharges by approximately 50% and colour by 60%. Discharges of organochlorines will be reduced by approximately 35% to 50% (Norström 1987).

Effects on effluent characteristics

There is much more published information on reduction of acute toxicity with oxygen delignification than there is for extended cooking. An overall 50% reduction in amount of toxicity (i.e. Toxic Units per tonne of pulp) has been claimed by Arhippainen (1987), and reductions of 50% to 70% in acute toxicity to fish are listed by Idner (1987). There was a definite reduction of toxicity in Microtox tests, in which the toxic concentration was raised from 4%, for bleach plant effluents without O_2 to 33% with O_2 pretreatment (Germgård 1985). In the same research project, mutagenicity of chlorination effluent was reduced from a response level of 600 to levels of 20 to 40 with O_2 delignification. Some comparisons do not show such great advantages, for example, effluents collected from mills with and without oxygen delignification did not yield clear differences in toxicity (IPK 1982). Such comparisons are complicated by the fact that many aspects of mill design and operations effect the toxicity of the mill effluent. The laboratory tests of bleaching carried out by Wong (1978) were inconclusive about toxicity reduction by oxygen delignification, since the authors state that much of the measured toxicity was caused by residual molecular chlorine.

Addition of an oxygen delignification stage to a conventional bleach plant will reduce the toxicity of the untreated effluent substantially, but the extent of the reduction will depend on several factors. Since a well designed and operated biological treatment system will raise the LC_{50} of any bleach plant effluent to 100%, the reduction in the acute lethality achieved by oxygen delignification may become unimportant in practice.

The organic material removed from the pulp in the oxygen delignification stage is routed to the recovery boiler and burned, recovering energy and chemicals as well as destroying organic pollutants, including presumably some of the non-biodegradable substances found in treated effluents. The material burned in the recovery boiler does not contain chlorinated organic substances, since chlorine compounds are added to the pulp only after the oxygen stage and there is no process path for chlorine used in bleaching to reach the boiler.

While oxygen delignification has a similar effect on lowering AOX discharges as high chlorine dioxide substitution, the use of oxygen delignification is more effective in reducing chronic toxic effects associated with persistent, non-chlorinated, compounds in kraft black liquor (MFG 1991a). According to Borton (1991) the concentrations of effluents from mills using oxygen delignification which caused a 25% reduction in the numbers of young produced in receiving waters were three times higher than for conventional mills. Borton's work was with US bleached kraft mill effluent that had been treated biologically in an efficient aerated stabilization basin.

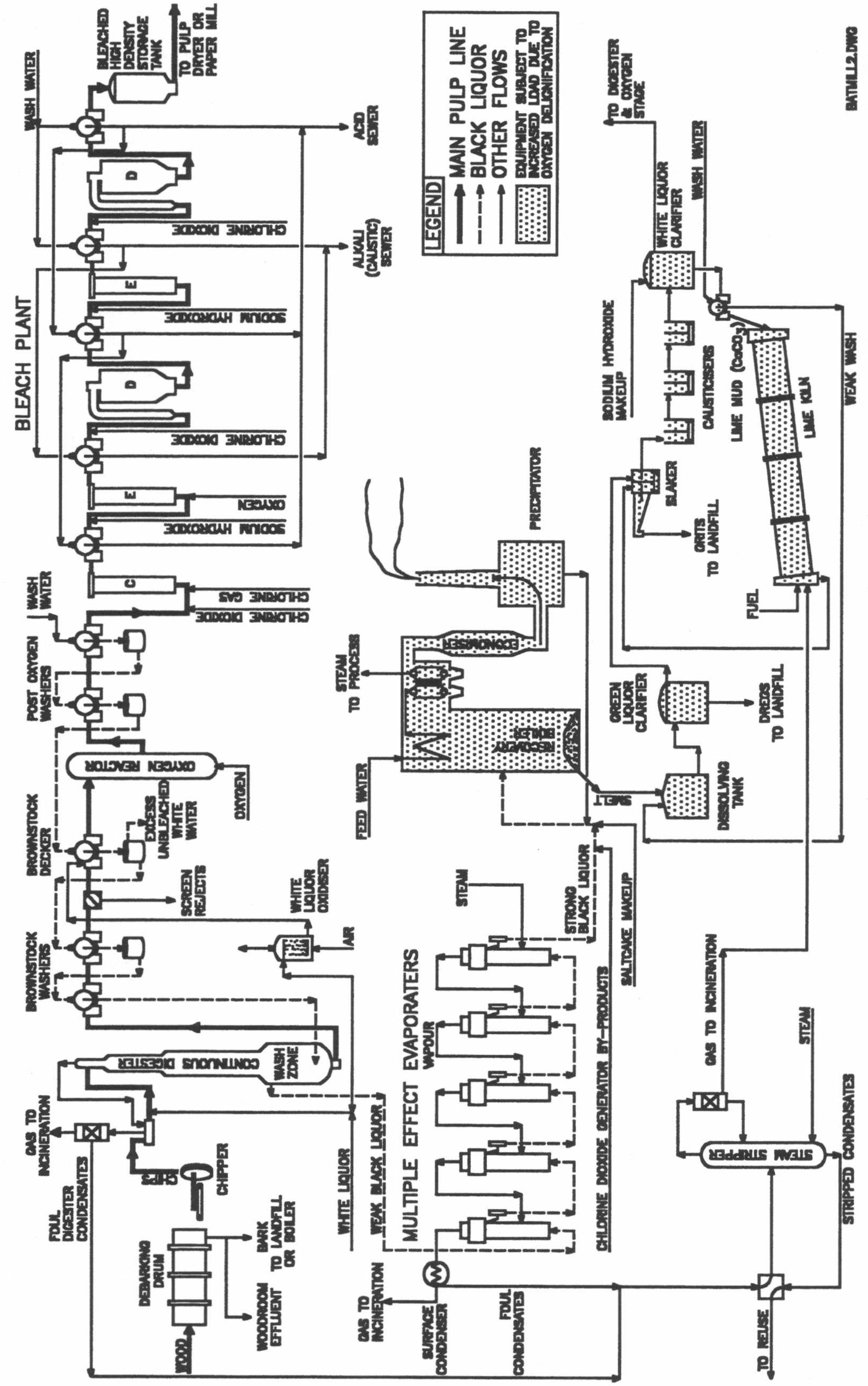


Figure 4 Typical kraft mill flowsheet with oxygen delignification

Most mills which have installed oxygen delignification systems have also taken steps to ensure that the preceding screening operations operate on a closed cycle (a "closed screen room"). While this is desirable for the reduction of BOD and colour, it increases the load on the mill's recovery boiler. Where it is desired to use oxygen delignification to reduce the discharge of chlorinated organic compounds, it is technically feasible to operate with an open screen room to reduce the amount of organic material returned to the recovery boiler. However, this is not normal practice.

Oxygen delignification is demonstrated technology that has been widely accepted worldwide, particularly in Alberta, Japan and Sweden. It is less commonly used in Canada than in most major pulp producing regions. The E.B. Eddy mill at Espanola has had two oxygen delignification systems since before 1980, but remained the only one in Canada until 1990. There are currently four other systems running in Western Canada, and Malette has commenced construction of an oxygen delignification system at the Smooth Rock Falls, Ontario mill. An oxygen delignification system is under construction at the Alberta Pacific mill at Athabasca. The geographic distribution of oxygen delignification systems is shown in Table 8, along with an indication to the extent of use of the process in each area.

Table 8 Geographic distribution of oxygen delignification in North America

	Bleached kraft capacity, air dry tonnes/day		
Location	Oxygen delignification	Total capacity	Fraction Oxy delig
Alberta	3,400	4,300	79%
BC	2,100	14,000	15%
Ontario	950	6,300	15%
Total Canada	6,500	31,000	21%
Total US	18,500	68,500	27%

There are no oxygen delignification installations in provinces omitted above. Production data are from various sources including Lockwood-Post's directory, oxygen delignification system vendors and personal contact, and may not be completely consistent, but do indicate relative status of installations. Projects under construction are included, but not those which are merely "announced"

There are no published surveys of the reasons behind the installation of oxygen delignification systems. Personal contact with several industry personnel closely involved in decisions both for and against oxygen delignification indicate that environmental pressures, mostly from regulatory authorities but also public opinion and customer interest, have been the major factor leading to installations. The authors are unaware of any regulations requiring the installation of this process, but personnel in several regulatory authorities have indicated verbally that no expansions or new bleached kraft mills would be authorized without incorporation of oxygen delignification. When examining the extent of adoption of the oxygen delignification process by various companies, it is apparent that there are clear corporate preferences, with some major bleached kraft pulp producers (Champion International and Union Camp) using the process for virtually all their bleached pulp, and others not at all. The installations include greenfield mills, major rebuilds and straightforward retrofits in roughly equal proportions.

2.2.6 Ozone delignification

There has been considerable interest in using ozone to replace some of the chlorine and/or chlorine dioxide used to bleach kraft pulp. Since the effluents from an ozone delignification stage could be recycled to the recovery boiler for incineration, improvements in effluent quality can be expected. Ozone delignification would normally follow oxygen delignification. Ozone is not used in the Northern River Basins mills.

The first full scale ozone delignification systems were commissioned in 1992, and only two kraft mills use ozone delignification for full scale production at the time of writing (Monsteros, Sweden and Franklin Virginia). At least four more full scale ozone installations were under construction at the time of writing. Nutt (1992) reported that the bleach plant at Franklin was been operating successfully, using an OZEoD sequence, with all effluents except the final chlorine dioxide stage being recycled to the recovery system. He reported that the pulp is used on their paper machines and was not noticeably different from traditional softwood pulps. For the 82 ISO brightness pulp required for the Franklin paper machines, he reported savings in bleach chemical costs of 68% relative to a conventional DEDED bleaching process.

Munro (1992) presented extensive data on ozone delignification trials with Ontario hardwood, which showed that the effluent AOX could be lowered from 1 kg/tonne to 0.05 kg/tonne pulp with an OZEDnD bleaching sequence.

2.2.7 Chlorine gas free bleaching

Chlorine gas free bleaching requires, by definition, the elimination of the use of gaseous chlorine from the bleaching process. This method of bleaching is also known as "molecular chlorine free".

In most cases, mills eliminate chlorine by operating with 100% substitution in the first bleaching stage. This requires a chlorine dioxide generation systems on-site that would have been considered unusually large before 1990, but introduces little new technology. Most market kraft mills in Canada are now capable of operating in this mode, but many do so only when customers demand it, and are presumably prepared to pay the cost premium which is in the order of $20/tonne.

AOX emissions are reduced substantially compared to conventional operations, and dioxins will be below the detection level in the effluent (Luthe 1992). However, significant quantities of chlorate are formed, and have been detected in Alberta mills running with very high or 100% substitution of chlorine with chlorine dioxide.

2.2.8 Totally chlorine free bleaching

Approximately 20 bleached chemical pulp mills in the world are capable of producing totally chlorine free (TCF) pulp which is somewhat similar to bleached market kraft pulp, but with brightness about 70 to 80 ISO. These mills rely on large quantities of hydrogen peroxide as their bleaching agent, which raises the mill operating costs by in the order of $50/tonne pulp. While this pulp appears to the non-expert to be only slightly less bright than conventional market kraft pulp with a brightness of about 90 ISO, there is no doubt that there is a limited demand for the lower brightness pulps, since under 25% of world capacity for production of TCF pulps is utilized at the time of writing.

The only totally chlorine free market kraft bleaching line in operation, which produces full brightness pulp (88 ISO) at the time of writing is at Monsteros in Sweden. It uses conventional pulping, followed by oxygen, ozone and hydrogen peroxide. While the AOX discharge is essentially zero, and dioxins are presumably non-detectable in the effluent, the mill does not recycle the bleaching effluents after the oxygen stage to the recovery boiler, so the discharge of unchlorinated organics, colour, and COD must be similar to any mill with oxygen delignification. At the time or writing, the Monsteros mill had produced only hardwood pulp by this process, although the company has announced the intention to produce softwood pulps also. (Information on the Monsteros mill was obtained by personal communication).

2.3 Recovery of Kraft Pulping Chemicals

SUMMARY The spent kraft pulping liquor removed from the pulp in the washing stages contains virtually all the original cooking chemicals and organic material removed from the wood. The quantity of total dissolved material depends principally on the pulping yield and is typically 1500 to 1800 kg/tonne for kraft pulp. Typically 96% to 99.5% of the spent liquor is recovered, and the rest becomes part of the mill effluent. The efficiency and reliability of the chemical recovery system has a major impact on all effluent parameters except those related to chlorinated organics.

2.3.1 Process description

The fundamental recovery process cycle in which the cooking chemicals are regenerated and the organic residues burned to produce energy for process and power is shown in Figure 1 on page 9 and Figure 4 on page 20.

The weak black liquor removed from the pulp by the brown stock washers is concentrated in a steam heated multiple effect evaporator to about 50% dry solids. This liquor is further concentrated to about 65% to 80% solids concentration either by direct contact with recovery furnace flue gas or indirectly in a forced circulation steam heated evaporator, generally known as a concentrator.

The strong black liquor is then burned in a recovery furnace. The organic matter burns, providing heat for steam generation, while the sodium/sulphur salts accumulate in the hearth of the furnace as a molten smelt. At the high temperatures and controlled conditions employed, the Na_2SO_4 added to the black liquor as make-up for sodium and sulphur losses is reduced to Na_2S as follows:

$$Na_2SO_4 + 2C \xrightarrow{\text{840 deg C}} Na_2S + 2CO_2$$

The molten smelt, composed mainly of Na_2S, Na_2CO_3 and some unconverted Na_2SO_4, flows by gravity from the furnace and is mixed with weak wash, the filtrate from lime mud washing, in the dissolving tanks. The greenish colour of chromium from chrome ore used to form the furnace bed, is imparted to the mixture and it is universally referred to as green liquor.

The green liquor is pumped to a green liquor clarifier where carbonaceous ash residues and other impurities are removed by sedimentation. The settled residue, known as green liquor dregs, or simply dregs, is washed to remove soluble sodium salts. The dissolved salts are returned to the system while the dregs are either landfilled or discharged to the sewer. Typically about 0.5 kg dregs are generated per tonne pulp.

The clarified green liquor is then routed to the causticizing system where calcium hydroxide is added, in the slaker, to convert the sodium carbonate to sodium hydroxide according to the reaction below:

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$$

The reaction, which is rather slow, begins in the slaker and is completed in the causticizers, which are a series of agitated tanks immediately downstream of the slaker. The calcium carbonate formed from the reaction is quite insoluble and is settled out of solution in the white liquor clarifier. The clarified solution which overflows contains the two major active cooking chemicals, Na_2S and NaOH. This liquor is called white liquor and is ready for re-use in the digester.

The calcium carbonate removed from the white liquor clarifier is pumped to a lime mud filter where it is thickened and washed to recover sodium salts.

The thickened $CaCO_3$ is then calcined in a direct fired rotary lime kiln or in a fluidized bed calciner, which converts it to calcium oxide as follows.

$$CaCO_3 + heat \longrightarrow CaO + CO_2$$

The CaO produced is recovered and used in the slaker.

The only solid wastes are the slakers grits which are non-reactive lime and inert mineral matter and the green liquor dregs consisting of carbon, ash and some sodium. This material carries many trace metals in the form of hydroxides or carbonates. This exit from the process will assume greater importance as mills approach zero process effluent.

The principal organic discharge in the chemical recovery system is the evaporator condensate, discussed below.

2.3.2 Evaporators

The weak black liquor is delivered to the chemical recovery department at a concentration of about 14% to 18% solids, and this concentration must be raised substantially by evaporation before it can be fed to the recovery furnace. Specially designed vertical shell and tube heat exchangers called evaporators are normally used for this evaporation process, arranged generally as shown in Figure 4 on page 20.

Volatile organic compounds, principally methanol, condense in the shells of the surface condenser and the evaporators, and constitute a major BOD source. There is a discrete condensate stream from each of the several evaporator bodies, but the BOD distribution is very uneven. It is normal practice in the more modern mills to segregate the condensate streams to facilitate reuse. All the condensate is hot, and the less contaminated streams are suitable for use in the recausticizing and pulp washing departments.

The condensates are also contaminated with small quantities of black liquor carried over from the vapor heads of the evaporators. The designer's objective is to minimize this carry over, and in well designed adequately sized units, it is usually negligible. However, multiple effect evaporators are not easy to operate, particularly if they are overloaded or poorly instrumented, and liquor carry over is a frequent problem. Several kg BOD/tonne pulp can be transferred to the condensates by this carry over, and will pass through any condensate stripping system. More seriously, carry over can cause foam generation in a condensate stripper, and prevent its operation so that both the volatile BOD from the true condensates and the BOD of the black liquor, which is carried over, will be added to the mill effluent. The foam is known to be acutely lethal, and is probably a contributor to the sublethal components of the mill effluent that resist biological treatment.

Since the environmental aspects of evaporator condensates became important in the 1970s, considerable development has taken place in the design of systems. A modern evaporator running at its design capacity can operate with only a few percent of the carry over of black liquor of older or overloaded systems. Current evaporator design criteria require a maximum of 1 gram sodium carry over/tonne condensate.

2.3.3 Evaporator and digester condensates

Contaminated condensates from the evaporators and the digesters are similar and are usually treated together, if at all. The digester condensates are recovered from the vent of the digester blowing system which is located between the digester and the brown stock washers, but is not shown on the drawing due to lack of space. The source of digester condensates in a kraft mill equipped with a continuous digester are shown in Figure 4 shown on page 20.

These condensates contain a total of 8 to 15 kg BOD/tonne pulp. The BOD is caused by alcohols, ketones, terpenes, phenolics, resin and fatty acids, and the total reduced sulphur (TRS) compounds. Methanol is the most significant factor in the BOD load. Most of the organics are low molecular weight substances which are readily converted to water, carbon dioxide and other harmless compounds in a biological treatment system or the receiving waters.

Reported 96-hour LC_{50}s for contaminated condensates range from 0.04% to 17%, using fish as the test organism. Many of the contaminated condensate's components, such as the TRS compounds, and resin and fatty acids, are lethal at levels well below their concentration in contaminated condensates. The TRS compounds appear to be the dominant factor in contaminated condensate toxicity, but these are removed very effectively in biological treatment systems.

Contaminated condensates contain about 0.3 kg TRS (as S) per tonne pulp. Since some of the TRS compounds in the condensates are stripped in the aerated lagoons by the process of aeration, sewered contaminated condensates can represent a significant source of odour from a biological treatment system.

2.3.4 Soap recovery

Soap skimming has long been a part of the kraft process but in recent years has become more important. A major reason for this is that resin acids contained in the soaps are one of the major toxic components in pulping effluents and also have an adverse effect on biological waste treatment systems. Soap skimmings consist largely of the resin acids and fatty acids present in the original wood which on pulping become ionized in the alkaline liquor, forming their sodium salts. In the dilute spent cooking liquor these salts remain soluble, but during evaporation they "salt out". This usually occurs at a black liquor solids concentration of 25% to 35%. This material is termed soap and can be removed by a rotating paddle at the surface of the liquor in a skimming tank. Where maximum soap removal is desired, the skimmer is normally located part way along the evaporator chain, where the black liquor concentration is around 30%.

Approximately 80 kg soap is formed per tonne of kraft pulp, typically containing 40% resin acids and 30% fatty acids. The BOD of soap approaches 100,000 mg/L, and its LC_{50} for fish has been measured as 6 mg/L, which is much more toxic than most streams in a pulp mill, so it is obvious that soap will have a significant effect on effluent quality if it is discharged to the sewer.

An adequate retention time in the tank (1.5 to 2.5 hours) permits the soap to float to the top. The skimmed soap may be converted to tall oil on-site or sold to an external tall oil plant. Alternatively it can be burned in the recovery furnace, effectively destroying it and recovering the heat and chemical value.

Since the soap can represent up to 10% of the total heat load on the recovery boiler, there is an opportunity to reduce the load on the latter by burning the soap elsewhere. It is fairly common practice to ship soap to other mills for conversion to tall oil with incineration of the residue. Recently some mills have investigated burning the soap in the hog fuel boiler, although there is no published literature on actual operations.

If there is no soap skimming equipment installed, there is a tendency for layers of soap to form on top of black liquor storage tanks (particularly the first tank in the chain that is at a consistency of over 35%) where some of this overflows to the sewer. Some mills with lower soap content liquor can effectively control soap losses simply by intermittently pumping off this layer and incinerating it. If there are no specific measures taken to avoid soap discharge to the sewer, then it will raise the toxicity of the mill effluent. A spill can be disastrous, and in one case there was a twenty-minute overflow which caused fish mortality over 45 km of the Spanish River in Ontario.

Soap spills and minor overflows can be a major cause of toxicity and/or poor operation of biological treatment systems. Any mill operator who wishes to maintain a high quality of effluent must understand the soap balance in the system, and take action to reduce or eliminate discharges

2.3.5 White liquor production

The molten smelt which flows from the smelt bed in a recovery furnace is composed mainly of sodium carbonate and sodium sulphide. This smelt drops through steam shatter sprays into a dissolving tank where it is dissolved to form green liquor, which is then causticized by mixing lime and water in a slaker. The reaction in the slaker takes place at around 100 deg C.

The mixture of calcium carbonate, sodium sulphide, sodium hydroxide and water produced by the causticizer is routed to the white liquor clarifier where the calcium carbonate settles out. The clarifier product is white liquor, which is the principal chemical ingredient in the cooking liquor required in kraft pulping.

The settled mud is washed by dilution then rethickened in another clarifier known as the lime mud washer, and then thickened to about 70% consistency in a vacuum filter and re-calcined to quick lime, CaO, in the lime kiln. A few mills use fluidized bed calciners instead of lime kilns.

Virtually all mills with oxygen delignification systems use a portion of the white liquor to supply the necessary alkali required in the oxygen reactor. White liquor contains about 25% sodium sulphide (Na_2S), and the latter must be oxidized by contact with air or elemental oxygen, as shown in Figure 4 on page 20.

2.3.6 Recovery cycle effluents

Theoretically, the only effluents from the kraft recovery areas would be evaporator condensates, green liquor dregs, and slaker grits as discussed above. However, there are a number of intermittent discharges due to spills of black liquor which can be up to 20 kg/BOD per tonne pulp. Good design and operating practices will reduce these spills to a few kg/tonne, and a spill control system, is necessary to achieve a high level of environmental protection.

2.4 Mechanical-sulphite Spectrum of Pulping

SUMMARY Five of the nine mills in the Northern River Basins use a member of family of pulping processes that can best be considered as a continuous spectrum from the traditional low-yield sulphite pulp (not manufactured in the region), through Chemi-ThermoMechanical Pulp and ThermoMechanical pulp, to the traditional groundwood pulping process.

*It is **conventional** to consider those pulps in this spectrum with yields of over 80% to be **mechanical pulp,** while those of lower yield are categorized as **chemical pulp.** All the non kraft mills listed in Table 1 can be categorized as mechanical mills. Some characteristics of the spectrum from groundwood through to low-yield sulphite pulp are shown in Table 9 on page 30.*

2.4.1 Groundwood pulping

Also known as **Stone Groundwood (SGW)**, this was the earliest form of mechanical pulping used commercially, and is used by the Findlay mill at Mackenzie, BC

In this process, logs are forced into contact with a revolving grindstone in the presence of water to reduce the wood to a mascerated fibrous condition. The water applied cools, cleans, and lubricates the stone and conveys the pulp away from the stone. A few percent of the organics in the wood are solubilized, causing the water carrying the pulp to exert a BOD when discharged, and to be toxic. Refer to Table 9 on page 30 for typical values.

2.4.2 Thermomechanical pulping

Thermomechanical pulp **(TMP)** is produced by chipping debarked logs, then separating the fibers in a device known as a **refiner**, where the chips pass between two serrated plates, one (or both) of which are rotating. This process requires almost twice as much power as the above mentioned groundwood process, but the mechanical properties of the pulp are substantially better. BOD and toxicity are increased, as indicated in Table 9 on page 30. TMP refiners operate under pressure, and at temperatures over 100 deg C. The only installation using the process in the Northern River Basins is the Alberta Newsprint Company at Whitecourt.

2.4.3 Chemithermomechanical pulping

Chemithermomechanical pulping **(CTMP)** is quite similar to TMP, except that the wood chips are softened by pretreating with sodium sulphite. This leads to higher untreated BOD discharges, and indicated in Table 9 on page 30. However, the organic material is relatively easily degraded, as evidenced by the low BOD discharges from the CTMP mills in Alberta.

The quantities of resin acid discharged from CTMP mills are generally considered to be substantially greater than from TMP or groundwood mills. However, the data on Alberta mill effluents presented in Table 12 on page 51 do not support this. The toxicity of CTMP effluent was found to be greater than TMP, but not as much as the resin acid concentration (Servizi 1986).

2.4.4 Bleaching mechanical pulps

In the bleaching of mechanical pulp, the object is chiefly to decolorize the pulp without solubilizing the lignin. This is usually accomplished with either reducing or oxidizing agents. Both provide similar brightness increases although brightness reversion from reduction bleaching is greater than from oxidative bleaching. The hydrosulphites were the most commonly used brightening agents in the past, but the use of hydrogen peroxide is increasing rapidly since it is the only way of bleaching to high brightness. Peroxides are the bleaching agents of choice whenever high brightness is required, but are more expensive than hydrosulphites.

All bleaching processes used for mechanical pulps are totally chlorine free, so they do not generate any of the organochlorines that are the subject of considerable attention where kraft pulp is bleached.

2.4.5 Effluent generation by mechanical sulphite mills

The shrinkage due to mechanical pulp bleaching could add up to about 50 kg BOD/tonne pulp to the mill effluent. The data in the literature, and known to the author, on BOD discharges exhibit considerable scatter. Mills using mechanical pulping only can be expected to generate about 15 to 25 kg BOD/tonne pulp, while those using the bleached chemimechanical process may discharge somewhat over 100 kg/tonne. The discharges from these mills depend primarily on the efficiency of their biological treatment systems.

It is generally considered that the untreated effluents from bleached CTMP mills will contain more resin and fatty acids than effluent from mechanical pulp mills which do not bleach. However, most of these substances are removed in the biological treatment systems. There is no obvious difference between resin acid discharges from the Alberta newsprint mill, which manufactures TMP but does not bleach, and the other mechanical mills in Alberta where the pulp is bleached to high brightness.

It is clear from consideration of the mass balance of a mechanical-sulphite mill that the quantity of organic material released from the wood is related to the pulping yield by a relationship of the form:

Organic loss % = 100 x (1-Yield) where yield is expressed as a fraction
loss is expressed as kg/tonne pulp

The CTMP mill at Meadow Lake, Saskatchewan is an exception, since it has a recovery process for the organic matter, and operates without discharging any procedss effluent (Evans 1992).

2.4.6 Summary of pulping processes

Typical characteristics of the pulping processes of most interest to this report are summarized in Table 9. This tends to understate the complex and diverse industrial processes involved. The reader is cautioned that there will always be exceptional situations where data will fall outside the ranges given.

Table 9 Typical characteristics of the processes and effluents of various pulping processes

Type of pulp	Yield	BOD kg/tonne	Effluent flow m^3/tonne	Principal pulping chemicals	Chemical feed (total inorganic) kg/tonne
Mechanical-sulphite spectrum of pulping processes					
Low-yield sulphite	45-55%	40-100[4]	100-300	Na, Mg,SO_2	450
High-yield sulphite	55-75%	140-250	50+	Na, SO_2	200-400
Ultra high-yield sulphite	80-90%	50-100	50+	Na, SO_2	150
CTMP	88-92%	40-60	8-25	Na, SO_2	50
TMP	90-95%	25-50	8-20	None	0
Pressurized groundwood	93-96%	11-20	8-20		
Traditional groundwood	93-96%	10-15	50	None	0
Miscellaneous pulping processes					
Kraft (unbleached)	43-58%	15-30[5]	50-100	Na_2S, NaOH	50 (makeup)
Kraft (bleached)	40-55%	20-50	50-200	Na_2S, NaOH	50 (makeup)
Semichemical	75-80%	80-120	15-100	Na_2CO_3, SO_2 (perhaps)	150
Deinking (non tissue)	70-90%	10-40	2-100	HOOH, NaOH, $NaSiO_2$	
Waste paper	95% +	5-10	10-100	None	None

Most of the pulping processes are used in mills where paper production is integrated with the pulping operation. The paper making operation will typically generate little BOD relative to the pulping operation, but will generate a significant amount of wastewater. The discharges are mixed, so that while the above mentioned data on BOD generated indicate the total BOD in the effluent, the flows of wastewater will generally be much higher. The BOD discharge is characteristic of the process, whereas wastewater flows are quite dependent on equipment selected and operating practices, so can vary widely.

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[4] *Assuming modern sulphite waste liquor recovery.*

[5] *Assuming typical recovery of chemicals and waste liquors.*

3 EFFLUENT TREATMENT

SUMMARY External treatment is utilized as a supplement or an alternative to discharge control at source. It may involve a range of physico-chemical and biological measures. Primary treatment involves removal of suspended solids, normally in a gravity clarifier. Secondary treatment removes soluble organic materials, normally by biological treatment which primarily removes BOD, and acute toxicity. All the mills in the Northern River Basins have effective primary and secondary effluent treatment systems.

External effluent treatment systems can reduce discharges of some "priority pollutants" substantially, others are effected very little by passing through an effluent treatment system. **It is essential to recognize that today's biological treatment technology was developed for BOD and toxicity control, and that any reductions in the "unconventional" pollutants are largely gratuitous.** In most cases there is not yet sufficient knowledge available to optimize biological treatment for removal of the unconventional pollutants.

Nutrients (phosphorus and nitrogen) are of increasing concern, with phosphorus being the more important. **The discharges of phosphorus and nitrogen from pulp and paper mills will generally be increased by external biological treatment**, since these substances have to be added to the effluent to attain efficient BOD removal. As the untreated BOD discharge is reduced by inplant processes such as extended cooking and oxygen delignification, the need to add phosphorus is also decreased. Where an aerated stabilization basin (ASB) is used for biological treatment, the phosphorus discharges would also decrease. All the mills in the Northern River Basins use ASB.

3.1 Wastewater Treatment Classification

Wastewater treatment is usually classified as follows:

Primary treatment involves removal of total suspended solids. Normally this is achieved in a gravity clarifier or sedimentation basin. However, alternative processes include dissolved air flotation (DAF) and screening. Preliminary treatment, involving grit removal for inorganics and bar screening for removal of larger objects entering the wastewater treatment system, normally precedes primary treatment.

Secondary treatment implies removal of organic materials from mill effluents, particularly BOD and substances acutely lethal to fish and *Daphnia magna*. Biological treatment is by far the most common method of secondary treatment.

Tertiary treatment involves unit operations other than primary or secondary treatment, normally applied to the effluent from a secondary treatment system.

3.2 Biological Treatment Processes

There are many forms of biological treatment used to treat municipal and industrial effluents, and most have been investigated for at least one mill. Activated sludge treatment (AST), a "high rate" process, and aerated stabilization basins (ASB), a "low rate" process dominate the field in the pulp and paper industry. They seem likely to continue to do so. There are approximately 600 installations in the North American pulp and paper industry, and increasing numbers are being installed in Scandinavia and other pulp and paper producing regions. All nine mills discussed in this report have primary and biological treatment systems.

3.2.1 Activated sludge treatment (AST)

SUMMARY Activated sludge treatment (AST) is a widely used biological process normally applied to primary treated effluents. The principle is based on the building of a settleable sludge of microorganisms grown on the soluble materials in the effluent. The sludge is recycled within the process and excess sludge is concentrated and then incinerated or landfilled. The successful operation of an AST system involves the control of the varieties of microorganisms present in the reaction vessel, the food to microorganism ratio and the sludge age. Energy and chemical requirements for sludge handling make this process more expensive per tonne of removed BOD than an ASB system. AST can achieve lower BOD and TSS than aerated stabilization basins, but generates significant quantities of waste sludge and discharges higher quantities of nutrients than an ASB.

A number of high rate biological treatment processes are used for treatment of municipal and industrial wastewaters. The activated sludge process, developed around the turn of the century in England, is the only high rate biological treatment process that is widely used for treating pulp and paper mill wastewaters. Rotating biological contactors (RBC), trickling filters, extended aeration and many variations of the activated sludge process have all been installed. Most of the RBCs have been abandoned.

These processes operate with very high concentrations of microorganisms, and relatively short hydraulic retention times. BOD reduction is quite rapid, with treatment completed in 2 to 24 hours, resulting in compact installations. Generally, the higher the reaction rate, the more suspended solids are produced.

A typical primary effluent treatment system followed by an activated sludge system is shown schematically in Figure 5 and its operation can be described as follows.

The main effluent stream passes through a coarse screen, to a primary clarifier where the settleable solids are removed by simple sedimentation. The pH of the clarified effluent is adjusted, if it is not already close to neutral, and recycled sludge is added. After adding the necessary nutrients, the effluent flows into an aeration tank where it is violently agitated and oxygen is supplied, normally in the form of air, but industrial grade pure oxygen is sometimes used. In the aeration tank, a mixed population of bacteria and other microbiological life develops, feeding on the organic substances, oxygen and nutrients. The effluent then flows to the secondary clarifiers, where most of the biomass settles, and then the clarified effluent is discharged.

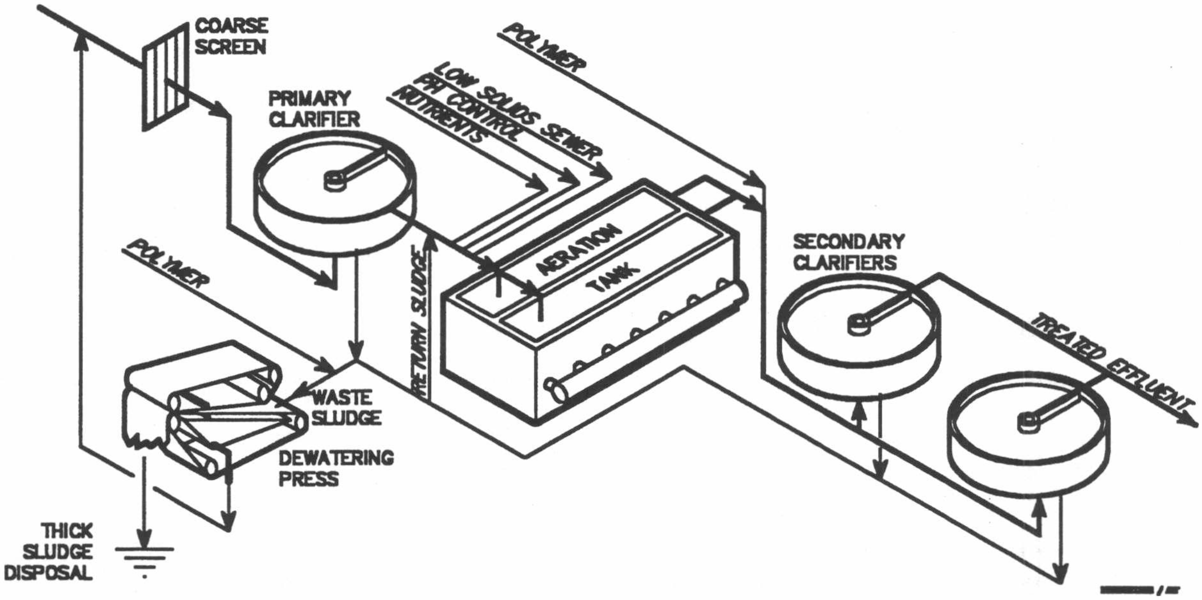

Figure 5 Flowsheet of typical activated sludge system

Some of the sludge produced is recycled to the aeration tank as shown. The excess sludge, in the order of 0.4 to 0.5 kg solids/kg BOD removed, must be dewatered and disposed of effectively. The quantity of waste activated sludge handled is a function of the solids retention time (sludge retention time) in the aeration tank and the food to microorganism loading ratio. A long sludge retention time and low F:M will result in the least quantity of waste activated sludge. The waste activated sludge is typically extracted from the treatment system for subsequent disposal at around 1% consistency. This requires energy, chemicals and a variety of complex equipment. Chemicals may represent one-third of the operating cost of the effluent treatment system, but are frequently overlooked or seriously underestimated in feasibility studies and other predictions of environmental compliance costs. The most widely used mechanical dewatering technologies are vacuum filters, belt presses and centrifuges.

3.2.2 Aerated stabilization basin (ASB)

SUMMARY Aerated stabilization basin (ASB) treatment is a biological process normally applied to primary treated effluents. The principle is based on long-term growth of microorganisms on the soluble materials in the effluent, without the sludge recycle that is characteristic of the activated sludge process. When the microorganisms die, the sludge is used as a substrate for other microorganisms, and thus the organic material causing BOD is digested. The successful operation of an ASB system involves the control of the non-digestible sludge so that low TSS and BOD are achieved in the final effluent without dredging of sludge being necessary. The energy requirements for an ASB system are lower than for an AST system and generation of sludge waste is avoided. However, the lowest attainable concentrations of BOD and TSS in ASB effluent are about the double those for AST.

The aerated stabilization basin (ASB) is a basin in which oxygenation is accomplished by mechanical or diffused aeration units and by induced surface aeration. The turbulence level maintained in the basin insures distribution of oxygen throughout the basin, but is usually (deliberately) insufficient to maintain all the bacterial solids in suspension. Besides providing oxygen, the aerators distribute soluble influent food throughout the basin for biological organisms to metabolize.

The ASB process is currently used at more North American pulp and paper mills than any other form of biological treatment system. A few Southern US mills still use large storage oxidation basins, and discharge effluent only during rainy seasons. There are no such installations of naturally aerated basins in Canada.

The ASB has been almost universally adopted by those kraft mills in the Canadian pulp and paper industry which already have secondary treatment systems. Other processes are likely to be selected for many of the non-kraft mills, including activated sludge using either air or oxygen, and perhaps rotating biological contactors, trickling filters, anaerobic systems and sequencing batch reactors.

Low temperature of the effluent is detrimental to biological treatment system operations, but there are some very successful ASB systems operating in climates as cold as Alberta (McCubbin 1991, appx C). The characteristically long retention of ASB systems makes them more susceptible to cold climates than AST. Most of the currently operating biological treatment systems in Canada are in kraft mills, which have a characteristic foam blanket which lowers heat losses. However, the non-kraft mills will not normally have a stable foam blanket, so that they will be more susceptible to winter weather. The reader is cautioned that there are a number of publications in the literature, usually originating in countries warmer than Canada, which provide procedures for predicting aerated stabilization basin temperatures in winter. If extrapolated to Northern Alberta or BC winter conditions, some will predict erroneously low temperatures for paper industry wastewaters.

ASBs convert some of the entering BOD into biomass, but, in contrast to most other biological treatment systems, are capable of digesting this biomass, so that the net generation of suspended solids is very much lower than for the conventional activated sludge process. This digestion of biomass, known as endogenous digestion, occurs close to the bottom of the basin, and it is essential that the level of mixing and location of the aerators be appropriate for it to take place. A well designed and operated ASB will run indefinitely without the dredging of sludge being necessary, providing the upstream primary treatment system is properly utilized.

The electrical energy required for aeration of an ASB will generally be at least as much as for an AST system for the same effluent, but the overall system will require somewhat less energy, since there is no slucge to dewater.

3.3 Nutrients

3.3.1 Nutrient addition

Biological treatment systems require carbon, oxygen, phosphorus, nitrogen and other trace materials to function. Sufficient carbon is always available, because normally the objective of the treatment system is to remove the organic carbon compounds from the effluent. Oxygen must be supplied by mechanical devices, most commonly surface aerators. Pulp and paper industry effluents generally do not contain sufficient nitrogen and phosphorus to maintain an optimum microbial population for BOD removal. It is usually necessary to add these nutrients to maintain the efficiency of treatment systems.

Aerated stabilization basins can treat pulp mill effluents successfully without the addition of phosphorus or nitrogen, particularly where retention times substantially exceed five days. In this case, there are some nutrients in the wastewaters, and the discharge of nutrients from ASBs is lower than from high rate biological systems. In general, BOD removal efficiency in paper industry ASBs can be expected to drop by up to several percentage points, if there are no nutrients added to the raw effluent, because growth is limited by nutrients and a decline in the reaction rates in aeration basins. To optimize this trade-off between nutrient and BOD discharges, the needs of the receiving waters have to be considered.

Because nutrients also have a significant impact on the specific microorganisms that predominate in ASB or AST, the lack of sufficient nutrients is widely recognized as being the main factor attributable to AST performance excursions in the industry. Jenkins (1991) has discussed this subject extensively.

High rate biological treatment processes, such as activated sludge, require substantially more nutrients than aerated stabilization basins if they are to approach their potential efficiency in removing BOD. It is frequently stated that BOD and nutrients in the input stream are required in the ratio of 100:5:1 BOD:N:P. However, optimization of pulp and paper effluent treatment systems that operate at high efficiencies has demonstrated that some require less nutrients, approximately 100:3.5:0.6 (Möbius 1991). The actual requirements are site specific, and must be developed by correlating performance and nutrient concentrations in the biological treatment final effluent with nutrient addition rates. Any fixed ratio fails to reflect various sludge ages and predicts equal dosing for all systems regardless of biomass production (Grau 1991). In some mills, design weaknesses lead to ineffective practices such as adding orthophosphates to the mill sewers just upstream of the lime mud addition point. In these situations, the lime will precipitate the H_3PO_4 and will remove the phosphorus. It is obviously essential that the nutrients added are actually made available to the microorganisms (Edde 1990). The cost of these chemicals is usually a significant factor in the operating costs of activated sludge plants.

Much of the added nutrient is removed from the system with the waste sludge, but it is generally accepted that 0.5 to 1.5 mg/L phosphorus will be discharged with the effluent, if suspended solids removal in the secondary clarifiers is efficient. The latter implies a suspended solids discharge concentration below 20 mg/L. In an exceptional case, at the Glatfelter mill in Spring Grove, Pennsylvania, one finds phosphorus concentrations consistently below 0.5 mg/L, (McCubbin 1991, Appendix C). However, phosphorus discharges from activated sludge treatment systems can often be much higher, usually due to excessive phosphorus addition or high suspended solids discharges. Kiuru (1990) presented examples of phosphorus discharges frequently over 2 mg/L, and occasionally over 5 mg/L at the mill at Rauma, Finland. The suspended solids discharge from the plant concerned was reported to be from 30 to about 180 mg/L, which is indicative of unsatisfactory operation, although it is a modern installation.

3.3.2 Control of phosphorus discharges

SUMMARY Phosphorus is a limiting nutrient for microbiological growth in biological treatment of pulp and paper mill effluent, and its control thus involves an accurate assessment of the need for adding it, normally in the order of 0.6 to 1:100 as the ratio of P:BOD. Long retention ASB systems often operate without addition of phosphorus. The quantities of phosphorus which have to be added to an AST can be limited by applying biological phosphorus control.

Concern over phosphorus discharges is related to the fact that algae growth in most fresh water ecosystems is phosphorus limited. Excessive concentrations of phosphorus may result in a eutrophied ecosystem, oxygen depletion and fish kill.

Control of phosphorus emissions may require a trade-off between attaining low BOD discharges and low phosphorus discharges. Part of the problem is that sufficient nutrient residual must exist in the wastewater **at all times** during the treatment process. Thus nutrient addition rates must be paced with BOD removals achieved. Whereas an effluent treatment plant treating a uniform BOD load may achieve a final effluent concentration as low as 0.2 mg/L, the same plant under varying load conditions will require a higher phosphorus concentration in the final effluent to assure the system is not operating in a nutrient limiting condition.

Pulp and paper mill effluents are typically deficient in phosphorus relative to the quantities required for the operation of most biological treatment systems. Therefore phosphorus must often be added in adequate amounts to avoid phosphorus limited growth and a decline in reaction rates in aeration basins. Phosphorus deficiency is a selective factor, frequently leading to the deterioration of sludge settleability and slow biodegradation of carbonaceous compounds (Eckenfelder 1985, Vuoriranta 1989). However, in some cases pulp mills discharge sufficient quantities of phosphorus with the untreated wastes.

In biological treatment plants handling pulp and paper mill effluents, the first step in phosphorus control is to define the criteria for adequate phosphorus feed. The minimal nutrient requirements for AST are in the range of 0.6 to 1:100 phosphorus:BOD ratio to assure phosphorus limited growth does not occur while still achieving optimal BOD removal during biotreatment (Edde 1968, Möbius 1991). Discharges of phosphorus have in the past been considered a secondary problem to BOD removal and TSS control. This attitude is changing rapidly. Wastewater discharges to the Great Lakes Basin are generally required to limit their discharges of total phosphorus to 1 mg/L or less under an agreement between the United States and Canada (Reid 1991, Great Lakes 1987). Regions where effluent phosphorus concentrations of 2 mg/L or less are required are summarized in Table 10. All these values are considered attainable by the relevant regulatory authority.

Table 10 Examples of effluent phosphorus standards

Region	P standard (mg/L)
USA	
Great Lakes	1.0 (if > 2640 m^3 per day)
Florida	1.0 (for lake, bay, impoundment or estuary discharge
Chesapeake Bay Basin*	
Pennsylvania (lower Susquehanna)	2.0
Maryland	0.2, 1.0, 2.0
Virginia (lower Potomac River)	0.2, 0.4, 0.5, 1.0
Washington, D.C.	0.23
Reno Sparks, Nevada	0.5
Lake Tahoe, California	1.0
Switzerland	1.0 or 85% removal for discharges to lakes
Sweden	$\leq$ 1.0

* Varies according to stretch of river. Above is a simplified representation of regulations which are sometimes complex, with local variations.

Chemical phosphorus removal

Phosphorus can be precipitated by the addition of coagulants such as aluminum, ferric or calcium salts or polyelectrolytes. They can be added in the secondary clarifier, but it is more common to have an add-on chemical treatment unit. This is primarily used when phosphorus discharge criteria are lower than can be achieved in a secondary biological effluent treatment plant. This is known as tertiary treatment.

3.3.3 Maintaining the nutrient allowance

In a multi-cell ASB with nutrient addition, it is possible that a phosphorus concentration shortfall will exist immediately at the head end of the ASB where there is normally high biological activity, high mixing energy and high phosphorus demand. The high mixing energy prevents deposition of biological organisms which are therefore displaced from the head end of the ASB. The nutrient demand at the head end of the effluent treatment system may deplete the available phosphorus in the wastewater. Between the head end and midsection of the ASB there may be a portion of the ASB where phosphorus concentrations are not adequate to meet nutrient demands and a growth limiting condition develops.

After this midsection growth limiting condition, due to a lack of nutrients, the wastewater will pass into a section of the treatment system where recovery of nutrients released from decomposing sludge at the bottom of subsequent aeration basin cells again makes available adequate nutrients. This will occur toward the end section of the ASB where adequate nutrients resulting from resolublization of biological organisms are recovered by the microorganisms.

The midsection nutrient deficiency may not be noticed if only the final effluent phosphorus concentration is monitored. A nutrient shortfall was observed at the midsection when monitoring throughout the ASB basin at Proctor and Gamble, Grande Prairie, Alberta. A similar problem was discovered and corrected several years ago at a Washington State ASB. A similar nutrient shortfall situation can also exist with "contact stabilization" or other modifications to AST, and avoiding it is essential for attaining optimum effluent quality. This is one example which demonstrates the need for competent technical supervision of aerated stabilization basins or ASB if efficient treatment is to be attained.

3.4 Removal of Metals in Biological Treatment

Metals cannot be destroyed, only redistributed in the environment. Biological treatment systems inevitably remove some proportion of metals from the effluent stream being treated. Analysis of whether this is environmentally desirable or not is beyond the scope of the present report. Generally, activated sludge systems will remove over half the metals in an effluent stream, concentrating them in the waste sludge, while aerated stabilization basins have less effect (McCubbin 1991, p 210). The concentrations of metals found in the effluent from the only three Northern River Basin mills require to monitor them were extremely low.

4 EFFLUENT CHARACTERISTICS

4.1 Chemical Characterization

The purpose of characterization of an effluent is to assist in the environmental impact assessment, particularly concerning the receiving water. The impact of an effluent is a function of both exposure and effects (Folke 1985). There are two ways to approach the impact assessment, the holistic and the fragmented approach.

4.1.1 The Holistic Approach

The holistic approach involves an exposure analysis based on the physical properties and chemical analysis of organic and inorganic materials as well as group variables. Effect analysis involves ecotoxological assessment of the entire effluent. Today, effect analysis is often based solely on laboratory testing, e.g. acute and (sometimes) chronic toxicity before and/or after aerobic stabilization of the effluent (biological treatment, biodegradation/weathering), whereas some of the long term effects, especially of pulp and paper mill effluents, only show in field studies or physical modeling using micro-ecosystems (Folke 1991, Folke 1992).

4.1.2 The Fragmented Approach

The fragmented approach assumes that the overall environmental impact of an effluent is a sum function of the hazardous properties of the individual compounds in the effluent, i.e. it involves the identification of all substances present, and an individual hazard assessment of each component:

Suspended solids
Readily degradable compounds
Slowly degradable compounds
Colouring compounds
Toxic compounds
pH-changing compounds
Inorganic salts
Residual auxiliary chemicals.

It is well known that the environmental hazard of a chemical is also a function of exposure and effect (Landner 1988), i.e. it involves a determination of the amounts released and the (eco)toxicity of each individual compound. Until now this approach has, to a large extent, been driven by the state-of-the-art of chemical analysis, i.e. in the 1960s DDT was *the* problem, in the seventies PCB and chlorophenols were in focus, and in the eighties *dioxin*-analysis was the state-of-the-art. Decisions made on the basis of analytical capability are unlikely to be the most rational, if potential environmental effects are not considered appropriately.

Chlorinated organics.

Recent Canadian research in the provinces of Saskatchewan, Alberta and British Columbia as well as by Environment Canada suggests that careful risk assessments are required, and that these analysis of the effects of substances concerned on the receiving waters must be considered (Swanson 1991; Kloepper-Sams 1991). We believe that this may change the focus in the pulp and paper mill effluents from dioxins towards polychlorinated phenols (see below). Dioxins may be more toxic, but discharges of polychlorinated phenols are millions of times higher. Reducing the rate of formation of polychlorinated phenols will normally reduce the rate of formation of PCDD/PCDFs, thus controlling these latter compounds more economically than a direct PCDD/PCDF control (Dahlman 1991). Much research has lately gone into reducing levels of AOX from bleached kraft mills (Basta 1991; Joshi 1991). However, the relationship between chlorinated group parameters (AOX, EOX etc.) and acute or chronic toxicity failed to show (O'Conner 1992; Folke 1991, 1992). Organochlorines are biosyntherized in nature to a very large extent (Nelson 1991, Grimvall 1991).

One effect of the general pressures to reduce or eliminate emissions of chlorinated organmic substances has been the development of practical technology for the complete eliminatin of chlorine compounds from at least some bleached kraft mills as discussed on page 22. This may well lead to the elimination of process effluents from such mills in the near future, at which point the complex debates over the significance of the various substances in the wastewaters would become academic.

Pulp and paper mill wastewaters are most frequently characterized only chemically by a limited of parameters. Commonly seen variables (in wastewater permits) are: Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD_{Cr}), Total Suspended Solids (TSS), Colour, Adsorbable (Extractable or Purgeable) Organic Halogens (AOX/EOX/POX), chlorophenolics, PolyChlorinated Dibenzo-*p*-Dioxins DbenzoFanes (PCDD/PCDF) and heavy metals. If ecotoxicity is addressed, it is normally only in terms of acute toxicity to fish and possibly crustaceans according to the Canadian or OECD test guidelines.

4.2 General Wastewater Variables

SUMMARY Traditionally BOD, TSS and acute lethality were the principal parameters used for evaluation of wastewater quality. These provide a basis for examining only the short term and local effects of effluent discharges, but are useful where gross amounts are discharged, as one finds in older mills without effluent treatment. In recent years attention in several parts of the world, including the Province of Alberta, has shifted to the longer term effects, requiring consideration of sub/acute toxic effects, the content of persistent and/or bioaccumulative substances in the effluents. The ratio of chemical oxygen demand (COD) to BOD provides an indication of the biodegradability of the effluents. High values for this ratio, as found in well treated effluents, indicate that little further reduction in organic content can be achieved by biological treatment. AOX provides an indication of the total amount of organochlorines. However, low AOX discharges (under about 2 kg/ADt) do not correlate with toxicity. The substances that are responsible for the remaining sub-lethal toxic effects from modern kraft pulp mills are non chlorinated compounds by nature. Indications are that steroids in the wood extractives play a major role in this regard.

Effluent testing methods are well standardized in most developed countries, but national standards are often not equivalent to each other. In particular, Scandinavian practices are liable to lead to higher BOD and much lower TSS values being reported, relative to Canadian practices. Previously, Sweden also used the TOCl method which gave lower values than the AOX method, most widely used today.

Colour is a parameter of concern in some parts of the world. Conductivity is a good indicator of the efficiency of process water usage, with low conductivity indicating that there is a good potential for success if a water conservation program is implemented

Traditionally, the following parameters have been considered for the evaluation of wastewater treatment plant performances: BOD, COD, DOC, TSS/VSS, NH_3/NH_4^+, NO_3/NO_2, Tot-N, Tot-P, and sulphide. These are generally the parameters that can be most effectively controlled by the traditional sedimentation and biological treatment processes which are used extensively to treat municipal wastewaters.

In recent years, many scientists and several regulatory agencies have expressed increasing concern about other parameters. A brief review of substances of current interest can be found in Tables 2 to 5, commencing on page 3.

The remainder of this chapter discusses individual parameters in more detail.

4.2.1 Biochemical oxygen demand

The oxygen demand exerted by the microorganisms during biological treatment is measured by the biochemical oxygen demand (BOD) test. The standard BOD test (APHA 1989) uses a five day sample incubation period at 20 deg C and this procedure is usually understood unless otherwise stated (In Sweden and Finland seven days are commonly used. There is no precise conversion factor between the two values, but as a rule of thumb BOD_5 constitutes about 85% of the BOD_7 value). The five day test does not give an absolute measure of the ultimate oxygen demand of the liquid waste, but its long acceptance and the lack of a more reliable standard dictate its continued use. **All references to BOD in this report should be interpreted as BOD_5, unless otherwise noted.**

This test can also give an indication of how the effluent will affect the oxygen balance of a receiving water. Because the method involves the use of biological inoculum, the variation coefficient of the method is quite large and systematic errors are easily introduced, i.e. inter-calibration exercises between laboratories proved the method less reproducible than many chemical analyses. However, BOD remains an important parameter for the design of treatment plants, and control of BOD in the effluent can be of importance for discharges to receiving waters that are vulnerable to oxygen depletion, such as the Athabasca and Wapiti Rivers.

BOD represents the fraction of the organic substances in an effluent that the natural ecosystems can generally assimilate quite well, except that where the assimilative capacity of the receiving water is exceeded, local damage, sometimes severe, can occur. BOD, by its nature, measures only non-persistent, non-toxic pollutants, and many environmental scientists consider it unfortunate that its long, and often useful, history has led to such heavy emphasis on reducing discharges. It is an important parameter to control the level of dissolved oxygen in a river and remains relevant in smaller rivers.

BOD and TSS were two of the most significant effluent parameters in pulp and paper mill wastes in the past, but are less important today because of the lower discharge rates and the development of more sophisticated knowledge of environmental effects. Discharges from Northern River Basins mills are well under 10% of the levels common when much of the general environmental literature was written, and comments in textbooks etc. must be considered in this context. Today careful analysis is essential before allocating resources to further BOD reduction, because it may often be more effective to focus the available resources on other parameters. BOD and TSS remain critical design parameters for biological treatment plants, and are important in many kinds of wastewater, which has led to extensive data on performance being available, and sophisticated technology being developed for BOD and TSS control.

4.2.2 Chemical oxygen demand

COD_{Cr} (or COD) measures oxygen demand of a sample by direct chemical oxidation (Chromic acid[6]) (APHA 1989). It is important to know whether or not the sample has been filtered prior to analysis. It is common practice in some European countries for the filtrate from TSS analysis to be analyzed for COD. In this case the

$$COD \approx COD_{GF/A} + \tfrac{1}{2}TSS_{GF/A} \quad \text{or} \quad COD \approx COD_{70\mu m} + \tfrac{1}{2}TSS_{70\mu m}$$

where GF/A refers to the glass fiber filters normal in North America, and 70 µm refers to the wire mesh common in Scandinavia. The results reported from Sweden in this report have been recalculated to unfiltered COD where applicable.

COD analysis can be performed quite rapidly, whereas it requires, by definition, 5 days to determine BOD. In many cases, COD may correlate quite well with BOD for a particular effluent. The difference between BOD and COD values for one sample provides an indication of the presence of persistent materials. The COD analysis is more precise method than the BOD analysis. A suitable COD regulation can protect the receiving water against oxygen depletion in the same way that the BOD regulation can be used. This philosophy is generally adopted by the Swedish and Japanese Environmental Protection Agencies. Efficient (>90%) biological treatment can remove in the order of 40% of the COD from pulp and paper industry effluents. Inplant process modifications generally reduce COD in direct proportion to BOD. For example, modification of a digester system to use the extended cooking technology discussed on page 11 could reduce both the BOD and the COD discharged by the subsequent bleaching operations by 30% to 60%.

The COD of a biologically treated effluent represents the fraction of the organic substances in an effluent that the natural ecosystems cannot readily degrade, but provides no indication as to whether these substances are harmful. Organochlorines are generally a fraction of COD, where the effluent sample originates in a process using chlorine.

COD/AOX or DOC/AOX ratios

The COD/AOX ratio reflects the chlorination rate of organic materials provided that the COD is determined for the bleach plant effluents, which is generally not the case for publicly available effluent data. A low ratio, below 20, reflects a high degree of chlorination and conversely a ratio above 40 reflects a low degree of chlorination, similar to naturally found AOX (Grimvall 1991).

4.2.3 Dissolved organic carbon (DOC)

DOC is an instrumental analysis in which a filtered water sample is burned and the evolved CO_2 is quantified by IR-detection, or it is catalytically reduced to methane which is subsequently burned and quantified in a flame ionization detector. Thus it is independent of

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[6] *Another COD method exists using potassium permanganate. However, this is basically used in drinking water analysis and is of no relevance for pulp and paper mill effluents. Consequently, COD is used in this report as a synonym for* COD_{Cr}.

the oxidation stage of organic carbon and does not include other elements such as hydrogen, sulphur and nitrogen (APHA 1989). The method may readily be adapted to pulp mill effluents (Folke 1984, Folke 1985). DOC is not widely used at present, but the method could have a potential in wastewater characterization. For an individual effluent, it is possible to correlate the measured DOC with COD and BOD. With bleach plant effluents, DOC has the advantage over COD in that the ratio between AOX and DOC is a direct measure of the degree of chlorination, i.e. the number of carbon atoms per chlorine atom. This is important in order to understand the nature of the measured AOX. Unfortunately, the international data base on DOC is rather limited, causing some difficulty in interpreting the data collected. A recent source is the Ontario MISA monitoring program (MISA 1991) where some mills reported DOC.

4.2.4 Total Suspended Solids (TSS) / Volatile Suspended Solids (VSS)

TSS is determined by passing a known amount of sample through a filter paper and measuring the change in weight (APHA 1989).

The question of impact of TSS on receiving waters is confused by the fact that TSS testing has historically been performed using a wide variety of filter media and methods, thereby making it difficult to evaluate impacts from different discharges on a uniform basis. Thus, the choice of filter is particularly important for pulp mill effluent due to the presence of fibrous materials. Filtration using glass fiber media is the generally accepted methodology in North America and apparently also within the EEC. However, a number of natural fiber filter papers have historically been used in non-standard methods. In the authors' experience much of the data on TSS reported prior to the 1980s was erroneously low because the glass fiber media filters used today give higher TSS concentrations than would be obtained from the non-standard natural fiber filter paper. The exact magnitude of this difference varies widely with two to tenfold increases having been reported. Thus, any effluent TSS discharge limitation must be established with consideration to the analytical procedures.

In Sweden, a 70 µm wire filter is frequently used for fibrous materials, and measurements can differ quite unpredictably from results obtained from the paper or glass fiber filters used in Alberta:

> $\frac{TSS_{GF/A}}{TSS_{70}}$ = from about 1.1 for concentrated samples to at least 5 for very dilute samples, such as the discharge from effluent treatment systems.

The differences between TSS values determined by the APHA (1989) method, using the fiberglass filters and the above mentioned 70 µm wire filter approach, are particularly marked when analyzing well treated effluents, since the suspended matter, normally consists of small particles, is present at low concentration, and is non-fibrous.

Suspended solids originate mainly from pulp fiber losses and biosolids formed in secondary treatment systems. In some locations, it is important to minimize the discharge of TSS, since they may disrupt the receiving water ecosystem, depending on the characteristics. TSS discharged by a well operated biological treatment system will generally not settle in the receiving waters, and can often be considered as "fish-food". On the other hand, TSS has been found in some cases to carry bioaccumulative organic compounds, including polychlorinated dioxins and other toxicants that may adsorb onto the solids.

The characteristics of suspended solids discharged from today's mills are very different from those prior to the 1970s, when many mills outside the Northern River Basins carpeted waterways with fiber, lime and bark. This must be considered carefully when evaluating environmental effects and when referring to older literature and textbooks.

Volatile suspended solids are a further characterization of the TSS in which the combustible organic content is determined. For the pulp mill effluents in Alberta, the difference between TSS and VSS can be expected to be low (For paper mill effluents the discharge of fillers and coatings may result in greater differences, but there are no such mills in Alberta.)

Control of TSS and VSS depends strongly on the performance of the biological treatment system. Internal measures for fiber recovery, such as white water savealls, effect discharges significantly only where there is no effluent treatment system.

The Northern River Basins make-up the only pulp manufacturing region known to the authors which has never had a mill without effluent treatment. Although the original system at Hinton in the 1950s and early 1960s provided only primary treatment and was primitive by today's standards, it was better than most of the mills in the world at the time.

4.2.5 Nitrogen and ammonia

The total amount of nitrogen compounds in an effluent can be determined by total Kjeldahl analysis (TKN). This method involves decomposition of the organic substances by heating with concentrated sulphuric acid. Nitrogen compounds present in higher oxidation states than amines, will have to be reduced by graphite or a similar agent prior to the digestion in which ammonium sulphate is formed. By adding sodium hydroxide, ammonia can be distilled off and the remaining liquor can be quantitatively back-titrated.

Not all organically bound nitrogen is accessible to plants and microbes to build proteins. A fraction of the nitrogen compounds, particularly from pulp mill effluents, is very persistent, but not necessarily toxic or bioaccumulative, and thus is of minor environmental importance. Another fraction of the total nitrogen can be removed in biological treatment plants.

Ammonia/ammonium ions are the most easily used nitrogen compounds. Ammonia is acutely toxic to fish. For rainbow trout LC_{50} = 1 mg/L free ammonia (Lloyd 1961) whereas ammonium ions are not toxic. The Food and Agriculture Organization (FAO) water quality criteria for aqueous ecosystems is 0.025 mg/L at temperatures above 5 deg C and $pH < 8$ (Alabaster 1980). The concentration of free ammonia depends on temperature and pH:

$$pK_a = 10.0625 - 0.03325 * \text{deg C}$$

$$[NH_3]\% = \frac{100}{1 + 10^{pK_a - pH}}$$

Assuming a river temperature of 5 deg C and pH = 7.2, a concentration of free ammonia of 0.025 mg/L corresponds to a concentration of ammonia plus ammonium ions of 12.4 mg/L.

At pH 8, this figure is reduced to 1.92 mg/L, but even at that pH the acute lethal concentration of ammonia plus ammonium is in the order of 80 mg/L. Therefore, ammonia toxicity is not generally a significant concern for pulp and paper mill effluent.[7]

In municipal sewage, there is a surplus of ammonia/ammonium ions. So in order to reduce fish toxicity, there is an interest in oxidizing ammonia to nitrate during biological treatment. This puts certain constraints on the design of municipal treatment plants, which are not relevant to pulp and paper industry effluent treatment, since these effluents are deficient in nitrogen compounds.

Nitrate and nitrite ions are normally insignificant in pulp and paper mill effluents because of this deficiency of nitrogen compounds. Plants and bacteria prefer ammonia/ammonium ions to nitrate/nitrite ions as the source of nitrogen, because this saves them the energy required to reduce nitrate.

The fraction of total nitrogen that is biologically available can vary widely from one mill to the other. Generally, the sum of the ammonium and nitrate nitrogen is the best indicator of the extent to which the effluent will contribute to eutrophication.

4.2.6 Phosphorus

Phosphorus may be combined with organic substances, and may be present as polyphosphates, orthophosphates or similar compounds. The aqueous chemistry of phosphorus is complicated and the interaction with heavy metals makes it very difficult to determine the environmentally desirable level, although in most cases, it is desirable to reduce phosphorus discharges. For example, the presence of phosphates precipitates many heavy metals such as mercury and cadmium in the sediment. In Sweden, there are examples where the presence of phosphate has made cadmium inaccessible to the biota, and a lowering of the phosphate level in that particular lake increased the concentration of cadmium in fish from the lake. The same can be said about mercury and several other heavy metals (MFG 1991). Although excessive levels of phosphate are undesirable from a eutrophication point of view, it may not be desirable to lower the levels without consideration of the interrelationship with heavy metals. For example, arsenic has severe effects on algae in lakes that are phosphorus limited, because plants mistake arsenic for phosphate in such cases.

Phosphorus presents a dilemma to regulators of the pulp and paper industry. It seems to be generally agreed that most receiving waters are affected by human activities and would benefit from reductions in phosphorus input, while the addition of the biological effluent treatment plants to pulp mills and others which can reduce BOD and other pollutants will result in increased discharges of phosphorus.

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[7] *There have been reports of biologically treated pulp mill effluent being toxic to fish due to ammonia formation during storage/transportation from sample site to laboratory.*

Furthermore, lakes become less vulnerable to acid rain if levels of phosphates are not too low, because phosphate precipitates toxic aluminum ions that are released at lower pH. Reasonable fish production is also dependent on the phosphorus level not being too low.

4.2.7 Sulphur

Sulphide may be present in black liquor from kraft pulping. The presence of other sulphur compounds such as sulphate in effluents may lead to formation of sulphides under anaerobic or anoxic conditions. Sulphides are very toxic, especially under acidic condition due to the formation of H_2S. However, sulphides are easily oxidized to sulphates under aerobic conditions in a treatment plant and are therefore insignificant in biologically treated pulp and paper mill effluents, such as one finds in the Northern River Basins.

4.2.8 Colour and turbidity

Colour and turbidity are not only of aesthetic concern, but they can reduce the penetration of sunlight into low-flow receiving waters and impede the growth of water vegetation, thus creating an imbalance in the receiving water ecosystem. Colour also contributes to taste problems and increase stability of some bivalent metal ions by chelation (Panchapakesan 1991). These variables are of concern in some parts of the world, due to the aesthetic concern, and the use of polluted waters as drinking water. Colour provides a rough indication of the relative quantities of lignin and related substances being discharged from a mill as the process is modified or operating practices change.

Colour is normally expressed in chloroplatinate units, where the colour of an effluent sample is defined as the concentration of a standardized solution of equal colour (APHA 1989). The value has the dimension of concentration, normally mg/L, so it is conventional to express total colour discharges as the equivalent mass discharge calculated by multiplying the flow by this concentration. Traditional kraft mills discharge 100 to 250 kg of colour per tonne production. As indicated in Table 11, the Alberta mills discharge less than average older mills.

Table 11 Colour of effluents from Alberta mills

	Colour kg/d	Colour kg/t
Hinton	109,099	126
Grande Prairie	128,825	159
Peace River	61,674	83
Whitecourt CTMP	9,326	16
Slave Lake	8,727	39
Whitecourt Newsprint	3,051	7

Colour expressed in APHA units

Colour from kraft mills is controlled by same inplant measures that reduces the amount of residual lignin in the pulp entering the bleach plant, e.g. extended cooking, oxygen and ozone delignification, enzyme bleaching aids, etc. If the brownstock screening system is used as a final wash for the unbleached pulp, by discharging unbleached whitewater, as shown in Figure 4 on page 20, then a significant quantity of coloured material can be discharged. This practice was very common in the past, but is less common in mills with modern washing and screening operations. In mills with oxygen delignification, it is normal to eliminate thais flow.

Nutt (1992) reported colour discharge of 1.5 kg/tonne pulp when bleaching softwoods with an OZEoD sequence and 0.5 kg/tonne when bleaching hardwoods with the same sequence to 82 ISO brightness. He did not present data directly on the colour discharges which would result from using the process to bleach to conventional market brightness, but his data indicated that if the brightness target were raised to 89 ISO, then the colour discharges would be about 2.5 kg/tonne for southern pine.

Biological treatment is not an effective means to control colour. External colour removal measures include chemical treatment with lime, ferric sulphate, or polymers, all of which create significant sludge disposal problems. Carbon adsorption, ozonation, and membrane processes include other expensive external treatment possibilities (Panchapakesan 1991). Several full scale external colour removal systems were operated for a few years in the US in the 1970s and were abandoned due to operating difficulties, poor performance and costs.

CTMP mills will have to control colour by water cycle closure and external treatment, and have fewer inplant options than a kraft mill. Enzyme treatment for the purpose of polymerizing and thus precipitating coloured materials is being researched. However the sludge handling problem would remain and would limit the value of the technique. The only effective process for control of colour discharges from a CTMP mill that is operating full-scale is at the Meadow Lake, Saskatchewan mill which operates on a closed cycle with no effluent discharge (Evans 1992)

4.2.9 Specific conductivity

Specific conductivity measures the ionized materials in the water sample, such as sodium, chloride, sulphate, ionized organics (acetic acid) and others. Pure water has very low conductivity, whereas sea water has a high conductivity. Water with a high conductivity tends to be more corrosive than water with low conductivity, and corrosion is frequently cited as one of the principal limiting factors in reducing water usage and effluent flows in mills by internal recycle. Therefore, conductivity data provide a useful indication of the likelihood of a water conservation program being successful (COD provides an indication of the extent to which high concentrations of organic substances may interfere with increased water recycle.) Conductivity is not normally measured in Alberta, but it was part of the Ontario MISA program. Bleached kraft mills in Ontario generally have conductivity exceeding 1500 µs/cm, but in some cases conductivity is closer to 1000 µs/cm, indicating possibilities for water savings. Ontario newsprint mills have conductivity exceeding 1000 µs/cm. Non-integrated paper mills will have lower conductivity than kraft mills, and frequently COD is the limiting factor for water closure of these paper mills. Generally, where conductivity is low relative to similar mills, the prospects for implementing a successful water conservation program are good.

4.2.10 Toxicity

The terms "toxic" and "toxicity", when used in Canada in the context of industrial effluents, generally refer to acute lethality to rainbow trout (96-hour LC50) or Daphnia magna (48-hour LC50). Effluents from modern pulp mills using appropriate inplant and external measures to control effluent discharges are non-toxic by this standard. However, it is also important to address sub-acute, or sub-lethal, effects. This is particularly the case for Alberta mills that are very modern by international standards, and discharge effluent that normally pass acute lethality tests.

The following terms have been adopted by many toxicologists associated with the "Group of Experts on the Scientific Aspects of Marine Pollution" (GESAMP), which is an international body supported by the UN, and other international organizations, to describe various levels of toxicity:

LC_{50} < 1mg/L	Highly toxic
LC_{50} 1-10 mg/L	Moderately toxic
LC_{50} 10-100 mg/L	Slightly toxic
LC_{50} 100-1000 mg/L	Practically non-toxic
LC_{50} >1000 mg/L	Non hazardous

This terminology is intended to be used to describe pure chemicals, or commercial products, generally in the context of quantities that are shipped. It is also applicable to specific compounds or groups of compounds (e.g. resin acids) in pulp mill waste, but is hardly relevant to the very dilute concentrations found in mill effluents. The Alberta pulp and paper industry wastewaters would all be classified as non-hazardous on this case. Sprague (1991) and Bonsor (1988) among others emphasized that sub-lethal effects may be more significant than acute lethality.

The classic review by McLeay (1986) covers the literature on aquatic toxicity of pulp and paper mill effluents until about 1985. Two recent reports prepared for the Ontario Ministry of the Environment discuss the environmentally important aspects of pulp and paper mill effluent toxicity in considerable detail (Sprague, 1991 for non-kraft mills and Bonsor, 1988 for kraft mills). The so-called Procter and Gamble study (NCASI 1989 A,B & C) focused on Scandinavian literature describing sub-acute toxicity of pulp mill effluents in comparison with the North American studies. Colodey (1989) published a review pointing towards chlorinated organics as the most important group responsible for the toxicity of bleached kraft mill effluents. A recent review by Colodey (1991) is more in line with the recent Scandinavian studies (Lehtinen 1991AB; Lehtinen 1991; MFG 1991AB), which suggest than non-chlorinated substances are also significant in those mills that have reduced discharges of organochlorines below traditional levels.

Conclusions from these reviews are that appropriate internal measures taken at kraft pulp mills combined with external treatment in ASB or AST prevent acute lethal toxicity and that the remaining sub-acute toxicity that can be characterized as "weak toxic effects" are not caused by any organochlorine substances, but rather neutral, non-chlorinated compounds.

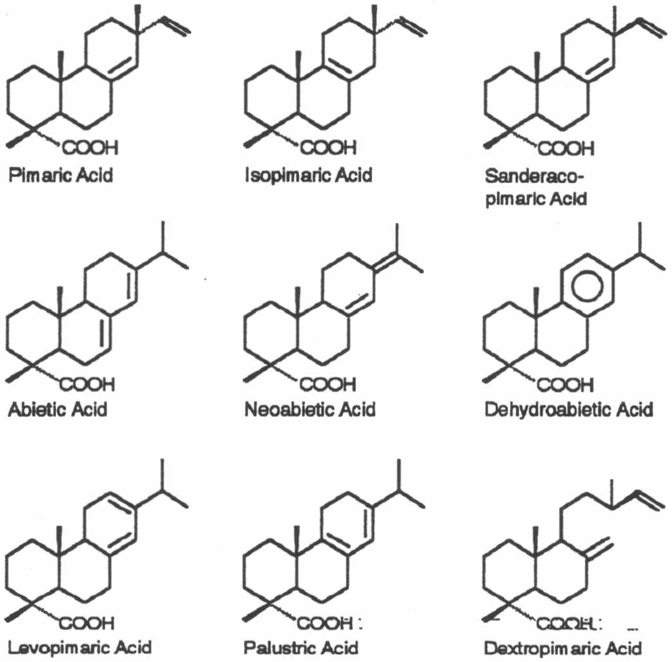
Steroids originating from wood extratives are suspected to be one important group of compounds (Lehtinen 1991AB, MFG 1991AB). These findings are confirmed by recent Canadian findings that bleached kraft mill effluent affects fish growth and that the mechanism involves significantly reduced testosterone levels in both prespawning and spawning female and male white suckers (Munkittrick 1991; Hodson 1990). Also, metabolic effects in liver and bile was observed (Smith 1992). NCASI failed to show similar growth inhibiting effects in rainbow trout where a full life cycle was completed in a 1.5% effluent flow through system (Hall 1991). Concern has been directed towards the tainting potential of 2,4-dichlorophenols reflected in the 0.2 µg/L Canadian Water Quality Guideline (Colodey 1991). This is particularly a problem with increased chlorine dioxide substitution, because this leads to increased concentrations of lower chlorinated phenols as compared to conventional chlorine bleaching. (Grimvall 1991, Borén 1991) points towards evidence of 2,4,6-trichlorophenol being formed after biochlorination of humic substances catalyzed by naturally occurring enzymes.

4.3 Resin Acids

SUMMARY Resin acids are synthesized naturally in trees and may be more concentrated in effluents from mechanical pulping than from chemical pulping operations. In kraft mill effluents, high concentrations may mean excessive losses of black liquor.

Resin acids are naturally occurring compounds in wood resins, particularly in pine and spruce. The amounts are particularly high in concentrated effluents from mechanical effluents. If high amount of resin acids are found in kraft mill effluent, their origin is frequently spills of black liquor and soap or black liquor carry-over (perhaps poor brown stock washing). Figure 6 shows the structure of the resin acids commonly found in effluents from softwood kraft mills.

In pulp mill effluents, a major fraction of the toxicity towards fish originates from fatty and resin acids (McLeay 1987). In the case of the Swedish Mönsterås kraft mill (SSVL 1990), about 14 g/ADt of resin acids (0.2 g/ADt is dichlorodehydroabietic acid), 8 g/ADt of saturated fatty acids and 1 g/ADt of unsaturated fatty acids were reported in the untreated effluent. Resin acids and unsaturated acids were reduced below 1 g/ADt by the aerated stabilization basin, whereas saturated fatty acids were reduced to only 5 g/ADt.



Pimaric Acid
Isopimaric Acid
Sanderaco-pimaric Acid
Abietic Acid
Neoabietic Acid
Dehydroabietic Acid
Levopimaric Acid
Palustric Acid
Dextropimaric Acid

Figure 6 Resin acids found in softwood

The data availalbe on discharges of resin and fatty acids from the alberta mills is shown in Table 12. The discharges from the kraft mills are generally similar to those from the Ontario mills with effluent treatment mentioned in Figure 7.

Table 12 Resin and fatty acids in Alberta mill effluents

Averages	**Resin & Fatty Acids** µg/L	**Total Resin Acids** µg/L	**Dehydro-abieic Acid** µg/L	**Resin & Fatty Acids** g/tonne	**Total Resin Acids** g/tonne	**Dehydro-abieic Acidt** g/tonne
Hinton		188			23.5	
Grande Prairie		184			13.4	
Peace River		794	174		59.0	12.9
Whitecourt CTMP		57			1.1	
Slave Lake	1,048			17		
Whitecourt News	82			2.7		
Maxima						
Hinton		2,000			297	
Grande Prairie		1,400			145	
Peace River		4,860	2,230		460	211
Whitecourt CTMP		130			3.3	
Slave Lake	8,300			168		
Whitecourt News	390			17		

Where data are not shown, mill does not routinely monitor the parameter concerned.
Data from samples from July 1990 until February 1992

The discharge rates of resin acids from Ontario mills found during the 1990 MISA monitoring program were quite variable, and illustrate the effects of effluent treatment systems, because only some mills have secondary treatment. Monthly average discharges from the Ontario kraft mills are summarized in Figure 7.

The two Ontario mills with very low discharges have aerated stabilization basins discharge low quantities of BOD (similar to the Alberta kraft mills). The Boise and CPFP, Dryden mills also have ASB systems, but these are only moderately efficient in removing BOD. The other mills lacked secondary treatment when the data were collected. The two kraft mills which also manufacture mechanical pulp had no secondary treatment when the discharges were determined, and had the highest discharge rates.

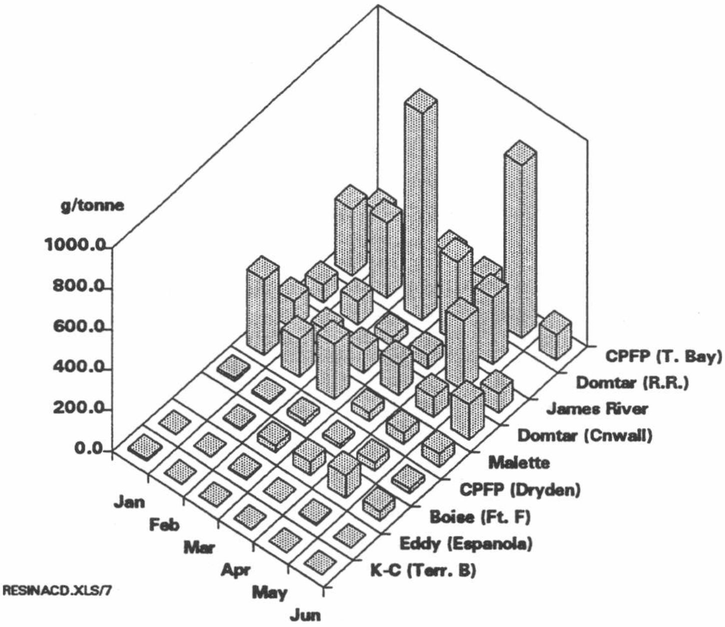


Figure 7 Resin acid discharges from kraft mills

4.4 Steroids

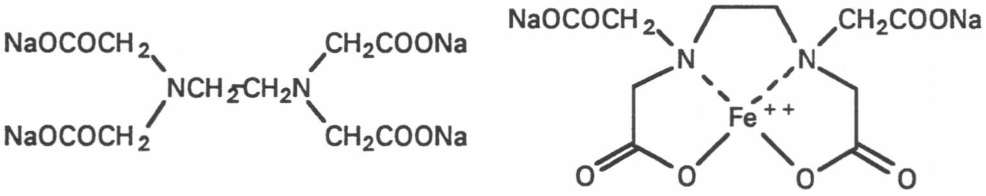
The observed effect on fish growth exposed to effluents from bleached kraft mill effluents can not be explained by any organochlorine compounds, because the effect is independent of the AOX level of the effluent (Lehtinen 1990). They are believed to be caused by metabolic disturbances, possibly at the hormone level, because the cholesterol level of fish liver was increased in disturbed fish. Resin acids or chlorophenols conjugates did not correlate with the observed effects either, and it is hypothesised that the steroids present in wood extractives are the cause of these effects.

There are no data available on steroid discharges by mills in the Northern River Basins. Steroids are present in many effluents, including treated municipal wastewaters.

4.5 Chelating Substances

Chelating agents, e.g. EDTA are used extensively in the new semi-bleached TCF pulp bleaching sequences for kraft pulps such as the *Lignox,* as well as for bleaching CTMP. EDTA may be discharged with the wastewaters.

Chelating or sequestering agents are usually large organic molecules that will bind cations and in particular will bind metals into an inactive or temporarily non-reactive form. Common chelating agents are EDTA, (ethylene diamine tetra-acetic acid) and DTPA (diethylene triamine penta-acetic acid). Figure 8 shows EDTA in its uncomplexed and complexed (chelated) form with ferric ions.



EDTA (trisodium edetate) EDTA (Ferro disodium edetate)

Figure 8 Structure of EDTA

Another member of the family that has been shown to be a "good stabilizer for peroxide" is DTPMPA (diethylene triamine pentamethylene phosphoric acid, May 1981).

There is voluminous literature, unrelated to pulp mills, on the roles of natural and artificial chelating agents in the functioning of ecosystems. The natural ones have major functions in keeping trace nutrients in the water as a reservoir for algae nutrition. There are many ecological concerns about man-made chelating agents in surface waters, ranging from the idea that trace mineral might be rendered unavailable to algae, to the opposite extreme that metals might be mobilized from the sediment and then taken up by aquatic organisms to their detriment. The degree of concern was best exemplified a couple of decades ago when another chelating agent (NTA) was proposed as a substitute for polyphosphate binding agents in detergents: there was great scientific debate and a surge of publications (e.g. a major report on ecological effects, IJC 1978).

In the course of the preparation of a detailed study of mechanical pulp and paper mills in Ontario, the literature was searched without finding any evidence of harmful environmental effects of chelating agents used in mills (Sprague 1991). The BCTMP mill of Millar Western Pulp Ltd. in Alberta had, in 1989, about 38 mg/L of DTPA and 12 mg/L of EDTA in the effluent, but concentrations in the river were never found to be above the detection level of 0.5 mg.L and no particular harmful effect was credited to the sequestering agents (Noton 1989, Sprague 1991).

IVL came to the same conclusion in a recent literature review (IVL 1989). EDTA complexes so strongly with ferric ions present in the process water that it does not exchange with other ions in the receiving water. EDTA and DTPA resists degradation during aerobic wastewater treatment, but some degradation takes place in carbon and nitrogen deficient natural waters. The main degradation pathway is photochemical degradation combined with biodegradation. These are hydrophilic compounds and do not bioaccumulate and must consequently be regarded contaminants rather than true pollutants (Folke 1991).

Some Swedish permits for (C)TMP mills include a 1 kg/tonne limit on discharges of chelating agents. This was based on the "precautionary principle", rather than on any known or suspected environmental effects (personal contact Agneta Mellin, SNV, 1990).

4.6 Adsorbable Organic Halogen (AOX)

SUMMARY AOX is an analysis of organohalogens that are adsorbable on activated charcoal. In a pulp mill effluent, AOX is the best known analytic procedure for quantifying the mass of chlorinated organic compounds. It measures more of the total amount than any other currently used single analytical test. AOX consists of approximately 80% high molecular mass materials (> 1000 dalton), 19% relatively hydrophilic (water soluble) low-molecular mass compounds, 0.09 % relatively lipophilic (fat soluble, potentially bioaccumulative) compounds, and 0.1% highly lipophilic (bioaccumulative) compounds. The exact composition varies considerably depending on its origin. If high molecular weight AOX is diluted with distilled water, a major fraction of it breaks down into lower molecular mass AOX. Low chlorinated AOX is proven to be biosynthesized in aquatic and terrestrial ecosystems. The AOX materials in effluents include chemically unstable fractions that can be dechlorinated by chemical action or can be partially broken down in biological treatment plants. Some components are persistent and may remain in the environment for sometime.

The determination, expressed in international conventions and by national regulators in many countries, to eliminate AOX from pulp mill effluents is based on a questionable argument: "Some chlorinated organics are known to be hazardous. Therefore, all chlorinated organics are potentially hazardous and should be regulated". As an effluent control parameter AOX lacks the correlation between discharge and effects on ecosystems. A kraft pulp mill where AOX formation has been reduced below about 2 kg/t pulp, normally produces an effluent with fairly harmless chlorinated organics, which furthermore seem to be similar to naturally formed organochlorides.

AOX is an instrumental analysis of organically bound halogens (chlorine, bromine, iodine) that can be adsorbed on granular activated charcoal. In pulp and paper mill effluents, chlorine is the only halogen present in significant quantities. Organohalogens that are not adsorbable on this charcoal bed, are not included in this analysis. The Swedish TOCl analysis is similar in that it uses XAD-resin to adsorb and desorb organochlorines to analyze different fractions. The actual chemical composition of effluent AOX varies from one effluent to another, and two AOX samples cannot easily be compared. For example, the ratio of chlorine to carbon varies significantly. One AOX value may be due to highly chlorinated matter with a significant proportion of bioaccumulative compounds, whereas another figure may arise from low-chlorinated matter that is equivalent to the organochlorine matter that is biosynthesized in aquatic ecosystems (Grimwall 1991). In all cases, a fraction of AOX consists of chemically unstable or readily biodegradable materials, which are easily mineralized (decomposed to harmless chloride) in any biological treatment plant. The AOX materials which are not mineralized during biological treatment may be regarded as more persistent in the environment, and a fraction of this material may even bioaccumulate. Therefore, this AOX fraction is potentially the most hazardous one.

Extractable organochlorines (EOCl) using hexane and persistent extractable organochlorines (EPOCl) (treatment with sulphuric acid adsorbed to kisel gel) were also determined in the Mönsterås study (SSVL 1990). EOCl was reduced from 8.5 g/ADt to 1.5 g/ADt during treatment, whereas EPOCl remained approximately the same at 0.5 g/ADt. Earl and Reeve (1989, 1990) reported laboratory values for EOCl being closely related to the amount of chlorine used in the first bleaching stage. The sequence $D_{60}CE$ on a Kappa 30 unbleached pulp and a chlorine multiple of 0.14 resulted in EOCl of 12 g/ADt being formed (Earl 1989, 1990).

Conventional chlorine kraft bleaching leads to a high molecular mass fraction with the elementary composition (IPK 1982):

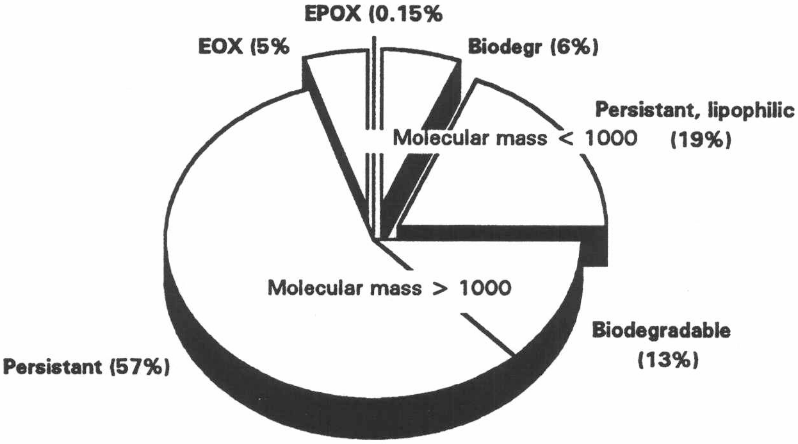
Untreated: $C_9 H_9 O_4 Cl$ to $C_{10} H_{14} O_7 Cl$

An atomic analysis of the high-mass fraction of AOX at the Mönsterås bleached kraft mill in Sweden gave the following elementary composition (SSVL 1990):

Untreated: $C_{27.7} H_{31.8} N_{0.1} O_{17.5} S_{0.4} Cl_{1.0} Na_{0.4} Ca_{1.2}$

Treated: $C_{29.7} H_{38.1} N_{0.3} O_{19.2} S_{0.8} Cl_{1.0} Na_{0.9} Ca_{1.4}$

Apart from insignificant hydrolysis, biological treatment does not seem to affect the elementary composition of this high mass material. An oxidative degradation and subsequent analysis of aromatic carboxylic acids revealed the same kind of aromatics as are the precursors for the chlorophenolics. There were insignificant differences in the findings in the treated and untreated effluent. Molecular masses show maxima in the range from 1,500 to 15,000 for both treated and untreated effluents. The chlorination ratio of aromatic structures is somewhat lower for this high mass material than for low mass compounds.More recent results show that high molecular mass organic materials in softwood and hardwood bleached kraft mill effluents produced under comparable conditions may differ significantly in molecular mass and contents of functional groups (Mörck 1991). This study showed that highly chlorinated monomeric phenolic compounds could not be released from high molecular mass organic AOX originating from "modern" bleach kraft pulp mill effluents. A typical example of the breakdown of the types of organochlorines that are to be found in an untreated softwood kraft effluent is shown in Figure 9. The AOX of the effluent was 1.9 kg/ADt. The annual average reduction of AOX across the ASB at the mill was reported to be 42%, corresponding to 1.1 kg/ADt in the treated effluent. About 20% of the production is based on hardwood, so the combined annual figure is below 1 kg/ADt. A fraction of the EOX is also biodegradable.



JPIEFIGS.XLS Chart

Untreated bleached softwood kraft pulp mill effluent from Mönsterås. Data has been recalculated from SSVL (1990)

Figure 9 Approximate composition of AOX

Figure 9 presents an estimate of the constituents making up the AOX of untreated effluent at the Mönsterås bleached kraft mill in Sweden. (McCubbin 1991, Appendix C). The data originate from the "three bleach line" study in Sweden (SSVL 1990).

New evidence indicate that high molecular mass AOX is only held together by hydrogen bonds, i.e. with no co-valent bonds. If high molecular mass AOX is diluted with distilled water a major fraction of it brakes into lower molecular mass AOX (Jokela 1992). This explains why high molecular mass AOX has never been found to accumulate in sediments.

The Extractable Organic Halogen (EOX) method has not been standardized. If analyzing for EOX, an appropriate protocol distinguishing EOX from POX (Purgeable organohalogens) should be used. Otherwise EOX may just be an estimate of chloroform.

4.6.1 Calculation of AOX content of effluent

SUMMARY An equation was developed to predict the AOX discharge rate for possible process modifications. It is similar to equations used by others, but coefficients were adjusted to fit known data on the Ontario kraft mills gathered during the 1990 MISA monitoring program.

To evaluate alternative processes for improving mill effluent quality, it is necessary to be able to predict the AOX discharge rate for any proposed process modification.

Germgård (1983) proposed the following equation for calculation of the organically bound chlorine (TOCl)[8] discharge from kraft bleach plants, and it has become quite widely accepted.

$$\text{Organically bound chlorine} = k \times (C + \frac{H}{2} + \frac{D}{5}) \text{ kg/tonne pulp}$$

where k is a constant in the range 0.07 to 0.11 if C,H, and D are in the units kg/tonne pulp
and the Organically bound chlorine is determined according to the TOCl analysis procedure described by Sjöström (1981)
C is total molecular chlorine charge
H is hypochlorite charge, as equivalent molecular chlorine (=1.05 x NaOCl)
D is chlorine dioxide charge as equivalent molecular chlorine (= 2.63 x ClO_2)

The authors reviewed a number of publications, and discussed the problem of predicting AOX discharges with several scientists with extensive experience in measuring AOX discharges, and the consensus seems to be that the above mentioned equation is the best available at present, but that selecting the appropriate value for "k" is open to some discussion. It appears that the value of "k" should decrease somewhat for chlorine dioxide substitution over 70% (Liebergott 1991).

The above equation has been quite widely used in Scandinavian literature. Many statements in both Scandinavian and North American literature which one might presume to be based on chemical analysis of mill or laboratory effluent streams are actually based on the equation; although the authors rarely mention the value they selected for the "k" factor.

The data available from the 1990 MISA monitoring program (MISA 1991) provide more information on mill AOX discharges than has been available in the past, since analyses were conducted three times a week. Unfortunately, the relevant mill operating conditions and effluent treatment plant input AOX concentrations were not recorded simultaneously, so it is not possible to conduct a rigorous comparison of the foregoing equation with the measured AOX discharges.

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[8] In this section, note that "TOCl" refers specifically to the values obtained by analysis using ultra filtration and XAD resin according to Sjostrom (1982).

Earlier literature proposed values from 0.05 to 0.07 for k, but analysis of the MISA monitoring data (MISA 1991) indicates that a **value of 0.08 is the most appropriate for "k", up to 70% substitution, but that lower factors are appropriate for higher substitution levels.** The foregoing equation ignores any treatment of the bleach plant or whole mill effluents, but a review of the literature and comparison with the data in MISA 1991 indicates that an **aerated stabilization basin can remove approximately 40% of the AOX entering.**

The original equation proposed by Germgård was based on bleaching with chlorine dioxide substitution rates under 70%. Liebergott (1991) presented curves indicating effectively that "k" declines at substitution rates over 70%. The authors have therefore used a modified value for "k" as follows where substitution is over 70%:

The calculations of AOX discharges in this report are based on:

$$\mathrm{AOX} = k \times (C + \tfrac{H}{2} + \tfrac{D}{5}) * (1\text{-}e_B) \text{ kg/tonne pulp}$$

Where e_B is the AOX removal efficiency of the biological treatment system,
40% for ASB,
33% (Rempel 1991) for activated sludge.

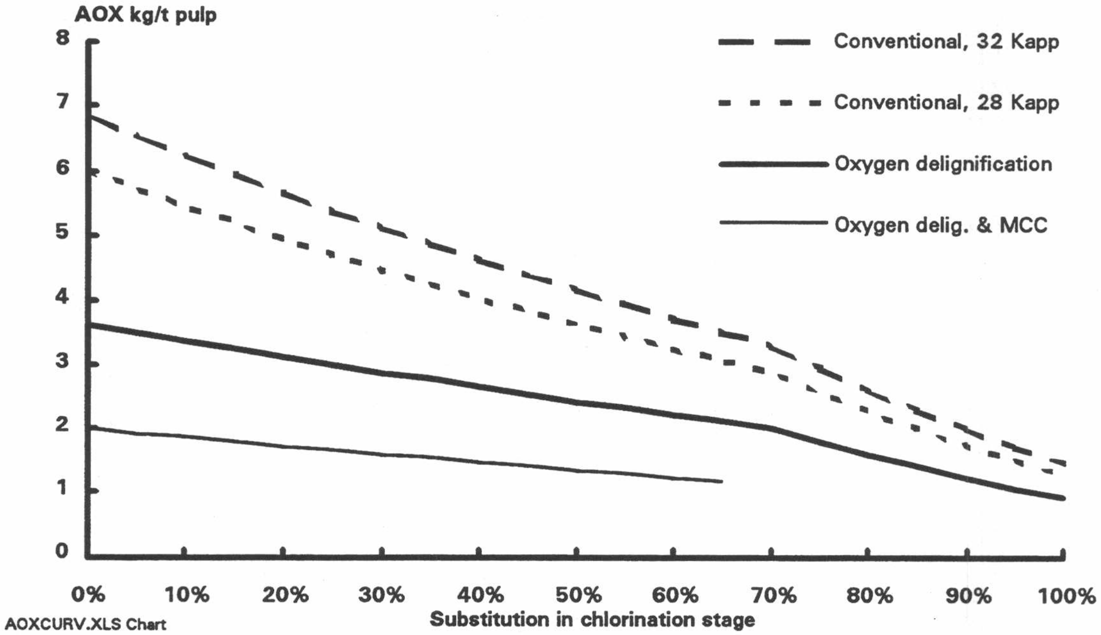
k = 0.08 when the bleach plant is operating with less than 70% chlorine dioxide substitution in the first stage, and
$k = 0.08 \times (1.7 - (\frac{\%\ \text{substitution}}{100}))$ where substitution is greater than 70%.

Andrews (1991) and personal communication with several mill staff responsible for full scale pulp production trials with 100% chlorine dioxide substitution confirm that the values calculated from these equations are realistic.

The above equation is **probably as reliable as many of the calculations used in designing mill processes, it must be recognized that the prediction of AOX discharges is far from an exact science,** and lacks the years of experience underlying predictions of discharges of traditional pollutants. The curves in Figure 10, taken from McCubbin (1991 Fig 23), present the results of calculations from this equation for various pulping and bleaching conditions, for softwood pulps.

AOX discharges from hardwood will normally be substantially lower than shown in Figure 10, since lesser quantities of chlorine based compounds are required to bleach hardwood.

The focus on AOX as a regulatory parameter was probably more appropriate to the pulping processes and level of scientific knowledge in the 1908s than today (Berry 1991, Folke 1989 1990 1991 and 1992). It attracted attention to the problems of toxic effects from kraft pulping when bleaching sequences and operating practices were used that produced to 5 to 15 kg AOX per tonne pulp.



AOX discharges prior to biological treatment. Calculated by the authors using the equations discussed in text.

Figure 10 AOX discharges for various pulping and bleaching conditions (softwood)

Today AOX can be considered to have served its purpose as a regulatory parameter in many locations, in that there is no longer any meaningful relation between the AOX content and biological/ecological effects of current mill effluents where AOX is usually under 2 kg/tonne. This is not simply because of a reduction in the mass discharge of AOX, but because the inplant process modifications that have been used by mills to lower AOX values have changed the characteristics of the effluents to the extent that AOX is of severely limited environmental significance.

External effluent treatment in aerated stabilization basins or activated sludge plants reduces AOX by proportions ranging from nil to 65%, with most data being in the range of 25% to 45% reduction (Wilson 1991). There is a lack of correlation between the specific AOX discharge and the effects on ecosystems as discussed below. The fraction of AOX which consists of polychlorinated organics is the most important for the environment, and can be defined by total polychlorinated phenolics [Folke 1989]. This is the sum of the contents of tri- and tetrachlorophenolic compounds, such as phenols, guaiacols, catechols and trichlorinated syringols (see below). Berry (1991) discussed the same concept, referring to the chlorophenolics in terms of their pentachlophenol toxicity equivalent (TEQ) and showing that the TEQ value is extremely low in effluents from mills that have implemented inplant measures to lower AOX below about 2 kg/tonne pulp.

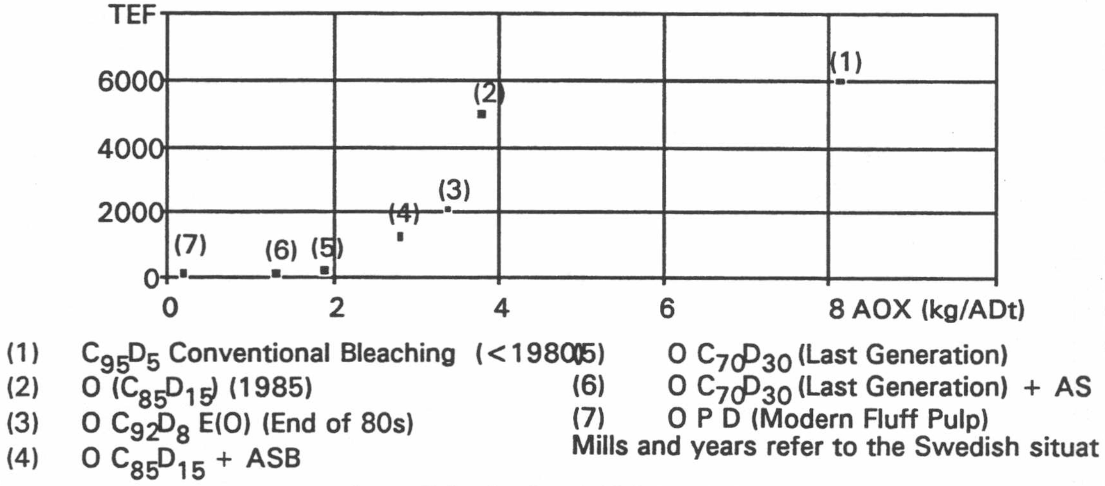
External effluent treatment in aerated stabilization basins or activated sludge plants is only modestly effective in reducing polychlorinated organics. However, reduction of high AOX emissions by means of internal measures in the mill can provide effective protection of the environment, provided cost effective and energy saving processes are used. A kraft pulp mill where the chlorine multiple in the first CD-stage in the bleach process has been reduced to less than about 0.15, and/or the Kappa number of the unbleached pulp is below 20, corresponding to formation of 1.5 to 2 kg AOX/tonne, normally produces an effluent with relatively harmless chlorinated organics, which seem to be fairly similar to naturally formed chloro-organics. Non-chlorinated substances, such as wood extractives, are responsible for the remaining weak environmental effects of such effluents.

The biological effects of effluents from mills using different bleaching and external treatment concepts have been assessed using a variety of biological test methods, ranging from acute lethality tests, through medium-term laboratory tests of sub-acute or chronic effects to complex, multispecies tests in outdoor model ecosystems.

A series of medium-term laboratory tests for sub-acute effects in zebra fish and *Ceriodaphnia* were carried out, where the "Lowest Observed Effect Concentration" (LOEC) was determined for two different end-points:

A. Reproduction and survival of embryo/larvae, and

B. Induction of adverse effects during gametogenesis in fish, determined as reduced stress tolerance in the offspring (Landner 1985, Neilson 1990).



Source Folke, Landner & McCubbin 1992

TEF$_{SA}$[9] determined for end-point B (see text).

Figure 11 AOX vs. toxicity emission factor

Based on data from such tests (Neilson 1991), one can conclude (refer to Figure 11):

(i) The amount of sub-acute toxicity, expressed as TEF$_{SA}$ (where TEF$_{SA}$ = 100/LOEC x wastewater flow per tonne of pulp) for a mill using a conventional bleaching sequence, typical for the years before 1980, is about 1,000 for end-point A and 6,000 for end-point B. This serves as a reference for the "worst case".

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[9] *TEF is used mostly in North America to refer to acute lethality. Therefore, we have used the subscript SA= Sub-Acute*

(ii) Introducing oxygen delignification without any other major change in the bleaching sequence, will reduce the TEF_{SA}-values to 500 (A) and 5,000 (B). This is the technology typical around 1985 in Sweden and is becoming widespread in the USA and is used in the Hinton and Peace River mills.

(iii) Reduction of the washing loss[10] and carry-over of substance from the oxygen stage to the chlorination stage and better control of the bleaching process. This includes oxygen reinforcement of the extraction stage, as was the practice in many Swedish and Alberta mills at the end of the 1980s it reduces the TEF_{SA}-value for one of the end-points (B) to about 2,100, but do not change the TEF_{SA} for the end-point A.

(iv) The best bleaching practice used in Sweden at the beginning of the 1990s, oxygen delignification, followed by a 70% substitution of the active chlorine in the chlorination stage produces an effluent giving TEF_{SA}-values of 170 (A) and 250 (B), respectively. This is similar to the Hinton and Peace River kraft mills[11].

(v) It was demonstrated that external treatment of the effluents in an aerated stabilization basin with a retention time of 8 to 9 days and operated with an anoxic pre-zone for effective elimination of chlorate in the effluents, resulted in efficient reduction of most pollutants (Haglind 1991) (Figure 12). Furthermore, it was found that, irrespective of the level of sophistication of the washing and bleaching technology, the treatment will produce an effluent which has two to four times lower TEF_{SA}-values than the effluents before the external treatment. However, the reduction in AOX as a result of the external treatment was normally only around 30% to 40 %, to be compared with the much greater reduction in toxicity.

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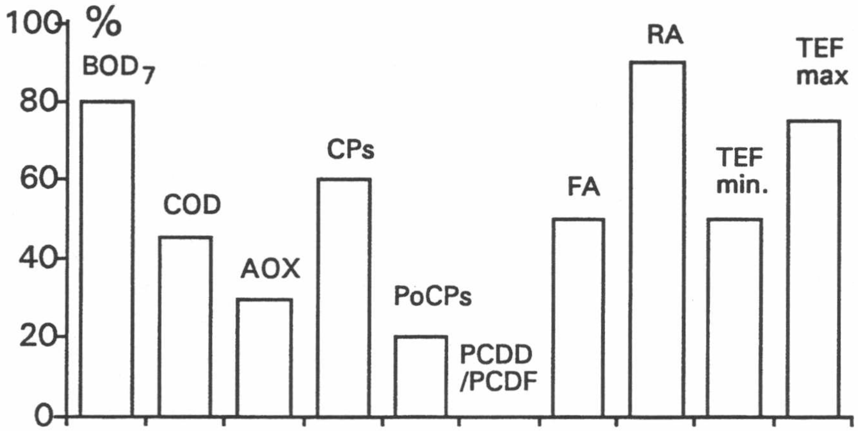
[10] *Washing losses under 10 kg saltcake/tonne pulp are considered low.*

[11] *The current trend toward replacing all the chlorine in the first bleaching stage with chlorine dioxide will presumably achieve at least as good a result.*



CPs = chlorinated phenolics

PoCPs = polychlorinated phenolics

FA = fatty acids

RA = resin acids

TEF_{SA} = toxicity emissi factor.

Source> (Folke, Landner & McCubbin 1992)

Figure 12 Reduction of pollutants in an aerated stabilization basin.

(vi) Compared with the externally treated effluents (aerated stabilization basin) from mills using the "last-generation" cooking, washing and bleaching technology, but only 30% chlorine dioxide substitution (about 30 % of the active chlorine in the chlorination stage as D, giving an AOX in the treated effluent of 1.3 kg/ADt), bleaching sequences with 100 % substitution and AOX levels of 0.1 to 0.2 kg/ADt do not further reduce the TEF_{SA}-values (Haglind 1991, Brunsvik 1991).

The above conclusions are further substantiated by the results of long term experiments (about 5 months duration) where sub-littoral brackish-water communities from the Baltic Sea were exposed to various effluents in 8 m^3 outdoor test tanks. Tank studies were supplemented by medium-term exposures of rainbow trout, followed by assessment of the physiological and biochemical status of the fish. The combined results from these comprehensive biological tests indicated that there is no correlation between the amount of AOX being formed during the bleaching and the composite biological response (Lehtinen 1991). The effluent from a mill producing unbleached kraft pulp showed a composite biological response which was stronger than that obtained with effluents from mills with bleaching and AOX levels up to about 4 kg/ADt (Brunsvik 1991, Landner 1991). However, the effluents from the production of unbleached pulp are difficult to compare directly with those from bleached production. The only conclusion which is justified at this stage is that compounds other than chlorinated organics significantly contribute to the overall toxicity of pulp mill effluents, if AOX discharges are under about 4 kg/tonne, as is now becoming normal in Canada.

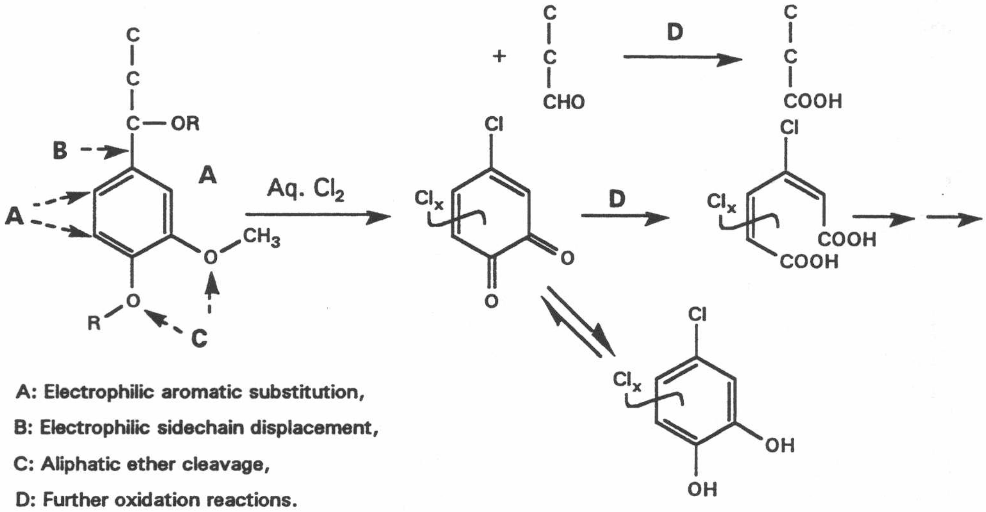
4.7 Formation of Organochlorine Compounds

SUMMARY The reaction of chlorine and/or hypochlorite with lignin residuals from the cooking process creates organochlorine compounds. These take many forms and those that have been identified total in excess of 300 compounds. Of these compounds the chlorophenolics are probably the better known group of compounds.

The main pathway for the formation of organochlorine compounds is the reaction of elemental chlorine or hypochlorite with lignin residues from the cooking process.

4.7.1 Chlorophenolics

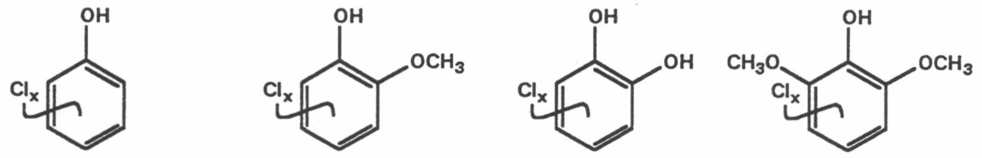
Chlorophenolics are formed in the C-stage after electrophilic sidechain displacement reactions of lignin residuals which can be followed by one or several aromatic substitution reactions (up to four chlorine atoms may be added to non-chlorinated phenolic precursors). Precursors may originate from the delignification processes occurring during cooking or by the oxidation reactions of chlorine. Often chlorophenolics formed in the C-stage are only extracted in the E-stage due to the non-ionized (water insoluble) form they have in the C-stage.



A: Electrophilic aromatic substitution,
B: Electrophilic sidechain displacement,
C: Aliphatic ether cleavage,
D: Further oxidation reactions.

Figure 13 Reaction pathways for lignin residuals with chlorine

The phenolic structures that may be formed by these reactions are summarized in Figure 14.



Chlorophenols Chloroguaiacols Chlorocatechols Chlorosyringols

Chlorovanillins Chlorosyringaldehydes

Spent bleach liquors from hardwood and softwood fibers (Carlberg 1991)

Figure 14 Chlorophenolics found in chemical pulp waste waters

The type and amount of chlorophenolics to be found in different spent bleach liquors depend on the raw material, the pulping process and the amount of chlorine used for bleaching. Bleach plant effluents from softwood kraft pulp normally contains the highest amounts of chlorophenolics, i.e. the chlorinated phenols, guaiacols, catechols, and vanillins. Bleach effluent from hardwood pulp contain smaller amounts than softwood, but syringols may be present, which are not found in softwood effluents, as precursors are lacking in the softwood lignin.

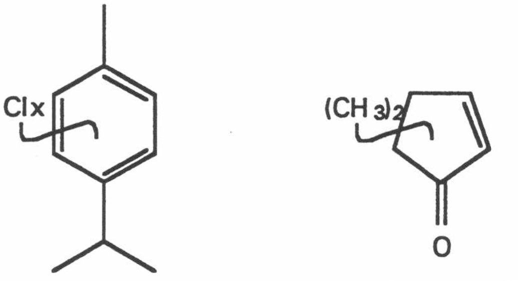
Recent results from the studies of the Mönsterås mill indicate that when oxygen delignification is used prior to a C/D stage with a low chlorine multiple, mainly dichlorinated phenolics are formed (~27 g/ADt) with less monochlorinated (~7 g/ADt) and trichlorinated phenolics (~10 g/ADt). Hardly any tetrachlorinated phenolics are formed during bleaching (SSVL 1990). The same study includes data on the ASB performance which also indicate that monochlorinated phenolics are essentially removed, and dichlorinated phenolics are reduced to one-third, whereas tri- and tetrachlorinated phenolics resist biological degradation in the treatment system. (The latter types of phenolics are by far the most hazardous fraction.) The total reduction of chlorophenolics during ASB treatment was 58%. These types of chlorophenolics are derived from phenols, guaiacols, catechols and vanillins as could be expected from softwood pulping. The total level of chlorinated phenolics (40 to 45 g/ADt) is significantly lower than reported from bleach plants without oxygen delignification (80 to 250 g/ADt).

The environmental fate of pulping compounds has been studied at Grand Prairie, Alberta, after major process changes. The Grand Prairie plant is a 285,000 tonnes per year bleach kraft pulp mill using a DcEoHDED bleach sequence (the latest process change in 1990 being an increased ClO_2 in the Dc stage, up from 25% to 70%) and a 7 days ASB (Joshi 1991). As a result AOX decreased 15% to 20% color by 30% to 40%, polychlorinated phenols by 60% to 80%, and the carbon to chlorine ratio increased by 10% to 20%. Polychlorinated phenols in untreated the effluent was reduced from 13 g/ADt to 4 g/ADt after the process change and from 3 to 1 g/ADt in the treated effluent. This is a remarkable reduction, particularly with respect to the ASB system which showed a considerably better percentage reduction of polychlorinated phenols than the Mönsterås ASB.

The presence of di- and trichlorophenols found during the MISA program in a bleach plant effluent (Chapman 1992) can be taken as an indication of the presence of chlorinated guaiacols, catechols and other lignin related chlorophenolics as well[12]. The other chlorophenols analyzed in the MISA program, i.e. 2,3,4, 2,3,5, 2,4,5-trichlorophenols, tetrachlorophenols and pentachlorophenols cannot be formed from direct chlorination of phenol at atmospheric pressure, and probably originate outside the bleach plant itself, e.g. wood preservatives.

4.8 Lipophilic, Neutral Organochlorines

Around 60 lipophilic pollutants have been identified by GC/MS (gas chromatography/mass spectrometry) analysis in the effluents from the Mönsterås mill in Sweden. Most of those were reduced significantly during biological treatment in ASB, but higher chlorinated ones tend to be more stable. Treatment with sulphuric acid eliminated most of the lipophilic compounds except chlorinated phenolics, chlorinated and non-chlorinated p-Cymens and trimethyl-2-cyclopentenone.



p-Cymen

Trimethyl-2-cyclopentanon

Figure 15 Compounds that are not degraded in biological treatment (ASB)

Chloroform, chloro-acetones, aldehydes and acetic acids may be formed in both C, E, and H pulp bleaching stages (Dallons 1990, Hrutfiord 1990):

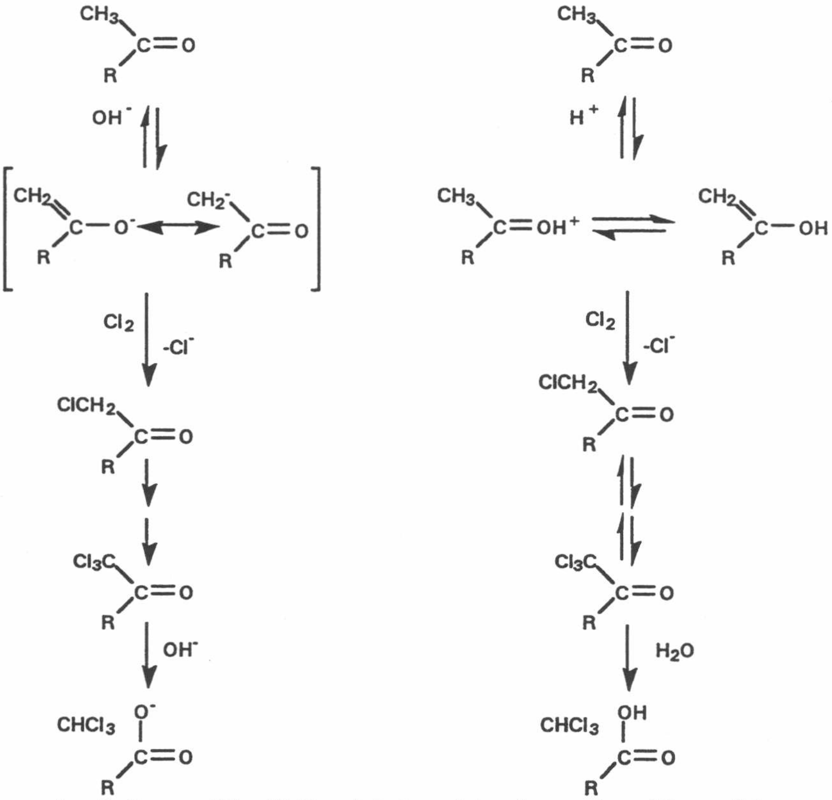
The H-stage is by far the largest chloroform producer, 150 to 200 g/ADt or 5 to 15 times the magnitude of C, E, and D-stages combined, and the magnitude of the hypochlorite charge is the dominant factor affecting the amount of chloroform produced in the H-stage. The classical haloform reaction is the main reaction responsible for chloroform formation from methyl-ketones (from lignin precursors). This reaction is most efficiently catalyzed by alkaline conditions as shown in Figure 16.

---

[12] *The 1990 monitoring program did not include these substances, apparently because of the lack of defined testing protocols.*

Chloroform intermediates are also formed in the C-stage, and chloroform is formed upon treatment with hypochlorite. If the intermediate compounds are only subjected to a neutral or basic pH environment, methylene chloride may be formed instead.

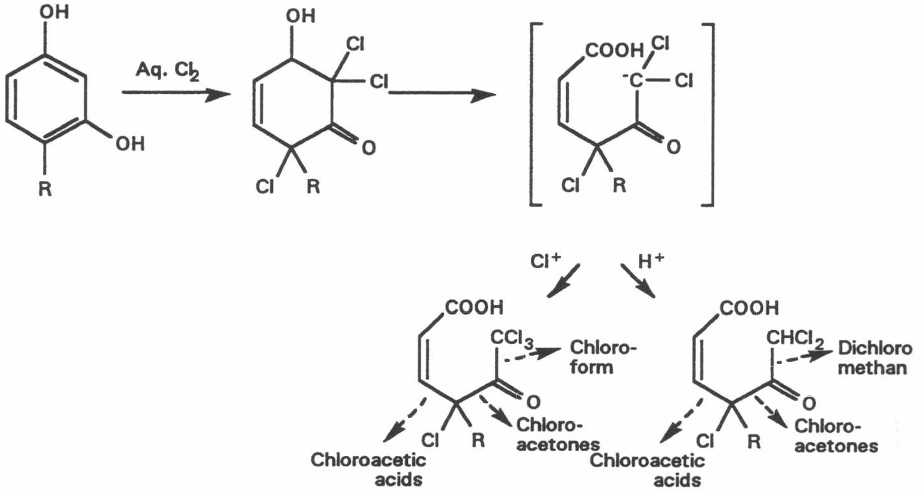
Meta-dihydroxylated aromatic compounds and several other hydroxy and carbonyl structures which may be formed from lignin are precursors for the formation of chloromethanes, chloroacetic acids and chloroacetones when reacted with chlorine in acidic media.



Most effective under alkaline condition (H-Stage), but can take place under acidic condition as well (C-stage)

Figure 16 The classical haloform reaction

The meta-substituted catechol-precursor may be formed by many reactions taking place in an acidic media containing elemental chlorine, i.e. C or C/D-stages. Thus, the elimination of the hypochlorite-stage of older bleach plants does not itself prevent chloroform formation, although the classic alkaline catalyzed haloform reaction in hypochlorite stages accounts for the greater fraction of chloroform. A typical CEHDED bleach sequence results in releases of chloroform of 240 to 300 g/ADt. In fact, levels exceeding 1,200 g/ADt have been reported by NCASI (Dallons 1990). In the case of Mönsterås, only 7 g/ADt of chloroform was reported in the untreated effluent, and this was eliminated during ASB treatment (<0.1 mg/ADt). A typical C_d E D E D bleach line has been reported to discharge 10 g/ADt of chloroform from the C_d stage, and 30 g/ADt from the E1-stage (IPK 1982). This indicates the extent of the reduction in chloroform discharges when hypochlorite bleaching is eliminated.

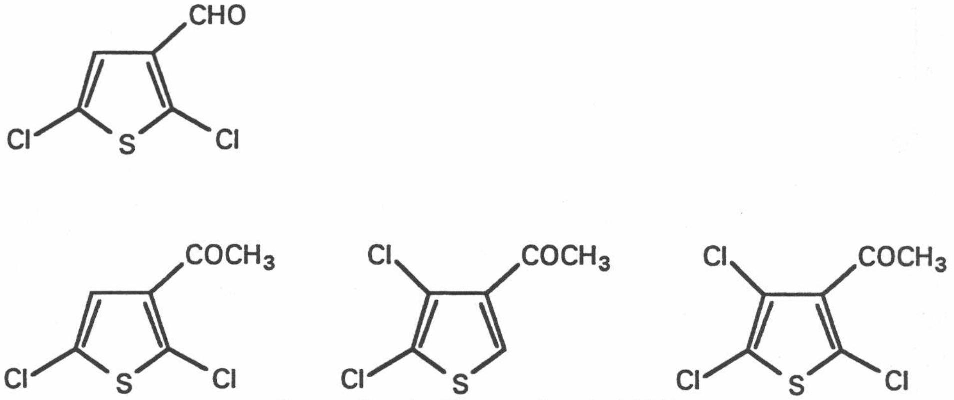


Formation of chloromethanes, chloroacetic acids and chloroacetones in chlorine bleach plants with or without H-stages

Figure 17 Mechanism of formation of chloro-organics

The untreated effluent from Mönsterås contained around 9.5 g/ADt of 1,1-dichloro-dimethylsulfone ($CHCl_2SO_2CH_3$), and this compound was only reduced to 6.5 g/ADt during treatment (30% reduction). Only very low levels of chloroacetones were found in the influent, and none in the effluent. Di- and tetrachlorinated acetic acids (~ 64 g/ADt) are virtually eliminated during biological treatment, but these levels are even significantly lower than previously reported values (300 to 1200 g/ADt) (IPK 1982) even before biological treatment. Chlorinated veratroles were not found in the effluent as could be suspected from the work of Nielson (Folke 1991).

Di- and trichlorinated 3-formyl/acetylthiophenes have been identified in bleached kraft mill effluent (Lunde 1991). Refer to Figure 18. Three-substituted thiophenes are formed from cellulose and glucose when treated in a kraft process and are the precursors of the chlorinated ones.



Source: [Lunde, Skramstad et al., 1991]

Figure 18 Chlorinated thiophenes identified in bleached kraft mill effluent

Chlorinated thiophenes have a high potential for bioaccumulation and they have been found to be weakly mutagenic.

4.9 Polychlorinated Dioxins and Furans (PCDD/PCDF)

SUMMARY The PCDD/PCDF compounds have been identified as a group of compounds with varying degrees of toxicity. 2,3,7,8-TCDD has been identified as the most toxic of this group and the toxicity of the others are related to TCDD in setting toxicity equivalent factors. The most important factors in minimizing the PCDD/PCDF content appear to be a, low chlorine multiple, and high chlorine substitution. PCDD/PCDF are removed to some extent in biological treatment through adsorption in the sludge. Dechlorination takes place more readily under anaerobic conditions, i.e. in the sludge. The detection limit for TCDD/TCDF is reported to be 10 pg/L based on high resolution analysis.

The NCASI 23 mill study (Dallons 1990) reports a detection limit for TCDD/TCDF of 10 pg/L based on their high resolution GC/MS procedure. This is a statistically based limit where data will be normally distributed. It is possible to actually recognize TCDD/TCDFs in treated pulp mill effluents at levels as low as 1 pg/L, but it will be impossible to apply normal distribution statistics to the results, so for most practical purposes, 10 pg/L is a usable limit of detection for pulp mill effluents.

The data on the dioxin content of mill effluents collected in Alberta in 1991 and 1992 were based on procedures that are capable of detecting 2,3,7,8 TCDD in concentrations down to about 0.5 to 3 ppq, depending on practical considerations such as sample size and contamination.

Various systems have been used to convert a multitude of PCDD/PCDF levels into a simpler expression, e.g. by the use of toxic equivalent factors as shown in Table 13.

The rationale behind these systems is that 2,3,7,8-TCDD is the most toxic of all the isomers, and that isomers with more chlorine atoms having the 2,3,7,8-substitution pattern potentially degrade to 2,3,7,8-TCDD and are often more toxic than other isomers. The original Eadon and NATO toxicity emission equivalents have been supplemented as new knowledge has emerged. We consider that either the USEPA or the Nordic model are probably more appropriate for regulatory authorities in the future.

There is a critical difference between the Eadon and USEPA equivalency factors on the one hand, and the NATO and Nordic on the other. **The Octa-chlorinated dioxins and furans are considered to have zero toxic equivalents in former scales, but to be equivalent to 1/1000th of TCDD in the latter.** The Octa homologues were the principal dioxins/furans found in the non-kraft mills in the 1990 MISA monitoring program. These were found in the effluents from a non-kraft mill processing waste papers.

Table 13 Toxic equivalency factors for PCDD/PCDF

Homologue	NATO	Eadon	Nordic 1987	USEPA (1987)
Dioxins				
2,3,7,8-TCDD	1.0	1.0	1.0	1.0
All other TCDDs	0.0	0.0	0.0	0.01
1,2,3,7,8-PCDD		1.0	0.5	
2,3,7,8-substituted PCDDs	0.5			0.5
All other PCDDs	0.0	0.0	0.0	0.005
2,3,7,8-substituted HxCDDs	0.1	0.03	0.1	0.04
All other HxCDDs	0.0	0.0	0.0	0.0004
1,2,3,6,7,8-HpCDD		0.0	0.01	
2,3,7,8-substituted HpCDDs	0.01			0.001
All other HpCDDs	0.0	0.0	0.0	0.00001
OCDD	0.001	0.0	0.001	0.0
Furans				
2,3,7,8-TCDF	0.1	0.33	0.1	0.1
All other TCDFs	0.0	0.0	0.0	0.001
1,2,3,7,8-PCDF	0.05	0.33	0.01	0.1
2,3,4,7,8-PCDF	0.5	0.33	0.5	0.1
All other PCDFs	0.0	0.0	0.0	0.001
2,3,7,8-substituted HxCDFs	0.1	0.01	0.1	0.01
All other HxCDFs	0.0	0.0	0.0	0.0001
2,3,7,8-substituted HpCDFs	0.01	0.0	0.01	0.01
All other HpCDFs	0.0	0.0	0.0	0.00001
OCDF	0.001	0.0	0.001	0.0

In the USA and Canada, the NATO-units system is commonly used. There is no formally defined standard in Alberta.

PCDD/PCDF appears to be formed entirely at the first C/D-stage (Dallons 1990). The actual amounts of PCDD/PCDF formed depend on the concentration of molecular chlorine in this stage and the concentration of DBD and DBF precursors in the brown stock. The chlorination factor appears to be the most important of the two. Hrutfiord (1990) found that compression wood was a likely source of unchlorinated DBD and DBF built into the lignin structure and chlorine side-chain displacement releases the PCDD/PCDFs.

Quantities discharged

The data available on the quantities of 2,3,7,8-TCDD and 2,3,7,8-TCDF by the Alberta mills are summarised in Table 14. Most of the data would have been considered to be below the detection limit a few years ago.

Table 14 Dioxin discharges from Alberta kraft mills

	2,3,7,8 TCDD pg/L	2,3,7,8 TCDF pg/L	2,3,7,8 TCDD µg/day	2,3,7,8 TCDF µg/day	2,3,7,8 TCDF µg/ton	2,3,7,8 TCDF µg/ton	TCDF to TCDD ratio	TEQ µg/ton
Hinton	7.3	14.9	773.9	1,629	1.3	2.1	1.7	1.5
Grande Prairie	5.2	28.4	288.5	1,551	0.5	2.2	4.7	0.7
Peace River	1.8	4.5	114.1	290	0.4	0.9	2.1	0.5

The analytical detection methods used were more sensitive than those used for some previous studies.

US pulp mill effluents show contents of 2,3,7,8-TCDD ranging from the detection level of around 1 µg/ADt up to 500 µg/ADt (Dallons 1990). The samples for Dallons data were mostly collected in 1988 and 1989.

According to Dallons the most important factors in minimizing the content appear to be (1) low Kappa number prior to bleaching, (2) low chlorine multiple and (3) high chlorine dioxide substitution (1990). While cautioning readers that the effects of any one process technology were not necessarily transferable to other mills, Dallons noted that the two mills which used oxygen delignification out of the 23 examined had the lowest emissions of TCDD.

Berry (1991) differs from Dallons on one key point. Berry showed that the Kappa number entering the first chlorine based bleaching stage had little effect on the formation of dioxins, although he agreed on the other points. The apparent correlation of low dioxin discharges with the existence of oxygen delignification may be due the fact that mills with oxygen delignification tend to have more modern, better instrumented bleach plants and also that many have taken advantage of the drop in bleach chemical demand to increase the level of chlorine dioxide substitution.

In the USA, a number of mill studies have been conducted. In 1986, the USEPA and the industry performed a cooperative 5 mill screening study (NCASI 1988b). 2,3,7,8-TCDD was found in seven of nine bleached pulps collected at those five mills ranging from 3 to 51 ppt, and 2,3,7,8-TCDF was found in eight of the nine bleached pulps at levels ranging from 8 to 330 ppt. Wastewater concentrations of 2,3,7,8-TCDD ranged in three of the five mills from 15 to 120 pg/L, and 2,3,7,8-TCDF was found in four of the five mill effluents at levels from 11 to 2,200 pg/L. PCDD/PCDF was found to be more than 90% transferred to the sludge and suspended solids during wastewater treatment. Since the samples were collected for this study, most mills have implemented aggressive measures to reduce dioxin formation, and current discharges in the US are much lower (USEPA 1990).

This study initiated another cooperate screening study to include all 104 bleach plants in US chemical pulp mills in 1988 (USEPA 1990). Results indicate that TCDD/TCDF concentrations in sludge and final pulp are more than 1000 times greater than treated effluent concentrations, and that there is a great variation in concentration between different mills. Also TCDF tended to be 50 to 100 times higher in concentration than TCDD (This is not true of more recent data on Alberta mill effluents, as indicated in Table 14). Extremes in sludge concentrations are 1,400 ppt (TCDD) and 17,000 (TCDF) down to 3 ppt (TCDD) and 50 (TCDF). Effluent concentrations ranged from 320 pg/L (TCDD) and 4,000 (TCDF) to below the level considered as the detection limit at the time (10 pg/L).

2,3,7,8-TCDD, and PCDD/PCDF in general, leave the process by three paths, with pulp, with effluent to the receiving waters, and in effluent treatment plant sludges. The above mentioned 104 mill study demonstrated that partitioning is very roughly one-third via each path, but wide and unexplained variations were found.

Experience in contolling discharges of dioxins

On the basis of an extensive review of recent operating experience in almost 50 Canadian bleached kraft mills, Luthe *et al* (1992) suggest that dioxins and furans in the final mill effluent will be non-measurable if the Active Chlorine Multiple (ACM) is below a threshold value, which in turn depends on the extent of chlorine dioxide substitution. ACM is calculated as the ratio of total active chlorine applied to the first chlorination stage to the incoming kappa number. Luthe suggests that this limiting ACM can be calculated as 24 / (150 - ClO_2 Substitution %). These conclusions apply only if dioxin precursors (normally in defoamers) have been eliminated, as is now normal practice in Canada and is believed to be the case in the US.

Substitution %	Limiting ACM
0.	0.16
5.	0.17
10.	0.17
15.	0.18
20.	0.18
25.	0.19
30.	0.20
35.	0.21
40.	0.22
45.	0.23
50.	0.24
55.	0.25
60.	0.27
65.	0.28
70.	0.30
75.	0.32
80.	0.34
85.	0.37
90.	0.40
95.	0.44
100.	0.48

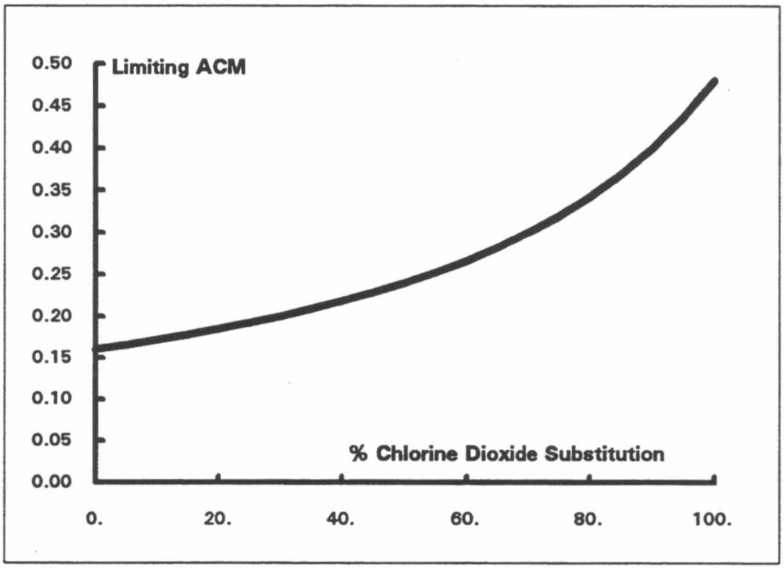


Figure 19 Active chlorine multiple required to eliminate measurable formation of TCDD/F

If we manipulate the above equation to calculate the substitution level, it becomes:

Substitution % = (150 * ACM - 24)/ACM, which was used to prepare the following table and graph.

Luthe defines mill discharges as "non-measurable" if the discharge of 2,3,7,8 TCDD is under 10 ppq. and the discharge of 2,3,7,8 TCDF is under 30 ppq. They prefer to avoid using the concept of detection level, since any measurement close to the detection level is liable to be inaccurate. These criteria are not as low as some may wish, but it were considered by

Luthe and her co-workers to be the lowest values which could be determined with reasonable confidence at the time of writing (early 1992). It is probable that many of the mill effluents described as having "no detectable" concentrations of 2,3,7,8 TCDD actually contain very much less than 10 ppq, so they would remain "non-detect" if judged by a more stringent criterion that may well become practical as laboratory experience advances.

Mills can be expected to achieve discharge rates well below those mentioned above by optimizing the relatively new bleach sequences introduced in the past few years to reduce the formation of organochlorines in general, and dioxins in particular.

4.10 Chlorate

Chlorate is found in the effluents from bleached kraft mills, particularly those which practice high chlorine dioxide substitution. Discharges of chlorate from kraft mills were not considered significant until recently, when the desruction of benthic flora (described below) occurred near the outfall of a Swedish bleached kraft mill. At the time the mill did not have a secondary treatment system.

The current trend in the kraft pulp industry, particularly in Canada, is to increase chlorine dioxide substitution. A few years ago, most mills operated with chlorine dioxide substitution under 20%, whereas 70% is common today, and many mills operate at 100% substitution, thus eliminating the use of gaseous chlorine. The principal objective is to reduce the discharges of organochlorines, with particular reference to AOX, dioxins and furans. As discussed elsewhere in this document, these measures have been successful in attaining their objective.

Chlorate discharges are not routinely measured in Alberta but data collected by the Ministry of the Environment have indicated that the Alberta kraft mills discharge chlorates. All use high chlorine dioxide substitution.

Chlorate has shown to be lethal to the bladder-wrack (Lehtinen 1988). The chlorate-induced damage to this and other brown algae has been shown to cause extensive secondary effects on the littoral, rocky hard-bottom ecosystem as shown in model ecosystem experiments (Lehtinenn 1988, MFG 1988). The disappearance of the bladder-wrack reduced the production of benthic macrofauna, i.e. several species of invertebrates which grew in the bladder-wrack zone lost their ecological niche. Thus, it has been indicated that the disappearance of a component of an ecosystem might result in a decreased fish production at least locally in the damaged area. However, the influence might be of larger magnitude than expected. For instance the Baltic herring is dependent for spawning upon rigid substrates such as the bladder-wrack (Folke 1991). Theoretically, it can be expected that the local disappearance of the bladder-wrack might result in a decreased recruitment of larvae of the free-swimming population. Conclusive data in this matter are lacking so far.

The mechanism of chlorate toxicity to plants is related to its three-D molecular similarity to nitrate (ClO_3 vs. NO_3). Thus, receiving waters that are nitrogen insufficient will be more vulnerable than receiving waters that are phosphorous insufficient.

There is a lack of information on the effects of chlorate in freshwater receiving pulp mill effluent. Such waters are generally phosphorus limited, and the conditions in a Northern Canadian river are quite different from the Baltic.

4.11 Metals

Metals enter pulp mills with the wood, chemicals and water. They may exit the mikll in the product, waste sludges or in the effluent. Only three mills in the Northern River Basins monitor metals contents of their effluents routinely. The data collected over a two year period are summarised in Figures 20 and 21.

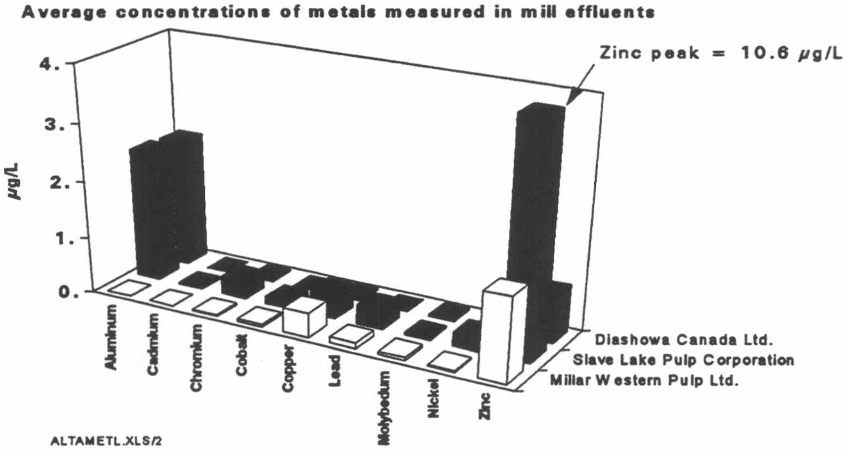


Figure 20 Average metals discharges

The few peak values in Figure 21, particularly for zinc, are so much above the average that one must question the reliability of the data. One mill in the Ontario MISA program measured unusually high zinc concentrations, but were never able to reproduce the data, despite extensive testing and investigation over several months (McCubbin 1991, p 139)

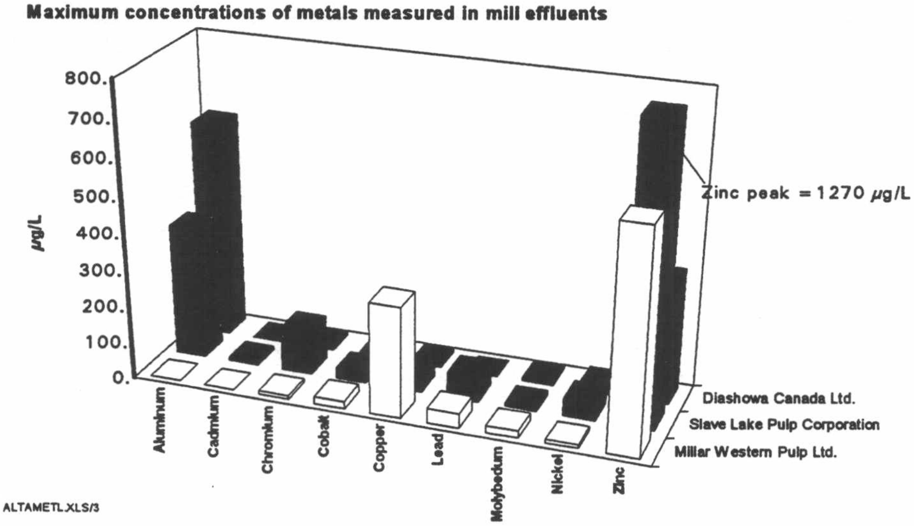


Figure 21 Maximum metals discharges

The most comprehensive data collection of metals discharged in pulp mill effluents is probably the MISA data base. The data collected on metals concentrations in the mill effluents during the whole twelve months of the 1990 effluent monitoring program (MISA 1991) are presented below for comparison with the Northern River Basins mills.

The average concentrations of each metal found in each sub-sector of the Ontario pulp and paper industry are shown in Figure 22 and the maximum values reported in MISA (1991) in Figure 23. It is noticeable that the highest metals discharge concentrations were from the corrugating mills, but there is no obvious explanation for this. One of these mills used exclusively virgin pulp at the time, while the other used about 35% wastepaper.

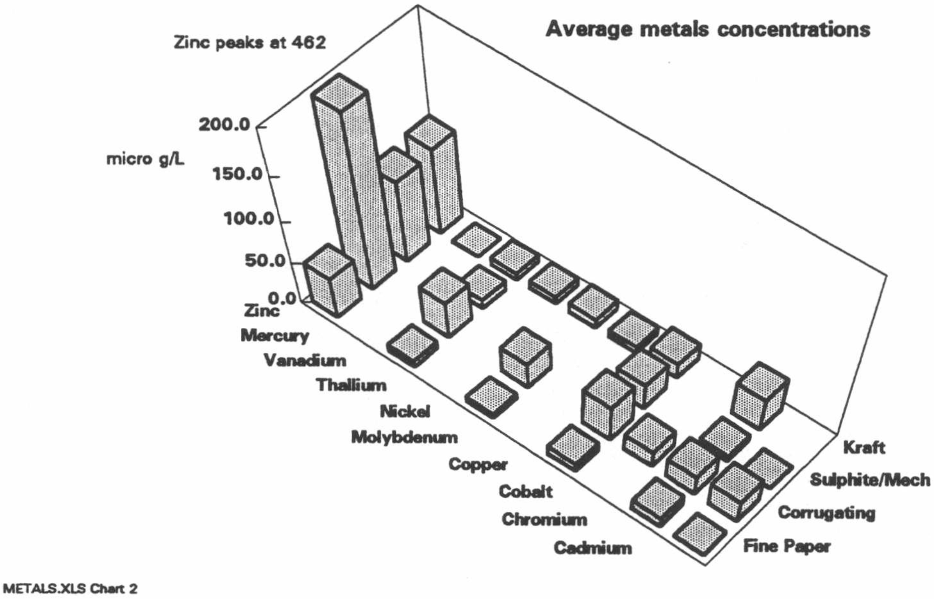


Figure 22 Metals concentrations in Ontario pulp and paper mill effluents (averages)

Copper, zinc, mercury and cadmium are known constituents of wood, because growing trees accumulate these metals when exposed to them. Cadmium and mercury are by far the most significant priority pollutants. No analytical results on the influent to the mills were included with the MISA data. It is possible that some of these metals were present in the raw water.

Aluminum is used worldwide to reduce COD, AOX and toxicity of effluents (Folke 1991). When used, proper clarifier operation is important to minimize discharges, but aluminum is hardly a priority problem except in particularly vulnerable receiving waters. Aluminum becomes very toxic to aquatic life at low pH values, i.e. an effect of acid rain. Ferric chloride or polyelectrolytes have been proposed as alternative agents for chemical coagulation in some cases, but would create significant sludge disposal problems.

Aluminum is widespread in nature. Sprague (1991) presented calculations showing that at least one Ontario newsprint mill which used aluminum salts (alum) extensively in paper making was actually a sink for aluminum, since the discharge concentration was lower than the natural water used in the mill.

Copper salts are generally used in wood protection, fungicides and toxic pigments in anti-fouling agents. Trace amounts of copper for use in co-enzymes are essential to all life, but in slightly higher amounts copper can be very toxic to fish and algae (Landner 1989). Copper tends to accumulate in phytoplankton, and to a smaller degree in higher organisms. In fish, copper is accumulated in liver, gills and bones.

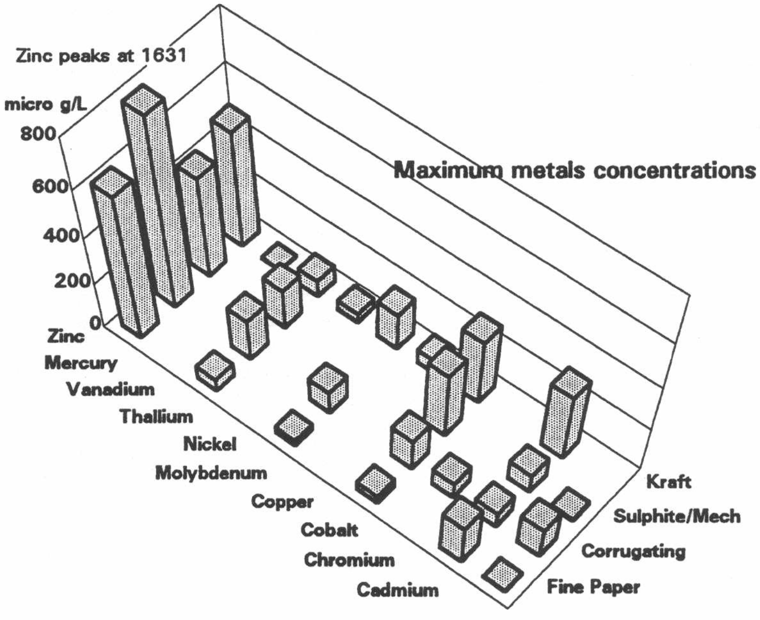


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Figure 23 Metals concentrations in Ontario pulp and paper mill effluents (maxima)

Mercury is used in older chlor-alkali plants and may be carried to the bleach plants by chlorine gas. In the past phenyl-mercury acetate was used for control of fungi in the pulp and paper industry, but has not been used in Canadian mills since the late 1960s. It is not known whether the only mill in the Northern River Basins which was operation at that time, at Hinton, ever used mercuric fungicides. Today the main use of mercury is in batteries, electronic instruments and for dental purposes. Mercury is bioaccumulates in its alkyl-mercury form (BCF > 100,000) and is very toxic to aquatic species. Although mercury can be concentrated in biosludge, it is most effectively controlled at the source, i.e. by closing chlor-alkali plants using mercury cells, by avoiding its use for dental purposes etc. In the past, most kraft pulp mills discharged mercury which entered the mill as a contaminant in purchased sodium hydroxide, but this problem was successfully addressed by the industry in the 1970s and early 1980s.

Zinc is the most widespread heavy metal in nature. High concentrations can be toxic, but low concentrations are essential to make proteins function. Its concentration in lakes depends on the acidity of the lake, and is thus connected to acid rain. The main source of zinc in pulp mill effluents is the wood. Zinc has a high acute toxicity to many species in laboratory testing. In nature this is seldom the case, because zinc is associated with humic materials and other organic matter and is hence non-bioavailable (SNV 1988). Furthermore, zinc is known to have an antagonistic effect on mercury and cadmium in fresh water lakes (Lindeström 1982). This means that the presence of zinc in the water body suppresses the accumulation and effects of mercury and cadmium. Therefore, one should be reluctant to reduce the discharge of zinc into water bodies that are contaminated with mercury and cadmium.

Zinc is often mentioned in literature on pulp and paper mill wastes, because zinc hydrosulphite was used for brightening groundwood pulps for newsprint in the past. Zinc was one of the first toxic substances discharged by the pulp and paper industry to be regulated by the USEPA, and has perhaps received a disproportionate amount of attention because of this. It is many years since zinc hydrosulphite was used in Canadian pulp and paper mills, and it has probably never been used in the mills in the Northern River Basins.

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APPENDIX A

TERMS OF REFERENCE

Although the complete Terms of Reference are provided in this Appendix, this document is only intended to satisfy part "1. Literature Review".

NORTHERN RIVER BASINS STUDY

SCHEDULE OF TERMS OF REFERENCE

PROJECT 2111-A1: EFFLUENT CHARACTERIZATION, PULP MILL DATA REVIEW

1. LITERATURE REVIEW

Objective

The general objective is to prepare a concise overview of generic CTMP and Kraft pulp mill effluent quality which will serve as a reference document for the Northern River Basins Study.

Requirements

1. Consider recent significant reviews of pulp mill effluent quality, particularly those of McLeay; Bonsor, Sprague, McCubbin; Procter and Gamble; PAPRICAN/Voss et al.; Kringstad, McKague.

2. Review pertinent scientific papers and ongoing research that provide relevant information more recent than the above reviews.

3. Prepare a concise overview of CTMP and kraft pulp mill effluent quality, based on the above, which organizes the information around pertinent subjects including (but not necessarily limited to):

    - effluent constituents/parameters
    - type of mill, production level, CLO_2 substitution level, wood furnish, etc.
    - volume of effluent
    - effluent treatment characteristics, including type of process, hydraulic retention time, etc.

4. Submit a draft report by April 30, 1992. Prepare a final report incorporating review comments three weeks after receipt of the reviewed draft report. Supply ten (10) copies and the camera ready original of the final report.

2. DATA COMPILATION

Objective

The general objective is to compile recent, pertinent data held by Alberta Environment, Environment Canada, and Fisheries and Oceans Canada on the quality and quantity of pulp mill effluents in the Peace and Athabasca River Basins.

Requirements

1. Assemble pulp mill effluent data, whether electronic or hard copy, held by Alberta Environment and Environment Canada. Focus on data obtained since mill start-up, expansion, or upgrade (about 1990 for most mills).

2. Enter all data for a selected pulp mill in Lotus 1-2-3 format, and prepare tables, graphs and statistics of the data. Review this output with the Project Manager.

3. Modify the data system as agreed with the Project Manager. Enter all remaining data for pulp mills and prepare appropriate tables, graphs and statistics.

4. Assess the data and provide a brief interpretation of any key points and findings.

5. Prepare a concise technical report on the data system including a guide for users, dictionary, and any other pertinent specifications of the electronic data submission. Submit this report plus compiled data, tables, graphs and statistics and interpretations in draft form by May 30, 1992. Prepare a final report incorporating review comments three weeks after receipt of the reviewed draft report. Supply ten (10) copies and the camera-ready original of the final report.

3. QUALITY ASSURANCE

Objective

The Contractor will prepare a document or guide containing all of the information and procedures for sampling, analyzing and reporting to ensure consistent, reliable data on effluent quality is generated by industry.

Requirements

Prepare a procedures manual for pulp mill effluent sampling, analysis and reporting, which includes (at a minimum):

1. Layouts for each mill clearly identifying the sampling locations specific to each parameter to be sampled (plant-size layout information is obtainable from Alberta Environment).

2. Listing of each parameter to be sampled, the location to sample, the type of sample (grab or composite), sample volume, preservation techniques, sample transport, maximum storage time, labelling and any other information. This should be broken down on a mill specific basis - reflecting the different parameter requirements of each mill.

3. Example chain of custody form and checklist to be used for those samples (chlorinated phenolics, dioxins, etc.) where it would be deemed necessary.

4. Appendices clearly outlining and containing the lab methods and protocol to be used for each parameter and any specific conditions to ensure consistent results.

5. The type of data reporting format and data checking/verifying to be performed on all data.

6. The type of lab QA/QC information which should accompany each data report.

7. The protocol that should be followed for those samples or analysis that fail QA/QC specifications.

8. The protocol that should be used for split sampling between industry and government.

9. The procedures to follow up and resolve inconsistent split sample results.

Submit a draft report by April 30, 1992. Prepare a final report incorporating review comments three weeks after receipt of the reviewed draft report. Supply ten (10) copies and the camera-ready original of the final report.

The Department will attempt to obtain and provide access to information requested and/or required by the Contractor which is, or will be, held by Alberta Environment, Environment Canada and the Northwest Territories.

APPENDIX B

GLOSSARY

Glossary

This glossary is intended to assist readers unfamiliar with the technical terminology in the report. Many terms are standard in the fields of pulp and paper technology or environmental science, and are presented here for the readers convenience. Readers are recommended to refer to Smook (1990) for a more complete glossary of pulp and paper industry terminology.

Some terminology is not at all standardised. The authors have attempted to define all such terms used in the report in this glossary, in the context of their use herein.

2,3,7,8-TCDD	Tetrachlorodibenzo-p-dioxin.
2,3,7,8-TCDF	Tetrachlorodibenzofuran.
Activated sludge process	Biological treatment where micro-organisms are decanted after the principal reaction vessel and recycled to the effluent stream. Also known as "Activated Sludge Treatment" or "Waste Activated Sludge Treatment".
Active chlorine multiple	In a mixture containing molecular chlorine and chlorine dioxide. This quantiity represents the oxidizing power of the molecular chlorine and chlorine dioxide expressed as molecular chlorine equivalents. The active chlorine multiple is calculated as follows: $\frac{(Cl_2 + ClO_2 * 2.63)\% \text{ on o.d. pulp}}{\text{Kappa number of the unbleached pulp.}}$
Acute	With reference to toxicity, happening quickly, usually within 4 to 7 days for fish. Can describe an effect, or the duration of a test, e.g. an acute test. An acute effect could be a mild or sublethal one.
ADI	Acceptable Daily Intake. The amount of a substance that is considered "safe" to take into the body, on a daily basis, for a lifetime. This is almost always for humans. The value of ADI is decided by a regulatory body, after considering relevant scientific data.
Aerated stabilization basin	Biological treatment process characterized by absence of sludge recycle and by a long hydraulic retention time (typically several days).
Aerobic treatment	Refers to biological processes to treat effluents, in which the principal reactions take place in the presence of dissolved oxygen.

Air dry	The term "Air dry" refers to pulp and signifies 90% dry fibre and 10% moisture (1 ADt = 900 kg OD pulp). The abbreviation t_{90} is frequently used in Scandanavia.
Anaerobic treatment	Refers to biological processes for effluent treatment in which the principal reactions take place in the absence of dissolved oxygen.
AOX	Adsorbable Organic Halogens. A measurement of the amount of chlorine attached to organic substances. The amount of AOX measured in a sample according to a German standard test (DIN 39-409) or similar tests. Chlorine is the only halogen used in significant quantities in pulp mills. The measurement is expressed as weight of the halogens (chlorine), not the weight of the entire organic molecule.
ASB	Refer to aerated stabilization basin.
AST	Activated Sludge Treatment. Synonymous with activated sludge pocesss.
Atomic Chlorine	refers to any form of chlorine, combined with other elements or molecular *(qv)*
Atomic chlorine multiple	In a mixture containing molecular chlorine and chlorine dioxide, this quantity represents the total chlorine present in the system. Atomic chlorine refers to any form of chlorine, that is, molecular chlorine and chlorine combined with other elements; eg. ClO_2, NaOCl, etc.combined or molecular. The atomic chlorine multiple is calculated as follows: $\frac{(Cl_2 + ClO_2 * 2.63/5)\% \text{ on o.d. pulp}}{\text{Kappa number of the unbleached pulp.}}$
AVG_{30}	30 day rolling average performance of a treatment plant: $AVG_{30} = \frac{\sum_{i=1}^{n} x_i}{n}$ where n= number of data points in that 30 day period. The term is used to evaluate the performance of a treatment plant. Outliers are included in the measure, so that in the case of extreme outliers, the AVG_{30} may exceed the MAX_{95} which excludes outliers. Performance may refer to concentration, mass or other effluent characteristic measured on a 24 hour composite sample of mill effluent.

AVG_{95}	Annual 95th percentile of the distribution of daily performance of a treatment plant. Essentially the long term average discarding the top and bottom 2.5% of values. An approximate calculation has been used in this report: $AVG_{95} = \frac{\sum_{i = (0.025 * n)_{\text{o dec.}}}^{(0.975 * n)_{\text{o dec.}}} x_i}{n}$ where n = number of data points in that 30 day period. Performance may refer to concentration, mass or other effluent characteristic measured on a 24 hour composite sample of mill effluent.
BCTMP	Bleached Chemi-Thermomechanical Pulp.
Benthic	An adjective describing organisms that live on the bottom in a body of water, or non-living things that are on the bottom, or part of the bottom. Most often used for "benthic invertebrates". Benthos is a noun referring to the assemblage of organisms that live in, on or near the sediment or other substrate of a body of water.
Bioaccumulation	A general term, meaning that an organism stores within its body, a higher concentration of a substance than is found in the environment. This is not necessarily harmful. For example, freshwater fish must bioaccumulate common salt if they are to live. Many toxicants, such as arsenic, can be handled and excreted by aquatic organisms, so that they are not included among the dangerous bioaccumulative substances.
Bioassay	This term can be used for toxicity tests with fish, but it is probably best to reserve it for the formalist procedures used in testing the potency of drugs (pharmaceuticals).
BK, BKM, BKME.	Abbreviations for Bleached Kraft, Bleached Kraft Mill, and Bleached Kraft Mill Effluent. All refer to a pulp mill that operates by the kraft or sulphate process, and bleaches some or all of the product.
Black liquor	A liquid in the kraft process, composed of spent pulping chemicals and wood residues. Weak black liquor refers to concentrations under 20% solids, strong black liquor to concentrations over 50% solids.
Bleaching	In the context of this report, refers to raising the brightness of chemical pulps by selective chemical removal of residual lignin and other coloured materials. Refer also to "brightening". Most bleaching processes use chlorine compounds.

Blow tank	A tank which receives the pulp discharged (blown) from the digester in a chemical pulp mill
BOD	Biochemical Oxygen Demand is a property of water or wastewater, determined by measuring the quantity of oxygen consumed by a sample under controlled conditions (20 deg C, neutral pH) for a defined time period. The most commonly used period in North America is 5 days which is sometimes written as BOD5. BOD is expressed as mg/L ("parts per million"), the same unit as is customary for dissolved oxygen, or simply as a weight, as in "kg of BOD per tonne of pulp".
Bone dry(BD)	Outdated term for oven dry (qv).
Bound soda	In brown stock washing, soda that is retained in the pulp by physical/chemical forces, is referred to as bound soda. Mill control tests sometimes exclude bound soda in routine tests and account for it by a predetermined factor. Normally expressed as Na_2SO_4.
Brightening	Chemical modification of lignin and other coloured components of high yield pulps in the mechanical-sulphite spectrum to raise brightness. The coloured components are not removed, in contrast to bleaching processes (*qv*). Brightening processes do not use chlorine compounds.
Brightness	A measure of the whiteness of paper as compared to a standard.
Brown stock	Kraft slush pulp prior to bleaching. Unbleached pulp from an alkaline pulping process.
Carcinogenic	Capable of causing cancer.
Caustic	Commonly used name for sodium hydroxide.
Caustic extraction	Bleaching stage where highly coloured organics are dissolved with alkali, normally NaOH.
Causticiser	A tank used to allow calcium hydroxide and sodium carbonate to react and form sodium hydroxide and calcium carbonate.
Chemical pulp	Wood pulp which has been manufactured by chemically separating the fibres that make up solid wood. Kraft and sulphite are the most common examples. The term chemical contrasts with mechanical, (qv). Since the 1970's, a significant and increasing proportion of wood pulps have been hybrid mechanical/chemical.

Chlorine-compound-free	Pulp bleached without any chlorine compounds. In a traditional bleach plant this would imply elimination of use of chlorine, chlorinie dioxide and hypochlorite.
Chlorine dioxide substituton	Although an unprecise expression, this term generally refers to the practice of replacing the bleaching function of molecular chlorine with chlorine dioxide.
Chlorine equivalent	Refer to "Equivlalent chlorine"
Chlorine free	Poorly defined term. Some users mean pulp which is bleached without the use of molecular chlorine, when it usually refers to pulp bleached with 100% chlorine dioxide substitution in the chlorination stage. Others mean chlorine-compound-free when using this term. Refer also to molecular chlorine.
Chronic	Long-lasting or continued. Can refer to the effect or the duration of exposure. In mammalian toxicology, usually signifies exposures lasting at least one-tenth of a lifetime. In aquatic toxicology, is sometimes used to mean a full life-cycle test.
CMP	Chemimechanical Pulping. Chips are pretreated with a chemical at an elevated temperature prior to atmospheric refining to produce a pulp yield over 80%.
COD	Chemical Oxygen Demand. A similar concept to BOD, except that the measurement is of oxygen consumed, based on rapid chemical oxidation of the sample. BOD and COD are generally poorly correlated.
Condensate	Water condensed from steam which has come into contact with a surface at a lower temperature during a process. Contaminated or foul condensate usually refers to a condensed vapor from evaporation of black liquor or other spent pulping liquor.
Coniferous trees	Cone-bearing and evergreen trees, such as spruce, hemlock, Douglas fir, pine.
Consistency	Weight per cent of moisture free, or air dry (as specified) fibres in a suspension of pulp fibres in water.
Conventional bleaching	Refers to the bleaching of kraft pulps obtained by conventional pulping to market brightness by the sequential use of the following stages: chlorine with no more than 10% substitution of molecular chlorine with chlorine dioxide; sodium hydroxide with or without oxygen; chlorine dioxide or sodium hypochlorite or both; sodium hydroxide; and chlorine dioxide.

Conventional pulping	Conventional pulping refers to the pulping of softwoods to obtain a bleachable grade of pulp with a lignin content measured as 30 Kappa number, plus or minus 5 units, using co-current continuous digesters or conventionally blown batch digesters.
Cook	Normal term in the pulp and paper industry for the chemical pulping process in the digester where the fibre is separated from lignin by chemicals under conditions of elevated temperature and pressure.
CTMP	Chemi-thermomechanical pulping. Similar to TMP. Chemical is added to the chips either prior to or during the presteaming of the chips with first-stage refining at an elevated temperature of over 100 deg C and any subsequent refining at atmospheric pressure. Retention time and pressure in the presteaming device is normally such that yields are in the 90% plus range.
DBD	Dibenzo-p-dioxin. A precursor present in certain raw materials, when chlorinated it can be converted to TCDD.
DBF	Dibenzo-p-furan. A precursor which is detectable in chips, unbleached pulp and raw material supplies or additives. When chlorinated it can be converted to TCDF.
Decanter (turpentine)	A tank used to separate turpentine from condensate.
Deciduous trees	Hardwoods or broadleaf trees which lose their leaves in winter, such as alder, maple, oak, birch, cottonwood.
Decker	An apparatus for dewatering pulp by filtering the fibres out on a mesh covered drum.
Defiber	Break wood down into separate fibres, usually by mechanical means, to make wood pulp.
Dilution factor	A measure of the efficiency in pulp washing when the pulp is well washed. Mathematically the dilution factor is the ratio of incoming water consumed to oven dry pulp washed.
Dissolved solids	Substances that are dissolved in the water, and will pass through the filter used in the standard method of measurement. They are measured by evaporating the water and weighing the solids that are left behind.
DO	Dissolved oxygen, normally measured in milligrams/litre and widely used as a criterion of receiving water quality.

EC50	Median effective concentration. As LC50, except that it may apply to any effect, lethal or non-lethal. The effect as well as the exposure-time must be specified.
Ecosystem	An interacting system of all living organisms in a circumscribed region of similar characteristics, and the non-living substrate, nutrients, energy, and other environmental components.
Effluent	A waste material discharged into the environment. In this report, the effluent refers to the liquid waste with its suspended and dissolved materials, which is discharged into surface waters.
Effluent standard	A regulation concerning the quality of a liquid waste, or the concentrations of substances that it may contain. This standard applies "at the end of the pipe".
Elemental chlorine	Refers to chlorine used to bleach pulp when applied as a component of some other compound, normally chlorine dioxide, hypochlorite (sodium or calcium), or chlorine monoxide. The authors have generally avoided this term in the report, using "Atomic Chlorine" *(qv).*
EMPPL	Effluent monitoring priority pollutants list. A list of substances considered environmentally significant by the Ontario Ministry of the Environment. Very similar to the USEPA Priority Pollutants List.
EOX	Extractable organohalogenes using a non- or semipolar solvent such as hexane or ethylacetate for the extraction. Extractable chlorines (EOCl) or persistent, extractable organohalogenes are variations of the analytical procedure.
Equivalent chlorine	The term "chlorine equivalent" is widely used to define the "equivalent bleaching power" of the popular bleaching chemicals. It refers to a simple comparison of free electrons available to oxidize lignin in the bleaching reactions. Common values are: Chlorine = 1 Oxygen = 2 Hypochlorite = 2 Hydrogen Peroxide = 2 Chlorine Dioxide = 2.63 Ozone = 3 In practice, the actual values vary somewhat, but the above values are useful for rapid estimates. With the disappeance of chlorine from an increasing number of bleach plants, the term **"oxidizing equivalent"** is being used rather than "chlorine equivalent"

Exit	In the context of this study, refers to materials leaving a process, system or plant.
Extended cooking	A sub-set of extended delignification processes which are implemented in the digester.
Extended delignification	Refers to a variety of processes developed over the past twenty years to extend delignification of kraft pulps beyond the traditional levels of Kappa of about 30 for softwoods and 15 for hardwoods, without using chlorine compounds As used in this report, it would include extended cooking (*qv*), oxygen delignification, ozone delignification and any other delignification process prior to the bleach plant.
F:M ratio	Food to Microorganism ratio. Term used in biological effluent treatment to designate ratio of "food" (normally expressed as BOD) to biomass in a biological reactor
Fillers	Minerals, synthetic mineral-like material used to fill voids which occur between fibres. Many printing and writing papers contain substantial amounts of filler. Standard newsprint does not contain fillers.
Filter	A device used to separate suspended solids from a liquid or gaseous carrier.
Filtrate	The liquid that passes through a filter. In pulp processing, filtrate is usually white water.
Free soda	In brown stock washing, soda that can be washed from the pulp by a standard washing and filtering test. Free soda and bound soda constitute the total soda loss . Synonymous with washable soda.
Furnish	The specific mixture of raw materials, both pulp and chemicals, from which a particular grade of paper is manufactured, ready to be delivered to the paper machine.
Green liquor	A liquid in the kraft process composed of the chemicals obtained from the recovery furnace. Primarily sodium sulphide and sodium carbonate in aqueous solutions.
Grits	In kraft mills, the inert lime rejected from the slaker in the recausticising department, includes impurities such as sand and unconverted limerock or limemud.
Groundwood or GWD	Stone Groundwood. Commonly called groundwood pulp. Logs are torn into separate fibres by being forced into contact with a rotating grindstone. The axes of the log and stone are parallel. The oldest widely used pulping process. May also refer to Refiner Groundwood.

Hemicellulose	Portion of wood fibre consisting of sugar-like substances intimately associated with cellulose in the fibre wall and removed mainly in the cooking process.
Hog fuel	Term for wood waste fuel widely used in pulp and paper industry boilers. It includes some of the following: bark; sawdust; reject chips; sticks; branches; cutoffs; and other sawmill and wood harvesting wastes. A major component is usually bark.
HYS	High-yield Sulphite. Normally refers to sulphite pulping in the yield range of 55% to 80%.
In-plant	As used in this report refers to water pollution abatement measures which rely primarily on modifications to the production process or operating procedures. Examples include reuse of water, replacement of liquid ring vacuum pumps with dry pumps, replacement of open screens with closed screens to reduce accidental spills, improved process control and operator training.
K No.	Synonymous with Permanganate No. (*qv*).Permanganate No. A mill test that measures the degree of cooking, or delignification of kraft pulp. Although, it is related to lignin content, it does not have a linear relationship to it. For both high yield and low lignin content pulps, the Kappa number was developed to provide a linear measure of lignin over a wide test range.
Kappa Number	A measure of lignin in pulp, according to a standard laboratory procedure. Bleachable grades of unbleached kraft pulp generally have a Kappa number from 5 to 35, depending on the wood species and the extent of delignification. When extended delignification is practiced in a mill, the wide range of lignin content is more accurately reflected by the Kappa number than by the K number.
KM, KME	Kraft mill and kraft mill effluent. See BK.
Knotter	A type of screening device used to separate knots and other large, oversized and unwanted material from wood pulp.
Kraft pulp	Pulp produced by the kraft process. Also known as sulphate pulp.
LC_{50}	Median lethal concentration. The concentration of a substance that is estimated to kill half of a group of organisms. The duration of exposure must be specified (e.g. 96-hour LC_{50}).
Lethal	Causing death, or sufficient to cause death.
Machine dry	The degree of dryness of pulp, or more commonly paper, as it leaves the drying machine.

Machine finish (MF)	The normal finish applied to the paper when manufactured on a paper machine equipped with conventional dryers (differentiated from a Yankee dryer).
Market pulp	Pulp products such as bleached or chemical pulps or mechanical pulp sold to customers outside the producing company for machine furnish.
MAX_{95}	Annual maximum of the 95th percentile of daily performance of a treatment plant. Excludes the 5% most extreme values that reflect malfunctioning of the treatment plant or the mill. An approximate calculation has been used in this report: $MAX_{95} = x_{(i=0.95*n)}$ where n = number of data points in the period. Daily performance is better than MAX_{95} 95% of the time. Performance may refer to concentration, mass or other effluent characteristic measured on a 24 hour composite sample of mill effluent.
Maximium daily discharge	Highest value of concentration, mass or other effluent characteristic measured for one day on a 24 hour composite sample of mill effluent.
MBC	Modified Batch Cooking. Generally refers to modifications to batch cooking processes intended to reduce the Kappa number of the product while preserving or enhancing strength.
MCC	Modified Continuous Cooking. Generally refers to modifications to continuous cooking systems manufactured by the dominant technology vendor (Kamyr Inc), to reduce the Kappa number of the product while preserving or enhancing strength.
Mechanical pulp	Wood pulp which has been manufactured by physically tearing apart the fibres that make up solid wood. Groundwood, TMP and RMP are the most common examples. The term mechanical contrasts with chemical (qv). Since the 1970's, a significant and increasing proportion of wood pulps have been hybrid mechanical/chemical.
mg/L	Milligrams of the substance in question, contained in one litre of solution. Roughly speaking, parts per million. This is the common unit for assessing water quality.
MISA	Municipal/Industrial Strategy for Abatement. Ontario Ministry of the Environment program which has a principal goal of reducing the discharges of water pollutants, particularly toxic and or persistent substances.

ML(V)SS	Mixed liquor suspended solids. Term used in biological treatment referring to the concentration of suspended solids in the biological reactor. "V" refers to the Volatile fraction, and is used to indicate the concentration of organic matter.
Molecular chlorine	As applied to bleaching and substitution refers to industrially pure Cl_2, normally applied to the pulp in gaseous form. The term is used to distinguish this from chlorine used in the form of a compound such as chlorine dioxide or sodium hypochlorite.
Molecular chlorine free	Refers to pulp bleached without use of molecualr chlorine (chlorine compounds may be used).
Molecular chlorine multiple	In a mixture containing molecular chlorine and chlorine dioxide, the molecular chlorine multiple represents the chlorine present in its molecular form and is calculated as: [Cl_2, % on OD pulp]/Kappa number of the unbleached pulp. If no chlorine dioxide is mixed with the chlorine, then active, atomic and molecular chlorine multiples are all equivalent to one another.
Mutagen	A chemical that causes an alteration of the inherited genetic material, i.e. the DNA of the genes. In the narrow sense, the chemical alters the genetic material of paternal or maternal sex cells.
NCASI	The National Council for Air and Stream Improvement - a US environment research organization sponsored by the US pulp and paper industry.
NCG	Non-condensable gases are gases emitted from several parts of the kraft pulping process which do not condense in the commonly installed condensing equipment. TRS and/or methanol are the predominant components.
NOEC	The no-observed-effect concentration. The highest concentration in a sublethal test that does not cause a significant adverse effect, in comparison to the controls.
NOEL	No-observed-effect level. Similar to NOEC

Non-detectable	Refers to failure to detect a substance when analysing a sample. The minimum level of detection depends on many factors in addition to the characteristics of the substance itself, so the threshold of detection cannot be defined simply. In some cases, (e.g. Environment Canada 1991 proposed regulations for dioxins) "non-detectable" refers to a defined, normally very low, concentration. In Ontario, the term "non-detectable" is defined with reference to the accepted detection limit for a defined analytical procedure. The lower limits of detection of most pollutants are decreasing rapidly, due to extensive research, so that caution is required in interpreting the term "non-detectable"
NPOX	Non-purgeable organic halogen (See also AOX, POX)
NSPS	New Source Performance Standards. Term used by the US EPA and some states to refer to a set of effluent and atmospheric emission standards that new plants must comply with. Generally very stringent.
OD	Refer to oven dry.
Oligotrophic	The condition of a lake which has low productivity because of lack of nutrients. The water would be clear. Lake Superior is oligotrophic.
Organochlorine	Chlorine which is combined with organic molecules or bound to them. Many organochlorines are formed in bleaching processes whenever chlorine or chlorine based compounds are used. Thousands of chlorinated organic compounds exist, but only a small proportion of those in pulp mill effluents have been identified. AOX is one of many ways of measuring organochlorines, and it expresses the result the weight of organically bound chlorine, not the weight of chlorinated organic molecules.
Oven dry (OD)	Pulp or paper dried in an oven by a standard laboratory procedure to the point where it contains no moisture. The term Bone Dry (BD) is commonly used synonymously (this is now obsolete). When applied to market pulp, oven dry weight divided by 0.9 by definition of the pulp (see Air dry) equals the air dry weight.
Oxidation efficiency	(As applied to kraft black liquor) Percentage reduction of sodium sulphide concentration in the black liquor after it has been oxidized by blowing air or oxygen through the liquor, as applied to black liquor oxidation processes.
Oxidising equivalent	Refer to equivalent chlorine.

Particulate emissions	Generally, this consists of all solid material discharged from a stack or vent. Specifically the particulate flow is defined by a standard test method. Particulate emissions are usually expressed as mg/m3.
PCDD	Polychlorinated dibenzo dioxins. Refers to a family of substances. Refer also to 2,3,7,8-TCDD
PCDF	Polychlorinated dibenzo furans. Refers to a family of substances. Refer also to 2,3,7,8-TCDF
PGW	Pressurized stone groundwood. Similar to groundwood, except that the logs are ground under pressure at temperatures around 100 degrees C. This process was developed recently.
pH	A measure of the acid or alkaline nature of water or some other liquid. Specifically, pH is the negative logarithm of the hydrogen ion concentration (H3O+). Practically, pH 7 represents a neutral condition in which the acid hydrogen ions balance the alkaline hydroxide ions. Values of pH below 7 represent acid conditions and values above 7 are alkaline. A change of one unit, for example from 7 to 6, represents a ten-fold increase in hydrogen-ion activity, and thus a ten-fold increase in the "acidic" nature of a water. Soft northern waters would typically range from pH 6 to 7.5; hard waters would usually be close to pH 8. The pH of the water can have an important influence on the toxicity of chemicals in effluents.
Pollution	With reference to water pollution, the addition of something to the water, resulting in a measurable effect, which is deleterious to some use of the water by living organisms including humans.
POX	Purgeable organic halogen (see also AOX, NPOX)
Precipitator (electrostatic)	A piece of equipment which uses electrostatic forces to recover solids from a gas stream by the use of high voltages applied to plates or wires in the stream.
Precursors	A group of unchlorinated dioxins/furans which have the potential to be transformed into chlorinated dioxins/furans during combustion or treatment with elemental chlorine such as in the pulp bleaching process.
Pretreatment	Describes initial treatment processes before an effluent reaches primary treatment. The processes are designed to remove grit, coarse material and debris, to neutralize acid or alkaline wastes, and to equalize the effluent characteristics and flows. This is carried out by mixing the collected effluent streams and directing occasional large flows or concentrated streams to spill tanks or basins. This is a normal part of pulp mill operations.

Primary treatment	This is intended to remove suspended solids from the effluent and normally includes dewatering the recovered settled solids or sludge to facilitate disposal to landfill or by combustion. Primary treatment is a pre-requisite for most secondary treatment processes.
PRMP	Pressure refined mechanical pulp. Similar to PTMP except that the chips are not presteamed at an elevated temperature prior to refining which is customary for TMP and PTMP systems.
PTMP	Tandem or "pressure/pressure" thermomechanical pulping. Similar to TMP except that both primary and secondary stages of refining are pressurized. This approach is becoming so common in new installations that the term "TMP" may be used.
RDH	Rapid Displacement Heating. Process modification to improve heat economy and lower product Kappa number for batch pulping systems in kraft mills. This is a Beloit process.
Recovery furnace	A unit used to burn recovered cooking liquor to produce steam and to recover cooking chemicals. Frequently known as the recovery boiler.
Refiner	As applied to pulping wood, or modifying pulp fibres in paper making. A device which separates fibres by passing the wood chips through a narrow gap between rotating and stationary plates with serrated surfaces. Since the early 1970s, refiners have become the mainstay of most pulping processes except kraft.
Refiner groundwood	Mechanical pulp made by separating wood chips into discrete fibres in a refiner.
Residue filtered	(RSF) Term used in many MOE documents for dissolved solids.
Residue particulate	(RSP) Term used in many MOE documents for suspended solids (q.v.).
Retention aid	Generic group of chemicals used in small quantities to improve the retention of fine fibres and fillers on paper machine wires. Widely used in fine papers, they may be used in almost any type of paper mill.
Reversion	Tendency of a pulp or paper sheet to lose brightness with time. Typically several brightness points are involved, over time spans of days to months.
RMP	Refiner mechanical pulp. Atmospheric refining with no pretreatment.

Saveall	Equipment used to recover fibres and filler from the white water. Usually a wire-covered rotating drum or wire-covered discs. Vacuum is employed to draw the water through the wire. Today, the "wires" are usually plastic. There are several other types of save-alls working on a sedimentation or flotation principle.
Screen room	A common term for the screening and cleaning department which usually follows a pulping operation.
Scrubber	A piece of equipment used to remove certain gases or solids from a gas stream normally utilizing a spray of liquid, such as water or an aqueous solution of reactant. Dry scrubbers are used for some applications.
Secondary treatment	A stage of waste treatment in which micro-organisms decompose organic constituents in the effluent. In the process, they use oxygen for their metabolism and to oxidize the waste material. Most secondary treatment processes also reduce toxicity.
Shives	A small bundle of fibres that has not been separated completely in the pulping operation.
Shrinkage	A term normally applied to the pulp loss in bleaching due to removal of lignin. Usually expressed as percent. Pulp typically shrinks about 7% on bleaching. It also refers to losses in deinking.
Sludge filter	A piece of equipment used to concentrate suspended solids by removing water from them. The solids are recovered after settling in a clarifier.
Smelt	The inorganic chemicals that are obtained in molten form from the recovery furnace.
Soda loss	The loss of sodium salt due to imperfect washing of the pulp, or in the recovery of sodium compound in the chemical recovery system. For pulp washing the measure should include both bound and free soda, and for clarity reports should state what is included. The intent is to include all soda leaving with the pulp..
Stock	A general term for a suspension of pulp fibre in water; usually implies a consistency between 0.2% and 15%. A papermaker's terms for the beaten, refined and mixed materials (furnish) in a water suspension as supplied to the paper machine (also called "stuff").
Stock preparation	A term for the operation which occurs between pulping or bleaching and formation of the web on the paper machine. The operations may include blending of several pulps, addition of colour, filler and other materials and chemicals.

Sublethal	A concentration or level of a substance that would not directly cause death. An effect that is not directly lethal.
Sulphate pulp	A term that is often used for kraft pulp, especially in Scandinavian literature.
Sulphidity	In white liquor, the percentage of sodium sulphide to sodium sulphide plus sodium hydroxide, with all compounds expressed as sodium oxide.
Sulphite pulp	A chemical pulp which is manufactured by separating the fibres of wood chips by cooking (qv) them in a hot solution of sodium, magnesium, calcium or ammonium sulphite and sulphur dioxide under pressure.
Suspended solids	Particles of matter suspended in the water. Measured as the oven dry weight of the solids, in mg/L, that are retained on a standard filter paper. Less than 25 mg/L would be considered clean water, while an extremely muddy river might have about 200 mg/L of suspended solids. The term "Total Suspended Solids" (TSS) is now the correct term to use in North America, and it is rare to report suspended solids other than as Total Suspended Solids, although the suspended solids component of a wastewater can be broken down analytically into many subdivisions if desired. In Sweden the TSS analysis is carried out with 70 micron wire filter which is much more open than the APHA standard used in North America and results in lower TSS values.
t_{90}	Refers to air dry tonnes. Commonly used in Scandinavian literature, but little used in North America where the normal abbreviaiton is ADt.
TCDD/TCDF	In this report TCDD/TCDF refers to 2,3,7,8-TCDD and 2,3,7,8-TCDF.
TEF	Toxicity Emission Factor. A measure of the amount of toxicity discharged in an effluent. It is the toxicity of the effluent multiplied by the volume of effluent discharged for each tonne of production at the mill. The calculation is usually based on the lethal concentration of the effluent (LC50) to trout or other fish. Since toxicity is the reciprocal of LC50, TEF is equal to 100 times the number of cubic metres of effluent discharged per tonne of product, divided by the LC50 as a percentage. The numerical value of TEF may be thought to represent the number of m^3 of "just-barely-lethal" effluent that are discharged for each tonne of product. (TEF may also be obtained by dividing the TER by the daily production.)

TER	Toxicity Emission Rate. Similar to TEF, but a measure of the amount of toxicity discharged in an effluent during unit time, usually during one day. It equals the toxicity of the effluent multiplied by m^3 of effluent per day. TER is equal to 100 times the number of m^3 of effluent per day, divided by the LC50 as a percentage.
Tertiary treatment	This is a final process of effluent treatment after primary and secondary treatment steps. It embraces a broad range of processes used to remove items such as colour, odour, taste, and toxicity. It is often used for removing nutrients, especially phosphorus, from municipal effluents.
TMP	Thermomechanical pulp. Chips are steamed and refined at an elevated temperature in a "primary" refiner, normally followed by second-stage atmospheric refining.
TOCl	Total organically bound chlorine. Quantity of organically bound chlorine in a sample, determined according to a method described by Sjostrom (1982). This is similar to the measurement of AOX, except that the TOCl is sorbed onto XAD (ion-exchange resin), instead of activated carbon. This is a measure of the total chlorine in organic compounds, many of which may be unidentified. This term has been replaced by AOX in most countries.
TOX	Abbreviation commonly used to refer to the Total organic halogen analytical procedure defined by APHA et al (1989). This provides a measurement that is essentially the same as AOX.
Toxic	Generally, describes a substance, a dose, or a concentration that is harmful to a living organism by means of chemical action. **In the context of this report, "toxic" refers to acute lethality to rainbow trout (96-hour LC_{50}) or *daphnia magna* (48-hour LC_{50}), as determined by standard tests,** unless otherwise noted. It bears little or no relationship to the toxicity of an effluent to humans, toxic effects on algae, plants or bacteria, or the persistence or bioaccumulative properties of the substances.
Toxicity	The quality or action of being toxic. The action of causing severe biological damage.
Toxicity test	Any test in which the harmful action of a substance is measured by observing the effect it has on a living organism, organisms, or some living system.
Toxicology	A branch of science. A discipline studying the actions and mechanisms of toxic substances. The word could also be used to describe the body of knowledge that has been accumulated, with the implication that the information is at a fairly high scientific level.

TRMP	Thermo-refiner mechanical pulp. Chips are presteamed at a temperature over 100 deg C and then refined at atmospheric pressure.
TRS	Total reduced sulphur. A general term for sulphur gases emitted from the kraft process, excluding sulphur dioxide and trioxide. Generally considered to include hydrogen sulphide, dimethyl sulphide, dimethyl disulphide and methyl mercaptan. These gases are the principal cause of the classic kraft mill odour. They are generated by the reaction of sodium sulphide with some of the wood components. TRS is normally expressed as elemental sulphur.
TSS	Total suspended solids (qv). See suspended solids.
Turbidity	An attribute of water, causing scattering of light as it passes through the water. Usually caused by fine suspended particles, but may be caused by colour.
ug/L.	Micrograms per litre. Roughly speaking, a part per billion, or only one-thousandth of the strength of one mg/L.
USEPA	United States Environmental Protection Agency.
Washable soda	Refer to free soda.
Water quality criterion	(Plural: criteria) In the broad sense, a criterion is a number which may be used for judgement. In aquatic toxicology, w.q.c. commonly means the highest concentration which is not expected to cause an appreciable effect on an aquatic system or its users. The number is derived from available scientific data. There may be several sets of criteria for the same substance, e.g. for drinking water, industrial use, etc. These criteria always apply after dilution in the receiving water.
Water quality objective	Similar to water quality standard except that it is merely an expression of a desirable goal, and does not have the same force as a regulation, nor is there a penalty for transgression.
Water quality standard	A maximum concentration of a pollutant, or a maximum or minimum level of some characteristic such as pH, which is not to be transgressed in a body of water. These numbers are promulgated by a government or its agency by means of laws or regulations. They may or may not adhere closely to criteria.
White liquor	A liquid in the kraft process composed of the chemicals used in the digester to cook the wood chips. Primarily sodium sulphide and sodium hydroxide in aqueous solution.

White water	Abbreviated WW, a general term for water removed from a pulp suspension and containing a small amount of fibre and/or additives. On a paper machine, the excess water drained through the wire from the furnish. The use of the term "white water" usually implies low dissolved solids content, and a suspended solids content up to about 1000 mg/L, mostly of fine material. Always white or beige when white paper is produced, white water contains pigments when coloured paper is being made, and can be any colour.
Zero concentration	Zero concentration of any substance. is unattainable in to-day's world of rapid advances in analytical chemistry. A substance may be non-detectable (*qv*), but it is scientifically inaccurate to state that the concentration of any substance in an effluent sample is zero. The authors have, therefore, refrained from such terms as "zero concentration" or "elimination" of discharges of specific substances, unless they are qualified by adjectives such as "virtual", or in a special situation such as "a waste stream is totally eliminated".
Zero effluent	For the purpose of this report zero effluent is taken to mean elimination of liquid process effluent from a pulp or paper mill, without transferring an unreasonable load to the airshed or soil.

Unit conversion factors

Unless otherwise stated, all units in this report are stated in the Système International (SI).

Conversion factors between traditional and SI units are shown on the following page.

CONVERSION FACTORS

1 kg (kilogram)	= 2.205 pounds (lb.)	[lb x 0.4536 = kg]
1 t (tonne)	= 1.102 short (US) tons	[s. tons x 0.9072 = tonnes]
	= 0.9842 long (US) tons	[l. tons x 1.016 = tonnes]
1 ADt	= 0.9 oven dry tonnes pulp	
1 m (metre)	= 3.281 feet	[feet x 0.3048 = m]
1 km (kilometre)	= 0.6214 miles	[miles x 1.609 = km]
1 hectare	= 2.471 acres	[acres x 0.4047 = hectares]
1 km^2	= 100 hectares	
1 km^2	= 0.3861 square miles	[sq. mi. x 2.590 = km^2]
1 L (litre) of water	= approx. 1 kg	
1 m^3 of water	= 1000 L	= approx. 1 tonne
	= 35.31 cubic feet	[cubic feet x 0.02832 = m^3]
	= 220.0 Imp. gal.	[Imp. gal. x 0.004546 = m^3]
	= 264.2 U.S. gal.	[U.S. gal. x 0.003785 = m^3]
1 m^3/t	= 199.6 Imp. gal./short ton	[1000 gal/ton x 5.011 = m^3/t]
	= 239.7 U.S. gal./short ton	[1000 gal/ton x 4.171 = m^3/t]
1 kg/tonne	= 2 lb/short ton	[lb/ton x 0.5000 = kg/t]

Fractional Units

1 tonne	(metric tonne)	= 10^6 g	= 1000 kg
1 kg	(kilogram)	= 10^3 g	= 1000 g
1 g	(gram)	= 1 g	= 1000 mg
1 mg	(milligram)	= 10^{-3} g	= 1000 μg
1 μg	(microgram)	= 10^{-6} g	= 1000 ng
1 ng	(nanogram)	= 10^{-9} g	= 1000 pg
1 pg	(picogram)	= 10^{-12} g	= 1000 fg
1 fg	(femtogram)	= 10^{-15} g	= 1000 ag
1 ag	(attogram)	= 10^{-18} g	

Approximate Equivalents (frequently used interchangeably)

1 g/L	= 1 g/kg	= 10^{-3} g/g	= "1 part per thousand"
1 mg/L	= 1 mg/kg	= 10^{-6} g/g	= "1 part per million"
1 μg/L	= 1 μg/kg	= 10^{-9} g/g	= "1 part per billion"
1 ng/L	= 1 ng/kg	= 10^{-12} g/g	= "1 part per trillion"
1 pg/L	= 1 pg/kg	= 10^{-15} g/g	= "1 part per quadrillion"