Canadian Environmental Protection Act

Priority Substances List
Assessment Report No. 2

Effluents from Pulp Mills Using Bleaching

Government of Canada / Gouvernement du Canada
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CANADA'S GREEN PLAN

Canadian Environmental Protection Act

Priority Substances List Assessment Report No. 2

Effluents from Pulp Mills Using Bleaching

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Preface

Worldwide technical literature, together with unpublished information on effluents from pulp mills employing chlorine bleaching, have been studied to determine whether these effluents are "toxic", as defined under Section 11 of the *Canadian Environmental Protection Act* (CEPA), to the environment, to the environment on which human health depends, or to human health. The impacts of chlorinated "dioxins" and "furans" were not examined specifically in this report, even though they are found in bleached pulp mill effluents, since they were specifically nominated to the Priority Substances List for independent assessment. Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD), characteristic of pulp mill effluents, are currently regulated under the *Fisheries Act* as deleterious substances; therefore, they were not examined specifically in this assessment of effluents from bleached pulp mills.

This report is an assessment of the risk associated with the release of chlorinated organic material in bleached pulp mill effluents and therefore of the need to invoke the *Canadian Environmental Protection Act*. It also contains an overview of CEPA, the risk assessment criteria employed, a brief description of the scope of the investigation, an overview of factual data, and the conclusions of the risk assessment.

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* The units of concentration employed throughout this report are parts per trillion (ppt), parts per billion (ppb), and parts per million (ppm) on a weight per volume basis for water (e.g., 1 ppm = 1 mg/L, 1 g/m^3, etc.) or on a weight per weight basis for aquatic organisms and sediment (e.g., 1 ppm = 1 µg/g, etc.).

Avant-propos

On a étudié de la documentation technique du monde entier ainsi que des données inédites portant sur les effluents des usines de pâte blanchie au chlore pour déterminer si ces effluents sont toxiques au sens de l'article 11 de la *Loi canadienne sur la protection de l'environnement (LCPE)*, c'est-à-dire sont nocifs pour l'environnement, pour l'environnement dont dépend la vie humaine ou pour la santé des humains. Dans le présent rapport, on n'a pas étudié de façon particu1ière les effets des dioxines et des furanes chlorés, bien que ces composés se retrouvent dans les effluents des usines de pate blanchie, puisqu'il était expressément indiqué dans la Liste des substances d'intérêt prioritaire qu'ils devaient faire l'objet d'une évaluation distincte. La teneur en matières en suspension (MES) et la demande biochimique en oxygène (DBO) caractéristiques des effluents des usines de pate blanchie sont actuellement rég1ementées en vertu de la *Loi sur les pêches* en tant que substances nocives; c'est pourquoi elles n'ont pas non plus été étudiées de façon particu1ière dans la présente évaluation des effluents des usines de pâte blanchie.

Le présent rapport évalue le risque lié au rejet de matières organiques chlorées dans les effluents des usines de pâte blanchie et, par conséquent, la nécessité d'invoquer la *LCPE*. Il donne également un aperçu de Ia *LCPE*, les critères d'évaluation du risque employés, une brève description de la portée de l'étude, un aperçu des résultats ainsi que la conclusion de l'évaluation du risque.

Les unités de concentration emp1oyées dans le présent rapport sont les parties par billion ou 10^{12} (désignées par 1'abréviation «ppt», *pour parts per trillion*), les parties par milliard ou 10^{9} (désignées par 1'abréviation «ppb», *pour parts per billion*) et les parties par million ou 10^{6} (ppm), en unités de masse par unité de volume pour l'eau (par exemple, 1 ppm = 1 mg/L, 1 g/m^3, etc.) on en unités de masse par unité de masse pour les organismes aquatiques et les sédiments (par exemple, 1 ppm = 1 µg/g, etc.).

Table of Contents

List of Figures

List of Tables

Summary

There were 47 pulp mills employing chlorine bleaching in operation in Canada at the time of writing this risk assessment report. The molecular chlorine or chlorine-containing compounds currently used as bleaching agents by the pulp and paper sector react with materials released from wood during the pulping process, resulting in the formation of chlorinated organic compounds which are in part discharged into the aquatic environment via effluents.

Canadian mills are estimated to use over 610 000 tonnes of chlorine annually to produce over 10 million tonnes of bleached pulp and to release over a million tonnes of chlorinated organic compounds to the aquatic environment. The assessment report concentrates upon these materials, in accordance with the recommendation of the Report of the Ministers' Priority Substances Advisory Panel (1988) to consider the "full range of compounds found in those effluents, particularly organochlorine compounds." Other materials commonly found in bleached pulp mill effluents include resin and fatty acids and these were examined briefly.

This assessment report does not include polychlorinated dibenzodioxins and polychlorinated dibenzofurans, total suspended solids (TSS) or biochemical oxygen demand (BOD) in the evaluation of bleached pulp mill effluents. The dioxins and furans were not considered as they were concluded to be "toxic" under Sections 11(a) and 11(c) of the *Canadian Environmental Protection Act* (Reported in Priority Substances List Assessment Report No. 1 and published in the Canada Gazette, Part 1, March 17, 1990, p.949). A preliminary review of other organochlorine components of bleached pulp mill effluents found insufficient data to be able to judge their impact on the quality of fish for human consumption or on drinking water. TSS and BOD are regulated under Sections 34 and 36 of the *Fisheries Act*.

The chemical composition of bleached pulp mill effluents is variable and not well characterized. Approximately 250 compounds have been identified in bleachery effluents but many more remain unidentified. Thus, substantial quantities of chlorinated organic compounds, both of known and of unknown composition, enter the Canadian aquatic environment from bleached pulp mill discharges.

Many of these chlorinated organic compounds are persistent and have been detected in water, sediments and biota up to 1400 km

from bleached pulp mills outfalls. Compounds with low chlorine substitution degrade within hours to days, whereas highly chlorinated organic compounds may persist from days to weeks or longer. Persistence may be longer in winter, especially under ice. Some chlorinated organic compounds can be biologically degraded or transformed and transformation may lead to more persistent and bioaccumulative compounds. Chloroveratroles, for example, transformation products of chloroguaiacols which are unique to bleached pulp mill effluents, are capable of accumulating in fish up to 25 000 times the concentration in water. Some other chlorinated organic compounds detected in biological tissues downstream of bleached pulp mills reflect repeated or long-term exposure rather than high bioaccumulative potentials.

Seventy-five percent of Canadian bleached pulp mills discharge effluents that are acutely lethal to fish, sometimes at concentrations as low as 3.2% effluent. A few individual chlorinated organic compounds in these effluents approach or surpass concentrations that cause mortalities in aquatic organisms ranging from algae to fish. Seventy percent of Canadian freshwater bleached pulp mills discharge whole effluent that, even upon dilution by the receiving waters, are at levels which cause chronic effects. Chronic effects, such as reproductive anomalies, biochemical changes, and behavioural alterations in aquatic organisms, have been observed in Canadian field studies at 0.5 to 5 % whole effluent. Laboratory studies using individual chlorinated organic compounds that are commonly discharged from bleached pulp mills have demonstrated such chronic effects as deformities, and embryo and larval mortalities in fish. These chronic effects include significant irreversible factors which jeopardize the continuance of the species and the integrity of the ecosystem.

Thus, the levels of whole effluents discharged from Canadian bleached pulp mills to the aquatic environment and the resulting acute and chronic effects observed both in the field and in the laboratory combine to represent a significant risk to the aquatic ecosystem.

Based on these considerations, the Minister of Environment and the Minister of Health and Welfare have accepted the conclusion that the substance "Effluents from Pulp Mills using Bleaching" is entering the environment in a quantity or concentration or under conditions having an immediate and long-term harmful effects on the environment. This substance is therefore considered to be "toxic" as defined under Paragraph 11(a) of the *Canadian Environmental Protection Act*.

Acknowledgements

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Section 1

The *Canadian Environmental Protection Act*

The *Canadian Environmental Protection Act* [1,2] was created to protect the environment and human health from adverse effects associated with the entire life cycle of substances (manufacture, distribution, use, transportation, storage and disposal). The Ministers of Environment and of National Health and Welfare share responsibility for the Act and are required under the Act to assess the effects of selected substances on the environment, on the environment on which human health depends, and on human health.

The *Canadian Environmental Protection Act* (CEPA) is federal legislation which incorporates and expands upon the *Environmental Contaminants Act* (1975) (temporarily excluding Subsection 4(6)), the *Clean Air Act* (1971), the *Ocean Dumping Control Act* (1975) and Part III of the *Canada Water Act* (1970). Through the amalgamation of these Acts, CEPA provides a comprehensive total ecosystem approach to the protection of our air, water, soils, and the marine environment. CEPA does not, however, have any jurisdiction over subject matter regulated by such statutes as the *Fisheries Act*, the *Food and Drug Act* and the *Pest Control Products Act*. In instances where an aspect of a substance is regulated by any other federal statute, Section 34(3) of CEPA will not permit the making of a regulation.

CEPA defines substances as "any distinguishable kind of organic or inorganic matter, whether animate or inanimate". Included in this definition are chemicals, products of biotechnology, and mixtures including emissions and effluents. CEPA defines a substance as "toxic" if it can cause direct or indirect harmful effects on the environment or human health.

Section 12 of the Act requires the Ministers to compile a Priority Substances List (PSL). Following consultation with academia, industry, environmental public interest groups, and provincial governments[3], a list of 44 substances was compiled and published in 1989[4]. Section 12 also permits the Minister to amend this list from time to time.

Assessment reports for each of the substances on the PSL are required and are expected to be completed within three to five years of the PSL publication date. The order in which substances are addressed depends on the amount of investigation required, their status with respect to the development of regulations, and the degree of environmental or public concern.

For the purpose of assessing a substance's toxicity or for developing regulations, Sections 16 and 18 of CEPA allow the Minister of the Environment to require persons to provide toxicological or quantitative information and samples of the substance(s) in question. Any person to whom such a Notice is directed (such as: manufacturers or users) must comply subject to the penalties provided in Section 112 of the Act.

According to Section 11 of the Act, a substance is "toxic" if it: "is entering or may enter the environment in a quantity or concentration or under conditions:

a) having or that may have an immediate or long-term harmful effect on the environment;

b) constituting or that may constitute a danger to the environment on which human life depends; or

c) constituting or that may constitute a danger in Canada to human life or health."

If a substance is deemed to be "toxic" to the environment and/or human health, the Ministers of Environment Canada and Health and Welfare Canada may recommend the development of regulations. The Governor in Council, if satisfied with the evidence declaring a substance "toxic", and on the recommendation of the Ministers, may order the substance to be placed on the List of Toxic Substances in Schedule I of CEPA (Section 33(1)) and regulations to be enacted. A substance may be added to this List in advance of the development of regulations.

Section 2

Risk Assessment Criteria

The goal of this CEPA risk assessment is to determine the degree of environmental risk from effluents discharged by pulp mills using chlorine bleach. For purposes of this report, "discharge" is defined as the release or entry of a substance into the environment under current manufacturing conditions.

Four discrete approaches to risk assessment are available:

- field evidence of harmful effects on biota caused by exposure to bleached pulp mill effluents can be taken as evidence of a high degree of risk;

- measured aquatic exposure data can be correlated with laboratory environmental effects data; if, for example, the level of a tested substance in the environment approaches or exceeds the concentration known to induce chronic effects, then the degree of risk that chronic effects will occur in aquatic species will be very high;

- evidence of a threat to any species named in the vulnerable, threatened or endangered categories by the Committee on Status of Endangered Wildlife in Canada or designated as endangered by the provinces or territories, or to the habitat of such species, represents an unacceptable risk; and

- the presence of residues or metabolites in biota exposed to bleached pulp mill effluents corresponding to or exceeding known threshold levels is also strongly predictive of either short- or long-term harmful effects.

In instances where there is evidence of any one or more of these criteria, the substance would be deemed to be "toxic" pursuant to Paragraph 11(a) of CEPA.

No Canadian information was found concerning the exposure of endangered species within the zone of influence of bleached pulp mills or information showing residues in excess of threshold levels in biota or tissues either for whole bleached pulp mill effluents or for any of their known constituents.

Many factors influence the degree of "immediate or long-term harmful effect on the environment" (Paragraph 11(a) of CEPA). "Harmful effect" is not defined in the Act. For the purposes of this risk assessment report, "immediate harmful effect" includes acute toxicity and "long-term harmful effects" includes significant, irreversible, chronic effects which will continue (or worsen) during the entire period of exposure of the ecosystem to the substance. Ideally a risk assessment involves the comparison of exposure levels with harmful effects levels using both field and laboratory data on the most sensitive known species over at least one full life cycle. Frequently, however, as in the present investigation, initial field observations have not yet been followed up with laboratory studies, and specific stages of a sensitive organism's life-cycle remain to be investigated. The approach taken in this risk evaluation is to place the greatest weight on the most sensitive species for which field data or laboratory data are available.

A major component of this risk assessment involved the critical examination of the quality and quantity of the data associated with a variety of bleached pulp mill effluent studies. The criteria for assessment of this type of information included: determining

whether or not the reference sites were uncompromised; evaluating the statistical and analytical methods employed; comparing limits of detection and quantitation with reported concentrations; examining the consistency of reported data with other related information; and evaluating observed field effects for causality by means of criteria originally established by Popper[5],i.e., determining the degree to which other controlled parameters, such as BOD, could influence the observed effects. Authors, experts or peers were often consulted when questions of data quality or interpretation arose. In cases where insufficient information was available, reasonable estimates were made on the basis of related data or "worst-case" estimates were produced.

The conclusion of this report is based on a synthesis of the results of all of the above critical evaluations, i.e., it is based on the weight of all available evidence. New information, especially in key areas such as amounts released to the aquatic environment, exposure levels, observed effects in the field, and harmful effects levels could modify or change our estimate of the degree of risk.

Section 3

Scope of the Investigation of Effluents from Pulp Mills Using Bleaching

The risk assessment process involves searching chemical, biological, medical, legal, technological, and environmental literature and supplementing this information, where possible, with actual testing, monitoring, and research. Information of particular importance includes environmental effects and human toxicity data, as well as data dealing with the routes, levels and effects of short- and long-term exposure. Additional information, in this instance, was acquired through a CEPA Section 18 notice requiring bleached pulp mills to submit specific information about their operations and discharges.

Chlorinated organic constituents of effluents from bleached pulp mills are the primary focal point of this assessment report, as recommended by the Ministers' Priority Substances Advisory Panel[3]. Chlorinated "dioxins" and "furans" (also found in bleached pulp mill effluents) were evaluated in a previous assessment report[6].The effects of Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD) (characteristic of pulp mill effluents) were not evaluated as they are regulated under the *Fisheries Act.*

The toxic effects of bleached pulp mill effluents on human health have not been widely studied. The toxicity of dioxins and furans, as well as their potential to harm human health, has been well established and they were the first substances on the Priority Substances List (PSL) to be declared "toxic" under CEPA. Insufficient data were found in a preliminary review on other organochlorine components of bleached pulp mill effluents to be able to judge their effects on the quality of fish for human consumption or on drinking water. This assessment therefore focused on the environmental impacts of pulp mill effluents.

Similarly, no information was found which suggested that any of the constituents of bleached pulp mill effluents affected the environment on which human health depends. "Toxic" effects as defined by Paragraphs 11(b) and 11(c) of the Act, therefore, are beyond the scope of this assessment. This does not preclude future use of CEPA in these areas should new information arise.

This investigation of effluents from pulp mills employing bleaching included the following activities:

1. The technology of bleached pulp manufacture was studied to provide a basis for evaluating biological information.

2. The physical and chemical properties of selected chlorinated organic compounds in bleached pulp mill effluents were reviewed. Particular emphasis was placed on those properties that influence chemical analysis, environmental persistence and distribution, and aquatic toxicity.

3. The complexity of bleached pulp mill effluents was explored and available information on generic and specific releases from bleached pulp mills to the aquatic environment was evaluated.

4. Analytical methods employed to measure organochlorine concentrations in bleached pulp mill effluents were examined. Particular emphasis was placed on surrogate measurements, such as Adsorbable Organic Halogen (AOX),

for the estimation of the organochlorine Content in effluents and receiving waters.

5. Existing and proposed guidelines, regulations, and legislation relating to the control of organochlorine pollution of the aquatic environment by bleached pulp mills were reviewed and compared for Canada, the United States, Scandinavia, and Europe.

6. Canadian statistics on quantities of chlorine consumed, effluents discharged, and bleached pulp produced were collected and analyzed, and an estimate of the chlorinated matter released was made.

7. The environmental distribution and fate of chlorinated substances released in bleached pulp mill effluents were investigated. Particular emphasis was placed on the manner in which bleached pulp mill effluent constituents are partitioned among various environmental compartments (water, sediments, and biological tissues), how long they persist in these compartments, the potential for physical and biological degradation and the transformation, and the degree to which they are bioaccumulated in the aquatic environment.

8. Canadian levels of chlorinated organic compounds detected in bleached pulp mill effluents, receiving waters, sediments, and aquatic organisms were reviewed and compared when possible with the levels found in Scandinavia. This information was examined for organochlorine concentration gradients in the aquatic environment to determine if the exposure levels involved in extensive Scandinavian studies are comparable to those found in Canada.

9. The acute and chronic toxicities to aquatic organisms associated with whole bleached pulp mill effluent and its known organochlorine constituents were reviewed for both field and laboratory conditions. Emphasis was given to relating, where possible, the levels of these compounds measured in water, sediments, and biota to the levels required to induce acute or chronic effects in exposed aquatic life. Comparable data on exposure and effects from other countries were included, when available.

Section 4

Overview of Findings

4.1 Scientific and Technical Literature

A survey of the published and unpublished scientific literature on bleached pulp mill effluents, including two recent unpublished reviews by A.G. Colodey[7] and by J.B. Sprague and A.G. Colodey[8], together with comments from selected reviewers provided much of the background information necessary for this risk assessment.

The acute lethality of pulp mill effluents has been documented extensively in the scientific literature, but there has been less emphasis on chronic toxicity or fate. The present world trend of rapidly increasing environmental awareness, coupled with the relatively recent discovery of chlorinated dioxins and furans in bleached pulp mill effluents, however, has spurred a greater research effort, particularly in the areas of chronic effects and fate. As a result, scientific information on such topics as bleached pulp mill effluent composition, effects, and ultimate fate is expected to improve dramatically in the next few years.

4.2 Definitions of Bleached Pulp Manufacturing Processes

4.2.1 Pulping

The main objective of the pulping process is to separate cellulose fibre from lignin to free the fibres for papermaking. The two main types of pulping processes are mechanical and chemical. Mechanical pulping utilizes heat and mechanical forces to break down the lignin and results in a light-coloured pulp which requires little bleaching. This report focuses on chemical wood pulping as recommended by the Ministers' Priority Substances Advisory Panel[3].

As the name implies, chemical pulping uses a mixture of chemicals to separate the cellulose fibres from the lignin. The two major chemical processes are kraft and sulphite pulping. Kraft pulping is carried out in an alkaline medium and releases fibres by dissolving lignin in a caustic solution of sodium hydroxide and sodium sulphide. In contrast, the sulphite process is carried out under acidic conditions and solubilizes lignin through sulphonation using a solution of sulphur dioxide and alkaline oxides such as sodium, magnesium, ammonium, or calcium[9],Both chemical processes produce a relatively dark-coloured pulp which requires bleaching. The vast majority of the 47 bleached pulp mills in Canada employ the kraft pulping process (five mills employ the sulphite pulping process).

Oxygen delignification, which may be employed as an additional stage in either the sulphite or kraft pulping process, breaks down the lignin further, reducing the amount of bleaching agent required in the subsequent stage.

4.2.2 Bleaching

The bleaching of cellulose fibres is an extension of the delignification which commenced in the pulping stage. Mechanical pulp is generally brightened by hydrogen peroxide. As no chlorine or chlorine- based chemicals are used, no chlorinated organic compounds are generated.

Bleaching of chemical pulps is generally a complex process consisting of a series of stages, each of which may use several chlorine-based chemicals. In the first stage, the pulp is dispersed in water and contacted with a chlorine-water solution. More recently, chlorine dioxide has been substituted

for a growing percentage of the chlorine gas at this stage to reduce the formation of chlorinated organic compounds. Chlorine and chlorine dioxide are effective in breaking down lignin, but little colour is removed at this stage. The second stage of bleaching is usually caustic extraction. The caustic solution (sodium hydroxide) dissolves most of the modified lignin. In the third stage, chlorine dioxide or hypochlorite are added to the pulp. Subsequent bleaching stages and the chemicals used depend on the brightness required and the quality demands of the finished products[10].

The locations of Canadian pulp mills that employ chlorine-bleaching are shown in Figure 1.

4.2.3 Effluent Treatment

The effluents from pulping and bleaching operations are combined and, in most cases, treated prior to discharge. Primary treatment removes suspended solids through screening and settling, thereby reducing the biological oxygen demand (BOD) of the effluents on the aquatic environment. Secondary treatment involves contact with bacteria which decompose organic substances in the effluent. This process removes oxygen- consuming substances and also many substances toxic to fish. In Canada, 49% of bleached pulp mills employ secondary treatment, 43% employ only primary treatment, and 9% of the mills employ no effluent treatment. These statistics can be further broken down as follows:

	Number of Mills	
	Inland	Coastal
No treatment	2	2
Primary treatment only	12	8
Secondary treatment	20	3

In contrast, all U.S. bleached pulp mills are required by law to apply secondary treatment to their effluents.

4.3 Important Chemical and Physical Properties of Chlorinated Organic Pulp Mill Effluents

A chlorinated organic substance is any organic compound that has one or more chlorine atoms attached to the molecule. On the other hand, the term organochlorine (a short form for "organic chlorine"), refers to the chlorine (only) that is attached to a chlorinated organic molecule. This distinction is quite important in consideration of the weights of material involved. For the compounds found in bleached pulp mill effluents, the mass (weight) expressed as organically bound chlorine is usually about 1/13 (8%) of the mass of the same compounds expressed as chlorinated organic substances[11].

It is beyond the scope of this assessment report to discuss the physical and chemical properties of all the individual chlorinated organic substances found in bleached pulp mill effluents to date. Interested readers are referred to a recent review[12] which describes many environmentally relevant properties of over 250 chemicals identified in pulp mill effluents. Of particular environmental importance are the general characteristics of chlorinated compounds, such as: specific octanol/water partition coefficients; water solubilities; vapour pressures; and bioconcentration potentials. In comparison with their nonchlorinated analogues, chlorinated organic compounds may become: more toxic[13-19]; more lipophilic and therefore bioaccumulative [12,17,20,21]; less biodegradable [15,19,22]; and mutagenic [15,20,23,24].

4.4 Composition of Chlorine-bleached Pulp Mill Effluents

Generally, unbleached pulp mill effluents contain resin acids and soaps, fatty acids,

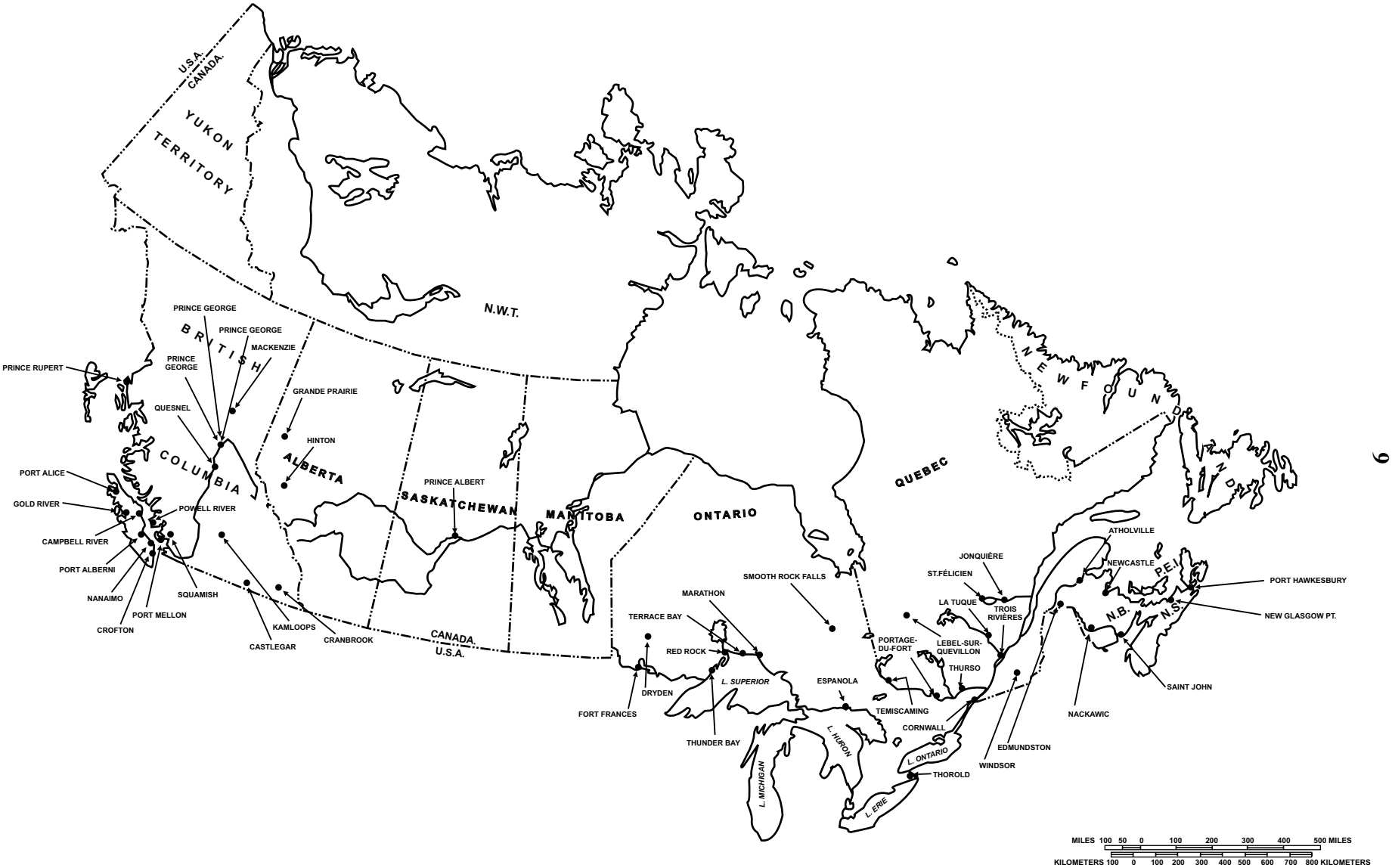


Figure 1 Locations of Canadian Pulp Mills Employing Chlorine Bleaching

diterpene alcohols, and phytosterols. After chlorine bleaching, the effluents contain these chemicals as well as chlorinated phenols, chlorinated acids, alcohols, aldehydes, ketones, sugars, and aliphatic and aromatic hydrocarbons [8,9,12,25](see Figure 2). Numerous volatile sulphur-containing compounds are also found in pulp mill effluents[25].

It has been estimated that only 10 to 40% of the low molecular weight (mw < 1000) chlorinated organic compounds in bleached pulp mill effluents have been characterized[9,16,26-28]. In general, the majority of the chlorinated organic compounds in bleachery effluents, approximately 70 to 80%, are of high molecular mass (mw > 1000)[9,29-31]. Many of the high molecular mass chlorinated organic compounds formed during the pulping and bleaching processes, are transformed in either secondary treatment lagoons or the receiving environment, into often more toxic and persistent low molecular mass compounds; compounds of mw < 1000 are able to pass through biological membranes while those of a higher molecular weight are rarely able to do so[9,29].

Complicating the characterization of pulp mill effluents are the effects of such factors as the type of wood used, in-plant processes (including bleaching sequences) and the effluent treatment procedures employed[29]. In general, softwood produces greater quantities of phenolic by-products than hardwood. Chlorinated softwood effluent contains chlorophenols, chloroguaiacols, chlorocatechols, and chlorovanillins. In addition to the previously mentioned chlorophenolics, hardwood effluents also contain chlorinated syringols and chlorinated syringaldehydes[32] .

The type of pulping and bleaching procedures employed by a mill, influence the character of the effluent. The most common chlorinated phenolics in bleached kraft pulp mill effluents are tri- and tetra-chloroguaiacols, whereas trichlorophenol is the principal chlorinated phenol in bleached sulphite discharges (see Figure 3). The substitution of chlorine dioxide for chlorine in the bleaching stage also alters effluent composition. In one instance, catechols and guaiacols together comprised 77% of the total chlorinated phenolic content when chlorine alone was used in the bleaching stage. When a 70:30 $C10_2$:C_{12} ratio was used in the first stage, the catechol and guaiacol portion decreased to 46%, and at 100% chlorine dioxide substitution, only 10% of the chlorinated phenolics were of the catechol and guaiacol type[33].

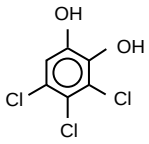
Many chlorinated compounds have been reported in untreated effluent from the bleaching process, but comparatively few have been reported in biologically-treated bleached kraft and sulphite mill effluent[9,26,28].

For an exhaustive listing of chemicals found in pulp mill effluents to date readers are referred to references 9, 12 and 25.

4.5 Analytical Methodology for Chlorinated Organics in Bleached Pulp Mill Effluents

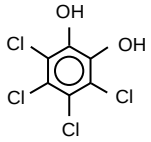
Many analyses have been performed on individual constituents of pulp mill effluents, chiefly by gas-liquid chromatography (GLC) [16,30,34-37]; Because of the variables known to affect the composition of these effluents and since it is unlikely that all chlorinated compounds in bleached pulp mill effluents will ever be identified, it is not practical to attempt to completely characterize effluents on the basis of individual substances. It is more reasonable as an interim measure, therefore, to measure the total organic chlorine loading from bleached pulp mills in the aquatic environment.

Generic tests, such as Adsorbable Organic Halogen (AOX) and Extractable Organic Chlorine (EOCl), provide indices of total organochlorine concentrations in effluent, receiving waters, sediments, and biota[38].



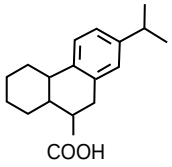
345-TC C

3,4,5,-Trichlorocatechol



TECC

Tetrachlorocatechol



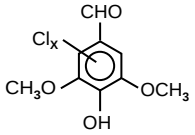
Dehydroabietic Acid

$C_{18}H_{32}O_2$

Linoleic Acid

$CH_3—OH$

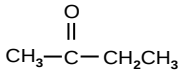
Methanol



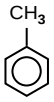
Chlorinated syringaldehyde

$C_6H_{12}O_6$

Glucose



2-Butanone



Toluene

$C_{15}H_{32}$

Pentadecane

Figure 2 Compounds Detected in Canadian Bleached Pulp Mill Effluents

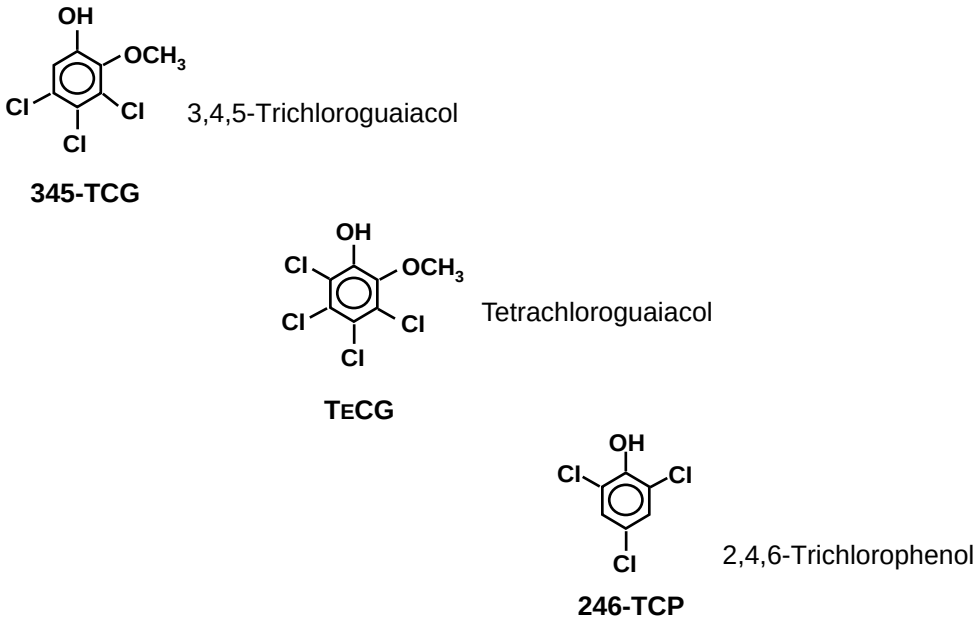


Figure 3 Specific Compounds Discharged from Bleached Pulp Mills

Adsorbable Organic Halogen is a widely accepted generic measurement used throughout this report to indicate the organic chlorine loading by a pulp mill using chlorine bleaching. In this procedure, a water sample is passed through activated carbon to adsorb organic substances. After the carbon has been washed to remove inorganic halides, it is combusted and the gaseous products are analyzed for total halogens. in effluents from bleached pulp mills, the halogen ("X") component of AOX is almost entirely chlorine.

Other surrogate measurements used to detect organic chlorine downstream of bleached pulp mills include EOC1, Total Organic Chlorine (TOC1) and Total Organic Halogen (TOX). Extractable Organic Chlorine is the analytical method used to determine the extractable organic chlorine from sediments and animal tissue samples. The TOC1 method has been frequently used, particularly in Scandinavia. This is a measure similar to AOX, but yields a result that is often about 75% of the AOX value([8]). Total Organic Chlorine values may be converted to AOX by using formulae developed from a bank of corresponding TOC1 and AOX determinations made at the Pulp and Paper Research Institute of Canada (PAPRICAN)([33]). The TOX method is sometimes used in the United States, and is very similar to the AOX method([29]).

Adsorbable Organic Halogen is the measurement most commonly used to analyze bleached pulp mill effluents because of its repeatability, comparative ease of use, and low cost. One of the major limitations of surrogate tests, however, is that they do not provide estimates of the potential toxicity, persistence, or bioaccumulation of specific chlorinated organic substances. Equal AOX or equal EOC1 values indicate neither identical composition of effluents nor equivalent toxicity to aquatic life.

The concentration of organic chlorine recoverable from sediment and/or animal tissue samples depends on the extraction and analytical techniques used[(39)] and on the lipophilicity of the chlorinated organic compounds. Chlorinated organics of low

lipophilicity would not be adsorbed by sediments and would have a short half-life in animal tissues. The amount of chlorinated organic compounds recovered from sediment samples is also very dependent on the sediment composition, e.g., sediment with a high organic carbon content would be expected to have a much higher EOCI value than sandy sediment[40].

The Pulp and Paper Research Institute of Canada in collaboration with Environment Canada have developed a draft protocol for the determination of Adsorbable Organic Halogen (AOX) in pulp mill effluents. The draft protocol is undergoing round-robin testing throughout Canada. Interested readers on AOX analytical methodology are also referred to Sjostrom *et al.* [41] in which two TOX methods are compared.

4.6 Regulations Governing Pulp and Paper Mill Effluent

4.6.1 Canadian Regulations

Canadian pulp mills have been regulated under the Pulp and Paper Effluent Regulations section (s.36-42) of the *Fisheries Act* since 1971. At present, the regulations apply only to mills that were built, expanded, or modified after promulgation of the Act. Mills that were built before 1971 are not regulated[29, 42].

The federal government is extending the application of the Pulp and Paper Regulations to include all mills and, among other things, is developing stricter enforcement policies to verify compliance. The revised regulations are expected to be published in the Canada Gazette in 1991. Regulations are also being developed to control the discharge of chlorinated dibenzo-dioxins and -furans from bleached pulp mill effluents.

At the provincial level, Ontario has established AOX discharge limits for kraft mill operating licences issued by the province[43]. Ontario plans to introduce regulations under its Municipal-Industrial Strategy for Abatement (MISA) program in 1992 to control bleached pulp mill effluent discharges. These may include setting stricter discharge limits in kraft mill operating permits based on best available technology and economic feasibility.

The provincial government of British Columbia has announced that they intend to regulate organochlorine discharges from their kraft pulp mills and have proposed AOX limits[43]. The controls include a regulatory schedule for source control of chlorinated organic substances and mandatory installation of secondary treatment at all mills in British Columbia which employ chlorine bleaching by 1991. The announcement followed the federal government's decision in 1988, and again in 1989, to close several west coast fisheries adjacent to coastal bleached pulp mills because of high levels of dioxin[44].

The Quebec provincial government has announced AOX limits which their bleached kraft pulp mills must attain by 1993.

Although Alberta has not announced AOX limits, the provincial government has decreed that all four of the new or expanding bleached kraft pulp mills in Alberta must install state-of-the-art technologies[44,45]. The latest Alberta-Pacific (ALPAC) proposal suggests extended delignification, 100% chlorine dioxide substitution and peroxide bleaching to achieve an AOX loading of less than 1 kilogram per Air Dried tonne of pulp (kg/ADt)[46].

Provincial regulatory schedules for controlling the discharge of organochlorine compounds from pulp mills which employ chlorine bleaching are summarized in Table 1.

4.6.2 Foreign Regulations

The greatest European regulatory action towards the reduction of organochlorine levels has occurred in Scandinavia[9]. Swedish authorities are focusing upon processes within pulp mills to reduce the

production of total chlorinated organics rather

Table 1 Regulatory Schedule for Discharge of Organochlorine Compounds from Pulp Mills which Employ Chlorine Bleaching

Location	AOX discharge (kg/t)	Target Date
Ontario (kraft mill permit)	2.5	1991
Quebec (Existing softwood)	2.5	1993
(Existing hardwood)	1.5	1993
(New softwood)	1.5	1993
(New hardwood)	1.0	1993
Alberta (kraft mill permit)	1.5	1990
British Columbia	2.5	1991

than on studies of specific organochlorines that may have detrimental environmental effects[47]. By 1990, all Swedish bleached kraft pulp mills except two, will have installed oxygen bleaching[29]. Finland, on the other hand, is focusing much of its effort on low molecular weight chlorinated organics, which are associated with acute and chronic toxicity, in the belief that the installation of secondary treatment facilities will sufficiently reduce the total amount of chlorinated organics released to the aquatic environment[47,48]. Pulp mills in Sweden and Finland must also apply for a licence or permit to pollute the aquatic environment[29].

The German and French regulatory approach is to tax the pulp mill based on the amount of organochlorines in effluents[44]. The onus is on the mills to implement or develop the technology necessary to reduce the levels of chlorinated organic substances discharged to the receiving waters.

The regulatory schedules of some European countries as of late 1988 for source-control of chlorinated organic compounds[8] are shown in Table 2.

The United States is intending to reduce levels of chlorinated organic substances by regulating chlorine consumption by the mills. Although the Environmental Protection Agency (U.S. EPA) has not taken any formal action as yet, it is believed that the United States will adopt a generic (AOX) approach to organochlorine control[8]. As of October 1988, the U.S. EPA described a "Proposed Interim Chlorine Minimization Program" with several stages of reduced chlorine use, tests of effluents, and reporting[49].

4.6.3 Non-regulated Parameters

The regulating of organochlorines in bleached pulp mill effluents is a relatively new concern. All countries, including Canada, are comparatively similar in their existing or proposed regulations. They are primarily concerned with setting AOX limits and with incorporating state-of-the-art process and treatment technology. However, numerous areas are not regulated. No Canadian provincial, federal or foreign regulations were found which pertain to the disposal of chlorinated organic contaminated sludge from

Table 2 European Regulatory Schedules for Source-Control of Chlorinated Organic Compounds

Location	TOC1 or AOX Discharge (kg/t)	Target Date
West Germany	1.0	1989
Finland	2.5	1994
Norway	2 to 2.5	1991
Baltic	2.5	1994
Sweden	1.0 to 2.0	1992
Sweden	0.5 to l.0	1995
Sweden	0.3 to 0.5	1999

the secondary treatment lagoons. Presently, only two methods exist for the disposal of sludge: incineration, which is currently a suspected source of dioxin[50] and dumping at landfill sites[47]. Also absent are regulations on emissions to the atmosphere, chlorine consumption by the bleached pulp mills, "safe" organochlorine levels in fish for human consumption, or long-term studies of the aquatic biota.

4.7 Quantities of Chlorinated Organic Compounds Entering the Environment

Bleached pulp and paper industries use large amounts of water, consume considerable quantities of chlorine, and discharge large quantities of chlorinated organic matter into rivers, lakes, and oceans[42].

The pulp and paper industry is the largest single commercial user of water in Canada. In 1989, the total mill effluent discharged from Canadian bleached pulp mills averaged 137 cubic metres per tonne or 104 000 m^3/d (ranging from: 25 300 to 311 100 m^3/d) which is roughly equal to the flow of the St. Lawrence River at Cornwall, Ontario or to that of the Columbia River in British Columbia. Total mill effluent volumes depend on the grade and amount of pulp being produced.

Canadian bleached pulp mills consumed an average of 47.8 tonnes of chlorine per day (ranging from: 2.5 to 175.0 t/d) in 1989. Chlorine useage by pulp mills depends on the type of wood used, the pulping and bleaching systems employed, and the desired grade of the final product. On average, in 1989, Canadian pulp and paper mills bleached 678 tonnes of pulp per mill per day (ranging from: 100 to 1 430 t/d).

It is estimated that the cumulative discharge of organic chlorine by bleached kraft pulp mills to Canadian receiving waters in 1989 was 86 000 tonnes (or 1 000 000 tonnes of chlorinated organic compounds).

Laboratory studies have shown a linear relationship exists between the amount of elemental chlorine added as either molecular chlorine or chlorine dioxide and the formation of AOX[51]. Less AOX is produced when

chlorine dioxide is the principal bleaching agent. No commercially proven method, however, is available to bleach pulp to the level of brightness currently demanded by the market without the use of chlorine-containing bleaching agents[29].

In principle, numerous internal and external plant methods exist for reducing organochlorine discharges from bleaching plants. Internal mill measures which can be applied are:

1) extended and/or oxygen delignification;

2) more efficient washing of pulp before bleaching;

3) replacement or substitution of chlorine by chemicals with lower or no chlorine content or reactivity (e.g., chlorine dioxide, hydrogen peroxide); and

4) recovery of spent bleaching liquors[33,48,52]

Secondary treatment of bleach plant effluents is the optimal external measure for reducing organochlorine concentrations[7,8,52].

4.8 Environmental Fate and Levels

4.8.1 Fate and Persistence of Chlorinated Organic Compounds Discharged from Bleached Pulp Mills

Adsorption. The adsorption of hydrophobic chlorinated organic compounds by sediments and suspended particulate matter is an important factor influencing the distribution and fate of chlorinated organic compounds in the aquatic environment[34-53]. This is evident from the observed declining concentration gradients in sediments and water with increasing distance from bleached pulp mill effluent outfalls[40,53,54].

The adsorption of constituents of bleached pulp mill effluents on sediments and suspended particulate matter depends on pH, the organic carbon content of the potential sorbent, and the partition coefficients of the chlorinated organic compounds between the water and solid phase[55-57].

Chlorinated organic compounds bound to sediments and suspended particulate matter are not necessarily unavailable to the aquatic biota. Organochlorine concentrations have been found in benthic invertebrates, which live and/or feed on sediments in waters receiving effluents from pulp mills using chlorine bleaching[30,35,40,58-65]. Fish feed on these contaminated benthic invertebrates, thereby accumulating organochlorines[25]. These are then further accumulated by fish-eating birds[25].

Laboratory and field investigations have both shown that sedimented chlorinated material originating from bleached pulp mills can act as a continuing source of organochlorine compounds to the aquatic environment[66]. For example, comparable concentrations of extractable organic chlorine (EOCI) were measured in lipid of fish caught sixteen months after the closure of a Norwegian sulphite pulp mill and when the mill was in operation[66]. Samples collected 3.5 years after the mill had closed found AOX (TOC1) concentrations in water to have returned to background levels and fish tissue concentrations (EOC1) to have decreased by 90% of the pre-closure levels. Although no sedimentation rate and transportation studies were conducted, it was concluded that sufficient natural sedimentation had occurred to cover the contaminated sediments, thereby making the chlorinated organic compounds less available to the aquatic environment[66].

Volatilization. Studies have demonstrated that some chlorinated lipophilic substances, such as chlorophenols, originating from bleached pulp mills are volatile and that a low percentage can be expected to escape to the air when discharged into well-mixed receiving waters[59-67]. However, recent Canadian winter monitoring studies of rivers completely covered by ice reveal that volatilization has no role in the removal of,

for example, chloroguaiacols, from the aquatic environment and that the chlorophenols are in fact quite persistent under ice[68, 69].

Photolysis. Many chlorophenol isomers found in bleached pulp mill effluents are degraded to some extent by ultraviolet (UV) light[57]. Photolysis dechlorinates the molecule[70,71] but the rate is affected by the number and position of chlorine substituents on the molecule[57]. For example, dichlorophenols and chloroguaiacols are expected to be stable to light in the aquatic environment and remain in the water column for hours to days and weeks to months, respectively[72]. Turbidity and colour of the receiving waters limits the pentration of light and therefore inhibits photolysis.

Biodegradation. Chlorinated organic substances can be metabolized by certain microorganisms in water[71,72,73,74] and sediment[73, 75] This decomposition is often quite rapid with half-lives ranging anywhere from hours to days[57].

Many factors influence the rate of biodegradation of chlorinated organic compounds in bleached pulp mill effluents. Generally, compounds which are highly chlorinated or have chlorine atoms situated in the meta position are more stable, more resistant to microbial degradation and, therefore, more persistent in the aquatic environment than those without[76].

Microorganisms that have been previously exposed to a chlorinated organic compound are usually able to metabolize it immediately when re-exposed, and at a faster rate than non-acclimated organisms[74, 77]. Microorganisms not previously exposed often exhibit a lag time of as much as several days before they begin to degrade the compound[78]. Similarly, prior exposure to a structurally-related compound can facilitate the metabolism of chlorophenols, indicating that the enzyme induced by the original compound is somewhat nonspecific[57, 79] .The time lag exhibited by non-acclimated microorganisms has implications when considering the construction of a bleached pulp mill in an area previously uncontaminated by constituents of bleached pulp mill effluents. The effects on the aquatic environment would predictably be greatest during the initial operations.

Many researchers have concluded that biodegradation between the water-biofilm interface and not volatilization is the major factor influencing the fate of dehydroabietic acid and chlorophenols in the aquatic environment[72,80,81]. For example, turbidity or a rocky substrate with little biofilm degradation would result in the retention of chlorophenols in the water column for weeks. Photolysis photodegradation) would then become the primary degradation pathway[72] .

The results of laboratory studies suggest that biodegradation is most rapid in aerobic soils and sediments, and is reduced in anaerobic or nutrient-poor habitats[57]. Field studies support these conclusions, since sediment cores, which contain layers several decades old and are presumably anaerobic, contain detectable levels of tetrachlorophenol, pentachlorophenol, and dehydroabietic acid[18,82-84]. Dehydroabietic acid, a resin acid commonly discharged in pulp mill effluents, was found to remain in sediments for 21 years[80].

The rate of removal of chlorinated organic compounds in wastewater treatment facilities depends greatly upon operating conditions and can be quite low[27, 38, 85]. Bleached pulp mill effluent constituents most resistant to microbial degradation (5-day aerated lagoon) and, therefore, most likely to be discharged into receiving waters are dichlorodehydroabietic acid and tetrachloroguaiacol (degradation rates of 18 and 8.4 µg/mg biomass/d, respectively)[25]. Chlorinated phenols, guaiacols, catechols, vanillins, and veratroles are also easily detectable in biologically-treated, as well as

nonbiologically-treated, bleached pulp mill effluents[9,32,81].

An analysis by a Canadian "state-of-the-art" bleached kraft mill of its biologically-treated effluents found its aerated lagoons effectively treated chlorinated vanillins and guaiacols with up to 82% and 76% removal, respectively[86]. In contrast, the same lagoons were not as effective in removing chlorinated catechols (12%) and phenols (44%). In comparison, the lagoons of a similar European pulp mill were only capable of removing between 13% and 54% of the chloroguaiacols from the effluents[50].

Biotransformation. Some chlorinated organic compounds from bleached pulp mill effluents can be biologically transformed into more toxic, more accumulative compounds, such as chloroanisoles and chloroveratroles in high yields[87-89]. Through bacterial *O*-methylation, 3,4,5-trichloroguaiacol is transformed into 3,4,5-trichloro -veratrole, -syringol, and -catechol[90].

The possibility that the biotransformation of chloroguaiacols was a laboratory artifact, and did not occur in the natural environment, was resolved by finding elevated concentrations of chlorinated veratroles in Baltic Sea fish tissue[88,89] and sediments[54] in the vicinity of bleached pulp mill outfalls. Since no other source of polychlorinated veratroles is known, it must be concluded that these substances originated from microbial transformation of the corresponding guaiacols[90].

Although chloroveratroles have been detected in Canadian bleached pulp mill effluents and receiving waters[69,91], they have not been sought in Canadian fish tissue. It is believed that fish have inducible liver de-*O*-methylation enzymes which quickly convert chloroveratroles back to chloroguaiacols and chlorocatechols[92]. This conjecture is supported by laboratory experiments with zebra fish in which chloroveratroles within the fish were de-*O*-methylated to the corresponding chloroguaiacols and chlorocatechols and excreted as aqueous sulphate and glucuronide conjugates[93].

O-methylation is expected to be restricted to aerobic or at least micro-aerophilic locations[94]. Oxygen-depleting fibre mats often cover the sediments in the immediate vicinity of bleached pulp mill outfalls rendering the sediments anoxic by extensive microbial activity. In a laboratory study, chloroveratroles and chloroguaiacols were rapidly de-*O*-methylated to the corresponding catechols[95]. These findings explain the failure to recover chlorinated veratroles from anaerobic sediments. The study also revealed an anomaly as chloroguaiacols were not recovered[95]. A possible explanation for the difference in the chemical extractability of chloroguaiacols and chlorocatechols may be that these compounds are "bound" in sediments by different mechanisms. Further experiments[95] have shown chlorocatechols to be unstable under anaerobic conditions.

A laboratory experiment using low substrate concentrations of 3,4,5-trichloroguaiacol under anoxic conditions resulted in 3,4,5-trichloroveratrole as the biotransformation product; however, at higher concentrations, 3,4,5,-trichlorosyringol and 1,2,3-trichloro-4,5,6-trimethoxybenzene became the dominant products[94].

Bioaccumulation. Many toxic anthropogenic organic compounds enter the aquatic environment. There, living organisms have developed internal mechanisms for the sequestering, detoxification and/or elimination of these compounds for self-protection. Some chlorinated organic compounds which are discharged from bleached pulp mills are, however, bioaccumulative, magnifying the potential harmful effects to the organisms and to other organisms which feed upon them.

The potential for aquatic organisms to accumulate constituents of bleached pulp mill effluents above background (water)

concentrations (bioconcentration factor or BCF) is usually small[57]. The results of several laboratory BCF studies of compounds discharged from bleached pulp mills are listed in Table 3.

Tetrachloroveratrole, a biotransformation product of bleached pulp mill effluents, has the potential to be accumulated in fish tissue 25 000 times above the background concentration[25,89]. Again, the importance of understanding the fate of both products and by-products found in bleached pulp mill effluents is emphasized.

The results of most bioaccumulation studies indicate that bioconcentration of chlorophenols is positively correlated with the number of chlorine atoms present in the molecule[96]. The higher BCF with increasing chlorine substitution most likely results from the high partition coefficient or the lower dissociation constant[57]. Other experimental conditions, such as length of exposure, exposure concentration, pH, ionic strength, water hardness and salinity, may also contribute to the substantial range of BCF values[97].

Clearance rates by fish of certain lipophilic and bioconcentrating chlorinated phenolic compounds present in bleached pulp mill effluents are rapid[58]. For example, 2,4,6-trichlorophenol and tetrachloroguaiacol were eliminated from rainbow trout livers 21 and 10 days, respectively after dosing was discontinued[58]. Similarly, 84 to 92% of 2,4,5-trichlorophenol was lost from fathead minnows in the first day after exposure[98]. The rapid elimination of these contaminants by fish in laboratory studies may indicate that the observed bioaccumulation in field situations is a result of long-term, low-level exposure rather high bioaccumulative potentials[58]. In nature, however, many aquatic organisms cannot or will not leave contaminated waters[29,99], and, therefore, the effectiveness of detoxification via excretion is limited in practice.

4.8.2 Levels and Distribution of Chlorinated Organic Compounds in the Aquatic Environment

Water. In 1989, the Canadian Pulp and Paper Association (CPPA) conducted a National Dioxin Characterization Program of Canada's 47 bleached chemical pulp mills. Effluent samples were analyzed by private consultants. The CPPA monitoring program included AOX measurements and the results are listed in Table 4.

Only with good design and careful management can effluent treatment result in a low AOX value. The lowest AOX value in 1989 for a Canadian bleached pulp mill with no effluent treatment was 3.0 kg/ADt; one mill with primary treatment achieved an effluent AOX level of 1.0 kg/ADt, while the best result for a Canadian mill with secondary effluent treatment was 0.5 kg/ADt. Poor design or management of an effluent treatment facility, however, may lead to values above 10 kg/ADt.

Inland Canadian pulp mills using chlorine bleaching, discharge effluents which may form a substantial portion of the immediate receiving waters. At one mill, the river flow of the immediate receiving waters was only four times that of the effluent, so that the mill provided 20% of the watercourse flow. On average, the effluents from the 24 Canadian bleached pulp mills situated inland on rivers have been estimated (based on AOX levels compiled by the CPPA monitoring program in 1989) to comprise 2.8% of the immediate receiving waters during minimum flow conditions. The estimated concentration range of total chlorinated organic substances in the final effluent and in the immediate receiving waters during mean and minimal daily watercourse flows are shown in Table 5.

The concentration of chlorinated organic compounds in the effluents discharged from bleached pulp mills is diluted upon mixing with the immediate receiving waters; however, during low flow conditions, some

Table 3 Bioconcentration Factors of Compounds Discharged from Bleached Pulp Mills

Chemical	Organism	BCF	Reference
2-Monochlorophenol	Bluegill	214	100
2,4-Dichlorophenol	Brown trout	10	25
2,4, 6-Trichlorophenol	Snail (adult)	3 020	101
2,4, 6-Trichlorophenol	Marine worm	20 269	102
2,4,5-Trichlorophenol	Fathead minnow	1 900	98
2,3,4,6-Tetrachlorophenol	Blue mussel	45-60	103
2,3 ,4,6-Tetrachlorophenol	Roach	200	104
2,3,4,5-Tetrachlorophenol	Marine worm	17 625	102
2,3,5,6-Tetrachlorophenol	Catfish (liver)	8 608	105
Pentachlorophenol	Roach	60	104
3,5-Dichlorocatechol	Brown trout	2	25
Tetrachlorocatechol	Brown trout	4	25
3,4,5-Trichloroguaiacol	Rainbow trout	268	106
4,5 ,6-Trichloroguaiacol	Rainbow trout	98	106
4,5,6-Trichloroguaiacol	Bleaks	390	25,107
Tetrachloroguaiacol	Bleaks	400	25,107
Tetrachloroguaiacol	Rainbow trout	189	106
Tetrachloroveratrole	Zebra fish	25 000	25,89
Chlorovanillins	Rainbow trout	<5	106
3,4,5-Trichlorosyringol	Rainbow trout	125	106

receiving waters do not have adequate dilution capacity. Data from field measurements of effluent dilutions in several eastern Canadian rivers and lakes concur with these estimates[25,36,108-111]. Even when mills are situated on lakes, the effluent may exist in measurable concentrations over a large area. Two mills located on Nipigon Bay in Lake Superior, required a distance of 4 km to achieve a dilution to 0.1% of effluent[36,103].

Table 4 Canadian Adsorbable Organic Halogen Measurements (1989)

Region	Number of Mills	AOX (kg/ADt) Range	AOX (kg/ADt) Mean
Pacific & Yukon	18	0.8 to 14.9	5.0
Western & Northern	3	1.1 to 2.9	2.2
Ontario	10	0.5 to 8.0	3.1
Quebec	9	0.6 to 7.9	3.1
Atlantic	7	1.2 to 5.9	3.4

Table 5 Range of AOX Concentrations in the Effluent and Immediate Receiving Waters During Mean and Minimal Daily Watercourse Flows (Freshwater)

	Range of AOX Concentrations (ppm)
Final effluent	3.8 to 62.5 (mean 26.6)
Immediate receiving waters, mean flow	0.003 to 3.7 (mean 0.32)
Immediate receiving waters, minimal flow	0.008 to 12.5 (mean 1.07)

The most consistently measured chlorinated organic compounds in waters receiving bleached pulp mill effluents are chlorophenolics[40,60-65].The range of concentrations detected along the British Columbia coast in the general vicinity of bleached pulp mills is:

2,4,6-Trichlorophenol	1.6 to 20.0	ppb
2,3,4,6-Tetrachlorophenol	1.0 to 7.1	ppb
Pentachlorophenol	1.7 to 2.8	ppb
3,4,5-Trichloroguaiacol	8 to 30.5	ppb
Tetrachloroguaiacol	1.1 to 58.5	ppb
3,4,5-Trichlorocatechol	1.0 to 16.0	ppb
Tetrachlorocatechol	3.0 to 17.0	ppb

Future coastal monitoring studies in British Columbia must analyze for other chlorinated organic compounds as the levels of those compounds sampled do not adequately reflect the total effluent AOX. For example, the AOX concentrations in effluents from five coastal bleached pulp mills ranged from 16 to 48 ppm[60-63,65].

Chloroveratroles, products of biotransformation, have been detected in the effluents of bleached pulp mills; they have not, however, been detected in the receiving waters[69,81,91]. Concentrations of dichloroveratrole, 3,4,5-trichloroveratrole and 1,2,3,4-tetrachloro- 5 ,6-veratrole have been found in bleached pulp mill effluents at 7, 36 and 28 ppb, respectively[69,81,91].

Concentration gradients of AOX, resin acids, and specific chlorinated organics, which are associated with pulp mills using chlorine bleaching, have been observed in Canadian waters[63,81,112]The AOX concentration declined, for example, from 102 ppm at 1 km to less than 10 ppm at 7 km from the outfall of a coastal bleached pulp mill[64]. Dehydroabietic acid concentrations ranged from 130 ppb in the effluent to 100 ppb at 1.0 km and finally to 0.1 ppb over 6 km away from a bleached pulp mill on Nipigon Bay[81]. A recent monitoring study on the St. Maurice River in Quebec revealed concentrations of 3,4,5-trichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachloroguaiacol, 2,4,6-trichlorophenol and 2,4-dichiorophenol to be 80, 35, 30, 30 and 18 ppt, respectively, immediately downstream of the outfall of a bleached pulp mill[112]. The concentrations of these compounds decreased logarithmically to 45, 9, 4.5, 10.5 and 5.5 ppt, respectively, over a distance covering 96 km. AOX levels decreased at a significantly slower rate.

Gradients of AOX and chlorinated organic compounds have also been observed downstream of bleached pulp mills in Scandinavia[113].Finnish and Swedish studies of the Gulf of Bothnia found AOX levels highest near the outfall of bleached pulp mills (260 ppb) and only falling to background levels after 15 km and 12 km, respectively [113, 114]. It has been reported that the natural background level of AOX in both marine and fresh Scandinavian waters ranges from 10 to 50 ppb[66,115,116]. These levels have been attributed to naturally occurring organic acids, e.g., humic and fulvic acids, which can have chlorine concentrations of 0.1 to 1% [115].

Numerous Canadian studies have discovered bleached pulp mill-generated chlorinated organic compounds in fresh water over 600 km from the source[41,50,68,81,117-122] A monitoring survey of the Athabasca River in November 1988 found concentrations of 3,4,5-trichloroguaiacol and tetrachloroguaiacol 20 km downstream of a bleached pulp mill to be 307 and 186 ppt, respectively. No chloroguaiacols were detected above the mill[118]. A later analysis of chlorophenols (February, 1990) detected relatively high levels of these chloroguaiacols (30 and 40 ppt, respectively) 650 km downstream of the same outfall[68]. Other chlorinated organic compounds specific to bleached pulp mill effluents, such as acetosyringol (5 to 50 ppb) and vanillin (0.1 to 0.5 ppb), have been detected in the Athabasca River over 20 and 200 km downstream of the mill, respectively[69].

The long-range transportation of bleached pulp mill effluents has also been demonstrated in coastal [40,41,60-65,117,120]. Furthermore, effluent "slugs" have been observed to remain in the marine water column at the same depth as the mill outfall for over 36 km [40,60-65]. Surface AOX measurements, therefore, may not accurately reflect the effluent concentration or demonstrate an AOX gradient in the receiving waters. At the outfall of one coastal mill (2 m below the water surface), for example, the AOX level was 357 ppb and an obvious concentration gradient was observed at the same depth over a distance of 36 km at which the concentration was 64 ppb[65] .The surface AOX concentration, in comparison, was only 14 ppb at the outfall and decreased rapidly with increasing distance to non-detectable. It is important to remember that considerable amounts of high molecular weight compounds may be accessible for biological degradation and transformation to potentially bioaccumulative and toxic substances at even greater distances from the general vicinity of the bleached pulp mill effluent discharge site[41].

Several studies have documented changes in AOX and chlorophenol concentrations in receiving waters as a result of winter conditions[68,114,119,123,124] example, the Fraser River has an average winter bleached pulp mill effluent concentration of 3% [123], but the annual effluent concentration of the river is estimated to be 1 to 3%[123]. Chlorophenols have been detected in Lake

Athabasca, which is 1400 km downstream of the nearest bleached pulp mill outfall, when the Athabasca River is frozen over[125]. A Finnish freshwater study found AOX and chlorophenol levels to be elevated during winter months[114]. These data demonstrate the major influence of ice cover on the persistence of otherwise fairly volatile compounds in the aquatic environment. Ice cover prevents evaporation and reduces photolytic and bacterial decomposition.

Sediments. Canadian monitoring studies suggest widespread contamination of sediments by chlorinated organic compounds discharged from pulp mills using chlorine bleaching[40,60-65,126,127]. Tetrachlorocatechol and chloroguaiacols are present in Fraser River sediments up to 50 km and 700 km, respectively, downstream of the nearest bleached pulp mill[126,127]. Large concentration ranges of chlorinated organic compounds unique to the effluents of bleached pulp mills have been found in the coastal sediments of the Strait of Georgia, British Columbia[40,60-65]. For example, the concentrations of trichloroguaiacol, tetrachloroguaiacol, trichlorocatechol and tetrachlorocatechol ranged from nondetectable to 606, 893, 630, 1000 ppt, respectively within a 3 km range of the mills[60-63,65]. Tetrachloroguaiacol was detected (2.0 ppt) in coastal sediments over 36 km from the nearest bleached pulp mill[65]. Chlorophenols, such as di-, tri-, tetra- and penta-chlorophenol, were also identified throughout this British Columbia survey area[40,60-65].

Recent Canadian monitoring studies have revealed concentration gradients of individual chlorinated organic compounds in sediments with increasing distance from bleached pulp mill effluent outfalls[40,60-65]. Concentrations of these compounds in sediments along the British Columbia coast were greatest closest to the mill outfalls and, in most cases, decreased in a north-south direction. In contrast, the EOC1 sediment concentration demonstrated no discernible gradient but remained consistently at 10 ppb within the Strait of Georgia[60-63,65], and therefore is of limited usefulness in monitoring.

Trace amounts of tri- and tetrachloroveratroles (<5 ppt) were detected in sediment extracts near an Atlantic coastal bleached mill[91]. The presence of chloroveratroles at this site may be explained by the flushing, and presumably, aeration influence of the tides[91]. Also, dehydroabietic acid, a predominant resin acid found in sediments adjacent to bleached pulp mill effluent outfalls, was detected 1 km from a bleached pulp mill on Nipigon Bay, Lake Superior at 150 ppb[81] and ranged between 5 to 100 ppb within the surficial sediments[80].

The sediments of the Gulf of Bothnia have been extensively sampled and analyzed for specific and general chlorinated organic compounds[128-129]. Numerous studies have found gradients of individual chlorinated organic compounds and of EOC1 in sediments near various Swedish pulp mill effluents. The predominant chlorinated organic compounds unique to bleached pulp mill effluents which are found in the sediments of the Gulf of Bothnia within 1 km of an outfall are 2,4,6-trichlorophenol, 4,5-dichloroguaiacol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol[54]. Sediment EOC1 concentrations ranged from 500 to 6000 ppb within 10 km of bleached pulp mills and fell to background levels at a distance of 20 km[130].

Background levels of extractable organic chlorine (EOC1) in the Baltic and Swedish coastal fjords and in lake sediments ranged from 10 to 30 ppb[115,130]. These background EOC1 levels are considered to reflect contamination from the atmosphere with an anthropogenic source, or perhaps naturally occurring chlorinated organic acids[115,131]. Diffuse leakage of EOCI from land sources did not explain the gradients found near pulp mills[128]. Petrochemical, steel and municipal sewage discharges were also eliminated as major sources of EOC1[130].

Animal Tissues. Chlorophenol and chloroguaiacol uptake has been reported in muscle tissue of whitefish (*Prosopium williamsoni*), suckers (*Catostomus macrocheilus*), pink salmon (*Oncorhynchus gorbuscha*) and chinook salmon (*Onchorhynchus tshawytscha*) inhabiting a 650-km stretch of the Fraser River[117,122,132]. Overwintering juvenile chinook salmon, collected in the lower Fraser River, 117 km from the mouth and over 650 km downstream from the nearest bleached pulp mill effluent outfall had body burdens of tri-, tetra- and penta- chlorophenol averaging (on a wet weight basis) 10.7, 15.2 and 38.3 ppt[122]. Trichloroguaiacol and tetrachloroguaiacol were also found in salmon over 650 km downstream of the bleached pulp mills at levels of 48 and 24 ppt, respectively[122]. The highest concentrations of these two substances (304 and 136 ppt, respectively) were found 8 km below the nearest outfall on the Fraser River[122]. Because these chinook salmon were juveniles (fry and presmolts) and as such have never entered marine waters, and since chloroguaiacols are unique to bleached pulp mills, it can be assumed that the chlorinated organic body burdens found in fish in the lower Fraser River represent the accumulation of chloroguaiacols discharged from the mills over 650 km upstream. Furthermore, in laboratory studies, chinook salmon bioconcentrated chloroguaiacols from Fraser River water[122], substantiating the widespread contamination along the Fraser River system.

Tri- and tetra-chloroguaiacol have been found in the liver and muscle of burbot (*Lota lota*) and walleye (*Stizostedion vitreum*) in the Slave River, NWT at 2.13 and 0.95 ppt, respectively[131a]. This sampling site is over 1 500 km downstream of the nearest bleached pulp mills which are located in Alberta.

Chlorinated organic compounds generated by pulp mills using chlorine bleaching are also widespread in coastal waters [40,60-65]. Five bleached pulp mills spanning approximately 200 km of the British Columbia coast were studied. In one instance, tetrachloroguaiacol was detected in fish muscle (8.0 ppt, wet weight) over 36 km from the nearest mill[65].

Numerous monitoring surveys have been conducted along the British Columbia coast in the past year[40,60-65] and several trends can be noted. Generally, only highly chlorinated phenolic compounds, such as trichloroguaiacol, tetrachloroguaiacol, and trichlorocatechol excluding tetrachlorocatechol, have been accumulated by clams, oysters, shrimp, crabs, and fish. An exception is pentachlorophenol which was usually present at no more than the detection limit; in one instance, however, 9.0 ppt (wet weight) of pentachlorophenol was detected in the hepatopancreas of crabs 1.5 km from a bleached pulp mill effluent outfall[65]. Tissue concentrations of these chlorinated phenols ranged from nondetectable to 6.0 ppt for clams, oysters, and shrimp; 13 ppt for crabs; and 7.0 ppt for [60-63,65].

Trichloroguaiacol was the chlorinated phenolic compound most often detected and in the greatest concentrations in fish[61-63,65]. The maximum concentrations of trichloroguaiacol (13 ppt) occurred in fish captured within the immediate receiving waters although tetrachloroguaiacol was detected at 36.0 ppt over 6 km from one mill[65]. A maximum concentration of 100 ppt tetrachloroguaiacol was discovered in crabs 1 km from the mill[65].

Chlorinated compounds have also been detected in shellfish and fish collected near the outfall of a bleached pulp mill on the Atlantic coast; however, the maximum concentrations are almost three orders of magnitude greater than those found in organisms along the Pacific coast:
2,4-dichlorophenol (3.73 ppb), 2,4,6-trichlorophenol (3.48 ppb), trichloroguaiacol (2.4 ppb), tetrachloroguaiacol (2.13 ppb) and pentachlorophenol (7.9 ppb)[91]. It should be noted that the bleached pulp mill on the

Atlantic coast closest to where the fish were captured does not treat its effluents, whereas the majority of the Pacific coast mills subject their effluents to primary treatment.

Dehydroabietic acid has been detected using Gas Chromatography/Mass Spectrometry (GCMS), but not quantified, in various fish species from Nipigon Bay, Lake Superior[133]. Seston, found 4 km downstream of a bleached pulp mill effluent outfall in the same bay, had levels of 35 ppb dehydroabietic acid and a concentration gradient was observed[81].

Surveys of the Strait of Georgia, B.C. also revealed an organochlorine concentration gradient in animal tissues with increasing distance from the bleached pulp mills[60-63,65]. These gradients, observed in crabs and fish only, indicate continuous exposure, possible persistence, and, most importantly, bioaccumulation of bleached pulp mill generated chlorinated organic compounds by aquatic organisms. Fish demonstrated a typical concentration gradient with levels consistently falling with increasing distance from the bleached pulp mill effluent outfall([61,63-65]. On the other hand, the concentrations of chloroguaiacols in crabs near outfalls peaked (7.8 to 13 ppt) 4 km from these mills([62,63]) and then decreased with increasing distance from the mill[61-63]. The survey results indicated that clams, oysters, and shrimps are poor indicators of contamination by chlorinated organic compounds generated by bleached pulp mills, since they do not reflect levels found in sediments, fish, and crabs at similar distances from the outfalls[60-63,65].

Laboratory and field studies have demonstrated that hepatopancreas and liver are the organs which accumulate concentrations of chlorinated organics discharged from bleached pulp mills at levels most similar to those in water[40,60,62-65,134,135]. Skeletal muscle tissues display the lowest potential for bioaccumulation[40,60,62-65,134,135].

Swedish investigators have reported EOC1 concentration gradients in animal tissues which reflect those found in sediments and water [136].

A Swedish study on a mill undergoing "start-up" conditions (at Norrsundet), found the highest EOC1 concentrations in perch muscle closest to the mill (>400 ppm) and a decrease with distance to 50 to 120 ppm at 11 km. Extractable Organic Chlorine levels in perch near an unbleached mill in Sandarne were 12 to 66 ppm and did not demonstrate a gradient with distance. Snails (*Lymnea* sp.), collected near the same bleached kraft mill (Norrsundet), had EOC1 levels approximately ten times the concentrations (0.7 ppm) in snails from an area not receiving effluents from bleached pulp mills [8]. Fish, sampled in a Norwegian lake, were found to maintain consistent EOC1 concentrations (220 to 620 ppm) up to 16 months after the closure of a bleached sulphite mill[66]. Extractable Oragnic Chlorine concentrations in fish tissue returned to background levels 3.5 years after the mill closure. Of particular interest is the fact that fish tissue concentrations of individual chlorinated organic compounds, such as mono- and di- chlorocymene and tri-, tetra- and penta- chlorophenol, fell to nondetectable levels (<60 ppb) within the same 16-month period[66]. Clearly, other chlorinated organic substituents of bleached pulp mills that were not individually measured in the study were responsible for the continued elevation of EOC1 concentrations in fish. Fish have been found to contain up to 2000 ppm of organic chlorine in fat tissue; however, the identified compounds accounted for only a few percent of the total amount of chlorine measured[66].

Although chloroveratroles have not been detected in Canadian fish, they have been detected in fish tissue in the Baltic Sea (400 ppb in liver fat)[89]. Possible explanations for the discrepancy are that Canadian researchers do not analyze fish tissue for chloroveratroles or that

concentrations in Canadian receiving waters do not reach levels which affect the enzymic de-*O*-methylation of chloroveratroles to chloroguaiacols and chlorocatechols.

Few, if any studies, have been conducted to date on chlorinated organic compounds discharged from bleached pulp mills concerning their fate, distribution, and levels in aquatic plants or in wildlife.

4.9 Effects of Bleached Pulp Mill Effluents on the Aquatic Environment

4.9.1 Acute Lethality

Some attempts have been made to assess the acute toxicity of whole effluent from bleached pulp mills by assuming that each individual chlorinated organic compound contributes to the overall toxicity[126,137]. An estimate of this type based on nine representative compounds common to bleached pulp mill effluents (chlorinated catechols, guaiacols, phenols, resin acids and fatty acids) resulted in a predicted additive toxic action of 2.2 times the observed lethal level[137], whereas another study estimated a toxicity of only 0.2 of the measured lethal level[138]. Clearly, the most accurate evaluation will result from the direct measurement of toxicity of whole bleach plant effluent, or direct comparison of effects of bleached with unbleached pulp mill effluents[8].

Effluents from the bleaching stage account for approximately half of the acute lethality of bleached pulp mills' total discharged effluents[8].

Toxicity Emission Factors (TEF), the total amount of toxic material discharged by a pulp mill per tonne of pulp produced, in one mill, for example, ranged from 300 to 740 TEF for bleach plant effluent to 610 to 1400 units for the whole mill effluent [36,139].The toxic contributions of the various streams within bleached pulp mills, when totalled, produce a reasonably accurate estimate of the toxicity of whole effluent[8].

The concentrations of compounds found in biotreated bleached effluents, excepting tetrachloroguaiacol, trichlorophenol, and chlorodehydroabietic acid, are a small fraction of the levels that are acutely lethal to fish or other aquatic life[25]. The concentration range (ppb) of bleached pulp mill-generated compounds found in biologically-treated kraft and sulphite pulp mill effluents as well as their corresponding LC_{50}s to aquatic organisms are listed in Table 6.

Three quarters of the effluents from the 47 Canadian bleached pulp mills are acutely toxic to trout (data gathered under the Fisheries Act). Analysis of these data suggests a correlation between the results of acute lethality tests and the degree of wastewater treatment. Almost all effluents from Canadian bleached pulp mills which have primary or no effluent treatment are acutely lethal. At one such mill, the lethal concentration for rainbow trout occurred at 3.2% whole effluent. Only halt of the biologically-treated bleached pulp mill effluents in Canada are not acutely lethal to trout at 100% whole (undiluted) effluent. Biologically-treated effluents from two Ontario kraft mills were more lethal (LC_{50} of 21%) than six equivalent Ontario mills with primary effluent treatment only (LC_{50}>32%)[140,141]. No correlations were observed between effluent AOX concentrations and effluent toxicity.

It has been estimated that 16% whole effluent is the mean lethal concentration (LC_{50}) for Canadian bleached mills[8]. Effluents from bleached pulp mills comprise anywhere from <1 to 20% of the immediate receiving waters; therefore, the possibility for kills of aquatic organisms is real.

For many Canadian bleached pulp mills, acute lethality to fish would not be expected outside a small plume after the dilution of effluents in the receiving water, as long as the effluents are rapidly diluted 20-fold[8]. Unfortunately, many instances exist where the

Table 6 Concentration Range and LC_{50}s of Bleached Pulp Mill-generated Compounds Found in Biologically-treated Effluents from Kraft and Sulphite Pulp Mills

Compound	96-h LC_{50} (ppb)	Effluent Concentration Kraft	Effluent Concentration Sulphite	Reference
2,4-Dichlorophenol	2800	9 to 15	4 to 10	25
Dichloroguaiacols	2300	22 to 100	6 to 12	25,142
Dichlorocatechol	500 to 1000	12 to 90	-	25,142
2,4,6-Trichlorophenol	450 to 2600	1 to 51	3 to 764	25
Trichloroguaiacols	700 to 1500	10 to 340	16 to 39	16,25
Trichlorocatechols	1000 to 1500	120 to 270	-	25,142
Tetrachlorophenol	500	-	-	96
Tetrachloroguaiacol	200 to 1700	10 to 620	12 to 130	16,25
Tetrachlorocatechol	400 to 1500	22 to 420	-	25,96
Pentachlorophenol	200	-	-	96
Dehydroabietic acid	500 to 2000	-	-	143
Chlorodehydroabietic acid	600 to 900	10 to 750	10 to 900	25,143
Dichlorodehydroabietic acid	600 to 1200	10 to 420	10 to 40	16,25

discharge of effluents into rivers, lakes, and coastal waters does not result in rapid dilution[25,36,41,50,110,111,144] In addition, in most locations, chronic as well as acute effects can result, possibly extending over large areas[8].

Generally, the levels of individual compounds specific to bleached pulp mill effluents detected in the Canadian aquatic environment, particularly those which are chlorinated, are well below levels demonstrated to cause 96-h acute lethality. Some effluent concentrations of individual compounds, however, did approach the 96-h LC_{50}. For example, dehydroabietic acid maintained a consistent concentration (25% of the LC_{50}) in the effluents and in the immediate receiving waters of Nipigon Bay[143]. Levels of dichlorophenol, trichlorophenol, trichloroguaiacol, and tetrachloroguaiacol were detected in fish at 23%, 29%, 50% and 95% of their respective LC_{50}s in the nontreated effluents of an Atlantic coast bleached pulp mill[91].

Fish are generally more sensitive than invertebrates to the lethal action of bleached pulp mill effluents [8,25].There is a significant correlation ($r^2 = 0.68$) between low molecular weight (mw<1000) TOX discharges and acute toxicity (based on trout bioassays); therefore, low molecular weight TOX may be used as a reasonably accurate indicator of toxicity to

fish[47,145]. There is no compelling evidence that indicates common species of fish differ greatly in their resistance to lethal levels of bleached pulp mill effluents[146,147], although rainbow trout (*Salmo gairdneri*) are the species used most often [25]. It is difficult to compare sensitivities of species to the lethal action of bleached pulp mill effluents from the existing literature as various stages of the life cycle are studied. For example, trout are more sensitive to the effluents of bleached pulp mills than the crustacean *Gammarus*, generally considered a susceptible organism, which in turn are more sensitive than mosquito larvae. The waterflea, *Daphnia magna*, and midge larvae are more resistant to the lethal action of these effluents than are rainbow trout[147,148].

Swedish studies found acutely toxic effects at much lower concentrations than are generally determined by North American research. Field and artificial ecosystem studies indicate consistent measurable effects at 0.25% effluent (0.01 of the LC_{50}) and occasional meaningful effects at 0.1% effluent or 0.004 LC_{50}[8]. The discrepancy in lethal concentrations between North American and Scandinavian aquatic environments may be a result of:

1) lower water consumption and therefore higher "end-of-pipe" concentrations from Scandinavian mills;

2) Scandinavian pulp mill effluents generally receive primary treatment only; and

3) other toxicants in the Baltic Sea may have either a synergistic effect with those discharged from bleached pulp mills or may act independently of them, lowering the apparent effect-concentrations.

Many other components of bleached pulp mill effluents can cause mortality of aquatic organisms. Lethality may be caused by extremes in temperature, pH, and dissolved oxygen[8,149,150]. Studies have also demonstrated that toxic effects of these effluents to sockeye and coho salmon are enhanced under low dissolved oxygen (hypoxic) conditions[149].Researchers and literature reviewers have concluded that, in general, a reduction in dissolved oxygen from 100% to 80% of air saturation will cause increased mortality of fish exposed to some of the contaminants generated by pulp mills using chlorine bleaching[151,152].

Many of the other variables involved in bleached pulp mill processing, such as the type of wood, the bleaching sequence, and the degree of effluent treatment, affect the lethality of the effluents to aquatic organisms[8,29,33,140,141,153,154]. Softwoods are more acutely toxic to *Daphnia*, for example, than hardwoods pulped under comparable conditions[153]. The greater the chlorine dioxide substitution for chlorine during the bleaching process, the less toxic the effluent (e.g., as the chlorine to chlorine dioxide ratio decreases from 90:10 to 35:65 to 10:90, the toxicity decreases)[33]. Well designed, operated, and managed secondary effluent treatment facilities are estimated to remove between 50% and 90% of the effluent acute toxicity[8,29,154].

4.9.2 Chronic Effects

Unlike acute lethality, chronic toxicity normally does not result in the immediate death of an organism upon exposure to a pollutant. Chronic effects typically develop after continuous, long-term exposure to low doses of toxic material. In many instances, the effects a pollutant may exert on the individual organism, although subtle, may be important to the continuance of the species, e.g., reproduction, growth, or survival.

As difficult and important as it is to identify the exact effect a compound may have on an organism, it is often even more difficult to identify the ecological significance of these often subtle responses in the population[155]. Unfortunately, there is incomplete

information on the chronic effects of individual chlorinated organic compounds discharged in bleached pulp mill effluents. Also, predicting the toxicity of a mixture of these compounds from that of the individual components, which is achievable in the case of acute toxicity, is at present a nearly hopeless task at the chronic level.

The literature on chronic toxicity of whole bleached pulp mill effluents is extensive[7,156-163], and detailed reviews have been provided by Canadians Davis, Kovacs, and McLeay[126,161-163]. Many countries have conducted various chronic studies using whole effluent. Swedish researchers have examined effluents from various bleaching processes through the use of artificial ecosystems. The National Council for Air and Stream Improvement (NCASI), an affiliation of the U.S. pulp and paper industry, has conducted long-term studies on warm and cold water artificial streams using well-treated secondary effluents[164,168].

The known chronic effects of bleached pulp mill effluents on the aquatic environment are categorized and summarized in the following text.

Reproductive and Life-cycle Effects. Reproductive performance of aquatic organisms exposed to bleached pulp mill effluents for one or more entire life cycles should be among the most sensitive and relevant evaluations of chronic effects. Unfortunately, most researchers have conducted experiments which deal with effects only on early life-cycle stages or some limited aspect of reproduction.

Reduced gonad size and inhibited gonad development have been observed in fish downstream of bleached pulp mill outfalls[112,169-171].The gonad-somatic index (relationship between gonad and body size) was significantly smaller in white suckers (*Catostomus commersoni*), particularly mature adult females, up to 96 km downstream of a Quebec bleached pulp mill compared to the controls[112]. Sexually immature adult smallmouth bass (*Micropterus sp*.) and white suckers have been found downstream of bleached pulp mill effluent outfalls in the St. Maurice River, Quebec and Terrace Bay, Ontario, respectively[112,172]. Bleached pulp mill effluent concentrations in the receiving waters were not estimated in either study to determine the level associated with reduced gonad size and inhibited gonadal development in fish. These effects, however, occurred only in areas exposed to the effluents and did not occur in the control sites. In some instances[112], individual chlorinated organic compounds specific to bleached pulp mill effluents were measured in the receiving waters; however, no laboratory effects studies were conducted to prove possible causality. Similar observations were made with perch (*Perca fluviatilis*) in the Baltic Sea 10 km from a bleached kraft pulp mill[170]. No changes in female gonad development were observed near an unbleached kraft pulp mill in Sweden[136].

Swedish studies on fish in the vicinity of these outfalls showed that embryos had high levels of deformities, were generally smaller at hatching, and therefore had lower hatching success. Eggs laid in clean areas hatched successfully[173]. Experimental stream studies found an increased number of egg mortalities and a reduction in hatching success of trout exposed to 1.3% effluent[168]. No Canadian field studies relating to the hatching success of fish have been reported. NCASI findings and conclusions are similar to those of the Swedish investigations in that the decrease in hatching success could be attributable to poor quality sperm or eggs produced by the parents exposed to whole bleached pulp mill effluent[168,173].

Laboratory experiments have found 5-chlorouracil and 4-chlororesorcinol, which the authors suggest are formed by the reaction of chlorine with organic matter, to significantly lower ($P<0.05$) the hatching success of carp eggs at concentrations as low as 1.0 ppb[174]. Significant effects both on

embryo and on larval mortality of zebra fish (*Brachydanio rerio*) were demonstrated with pentachloroanisole and tetrachloroveratrole, products of biotransformation, at 2.8 ppb and 100 ppb, respectively[78]. The fecundity of the harpacticoid copepod (*Nitocra spinipes*), a marine crustacean, was reduced by 50% at 37 ppb of tetrachloroguaiacol[107].All the various field and artificial stream studies performed dealt with the observed effects on aquatic organisms of whole bleached pulp mill effluents. No effort was made to determine which chlorinated organic compound(s) were responsible for the observed embryo and hatching effects.

Multi-generation laboratory studies using killifish (*Rivulus marmoratus*), zebra fish, and viviparous blennies (*Blennius viviparus*) have revealed that offspring of parental fish exposed to bleached pulp mill effluents are sensitized to these effluents[89,175,176]. Parental mortality, hatching success and egg deformities of killifish exposed to 2,3,4,6-tetrachlorophenol at 5 to 20% of the 96-h LC_{50} (0.055 to 0.22 ppm) were similar to the control fish. There was, however, a clear dose response to the organochlorine compound in the survival of the offspring. Offspring of exposed parents suffered mortalities, and fin and gill erosion[176]. Other studies, involving the exposure of zebra fish and viviparous blennies to individual chemical constituents of bleached pulp mill effluents and 2.5% whole effluent, respectively, found similar results; concentrations of trichloroguaiacol, tetrachloroguaiacol, trichlorocatechol, tetrachlorocatechol, trichloroveratrole, tetrachloroveratrole, and pentachloroanisole which did not kill the parents did cause mortalities to larvae and unborn fry at 200, 200, 200, 150, 300, 50, and 2.8 ppb, respectively[89].

Recruitment failure (maintenance or growth of a specific stock of species through maturation of offspring) was observed in fish, particularly in those species with free swimming (pelagic) larvae, near the outfall of a Swedish bleached pulp mill effluent[173]. The recruitment damage caused low parental stock densities, and the population was sustained largely by immigration[173]. Percent effluent concentrations in the receiving waters were not reported.

Biochemical and Physiological Changes. Whole bleached pulp mill effluent has been shown in field and laboratory studies to elicit biochemical and physiological changes in fish[112,172,177-181]. Liver and blood parameters are most commonly examined for these biochemical and physiological disturbances.

Liver enzyme induction has been demonstrated in Canadian field populations of fish near bleached pulp mills. Preliminary data from studies at St. Maurice River, Quebec and Terrace Bay and the Kaministiquia River, Ontario found a 5 to 10-fold increase in hepatic mixed function oxidase (MFO) in white suckers downstream of the bleached pulp mills[107,172,180]. Whole effluent concentrations in the receiving waters were not reported. Juvenile chinook salmon (*Oncorhynchus tshawytscha*) captured near bleached pulp mills on the Fraser River showed up to 55-fold induction of 7-ethoxyresorufin-*O*-deethylase (EROD), a mixed function oxidase of the liver[182]. Induction of EROD is a sensitive subcellular response to the presence of certain toxic compounds. Fish in the Baltic Sea exhibited a definite gradient response to bleached pulp mill effluents, with EROD induction occurring up to 10 km from the source[169]. Suckers inhabiting the Kaministiquia River downstream of a bleached pulp mill also showed a 3.3-fold reduction of UDP-glucuronyl-transferase[180].

A study of locations 2.5 km or less downstream of a bleached pulp mill on the Wapiti River, Alberta showed that fish carrying residues of mill-derived chlorinated organic compounds had reduced levels of liver glycogen even though the biologically-treated effluent was nonlethal in acute toxicity tests[34]. Juvenile coho salmon

(*Oncorhynchus kisutch*) exposed to laboratory-treated bleached pulp mill effluent had significantly decreased liver and muscle glycogen reserves at 0.2 and 1.0 of the LC_{50} value [183]. Changes in liver glycogen and enzyme activation levels may cause increased energy expenditure and other physiological dysfunctions related to steroid hormone imbalance and reproductive inhibition [158,159,171,184,185]. The dependence of fish on muscle glycogen reserves suggests the impairment of stamina, making the fish more susceptible to fishing pressure, predation and/or starvation[183].

Reduced gonad size and gonad immaturity, observed in white suckers downstream of bleached pulp mill effluent outfalls on the St. Maurice River, Quebec and Terrace Bay, Ontario, are reflected in imbalances of steroid hormone levels[112,172]. Serum levels of testosterone were significantly reduced in male suckers at both sites. Female suckers downstream of the Terrace Bay mill exhibited significantly-reduced serum levels of estradiol [172]. On the other hand, female suckers in the St. Maurice River had raised estradiol concentrations up to 96 km downstream of the bleached pulp mill[112].

Swedish field studies demonstrated a biochemical and physiological response gradient in fish with the disturbances being most pronounced in fish living up to 4.5 km from the outfall of bleached pulp mills. Disruptions in enzyme levels could still be found in fish caught 8 to 10 km from the kraft pulp mills [113,169,170]. When the total Swedish field results are compared to laboratory exposures, however, only the liver somatic index and the EROD effects appear to have any significance. Liver enlargement and EROD induction may be linked to the parallel observation of impaired ovarian maturation in a minority of Norrsundet perch[186].

Few studies have attempted to identify the fraction(s) of whole effluents responsible for the induction of biochemical and physiological changes in aquatic organisms[137,186]. Laboratory investigations of resin acids have found varying degrees of enzyme induction [178,187]. A mixture of resin acids significantly increased liver EROD activity of channel catfish (*Ictalurus punctauls*) but only slightly induced EROD activity in trout [178,187]. In the trout study, however, the induction abilities of resin acids were compared with those of 2,3,7,8-TCDD -an extremely strong (200 x) inducer of trout liver EROD at low doses. Unfortunately, biochemical studies are in their infancy and no effort has been made to distinguish between the potency of the inducer and the degree of induction. No studies were found that investigated the ability of specific chlorinated resin acids common to bleached pulp mill effluents to elicit biochemical and physiological disturbances in aquatic organisms.

Few laboratory enzyme activation studies have been conducted with chlorinated organic compounds other than chlorinated dioxins and furans. A chlorinated phenolic mixture, composed of dichlorophenol, pentachlorophenol and tetrachlorocatechol, significantly increased hepatic catalase and palmitoyl coenzyme-A oxidase (PCO) activity in channel catfish[178]. Upon separation of the mixture, pentachlorophenol was found to be responsible for these biochemical disturbances. Increases in peroxisomal enzyme activities, such as PCO, in exposed fish are of concern because of the correlation between such increases in enzyme activities and hepatocarcinogenesis in mammalian models [178].

Morphology. Various degrees of skeletal deformities as well as fin and gill erosion have been reported in fish from areas near bleached pulp mill discharge [171,188-190]. High incidences of spinal deformities (e.g., curvature of the spine) have been found in fish near bleached and unbleached pulp mills in the Baltic Sea[171,188-190]. Unfortunately, field studies have neither identified the constituent(s) nor the concentration of pulp

mill effluents necessary to invoke these responses. The existence of these deformities, however, suggests that either a chemical(s) common to both bleached and unbleached pulp mill effluents (e.g., resin acids) or some other factor that may be non-pulp mill-related (e.g., other Baltic Sea pollutants such as polycyclic aromatic hydrocarbons)[191], are responsible for these particular changes in morphology. It must be kept in mind that effluents from Scandinavian pulp mills have, at best, undergone primary treatment and that aerated lagoons readily biodegrade such substances as resin acids[163]. Laboratory studies have not demonstrated the induction of severe spinal deformities.

Vertebral deformities, which impair the strength of spinal columns, have been induced in laboratory studies and observed in Canadian field studies[37,89,90,192].Juvenile fourhorn sculpin (*Myoxocephalus quadricornis*), exposed to 0.5 ppm tetrachloro-1,2-benzoquinone (TCQ) for 4.5 months, developed vertebral deformities and vertebrae weakness[192]. Another study induced vertebral deformities in zebra fish at 2.8 and 50 ppb of pentachloroanisole and tetrachloroveratrole, respectively[89]. Tetrachloroveratrole has been detected in fish collected near Swedish bleached pulp mill effluent outfalls at 40 to 400 ppb (liver fat)[89]. It is noteable that the laboratory induced vertebral alterations demonstrated in fish are a result of exposure to biotransformation products - compounds that are generally not looked for in bleached pulp mill effluents.

Pike (*Esox lucius*) near bleached pulp mills in the Baltic Sea were found to have severe skull deformations (bull-head)[113]. Bull-headed pike have not been found in the Baltic Sea every year sampled[113], nor has the bull-headed phenomenon been observed by other countries or in other species of fish. The scientific literature shows no laboratory induction of skull deformities.

Conversely, fin and gill erosion, which have been observed in perch near bleached kraft mills in the Baltic Sea, can be induced in the laboratory[176,193]. Fish exposed to 1.6 to 4% (0.1 to 0.25 LC_{50})untreated effluents for 40 to 60 days had higher incidences of fin necrosis and damaged gills than the unexposed fish. These changes may indicate a loss of resistance by the fish to bacterial pathogens and a significant stress-related effect of these effluents[193].In a previously mentioned laboratory experiment, which demonstrated a heightened sensitivity by offspring of parents exposed to 2,3,4,6-tetrachlorophenol (TeCP), fin and gill erosion were induced at 0.055 to 0.22 ppm (5 to 20% LC_{50}) of 2,3,4,6-TCP[176].

Mutagenicity. Bleached pulp mill effluents have been found to be mutagenic using standard tests[194-196]. Untreated whole bleached pulp mill effluent is usually weakly mutagenic[25,197-200]. The strongest mutagenic component of these effluents is generally effluent from the bleaching stage, but the addition of the caustic extraction effluent substantially reduces the concentration[24,25,195,197-199,202].

Studies have shown that many of the mutagenic compounds in spent bleach liquors from kraft and sulphite pulp mills are the same[203]. The concentrations of the identified mutagens in the effluents from chlorinated kraft pulp are, however, much higher than those reported in effluents from chlorinated sulphite pulps[204]. This indicates that the kraft pulping process creates more precursors of mutagenic compounds than the sulphite pulping process[203]. Also, oxygen delignification of sulphite pulp but not kraft pulp before chlorine bleaching increases the mutagenicity of the effluent[203,205].

Of the 27 mutagenic compounds isolated and identified, no particular pattern emerges, although three-quarters of the compounds contain chlorine[25]. The most abundant mutagenic compounds in effluents from bleached pulp mills are chloroform, 2,4,6-trichlorophenol[206], chloroacetones[203,207], 2-chloropropenal and

3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone[204]. The concentrations do not, however, approach those required to induce mutagenicity. For a more complete listing of mutagenic compounds in bleached pulp mill effluents, interested readers are referred to references 26 and 199.

There are few field observations to confirm the laboratory studies on mutagenicity of pulp mill wastes. Japanese researchers report an apparent association between bleached pulp mill effluents and neoplasms in fish[208,209]; however, details, such as controls and pulp mill processes are poorly documented. Two of the chemicals identified by the Japanese, 2,4,6-trichlorophenol and tetrachloroguaiacol, are known mutagens.

Mutagenic compounds can be eliminated or reduced in concentration through such mill processes as: the addition of alkali to the spent bleaching liquor[197,203]; increased chlorine dioxide substitution for chlorine [24,195,197,198,202]; and secondary waste treatment[197].

Carcinogenicity. A number of compounds found in bleached pulp mill effluents have been identified as carcinogens on the basis of standard methods of mammalian testing. Among these are chloroform, carbon tetrachloride, and safrole[9,210-212]. Some other compounds, such as various chlorinated benzenes and phenols, epoxystearic acid and dichloromethane, have been classified as suspected carcinogens[9].

Physiological alterations have been found in white suckers downstream of a bleached pulp mill on the Kaministiquia River, Thunder Bay, Ontario. Fish exposed to these effluents exhibited increased incidences of liver neoplasms (2.1%) and bile duct disease (21%) compared to control fish[180]. In relation to the liver neoplasms, non-carcinogenic effects have also been observed. Significant liver enlargement has been demonstrated in white suckers of the St. Maurice River up to 96 km downstream of the bleached pulp mill effluent outfall [112].Swedish field and laboratory studies have also demonstrated liver enlargement in fish collected near outfalls of bleached pulp mills[170,177]. No effort was made to determine which chlorinated organic compound(s) were responsible for the observed effects.

4.9.3 Other Effects

Behaviour Modification. Limited information exists on the behavioural response of aquatic organisms to whole effluent. Unfortunately, the information that does exist cannot differentiate which fraction of bleached pulp mill effluent, such as chlorinated organic substances, BOD, dissolved oxygen, pH, turbidity or suspended fibres, is responsible for behavioural modification[151,213-215].

Laboratory experiments, which regulated such parameters as BOD, dissolved oxygen, and suspended fibres, demonstrated limited or no behavioural response by fish[216,217]. Conversely, field studies and in situ bioassays have observed both avoidance and preference behaviour by fish exposed to bleached pulp mill effluents[151,213-215]

In situ bioassays have demonstrated that several species of juvenile fish, which by nature are surface water oriented, avoid surface waters receiving bleached pulp mill effluents for up to 10 km from the source[99,151,215].Furthermore, mortalities occur when these fish are confined, by caging, to surface waters near the outfalls[151,215].

Lethal conditions have been reported in the surface waters of many Canadian west coast estuaries during salmon spawning migrations[151]. Successful migration or survival of salmonids is not guaranteed by "diving" beneath the surface waters as in situ bioassays have shown that lethal conditions exist at depths greater than 4.0 m[151,213]. Dissolved oxygen and pH have been shown statistically to be the most significant water quality parameters in explaining the depth preferences by fish[151,215]. Surface water

discharge of pulp mill effluent inhibits phytoplankton photosynthesis in the deeper waters, resulting in depressed levels of dissolved oxygen[213]. Researchers have found that the toxic effects of pulp mill effluent to salmonids are enhanced under hypoxic conditions[149,218].Temperature and salinity have been eliminated as possible influences on avoidance behaviour since fluctuations are within ranges tolerable to the fish[151,213]

A telemetry study conducted on white suckers in Nipigon Bay, Lake Superior found fish became disoriented for as much as several hours, then appeared to search for "background" conditions when released into high discharge concentrations of bleached pulp mill effluents (>15% dilution by volume)[214]. Fish released into low discharge concentrations (<15%) immediately initiated an avoidance reaction. No effort was undertaken to determine which constituent(s) of the effluents or which water quality parameters were responsible for the behavioural modification. A density analysis of the aquatic organisms in areas near bleached pulp mill effluent outfalls revealed fairly dense populations of fish and benthic invertebrates of limited species diversity, seemingly contradicting the observed avoidance behaviour[214,219-220]. However, telemetry indicated that the residence time of fish in the area of altered water quality was short[214]. The preference behaviour of certain fish species for areas of affected water quality suggests that the feeding response to high benthic biomass and the innate behavioural trait to occupy surface waters overrides the avoidance reaction to the effluents even under adverse (lethal) conditions [151,214,221]. It is likely that these fish will continually strive to occupy specific habitats, probably to their detriment[151].

Swimming stamina and ventilatory water flow were impaired in juvenile coho salmon at 20% of the 4-day LC_{50}[25]. Sublethal concentrations of filtered, aerated, neutralized effluents from bleached pulp mills reduced arterial oxygen tension in salmon at 33 to 47% of the 96-h LC_{50} (static bioassay)[222]. Davis concluded that “it seems highly likely that a toxic mechanism affecting swimming ability in bleached pulp mill effluents is related to ventilatory abnormality and reduced oxygen saturation of arterial blood”[222]. As this study dealt with aerated, neutralized, filtered effluents, probably most of the more volatile toxicants were absent, as they would be in all 96-h LC_{50} tests.

Bleached pulp mill effluents have been found to affect organisms that salmon feed upon. Static 117-h bioassays with these effluents interfered with the reproductive behaviour of the marine amphipod, *Anisogammarus pugettensis* and, at high concentrations (40% of whole effluent), mating ceased[223].

It is highly probable that the combined effects of chemicals and water quality parameters associated with bleached pulp mill effluents exert significant influence on preference-avoidance behaviour[151,214,215].

Species Diversity. Numerous studies have documented shifts in species dominance near pulp mills using chlorine bleaching[214,224-226] It is difficult to establish a cause and effect relationship between bleached pulp mill effluents and changes in species diversity, as a clear separation cannot be made between the influence of eutrophication and specific chlorinated organic compounds[214,225].

A study at Nipigon Bay, Ontario observed a species shift from perch to suckers downstream of a bleached pulp mill which employs primary effluent treatment. The observed species shift is likely the result of the fishes response to both the effluent and the habitat alterations (e.g., eutrophication)[214].

Species shifts have also been identified in the Baltic Sea[225,226]. Virtually no shallow water fish were found within 1000 m of the Norrsundet bleached pulp mill compared to an abundance of shallow water fish within 100 m of the unbleached pulp mill in Sandarne[226].

A superabundance of small shallow water species, known to inhabit areas of eutrophication, could be found up to 6 km from the bleached mill. Populations of larger, deeper-water fish were depressed for up to 4 km from the bleached pulp mill[225].It is implied that bleached pulp mill effluents affect species diversity through a combination of eutrophic and toxic properties. The limitations of the Norrsundet study, such as the abnormally high chlorine loading to the aquatic environment, as a result of in-plant process changes and the lack of secondary treatment, were taken into consideration. Situations exist in Canada, however, where poor or nonexistent effluent treatment results in the release of relatively high levels of organochlorines and also produces turbidity which may influence species diversity very close to the mills[214].

Evidence exists that bleached pulp mill effluents affect the dominance of floral species. The community structure of the periphyton in a southern U.S. river shifted toward a heterotrophic population near the bleached pulp mill effluent discharge point but recovered to control characteristics at downstream stations[224]. A more widespread situation exists in the Baltic Sea.

Particular constituents of bleached pulp mill effluents have been identified as the reason for shifts in species populations. Chlorate, which is a by-product of chlorine dioxide bleaching and is released in bleached pulp mill effluents, is highly toxic to seaweeds, particularly brown algae[29,52,227]. Through laboratory, model ecosystems and field testing, chlorate has been identified as the causal agent for the disappearance of the bladder-wrack community (*Fucus vesiculosus*) in the Baltic Sea[228,229]. Chlorate levels of 10 to 20 ppb are sufficient to reduce *Fucus* numbers[227]. No chlorate levels within the immediate receiving environment were reported.

Fucus, a genus of brown alga, is abundant in shallow, hard bottom environments and is found along the east and west coasts of Canada and in the Baltic Sea. The bladder-wracks are one of the most important plant components of the Baltic coastal ecosystem and form a prominent spawning, nursery and feeding area for a great number (>70%) of the macroscopic animal species, including fish[230]. Severe decreases in crustacean and gastropod populations have occurred as a result of the disappearance of *Fucus*[231]. From these studies, extending no more than one year, it was confirmed that the elimination of *Fucus* from the system induces a shift from the herbivorous and omnivorous species to detritivorous fish species[231]. Based upon the model ecosystem data, it is estimated that an area supported by a healthy *Fucus* population would have an annual fish production of 12 to 15 tonnes. Presently, however, it is estimated that the decrease in annual fish production, due to spawning and nursery habitat destruction and a shift in food species, would be in the order of 10 tonnes[227].

The substitution of chlorine dioxide for chlorine will enhance the generation of chlorate. Secondary biological treatment systems reduce chlorate concentrations to environmentally safe levels[29]; however, the majority of the Canadian coastal bleached kraft mills do not employ secondary treatment. *Fucus* populations and chlorate levels have not been monitored in Canadian waters; therefore, the effect of chlorate discharged from pulp mills using chlorine bleaching on *Fucus* and on its habitat is unknown.

Tainting. Whole bleached pulp mill effluents can cause tainting in commercial species of fish and shellfish. Several reviews list constituents of bleached pulp mill effluents responsible for tainting[126,163,232,233]. Fish tainting may be caused by chlorinated or nonchlorinated components of bleached or unbleached pulp mill effluents. It may also arise from naturally occurring water contaminants. This makes identification of

the causative agents in bleached whole mill effluents difficult[38].

Bleaching was not considered to be a significant contributor to tainting[138] until recent work found that biotransformation products of chlorophenols, tri- and tetra-chloroveratrole, cause tainting[89]. Simple aeration and/or secondary waste treatment may reduce tainting by a factor of 2 to 10 [234-236].

The degree of tainting contributed by specific effluent constituents or their derivatives has yet to be determined[38]. Whole bleached pulp mill effluent can cause tainting in fish at concentrations as low as 0.5[234,235,237-239]. For perspective, concentrations of 1% elicit the more sensitive sublethal effects in fish[234]. Field studies confirm that tainting may occur at that concentration, although some results appear to be confounded with natural "off-flavours". For example, a field study on the Ottawa River found fish that had been caged for 48 hours became tainted as far as 2.5 km downstream of the bleached pulp mill effluent discharge site[240].

Section 5

Risk Assessment, Conclusions and Future Considerations

5.1 Source Assessment

In Canada, as of July 1990, there were 47 pulp mills (42 kraft and five sulphite) which use chlorine bleaching. Much variety exists among these mills resulting in different effluent qualities, for example: pulping, bleaching and wastewater treatment processes; type of wood pulped; and the quality of the pulp product. Many of these bleached pulp mills are integrated; therefore, in addition to their production of bleached pulp, the mills (53%) also produce such semi-bleached and unbleached pulp and paper products such as newsprint and paperboard.

In 1989, the Canadian bleached pulp industry discharged between 25 000 and 310 000 m^3 of wastewater per day per mill. Pulp mills consumed between 10 to 110 kg of chlorine per day per tonne of pulp produced (or 2.5 to 175 tonnes of chlorine per day). This produced approximately 100 to 1 400 tonnes of bleached pulp per day. On this basis, it is estimated that 610 000 tonnes of chlorine were used to produce 10.2 million tonnes of bleached pulp in 1989.

Effluents from pulp mills using chlorine bleaching contain a wide variety of chlorinated and unchlorinated organic compounds. The chlorinated compounds are produced as a result of complex reactions between lignin and its breakdown products, released during the chemical pulping process, and the chlorine bleaching agent. It is estimated that the Canadian pulp and paper sector discharges over one million tonnes of chlorinated organic material to the aquatic environment annually.

Seventy to eighty percent of the dissolved matter in bleached pulp mill effluents consists of high molecular weight chlorinated organic compounds. Although approximately 250 individual compounds have been characterized in bleachery effluents, they have been estimated to represent only 10 to 40% of the total low molecular weight materials present. High molecular weight chlorinated materials are not generally considered to represent a direct threat to aquatic biota, however, they have been observed to be microbiologically transformed or degraded into low molecular weight compounds that add to the total low molecular weight loading.

The predominant classes of low molecular weight compounds reported in Canadian bleached pulp mill effluents are: chlorinated and nonchlorinated resin and fatty acids, phenols, alcohols, aldehydes, ketones, sugars and aliphatic and aromatic hydrocarbons. Numerous volatile sulphur-containing compounds, such as hydrogen sulphide, thiophenes, and methyl mercaptan, are also found in bleached pulp mill effluents. The composition of bleached pulp mill effluents is not constant from mill to mill but depends on, for example, the chemical pulping and bleaching processes and the degree and type of wastewater treatment. For example, tri-and tetra-chloroguaiacols are the major low molecular weight chlorinated phenolics in bleached kraft mill effluents, whereas 2,4,6-trichlorophenol is the predominant chlorinated phenol discharged from bleached sulphite mills.

As the majority of chlorinated organic materials released in bleached pulp mill effluents have not been identified, analytical efforts have focused on developing general indicators or surrogate measures of the total quantity of chlorinated organic compounds in

a particular environmental matrix. For water, the most commonly used approach is known as the Adsorbable Organic Halogen (AOX) analytical method. The halogen component ("X") of bleached pulp mill effluents is almost entirely composed of chlorine. The AOX method is only applicable to water and not to sediments and tissues; therefore, another related method, known as Extractable Organic Chlorine (EOC1), may be used to determine the organochlorine content of sediments and biological tissues. The major limitation of such surrogate tests is the fact that equal AOX values (or equal EOC1 values) give no indication of effluent composition nor of its potential toxicity, persistence, or fate.

Adsorbable Organic Halogen values measured in Canadian bleached pulp mill effluents in early 1989 ranged between 0.5 and 14.9 kg per air-dried tonne of pulp (kg/ADt) with an average of 3.8 kg/ADt. The AOX level in bleached pulp mill effluents is directly related, for example, to the degree of chlorination applied during the bleaching process and to wastewater treatment. The greater the degree of chlorine dioxide substitution for chlorine as the bleaching agent, the lower the AOX value, in general. In addition, effluents from bleached pulp mills which employ secondary wastewater treatment have lower AOX values than those mills with either primary or no effluent treatment facilities.

The 47 Canadian bleached pulp mills together annually discharge over one million tonnes of chlorinated organic compounds to the aquatic environment. Approximately 250 compounds have been identified but many more remain unidentified. The chemical composition of bleached pulp mill effluents is complex, variable, and not well characterized. Thus, substantial quantities of chlorinated organic matter, both of known and unknown composition, enter the Canadian aquatic environment from bleached pulp mill discharges.

5.2 Distribution and Fate Assessment

A number of chlorinated organic compounds generated by pulp mills using chlorine bleaching have been detected and measured in effluents, water, sediments and biota. Water currents, sediment composition, salinity and temperature gradients, and discharge depth of bleached pulp mill effluents affect the distribution of organochlorine throughout the aquatic environment. Tetrachloroguaiacol, for example, has been detected in all aquatic environmental compartments at distances varying up to 1400 km downstream from the nearest bleached pulp mill outfalls.

The persistence of chlorinated organic compounds over time within various aquatic environmental compartments depends on such variables as the water pH, organic carbon content of suspended particulate matter and sediments, presence of a biofilm layer, partition coefficients, water solubility, temperature, light, and microbial population of the receiving environment, but the two most influential variables are the degree of chlorine substitution in the discharged compound and the time of year. Compounds with low chlorine substitution (e.g., dichlorophenols) biodegrade within hours to days whereas highly chlorinated organic compounds may persist within the aquatic environment anywhere from days to weeks or longer, especially in winter. Substances such as chloroguaiacols, therefore, have been discovered in water hundreds of kilometres downstream of bleached pulp mill effluent outfalls during winter conditions. Findings of long-range transportation of chlorinated phenols under ice are not unexpected; however, Canadian field studies have predominantly been conducted in the summer months rather than on a year round basis. Also, under conditions of low flow, particulate matter may settle out relatively close to the outfall; however, under conditions of high flow, for example, a spring freshet or a coastal storm, resuspension

occurs which may distribute the contaminated sediments over greater distances.

Nonchlorinated resin acids, such as dehydroabietic acid, have also been found to persist both spatially and temporally within the various environmental compartments (water, sediments and biota), especially where the mills concerned did not practice adequate secondary wastewater treatment.

Some chlorinated organic compounds can be microbially degraded in water or sediments and metabolized in tissues. Generally, the rate of decomposition depends on such factors as: the degree of chlorine substitution of the organic molecule; the organic carbon content of the substrate; ambient oxygen concentration; temperature; and the previous exposure of bacteria to individual or structurally-related chlorinated organic compounds generated by bleached pulp mills. Dichlorodehydroabietic acid and tetrachloroguaiacol are the most resistant to bacterial degradation of the well-characterized compounds discharged in bleached pulp mill effluents and, as such, are commonly detected in biologically-treated wastewaters and in the aquatic receiving environment.

The degree of wastewater treatment that these effluents receive can greatly influence both the levels and the types of compounds detected in the receiving waters. Bleached pulp mill effluents from well-managed, biologically-treated, aerated lagoons would be expected to contain less chlorophenols and their associated by-products than those mills with minimal or no wastewater treatment facilities. This is a general observation within the Canadian bleached pulp and paper sector.

Chlorinated organic compounds may also be microbially transformed into more persistent and bioaccumulative compounds. Biological transformation of chloroguaiacols and chlorocatechols, for example, occurs under aerobic conditions producing chloroveratroles and chloroanisoles, respectively. Under anoxic conditions, the reverse reaction takes place. The biotransformation products of chloroguaiacols, therefore, would not be expected and have not in fact been detected in the anaerobic sediments in the immediate vicinity of bleached pulp mill effluent outfalls. Chloroveratroles have, however, been detected in aerobic bleached pulp mill effluents, receiving waters and sediments in Canada and in fish tissues from the Baltic Sea.

Most chlorinated organic compounds generated by bleached pulp mills are not appreciably bioaccumulated within the tissues of aquatic organisms, however, trichlorophenols, tetrachlorophenols and chloroveratroles are often accumulated far above those concentrations found in water. Chloroveratroles are capable of accumulating in fish up to 25 000 times the concentration in water. The bioaccumulation of chloroveratroles is of particular interest as they are products of biotransformation and are not monitored within the various environmental compartments.

Chlorinated organic compounds from bleached pulp mills have been detected in water, sediments, and biota up to 1400 km from bleached pulp mill outfalls. Compounds with low chlorine substitution degrade within hours to days whereas highly chlorinated compounds may persist from days to weeks or longer. Persistence is longer in winter especially under ice. Some chlorinated organic compounds can be biologically degraded or transformed, and transformation may lead to more persistent and bioaccumulative compounds. Chloroveratroles, for example, transformation products of chloroguaiacols, are capable of accumulating in fish up to 25 000 times the concentration in water. Other compounds detected in fish tissues reflect repeated or long-term exposure rather than high bioaccumulative potentials.

5.3 Exposure and Effects Assessment

Seventy-five percent of Canadian bleached pulp mills discharge effluents that have been shown to be acutely lethal to rainbow trout in mandatory laboratory tests. Canadian effluent concentrations as low as 3.2% have been reported to cause mortalities in fish, and the average concentration required to kill 50% of the test organisms within 96 hours (96-h LC_{50}) is 16% effluent. A strong correlation exists between the results of the acute toxicity tests and the degree of wastewater treatment employed. Effluents from bleached pulp mills which employ well-managed secondary treatment are often nontoxic to rainbow trout, whereas those from mills with only primary or no wastewater treatment are toxic. Accidental spills and in-plant malfunctions can also contribute to acute toxicity. The acute lethality of whole bleached pulp mill effluent to aquatic organisms is also enhanced during periods of depressed, dissolved oxygen levels.

There is an appreciable amount of lethal toxicity information on some of the individual chlorinated organic compounds generated by bleached pulp mills, with 96-h LC_{50}s ranging from 200 to 2 800 ppb. Chlorinated phenolics, particularly guaiacols and catechols, and chlorinated resin acids have been identified as major toxicants in bleached pulp mill effluents. Although few bleached pulp mill effluents have been monitored for individual chlorinated organic compounds, the limited information suggests that the concentration of any single compound in the effluent does not usually approach its 96-h LC_{50} even if the effluent taken as a whole is acutely toxic. Concentrations of tetrachloroguaiacol, trichlorophenol, and chlorodehydroabietic acid, however, on occasion approach or surpass the 96-h LC_{50} concentrations. It is important to note that differences are small between acutely toxic and nontoxic concentrations of chlorinated compounds to specific organisms. For instance, in solutions of tetrachloroguaiacol, 100% fish mortality occurred by 96 hours at a concentration of 350 ppb, but there were no deaths after this interval of time at a concentration of 300 ppb.

In addition to the acute lethality of effluents from bleached pulp mills, whole bleached pulp mill effluents have been observed to cause such chronic toxic effects as reproductive anomalies, deformities, biochemical changes and behavioral alterations in aquatic organisms. In general, chronic effects were observed in the Canadian aquatic environment at 0.5 to 5% bleached pulp mill effluent (e.g., at concentrations of only one-tenth of the 96-h LC_{50}). Artificial stream studies conducted by the U.S. National Council for Air and Stream Improvement (NCASI) are compatible with Canadian findings in that they demonstrate chronic toxicity at the same dilution level of the effluents. Laboratory studies of individual chlorinated organic compounds induced such chronic effects as vertebral deformities, and embryo and larval mortality in fish at levels as low as 2.8 ppb.

The effluents from bleached pulp mills are diluted by local receiving waters to a degree which depends upon watercourse flow, tides, time of year, and other factors. Prom the limited data available, predominantly from freshwater mills, the receiving waters even after dilution in the mixing zone usually have concentrations of bleached pulp mill effluents well into the range necessary to exhibit chronic effects. In fact, seventy percent of the Canadian bleached pulp mill effluents discharged to freshwater systems are not diluted below the concentrations which have been associated with chronic effects.

The acute or chronic toxicity of whole bleached pulp mill effluent cannot be explained by the toxicity of individual chlorinated organic compounds which have so far been characterized. The toxicity of those individual chlorinated organic compounds generated by bleached pulp mills which have been studied in the laboratory does not summate to more than a few percent of the observed toxicity of the effluents. The

few detailed biological studies conducted downstream of representative Canadian bleached pulp mills all demonstrated continued and repetitive chronic effects on the aquatic biota. The observed chronic effects, such as reproductive anomalies, are significant irreversible factors which jeopardize the continuance of the species and the integrity of the ecosystem.

Seventy-five percent of Canadian bleached pulp mills discharge effluents that are acutely lethal, and even after dilution by the receiving waters seventy percent of the freshwater bleached pulp mill effluents are still within the range of chronic toxicity. The chronic effects observed downstream of Canadian bleached pulp mills include significant irreversible factors which jeopardize the continuance of the species and the integrity of the ecosystem.

5.4 Risk Assessment

Canadian bleached pulp mills discharge over one million tonnes of chlorinated organic materials to the aquatic environment annually. Some constituents of this material are of high spatial and temporal persistence; some demonstrate a large potential for bioaccumulation. Some individual chlorinated organic compounds have been isolated from bleached pulp mill effluents at levels which often approach or surpass concentrations that cause acute toxicity. The summated toxicity of all these chlorinated organic compounds represents a high level of risk.

Seventy-five percent of the effluents from Canadian bleached pulp mills are acutely toxic to rainbow trout. Even after dilution by the receiving waters, seventy percent of the effluents from freshwater bleached pulp mill produce significant chronic effects which jeopardize the continuance of the species and the integrity of the ecosystem. Thus, the levels of whole effluent discharged from Canadian bleached pulp mills to the aquatic environment and the acute and chronic toxic effects observed both in the field and in the laboratory combine to represent a significant risk to the aquatic ecosystem.

5.5 Conclusion

The conclusion based on this risk assessment, is that the substance "effluents from pulp mills using bleach" is entering the environment in a quantity or concentration or under conditions having immediate and long-term harmful effects on the environment. Effluents from pulp mills employing bleaching are therefore considered to be "toxic" as defined under Paragraph 11(a) of the *Canadian Environmental Protection Act*.

5.6 Future Considerations

Numerous and extensive information gaps were observed during the evaluation of data on bleached pulp mill effluents. Information gaps that have been identified and should be filled include acute toxicities and chronic effects of individual chlorinated organic compounds, especially chlorinated phenolics, which constitute a significant portion of the toxic loading of bleached pulp mill effluents.

The evaluation of bleached pulp mill effluent studies revealed many errors in experimental design. Future field studies should endeavor to select enough suitable control sites so that, for example, appropriate statistical analyses can be applied.

Due to the complexity of bleached pulp mill effluents, analytical methods should be focused on developing general indicators or surrogate measures of the total quantity of chlorinated organic compounds in particular matrices. These surrogate measures include AOX for water and EOC1 for sediments and biological tissues. It should be emphasized, however, that the AOX and EOCI parameters have many severe limitations. Of primary importance is their inability to provide an accurate estimate of the potential toxicity, persistence or bioaccumulation of specific chlorinated organic compounds. Efforts must

be made to determine and report all limits of detection and of quantitation for all analytical methods employed

The amount of chlorinated organic compounds formed during the pulping and bleaching processes must be reduced. Such in-plant process changes as oxygen delignification, improvements in pulp washing and substituting other bleaching agents for chlorine gas will reduce the amount of chlorinated organic compounds produced by a bleached pulp mill. In addition, the amount of chlorinated organic compounds released will be reduced through the installation of secondary wastewater treatment facilities where these do not already exist. It should be noted, however, that wastewater treatment leads to the generation of sludges which contain large amounts of chlorinated organic compounds for which as yet no monitoring or disposal strategy has been developed.

Many of the reported acute and chronic toxic effects have been associated with chlorinated phenolic compounds. Accordingly, future considerations should include the monitoring of a range of these compounds in bleached pulp mill effluents, water, sediments and animal tissues, together with their environmental effects. A strategy should also be devised to compel the bleached pulp industry to undertake biomonitoring of the local aquatic ecosystem. The data generated from this enforceable monitoring program would allow the organochlorine concentrations and aquatic effects at Canadian bleached pulp mills to be compared and contrasted. Only then will it be possible to determine if the proposed *Fisheries Act* national effluent regulation and the CEPA dioxin and furan effluent regulations are adequately protecting the aquatic environment or if a need for further regulations exists.

The members of the Task Group on "Effluents from Pulp Mills using Bleaching" believe that mandatory reporting by mills of their output of organically bound chlorine and of a range of chlorophenolic compounds in effluents, water, sediments or biological tissues should be established. Environmental effects monitoring should also be required. Given the difficulty of dealing with these contaminants, and their transformation products, future regulations if necessary should place maximum emphasis on preventing the formation of chlorinated organic compounds through the use of alternative technologies and better process control. Properly designed and managed secondary effluent treatment will also reduce the organic chlorine loading to the aquatic environment.

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