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Developing Options for Technology-Based Standards for the Pulp and Paper Sector in the Great Lakes Basin.

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Acronyms

AOX	Adsorbable Organic Halides
BAT(EA)	Best Available Technology (Economically Achievable)
BCT	Best Conventional Pollution Control Technology
BOD	Biochemical Oxygen Demand
BPT	Best Practicable Pollution Control Technology
CEPA	Canadian Environmental Protection Act
CIELAP	Canadian Institute for Environmental Law and Policy
Cl2	Chlorine Gas
ClO2	Chlorine Dioxide
COD	Chemical Oxygen Demand
CPPA	Canadian Pulp and Paper Association
CWA/FWPCA	Clean Water Act/Federal Water Pollution Control Act
DMR	Discharger Monitoring Report
EPA	Environmental Protection Agency
GAC	*Granular Activated Carbon Adsorption*
GLWQA	Great Lakes Water Quality Agreement
IJC	International Joint Commission
KG	Kilogram
MISA	Municipal-Industrial Strategy for Abatement
MOE	Ministry of the Environment
NaOH	Sodium Hydroxide
NPDES	National Pollutant Discharge Eliminating System
NSPS	New Source Performance Standards
OWRA	Ontario Water Resources Act
PAC	*Powdered Activated Carbon Adsorption*
PCDD	Polychlorinated-dibenzo-dioxins
PCDF	Polychlorinated-dibenzo-furans
PCP	Pentachlorophenol
PPB	Parts per Billion
PPM	Parts per Million
PPT	Parts per Trillion
TCP	Trichlorophenol
TOC	Total Organic Carbon
TOCL	Total Organically Bound Chlorine
TOX	Total Organic Halides
TSS	Total Suspended Solids
WPCP	Water Pollution Control Plant
2,3,7,8-TCDD	2,3,7,8-Tetrachlorinated-dibenzo-dioxin

Executive Summary

This report examines the role of technologies in attaining zero discharge from the pulp and paper industry. The industry is one of the oldest economic sectors in North America with 76 pulp and paper mills in the Great Lakes basin.

The Great Lakes are one of the most important natural resources in North America, but they have been continuously contaminated by industrial, agricultural and recreational activities. The need for international cooperation to deal with common pollution problems led to the signing of the Great Lakes Water Quality Agreement (GLWQA) in 1972, by the governments of Canada and the United States. The GLWQA was revised in 1978 and strengthened in 1987, and contains a number of important policy commitments, including the promise of zero discharge of persistent toxic substances.

This report examines some of the technical issues associated with achieving zero discharge in the pulp and paper industry. Specifically, the objectives of this report are:

(1) to summarize technology-based pollution abatement programs in the U.S. and Canada;

(2) to establish discharge loadings for specific pollutants on a basin-wide level;

(3) to review and assess existing technologies;

(4) to establish best available technology (BAT) options to prevent the discharge of a selected group of contaminants; and

(5) to recommend technology-based actions, with the goal of zero discharge, based on the pollution prevention approach.

Technology-based Regulatory Framework in the United States

Technology-based water pollution abatement programs in the U.S. are regulated under the Federal Water Pollution Control Act (FWPCA), which is now known as the Clean Water Act (CWA). In 1972, the FWPCA required the Environmental Protection Agency (U.S. EPA) to develop effluent limits for various industrial sectors, including pulp and paper mills. The U.S. EPA was also required to develop a National Pollutant Discharge Eliminating System (NPDES) for each industry.

Under the 1977 amendments of the CWA, pulp and paper mills were required to install best practicable pollution control technology (BPT), best available pollution control technology

(BAT), and best conventional pollution control technology (BCT).

Technology-based Regulatory Framework in Canada

In Canada, the federal government's effluent guidelines are developed under the Fisheries Act and the Canadian Environmental Protection Act (CEPA). The provinces either enforce the federal requirements as minimum standards, or implement more stringent requirements as necessary on a site specific basis.

The Fisheries Act guidelines for the pulp and paper industry were first promulgated in 1971. Currently, more stringent limits for conventional pollutants are proposed in new regulations under the Fisheries Act. Similarly, limits for chlorinated dioxins and furans in pulp and paper mill effluents are being developed under CEPA.

The Ontario Water Resources Act and the Environmental Protection Act provide legislative authority for pollution abatement programs in Ontario. Industrial sectors in Ontario are required to obtain Certificates of Approval from the Ontario Ministry of the Environment for the construction and operation of pollution control facilities in their plant.

The Ontario pollution abatement program for pulp and paper mills started in the early 1960's. This achieved some success in reducing conventional pollutants, and a series of Control Orders from mid-1970's reduced the discharges of conventional pollutants even further.

The Ontario government is currently developing the Municipal Industrial Strategy for Abatement (MISA) to address the discharge of toxic substances into Ontario's waters. Although substantially delayed, this program will ultimately produce enforceable, technology-based standards for industrial dischargers.

Pulp and Paper Manufacturing Processes

The four main processes in the manufacturing of pulp and paper products include raw material preparation, pulping, bleaching and paper-making.

During pulping, wood chips are reduced to a fibrous form by mechanical, chemical or semi-chemical means. The objective of the pulping process is to separate the cellulose fibres from other wood materials. About half of the wood raw material is cellulose fibre, while the other half is lignin, hemicellulose and other extractive compounds that cement and strengthen the fibres.

In chemical pulping, chemicals are used to dissolve lignin and free the fibres from one another. Since some of the fibre will be lost during chemical pulping, the pulp yield is only 40% to 55% of the original wood. In the case of mechanical pulping, the fibres are separated by the application of mechanical energy, giving a yield of over 90% of the original substrate.

To produce white paper, the chemical pulps are bleached in successive stages using molecular chlorine and/or chlorine dioxide. The use of chlorine causes the formation of chlorinated organic substances, which may include dioxins and furans. Generally, mechanical pulps do not require a high degree of brightness and are usually brightened with sodium hydrosulphite or hydrogen peroxide.

Effluent Treatment Technologies

Even though mills undertake various control measures to reduce the pollutants in the effluents, including in-plant and end-of-pipe treatment technologies, their effluents contain many toxic substances.

In-plant control measures in a pulp and paper mill consist of effluent reductions, chemical substitutions, chemical recoveries, spill control systems and process changes. End-of-pipe treatment technologies include primary treatment systems, which remove suspended inorganic and organic materials, and secondary treatment systems, which reduce BOD and other dissolved organic materials. Some mills may use tertiary treatment systems, which are designed to further improve waste water quality.

All 20 Ontario mills discharging into the Great Lakes provide primary treatment systems, whereas only seven mills have installed secondary treatment systems.

There are 56 pulp and paper mills in the United States portion of the Great Lakes basin. Most mills in the United States provide secondary treatment systems in addition to the primary treatment systems, while two mills also employ tertiary treatment systems.

Developing Best Available Technology Options

The total amount of chlorinated organic substances released into the Great Lakes is used to compare different BAT options. Over 200 of the 300 substances identified in bleached chemicals pulp mill effluents are chlorinated organic substances, and many are toxic, bioaccumulative and persistent. Indeed, both Canadian and American studies have shown the presence of 2,3,7,8-TCDD and

2,3,7,8-TCDF (two of the most toxic forms of chlorinated dioxins and furans) in the pulp, sludge and effluent of mills using chlorine compounds for bleaching.

In calculating the loading reductions of chlorinated organics based on a BAT option, several limitations were encountered and assumptions made. However, the main thrust of this study is a comparative analysis, examining which technologies can reduce persistent toxic substances to the furthest degree possible.

Technologies for Reducing and Eliminating Chlorinated Organics

Several technologies are immediately available to reduce the amount of chlorinated organic pollutants, including:

(1) secondary treatment and ultrafiltration;
(2) oxygen delignification;
(3) extended delignification;
(4) chlorine dioxide substitution; and
(5) use of non-chlorine bleaching agents such as hydrogen peroxide and sodium hydrosulphite.

One emerging technology is ozone bleaching; it has been successfully used in several pilot plant runs and will be commercially available in the near future. Other technologies used to conserve water and to reduce energy consumption may also help to reduce the amount of chlorinated by-products in the waste stream.

However, the development of environmental technologies must take into account policy goals by governments as expressed in law and policy. Most importantly, the governments of Canada and the United States have committed themselves to the goal of "virtual elimination of persistent toxic chemicals" under the Great Lakes Water Quality Agreement. This Agreement also states that regulatory strategies must be undertaken in the "philosophy of zero discharge". This commitment suggests a preventative approach by examining process and product reformulation, substitutions and the like. In the context of the pulp and paper industry, the preventative approach suggests that the use of chlorine compounds for bleaching should be eliminated.

Moreover, as a more general policy issue, the use of white paper products should be re-examined. Items such as toilet paper, writing paper, sanitary napkins, diapers and many others do not need to be white and thus do not need to be bleached or brightened. In essence, their colour does not diminish their purpose.

Recommendations

Recommendation 1: MONITORING OF PRIORITY POLLUTANTS

One of the requirements of a BAT must be the continuous monitoring for persistent priority pollutants until zero discharge mills are achieved. Such monitoring should be implemented immediately for all types of mills.

Recommendation 2: MECHANICAL MILLS

All new mechanical mills should be built using the zero-effluent technology. This is an available technology with two such mills starting production in 1992 in western Canada. Existing mechanical mills, which still discharge effluents into surface waters, should upgrade their operations to zero-effluent mills by the year 2000.

Recommendation 3: SULPHITE MILLS

All new sulphite mills should use the oxygen delignification and hydrogen peroxide bleaching technologies. All chlorine-using sulphite mills should convert to chlorine-free bleaching, using oxygen and hydrogen peroxide, by 1996.

Recommendation 4: KRAFT MILLS

New kraft mills, which do not require high brightness for their products, should use the Lignox method without chlorine dioxide bleaching. New kraft mills, which do require a high degree of brightness for their products, should use oxygen and ozone to delignify the pulp, and hydrogen peroxide and sodium hydrosulphite to bleach and brighten it. In addition, all new kraft mills should install a secondary treatment plant.

Existing kraft mills should convert to the Lignox method or the oxygen/ozone/hydrogen peroxide/sodium hydrosulphite method by the year 2000. Furthermore, such mills should install a secondary treatment plant by the 1994.

1. Introduction

This report is a case study of the role that technology can play in attaining zero discharge in the pulp and paper industry in the Great Lakes. The waters of the Great Lakes basin are utilized for many purposes, including drinking water, industrial processing, shipping, agricultural irrigation, and recreational and commercial fishing.[1] However, industrial and agricultural activities in the Great Lakes basin have created an increasing number of environmental problems.

At the turn of the century, the primary environmental concern was bacterial contamination of drinking water which caused epidemics of cholera and typhoid. In the 1950's, the major concern was the eutrophication of Lake Erie resulting from enormous phosphorus loadings. In the early 1960's, scientific data turned the concern to toxic pollutants, many of them persistent toxic chemicals.*

Today, the waters of the Great Lakes are still contaminated with hundreds of toxic and persistent chemicals from hundreds of industrial facilities operating in the basin. Available information reveals that many species of fish and wildlife in the Great Lakes basin suffer from cancerous tumours, reproductive defects and population collapses.[2]

The need for intergovernmental cooperation to deal with the contaminants in the Great Lakes basin led to the signing of the Great Lakes Water Quality Agreement (GLWQA)in 1972 by the governments of Canada and of the United States. The GLWQA was renegotiated in 1978 and amended in 1987.

The GLWQA commits the two federal governments, in cooperation with the Province of Ontario and the eight Great Lakes States, to restore, preserve and protect the integrity of the Great Lakes ecosystem. Furthermore, the 1978 GLWQA and its 1987 amendments commit the two signatories to a number of policy obligations. Article II of the GLWQA establishes a commitment to eliminate or to reduce to the maximum extent practicable the discharge of all pollutants. It also mandates a special, more stringent regime pertaining to toxic substances so that

> "the discharge of toxic substances in toxic amounts be prohibited and the discharge of any or all persistent

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* Persistent toxic substances are those chemicals which are difficult to break down by physical, chemical or metabolic processes. Once in the environment, they have a tendency to remain for a long time and build up in various compartments of the environment.

toxic substances be virtually eliminated".[3*]

Furthermore, Annex 12 of the Great Lakes Water Quality Agreement lists a number of principles which governments are to abide by when undertaking regulatory strategies to deal with persistent toxic substances. The key principle in this regard is that, when designing new regulatory strategies, they must be undertaken in the "philosophy of zero discharge".[4] Annex 12 provides a directive requiring regulatory programs to work toward the complete elimination of all discharges of persistent toxic chemicals.[5]

The definition of "zero discharge" for the purposes of this report is the elimination of all inputs, to any medium, of any persistent toxic substances. Zero discharge suggests a pollution prevention approach that requires the use, generation, manufacture, production and release of chemicals be evaluated.

This definition suggests that all deliberate inputs of persistent toxic chemicals should be eliminated. However, this definition does not include natural or non-anthropogenic sources, and accidental and illegal releases which are beyond immediate control.

1.1. Purpose of this Report

This report is a case study of the role that technology can play in attaining the goal of zero discharge in the pulp and paper industry. Specifically, the objectives of this report are:

(1) to summarize technology-based pollution abatement programs in the U.S. and Canada;

(2) to establish discharge loadings for chlorinated organics on a basin-wide level;

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* CIELAP's proposed definition of "virtual elimination" is based upon the distinction found in the Great Lakes Water Quality Agreement between persistent and non-persistent toxic substances. With respect to persistent toxic chemicals, *virtual elimination* is defined as the elimination of all inputs, to any medium, of persistent toxic substances. This definition suggests that all deliberate inputs of persistent toxic chemicals would be eliminated. The elimination of these substances may not be "absolute", but only "virtual", since toxic chemicals may still be discharged by natural or non-human sources, or by those sources beyond immediate control (such as accidental and illegal discharges).

(3) to review existing and emerging technologies;

(4) to establish best available technology (BAT) options to prevent the discharge of chlorinated organics (costs of the different BAT options have not been considered for the purposes of this report); and

(5) to recommend technology-based actions, with the goal of zero discharge, based on pollution prevention.

It must be emphasized that the financial costs and benefits of the proposed BAT options have not been examined. The sole purpose of this report is to identify choices for pollution prevention, and it should be emphasized that BAT standards will not be developed based on costs.

1.2. Outline of this Report

First, the existing technology-based standards in the Great Lakes basin are reviewed, followed by a general review of the processes in a pulp and paper mill. Then, the pulp and paper industry in the Great Lakes is examined and pollutant loadings are calculated. Various BAT options are developed and applied to all pulp and paper plants around the basin to predict the resulting pollutant loadings. The final section summarizes the findings of this report and provides a series of recommendations.

1.3. Methodology

Several sources of information were investigated to assess the pulp and paper industry and their treatment facilities, including:

- reviewing published documents, discharge monitoring reports (DMRs), and permit applications for each existing mill on the U.S. side of the Great Lakes. These documents were obtained from the United States Environmental Protection Agency (U.S. EPA);
- analyzing the Ontario Ministry of the Environment's (MOE) first six-month (July 1990-Dec. 1990) MISA monitoring data for the pulp and paper sector;
- reviewing the literature in order to identify the available pollution prevention technologies and their removal efficiencies;
- contacting representatives of several research institutes and organizations including, the Canadian Pulp and Paper

Association (CPPA), the Pulp and Paper Research Institute of Canada, and the International Joint Commission (IJC); and

- o preparing a questionnaire for every mill discharging directly into the Great Lakes basin. The questionnaire included questions on the processes in each mill, bleaching sequences, and quantities of the bleaching chemicals used each year. Unfortunately, only four mills out of the 76 mills responded to the questionnaire.

Organochlorines, measured as AOX, were used to evaluate technologies because they are a family of compounds that frequently demonstrate properties of toxicity, persistence and bioaccumulation. AOX does not measure the precise toxicity of a given effluent, but combined with other measures, AOX is an important indicator of progress in reducing, and eventually eliminating, discharges of persistent toxic substances from pulp and paper plants.

2. Technology-Based Standards in Great Lakes Jurisdictions

Technology-based effluent standards are standards of performance. They are based on technologies that can be used to reduce the discharge of pollutants, such as *best available technology economically achievable* (BAT) and *best practicable pollution control technology currently available* (BPT). Once technology-based standards have been selected for an industrial sector, all facilities within that sector are required to meet those standards. This section summarizes the development of discharge standards in the United States and Canada.

2.1. Overview of the Regulatory Framework in the United States

In the United States, the development of technology-based effluent standards is regulated federally and not at the state level. Pulp and paper waste water abatement programs are administered through the Federal Water Pollution Control Act (FWPCA), currently known as the Clean Water Act (CWA).[6] In 1972, the FWPCA established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters".[7] The 1972 amendments to the FWPCA required the U.S. EPA to develop national effluent limits for the various industrial categories. Under this program, each direct discharger must apply for and obtain a National Pollutant Discharge Elimination System (NPDES)* permit from either the Federal government or from the State.[8]

The NPDES permits, which are issued for a period of five years, include effluent limits specifying the quantity of the pollutants that can be discharged. The permits also contain self-monitoring requirements, dates for construction of treatment-facilities, and other means to achieve the required effluent limits.

The amendments to the FWPCA in 1972, and to the CWA in 1977, required a two step process for reducing the levels of pollutants:[9]

(a) by July 1, 1977 achieve best practicable control technology (BPT) standards for all pollutants, and

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* The NPDES is a program established under the authority of the Clean Water Act for the purpose of issuing and enforcing permits regulating the discharge of pollutants. NPDES permits are generally administered by the U.S. EPA, but individual States may develop water management plans to which NPDES permit authority is then transferred.

(b) by July 1, 1984 provide best conventional control technology (BCT) for conventional pollutants and best available control technology (BAT) for all toxic and non-conventional pollutants.*

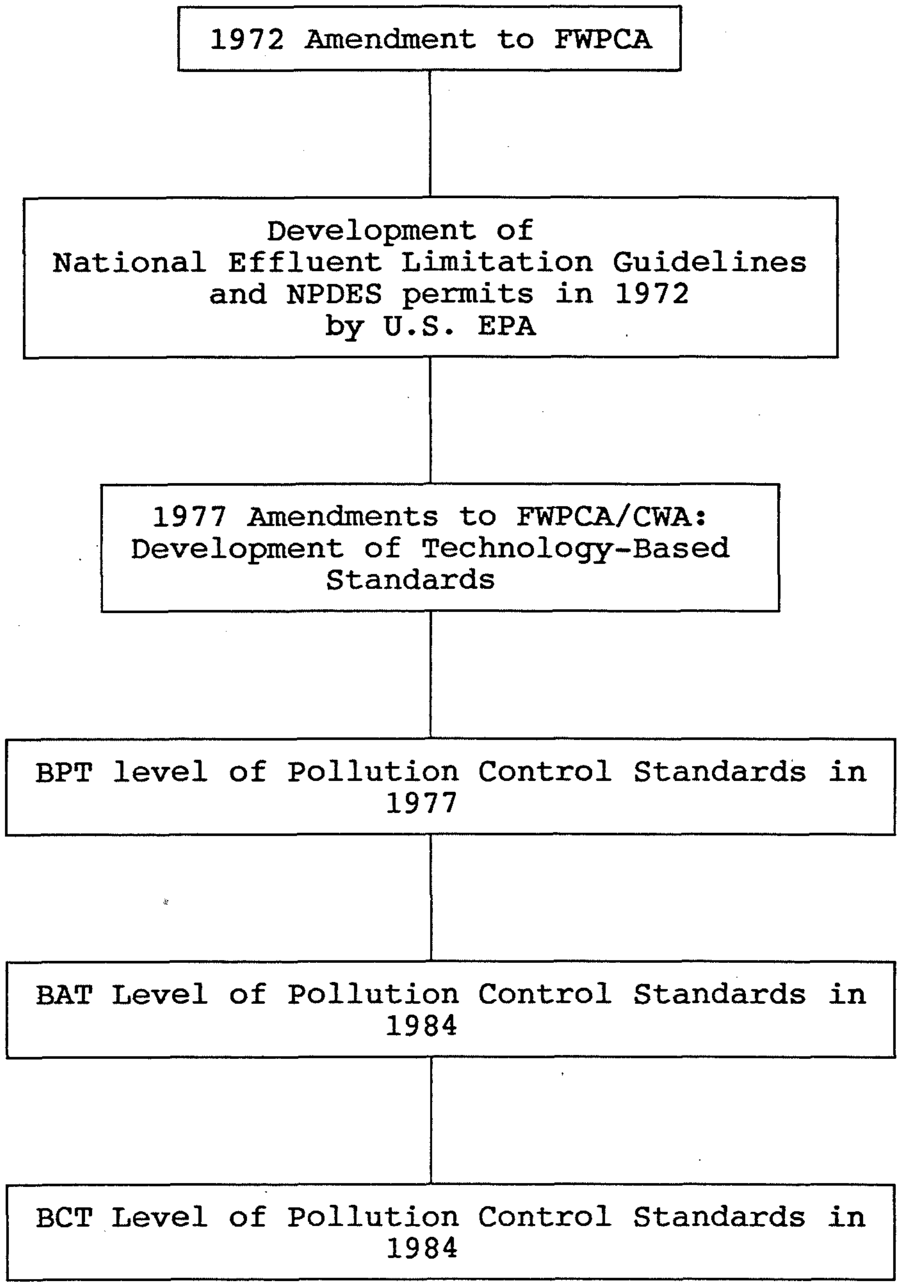
Table 1 provides a description of each type of U.S. technology-based standard, while Figure 1 is a chronological history of the development of technology-based effluent limits for the pulp and paper industry in the United States.

Table 1. Technology-Based Standards for the Pulp and Paper Industry in the United States.

Standard	Date	Description
Best Practicable Technology (BPT)	1977	BPT-based discharge limit were to be established for industrial dischargers by 1977. Depending upon the industrial category, the limits may include conventional, non-conventional and toxic pollutants.
Best Conventional Technology (BCT)	1984	These contaminant limits of conventional pollutants cannot exceed those of BPT, unless the additional removal of conventional pollutant by BCT can be achieved cost effectively.
Best Available Technology (BAT)	1984	BAT limits are the maximum allowable discharge levels for toxic pollutants (see Appendix A for the current BAT limits for pulp and paper mills).

* Conventional pollutants include biochemical oxygen demand (BOD), total suspended solids (TSS), oil and grease, faecal coliform and pH. The term "conventional pollutant" identifies a pollutant that can be treated by a conventional secondary waste water treatment plant. A toxic pollutant is a chemical that can cause adverse human health and/or aquatic life impacts. The 1977 <u>CWA</u> included a list of 65 classes of compounds that the U.S. EPA was to consider, as minimum, as potentially toxic pollutants. Non-conventional pollutants include total organic carbon (TOC), chemical oxygen demand (COD) and ammonia.

Figure 1. Chronological Overview of Technology-Based Standards for the Pulp and Paper Industry in the United States.



2.1.1. History of Limits Development for the Pulp and Paper Industry in the U.S.

In promulgating effluent limits and standards, the U.S. Environmental Protection Agency (EPA) conducted a two-phase implementation strategy. In the first phase (May 1974), guidelines were issued for the unbleached kraft, semi-chemical, and paperboard from waste paper subcategories. The second phase, (January 1977), established effluent limits for most of the remaining subcategories.

In order to develop and promulgate standards, the U.S. EPA undertook a comprehensive program to evaluate the status of pulp and paper dischargers. The major tasks of the program included the identification of the volume of water used, the manufacturing processes employed, the sources of waste waters within each pulp and paper plant, and the constituents of waste waters including toxic pollutants. The U.S. EPA then studied the control technologies, including both in-plant and end-of-pipe treatment technologies, which are in use, or capable of being used, to control or treat pulp and paper effluents.

The U.S. EPA also estimated the costs of each control and treatment technology for the various industrial subcategories. Upon consideration of these factors, the Agency identified various technology-based standards:

- o BPT (best practicable control technology currently available);
- o BAT (best available technology economically achievable); and
- o NSPS (new source performance standards).

The final regulations, however, do not require the installation of any particular technology. Rather, the regulations require dischargers to achieve effluent limits with any available technology they may choose.[10]

Based on the U.S. EPA study of existing regulations, and on data from an extensive sampling program of the pulp and paper industry, BAT effluent standards were promulgated in 1984.[11]

The factors considered in establishing BAT level of controls included: the cost of applying control technologies, the age of process equipment and facilities, the process employed, process changes, the engineering aspects of applying various types of control technologies, and non-water quality environmental consideration such as energy consumption, solid waste generation, and air pollution. In assessing a BAT, the Agency gave substantial weight to the financial costs of establishing effluent limits.[12]

2.1.2. Current Effluent Limits

The U.S. EPA decided to regulate three toxic pollutants from the discharges of pulp, paper and paperboard industries: zinc, trichlorophenol (TCP) and pentachlorophenol (PCP). It is noteworthy that these BAT regulations did not establish limits for other chlorinated organic substances such as AOX, dioxins or furans.

The Agency required the substitution of TCP and PCP since they are not effectively removed by primary or biological treatment.[13] Indeed, TCP and PCP can be replaced by formulations that do not contain these toxic pollutants.[14] However, the total removal of PCP and TCP is not achieved because some recycled paper is contaminated with low levels of PCP. Furthermore, low levels of TCP are formed when pulp is bleached with chlorine or chlorine-containing compounds.[15] Appendix A contains the U.S. BAT effluent limits for PCP, TCP and zinc from pulp and paper mills.

Currently, the U.S. EPA is reviewing the BAT limits for the pulp and paper industry and the new limits are to be promulgated by 1995. These regulations will include limits for dioxins, furans and other chlorinated organics, and new regulations will also be set for conventional pollutants.[16]

2.2. Overview of the Canadian Regulatory Framework

In Canada, environmental protection is a shared responsibility between the federal and provincial governments. The federal government develops nation-wide baseline effluent guidelines for specific industrial sectors. The provinces enforce either the federal requirements as a minimum, or establish more stringent requirements as necessary on a site specific basis. The following sections describe the federal and provincial regulatory requirements in more detail.

2.2.1. History of Limits Development at the Federal Level

In the late 1960's, the Canadian Government developed regulations under the Fisheries Act aimed at reducing the discharge of "deleterious substances" into both fresh and marine waters. Under the Act, pulp and paper effluent regulations were promulgated in 1971 for new and expanded mills. The regulations limited the allowable discharges of total suspended solids (TSS) and biochemical oxygen demand (BOD).[17] In addition, the final effluent had to pass a toxicity test.

The federal government is currently undertaking new initiatives to improve the existing federal regulations for pulp and paper mill effluents. The first component of the strategy is to tighten regulations under the Fisheries Act for conventional pollutants. The second component involves regulations under the Canadian Environmental Protection Act (CEPA) to limit dioxin and furan discharges.

The regulations passed pursuant to CEPA are divided into two sets of regulations. The first set will control the sale or use of defoamers containing dioxins and furans, and to ban the sale and use of wood containing polychlorinated phenols.[18] The second set of regulations will apply to mills that use a bleaching process.[19] These mills will be prohibited to release any measurable amount of 2,3,7,8-TCDD or 2,3,7,8-TCDF.[20]

New regulations under the federal Fisheries Act propose will place more stringent limits on effluent discharges for three contaminants: total suspended matter (TSM), biochemical oxygen demand (BOD) and acutely lethal effluents.

It is anticipated that the CEPA and Fisheries Act regulations will be promulgated in the middle of 1992.

2.2.2. History of Limits Development at the Provincial Level

The Ontario Water Resources Act and the Environmental Protection Act provide legislative authority for pollution abatement programs in Ontario. The legislation prohibits the discharge of pollutants that adversely affect the quality of air, water and land.

Industrial sources are required to obtain a Certificate of Approval from the Ontario Ministry of the Environment (MOE) for installing pollution control measures. Schedules for program implementation and limitations on operations, including legally enforceable effluent requirements, may be included in the Certificate. The Certificates of Approval are issued on a case-by-case basis.

In the early 1960's, the Ontario government started a program through the Ontario Water Resources Commission to investigate the quality and quantity of pulp and paper mill effluents. The results showed that the effluents contained large quantities of waste products, particularly suspended solids and oxygen demanding waste.[21] These findings resulted in the development of a pulp and paper abatement strategy which was formulated in the late 1960's. This strategy established a five year abatement plan which called for large reductions in the discharge of suspended solids within two years, and large reductions in the discharge of oxygen demanding wastes within five years. The strategy also recommended certain in-plant control and waste treatment technologies which were available at that time to meet the requirements.[22]

Some success was achieved as a result of these two initiatives. By the mid-1970's, most Ontario mills had installed facilities for the removal of suspended solids which brought them into compliance with the federal guidelines and/or requirements. At some locations, Ontario required additional suspended solids reduction based on local effects on aquatic systems. These were forced upon industry by a series of Control Orders. (A Control Order addresses site specific problems at a given mill, describing the remedial actions and time period required to complete abatement measures).

The existing provincial regulations lack limits for toxic and persistent toxic substances. In order to overcome the shortcomings of the existing regulations and to create a set of enforceable environmental standards, the Ontario Ministry of the Environment (MOE) is developing a technology-based program called the Municipal-Industrial Strategy for Abatement (MISA).

MISA, which was announced by the Government of Ontario in 1986, has as its goal the virtual elimination of persistent toxic substances. To achieve this goal, the Ontario MOE decided to use an approach similar to the U.S. model:

(a) monitoring data: a monitoring regime for direct dischargers to identify what chemicals and in what quantities are being discharged;

(b) technology-based standards: setting effluent limits based on the application of Best Available Technology Economically Achievable (BATEA); and

(c) water quality standards: based on local conditions, setting more stringent limits to improve water quality. The water quality standards are based on the desired quality of the receiving water.

Under MISA, industries are divided into nine industrial sectors and sewage treatment plants. BAT standards are being developed for each sector. They include:

- Electric power generation
- Industrial minerals
- Inorganic chemicals
- Iron and steel
- Metal casting
- Metal mining & refining
- Organic chemicals
- Pulp and paper
- Petroleum refining
- STPs (WPCPs)

No BAT limits have been promulgated to date; a draft BAT limit regulation for the pulp and paper sector is expected sometime in early 1992. The only product of MISA so far are the monitoring data, and details on the MISA monitoring of pulp and paper mills can be found in Appendix B.

3. Overview of Pulp and Paper Processes and Pollution Controls

The production of pulp and paper involves several standard manufacturing processes including raw material preparation, pulping, bleaching and paper-making processes. The purpose of this section is to summarize these processes and associated pollution controls. This section also describes the waste water treatment technologies currently in use in Canada and the United States.

3.1. Raw Material Preparation

Preparation of raw materials involves log washing, debarking and chipping of wood. Upon arrival at the mills, the wood logs may carry a substantial quantity of solid material including soil and bark which have to be removed. Debarking may be achieved through wet or dry processes. One method of wet debarking uses high pressure water jets to separate bark and log. The log washing and wet debarking of raw materials consume a large volume of water, and the resulting effluent contains significant levels of BOD and TSS, along with resin acids from the bark, which can be toxic to fish.

Dry debarking consumes much less water, and wastes from this process are generally burned or land-filled. Generally, newer mills use dry debarking because the effluent treatment for wet debarking is very costly.

The clean, debarked logs are then reduced to wood chips by means of a rotating flywheel faced with knives which act as cutting blades. The chips are screened and those not suitable for pulping are sent to a boiler to be used as fuel. The accepted chips are sent to the pulping process.

3.2. Pulping and Bleaching Technologies

The objective of the pulping process is to separate the cellulose fibres from lignin, hemicelluloses and other wood substances*. Pulping is a process during which the wood chips are reduced to a fibrous mass by mechanical, chemical or semi-chemical means. Depending on the tree species, approximately 40% of the wood is cellulose. Almost all of the lignin must be removed to make the pulp white, and this is accomplished in a multi-step bleaching procedure. The following sections briefly explain the different types of pulping processes.

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* Lignin is a complex, relatively non-degradable organic compound of wood which cements the wood fibres together.

3.2.1. Mechanical Pulping

In mechanical pulping, the fibres are separated by mechanical energy such as grinding and chopping. Mechanical pulps are characterized by yields of over 90 percent of the original substrate because the lignin is not removed from the pulp. Paper produced from this pulp is relatively stiff and not as strong as chemical pulps. Newsprint typically contains between 80 and 100% mechanical pulp, and other paper products such as printing and writing papers, carton board and lightweight coated papers also contain a certain percentage of mechanical pulp.

3.2.2. Chemical Pulping

Chemical pulping degrades and dissolves the lignin and leaves behind most of the cellulose and hemicellulose fibres. Because most of the lignin is removed during chemical pulping, the yield ranges from 40% to 55% of the original substrate. The high cellulose content of chemical pulps allows the manufacturing of high quality, flexible and well bonded products, including fine papers. Overall, the fibres of chemical pulps are used for their length and strength, and are utilized to reinforce almost all paper and board grades.

The two principal chemical pulping methods are the kraft process (alkaline) and the sulphite process (acidic). The kraft process has become dominant because of advantages in chemical recovery and pulp strength.

(a) Kraft Pulping (Alkaline)

The kraft process involves cooking the wood chips in a solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). This alkaline condition causes a breakdown of the lignin molecule into smaller segments whose sodium salts are soluble and can thus be removed. Kraft pulps produce strong paper products, but the unbleached pulp is characterized by a dark brown colour. The kraft process is associated with malodorous gases, principally organic sulphides, which are an environmental concern.

The kraft process is suitable for almost all species and types of wood, but is preferred for resinous softwood such as fir and hemlock.

(b) Sulphite Pulping (Acidic)

In the sulphite process, a mixture of sulphurous acid (H_2SO_3) and/or bisulphite ion (HSO_3^-) is used to solubilize the lignin. The chemical reactions remove the lignin as salts of lignosulphonic acid while the molecular structure of the fibre is left largely intact. Sulphite pulps are associated with the production of many types of paper, including tissue and writing papers.

Sulphite pulp is lighter in colour than kraft pulp and can be bleached more easily, but the paper sheets are weaker than equivalent kraft sheets. The sulphite process works well for softwood such as spruce, fir and hemlock, and hardwood such as poplar and eucalyptus. A greater sensitivity to wood species, along with weaker pulp strength and the greater difficulty in chemical recovery, are the major reasons for the decline of sulphite pulping relative to the kraft method.

3.2.3. Bleaching of Pulp

Bleaching of Kraft Pulp

Following the chemical pulping stage, some of the lignin, which causes the pulps' brown colour, remains in the pulp. As a result, the pulp is treated with chemicals to remove the lignin and enhance its brightness. The extent of bleaching depends on the degree of brightness required, which varies according to the end use of the pulp.

Chlorine is the choice of bleaching agent and it is at this stage that persistent and bioaccumulative chlorinated compounds are formed. Also, in most kraft mills, this stage is the source of about half the BOD, all the organochlorines and much of the toxicity in the effluent.[23]

The residual lignin (approximately 5-10%) is removed by a multi-stage bleaching procedure. The process generally starts with a chlorine treatment, which converts lignin to compounds which are soluble in alkali and subsequently can be washed out with caustic sodium hydroxide. This process is called the delignification stage. Following delignification, oxidative bleaching is carried out with either sodium hypochlorite and/or chlorine dioxide as the bleaching agent.[24]

It is a common practice for mills to substitute small quantities (5%-15%) of chlorine dioxide in place of molecular chlorine during the bleaching process. Since 1 kg of molecular chlorine dioxide can replace approximately 2.63 kg of chlorine, there is a net reduction in the amount of chlorine used. The highest level of chlorine dioxide used in an operating mill is 100%.

The generation of chlorinated organic compounds during the chlorination and extraction stages is proportional to the amount of chlorine consumed, whether it originated from molecular chlorine or chlorine dioxide. The only advantage of using chlorine dioxide as opposed to molecular chlorine is that less material is needed to reach the same brightness.[25]

Bleaching of Sulphite Pulp

Sulphite pulp is less coloured than kraft pulp and therefore requires less bleaching. In the past, sulphite mills employed a three-stage sequence of chlorination, caustic extraction and hypochlorite or chlorine dioxide bleaching. However, environmental concerns with the use of chlorine caused most mills to use hydrogen peroxide as a bleaching agent. As a result, there are only two sulphite mills in the Great Lakes basin which still use chlorine compounds.[26]

Brightening of Mechanical Pulp

Mechanical pulp does not require a delignification stage because lignin is left in the pulp and requires only brightening or de-colouration. Sodium hydrosulphite is the most common agent used to brighten the pulp, but hydrogen peroxide is used whenever high brightness is required. The effluents from mechanical pulp have high BOD values, but unlike effluents from sulphite and kraft pulp, the mechanical pulp effluents contain no chlorinated organics or dioxins.

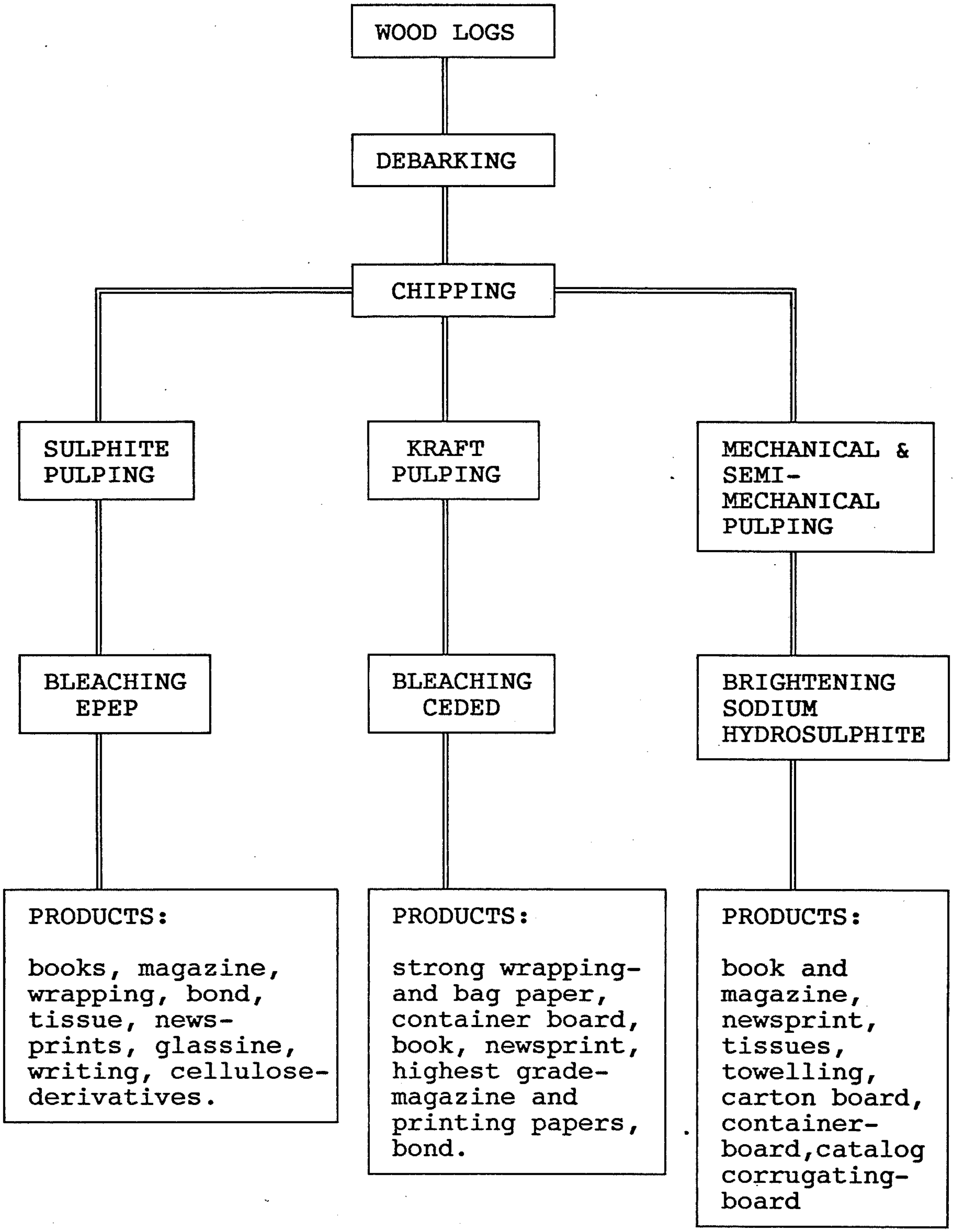
3.2.4. Paper-making

Paper products are made by blending various types and grades of pulp with a variety of additives. The pulp is diluted by adding water and is then passed through a headbox that distributes the fibre uniformly over the width of the paper to be formed. The suspended fibre is then deposited on a web or screen from which the water is drained. The wet paper sheets are then pressed between rollers and dried by heating.

Many other materials may be added to the fibres to provide the unique properties of the many types of paper used today. If printing paper is made, fillers such as clay, calcium carbonate, talc, or titanium dioxide can be added to improve smoothness, brightness and opacity. To increase ink or water resistance, paper makers add resin or starch.

Figure 2 summarizes the different pulp and paper processes. The different pulps (kraft, sulphite and mechanical) are generally mixed in certain proportions for the different paper products indicated in Figure 2.

Figure 2. Basic Processes in a Pulp and Paper Mill



3.3. Pollution Abatement Technologies[27]

The quality of waste water discharges from pulp and paper mills can be controlled by in-plant and end-of-pipe treatment systems. In-plant systems include alternative pulping and bleaching technologies, while end-of-pipe systems only focus on treating the resulting effluents. This section summarizes the available and emerging in-plant and end-of-pipe treatment systems.

3.3.1. Available Pulping Technologies

Extended Delignification

Extended delignification prolongs the cooking process to produce pulp with lower lignin content, thus reducing the demand for bleaching chemicals. The use of this technology is increasing rapidly because it reduces the amount of organochlorines, BOD and COD discharged. This process is especially effective in combination with oxygen delignification and chlorine dioxide substitution.

Oxygen Delignification

The pulp is delignified with oxygen under pressure in an alkaline environment, which reduces the chemical requirements for pulp bleaching and the number of conventional bleaching stages. It has been shown that oxygen delignification reduces BOD (40-55%), COD (45-55%) and organochlorines (35-87%).

3.3.2. Emerging Pulping Technologies

Peroxide Delignification

Hydrogen peroxide is used to delignify the pulp in an alkaline environment, resulting in a delignification efficiency of 22-29% for kraft hardwood and 25-42% on kraft softwood.

Nitrogen Dioxide Pretreatment

The so-called Prenox treatment for kraft pulp occurs under acidic conditions with 1-2% nitrogen dioxide, and is applied after the digestion and before oxygen delignification. Pilot studies indicate that 70-80% delignification is possible and that chemical costs are reduced. This technology is promising but has not been tested at a full-scale mill.

3.3.3. Available Bleaching Technologies

Chlorine Dioxide Substitution

Chlorine dioxide (ClO_2) may replace some or all of the molecular chlorine (Cl_2) in the first bleaching stage. Because it reduces the amount of organochlorines and COD discharged, as well as the cost of bleaching, this chemical substitution is increasing rapidly.

3.3.4. Emerging Bleaching Technologies

Oxygen, Hydrogen Peroxide, Ozone, Sodium Hydrosulfite and Caustic Soda Bleaching

Several research activities and pilot studies have demonstrated that pulp can be bleached without the use of chlorine compounds. Bleaching softwood kraft pulp with different sequences of oxygen, ozone, caustic soda, hydrogen peroxide and sodium hydrosulfite produces high brightness pulps with similar strength qualities as conventional pulps.[28]

3.3.5. End-of-Pipe Treatment Technologies

Primary Treatment Systems

Primary treatment systems are used to remove suspended inorganic and organic materials. The primary treatment is accomplished by gravity separation through mechanical clarifiers or sedimentation lagoons.

Mechanical clarifiers consist of a large circular tank equipped with sludge removal rakes. Settled solids deposited on the clarifier floor are drawn to the centre by the rotating mechanical raking system and are drawn off and de-watered prior to disposal. Chemicals such as lime or certain polymers may be added to improve the settlement of solids.

Sedimentation lagoons are simple shallow basins which allow suspended solids to deposit on the bottom of the basin. Cleaning the basins is accomplished with earth moving equipment.

Sludge produced by these primary treatment systems is de-watered and then incinerated, land-filled, or sometimes spread on agricultural land.

Secondary Treatment Systems

Secondary treatment of pulp and paper mill effluents is designed to reduce BOD associated with dissolved organic materials. The most commonly used treatment systems are aerated lagoons. Other available methods include activated sludge using either air or oxygen, rotating biological contactors, trickling filters or anaerobic systems.

While most secondary treatment systems reduce the BOD by 70% to 95%, rendering the effluent non-lethal to fish, the sludges from this process are generally contaminated. Depending on the mill processes, the sludge from secondary treatment systems may contain large quantities of chlorinated organic substances. A U.S. study revealed that there are measurable concentration of 2,3,7,8-TCDD (up to 240 parts per trillion) and 2,3,7,8-TCDF (up to 2300 ppt) in waste water sludges.[29] A similar study by the Canadian Pulp and Paper Association, showed maximum concentrations of 88 ppt for 2,3,7,8-TCDD, and 1400 ppt for 2,3,7,8-TCDF in the sludges.[30]

Tertiary Treatment Systems

The components remaining in the effluent after primary and secondary treatment include residual suspended solids, residual BOD, nutrients, colour and chlorinated organic compounds. Tertiary treatment systems are not commonly used in the pulp and paper industry, although several different types exist.

(a) A *sand filtration system* is a commonly used tertiary system in pulp and paper mills. Its function is to reduce the suspended solids content of the final effluents.

(b) *Granular activated carbon adsorption* (GAC) has been used for many years at municipal and industrial facilities to purify potable and process water. GAC treatment usually consists of one or more carbon beds or columns which are used to remove organic substances from waste water.

(c) *Powdered activated carbon adsorption* (PAC) treatment systems involve the addition of powdered activated carbon to biological treatment systems. The adsorbent quality of carbon aids in the removal of organic materials in the biological treatment process. In addition, PAC enhances colour and also reduces the chemical oxygen demand (COD).

4. An Overview of the Pulp and Paper Industry in the Great Lakes Basin

The pulp and paper industry is a significant source of conventional and toxic pollution to the Great Lakes.[31] There are a total of 76 pulp and paper mills in the Great Lakes discharging waste water into the basin.

4.1. Pulp and Paper Mills in Ontario

The pulp and paper industry is one of the leading sectors in Canada's economy. It is also a significant water consumer and a major source of water pollution, while, at the same time, being a recipient of public funds.[32] For example, Ontario's pulp and paper plants have received subsidies of $187 million under a six-year modernization programme (1979-85). One of the intentions of this programme was to provide funds for pollution abatement, and although some success was achieved, pulp and paper mills continue to be a significant source of pollution.

Of the 27 Ontario mills, 20 are discharging either directly into the Great Lakes or into one of the connecting channels to the Lakes.[33] The total discharges of such mills into the Great Lakes accounted for 1.13 million cubic meters per day (300 million gallons per day).[34]

Most of the conventional pollutants are not persistent or bioaccumulative, and thus do not pose a long-term environmental problem. However, they may be lethal to aquatic organisms immediately after being discharged. A recent report by the Ontario Ministry of the Environment identified the significant degree of pollution from pulp and paper mills which do not use chlorine. Table 2 summarizes the loadings of such mills into Ontario rivers and lakes.

Table 2. Annual Pollutant Loadings from Non-Chlorine Pulp and Paper Mills in Ontario (tonnes/year).

Mills Subcategory	Conventional Pollutants	# of Priority Toxic Pollutants
Sulphite-Mechanical	329,443	966
Corrugating	5,306	19
De-inking/ Fine Paper/Tissue	25,024	221

Source: MOE, 1991.[35]

Pulp and paper mills in Ontario manufacture a variety of products ranging from newsprint (accounting for over half of the production), to products such as bleached kraft, ground-wood specialty papers, fine papers, liner board, corrugating medium, paperboard and tissue products.[36] A summary of Ontario mills, including their production capacities, effluent treatment systems and discharge volumes is provided in Table 1 of Appendix D.

4.2. Pulp and Paper Mills in the United States

In the United States, 56 pulp and paper mills discharge waste water directly into the Great Lakes basin. These mills were required to provide best practicable control technology (BPT) for their waste waters by 1977. Additional restrictions were placed on the release of pentachlorophenol, trichlorophenol and zinc in 1982 with the result that the industry in the Great Lakes basin had switched to use fewer toxic materials by 1984.[37]

Many mills in the United States employ secondary treatment systems. Of the 56 mills, 35 provide clarification in addition to secondary treatment, 33 provide biological treatment, two provide clarification plus post-settling basins, and one provides reverse osmosis and hyper-filtration.[38] Detailed information on each American mill operating in the Great Lakes is provided in Table 2 of Appendix D.

4.3. Priority Pollutants Detected in Pulp and Paper Mills Effluents

Large quantities of water are used during the various operations in a pulp and paper mill. In pulping operations, water is used for dilution, for washing and cleaning, and for facilitating process mechanisms. Water is also used to transport the wood within the mill and to carry the separated fibres through the bleaching, refining and sheet-forming phases of paper manufacturing.

During all these operations the water can become polluted with many types of contaminants. Indeed, as Table 3 shows, waste water from pulp and paper mills contains a variety of toxic, persistent and bioaccumulative chemicals.

Nearly 300 different compounds have been identified in bleached chemical pulp mill effluents, of which about 200 are chlorinated organic compounds.[39] About 75 to 85% of the organically-bound chlorine in bleached kraft mill effluent is high molecular weight material. Appendix E summarizes the concentrations of all contaminants found in Ontario's kraft mills, while Appendix F reviews the formation and concentration of dioxins and furans in pulp and paper mills.

Table 3. Selected Contaminants of Concern Identified in Pulp and Paper Mill Effluents.

Halogenated Volatiles	Extractables
Bromodichloromethane	Dibutyl phtalate
Carbon tetrachloride	2,4-dichlorophenol
Chloroform	4,5-dichloroguaiacol
Chloropropenal	2,4,6-trichlorophenol
Dichloroacetone	3,4,5-trichloroguaiacol
Dichloroethane	4,5,6-trichloroguaiacol
Methylene Chloride	Pentachlorophenol
Pentachloroacetone	Phenol
Pentachloropropene	2,3,4,5-Tetrachlorocatechol
Tetrachloroacetone	3,4,5,6-Tetrachloroguaiacol
Tetrachloroethane	
Tetrachloropropene	
Trichloroacetone	

Total Metals	Non-Halogenated Volatiles	Chlorinated Dioxins and Furans
Aluminum	Benzene	
Cadmium	Toluene	
Lead	Dimethyl Sulphide	
Mercury	Dimethyl Disulphide	
Zinc		

5. Developing BAT Options for Pulp and Paper Mills

Having reviewed the technological basis of pulp and paper mills, this section summarizes the AOX loading data as well as the assumptions and information used to develop the technology options for the industry.

The virtual elimination of persistent toxic substances is the ultimate goal in defining BATs. However, it is not expected that this goal is achievable immediately. Therefore, a number of successively more stringent standards need to be developed. The first step in the setting of such limits requires that specific contaminants be selected for regulation. The second step in attaining virtual elimination is to define a BAT which meets an initial limit. The final steps will require more stringent limits until virtual elimination is achieved.

5.1. Current Loadings of Chlorinated Organic Substances

The discharge of chlorinated organic compounds (measured as AOX) is a topic of growing concern for the pulp and paper industry. Although AOX does not measure the precise toxicity of a given effluent, AOX is an important indicator of progress in reducing, and eventually eliminating, the discharge of persistent toxic substances from pulp and paper mills.

The elimination of organic pollutants, particularly dioxins and furans, is becoming a major issue throughout industrial countries. Considering their toxicity to fish, their bioaccumulation in many organisms, their persistent nature, and their health threat, many have argued that chlorinated organic compounds ought to be completely eliminated.

Acute toxicity of chlorine-bleached kraft effluents is due, in part, to material of molecular weight less than 1000. Compounds of higher molecular weight are generally less toxic because large molecules are thought to be unable to penetrate cell membranes and to exert toxic effects. Chlorinated organic substances with molecular weight less than 1000 were found to comprise about 30% of the chlorinated effluents from pulp and paper mills.[40] Such molecules resist degradation in the environment, that is, they are very persistent, and many of them are toxic and tend to bioaccumulate in wildlife.[41]

Appendix G summarizes the analytical methods of measuring chlorinated organic compounds.

In order to assess technologies, removal efficiencies were applied to current loadings to predict the resulting contaminant loadings. However, establishing current loadings is a difficult task since pollutant discharge information is often incomplete.

Therefore a number of estimates and assumptions are used to obtain basin-wide industry loadings, including:

(1) The AOX loadings for Ontario mills are calculated using the MISA six-month monitoring data (January 1990 to June 1990).

(2) Because no comprehensive measurements of AOX are available for U.S. mills, their organochlorine discharges were estimated using Ontario data.* Specifically, the Ontario MISA data is used to calculate an average U.S. AOX discharge based on effluent volumes for similar Ontario mills. CIELAP recognizes that, at best, this extrapolation can only be regarded as an estimate. However, what is important for this report is not the absolute number but the analysis of the loadings on a comparative basis.

Current Loadings

In total, the Great Lakes receive 75.3 million kgs or 165 million pounds of organochlorines per year from pulp and paper mills. Ontario mills contribute 40.87 million kgs, while U.S. mills discharge 34.41 million kgs of organochlorines into the Great Lakes.** These values form the baseline and are used to compare the different technologies.

5.2. Assumptions and Limitations in Developing BATs

Removal Efficiencies

Assessing the performance of the technologies takes into consideration that all mills have already acquired some basic control technologies. For example, all mills in the Great Lakes have installed primary treatment systems.

Several sources were used to obtain AOX removal efficiencies, but they are primarily based on work undertaken by Bonsor and colleagues.[42] One option, however, is exclusively

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* A survey was sent to each pulp and paper mill in the Great Lakes basin to request information on their bleaching sequences, chlorine usages etc. Among other objectives, CIELAP hoped to use this information to arrive at a better AOX estimate for U.S. mills. Unfortunately, only four mills responded and thus, the MISA estimate had to be used for U.S. mills.

** Please note that all Ontario mills taken together discharge over 61.7 million kgs of organochlorines into provincial waters. However, not all Ontario pulp and paper mills discharge into the Great Lakes basin (see Appendix D for a list of mills discharging into the Great Lakes).

based on Eka Nobel's estimation.[43] For each option, the current annual loadings of AOX are compared against the AOX removal by the given technologies.

Other Assumptions

(a) The financial costs and benefits of the BAT options have not been examined. The sole purpose of this report is to identify choices for pollution prevention, and it should be emphasized that BAT standards will not be developed based on costs.

(b) With exception of BAT option 1, the BAT options are applied across all mills, regardless of whether a particular mill already uses one component of the BAT option. This allows a better comparison between the different technologies.

(c) The BAT options also focus on water discharges only. Sludge management and air pollution from boilers deserve further study.

(d) The assessment of BAT options is considered to be of the general type as more detailed operation specifications and associated data remain unavailable.

(e) Issues such as energy consumption, secondary air emissions and noise implications have been omitted for the purposes of this study, but deserve further study.

6. The BAT Options

The purpose of this section is not to set discharge limits as with the strict definition of BATs, but rather to recognize choices which can eliminate the use, generation and discharge of persistent toxic pollutants. In essence, this is a comparative analysis, comparing various technological options for their ability to remove chlorinated organics (measured as AOX).

Generally, mechanical and sulphite mills do not discharge chlorinated organics and thus, the emphasis in evaluating alternative technologies focuses on kraft mills. As a result, the comparative analysis for the different technologies is done exclusively for kraft mills, while only a few comments are warranted for mechanical and sulphite mills.

6.1. Mechanical Mills

Because of tightening of the environmental regulations, many new mills are now considering the zero-effluent technology. That is, new mills can be built without any discharges into surface waters. Indeed, there are two mills currently under construction in Canada which will operate on a closed-loop system, the Millar Western mill in Saskatchewan and the Orenda Forest Products mill near Stewart, British Columbia. Both mills will be operational in 1992.

Millar Weston is a chemi-thermomechanical mill with a production capacity of 240,000 tonnes of pulp per year. The mill design will incorporate an effluent treatment system which will continually recycle the water used in the pulping process. The pulp will be used to produce tissues, paper towels, printing and writing paper.[44] Similarly, the Orenda will be an effluent-free groundwood mill, which first treats its water and then reuses it in the various pulping processes.[45]

6.2. Sulphite Mills

The are only two sulphite mills in the Great Lakes basin which still use chlorine compounds in their processes. In the past, most mills have switched to hydrogen peroxide with the aim of eliminating chlorine usage. Replacing chlorine with hydrogen peroxide in a closed-system will achieve a reduction of BOD (40%), colour (90%) and will eliminate chlorinated substances in the effluent.

6.3. Kraft Mills

Five separate AOX options are presented in this section, each having a different capacity to remove or eliminate the discharge of chlorinated organics. Each option is summarized first with its removal efficiency and resulting AOX loadings into the Great Lakes. An explanation of the technology follows, with world-wide examples of where the technology has been applied.

Option 1 **Best Available Technology in the United States**		
Steps: Molecular Chlorine Bleaching Aerated Lagoon		
AOX removal efficiency:		
Current AOX Loadings into the Great Lakes (tonnes/year)	Removal Efficiency	Option 1 Loadings (tonnes/year)
7,528.7	30%	6,719.5

Option 1: Best Available Technology in the United States

Chlorinated organics can be removed to some extent by treating effluents in aerated lagoons. While biological treatment systems such as aerated lagoons are in extensive use in the U.S., only five out of nine Ontario kraft mills employ such secondary treatment. Thus, the AOX loading reductions apply to Ontario mills only since most U.S. mills already have secondary treatment.

Although aerated lagoons offer some reduction in the level of AOX, the use of these lagoons does not eliminate chlorinated organics. In addition, aerated lagoons can create contaminated sludge which needs to be removed. However, the E.B. Eddy mill in Espanola, Ontario has used an aerated lagoon for eight years and generated only six inches of sludge because the lagoon was properly operated.[46]

Bryant and colleagues estimated that about 30% of the non-volatile AOX can be removed in such lagoons.[47] Various other studies have shown that aerated lagoons can remove between 16-68% of the AOX.[48]

Option 2 Best Available Technology in Ontario		
Steps:		
Oxygen Delignification		
Molecular Chlorine Bleaching		
Aerated Lagoon		
AOX Removal Efficiency		
Current AOX Loadings into the Great Lakes (tonnes/year)	Removal Efficiency	Option 2 Loadings (tonnes/year)
7,528.7	50%	3764.4

Option 2: Best Available Technology in Ontario

By using an oxygen delignification process, the generation of chlorinated organics is reduced significantly. Oxygen delignification, or oxygen bleaching, is applied prior to chlorine bleaching. The oxygen is used to reduce the amount of lignin, while maintaining the pulp's strength characteristics. As a result, less chlorine or chlorine compounds are required to bleach the pulp, reducing the amount of chlorinated organics in mill effluents.[49] In general, oxygen delignification reduces the discharge of chlorinated organic compounds by about 40% and BOD discharges by about 50%.[50]

Furthermore, the reduced use of chlorine gives an overall reduction of operating costs, because oxygen is less expensive than chlorine and because oxygen delignification requires significantly less energy and water.[51]

Considerable development work on oxygen delignification has been carried out over the past 20 years with a number of commercial plants in operation around the world. New environmental regulations in Sweden and Germany have prompted the pulp and paper industry to introduce oxygen delignification. In Sweden, thirteen of the country's fifteen bleached kraft mills have introduced, or are in the process of introducing, oxygen delignification.

The only Ontario mill with an oxygen system is the E.B. Eddy kraft mill in Espanola. This mill has been using oxygen delignification since 1977 for its softwood and since 1980 for its hardwood pulp. With oxygen delignification in place, the mill reported a 50% reduction in bleached plant effluents and a 30% saving in chemical costs.[52] Champion International in Palmyra, Michigan is another mill in the Great Lakes basin which has recently installed an oxygen system.[53]

A 50% removal efficiency has been applied to the current loadings based on the work by Norstom and by Bonsor and colleagues.[54]

Option 3 Chlorine Dioxide Substitution		
Steps: Oxygen Delignification Chlorine Dioxide Substitution Aerated Lagoon		
AOX Removal Efficiency		
Current AOX Loadings into the Great Lakes (tonnes/year)	Removal Efficiency	Option 3 Loadings (tonnes/year)
7528.7	60%	3011.5

Option 3: Chlorine Dioxide Substitution

The advantage of substituting chlorine dioxide for molecular chlorine is a reduced requirement of bleaching chemicals to reach the same pulp brightness. It is common practice for mills with a chlorine bleaching operation to substitute some of their molecular chlorine with chlorine dioxide. A bleach operation with no chlorine dioxide substitution may use up to 60 kg of molecular chlorine per tonne of pulp. A 30% chlorine dioxide substitution will reduce the chlorine consumption to 42 kg/tonne of pulp.

For this option, most of the molecular chlorine is substituted with chlorine dioxide. However, while reducing the amount of AOX, chlorine dioxide still generates chlorinated organic compounds and is thus not a completely acceptable alternative.

The 60% removal efficiency is based on the study undertaken by Bonsor and colleagues.[55]

Option 4 The Lignox Method		
Steps: Extended Delignification Oxygen Delignification Hydrogen Peroxide Bleaching Chlorine Dioxide Bleaching (if required) Aerated Lagoon		
AOX Removal Efficiency		
Current AOX Loadings into the Great Lakes (tonnes/year)	Removal Efficiency	Option 4 Loadings (tonnes/year)
7528.7	80%	1505.7

Option 4: The Lignox Method

Eka Nobel of Nobel Industries in Sweden has developed this method for bleaching pulp without using molecular chlorine. The process is based on two oxygen delignification steps, a bleaching step with hydrogen peroxide and a bleaching step with chlorine dioxide (if required).[56]

Although the Lignox method removes 80% of the AOX[57] compared to conventional kraft technologies, Eka Nobel found that it could sell a substantial amount of pulp that was not bleached with chlorine dioxide (ie. no AOX formed). That is, pulp bleached with only oxygen and hydrogen peroxide reaches a brightness of about 75% ISO, and because this is sufficient for many applications, the chlorine-free pulp is in greater demand.[58]

Option 5 **Chlorine-Free Bleaching for Kraft Mills**		
Steps: Oxygen Delignification Ozone Delignification Hydrogen Peroxide Bleaching Sodium Hydrosulphite Bleaching Aerated Lagoon		
AOX Removal Efficiency:		
Current AOX Loadings into the Great Lakes (tonnes/year)	Removal Efficiency	Option 5 Loadings (tonnes/year)
7528.7	100%	0.0

Option 5: Chlorine-Free Bleaching for Kraft-Bleach Mills

This option requires a process change as well as chemical substitution. Oxygen and ozone are used to delignify the pulp, while peroxide and hydrosulphite are used to bleach and brighten it.[59]

Chlorinated organics are not produced, since the use of chlorine-based compounds is eliminated. In addition, substantial reductions in biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are achieved. The end products will be similar to the conventional bleached pulp, with 90.1% brightness versus the 90.6% brightness of chlorine bleached pulp (see also Appendix H).[60]

This option is not yet in commercial use but has been tested extensively in pilot plants where it has shown good promise. The Union Camp Corporation currently has several pilot plants using ozone bleaching.[61]

Bleaching softwood kraft pulp with different sequences of oxygen, ozone, caustic soda, hydrogen peroxide and sodium hydrosulfite produces high brightness pulps with similar strength qualities as conventional pulps.[62] Thus, its commercial use remains just a question of time.

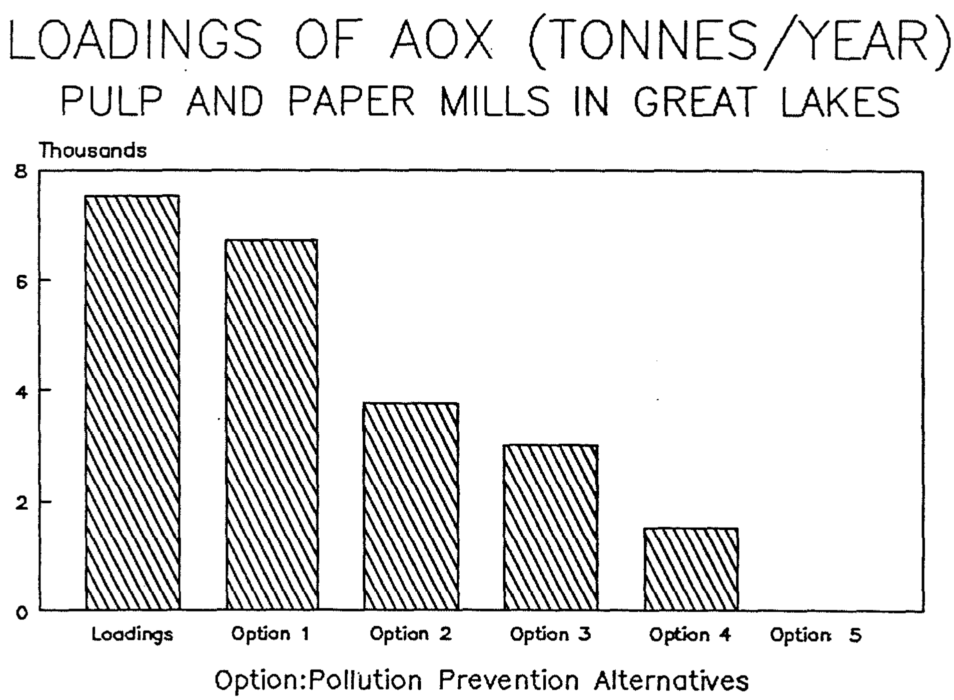
6.4. Summary of BAT Options

Table 4 summarizes the components of each option, while Figure 3 illustrates the loading reductions of the AOX options.

Table 4. Summary of AOX Reduction Options.

OPTION 1	OPTION 2	OPTION 3	OPTION 4	OPTION 5
chlorine bleaching aerated lagoon	chlorine bleaching oxygen de-lignification aerated lagoon	oxygen de-lig. chlorine dioxide bleaching aerated lagoon	oxygen and extended de-lignification hydrogen per-oxide and chlorine dio-xide bleaching (if required) aerated lagoon	oxygen and ozone de-lignification hydrogen per-oxide and sodium hydro-suphite bleaching aerated lagoon

Figure 3. Summary of Removal Efficiencies using the Various AOX Options.



7. Conclusion and Recommendations

The purpose of this report is to examine pollution abatement technologies, with an emphasis on pollution prevention, to approach the goal of zero discharge for the pulp and paper industry. This report does not attempt to set actual BAT limits or to examine the financial costs and benefits of each technology.

In eliminating discharges of chlorinated organic substances, it is necessary to examine two factors. First, the types of products which have been traditionally bleached do not really need to be bleached. The purpose of toilet paper, diapers, envelopes, writing paper and posters does not suffer from a light brown colour. Second, the technologies available to make white paper should be chosen in a way consistent with zero discharge.

Furthermore, market pulp is a commodity traded widely around the world, and markets for unbleached paper products are growing in countries all over the world. Some countries, for example Germany, impose taxes on the amount of AOX in pulp. Thus, unless the North American pulp and paper industry takes some action to reduce their chlorine usage, there is a possibility that they may lose their competitive position in the world market.

Regardless, from reviewing the available technologies, it has become obvious that chlorine compounds can be replaced in the pulp and paper manufacturing within the next few years. This will be an important step forward in keeping the promises made in the Great Lakes Water Quality Agreement. Therefore, CIELAP recommends the following:

Recommendation 1: MONITORING OF PRIORITY POLLUTANTS

One of the requirements of a BAT must be the continuous monitoring for persistent priority pollutants until zero discharge mills are achieved. Such monitoring should be implemented immediately for all types of mills.

Recommendation 2: MECHANICAL MILLS

All new mechanical mills should be built using the zero-effluent technology. This is an available technology with two such mills starting production in 1992 in western Canada. Existing mechanical mills, which still discharge effluents into surface waters, should upgrade their operations to zero-effluent mills by the year 2000.

Recommendation 3: SULPHITE MILLS

All new sulphite mills should use the oxygen delignification and hydrogen peroxide bleaching technologies. All chlorine-using sulphite mills should convert to chlorine-free bleaching, using oxygen and hydrogen peroxide, by 1996.

Recommendation 4: KRAFT MILLS

New kraft mills, which do not require high brightness for their products, should use the Lignox method without chlorine dioxide bleaching. New kraft mills, which do require a high degree of brightness for their products, should use oxygen and ozone to delignify the pulp, and hydrogen peroxide and sodium hydrosulphite to bleach and brighten it. In addition, all new kraft mills should install a secondary treatment plant.

Existing kraft mills should convert to the Lignox method or the oxygen/ozone/hydrogen peroxide/sodium hydrosulphite method by the year 2000. Furthermore, such mills should install a secondary treatment plant by the 1994.

Appendix A

U.S. Best Available Technology Standards for Pulp and Paper Mills.

BAT EFFLUENT LIMITATIONS
(kg/kkg or lbs/1000 lbs)

Subcategory	Maximum Day PCP[1]	TCP[2]	Zinc
Integrated Segment			
Dissolving Kraft	0.0025	0.016	NA
Market Bleached Kraft	0.0019	0.012	NA
BCT Bleached Kraft	0.0016	0.010	NA
Alkaline-Fine[3]	0.0014	0.0088	NA
Unbleached Kraft			
o Linerboard	0.00058	0.00053	NA
o Bag	0.00058	0.00053	NA
Semi-Chemical	0.0012	0.00043	NA
Unbleached Kraft and Semi-Chemical	0.00064	0.00059	NA
Dissolving Sulfite Pulp			
o Nitration	0.0030	0.019	NA
o Viscose	0.0030	0.019	NA
o Cellophane	0.0030	0.019	NA
o Acetate	0.0033	0.021	NA
Papergrade Sulfite[4]	*	*	*
Groundwood-Thermo-Mechanical	0.00097	0.00088	0.26
Groundwood-CMN Papers	0.0011	0.00099	0.30
Groundwood-Fine Papers	0.0010	0.00092	0.27
Secondary Fibers Segment			
Deink			
o Fine Papers	0.0030	0.0069	NA
o Tissue Papers	0.0030	0.0069	NA
o Newsprint	0.0030	0.0010	NA
Tissue From Wastepaper	0.0030	0.0011	NA
Paperboard From Wastepaper			
o Corrugating Medium Furnish	0.00087	0.00030	NA
o Noncorrugating Medium Furnish	0.00087	0.00030	NA
Wastepaper-Molded Products	0.0026	0.00088	NA
Builders' Paper and Roofing Felt	0.0017	0.00060	NA
Nonintegrated Segment			
Nonintegrated-Fine Papers			
o Wood Fiber Furnish	0.0018	0.00064	NA
o Cotton Fiber Furnish	0.0051	0.0018	NA
Nonintegrated-Tissue Papers	0.0028	0.00096	NA
Nonintegrated-Lightweight Papers			
o Lightweight	0.0059	0.0020	NA
o Electrical	0.0093	0.0032	NA
Nonintegrated-Filter and Nonwoven Papers	0.0072	0.0025	NA
Nonintegrated-Paperboard	0.0016	0.00054	NA

*Papergrade Sulfite Equations:

PCP = 0.00058 exp(0.017x)
TCP = 0.0036 exp(0.017x)
Where x equals percent sulfite pulp produced on-site in the final product.

[1]PCP = Pentachlorophenol

[2]TCP = Trichlorophenol

[3]Includes Fine Bleached Kraft and Soda subcategories.

[4]Includes Papergrade Sulfite (Blow Pit Wash) and Papergrade Sulfite (Drum Wash) subcategories.

NA = Not applicable.

Source: U.S. EPA, 1982. Development Document for Effluent Limitations Guidelines, New Source Performance Standards and Pretreatment Standards. EPA Report No. 440/1-82/025

Appendix B

MISA Monitoring Requirements for the Pulp and Paper Sector.

There are 27 pulp and paper mills located throughout Ontario which discharge their effluents into Ontario's waterways. From these 27 mills, 20 of them discharge their effluents into the Great Lakes basin.

Historically, pulp and paper mills discharged solids, dissolved organic and inorganic materials into the receiving waters. Until 1960 there were no regulations in place to limit these discharges. In the early 1960's remedial programs were developed by the Ontario government to reduce suspended solids and BOD.

Ontario's pulp and paper plants are to monitor their own effluents under the MOE's Industrial Monitoring Information System (IMIS) requirements. The data reported to the Ministry include:

- o biochemical oxygen demand (BOD5)
- o suspended solids
- o pH
- o total phosphorus
- o phenols
- o metals
- o toxicity test
- o nitrogen

Classification of Ontario Pulp and Paper Mills

After reviewing the operations at industrial mills and having determined the chemicals that are of concern at each mill, the Ministry classified mills into 4 categories:[63]

- Kraft (9 plants)
- Sulphite-mechanical (8 plants)
- Corrugating (2 plants)
- De-inking-board-fine papers-tissues (8 plants)

Contaminants and Frequency of Monitoring under MISA

The selection of contaminants and the frequency of monitoring were based primarily on the pre-regulation monitoring data, on the best practical judgement of the regulation writing sub-committee, and on the recommendation of the MISA advisory committee.

<u>A) Process effluents</u>

o Daily monitoring

This is used for conventional pollutants in all mills

1. Chemical Oxygen Demand/Dissolved Organic Carbon (COD/DOC)
2. Total suspended solids (TSS)
3. Specific conductance

- **Thrice-weekly monitoring***

1. BOD5
2. Resin and fatty acids
3. Chlorinated organic halides (AOX)**

- **Weekly monitoring**

1. Total phosphorus and nitrogen
2. Volatile suspended solids.
3. Aluminum
4. Zinc

- **Monthly monitoring**

1. Nitrogen and total phosphorus
2. Sulphide
3. Resin and fatty acids
4. Chlorinated organic halides (AOX)***
5. Chlorinated dioxins and furans****
6. Sector characterization

The remaining analytical test groups which are required to be monitored on a monthly basis for sector characterization are: total metals, mercury, sulphide (kraft only) volatile; halogenated volatile; non-halogenated, base neutral extractables, acid extractables, neutral extractables, resin and fatty acids, toxicity.

- **Bi-monthly monitoring**

1. Chlorinated Dioxins and Dibenzofurans*****

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* Only surrogate compounds are used for the thrice-weekly monitoring. The surrogate compounds for kraft mills are dehydroabietic acid (DHA) and dichlorodehydroabietic acid (DCHA). The surrogate compound for sulphite-mechanical and corrugating mills is dehydroabietic acid.

** Only kraft mills are required to monitor thrice-weekly for AOX.

*** Other than kraft mills, the mills which use chlorine compounds for brightening are required to monitor for AOX on a monthly basis.

**** Mills which use chlorine or chlorine derivatives for bleaching or brightening are required to monitor these compounds on a monthly basis.

***** For mills which do not use chlorine regularly.

- **Semi-Annual monitoring**

1. Chlorinated Dioxins and Dibenzofurans*
2. Open characterization

<u>B) Cooling water effluents</u>

- **Monthly monitoring**

COD/DOC, TSS, pH and specific conductance should be tested monthly to characterize cooling water effluents and to determine whether they are contaminated with process wastes.

<u>C) Waste disposal site effluents</u>

- **Monthly monitoring**

BOD5, suspended solids, nitrogen, phosphorus and pH are required to be tested on a monthly basis for any leachate which flows continuously from a waste disposal site.

In addition, total metals and mercury are also required to be monitored for any disposal site which receives chemical sludge or mud resulting from mill operations.

<u>D) Backwash effluents</u>

- **Monthly monitoring**

COD/DOC, pH and TSS are required to be monitored.

<u>E) Emergency overflow effluents</u>

- **Per event**

COD/DOC, TSS and specific conductance are required to be monitored.

<u>F) Storm water effluents</u>

- **Semi-Annually**

Storm water monitoring is being required on a limited basis at a number of mills.

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* For mills which do not manufacture or use bleached pulp.

Appendix C

Summary of In-Plant Control Measures for Pulp and Paper Mills.

PRODUCTION PROCESS CONTROL TECHNOLOGIES AVAILABLE FOR REDUCTION OF EFFLUENT VOLUME AND POLLUTANT LOADINGS

Woodyard/Woodroom
- Closeup or dry operation
- Segregate cooling water

Pulp Mill
- Reuse blow condensates
- Reduce thickener overflow (groundwood)
- Spill collection

Brown Stock Washers and Screen Room
- Add third or fourth stage washer
- Recycle more decker filtrate
- Cleaner rejects to landfill

Bleaching Systems
- Countercurrent or jumpstage wash
- Evaporate caustic extraction stage filtrate

Evaporation and Recovery
- Recycle of condensates
- Replace barometric condenser with surface condenser
- Boilout tank
- Neutralize spent sulfite liquor
- Segregate cooling water
- Spill collection

Liquor Preparation Area
- Installation of green liquor dregs filter
- Lime mud pond

Papermill
- Spill collection
- Improvement of savealls
- Use of high pressure showers for wire and felt cleaning
- Whitewater use for vacuum pump sealing
- Papermachine whitewater use on wire cleaning showers
- Whitewater storage for upsets and pulper dilution
- Recycle of press water
- Reuse of vacuum pump water
- Additional broke storage
- Installation of wet lap machines or other screening devices
- Segregate cooling water
- Cleaner rejects to landfill
- Fourth stage cleaners

Steam Plant and Utility Areas
- Segregate cooling water
- Lagoon for boiler blowdown and backwash waters

Recycle of Treated Effluent

Chemical Substitution

Source: U.S. EPA, 1982. Development Document for Effluent Guideline New Source Performance Standards and Pretreatment Standards. EPA Report No. 440/1-82/025

Appendix D

Production Capacities, Treatment Systems and Effluent Volumes for Pulp and Paper Mills in the Great Lakes Basin.

Table 1: PULP AND PAPER FACILITIES IN ONTARIO DISCHARGING INTO GREAT LAKES

FACILITY	TYPE	PRODUCTION (tons/day)	EFFLUENT TREATMENT	EFFLUENT DISCHARGE m3/day	RECEIVING WATER
Abitibi-Price Inc., Fort William	Groundwood Chemi-mechanical Paper making	235 GWP* 135 CMP** 383 Newsprint	Primary: Clarifier 3 Settling ponds	14,160	Thunder Bay Lake Superior
Abitibi-Price Inc., Iroquois Falls	Groundwood Sulphite Paper making	620 GWP 205 Sulphite 825 Newsprint	Primary: 2 Clarifiers	53,300	Abitibi River Lake Huron
Abitibi-Price Inc., Thunder Bay	Groundwood Sulphite Paper making	320 GWP 120 Sulphite 442 Newsprint	Primary: Clarifier, 2 Settling-lagoons	35,000	Thunder Bay Lake Superior
Abitibi-Price Inc., Provincial Papers	Groundwood Paper making	125 GWP 442 Fine and coated papers	Primary: Clarifier, Settling pond	47,000	Thunder Bay Lake Superior
Beaverwood Fibre Co.LTD, Thorold	Waste paper and board pulping, Paperboard formation	273 paperboard	Primary: Clarifier, Spill pond	14,000	Welland Canal Lake Ontario
Canadian-Pacific Forest Products LTD., Thunder Bay	Kraft Groundwood Sulphite Paper-making	910 GWP 300 Sulphite 1300 BKP*** 1170 Newsprint	Primary: 4 Clarifier	222,000	Kamanistikwia River Lake Superior
Domtar Inc., Fine Paper Div., Cornwall	Kraft Paper-making	400 BKP 200 Paperboard 600 Fine paper	Primary: Clarifier	102,400	St.Lawrence River
Domtar Inc., Containerboard Div.,Red Rock	Kraft Groundwood Paper-making	600 kraft pulp 150 GWP 50 Semi-bleached 600 Linerboard 200 Newsprint	Primary: Clarifier, Spill pond	91,000	Nipigon Bay Lake Superior
Domtar Inc., Fine Papers Div., St.-Catharines	Repulping Paper-making	200 Fine paper	Primary: Clarifier	9,752	Old Welland Canal Lake Ontario
Domtar Inc., Containerboard Div.,Trenton	Semi-Chemical Board making	130 SCP 282 Corrugating-medium	Recovery and Reuse of Spent Pulping Liquors	3,700	Trent River Lake Ontario
E.B.Eddy Forest-Product LTD., Espanola	Kraft Pulp-Bleaching Oxygen Delignification Paper-making	900 BKP 120 Kraft-Speciality paper Fine paper	Primary: Settling-Lagoon, 2 Clarifiers; Secondary: aerated Lagoon	117,600	Spanish River Lake Huron
Fraser Inc. Thorold	Deinking Paper making	270 Fine-papers	Primary: Clarifier; Secondary: High-rate biological-oxidation, Clarifier	25,300	Welland Canal Lake Ontario
James River Marathon LTD., Marathon	Kraft	440 BKP	Primary: Clarifier, Diffuser-outfall	64,530	Lake Superior
Kimberly Clark of Canada LTD., Huntsville	Paper making (Tissue)	95 Tissue	Primary: Clarifier, Polishing basins Percolation-bed (Winter) Spray irrigation (Summer)	425	Muskoka River Lake Ontario

FACILITY	TYPE	PRODUCTION (tons/day)	EFFLUENT TREATMENT	EFFLUENT DISCHARGE m3/day	RECEIVING WATER
Kimberly Clark of Canada, LTD., St. Catharines	Paper making	50 Tissue 35 Crepe 12 Fine Paper	Primary: Clarifier, Detention-basin	10,066	Old Welland Canal Lake Ontario
Kimberly-Clark of-Canada, LTD., Terrace Bay	Kraft	1200 BKP	Primary: 2 Clarifiers; Secondary: Aerated Lagoon	121,120	Moberly Bay, Lake Superior
MacMillan-Bloedel LTD., Sturgeon Falls Div., Sturgeon	NSSC**** Mechanical paperboard-formation, Hardboard-sheet formation	200 NSSC pulp 110 Chemical 200 Corrugating-medium 110 Hardboard	Primary: Clarifier	10,760	Sturgeon River Lake Huron
Quebec and Ontario Paper-Company LTD., Thorold	Deinking TMP Paper making	460 TMP pulping 540 Deinked-fibre 900 Newsprint	Primary: Clarifier; Secondary: High-rate biological-Treatment, 2 Clarifiers	85,000	Old Welland Canal Lake Ontario
Strathcona Paper Company, Strathcona	Waste paper and repulping paperboard-formation	165 Box board	Primary: 5 settling-ponds; Secondary: 2 aerated-lagoons	3,200	Napanee River Lake Ontario
Paperboard Industries Corporation, Trent Valley Paperboard Mills Div., Trenton	Waste paper and repulping paperboard-formation	279 Paperboard	Primary: Clarifier	2,400	Trent River, Lake Ontario

Table 2. Pulp and Paper Mill Description for Mills on the U.S. Side of the Great Lakes.

FACILITY	TYPE	PRODUCTION TONS/DAY	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
Abitibi-Price Corp. Alpena, MI	hardboard	S1S hardboard - 147 tons/day; S2S hardboard - 421 tons/day; defibrated wood pulp - 400 tons/day	Primary Treatment: clarifier, flotation; Secondary Treatment: aeration lagoons; Tertiary Treatment: sludge dewatering, air flotation	7.2	Thunder Bay River to Lake Huron
Big M Paper-board Palmyra Palmyra, MI	unbleached kraft mill	chipboard, tube and drum stock linerboard - 85 tons/yr	Primary Treatment: aeration lagoons	0.9*	River Raisin to Lake Erie
Champion Int-Quinnesec Mill Quinnesec, MI	bleached kraft mill	market bleached kraft - 822 tons/day; fine bleached kraft - 378 tons/day; nonintegrated-fine papers - 554 tons/day	Primary Treatment: clarifiers; Secondary Treatment: 2 aeration basins, 2 clarifiers, sludge dewatering	48.4	Menominee River to Lake Michigan
E.B. Eddy Paper Inc. Port Huron, MI	paper-making	non-integrated lightweight paper - 400 tons/day	Primary Treatment: air flotation, clarifiers	24.5	Black River to Lake Erie
Fletcher Paper Co. Alpena, MI	paper-making kraft mill	nonintegrated fine papers - 85 tons/day	Primary Treatment: coagulation, clarifier, sludge lagoons	3.8	Thunder Bay River & Lake Huron
French Paper Co. Niles, MI	fine paper mill	nonintegrated fine papers - 50 tons/day	Primary Treatment: rectagular clarifier; Secondary Treatment: circular clarifier, Unox oxygen reaction to maintain health of activated sludge	1.9	St. Joseph River to Lake Michigan
James River KVP-Parchment Parchment, MI	paper-making	nonintegrated fine papers - 460 tons/day	Primary Treatment: clarifier; Secondary Treatment: aeration lagoon	15.8	Kalamazoo River to Lake Michigan
James River KVP Port Huron, MI	paper-making	nonintegrated fine paper - 185.6 t/day; nonintegrated lightweight papers- 5.7 tons/day	Primary Treatment: air flotation, microstrainer	27.3	St. Clair River to Lake Erie
Kimberly Clark Munising Paper Munising, MI	paper-making	nonintegrated-fine papers - 146 tons/day; nonintegrated-filter nonwoven papers - 31.1 tons/day	Primary Treatment: settling pond	20.0	Lake Superior
Manistique Papers Inc. Manistique, MI	deink specialty paper	deink pulp - 300 tons/day	Primary Treatment: 2 clarifiers Secondary Treatment: clarifier, activated sludge system	13.8	Manistique River to Lake Michigan

FACILITY	TYPE	PRODUCTION TONS/DAY	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
Mead Corp-Publishing Paper Division Escanaba, MI	bleached kraft mill	market bleached kraft - 250 tons/day; fine bleached kraft - 800 tons/day; groundwood-fine papers 450 tons/day; nonintegrated-fine-papers - 450 tons/day	Primary Treatment: clarifier; Secondary Treatment: aeration lagoon, clarifier	131.1	Escanaba River to Lake Michigan
Menasha Group Otsego, MI	semi-chemical wastepaper corrugated medium	unbleached semi-chemical - 300 tons/day; paperboard from wastepaper - 420 tons/day; corrugated medium - 550 tons/day	Primary Treatment: aeration pond (disc saveall), clarifier; Secondary Treatment: aeration ponds	2.0	Kalamazoo River to Lake Michigan
Menominee Paper Co. Menominee, MI	paperboard	paperboard from wastepaper - 350 tons/day; nonintegrated-tissue papers - 50 tons/day	Primary Treatment; Secondary Treatment: activated sludge	1.2	Menominee River to Lake Michigan
Packaging Corp of America Filer City, MI	semichemical kraft mill	semi-chemical - 768 tons/day; soda carbonate- 600 tons/day	Primary Treatment: 2 clarifiers; Secondary Treatment: aeration pond	20.3	Manistee Lake and Lake Michigan
Performance Paper Inc. Kalamazoo, MI	unbleached kraft mills	nonintegrated-fine paper - 280 tons/day	Primary Treatment: 2 clarifiers	1.5	Portage Creek to Lake Michigan
Procter & Gamble Paper Cheboygan, MI	sanitary paper-making	paper-making - 140 tons/day; converted paper - 260 tons/day	Primary Treatment: air flotation unit, vacuum filter	4.6	Cheboyga River to Lake Michigan
Rock-Tenn Co. Otsego, MI	paperboard	paperboard from wastepaper - 250 tons/days	Primary Treatment: 2 clarifiers; Secondary Treatment: stabilization basins aerator lagoon	1.5	Kalamazoo River to Lake Michigan
Simpson Plainwell Paper Plainwell, MI	paper-making	coated and uncoated book and cover, release base, technical specialties- 260 tons/day	Primary treatment: clarifier; Secondary Treatment: clarifier, aerated tank	9.2	Kalamazoo River to Lake Michigan
Stone Container Ontonagon, MI	semichemical	corrugating medium - 690 tons/day; unbleached hardwoood - 575 tons/day	Primary Treatment: clarifier; Secondary Treatment: clarifier, activated sludge, gravity thickener, belt filter press	26.8	Ontonagon River to Lake Superior
Watervliet Paper Co. Watervliet, MI	pulp and paperboard	books, coated paper - 151 tons/day	Primary Treatment: spray irrigation	34.07	Paw-Paw River to Lake Michigan

FACILITY	TYPE TONS/DAY	PRODUCTION	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
Armstrong World Ind. Fulton, NY	unbleached kraft mill	kraft and wrapping tissue - 8 tons/day	Primary Treatment: air flotation, clarifier	8.5	Oswego River to Lake Ontario
Champion International Deferiet, NY	groundwood stone	unbleached softwood - 310 tons/day	Primary Treatment: 2 clarifiers; Secondary Treatment: activated sludge, aeration basin, clarifiers, sludge dewatering press and coil filter	43.5	Black River to Lake Ontario
James River Corp-Nat. Dam Division Gouverneur, NY	unbleached kraft mill	specialty tissue non-woven in jumbo rolls - 45 tons/day		0.8	Oswegatchie River
Knowlton Specialty Watertown, NY	unbleached kraft mill	photo envelope, phenolic impregnated technical specialty papers - 20 tons/day	Primary Treatment	20	Black River to Lake Ontario
Lyon Falls Pulp & Paper Inc. Lyon Falls, NY	sulphite	pulp high yield - 120 tons/day	Primary Treatment: flotation clarifier; Secondary Treatment: 2-stage lagoon (stabilization area)	15.9	Black River to Lake Ontario
Norfolk Paper Company Inc. Norfolk, NY	paper-making	bleached and natural papers, tissue, wrapping, waxing, bag and laminating - 55 tons/day	Primary Treatment: flotation clarifier	22.7	Racquette River to St. Lawrence River
Papyrus Newton Falls Newton Falls, NY	unbleached kraft mill	coated and uncoated books, gumming, label papers - 400 tons/day	Primary and Secondary Treatment	25.5	Trib. to Oswegatchie River
Potsdam Paper Mills Potsdam, NY	unbleached kraft mill	MF and MG specialty papers, kraft specialty bag and paper	Primary Treatment: 1-60' clarifier, sludge thickening	5.3	Racquette River to St. Lawrence River
Sealright Co., Eastern Div. Fulton, NY	sanitary food containers				Oswego River to Lake Ontario
Schoeller Technical Paper Inc. Pulaski, NY	unbleached kraft mill	photographic and industrial paper, greeting card and custom specialty technical papers - 100 tons/day	Primary Treatment: 1 clarifier, 2 settling basins	6.5	Salmon River to Lake Ontario
Specialty Paperboard, Beaver Falls, NY	groundwood refiner	unbleached softwood - 50 tons/day	Primary Treatment: 2 DAS flotation system, landfills; Secondary Treatment: settling pond, secondary aeration ponds, clarifiers	21.9	Beaver River to Lake Ontario

FACILITY	TYPE	PRODUCTION TONS/DAY	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
U.S. Gypsum-Oakfield Plant Oakfield, NY	unbleached kraft mill	news and manila lined chip gypsum board liner, in rolls - 105 tons/day		15.4	TR Oak Orchard C. (Whitney Creek) to Lake Ontario
Certain-Teed Products Corp. Avery, OH	felt mill asphalt roofing defibrated wood pulp	roofing felt - 90 tons/day; unbleached hardwood - 110 tons/day	Primary Treatment: clarifier, settling pond	15	Mud Brook to Lake Erie
Ivex of Ohio Chagrin Falls, OH	nonintegrated	kraft paper - 69.2 tons/day	Primary Treatment: screening, clarifier, flotation	2.7	Chagrin River to Lake Erie
United States Gypsum Co. Gypsum, OH	gypsum products paperboard mill mineral wool paints & allied products		Primary Treatment: clarifier Secondary Treatment: aerated lagoons, dewatering press	7.3	Sandusky Bay to Lake Erie
Appleton Papers Inc. Locksmill, Combined Locks, WI	chemi-mech. pulp paper-making	carbonless paper - 530 tons/day; chemical wood pulp - 200 tons/day	Primary Treatment: flotation, neutralization, dual clarifiers, flocculation, sedimentation, belt press; Secondary Treatment: clarifier, activated pure air sludge system, pressure filtration	21	Fox River to Lake Michigan
Badger Paper Mills Inc. Peshtigo, WI	sulphite paper-making	paper production - 163.8 tons/day; bleached hardwood/softwood - 120 t/day	Primary Treatment: sedimentation; Secondary Treatment: activated sludge	5.8	Peshtigo River to Lake Michigan
Fort Howard Paper Co. Fox River Green Bay, WI	deinking pulp and paper manufacturing	sanitary paper products from deinked pulp - 992.8 tons/day; from purchased pulp - 4.4 tons/day; caustic soda - 24.6 tons/day; calcium hypochlorite bleach liquor - 23.2 tons/day	Primary Treatment: clarifier, sedimentation; Secondary Treatment: belt filtration, chemical conditioning, activated sludge aeration	46	Fox River to Lake Michigan
Green Bay Packaging Inc. Green Bay, WI	paperboard NSSC	corrugated medium - 370.65 tons/day; NSSC - 220 tons/day	reverse osmosis/ hyperfiltration	7.4	Fox River to Lake Michigan
James River Corp. Green Bay, WI	sulphite mill paper-making	tissue grade paper-making - 465.4 tons/day; paper forming and coating operations - 51 tons/day; pulp - 163.7 tons/day; bleached hardwood - 160 tons/day	Primary Treatment: neutralization, screening, clarifier, sedimentation; Secondary Treatment: sludge belt filtration	38.2	Fox River via Backwash East River to Lake Michigan

FACILITY	TYPE	PRODUCTION TONS/DAY	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
James River Paper Co. Ashland, WI	deink	bleached deinked pulp - 65 tons/ day	Primary Treatment: clarifier; Secondary Treatment: activated sludge system, belt press	61.6	L. Superior via Chequamego
Kerwin Paper Co. Div. River Side Corp.; Fox River Appleton, WI	sulphite groundwood	secondary fibre - 96 tons/day; pulp - 64 tons/day	Primary Treatment: pH adjuster	7.8	Fox River to Lake Michigan
Kimberly Clark Corp. Neenah, WI	bleached kraft mill	rag pulp - 6.5 tons/ day; fine specialty paper - 130.1 tons/day; machine creped paper - 61.8 tons/day	Primary Treatment: sedimentation, screening, clarifier; Secondary Treatment: activated sludge flotation, chemical conditioning, belt filtration	12.3	Fox River to Lake Michigan
Kimberly Clark Corp. Lakeview Division, Fox River Neenah, WI	sanitary paper products	sanitary pulp and creped wadding tissue - 204.4 tons/	Primary Treatment: screening, sedimentation, flocculation, anaerobic treatment; Secondary Treatment: belt filtration centrifugation, chemical conditioning	12.3	Little Lake Butte Des Morts to Lake Michigan
Midtec Paper Corporation Kimberly Mill, Fox River Kimberly, WI	groundwood stone	coated publication paper - 998.9 tons/ day; groundwood pulp - 134 tons/day; unbleached pulp - 180 tons/day	Primary Treatment: 2 clarifiers; Secondary Treatment: aeration pond, belt filter, sludge press, surface water, sludge oxidation	40.7	Fox River to Lake Michigan
Niagara of Wisconsin Paper Co. Niagara, WI	groundwood stone	coated fine paper - 680 ton/day; groundwood pulp - 210 tons/day	Primary Treatment: clarifier; Secondary Treatment: 2-stage activated sludge system	21	Menominee River to Lake Michigan
Nicolet Paper Co. Fox River DePere, WI	paper manufacturing	off machine paper - 194.6 tons/day	Primary Treatment: pH control, 2 clar- ifiers, belt filter, sedimentation, screening	11.9	Fox River to Lake Michigan
P.H. Glatfelter Bergstrom Paper Division Neenah, WI	bleached paper making deinking	fine paper - 400.8 tons/day; deinked pulp - 214.5 tons/day; calcium acid sulphite - 63.7 tons/day	Primary Treatment: screening, clarifier flocculation, dechlor- ination, neutralization; Secondary Treatment: 2 stage activated sludge system, air-flotation sludge thickener and dewatering system	14.5	Little Lake Co. Butte Des Morts to Lake Michigan

FACILITY	TYPE	PRODUCTION TONS/DAY	EFFLUENT TREATMENT SYSTEM	EFFLUENT DISCHARGE (1000 M3/DAY)	RECEIVING WATER
Procter & Gamble Fox River PLT Green Bay Green Bay, WI	bleached sulphite deinking papermaking converting	sulphite pulp - 376 tons/day; deinked pulp - 113 tons/day; total tissue - 780 tons/day	Primary Treatment: flocculation, screening, flotation, anaerobic treatment, sedimentation; Secondary Treatment: activated sludge, pressure filtration	17.4	Fox River to Lake Michigan
Scott Paper Co. Oconto Falls, WI	bleach sulphite deinking paper converting	wetlap pulp - 70 tons/day; bleached softwood - 17 tons/day	Primary Treatment: clarifier, screening, flocculation, settling; Secondary Treatment, clarifier, activated sludge, neutralization, belt filtration	4.9	Oconto River to Lake Michigan
Scott Paper Co. in Menominee River Marinette, WI	nonintegrated manufacturing and converting	paper - 305.05 tons/day	Primary Treatment: neutralization, coagulation, sedimentation, clarifier, belt filtration, lagoon	22	Menominee River to Lake Michigan
Shawano Paper Mills Little Rapids Div. Shawano, WI	nonintegrated specialty	lightweight specialty papers and facial tissue papers - 169 tons/day	Primary Treatment: flocculation, clarifiers; Secondary Treatment: sludge dewatering press, lagoon	6.9	Wolf River to Lake Michigan
Superior Fibre Products-Superwood Corp. Weyerhauser, WI	wet process hardboard	hardboard - 154 tons/day	Primary Treatment: sedimentation, pH adjustment	2.5	Superior Bay to Lake Superior
Thilmany Pulp & Paper Co. Fox River Kaukauna, WI	unbleached kraft mill converted papers	unbleached kraft pulp - 384 tons/day; lightweight kraft specialty papers - 517 tons/day; kraft - 420 tons/day	Primary Treatment: screening, clarifier; Secondary Treatments: aerated lagoons, Unox activated sludge system	71.4	Fox River to Lake Michigan
Wisconsin Tissue Mills Menasha, WI	deinking	tissue paper from deinked pulp - 270 tons/day	Primary Treatment: clarifier, screening flocculation, flotation; Secondary Treatment: two-stage activated sludge treatment system, belt filtration, aeration; Tertiary Treatment: carbon filter	10.9	Little Lake Butte Des Morts to Lake Michigan

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Appendix E

Pollutant Concentrations from Ontario Kraft Mills as Measured under the MISA Programme.

PRIORITY POLLUTANTS DETECTED IN THE SULPHATE (KRAFT) SUBCATEGORY PROCESS EFFLUENT

PARAMETER	No.	F.D.(%)	MIN	MAX	AVG	UNIT
Adsorbable Organic Halide	687	100	.14	461.05	21.75	mg/L
Aluminum	245	100	3.83	6,840.00	1,834.52	ug/L
BOD, 5 day, Total Demand	699	100	.00	498.00	131.14	mg/L
COD	1427	100	20.00	3,840.00	644.94	mg/L
Chloroform	52	100	6.90	1,757.60	437.71	ug/L
DOC	175	100	4.55	181.00	119.86	mg/L
Hydrogen ion (pH)	1600	100	2.30	10.82	6.63	
Specific conductance	1601	100	33.00	4,200.00	1,570.32	usiem/cm
Total phosphorus	124	100	.20	2.40	.84	mg/L
Total suspended solids	1600	100	3.00	404.80	65.00	mg/L
Total Kjeldahl nitrogen	145	99	.00	16.65	3.84	mg/L
VSS	102	99	.00	220.00	62.55	mg/L
Zinc	243	97	.00	490.00	99.50	ug/L
Sulphide	52	96	.00	10.50	.49	mg/L
Ammonia plus Ammonium	145	87	.00	3.51	.61	mg/L
Dehydroabietic Acid	679	85	.00	6.60	.47	mg/L
Chromium	47	72	.00	300.00	40.55	ug/L
Chlorodehydroabietic Acid	53	68	.00	.81	.09	mg/L
Isopimaric Acid	53	68	.00	2.52	.14	mg/L
Total TCDF	54	67	.00	1.60	.14	ng/L
Dichlorodehydroabietic Ac.	679	66	.00	.72	.06	mg/L
Pimaric Acid	53	66	.00	.41	.04	mg/L
Abietic Acid	53	64	.00	2.27	.23	mg/L
Copper	53	64	.00	290.00	18.79	ug/L
Oleic Acid	53	64	.00	.43	.08	mg/L
Nitrate+Nitrite	145	63	.00	37.20	.61	mg/L
Neoabietic Acid	53	60	.00	4.50	.19	mg/L
Octachlorodibenzo-p-dioxin	54	54	.00	1.90	.20	ng/L
2,4,6-Trichlorophenol	53	51	.00	27.00	4.56	ug/L
2,4-Dichlorophenol	53	51	.00	8.10	2.08	ug/L
Vanadium	53	51	.00	70.00	8.39	ug/L
Toluene	52	48	.00	35.80	3.62	ug/L
Phenol	53	47	.00	186.00	19.20	ug/L
Molybdenum	53	45	.00	60.00	7.92	ug/L
Nickel	53	43	.00	160.00	11.09	ug/L
2,4,5-Trichlorotoluene	52	35	.00	1.41	.15	ug/L
Levopimaric Acid	43	35	.00	.09	.01	mg/L
Camphene	53	34	.00	85.00	5.36	ug/L
Mercury	52	33	.00	3.40	.09	ug/L
Thallium	53	32	.00	40.00	9.08	ug/L

No. = NUMBER OF ANALYSES
F.D. = FREQUENCY OF DETECTION ABOVE THE LABORATORY METHOD DETECTION LIMIT (%)
MIN = MINIMUM CONCENTRATION
MAX = MAXIMUM CONCENTRATION
AVG = AVERAGE CONCENTRATION IN THE PERIOD JANUARY 1 - JUNE 30, 1990
UNIT = UNIT OF MEASUREMENT

NOTE: Values less than the detection limit are treated as zero.
Minimum, maximum and average values are cited to two decimal places.

Source: Ontario Ministry of the Environment, 1991. Preliminary Report on the First Six Months of Process Effluent Monitoring in the MISA Pulp and Paper Sector. Toronto, Ontario.

PRIORITY POLLUTANTS DETECTED IN THE SULPHATE (KRAFT) SUBCATEGORY PROCESS EFFLUENT

PARAMETER	No.	F.D.(%)	MIN	MAX	AVG	UNIT
o-Cresol	53	32	.00	12.00	1.59	ug/L
Hexachlorobenzene	53	30	.00	2.21	.15	ug/L
Hexachlorocyclopentadiene	53	30	.00	.34	.02	ug/L
Lead	53	30	.00	80.00	6.58	ug/L
m-Cresol	51	29	.00	79.00	5.24	ug/L
Cadmium	53	28	.00	4.00	.62	ug/L
1,2,3-Trichlorobenzene	53	26	.00	3.05	.22	ug/L
Hexachlorobutadiene	50	26	.00	.16	.01	ug/L
Benzene	52	25	.00	12.50	1.35	ug/L
Octachlorostyrene	52	25	.00	.99	.04	ug/L
1,2,4-Trichlorobenzene	53	23	.00	.98	.05	ug/L
2,3,5-Trichlorophenol	53	23	.00	19.80	2.05	ug/L
Methylene chloride	52	23	.00	400.00	24.26	ug/L
Pentachlorobenzene	53	23	.00	1.26	.09	ug/L
Styrene	52	23	.00	14.40	.86	ug/L
Beryllium	53	21	.00	12.00	1.16	ug/L
Cobalt	53	21	.00	22.00	3.58	ug/L
Hexachloroethane	53	21	.00	.14	.01	ug/L
1,2,4,5-Tetrachlorobenzene	46	20	.00	.30	.02	ug/L
Total H7CDD	54	19	.00	.75	.02	ng/L
Total PCDF	54	19	.00	1.20	.04	ng/L
Total TCDD	54	19	.00	.79	.03	ng/L
p-Cresol	49	18	.00	13.00	.77	ug/L
Naphthalene	53	17	.00	8.60	.52	ug/L
m-Xylene and p-Xylene	52	17	.00	19.20	.66	ug/L
1,2,3,4-Tetrachlorobenzene	53	15	.00	.37	.02	ug/L
Phenanthrene	53	15	.00	19.90	1.13	ug/L
2,3,4,5-Tetrachlorophenol	49	14	.00	2.60	.17	ug/L
PCBT	8	13	.00	.26	.03	ug/L
Silver	53	13	.00	10.00	.81	ug/L
Fluoranthene	53	11	.00	9.00	.42	ug/L
Pentachlorophenol	53	11	.00	2.70	.17	ug/L
Total PCDD	54	11	.00	.09	.00	ng/L
Bromomethane	52	10	.00	390.00	9.42	ug/L
Chloromethane	52	10	.00	1,100.00	21.99	ug/L
1,2,3,5-Tetrachlorobenzene	46	9	.00	1.00	.03	ug/L
2,3,5,6-Tetrachlorophenol	53	9	.00	6.20	.27	ug/L
2,4-Dimethylphenol	53	9	.00	4.80	.24	ug/L
Indole	53	9	.00	6.20	.30	ug/L
Pyrene	53	9	.00	6.60	.25	ug/L
Total H6CDF	54	9	.00	.31	.01	ng/L

No. = NUMBER OF ANALYSES
F.D. = FREQUENCY OF DETECTION ABOVE THE LABORATORY METHOD DETECTION LIMIT (%)
MIN = MINIMUM CONCENTRATION
MAX = MAXIMUM CONCENTRATION
AVG = AVERAGE CONCENTRATION IN THE PERIOD JANUARY 1 - JUNE 30, 1990
UNIT = UNIT OF MEASUREMENT

NOTE: Values less than the detection limit are treated as zero.
Minimum, maximum and average values are cited to two decimal places.

PRIORITY POLLUTANTS DETECTED IN THE SULPHATE (KRAFT) SUBCATEGORY PROCESS EFFLUENT

PARAMETER	No.	F.D.(%)	MIN	MAX	AVG	UNIT
2,4,5-Trichlorophenol	53	8	.00	12.00	.62	ug/L
Bromodichloromethane	51	8	.00	6.60	.26	ug/L
Octachlorodibenzofuran	54	7	.00	.16	.01	ng/L
Total H6CDD	54	7	.00	.27	.01	ng/L
1,1-Dichloroethylene	52	6	.00	14.40	.36	ug/L
2,3,7,8 TCDD	54	6	.00	.08	.00	ng/L
2-Chlorophenol	53	6	.00	2.20	.06	ug/L
4-Chloro-3-methylphenol	53	6	.00	9.20	.19	ug/L
Acenaphthylene	53	6	.00	5.40	.22	ug/L
Total H7CDF	54	6	.00	.17	.01	ng/L
o-Xylene	52	6	.00	16.80	.39	ug/L
1,1,2,2-Tetrachloroethane	52	4	.00	14.40	.36	ug/L
1,2-Dichlorobenzene	52	4	.00	15.60	.34	ug/L
1,4-Dichlorobenzene	52	4	.00	9.60	.19	ug/L
2,3,4-Trichlorophenol	53	4	.00	28.00	.75	ug/L
2,4-Dinitrophenol	53	4	.00	1.80	.04	ug/L
2-Methylnaphthalene	53	4	.00	2.90	.06	ug/L
Bromoform	52	4	.00	340.00	6.79	ug/L
Chlorobenzene	52	4	.00	24.00	.51	ug/L
Chrysene	53	4	.00	1.70	.05	ug/L
Trichlorofluoromethane	52	4	.00	12.00	.27	ug/L
1,1,2-Trichloroethane	52	2	.00	22.80	.44	ug/L
1,1-Dichloroethane	52	2	.00	20.40	.39	ug/L
1,2-Dichloroethane	52	2	.00	16.80	.32	ug/L
1,2-Dichloropropane	52	2	.00	21.60	.42	ug/L
1,3-Dichlorobenzene	52	2	.00	13.20	.25	ug/L
2,3,4,6-Tetrachlorophenol	47	2	.00	1.80	.04	ug/L
4-Nitrophenol	53	2	.00	1.80	.03	ug/L
Acenaphthene	53	2	.00	.80	.02	ug/L
Anthracene	53	2	.00	1.60	.03	ug/L
Benz(a)anthracene	53	2	.00	.90	.02	ug/L
Carbon tetrachloride	52	2	.00	12.00	.23	ug/L
Cis-1,3-Dichloropropylene	52	2	.00	27.60	.53	ug/L
Dibromochloromethane	52	2	.00	16.80	.32	ug/L
Ethylene dibromide	52	2	.00	22.80	.44	ug/L
Tetrachloroethylene	52	2	.00	190.00	3.65	ug/L
Trans-1,2-Dichloroethylene	52	2	.00	16.80	.32	ug/L
Trans-1,3-Dichloropropylene	52	2	.00	44.00	.85	ug/L
Trichloroethylene	52	2	.00	12.00	.23	ug/L
Vinyl chloride	52	2	.00	116.00	2.23	ug/L

No. = NUMBER OF ANALYSES
F.D. = FREQUENCY OF DETECTION ABOVE THE LABORATORY METHOD DETECTION LIMIT (%)
MIN = MINIMUM CONCENTRATION
MAX = MAXIMUM CONCENTRATION
AVG = AVERAGE CONCENTRATION IN THE PERIOD JANUARY 1 - JUNE 30, 1990
UNIT = UNIT OF MEASUREMENT

NOTE: Values less than the detection limit are treated as zero.
Minimum, maximum and average values are cited to two decimal places.

Appendix F

The Formation and Concentration of Dioxins and Furans From Pulp and Paper Mills.

Chlorinated Dioxins and Furans

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic and persistent compounds. They consist of a number of chlorinated homologs (monochloro to octachloro) and a large number of isomers (135 chlorinated furans and 75 chlorinated dioxins).[64]

The most toxic form of PCDDs and PCDFs are those containing 4-6 chlorine atoms. The 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) are two of the most toxic forms of all PCDDs and PCDFs. These compounds are not made intentionally. They are unavoidable by-products created in the manufacture of other chemicals such as some herbicides and pesticides, or as a result of incomplete combustion of mixtures containing chlorine atoms and organic compounds.[65]

Discovery of dioxins and furans in pulp and paper mill effluents, sludges and products has raised concerns among the general public and in the environmental communities. Dioxins and furans are produced during the pulp bleaching processes.[66]

Formation of Dioxins and Furans in the Pulp and Paper Industry

(a) dioxin formation during the pulping stage

Raw materials such as recycled materials may contain dioxins or dioxin precursors. Trees may have been sprayed with 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and its precursor, 2,4,5-trichlorophenol (2,4,5-TCP) or 2,4-D pesticides, containing dioxin precursors and dioxins themselves. Some pulp mills use waste wood which may have been treated with pentachlorophenol or other preservatives contaminated with dioxins.

(b) dioxin formation during the bleaching stage

The bleaching of the pulp is the main source of dioxins in the pulp and paper process. A study of Ontario's kraft mills suggested that the chlorinated dioxins and furans are by-products of bleaching the pulps with chlorine or chlorine derivatives. This study revealed the presence of these chemicals in the sludges and effluents of the mills.[67]

During kraft bleaching, the delignification process is carried out using elemental chlorine. At this stage, as the chlorine reacts with phenol compounds in the lignin, the dioxin precursors are formed. The heat in the next stage, which involves alkaline extraction by adding hot sodium hydroxide, triggers the formation of dioxins from the chlorinated lignin components. The waste water from these two stages (i.e. chlorination and extraction) contains high levels of chlorinated organics.

(c) dioxin formation from the recovery/power boilers

Pulp and paper mill wastes, including wastes from bleach plants, are sometimes added to the recovery boilers where temperatures for the formation of dioxins are ideal. Thus, dioxins and furans escape through the smoke stack.

(d) dioxin in defoamers

Voss et. al. identified oil-based pulp mill additives, such as oil-based defoamers, as sources of dioxin and furan precursors. Oil-based defoamers may contain dioxin and furan precursors such as dibenzodioxin and dibenzofuran. In contrast, water-based defoamers are also available for use in pulp and paper mills, and studies have shown them to be free of dioxin and furan precursors.[68]

Tables 1 to 3 summarize the levels of TCDD and TCDF in waste water, sludge and pulp.

Table 1. Levels of TCDD/TCDF Found in Pulp and Paper Mill Waste water.

TCDD/TCDF Concentration (ppq)*							
		Kraft Mill			Sulphite Mill		
		Min.	Max.	Mean	Min.	Max.	Mean
EPA	TCDD	3	640	76	5	23	13
1990	TCDF	4	8400	476	3	840	112
CPPA**	TCDD	33	100	51	NA	NA	NA
1990	TCDF	8	480	51	NA	NA	NA
MOE	TCDD	ND	790	30	NA	NA	NA
1991	TCDF	ND	1600	140	ND	210	100

* part per quadrillion
** Canadian Pulp and Paper Association
NA not available
ND Not detected

Sources: U.S.EPA[69], CPPA[70] and MOE[71]

Table 2. Levels of TCDD/TCDF Found in Pulp and Paper Mill Sludge.

TCDD/TCDF Concentration (ppt)*							
		Kraft Mill			Sulphite Mill		
		Min.	Max.	Mean	Min.	Max.	Mean
EPA 1990	TCDD	0.9	1390	101	0.4	58	13
	TCDF	2.4	17100	797	0.7	584	99
CPPA** 1990	TCDD	2	88	26	NA	NA	NA
	TCDF	18	1400	302	NA	NA	NA

* part per trillion
** Canadian Pulp and Paper Association

Sources: U.S.EPA[72] and CPPA[73]

Table 3. Levels of TCDD/TCDF Found in Pulp.

TCDD/TCDF Concentration (ppt)*							
		Kraft Mill			Sulphite Mill		
		Min.	Max.	Mean	Min.	Max.	Mean
	TCDD						
EPA	HW+	0.4	56	8	2	15	7
1990	SW++	0.5	116	12	4	4	4
	TCDF						
	HW	0.8	661	56	1	323	73
	SW	0.7	2620	118	1	449	125
CPPA 1990	TCDD	1	12	3	NA	NA	NA
	TCDF	1	57	12	NA	NA	NA

* part per trillion
\+ hardwood
\++ softwood
NA not available

Sources: U.S.EPA[74] and CPPA[75]

The 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners have been discovered in fish collected downstream of some pulp and paper mills. The U.S. EPA's National Dioxin Study found 2,3,7,8-dioxin and/or furan in fish tissue near 83 of 96 pulp and paper mills surveyed that used chlorine to bleach pulp (up to 19 parts per trillion of TCDD). About 80% of the fish samples from the Great Lakes basin were found to have detectable levels of dioxin.[76] Because of these findings, the U.S. EPA has recommended to the States that they develop individual control strategies for every mill where 2,3,7,8-TCDD is detected in fish.

Appendix G

Analytical Methods for Measuring Chlorinated Organics.

There are several general methods of estimating the amount of chlorinated organic compounds, TOCl, AOX and TOX.

TOCl (total organically bound chlorine) is a general measure of the amount of chlorinated organic constituents in the effluent. The TOCl procedure involves extracting the chlorinated organics from the effluent sample by ion-exchange resin and ultrafiltration. The chlorine content of each recovered fraction is determined by combustion. Before analysis, the sample is aged for a week to stabilize the TOCl content, causing the more volatile chlorinated organics, such as chloroform, to escape. This method has been used extensively in Scandinavian countries. However, due to its complexity, TOCl is giving way to the AOX.[77]

AOX (adsorbable organic halides) is a simple and economical method for determining organically bound chlorine. It also has low data variability and thus, AOX is generally accepted as the best technique for estimating the total amount of chlorinated organics in effluent (reported as Cl). In this test, an effluent sample is treated with activated carbon, adsorbing most organic materials. The carbon is burned and all chlorinated organics are converted to hydrochloric acid which is absorbed in an aqueous solution and measured by microcoulometry. Thus, AOX formation is proportional to the amount of chlorine consumed during the delignification process (i.e. molecular chlorine or chlorine dioxide).[78]

TOX (total organic halides) is similar to AOX with the addition of a small proportion of volatile chlorinated organic which is excluded during AOX measurement. The proportion of volatile organics is generally under 5% in untreated whole mill effluents, although it can be significantly higher in specific streams within the mill. The volatile fraction is essentially zero in biologically treated effluents.[79]

In the TOX procedure, the organic material from the sample is concentrated on granular activated carbon. The carbon is then pyrolysed and the product gas is passed through a microcoulometric titration cell where the amount of halide present is determined.

The AOX and TOCl analytical procedures are significantly different and there is no explicit conversion factor between the two measurements. However, empirical data indicate that AOX is normally 10% to 30% higher than TOCl for most bleached kraft mill wastewaters.[80]

Appendix H

Brightness and Water Pollution for Different Bleaching Processes

In the laboratory, softwood was treated with oxygen (O), ozone (Z), sodium hydroxide (caustic soda) (E), hydrogen peroxide (P), and sodium hydrosulphite (Y). OZE(O)PY and ZO(ZW)PY sequences were able to produce pulp with brightness of 90.1% and 88.6% ISO, respectively. The effluent quality from this process is far better than the effluent from conventional bleaching (C/DEDED) and does not generate chlorinated organics. The fibre strength of these pulps is comparable to the pulp bleached by the conventional chlorine bleaching.[81] A comparison of pollutant amounts for conventional and non-chlorine bleaching processes is presented in Table 1.

Table 1. Comparison of Effluent Quality using Various Bleaching Processes on Softwood Kraft Pulp.[82]

Bleaching Sequence	Brightness %ISO	BOD*	COD*	TOCl*
C/DEDED	90.6	32	105	NA
C/DEODED	90.6	31	101	7
DCEODED	90.6	30	100	5
DEODED	NA	11	57	3
O	44	14	61	0
OC/DEODED	NA	18	50	4.5
ODCEODED	NA	16	43	1.7
OZEPY	90.1	38	129	0
OZPY	88.3	39	134	0
ZOZWPY	88.6	10	50	0

NA not available
C molecular chlorine
D chlorine dioxide
E sodium hydroxide
O oxygen
P hydrogen peroxide
W washing process
Y sodium hydrosulphite
Z ozone
* kg/tonne pulp

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2. See for example, T. Colborn, et. al., 1990. Great Lakes, Great Legacy?, the Conservation Foundation and the Institute for Research on Public Policy, Washington, D.C., p. 134.

3. The Great Lakes Water Quality Agreement, Article II, page 8.

4. Ibid., page 109.

5. Ibid.

6. Pulp and Paper Point Sources Task Force of the Water Quality Programs Committee, 1981. The Response of the Pulp and Paper Industry in the Great Lakes Basin to Pollution Abatement Programs. Report to the Great Lakes Water Quality Board, page 4.

7. U.S. EPA, 1982. Development Document for Effluent limitations Guidelines New Source Performance Standards and Pretreatment Standards for the Pulp, Paper and Paperboard and the Builders Paper and Board Mills Point Source Category. EPA report No. 440/1-82/025, page 19.

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9. U.S. EPA, 1982. Development Document for Effluent Limitations Guidelines New Source Performance Standards and Pretreatment Standards for the Pulp, Paper and Paperboard and the Builders Paper and Board Mills Point Source Category. EPA report No. 440/1-82/025, page 19.

10. Ibid., page 66.

11. Ibid., page 23.

12. Ibid., page 526.

13. Ibid.

14. Ibid.

15. Ibid., pages 529-530.

16. D. Anderson, Chief of the Commodities Branch, Industrial and Technology Division, U.S. EPA, Washington D.C., personal communication, March 13, 1991.

17. Pulp and Paper Effluent Regulations, Fisheries Act, C.R.C. 1978, c.830.

18. Proposed Pulp and Paper Mill Defoamer and Wood Chips Regulations, January 1991.

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20. Ibid.

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24. Ibid.

25. Earl, P.F. and D.W. Reeve, 1990. Chlorinated Organic Matter in Bleached Chemical Pulp Production Part VI Chlorinated Organic Compounds in Effluents. TAPPI Vol. 73., No. 1, pages 179-184.

26. Tim Martin, Pulp and Paper Researcher, Greenpeace Chicago, pers. comm., October, 1991. These two mills are on the U.S. side of the Great Lakes.

27. The following section is primarily based on: U.S. Environmental Protection Agency, 1990. Summary of Technologies for the Control and Reduction of Chlorinated Organics from the Bleached Chemical Pulping Categories of the Pulp and Paper Industry, Office of Water Enforcement and Permits, Washington, D.C.

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Compounds, October 1987, Las Vegas, Nevada, pages 1-14.

30. Canadian Pulp and Paper Association, 1990. CPPA National Dioxin Characterization Survey, Province: Ontario. CPPA News Release, February, 1990.

31. Great Lakes Water Quality Board, 1989. 1989 Report on Great Lakes Water Quality. Report to the International Joint Commission, Windsor, Ontario, page 21.

32. Campbell, M.E. and W.M. Glenn, 1982. Profit from Pollution Prevention: A Guide to Industrial Waste Reduction and Recycling. The Pollution Probe Foundation, Toronto, Ontario, page 219.

33. MOE, 1989. The Development Document for the Draft Effluent Monitoring Regulation for the Pulp and Paper Sector, March, 1989, page II-2.

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36. Ibid., page II-2.

37. Great Lakes Water Quality Board, 1985. 1985 Report on Great Lakes Water Quality. Report to the International Joint Commission, Windsor, Ontario, page 138.

38. Great Lakes Water Quality Board, 1989. 1989 Report on Great Lakes Water Quality Board. Report to International Joint Commission, Windsor, Ontario, pages 22-23.

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