AQUATIC TOXICITY OF PULP AND PAPER MILL EFFLUENT: A REVIEW

D. McLeay and Associates Ltd.

for

Environment Canada
Fisheries and Oceans Canada
Canadian Pulp and Paper Association
Ontario Ministry of the Environment

Report EPS 4/PF/1
April 1987

REVIEW NOTICE

This report has been reviewed by Environment Canada and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of Environment Canada. Mention of trade names or commercial products does not constitute recommendation or endorsement for use.

READERS COMMENTS

Readers who wish to comment on the content of this report should address their comments to:

John L. Betts
Industrial Programs Branch
Conservation and Protection
Environment Canada
Ottawa, Ontario
K1A 0E7

Pour obtenir un exemplaire français, prière de s'adresser à:

Publications de protection de l'environnement
Conservation et protection
Environnement Canada
Ottawa, Ontario
K1A 0E7

Cat. No. En 49-6/4-1E
ISBN 0-662-15335-9
BEAUREGARD PRESS LIMITED

PREFACE

This report was prepared for Environment Canada, Fisheries and Oceans Canada, the Canadian Pulp and Paper Association, and the Ontario Ministry of the Environment, as part of their shared effort to gain an understanding of current knowledge, concerns and monitoring techniques associated with the aquatic toxicity of pulp and paper mill effluents. The report constitutes an objective review and evaluation of publicly available documents and published reports that deal with this subject. The intent of the review was to undertake a critical assessment of the literature specific to the following topics:

- toxic constituents in mill effluents, receiving waters and sediments;
- laboratory monitoring for toxicity;
- toxic effects of mill effluents within receiving waters;
- bioaccumulation and elimination of organic constituents in mill effluents; and,
- bioassay tests for predicting the impact of whole mill effluents in the aquatic environment.

Each topic is considered separately in discrete chapters of the report, although concepts and information relevant to more than one chapter are included where and as appropriate.

The following computerized data bases were searched for relevant information, using discrete sets of key words:

Chapter 1: ASFA, AQUALINE, BIOSIS, CEN, PAPERCHEM
Chapter 2: AQUALINE, CEN, DIALOG, ENVIROLINE, PAPERCHEM
Chapter 3: AQUALINE, BIOSIS, CEN, DIALOG, ENVIROLINE, PAPERCHEM
Chapter 4: CEN, DIALOG, ENVIROLINE, FSTA, LIFE SCIENCES, PAPERCHEM

The series of technical reports prepared by the Cooperative Pollution Abatement Research (CPAR) program and the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) were searched manually, as were articles published during the period 1979 - 1984 in the following journals: **Aquatic Toxicology; Bulletin of Environmental Contamination and Toxicology; Environmental Pollution; Environmental Science and Technology; Journal of Fisheries Aquatic Science; Journal of the Water Pollution Control Federation; Marine Pollution Bulletin; Pulp and Paper Canada; TAPPI; Transactions of the American Fisheries Society;** and **Water Research.** Listings for the

U.S. Environmental Protection Agency's **Publications Bibliography Quarterly Abstract Bulletin** (1979 to 1984) and for the B.C. Research and Environment Canada (West Vancouver) libraries were also examined. Publicly-available reports, reprints and preprints were kindly provided following personal contacts with the regional U.S. Environmental Protection Agency (Seattle), the U.S. National Oceanographic and Atmospheric Administration (Seattle), U.S. Army Corps of Engineers (Seattle), Environment Canada, Fisheries and Oceans Canada, the B.C. Ministry of Environment, the Alberta Ministry of Environment, the Council of Forest Industries (COFI) of British Columbia, MacMillan Bloedel Limited and Weyerhaeuser Canada Limited; and in response to written requests mailed to informed persons and organizations within Canada (34), the U.S.A. (59), Sweden (18), Finland (16) and other countries (19).

Chapter 1 was written by Dr. B. McKague (B.C. Research, Vancouver) and Chapters 2 to 5 by Dr. D. McLeay. Initial drafts of all sections were evaluated critically by Dr. C.C. Walden (Forintek Canada Ltd., Vancouver). His substantial comments were incorporated, as appropriate. Other comments and suggestions for revision, as provided by the project sponsors, were considered and incorporated in our final revisions. The interpretations and conclusions presented in this report are solely those of the authors, and may or may not represent the viewpoints of the sponsoring agencies.

PRÉFACE

Le présent rapport a été préparé à l'intention d'Environnement Canada, de Pêches et Océans Canada, de l'Association canadienne des producteurs de pâtes et papiers et du ministère de l'Environnement de l'Ontario dans le cadre d'un effort conjoint visant à faire le point des connaissances, des problèmes et des techniques de surveillance reliés à la toxicité des effluents de l'industrie des pâtes et papiers pour la biocénose aquatique. Ce document est à la fois une étude et une évaluation objectives des ouvrages et des rapports publiés dans ce domaine et accessibles au public. Il s'agit d'une enquête bibliographique qui juge d'un oeil critique la documentation, eu égard aux sujets suivants:

- composition toxique des effluents, des eaux réceptrices et des sédiments;
- détermination en laboratoire de la toxicité de l'effluent de pâtes et papiers;
- toxicité de l'effluent de pâtes et papiers dans les eaux réceptrices;
- bioaccumulation et élimination des composants organiques de l'effluent de pâtes et papiers;
- prévision de la toxicité de l'effluent de pâtes et papiers pour la biocénose aquatique au moyen d'essais biologiques.

Chaque sujet a été traité séparément dans un chapitre du rapport, même si les notions de base et les données ont été reprises aux endroits appropriés lorsqu'ils s'appliquaient à plus d'un chapitre.

On a consulté les bases de données suivantes au moyen d'un certain nombre de mots-clés pour en retirer l'information pertinente :

Chapitre 1: ASFA, AQUALINE, BIOSIS, CEN, PAPERCHEM

Chapitre 2: AQUALINE, CEN, DIALOG, ENVIROLINE, PAPERCHEM

Chapitre 3: AQUALINE, BIOSIS, CEN, DIALOG, ENVIROLINE, PAPERCHEM

Chapitre 4: CEN, DIALOG, ENVIROLINE, FSTA, LIFE SCIENCES, PAPERCHEM

On a directement consulté les rapports techniques préparés par le CRRP et le NCASI ainsi que les articles publiés entre 1979 et 1984 inclusivement, dans les périodiques suivants: *Aquatic Toxicol.; Bull. Environ. Contam. Toxicol.; Environ. Poll.; Environ. Sci. Technol.; J. Fish. Aquat. Sci.; J. Water Poll. Control Fed.; Mar. Poll. Bull.; Pulp Paper Can.; TAPPI; Trans. Amer. Fish Soc.*; les *Water Res. Listings* préparées pour le U.S. EPA *Publ. Bibl. Quart. Abst. Bull.* (1979-1984) et les bibliothèques de B.C. Research et d'Environnement Canada (West Vancouver). On s'est procuré les rapports, les réimpressions et les préimpressions accessibles au public après contact personnel avec les employés régionaux de l'EPA (Seattle), de la NOAA (Seattle), du U.S. Army Corp. Eng.

(Seattle), d'Environnement Canada, de Pêches et Océans Canada, du ministère de l'Environnement de la Colombie-Britannique, du ministère de l'Environnement de l'Alberta, du COFI, de MacMillan Bloedel Limited et de Weyerhaeuser Canada Limited; certains documents ont été obtenus après demande écrite aux personnes et aux organisations pertinentes du Canada (34), des États-Unis (59), de la Suède (18), de la Finlande (6) et d'autres pays (19).

Le chapitre 1 a été rédigé par M. B. McKague (B.C. Research, Vancouver) et les chapitres 2 à 5 par M. D. McLeay. Chaque section a été examinée par M. C.C. Walden (Forintek Canada Ltd., Vancouver) dans sa version initiale, à laquelle on a intégré les commentaires de ce dernier. On a également examiné et incorporé les remarques et les suggestions formulées par les parrains du projet au moment de la rédaction définitive. Les interprétations et les conclusions que le lecteur trouvera dans ce rapport sont celles des auteurs et peuvent ou non représenter le point de vue des organismes parrains.

ACKNOWLEDGEMENTS

The sponsoring agencies (Environment Canada, Fisheries and Oceans Canada, Canadian Pulp and Paper Association, and Ontario Ministry of the Environment) which provided the financial support for this review are gratefully acknowledged. The advice and encouragement provided by the members of the Toxicity Subcommittee which coordinated this assignment (J. Betts, M. Gilbertson, D. Paavila and C. Innis) were particularly helpful. Dr. Gilbertson also served as the scientific authority for the project. Scientists who and agencies which responded eagerly to my request for technical information are too numerous to mention; however, without their knowledge and input this document would be lacking and they are thanked accordingly. All persons who reviewed the draft chapters and provided useful suggestions and criticisms are also thanked. The assistance of Ms. V. Essen (B.C. Research, Vancouver), Mr. A. Fabro (Environment Canada, West Vancouver) and their supporting staff in data acquisition is appreciated. Finally, the determined effort and skills of Ms. L. Borleske and Ms. L. McCormack in the typing and production of this report are acknowledged with gratitude.

TABLE OF CONTENTS

LIST OF TABLES

EXECUTIVE SUMMARY

Toxic Constituents in Mill Effluents, Receiving Waters and Sediments

Substantial information is available on the nature of the organic compounds present in pulp and paper mill effluents that are potentially toxic to fish. Most of the acute toxicity is attributed to resin and fatty acids, chlorinated phenols and, to a lesser extent, a broad group of neutral compounds. Concentrations of resin acids, fatty acids and chlorinated phenols in untreated and biotreated whole mill effluents are well documented, with the exception of mechanical pulping effluents.

Levels of resin acids in untreated pulp mill effluents often exceeded lethal limits. Reported total concentrations in whole mill effluents ranged from 100-25 000 µg/L in untreated kraft effluents, and from non-detectable levels to 16 000 µg/L in untreated sulphite effluents. Untreated mechanical pulping effluents from groundwood mills have been reported to contain from 1 300-80 000 µg/L resin acids, but information on levels in thermomechanical (TMP) and chemi-thermomechanical (CTMP) pulping effluent was not found in the published literature. Resin acid concentrations in untreated paper mill effluents ranged from 420 to 8 500 µg/L.

Biotreatment normally reduced resin acid concentrations to sublethal levels in effluents from all mill processes. Concentrations of unchlorinated resin acids usually decreased by 90% or more due to treatment, whereas chlorinated resin acids were more resistant to biological removal.

Fatty acids have been reported in untreated whole mill effluents in total concentrations ranging from 20 µg/L (sublethal) to 22 000 µg/L (above acutely lethal levels). Biotreated effluents contained only sublethal levels of fatty acids, indicative of their facile biodegradation.

Chlorophenolic compounds, namely chloroguaiacols, chlorocatechols and chlorophenols, arising from the bleaching of pulp, were normally present at sublethal levels in untreated whole mill effluents from bleached kraft and sulphite mills. Maximum total concentrations were normally in the range of 1 000-2 000 µg/L irrespective of bleaching variables. Biotreated effluents may contain up to 1 000 µg/L chlorophenols.

Recent environmental studies have provided some information on concentrations of potentially toxic mill effluent constituents in receiving waters and sediments. Dehydroabietic acid was the major resin acid reported in freshwater receiving sites. Concentrations ranged up to 1 930 µg/L in the immediate vicinity of one (Canadian) mill

discharging untreated effluent, and decreased to background levels at a distance of 3 km. Up to 600 µg/L dehydroabietic acid was present in receiving water 0.1 km from another (Finnish) mill discharging biotreated effluent but levels decreased to background within a few kilometres. Maximum detectable levels of other resin acids and fatty acids from the same mill were usually less than 100 µg/L at a distance of 0.1 km from the mill.

The total concentration of chlorophenols measured in freshwater sampled 3 km downstream from the nearest of three mills discharging biotreated bleached kraft effluent to the Fraser River (B.C.) was approximately 3 µg/L. Sub-microgram levels of specific chlorophenolic compounds were detectable 50 km downstream from these mills.

No reports were found documenting levels of resin and fatty acids in estuarine/marine receiving waters near mills. Sub-microgram levels of specific chlorophenols were present in estuarine/marine receiving waters near B.C. coastal bleached kraft mills discharging untreated effluent whereas up to 2 µg/L individual chlorophenolic compounds were present in the vicinity of similar mills in Sweden.

Dehydroabietic acid was the major resin acid reported in either freshwater or estuarine/marine sediment near mills. Levels ranged from 100-150 µg/g for surficial sediments within 1 km of mills discharging untreated effluents, to low µg/g levels at more distant sites. Levels of specific chlorophenols reported present in freshwater and estuarine/marine sediment near B.C. bleached kraft mills were $\leq$0.01 µg/g whereas surficial sediments collected within the vicinity of a number of bleached kraft mills in Finland and Sweden often contained higher (0.02-6 µg/g) levels. Tetrachlorocatechol was often the major chlorophenol reported in sediment, and was suggested as being a metabolite of other chlorinated compounds such as pentachlorophenol.

Laboratory Monitoring for Toxicity of Mill Effluents

Available 96-h LC_{50} data for juvenile rainbow trout exposed to untreated or primary-treated (clarified) pulp mill effluents of various types indicate that these effluents are normally acutely lethal, although dilutions of 100:1 to 20:1 or less will eliminate this effect. Primary treatment does not appreciably increase LC_{50} values, i.e., little reduction in acute lethal toxicity is evident due to fibre removal. No real difference exists for the acute lethal toxicity of unbleached, semi- or fully bleached kraft or sulphite whole mill effluents. Similarly, the toxicity of sulphite mill effluents is not appreciably dependent on the pulping bases (Na, Ca, Mg, NH_3) employed. Mechanical pulping effluents (stone or refiner) are somewhat more toxic than chemical pulping whole mill effluents, with 96-h LC_{50} values frequently within the range of 1-10%. Untreated or

primary-treated newsprint or fine paper mill effluents have a generally low acute lethal toxicity (LC_{50} values 25->100%). Only scanty information is available concerning the relative toxicity of TMP or chemi-thermomechanical pulping (CTMP) effluents, but no marked differences from other mechanical effluents are apparent.

Secondary (aerobic microbiological) treatment is effective in reducing the acute lethal toxicity (to fish) caused by conventional types of bleached or unbleached pulp and paper whole mill effluents. However, the treatment system must be properly designed and maintained, and protected from serious in-plant spills. When this is done, most conventional secondary-treated whole mill effluent samples are non-lethal, according to their LC_{50} values.

Conversion of LC_{50} values to toxic units and toxicity emission rates (TER) permits direct, linearly proportional comparison of toxic concentrations and quantities, without knowledge of the toxic constituents involved. On occasion, such calculations have been used to provide estimates of the relative quantities of toxic material discharged daily to the environment by one or more mills. Attempts to use the toxic unit concept to develop a chemical approach for predicting the acute lethal toxicity of pulp mill effluents, and to assess the relative toxic contributions of in-plant process streams, have proven largely unsuccessful.

In addition to fish bioassays, a number of short-term (48 h or less) bioassays with aquatic invertebrates or other non-fish organisms are now used in many countries for measuring the acute toxicity of effluents or chemicals. Non-fish toxicity tests most commonly employed are daphnia (freshwater) bioassays, algal bioassays and bacterial (e.g., Microtox) assays.

Laboratory bioassay tests with daphnia are being used in Canada and elsewhere for evaluating the acute toxicity of pulp and paper mill effluents, process streams and effluent constituents. Besides their inherent value for assessing the toxicity of a particular discharge towards a sensitive freshwater fish-food organism, other advantages of daphnia bioassays include the easy culturing and maintenance of the test species, simplicity of test apparatus, minimal effluent volume requirements, and a relatively short test duration (48 h). The Microtox microbial assay, which requires less than one hour to complete, is of value where the toxicity of an in-plant or final mill effluent requires definition prior to a decision as to containment, additional treatment or discharge. Shortcomings of the Microtox assay include a high capital cost, a periodically inconsistent performance for differing batch-cultures of the test microorganism, and unconfirmed (unpublished) reports of unreliable results for some pulp mill effluents. Where colour

concentrations are high, routine corrections are essential. Although the sensitivity of both Microtox and daphnia bioassays to pulp and paper mill effluents is, in general, similar to that of the 96-h LC_{50} rainbow trout test, tests with specific effluent samples often show dissimilar results. The oyster larval (seawater) assay has been used infrequently in recent years although the test appears to be sensitive to dilute concentrations of effluent and is applicable to the early life stages of a commercially relevant marine organism. Rapid tests for quantifying the toxicity of mill effluents to indigenous and cultured species of freshwater and marine algae are being developed and refined.

A review of the published literature on sublethal responses of aquatic life to acute or chronic exposure to pulp and paper mill effluents under controlled conditions indicates that our present understanding is based primarily on studies with kraft mill effluents and freshwater fish species. Our knowledge of sublethal effects (and median-effect concentrations) caused by newsprint, paper mill, TMP or CTMP effluents is extremely limited or absent altogether. Similarly, pertinent information with respect to sulphite whole mill effluents is also sparse at best, and does not permit any comparison of effects and effect-concentrations attributable to the differing commercial sulphite processes.

Brief (hours, few days) exposure of salmonid and other sensitive fish species to dilute concentrations of untreated or primary-treated whole mill effluents above 0.05 LC_{50} can cause diverse sublethal responses including stress and other metabolic effects, respiratory/circulatory effects, reduced tolerance to natural environmental variables, and behavioural alterations (avoidance or attraction responses). More prolonged (several days, months) exposure to these dilute concentrations of effluent under laboratory conditions does not result in fish mortalities; however, a number of diverse sublethal effects have been reported. Our present knowledge concerning the effects of dilute ($\leq$2%) concentrations of the various types of whole mill effluents on the reproduction, development and disease resistance of freshwater organisms is limited; such information for sensitive estuarine and marine species is cursory at best. The effects of these effluents on populations and communities of organisms have not been studied to any extent.

Studies conducted to date with secondary-treated pulp and paper mill effluents indicate that, in most instances, biotreatment markedly reduces the extent of their sublethal toxic effects. Notwithstanding, some instances of acute and chronic sublethal effects have been reported for secondary-treated whole mill effluents at strengths $\leq$1-5%, even though these effluents were not acutely lethal at full strength.

The lethal and sublethal bioassay tests undertaken with samples of pulp and paper mill effluents under controlled conditions have in most instances provided optimal or near optimal conditions of temperature and dissolved oxygen. Available evidence indicates that the toxicity of pulp and paper mill effluents to fish is enhanced with only moderate declines in the dissolved oxygen content, and that acclimation/test temperatures can modify the toxic responses of fish and fish-food organisms.

Certain diluent-water characteristics, namely pH and, to a lesser extent, alkalinity/hardness, can markedly influence the toxic effects of pulp and paper mill effluents and of the primary chemical constituents known to contribute to effluent toxicity. This is true not only for fish bioassays but also for tests with other organisms. The modifying effects of salinity and seawater chemistry on the toxicity of pulp and paper effluents are not understood.

Inter- and intra-laboratory acute lethal and other bioassay results for samples of pulp and paper mill effluents are subject to the differing conditions and procedures employed. Besides the modifying influences of diluent-water chemistry, controlled or uncontrolled test variables including the innate tolerance and acclimation history for the particular population of organisms used, aeration rates, loading densities, and the degree (if any) to which test solutions are renewed during the bioassay, may substantially affect the findings.

Toxic Effects of Mill Effluents Within Receiving Waters

Numerous studies have examined aquatic biota within waters adjacent to effluent discharges from pulp and paper mills for possible biological effects. Although receiving-water studies of individual fish and fish populations have been undertaken in Canada and abroad, the majority of surveys conducted have dealt with effects on infaunal invertebrate or phytoplankton/periphyton communities. Most of these investigations have not distinguished effects due to toxic effluent constituents from those caused by other effluent characteristics (i.e., temperature, colour, salinity, nutrients, settleable and suspended solids, pH, and oxygen demand).

Many of the reported studies have not performed concurrent water quality monitoring for natural variables (i.e., pH, temperature, salinity, dissolved oxygen) at the biological sampling stations, or have ignored the potential significance of their impact on the biological findings. Other data deficiencies common to the receiving-water studies include absent or incomplete information concerning effluent type and treatment, effluent characteristics, and concentrations of effluent or its (toxic) constituents within

these waters. The concurrent presence (or absence) of contaminants in receiving waters unrelated to the mill discharges was variously reported and considered, not examined/reported, or noted without consideration of their possible biological implications. The majority of these receiving-water studies incorporated a restricted number of sampling stations, often confined to the immediate waters adjacent to the outfalls. Studies that extended beyond this region normally did not attempt to determine effluent concentration nor its pattern of mixing and dispersal in association with the biological sampling sites.

Fish kills associated with pulp and paper mill discharges have been seldom observed. In situ studies conducted during the 1960s and earlier identified certain poorly flushed waterbodies that were acutely toxic to fish due to discharges of untreated mill effluent. These waters were often found to be oxygen-deficient. Findings of fish kills are now almost nonexistent and, when they have occurred, have been due to accidental in-plant spills or failures of effluent treatment systems. However a few Canadian receiving waters do contain zones adjacent to outfalls discharging untreated or primary-treated pulp mill effluent which are still inimical to fish survival (e.g., L'Etang Estuary and Neroutsos Inlet). These situations are caused at least in part to poor flushing rates, high oxygen demand of the effluent and/or deposited fibre. Such localized zones of influence are rare in Canadian receiving waters. No fish kills have been reported in any waterbodies receiving discharges of biotreated mill effluent.

Receiving-water studies with freshwater fish have not reported any definitive effects of untreated or treated pulp mill effluents on fish migration, avoidance, attraction, or other responses. One study reported a decreased liver enzyme function for rainbow trout held in cages at distances of up to 6 km from a mill discharging biotreated bleached kraft whole mill effluents (BKME). There are no other reports of biochemical or physiological changes for indigenous freshwater fish or those exposed experimentally to receiving waters. No receiving-water studies designed to examine the influence of mill effluent on reproduction, development or the disease resistance of freshwater fish have been found in the published literature. Surveys of fish distribution in Canadian or U.S. rivers receiving biotreated pulp and paper mill discharge have not identified any changes in downstream waters. Similar surveys for lakes or rivers receiving untreated or clarified effluents have indicated, variously, either increased fish abundance for waters proximate to the outfall, or a decreased yearly abundance associated with a combination of suspected causes including these discharges. Surveys of freshwater benthic macroinvertebrates have revealed numerous instances where species abundance and diversity have been

modified, often markedly and for considerable distances downstream, by the discharge of untreated or clarified mill effluents. Similar changes have not been reported for mills with effective secondary treatment of effluent prior to discharge. The changes in invertebrate communities that have been noted for waters receiving untreated or clarified discharges were frequently attributed to fibre deposits and oxygen-deficient waters. Surveys of phytoplankton and zooplankton communities in Canadian freshwaters adjacent to pulp mill outfalls have been somewhat limited, although effects, reported due primarily to effluent nutrients and colour, have been noted. Finnish studies indicate that significant toxic effects on indigenous planktonic communities can be anticipated in instances where untreated mill effluents are discharged to waters with limited circulation and flushing.

Fish studies conducted within estuarine or marine receiving waters have largely ignored examinations for histological, biochemical or physiological changes associated with mill discharges. For the limited surveys of fish condition or performance, findings have been equivocal and confounded by possible disease problems. Worthwhile studies of the possible influence of pulp mill discharges on the disease resistance of indigenous fish frequenting these waters have been extremely limited in number. However, isolated observations of increased incidences of liver lesions, gill parasites, and skin mucosal bacteria have been recently reported. Changes in the horizontal or vertical distribution of adult salmon migrating upstream through estuarine waters receiving untreated pulp mill effluent have been reported in two instances, although migration apparently was not impeded significantly. In situ behavioural studies have shown convincing evidence for the avoidance by certain salmonid fish species of untreated BKME and sulphite whole mill effluent (SME) introduced to surficial marine waters at two B.C. coastal sites. The contribution of toxic constituents to this response was unclear, as dissolved oxygen values in these surface waters were also depressed. The effects of mill discharges on populations of fish frequenting marine or estuarine waters adjacent to coastal mill outfalls have received only limited attention. Decreased fish abundance has been shown for waters within two regions where the dispersal of untreated or clarified effluent was poor and acutely lethal conditions prevailed in surface waters. Surveys of Pacific oysters have found decreased condition factors and increased numbers of abnormal or dead larvae exposed to coastal waters receiving untreated or primary-treated effluent. As with freshwater sites, numerous studies have found a decreased abundance and diversity of benthic macroinvertebrate communities in estuarine or marine waters at variable (and in some cases, appreciable) distances from mills discharging untreated or primary-treated pulp and paper mill effluents. Fibre deposits, in some cases associated

with hypoxic bottom conditions, appeared to be responsible in most instances. Light-dependent productivity of marine/estuarine phytoplankton has been shown to be depressed in some receiving waters due to effluent colour, although compensatory mechanisms may negate any real influence. Zooplankton have seldom been examined.

Bioaccumulation and Elimination of Organic Effluent Constituents

Current knowledge concerning the bioaccumulation and retention in aquatic life of pulp mill effluent constituents is sparse. For those constituents examined to date, data have related primarily to freshwater fish.

A number of laboratory studies have demonstrated that dehydroabietic and other resin acids can accumulate to an appreciable extent in certain tissues (blood plasma, liver, kidney, brain) of fish exposed to pure chemicals or to dilute strengths of BKME; although their accumulation in muscle tissue is low. The bioaccumulation of resin acids (pimaric, isopimaric, dehydroabietic and neoabietic) in liver and plasma of resident/caged freshwater or estuarine fish and in estuarine clams collected from waters receiving untreated pulp and paper mill effluents has also been demonstrated. Unchlorinated resin acids have been shown to accumulate rapidly (within two days) in certain tissues of exposed fish, but steady-state tissue concentrations due to prolonged exposures have not been ascertained. Rates for clearance of accumulated resin acids from specific tissues are also unknown, although resin acids accumulated in fish appear to be eliminated rapidly (within a few days) by their conjugation (detoxification) in the liver and excretion in the bile.

The bioaccumulation of chlorinated resin or fatty acids in aquatic organisms exposed to bleached pulp mill effluent in the laboratory or in receiving waters has, to our knowledge, not been studied. The uptake and elimination by aquatic life of fatty acids associated with effluent discharges also has received little attention.

Controlled bioaccumulation studies conducted with the chlorinated phenolic compounds known to be present in treated and untreated bleached whole mill effluents (trichlorophenol, tri-and tetrachloroguaiacol, chlorocatechols) indicate that these chemicals can accumulate in exposed organisms. The degree to which these chemicals can be taken up and stored in tissues of freshwater or estuarine/marine organisms is presently unclear, although the limited data available suggest a greater potential for accumulation of chloroguaiacols than that for chlorocatechols or di/trichlorophenol. Both the accumulation and subsequent excretion of tri- and tetrachloroguaiacol can occur rapidly (within one day).

Laboratory studies with fish exposed for one to eight weeks to dilute (2-2.5%) concentrations of kraft bleach plant or bleached whole mill effluents have demonstrated that appreciable quantities of trichloroguaiacol and, to a lesser extent, trichlorophenol and tetrachloroguaiacol can accumulate in fish livers or whole bodies. Subsequent transfer of exposed fish to uncontaminated water resulted in the clearance of these compounds within three weeks.

A limited number of field investigations have reported elevated levels of trichlorophenol, tri- and tetrachloroguaiacol in fish and shellfish captured within the vicinity of sulphite and/or kraft mills producing bleached pulp. For a number of freshwater, estuarine and marine sites downstream of untreated (freshwater, estuarine/marine) or treated (freshwater) mill discharges, the accumulations of trichlorophenol, trichloroguaiacol and/or tetrachloroguaiacol in fish liver tissue were significant, whereas concentrations of specific chlorophenolic compounds measured in fish muscle tissue or in whole-body tissues of shellfish were below the limit of detection or present only in trace quantities. Of the chlorophenolic compounds examined in field specimens, tissue concentrations of trichloroguaiacol were often highest. Results from one survey of a variety of freshwater species provided a limited indication that chloroguaiacols were biomagnified in higher food-chain organisms; however, confirmatory evidence is still required.

The bioaccumulation in fish of tri- and tetrachloroveratrole, two metabolites formed by the bacterial methylation of tri- and tetrachloroguaiacol, has been recently reported. Bioconcentration factors for each of these metabolites were high (several thousand), although each was cleared rapidly from fish tissues following their transfer to uncontaminated water. Accumulations of each metabolite were identified in liver and muscle-fat extracts from three species of estuarine fish captured in waters receiving discharges from bleached pulp mills.

The bioaccumulation of other organic constituents of pulp and paper mill effluents in aquatic life has not been examined to any extent. Certain chemicals (chlorobenzenes, chlorocymenes, chloroform, chloroethylenes, monoterpenes) have been identified in tissues of freshwater or estuarine/marine fish caught adjacent to waters receiving pulp and paper mill effluents. However, for a number of reasons these findings are suspect: similar tissue concentrations were reported in certain instances for specimens from more remote sites (chlorobenzenes, chlorocymenes, chloroethylenes); effluent/water concentrations of these constituents were not determined (terpenes, chloroform, chlorocymenes); or data were not developed for reference sites (chloroform).

Reports of off-flavours for edible aquatic life frequenting waters receiving pulp and paper mill effluents have been related primarily to freshwater fish. Many of these studies failed to demonstrate that the mill discharge was the cause. Evidence for off-flavours attributable to mill discharges was restricted to waterbodies where effluent mixing and dilution was minimal.

Reported evaluations of flavour impairment for commercially relevant aquatic species exposed experimentally to pulp and paper mill effluents were limited to studies with freshwater fish. Those investigations demonstrated that fish off-flavours can result from brief (one to seven days) exposure to unbleached or bleached kraft whole mill effluent. One study showed that significant off-flavours were caused by only one-hour exposure to dilute (0.5-1% untreated; 3-8% treated) BKME. Biotreatment of effluent reduced but did not eliminate its tainting propensity. Off-flavours in fish exposed to whole mill effluents or foul condensate were lost within a few days following transfer to fresh water. Little information was available concerning fish (or shellfish) tainting, attributable to sulphite whole mill effluents; and no flavour-evaluation data were found for mechanical, thermomechanical or paper mill effluents. Flavour-evaluation tests with mill process effluents indicated that dilute (<1%) concentrations of sulphite waste liquor or kraft condensates could taint fish, whereas kraft bleach plant and paper machine effluents were less involved.

The known or suspected contribution of specific effluent constituents to fish off-flavours was reviewed. Di- and trichlorophenol have reportedly caused tainting at strengths as low as 0.01 µg/L. Resin acids, organosulphur compounds, terpenes and cymenes have been proposed as potential off-flavour sources, although proof is lacking. No information was found concerning the contribution (if any) of chloroguaiacols or chlorocatechols to off-flavours in fish or shellfish.

Bioassays for Predicting the Toxicity of Mill Effluents Within the Aquatic Environment

The capability of a single-species (e.g., rainbow trout) acute lethal bioassay to predict the toxic environmental consequences of a whole mill effluent is limited. The LC_{50} bioassay is of limited sensitivity for evaluating the level of toxicity in an effluent under standardized conditions. This bioassay cannot predict any toxic (sublethal) effects which may be caused by the discharge of typical (non-lethal) biotreated pulp and paper mill effluents, nor can this test predict the long-term consequences for indigenous aquatic species exposed briefly or for extended periods to sublethal concentrations of mill effluent within receiving waters. Nonetheless, instances have been documented where

acute lethal bioassays have accurately predicted environmental improvement associated with decreased effluent toxicity (e.g., following the installation of biotreatment facilities); or toxic (lethal) environmental effects associated with mill effluents that are atypically high in toxicity and/or discharged to receiving waters where mixing and dilution are minimal.

Application factors have been derived for laboratory LC_{50} values in order to predict effluent concentrations within receiving waters which would not cause any toxic (sublethal) effects of consequence. This approach has merit when based upon extensive relevant sublethal data derived for the effluent type, receiving-water type, and fisheries resource in question (e.g., kraft mill effluent, freshwater and salmonid fish), together with a knowledge of effluent strengths within receiving waters. Such data could be derived on a site-specific basis, using the species of concern for extensive sublethal evaluations in conjunction with LC_{50} bioassays, and deriving an application factor accordingly. Such an approach is, however, unwieldy and depends on the correlation between acute lethal data and sublethal effects.

Acute lethal bioassays conducted in situ or with receiving-water samples can assess whether proximate waters receiving untreated mill discharges may cause short-term mortalities of sensitive indigenous aquatic life (e.g., oyster larvae or early life stages of other invertebrates or fish species). However, many such studies conducted to date have yielded erroneous results due to poor experimental designs or sampling strategies.

A number of sensitive, acute sublethal bioassay tests with fish or aquatic invertebrates (e.g., oyster larval assays for developmental anomalies; stress bioassays; tests for metabolic dysfunctions; avoidance/preference behavioural bioassays) have been developed and applied to pulp and paper mill effluents and receiving waters or samples thereof. These tests are promising tools for assessing treatment efficiency and residual (sublethal) toxicity of treated whole mill effluents, as well as the toxic zone of influence within receiving waters of untreated, partially or fully treated discharges. The utility of on-line, fully automated early warning systems which continuously monitor physiological responses of fish to untreated (diluted) or treated pulp mill effluents is presently being evaluated and shows promise due to their sensitivity, continuous nature and built-in alarm. The automated Microtox test can also provide an early warning of atypically toxic effluents, although this test is relatively insensitive and cannot detect any residual (sublethal) toxicity.

The use of chronic sublethal bioassay tests for assessing pulp mill effluents and receiving waters is necessary where concerns exist with respect to the long-term well-being of effluent-exposed organisms. Such concerns include possible influences on development, growth, reproduction, disease resistance/induction, and long-term survival. Complete and partial life-cycle studies with fish and aquatic invertebrates (e.g., daphnid species) have been and are continuing to be developed for this purpose. Sensitive organisms with rapid rates of growth and reproduction are available which permit these bioassays to be completed within one or two weeks, thus enabling their more routine application at reasonable cost. Other promising but seldom-used approaches for anticipating the toxic environmental consequences of mill effluents and their potential zone of effect include histological/physiological examinations of transplanted shellfish held in receiving waters at various distances from the mill outfall; benthos studies of larval settlement, survival and growth on artificial substrates positioned at appropriate sites; and multiple-species microcosm tests with dilute effluents and receiving-water samples for population and community effects. These latter approaches are research-oriented and need further development and refinement before their routine application is realized.

Toxicity bioassays with samples of mill effluent or receiving water cannot accurately predict the combined impact (due to other effluent characteristics besides toxicity) of mill discharges on fish habitat. Other techniques, including bioassays and chemical analyses of bottom sediments, substrate settlement studies and receiving-water/sediment surveys, have been employed successfully to evaluate the toxicity of effluent-contaminated sediment and the extent to which fish habitat may be affected.

Bioassays which determine the degree to which specific effluent constituents may accumulate in fish or shellfish tissues can forecast the likelihood of their uptake by indigenous organisms. Similarly, such studies can assess the biotransformation of effluent constituents, their partitioning into specific tissues, and their rate of elimination upon transfer of the organisms to effluent-free water. Available evidence from these uptake studies and from field surveys indicates little or no accumulation in edible tissues (e.g., fish muscle or shellfish soft tissues) for any of the effluent constituents examined to date.

The presence of significant off-flavours in edible fisheries products due to the presence of dilute pulp mill effluent in receiving waters can be predicted or verified by a combination of laboratory or in situ bioassays and taste panel evaluations. This proven but unwieldy approach enables a distinction as to the causative agent(s) (natural or otherwise) which may taint indigenous fish or shellfish species, and provides a means for

identifying specific effluent constituents and processes which are likely to contribute to off-flavours.

Current methods and strategies adopted by industrialized countries to monitor the toxicity of effluents and receiving waters were reviewed. An integrated approach, using a battery of appropriate bioassay tests together with effluent dispersal and water quality studies, while surveying individuals and populations of commercially relevant species for effect, is the most promising. Such studies are currently underway in Sweden, Finland and the U.S.A., and their findings should be timely and enlightening. As with these other countries, Canadian scientists and environmental regulatory personnel recognize the need for ecotoxicological bioassays to forecast and monitor the toxic environmental consequences of effluent discharges. A number of test procedures have been established within Canada and elsewhere for this purpose; others are being developed or require research and confirmation before routine application.

Conclusions

1. *Toxic Constituents in Mill Effluents, Receiving Waters and Sediments*

1.1 The nature of materials responsible for the acute lethal toxicity of conventional pulp and paper mill effluents to fish is well documented. Resin and fatty acids, derived from the wood furnish, and chlorophenolic compounds, derived from pulp bleaching, are the major materials responsible.

1.2 Levels of resin acids in untreated whole mill effluents often exceed concentrations reported to be acutely lethal to fish. Fatty acids are rarely present at lethal levels in untreated effluents. Biotreatment of conventional (kraft, sulphite, paper mill) effluents normally reduces levels of resin and fatty acids to sublethal levels.

1.3 Chlorophenols are normally present at sublethal levels in untreated whole mill effluents but remain significant components of biotreated effluents because of their resistance to biodegradation. Manipulation of bleaching cycles or partial substitution of chlorine by chlorine dioxide does not significantly reduce levels of chlorophenols in final mill effluents.

1.4 Non-acidic compounds, such as chloroform and the chloromethyl sulphones, are not present at acutely lethal levels in untreated or biotreated whole mill effluents.

1.5 Published data on concentrations of potentially toxic compounds in final discharged effluents from mills employing mechanical, TMP, CTMP and other

ultra high-yield pulping processes are notably lacking and their analysis needs to be addressed.

1.6 In terms of their potential environmental impact, the levels of all toxic chemicals in final discharged mill effluents need to be kept in perspective with respect to discharge volumes, a consideration beyond the scope of this review.

1.7 Of the naturally occurring resin acids present in high concentrations, dehydroabietic acid is the most persistent and is probably detectable in water and sediment near most mills, particularly where effluents are not biotreated. Traces of other resin acids are also likely detectable in the receiving environment, although in appreciably lesser amounts.

1.8 A variety of chlorophenols are present in receiving waters and sediments near mills discharging both untreated and biotreated effluents. Although only trace levels are normally detectable, the discharge of sublethal levels of the more environmentally persistent chlorophenols is potentially of more concern than the discharge of lethal levels of rapidly degradable resin and fatty acids, because more stable materials might accumulate or otherwise exert sublethal toxic effects while being widely dispersed.

1.9 Information is needed on the environmental fate of high molecular weight effluent constituents such as chlorolignin, as these may degrade to lower molecular weight, potentially toxic chlorophenol derivatives.

1.10 More knowledge is required concerning the environmental dispersal patterns for persistent mill-derived chlorophenolic compounds.

2. *Laboratory Monitoring for Toxicity of Mill Effluents*

2.1 The LC_{50} bioassay using rainbow trout and other sensitive aquatic organisms is a useful laboratory test for monitoring one aspect of the toxicity of pulp and paper mill effluents, i.e., to determine if the effluent sample is acutely lethal to these organisms and at what threshold (median effective) concentration.

2.2 The results derived from this bioassay are quantitative only insofar as they are viewed with respect to the test conditions and procedures employed. Although certain test variables have been standardized in recent years, others have not and the bioassay results are subject to their influence.

2.3 The toxic unit concept permits calculation of toxicity emission rates. These values, derived from LC_{50} and effluent flow data, are useful for providing estimates of the quantity of (acutely) toxic material discharged daily to the

environment at one or more mill sites. As with the LC_{50}, the numbers derived are not absolute and are relative to the specifics of the bioassay test.

2.4 Inasmuch as the toxic contributions of chemical constituents and individual mill process effluents are not consistently additive in effect, chemical assays are an unsuitable substitute for bioassays. The application of toxic units in these contexts is limited accordingly.

2.5 Rapid bioassay tests using daphnia or Microtox, although no more sensitive than LC_{50} tests with rainbow trout, offer a number of specific advantages and are amenable to assessments by researchers or mill personnel of modifications in effluent toxicity due to process changes, in-plant spills and altered treatment systems. These and other rapid toxicity tests (e.g., algal toxicity tests) using aquatic invertebrates or microorganisms should, however, be used to complement rather than replace fish bioassays.

2.6 The 48-h oyster larval bioassay should be re-examined to evaluate its relative sensitivity, reliability and worth for monitoring the acute toxicity of coastal mill discharges.

2.7 Further development of rapid toxicity tests with freshwater, estuarine and marine species of phytoplankton is desirable. Algal tests designed for monitoring effluent toxicity must be capable of distinguishing this effect from those caused by effluent colour or nutrients.

2.8 The LC_{50} fish bioassay is inappropriate for monitoring the residual (sublethal) toxicity of biotreated mill effluents and receiving waters, which in most instances are not acutely lethal to the test organisms. A number of rapid sublethal fish bioassays are now available and have proven useful (freshwater only), but the development of additional quantitative sublethal bioassays using freshwater, estuarine and marine organisms characteristic of those within our receiving waters is warranted.

2.9 A substantial amount of information exists concerning the acute lethal and sublethal toxic effects on freshwater-acclimated fish of exposure to untreated or primary-treated bleached and unbleached kraft and sulphite whole mill effluents under controlled conditions. Dilution of these effluents to concentrations equivalent to 0.05 of the samples' 96-h LC_{50} values eliminates the known physiological/biochemical reactions, although behavioural responses may still be evident.

2.10 Basic information is required regarding the toxicity and toxic effects caused by TMP and CTMP effluents, treated and untreated.

2.11 Insufficient data exist concerning the acute and chronic sublethal effects on fish and other aquatic life of exposure to dilute concentrations of biotreated whole mill effluent under controlled conditions.

2.12 Our knowledge of the influence of both untreated and treated whole mill effluents on the early developmental life stages of sensitive aquatic organisms, their reproduction and disease resistance is deficient. So too is our understanding of toxic effects and their significance at the population and community levels of organization. These information gaps should be given serious attention.

2.13 Laboratory (research) bioassays performed to investigate the extent to which specific effluent types may be deleterious to aquatic life should include testing under variable conditions of temperature and dissolved oxygen which typify the ranges characteristic of our receiving waters.

2.14 Laboratory or on-site controlled bioassays conducted with the intent of assessing the potential biological impact of a mill discharge within a particular receiving water, should use the receiving water source, taken upstream of the mill discharge, as the diluent water.

3. *Toxic Effects of Mill Effluents within Receiving Waters*

3.1 The vast majority of receiving-water studies conducted to date do not distinguish biological effects due to toxic effluent constituents from those caused by other effluent characteristics (e.g., colour, temperature, salinity, nutrients, oxygen demand, solids content). Such a distinction is necessary to discern the necessity for the controlled removal of toxic constituents from an effluent.

3.2 Very few of these receiving-water studies have attempted to define the toxic zone of influence caused by a mill discharge.

3.3 The demonstration of biological effects within receiving waters, associated with mill discharges, does not necessarily mean that the responses noted are deleterious to the environment.

3.4 The preponderance of receiving-water studies associated with pulp and paper mill discharges have examined biological changes in communities of benthic invertebrates, phytoplankton and periphyton. Although many site-specific

instances of effects have been demonstrated, few if any of these studies have shown that these changes resulted in adverse effects on fisheries resources.

3.5 Instances where significant environmental effects on aquatic life have been demonstrated are normally associated with pulp and paper mills discharging untreated or primary-treated effluent into poorly flushed waters with limited capacities for dilution and dispersal.

3.6 No studies have been found which show conclusive evidence of significant toxic effects within receiving waters which are attributable to typical biotreated mill effluent.

3.7 Reported receiving-water effects pertinent to the commercial fisheries include lethal (in exceptional cases only) and (in some instances) sublethal effects in captive fish; isolated findings of increased frequencies of fish liver lesions, gill parasites and skin mucosal bacteria; and observations of toxic effects in oysters. The frequency with which such effects occur, the (toxic) zones of influence and the relevance of these effects to exposed fish populations have yet to be ascertained for our waters.

3.8 Loss of habitat associated with fibre deposits, although a real and significant environmental impact at many receiving-water sites, is not related to effluent toxicity per se.

3.9 Application of the findings reviewed in this chapter to other discharge situations is, in most instances, vitiated by a lack of definition of effluent type, quality and treatment; effluent dispersal patterns and receiving-water concentrations; and/or the characteristics of the receiving waters.

4. *Bioaccumulation and Elimination of Organic Effluent Constituents*

4.1 Our present knowledge concerning the extent to which specific (toxic) effluent constituents bioaccumulate in exposed freshwater, estuarine or marine organisms is limited.

4.2 At the present time, we don't know at what level the concentration of any effluent constituent accumulated in fish or other aquatic life poses a threat to that organism (or to a commercial fishery resource), nor do we have any proven techniques for making such assessments.

4.3 Controlled-exposure studies with kraft bleach plant or whole mill effluents and with toxic effluent constituents show that unchlorinated resin acids, certain chlorophenolic compounds (di- and trichlorophenol, tri- and tetrachloro-

guaiacol, chlorocatechols) and chlorinated guaiacol metabolites (tri- and tetrachloroveratrole) can rapidly (days, weeks) accumulate in liver and certain other (fatty) tissues of fish and shellfish.

4.4 The elimination (clearance) from tissues of these compounds, following the transfer of exposed organisms to uncontaminated water, appears to be rapid (days).

4.5 The relative potential for bioconcentration of these effluent constituents has not been established, although available data for the chlorinated compounds suggest tetrachloroveratrole > trichloroveratrole > trichloroguaiacol > tetrachloroguaiacol > di/trichlorophenol > chlorocatechols.

4.6 The distribution (partitioning) of accumulated chemicals in the various fish tissues has not been studied intensively. Laboratory data indicate highest accumulations in liver and fatty tissues, with appreciably lesser (or undetectable) concentrations in muscle or whole-body tissues.

4.7 The limited number of field surveys of bioaccumulated effluent constituents in aquatic biota provide evidence that unchlorinated resin acids, chlorophenolic compounds and certain biodegradation products (chloroveratroles) can, in instances where effluent mixing and flushing is poor, accumulate in fish and shellfish. As with the laboratory findings, the results of these (freshwater, estuarine and marine) surveys indicate appreciably greater accumulations in fish liver than in muscle or whole-body tissues (where concentrations are frequently below the limits of detection).

4.8 The interrelationships between bioconcentration of effluent constituents and effluent type, treatment and receiving-water concentrations are presently unknown.

4.9 There is a need for more (comprehensive) field surveys to examine the degree of accumulation of effluent constituents (and metabolites) in exposed aquatic life. Additionally, more laboratory investigations should be undertaken which determine the bioconcentration potentials, elimination rates, mechanisms for detoxification/excretion and associated toxic effects for the known toxic pulp and paper mill effluent constituents and metabolites.

4.10 For fish and shellfish species exposed for a sufficient period (hours, days) to pulp mill effluent in waters with minimal mixing and dilution (i.e., effluent strengths $\geq$1%), off-flavours in edible portions are possible.

4.11 Evidence suggests that off-flavours imparted by mill effluents are rapidly eliminated following movement by the fish to clean water.

4.12 The few comparative flavour-evaluation studies conducted in the laboratory with treated and untreated samples of unbleached and bleached kraft whole mill effluent indicate that conventional biotreatment reduces the effluents' tainting propensity.

4.13 Flavour-evaluation studies, conducted in conjunction with chemical analyses of edible tissues, offer promise but have not yet identified the effluent constituents responsible for tainting.

4.14 No obvious relationship exists between effluent toxicity and off-flavours in fish or other edible aquatic life.

5. *Bioassays for Predicting the Toxicity of Mill Effluents in the Aquatic Environment*

5.1 The acute lethal bioassay test with rainbow trout is severely limited as a (sole) laboratory procedure for predicting the toxicity of pulp and paper mill effluents in the aquatic environment.

5.2 The applicability of this (and other) freshwater bioassay(s) to estuarine and marine environments has not been demonstrated.

5.3 The predictive worth of acute lethal bioassays is restricted because they cannot measure potential acute sublethal toxic effects nor assess long-term toxic effects due to either brief or prolonged exposures.

5.4 The value of acute lethal bioassays in predicting the likelihood of short-term lethal toxic effects on aquatic life frequenting the receiving waters can be enhanced by the selection of appropriate test species (for freshwater, estuarine or marine discharges), use of multiple species, and use of the receiving water as the diluent for the tests.

5.5 Meaningful site-specific predictions of toxic environmental effects, based on laboratory (lethal or sublethal) bioassays, cannot be made without worthwhile estimates of (seasonal) concentrations of effluent in the receiving waters.

5.6 Conventional laboratory bioassays with mill effluents cannot predict toxic effects due to possible toxic metabolites formed during effluent degradation.

5.7 A number of reasonably rapid and sensitive sublethal bioassays are now available for monitoring the toxicity of treated or untreated mill effluents and receiving waters to fish and other (lower) aquatic life under controlled

laboratory conditions and on-site. The worth of these promising bioassays in predicting the toxicity of mill discharges to indigenous aquatic life and defining possible toxic zones of influence within receiving waters remains to be proven.

5.8 Some of the more promising (predictive) aquatic bioassay tests/approaches include automated on-line physiological monitoring (fish) systems; acute stress bioassays; tests for metabolic dysfunctions and activation of detoxification mechanisms; behavioural assays; histopathological examinations; tests for developmental anomalies (e.g., oyster larval assay); partial or complete life cycle studies with selected aquatic species (e.g., daphnia); and multiple-species microcosm tests.

5.9 Toxicity tests with samples of mill effluent or receiving water cannot predict with any accuracy the extent to which a particular discharge may affect fish habitat. Such predictions require the inclusion of appropriate sediment bioassays in conjunction with the appropriate chemical analyses of sediments and overlying waters.

5.10 The ability of laboratory and in situ bioassay tests to predict the potential for bioconcentration in indigenous aquatic life of specific (toxic) mill effluent constituents has been demonstrated. So too has the application of a combination of controlled-exposure bioassays and organoleptic (flavour evaluation) studies for predicting the potential off-flavours in edible aquatic life due to mill discharges.

5.11 An integrated approach which includes a battery of sensitive effluent and receiving-water bioassay tests and test organisms appropriate to the receiving environment is now being applied (in various manners) by Sweden, Finland and U.S.A. in order to examine their capabilities for predicting and monitoring the toxic environmental effects of pulp and paper mill discharges. This approach offers considerable promise, although findings (as yet unavailable) from these comprehensive studies deserve our review to evaluate their predictive worth.

5.12 Assurance that this ecotoxicological bioassay approach can usefully predict the toxic environmental impact of mill discharges requires concomitant surveys of receiving-water quality, effluent dispersal and concentration, and the condition and abundance of populations of commercially relevant fish, shellfish and fish-food organisms at various sites adjacent to and distant from the outfalls.

LIST OF ABBREVIATIONS

AABT	algal assay bottle test
ADt	air-dried ton(ne)
AL	aerated lagoon
AS	activated sludge
BCF	bioconcentration factor
BKME	bleached kraft whole mill effluent
BPE	bleach plant effluent
BSME	bleached sulphite whole mill effluent
BW	brackish water
Cl_4C	tetrachlorocatechol
Cl_3G	trichloroguaiacol
Cl_4G	tetrachloroguaiacol
Cl_2P	dichlorophenol
Cl_3P	trichlorophenol
Cl_4P	tetrachlorophenol
CF	continuous-flow bioassay
COFI	Council of Forest Industries of British Columbia
CPPA	Canadian Pulp and Paper Association
CPAR	Committee for Pollution Abatement Research (Environment Canada, Ottawa, Ontario)
CTMP	chemi-thermomechanical pulping effluent
DDMS	dichlorodimethylsulphone
DDT	dichlorodiphenyltrichloroethane
DHA	dehydroabietic acid
EC_{50}	effective concentration causing a response for 50% of test organisms
EPA	Environmental Protection Agency (U.S.)
EPS	Environmental Protection Service (Environment Canada)
FW	freshwater
g	gram
h	hour
ISO	International Organization for Standardization
km	kilometre
KME	kraft whole mill effluent

L	litre
LC_{50}	(lethal) concentration causing the death of 50% of test organisms
mg	milligram
Mg^-	magnesium-based sulphite pulping
mL	millilitre
MPE	mechanical pulping effluent
Na^-	sodium-based sulphite pulping
NCASI	National Council of the Pulp and Paper Industry for Air and Stream Improvement, Inc. (New York, NY)
ng	nanogram
NH_3^-	ammonia-based sulphite pulping
NOAA	National (U.S.) Oceanic and Atmospheric Administration
NSSC	neutral sulphite semi-chemical pulping
°/oo	parts per thousand
O_2	oxygen
OECD	Organization for Economic Cooperation and Development (International)
PCB	polychlorinated biphenyl
PME	pulp mill effluent
S	static bioassay
SME	sulphite whole mill effluent
SS	semi-static (periodic renewal) bioassay
SW	seawater
TEF	toxicity emission factor
TER	toxicity emission rate
TMP	thermomechanical pulping effluent
TU	toxic unit
µg	microgram
UKME	unbleached kraft whole mill effluent
U.S. (USA)	United States of America
USME	unbleached sulphite whole mill effluent
v/v	volume/volume

GLOSSARY

Abiotic - devoid of life.

Acclimate - To become physiologically adapted to one or more environmental variables, usually under controlled laboratory conditions.

Acidic Fraction - Alkali-soluble organic constituents of pulp and paper mill effluent.

Acute Toxicity - A relatively short-term lethal or sublethal effect, usually defined as occurring within four days for fish and macroinvertebrates and shorter times for smaller organisms.

Algae - A group of aquatic plants, variously one-celled, colonial or filamentous, containing chlorophyll and/or other pigments and having no vascular system.

Algal Blooms - Proliferations of algae (microscopic aquatic plants containing chlorophyll and/or other pigments; variously one-celled, colonial or filamentous) within water.

Anadromous - Fish (e.g., certain salmonid species) which spend their early life stages in freshwater, enter the sea for a period of active feeding and growth, and return to freshwater to spawn.

Anoxic - Devoid of oxygen.

Anthropogenic - Of human origin; caused by man.

Aquatic - Growing, living in or frequenting water; occurring or situated in or on water; analagous to "terrestrial" for the case of land.

Aquatic Ecotoxicology - The science of the integrated assessment of toxic aggression on all biological communities of the environment.

Aquatic Toxicology - A study of the effects of toxic substance(s) on a target freshwater, estuarine or marine species.

Bacteria - Microscopic unicellular organisms, living singly or in columns within (in this instance) the aquatic environment.

Benthic - Inhabiting the bottom of streams, lakes or oceans.

Bioaccumulation - The uptake and storage in tissues of an aquatic organism of a chemical from the diet and/or the surrounding water.

Bioassay - The use of an organism or part of an organism as a method for measuring or assessing the presence or biological effect of one or more substances,wastes or environmental factors under defined conditions.

Bioconcentration - The accumulation in an aquatic organism of a chemical taken up directly from the water.

Bioconcentration Factor (BCF) - A constant of proportionality between the concentration (wet weight) of the chemical in the aquatic organism (C_O) and the water (C_W), as follows: $C_O = C_W \times BCF$.

Biomagnification - The accumulation in an aquatic organism of a chemical taken up through diet (via the food chain).

Brackish - Describes water having a salinity within the range of 0.5 to 17 o/oo (parts per thousand).

Carcinogenic - Able to cause cancer.

Chronic Toxicity - Long-term effects that may be related to changes in growth, metabolism, reproduction, disease resistance and death. Often signifies effects occurring over periods of at least one tenth of the life span of the organism.

Condition Factor - A measure of the plumpness or fatness of aquatic organisms. For oysters, values are derived based on the ratio of the soft tissue dry weight to the volume of the shell cavity.

Continuous-Flow Bioassay - Bioassay in which the solution to which the organism is exposed is replaced continuously in the test chamber at a controlled rate for the duration of the test. Also called a flow-through bioassay.

Crustacean - A class of mostly aquatic organisms having an outer skeleton ("exoskeleton") composed of chitin (nitrogenous polysaccharide). It includes daphnia, crabs, lobsters, shrimps and barnacles.

Daphnia - A freshwater micro-crustacean found in ponds, lakes or streams. Sometimes referred to as water fleas. Genus Daphnia.

Demersal - Being or living near bottom waters.

Effluent - Waste material (liquid and suspended solids) discharged into the aquatic environment.

Epibenthic - Aquatic organisms living on or just above the surface of bottom sediments.

Epidemiology - The field of science dealing with the relationships of the various factors which determine the frequencies and distributions of a disease or a physiological state in a human community.

Epifaunal - Animals living on or just above the surface of the bottom sediment of fresh, estuarine or marine waters.

Estuarine - Residing or situated in a semi-enclosed coastal body of water which has a free connection with the open sea and within which seawater is measurably diluted with freshwater derived from land drainage.

Fauna - The animal life present in fresh, estuarine or marine waters.

Fecundity - Ability to produce offspring rapidly and in large numbers.

Gonopodium - An elongation and modification of the anal-fin rays of certain male fish species, used to facilitate copulation.

Halocline - A vertical salinity gradient within a body of water that is greater than the gradients above and below it.

Hematocrit - Packed volume, following centrifugation, of circulating blood cells; expressed as a percentage of the whole blood volume. Values correspond primarily to erythrocyte (red blood cell) content.

Hypoxic - Oxygen deficient.

Indigenous - Belonging/found naturally in a particular body of water.

Infaunal - Invertebrate organisms living within the bottom sediment of fresh, estuarine or marine waters.

Lacustrine - Pertaining to a lake, or from a lake environment.

Lesion - Any pathology of tissue.

Leucocrit - Packed volume, following centrifugation, of circulating white blood cells (leucocytes), expressed as a percentage of the whole blood volume.

Lethal Toxicity - Causing or able to cause death by direct action.

Lignin - Naturally occurring phenolic polymer found between cell walls of woody tissues.

Lipophilicity - The measure of a substance's relative solubility in an oil-like matrix.

Macroinvertebrates - Invertebrate (without backbone) animals that are not microscopic.

Median Effective Concentration - The concentration of a specific toxicant (EC_{50}) which effects a specific response (i.e., avoidance, stress, loss of equilibrium) in 50% of the test organisms; usually within a given time.

Median Lethal Concentration - The concentration of an effluent or chemical which causes death of 50% of the test organisms, usually within a defined time period (e.g., 96-h LC_{50}).

Microsomal - Finely granular elements within the cytoplasm of cells.

Microtox - An automated (Beckman Instruments Inc.) rapid screening assay which determines the EC_{50} concentration of a chemical or effluent which reduces the amount of incident light emitted by a culture of fluorescent bacteria (Photobacterium phosphoreum).

Migratory - To pass, usually predictably (based on aquatic species), from one region or climate to another for purposes of feeding, breeding, etc.

Monomer - A fundamental structural unit of a system of repeating units.

Mutagenic - Ability to induce genetic mutations.

Mutation - A genetic change which, when transmitted to offspring, gives rise to heritable variation.

Nektonic - Free-swimming organisms, inhabiting the water column in lakes or oceans at various depths.

Neoplasm - Any new and abnormal growth in a tissue or organ, i.e., a tumour.

Neoplastic - Pertaining to or like a neoplasm.

Neutral Fraction - Alkali-insoluble organic constituents of pulp and paper mill effluent.

Palatable - Pleasing to the taste.

Parthenogenesis - A sexual reproduction from germ cells, without fertilization.

Partition Coefficient - The ratio of the equilibrium concentration or a chemical in equal volumes of two mutually immiscible liquids, in contact with one another.

Pelagic - Organisms inhabiting the water column and subject to the currents therein, i.e., not free swimming.

Periphyton - Attached freshwater or marine algae; mainly filamentous.

pH - A symbol for the degree of acidity or alkalinity of a solution; originally expressed as the logarithm of the reciprocal of the hydrogen ion concentration in gram equivalents per litre of solution.

Phytoplankton - Plant life, mostly microscopic, found floating or drifting in the oceans or large bodies of freshwater; forms the basis of most aquatic food chains as the main primary producer.

Plume - The main pathway for dispersal of effluent within the receiving waters, prior to its complete mixing.

Prey - Organisms hunted and consumed by predators for food.

Primary Treatment - Removal of particulate matter from an effluent, usually by sedimentation.

Proximate - Within the immediate vicinity.

Rapid Infiltration - A system for tertiary treatment of effluent, involving passage of effluent through a naturally occurring, porous soil bed, into receiving waters. Normally a number of soil beds are available and are alternated periodically. The principal function of this type of treatment is to remove effluent colour.

Riverine - Pertaining to a river.

Salinity - A measure of the quantity of dissolved salts in seawater. Formally defined as the total amount of dissolved solids in seawater - in parts per thousand (o/oo) by weight -

when all the carbonate has been converted to oxide, the bromide and iodide replaced by chloride, and all organic matter is completely oxidized.

Salmonid Fish - Fish belonging to the family Salmonidae (includes all species of salmon, trout, char, grayling).

Secondary Treatment - Microbiological treatment of an effluent as a means of reducing the dissolved organic loading; normally following primary treatment.

Sedimentation - Process by which matter settles to the bottom of a liquid.

Semi-Static Bioassay - Test in which the solution to which the organism is exposed is renewed periodically (usually at 24-h intervals) with a fresh test solution of the same concentration and composition.

Shellfish - Aquatic invertebrates with shells or carapace. Included are crustaceans (shrimps, prawns, crabs, lobsters) and molluscs (clams, mussels, oysters).

Sonic-Tagged - Equipped with an external or internal (stomach) ultrasonic transmitter, which permits tracking by telemetry of fish movements.

Static Bioassay - Test in which solutions to which organisms are exposed are not replaced during the exposure period.

Sub-Acute Toxicity - A lethal or sublethal effect extending beyond an acute (short-term) period and which may become chronic.

Sublethal Toxicity - Causing or able to cause deleterious effects (anatomical, behavioural, physiological, biochemical) within or towards an organism; may ultimately result in death if exposure is prolonged, or if organism is simultaneously/subsequently exposed to other environmental stressors.

Taint - To cause an unpleasant or off-flavour in food.

Tainting Propensity - Inclination or tendency to cause an off-flavour in food.

Teleost - Fish of order Teleostei, with skeleton completely ossified.

Threshold Concentration - The lowest concentration demonstrated or estimated to cause a detectable effect or response.

Tolerate - To withstand or endure.

Toxicity, Toxic - Adverse effect (lethal or sublethal) to a test organism caused by effluents or other aquatic contaminants. Toxic effects are a result of effluent concentration and exposure time, and are modified by variables such as temperature, chemical form and availability.

Toxic Unit (TU) - A concept for expressing the toxic strength or concentration of a chemical or effluent in terms of a multiple or fraction of its LC_{50} value, whereby 1 TU is equivalent to this value.

Toxicity Emission Factor - Represents the daily discharge of toxicity (based on an effluent's LC_{50} value) per unit of production. For pulp mills, this factor is determined by dividing the toxicity emission rate by the daily tonnage (odt) of pulp produced.

Toxicity Emission Rate - Represents the amount of toxicity (based on an effluent's LC_{50} value) discharged daily in an effluent. This value represents the product of the effluent's toxic units and the daily volume of the effluent released.

Tributary - Usually a smaller stream or river flowing into a larger one.

White Water System - The water recovered from formation of paper on the Fourdrinier machine; usually with a high degree of internal recycle within the paper mill.

Zooplankton - Animal life, usually microscopic, found floating or drifting in the water column of oceans or bodies of fresh water; form the bulk of the primary consumer link in aquatic food chains.

1 TOXIC CONSTITUENTS IN MILL EFFLUENTS, RECEIVING WATERS AND SEDIMENTS

1.1 Introduction

Numerous articles have been published in the last ten years concerning the nature of toxic constituents in pulp mill effluent. Brouzes (1976), Walden (1976), Hutchins (1979), and Walden and Howard (1981) all have reviewed the literature covering information acquired during the seventies. A large number of compounds have been identified in the various process streams and final effluents associated with the production of pulp and paper. The emphasis of research in this area is now on the determination of the concentrations of these compounds and their degradation products in receiving waters and bottom sediments, and the assessment of biological effects in the aquatic environment, particularly the longer-term implications associated with the discharge of the more persistent compounds.

It is important to realize that an evaluation of the toxicity of any complex organics-containing effluent is necessarily based on two types of measurements. The first involves identification of the organic constituents and subsequent quantification of their concentrations. Modern instrumentation has improved the limits of detection and the accuracy of this measurement, while decreasing costs, and simplified procedures have brought this capability within the reach of an increasing number of laboratories. However, before the role of these organic constituents as toxicants can be assessed, their toxicity must be established by undertaking or by reference to a second (biological) measurement, usually called a bioassay. A bioassay test measures the response of some biological parameter to the time-concentration effects of the toxicant. Under properly defined conditions it meets the requirements of any assay, namely that it is reproducible and produces quantitative data. Indeed, under empirical conditions the contribution of individual toxicants to the overall toxicity of complex effluents can be quantified. For this chapter, toxicity ascribed to the various organic constituents is restricted to their acute ($\leq$96-h) lethality to juvenile salmonid fish, usually rainbow trout, under controlled laboratory conditions. Information concerning the sublethal toxicity of effluent constituents and whole mill effluents is reviewed in Chapter 2.

The purpose of this review is to provide updated information on the nature and concentration of toxic constituents present in final discharged pulp mill effluent, receiving waters, and bottom sediments. The determination of constituent concentrations and their dispersal and persistence within the environment is a necessary and important

step in the overall assessment of their fate and effects. The effects of biotreatment on levels of toxic constituents in effluents from mills employing different processes are also reviewed. Gaps in information are identified which indicate specific problems still to be addressed.

Because of the large volume of literature available on effluent toxicity, information on volatile compounds, ubiquitous environmental contaminants (such as phthalate esters), and products from other forestry operations (such as pentachlorophenol from the logging industry) has been deliberately excluded. Similarly, toxicity associated with non-chemical components of mill discharges, such as suspended solids and fibres, is not reviewed.

1.2 Toxic Constituents in Mill Effluents

Most of the toxicity in pulp and paper whole mill effluents and process streams is attributed to resin and fatty acids, chlorinated phenols and, to a lesser extent, a broad group of neutral compounds. In this review, levels of these compounds in untreated and biologically treated effluents from mills employing different processes, i.e., kraft, sulphite or mechanical pulping, are documented. Primary-treated effluents are considered untreated, since levels of toxic constituents are not significantly reduced during the short residence time required for clarification (Easty et al., 1978; Willard, 1983). In instances where novel mill processes are used, for example, oxygen or chlorine dioxide bleaching, relevant information is included on any effects these processes have on levels of toxicants.

A number of recent descriptions of the various pulping processes are available (Beeland et al., 1979; Hutchins, 1979; Casey, 1980; Dellinger, 1980; McCubbin, 1983) and the reader is referred to these sources for specific information. Brief descriptions of the three major categories of pulp mills covered in this review, kraft, sulphite and mechanical, follow.

Kraft: The kraft process is the dominant chemical pulping process in Canada and other countries. In this process, wood chips are digested or "cooked" under pressure with a mixture of hot caustic soda and sodium sulphide. Lignin and wood extractives are solubilized, leaving the insoluble cellulose fibres as pulp. In an unbleached kraft mill, the product may be pulp or may be processed into unbleached kraft products such as linerboard and paper bags. In a bleached kraft mill, the bleached pulp has a variety of end uses, such as a component of newsprint and other papers. The chemicals are recovered from the spent (strong) black liquor and pulp washings (termed weak black liquor) through

a series of steps involving concentration, combustion, clarification and causticizing. Sulphur-containing gases, turpentine and tall oil by-products are produced during digestion and in the chemical recovery systems.

Sulphite: The sulphite process employs solutions of calcium, magnesium, ammonium or sodium sulphite as the cooking liquor. Cooking is done under either acidic or neutral (NSSC) conditions during which lignin is solubilized as ligninsulphonic acids. In the NSSC (neutral sulphite semichemical) process, separation of the pulp fibres is completed mechanically. Typical products of acidic sulphite processes include: a component of newsprint; fine papers; and highly bleached pulp (α-cellulose) for the manufacture of rayon. NSSC processes are used to produce unbleached products. Spent cooking liquor is not invariably processed for recovery of pulping chemicals. Recent improvements in sulphite processes have resulted in increased pulp yields.

Mechanical Pulping: Mechanical pulping involves conversion of wood into fibres by physical or mechanical grinding, aided in some cases by heat or chemicals. Stone groundwood and refiner groundwood pulp are produced by grinding short logs and chips respectively. Thermomechanical pulping (TMP) involves heating wood chips briefly under pressure with steam prior to mechanical refining. In chemi-thermomechanical pulping (CTMP), small amounts of sodium sulphite are included in the steaming process to improve softening of the chips prior to refining. All the mechanical pulping processes produce high yields of pulp since a large portion of the lignin is retained with the fibre. Mechanical pulp is a major component of newsprint, with the use of TMP for this purpose becoming more widespread in recent years.

1.2.1 Kraft Effluent. Because of its pre-eminent commercial position, more information has been compiled concerning toxic constituents in kraft effluents than for effluents from the other types of processes. Levels of resin acids which occur in kraft whole mill effluent are shown in Table 1.1. Both unbleached (UKME) and bleached (BKME) kraft whole mill effluents contain a wide range of concentrations of these compounds. In general, levels of the non-chlorinated resin acids appear higher in untreated UKME than untreated BKME, probably because of dilution of BKME by bleaching effluent. With the exception of the chlorinated dehydroabietic acids, bleachery effluents do not contain appreciable quantities of resin acids (Kringstad et al., 1984).

Notwithstanding the pooling of data in Table 1.1, the effectiveness of biotreatment on resin acid removal is clearly evident. A number of the references cited in the table provide information on resin acid levels in untreated and treated effluent

TABLE 1.1 RANGE OF CONCENTRATIONS (µg/L) OF RESIN ACIDS IN UNTREATED AND BIOTREATED WHOLE MILL EFFLUENTS DERIVED FROM VARIOUS PROCESSES

										Mechanical					
		UKME		BKME		USME		BSME		Groundwood		TMP/CTMP		Paper	
Resin acid	96-h LC_{50}[a] (µg/L)	untreated[b]	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated
abietic	700-1500	30-9970	<20-3630	<20-4800	<10-1780	520-4840	437-500	<10-1000	<10-100	210-16000	14-4200	-[c]	-	50-1900	50
chlorodehydro-abietic	600-900	-	-	<10-750	<1-260	-	-	<10-900	<10-450	-	-	-	-	-	-
dehydroabietic	800-1740	990-5780	<20-1930	<30-4580	<1-2140	700-4620	247-1100	<20-8500	10-700	490-15100	8-5800	-	-	227-4000	1000-3900
dichlorodehydro-abietic	600-1200	-	-	<10-410	<10-152	-	-	<10-40	<10-30	-	-	-	-	-	-
isopimaric	400-1000	70-4120	<20-1420	<20-4800	<10-930	100-5070	100-294	<10-300	<10-310	150-9300	12-7900	-	-	30-1200	780-800
levopimaric	700-1000	<10-2700	<10-30	<10-2400	<1-1190	100-510	200	<10-100	<10-60	80-22000	11-1800	-	-	12	-
neoabietic	610-730	<50-1200	-	<10-1000	<1-150	-	-	-	-	30-6800	<1-3800	-	-	29-450	-
palustric	500-600	-	-	90-100	80	-	-	-	-	300-7700	-	-	-	63	-
pimaric	700-1200	100-1830	<20-890	<20-1010	14-540	490-1140	20	<20-30	<20	20-6800	<1-5700	-	-	<20-610	500-800
sandaracopimaric	360[d]	-	-	-	-	-	-	-	-			-	-	9-275	45-110

[a] Median lethal concentration derived for rainbow trout under static bioassay conditions.
[b] May or may not be clarified.
[c] Not indicated/not determined/not applicable.
[d] Value for underyearling coho salmon.

References for Table 1.1

Resin acid	96-h LC_{50}	UKME	BKME	USME	BSME	Mechanical	Paper
abietic	1,2	3-5	3,4,6,7	3,4,7,8	3,4,8,9	1,4,10-12	3,13,14
chlorodehydro-abietic	2,15	-	3,4,6,7, 16	-	3,4,8,9	-	-
dehydroabietic	1,2,17	3-5	3,4,6,7	3,4,7,8	3,4,8,9, 18,19	4,10,11	3,13,14, 18
dichloro-dehydroabietic	2,15	-	3,4,6,7, 16	-	3,4	-	-
isopimaric	1,2	3-5	3,4,6,7	3,4,7,8	3,4,8,9	1,4,10,12	3,13,14
levopimaric	2	4,5	4	4,11	4,11	4	13
neoabietic	4	4	4,6	-	-	4	13,14
palustric	1,2,20	-	6	-	-	12,20	-
pimaric	1,2	3	3,6,7	3,7	3	1,4,10-12	3,13,14
sandaracopimaric	20	-	-	-	-		13

1. Leach & Thakore (1976)
2. Chung et al. (1979)
3. Easty et al. (1978)
4. Leach & Chung (1980)
5. Willard (1983)
6. Holmbom & Lehtinen (1980)
7. NCASI (1981a)
8. Howard & Leach (1978)
9. Walden et al. (1976)
10. Walden & Howard (1974)
11. Howard & Leach (1973)
12. Walden & Leach (1975)
13. Richardson & Bloom (1983)
14. Keith (1976)
15. Leach & Thakore (1975)
16. Claeys et al. (1980)
17. Davis & Hoos (1975)
18. Ball et al. (1978)
19. Peterman et al. (1980)
20. Leach & Thakore (1977)

from individual mills. These, and separate reports on resin acid biodegradability (Rogers et al., 1975; Leach et al., 1977; Chung et al., 1979; Willard, 1983) show that biological treatment normally reduces concentrations of non-chlorinated resin acids by at least 90%. Chlorinated resin acids are more resistant to biological treatment (Leach et al., 1977; Chung et al., 1979).

Concentrations of fatty acids in untreated and biotreated whole mill effluents from various processes are shown in Table 1.2. A comparison of LC_{50} values in this table with those for resin acids (Table 1.1) indicates that fatty acids are less toxic to fish than resin acids. Individually, the highest reported concentrations of these toxic constituents in untreated UKME and BKME are frequently below the 96-h LC_{50} values for various fatty acids, indicating their presence in sublethal amounts. The low levels shown for biotreated effluent indicate that fatty acids are readily degraded. Leach and Thakore (1977) reported that degradation of fatty acids occurred rapidly during bioassays, making determination of LC_{50} values difficult.

A comprehensive study of the levels of "Toxic and Nonconventional Pollutants" in untreated and treated effluents from different categories of pulp and paper mills in the United States has been carried out by the Environmental Protection Agency (Dellinger, 1980). The extensive data are reproduced, in part, in Appendix A. Concentration ranges for resin acids in untreated UKME for individual resin acids were as follows: abietic, 350-12 000 µg/L; dehydro-abietic, 330-27 600 µg/L; isopimaric, 78-1600 µg/L; and pimaric, 38-2500 µg/L. Treated UKME contained 0-250 µg/L abietic, 6-200 µg/L dehydroabietic, 0-32 µg/L isopimaric, and 0-60 µg/L pimaric acid. Corresponding levels for untreated and treated BKME respectively were 0-18 000 and 0-2500 µg/L abietic, 10-5200 and 0-1000 µg/L dehydroabietic, 0-1300 and 0-590 µg/L isopimaric, 0-1900 and 0-790 µg/L pimaric, 0-1600 and 0-700 µg/L chlorodehydroabietic and 0-86 and 0-65 µg/L dichloro-dehydroabietic acid. The range of concentrations is wider than that shown in Table 1.1, particularly for untreated effluents. Levels for treated UKME are lower than those shown in Table 1.1, but concentrations in treated BKME samples are generally similar. Marked reductions (48-99%) in average levels of abietic, dehydroabietic, isopimaric and pimaric acid were observed in dissolving kraft and unbleached kraft effluent for bag production, the two processes producing the highest average influent concentrations whereas somewhat lesser (32-67%) reductions were reported for the chlorinated dehydroabietic acids contained in dissolving kraft effluent. These results again indicate that chlorinated resin acids are more resistant to biodegradation than their non-chlorinated counterparts. In the same study, oleic, linoleic and linolenic acid levels reported in untreated UKME and

TABLE 1.2 RANGE OF CONCENTRATIONS (μg/L) OF FATTY ACIDS IN UNTREATED AND BIOTREATED WHOLE MILL EFFLUENT FROM VARIOUS PROCESSES

Fatty acid	96-h LC_{50} (μg/L)	UKME		BKME		USME		BSME		Mechanical		Paper	
		untreated[a]	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated	untreated	biotreated
dichloro-stearic	2500	-[b]	-[b]	<40-552	<40-268	-[b]	-[b]	<40	<40	-[b]	-[b]	-[b]	-[b]
epoxystearic	1500-3400	-[c]	-[c]	40-1540	<40	-[c]	-[c]	<40	<40	-[c]	-[c]	-[c]	-[c]
linoleic	2000-4500	<10-1160	<20-60	<20-9300	<20-500	90-14600	-[c]	<20-1110	<10-50	490-9000	23-1500	60-480	100
linolenic	2000-6000	<20-110	<20	<20-260	10-30	270-700	-[c]	<20-390	<20	<100-800	-[c]	<20-30	-[c]
oleic	3500-8200	40-2490	<20-120	30-7750	<20-2340	<50-6780	25	20-1040	10-370	230-4300	24-1400	50-430	80-400

a May or may not be clarified.
b Not applicable.
c Not indicated/not determined.

References for Table 1.2

Fatty acid	LC_{50}	UKME	BKME	USME	BSME	Mech.	Paper
dichloro-stearic	1	-	2	-	2	-	-
epoxystearic	3,4	-	2	-	2	-	-
linoleic	4,5	2,6	2,6,7	2,6	2,6	6,8,9	2,10
linolenic	4,5	2	2,7	2	2	9	2
oleic	4,5	2,6	2,6,7,11	2,6	2,6	6,8,9	2,10

1. Leach & Thakore (1977)
2. Easty et al. (1978)
3. Leach & Thakore (1975)
4. Chung et al. (1979)
5. Walden et al. (1976)
6. Leach & Chung (1980)
7. Holmbom & Lehtinen (1980)
8. Walden & Howard (1974)
9. Walden & Leach (1975)
10. Keith (1976)
11. NCASI (1981a)

BKME were generally at or below the respective individual LC_{50} values. Biotreatment reduced concentrations of fatty acids by over 70% in most instances to levels below 500 µg/L.

Data presented in Tables 1.1 and 1.2, and the results of the U.S. EPA (Dellinger, 1980) study, indicate that biotreatment effectively reduces the concentration of individual resin and fatty acids in kraft whole mill effluents to levels that, in most instances, are below acutely lethal values. As shown subsequently, certain resin and fatty acids persist in receiving waters and sediments downstream of mills discharging biotreated wastes. However, the precise environmental impact attributable to these individual components is unknown, and difficult if not impossible to determine. Certain mills, particularly those on tidewater, may discharge untreated effluent and, as a result, will discharge higher levels of resin and fatty acids than mills with biotreatment facilities.

Chlorophenols are produced in bleached kraft mills during the degradation of lignin with chlorine, and by chlorination of the phenolic residues, produced during pulping, which pass into the bleach plant with the unbleached pulp. Process-derived chlorophenols found in BKME include 2,4-dichlorophenol, 2,4,6-trichlorophenol, dichloroguaiacol (various isomers), 3,4,5- and 4,5,6-trichloro-guaiacol, tetrachloroguaiacol, 4,5-dichlorocatechol, 3,4,5-trichlorocatechol and tetrachlorocatechol (Claeys et al., 1980; NCASI, 1981a,b; Holmbom and Lehtinen, 1980; Kovacs et al., 1984). Other chlorophenols produced during bleaching, for example 2,6-dimethoxy-3,4,5-trichlorophenol (trichlorosyringol) from the bleaching of hardwood pulp (Holmbom and Lehtinen, 1980), and various chlorovanillins and protocatechualdehydes (Voss et al., 1980), are present at lower concentrations than reported in Table 1.3, at least in BKME (Kovacs et al., 1984). The presence of pentachloro-, tetrachloro- and 2,4,5-trichloro-phenol is regarded as originating from the use of slimicides or recycled waste paper (Ball et al., 1978; NCASI, 1982). The wood furnish may also contain penta- and tetrachlorophenol as a result of their application to lumber at sawmills.

Levels of chlorophenols in untreated and treated BKME are shown in Table 1.3. Values reported for chloroguaiacols include the corresponding cate-chol in some instances since the analytical method used did not distinguish these two groups of phenols. Most results reported after 1980 were obtained by a method (Coutts et al., 1979; Voss et al., 1981a) which allows distinction not only of the chlorocatechols and chloroguaiacols, but various isomers of the di-and trichloroguaiacols. For purposes of this review, the levels of di- and trichloroguaiacol include the combined levels of the isomers of each compound. As noted in Table 1.3, LC_{50} values are for 4,5-dichloro- and 4,5,6-trichloro-guaiacol.

TABLE 1.3 RANGE OF CONCENTRATIONS (μg/L) OF CHLOROPHENOLS IN UNTREATED AND BIOTREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES

Chlorophenol	96-h LC_{50} (μg/L)	BKME		BSME		References*		
		untreated	biotreated	untreated	biotreated	LC_{50}	BKME	BSME
dichlorocatechol	500-1000	12-90	1-120	-[c]	-	1	2-5	-
dichloroguaiacols	2300[a]	22-100	12-60	6-12	2-7	6	2,4,5	7
2,4-dichlorophenol	2800	9-15	2-51	4-10	2-8	6	3-5,8,9	3,7
tetrachlorocatechol	400-1500	22-420	2-240	-	2-5	1,10	2-5	3
tetrachloroguaiacol	200-1700	<10-620	<1-220	12-130	1-80	6,11,12	2-5,8,9, 13-15	7,13,14
3,4,5-trichloro-catechol	1000-1500	120-270	2-280	-	4-9	1	2-5	3
trichloroguaiacols	700-1000[b]	<10-340	<1-220	16-39	6-60	11,12	2-5,8,9, 13-17	7,13,14
2,4,6-trichloro-phenol	450-2600	<1-51	<1-61	3-764	3-30	6	2-5,8,9, 16,18	3,7,18

a 4,5-isomer.
b 4,5,6-isomer.
c Not indicated/not determined.

*References:

1. McKague (1981a)
2. Holmbom & Lehtinen (1980)
3. NCASI (1981b)
4. Kovacs et al. (1984)
5. Voss & Yunker (1983)
6. Voss et al. (1980)
7. Leuenberger et al. (1985)
8. Claeys et al. (1980)
9. NCASI (1981a)
10. Voss et al. (1981b)
11. Leach & Thakore (1975)
12. Chung et al. (1979)
13. Easty et al. (1978)
14. Leach & Chung (1980)
15. McKague (1981b)
16. Anon. (1984)
17. Ball et al. (1978)
18. NCASI (1982)

With the possible exception of tetrachloroguaiacol, concentrations of chlorophenols in untreated BKME (Table 1.3) do not exceed lethal thresholds. The cited ranges of concentrations for biotreated BKME are greater in some instances, whereas marked reductions in these constituents due to biotreatment are not apparent. The tri-and tetrachlorocatechols and guaiacols are present in higher concentrations in both untreated and treated BKME than any of the dichlorophenols or 2,4,6-trichlorophenol.

Somewhat lower levels (<30 µg/L) of 2,4-dichlorophenol, 2,4,6-tri-chlorophenol, trichloroguaiacol and tetrachloroguaiacol were reported for untreated BKME in the U.S. EPA study (Appendix). Levels in treated BKME were often below the detection limit.

The information available on levels of chlorophenols in untreated and treated kraft whole mill effluents indicates that, while concentrations of these constituents in untreated effluent are relatively low, biological treatment is not particularly effective in reducing these levels. A number of studies have reported that the chlorophenols in BKME are more resistant to bio-treatment than resin and fatty acids (Leach et al., 1977; Chung et al., 1979; Anon., 1982). Kringstad et al. (1984) reported that levels of chlorophenols are normally reduced by about 30%. The classic example for stability of chlorophenols, of course, is pentachlorophenol which is now an ubiquitous environmental contaminant (Rao, 1978; Jones, 1981, 1984). The U.S. Environmental Protection Agency has included 2,4-dichlorophenol and 2,4,6-trichlorophenol on the list of EPA Priority Pollutants because of their persistance in the environment. Nonetheless, simple calculations suggest that their combined contribution to the acute total lethal toxicity of BKME is only of the order of 0.5%.

A number of studies have been carried out to determine how levels of chlorophenols and toxicity of bleach plant effluents are related to bleaching techniques. Maximum production of chlorophenols, at 120% chlorine demand, occurred at a 1:1 ratio of chlorine and chlorine dioxide (Voss et al., 1980, 1981b,c). At higher levels of substitution, levels of chlorophenols dropped. Effects of chlorine dioxide substitution on toxicity have not been clearly established, although a slight reduction may occur (Kutney et al., 1984). Oxygen prebleaching has been claimed to reduce the quantities but not the spectrum of compounds subsequently appearing in the bleach plant effluent (Kringstad et al., 1984; Kringstad and Lindstrom, 1984). Data on the effects of oxygen prebleaching on levels of chlorophenols and toxicity of bleach plant effluent are limited (Wong et al., 1978; Anon., 1982; Nikki and Korhonen, 1983). Present information does not permit any

firm conclusions concerning the efficacy, if any, of modified bleaching techniques in reducing levels of chlorophenols in bleach plant and whole kraft effluents.

Although a number of toxic neutral compounds have been identified in kraft mill process streams, information concerning the levels of these compounds in final mill effluents is limited. Researchers have not directed any appreciable effort to these neutral compounds, since they account for only a limited fraction of total effluent toxicity. Chloroform, a volatile neutral compound with very low toxicity, is present at sublethal concentrations in BKME (Claeys et al., 1980; NCASI, 1977, 1982; Voss 1983). Typical concentrations range from 500-7000 µg/L in untreated BKME and 10-2000 µg/L in biotreated BKME. The highest concentrations of chloroform are in effluents from mills where the hypochlorite bleaching follows chlorination directly, without any intermediate caustic extraction stage (NCASI, 1983).

Leach and Chung (1980) reported that the combined levels of todomatuic acid and the neutral balsam fir extractive, juvabione, ranged from below 10 to 280 µg/L in treated BKME. Juvabione has an LC_{50} value of 1.5 µg/L for rainbow trout (Walden and Leach 1975; Leach et al., 1975), but is readily biodegraded. Chlorinated sulphones, particularly dichloromethyl methyl sulphone, have been reported in biotreated BKME at levels of about 500 µg/L (Voss, 1983). Although dichloromethyl methyl sulphone is not acutely lethal to rainbow trout at levels up to 10 000 µg/L (McKague, 1981a), it is resistant to biodegradation and little is known about its biological properties. Some evidence for its bioaccumulation has been reported (see Chapter 4). Other neutral terpenoids such as pimarol and isopimarol, camphor and fenchone (Hrutfiord et al., 1975; Holmbom and Lehtinen, 1980; Anon., 1984) have been reported in biotreated BKME, but corresponding toxicity data are not available.

1.2.2 Sulphite Effluent. Sulphite whole mill effluents contain the same resin acids, fatty acids and chlorophenols that are found in kraft mill discharges. Although fewer studies have been carried out on mills using the sulphite process, surveys by Easty et al. (1978), Howard and Leach (1978), Leach and Chung (1980) and NCASI (1981a) have shown that abietic, dehydroabietic, isopimaric, levopimaric and pimaric acid are present in untreated and treated unbleached sulphite whole mill effluent (USME) (Table 1.1). The ranges of concentrations in untreated USME are generally similar to those found in untreated UKME. As with untreated UKME, concentrations are highest for abietic (520-4840 µg/L), dehydroabietic (700-4620 µg/L) and isopimaric (100-5070 µg/L) acid. These same resin acids are also the principal ones found in biotreated USME although the

maximum reported concentrations are only 15-50% and 25%, respectively, of the corresponding values for biotreated UKME and BKME. Excepting dehydroabietic acid, the levels of non- chlorinated resin acids are distinctly lower in untreated BSME than in untreated USME, UKME or BKME. Similarly, the resin acid concentrations reported for biotreated BSME are generally lower than those found in treated USME, UKME or BKME.

Studies by the U.S. EPA (Dellinger, 1980; Appendix) also showed that abietic, dehydroabietic, isopimaric and pimaric acid were present in sulphite mill effluent. The ranges of concentrations reported for these resin acids in untreated sulphite effluent are generally lower than corresponding levels in untreated kraft effluents reported either in the same study or in Table 1.1. Abietic acid was found in concentrations up to 5200 µg/L, but all other resin acid concentrations were below 2000 µg/L. Individual levels of all resin acids in biotreated sulphite effluent were below 1000 µg/L.

The levels of fatty acids in USME and BSME (bleached sulphite whole mill effluent) shown in Table 1.2 are derived from only two studies (Easty et al., 1978; Leach and Chung, 1980). Nevertheless, the range of concentrations reported is very wide, particularly for linoleic acid (90-14 600 µg/L) and oleic acid (< 50-6780 µg/L) in untreated USME. It can be seen from Table 1.2 that biotreatment easily reduces concentrations of fatty acids to very low levels. Oleic acid was the major fatty acid reported by the U.S. EPA (Dellinger, 1980; Appendix), with concentrations ranging up to 1860 µg/L in untreated effluents from dissolving pulp operations. The same process also produced up to 1000 µg/L linoleic acid, and 800-850 µg/L epoxystearic acid. Biotreatment reduced levels of all fatty acids to less than 250 µg/L.

The combined data for whole mill sulphite effluent suggest lesser concentrations of resin acids in untreated and treated effluent than in the corresponding whole mill kraft effluents. A comparison between the two types of chemical pulping processes concerning fatty acids cannot be made, since information such as the softwood/hardwood mix used in the mill furnishes is not available. Similarly, any real difference between levels of resin acids in sulphite effluents attributable to the different pulping bases is less than the variation reported for the data which have been presented here. For example, Leach and Chung (1980) found levels of most resin acids in ammonium-base untreated BSME could be either higher or lower than in calcium-base untreated BSME.

Levels of chlorophenols reported in untreated BSME, except for 2,4,6-trichlorophenol, are below those reported for untreated BKME (Table 1.3). Dichlorophenols are all below 15 µg/L whereas trichloroguaiacols range from 16 to 39 µg/L and

tetrachloroguaiacol from 12 to 130 µg/L. Trichlorophenol is present at concentrations ranging up to 764 µg/L (NCASI, 1982), more than ten times the maximum concentration encountered in untreated BKME. Values for chlorinated catechols in untreated BSME have not been reported. Biotreated BSME contains lesser concentrations of chlorophenols than biotreated BKME (Table 1.3). The highest values, up to 80 µg/L for tetrachloroguaiacol and 60 µg/L for trichloroguaiacol, are three to four times lower than corresponding values for the same compounds in biotreated BKME. Results of the EPA study (Dellinger, 1980; Appendix) also showed that the maximum concentration for any chlorophenol in untreated BSME was 370 µg/L for 2,4,6-trichlorophenol. Levels of 2,4-dichlorophenol ranged up to 220 µg/L whereas both trichloro- and tetrachloroguaiacol were <10 µg/L. Di-and trichlorophenol were also found to be the major chlorophenols in biotreated BSME, present at up to 130 and 270 µg/L, respectively.

The results shown in Table 1.3 and in the Appendix suggest that levels of chlorophenols are generally lower in untreated and treated BSME than in BKME. The 2,4-dichloro- and 2,4,6-trichlorophenol are the predominant chlorophenols produced during the bleaching of sulphite pulp, whereas the chloroguaiacols predominate during production of kraft pulp.

The levels of chlorophenols in final whole sulphite effluent are clearly below the levels at which acute lethal toxicity would be a problem, even with inefficient biotreatment. Similarly, concentrations of the non-chlorinated phenols eugenol and trans-isoeugenol (Walden et al., 1976; LC_{50} 6500 and 3400 µg/L, respectively), in final discharged sulphite effluent are likely to be too low to constitute any major contribution to effluent toxicity. Concern with regard to these compounds must relate primarily to longer-term environmental implications.

More information is available concerning the neutral constituents of sulphite effluent than kraft effluent. The information relates principally to sulphite bleach plant effluent, although recent data have pertained to whole mill effluents. Reported chloroform levels have ranged from 40-1130 µg/L in untreated, and 8-330 µg/L in treated sulphite effluent (NCASI, 1977, 1982; Leuenberger et al., 1985). Some of these results are for effluents from the combined production of sulphite pulp and nonintegrated fine papers. Combined levels of juvabione and todomatuic acid reported by Howard and Leach (1978) and Leach and Chung (1980) ranged from 20 to 3200 µg/L in untreated sulphite effluent and from <10 to 200 µg/L in treated effluent. Juvabiol, which has an LC_{50} for rainbow trout of 1800-2000 µg/L (Walden and Leach, 1975; Leach et al., 1975), was reported by the former authors to be present in a sample of untreated BSME at approximately

1800 µg/L. Concentrations of chlorocymenes have been reported by Leuenberger et al., (1985) at levels of 55-167 µg/L in untreated and 15-18 µg/L in treated BSME. Although the toxicity of the chlorocymenes has not been reported, these compounds are chlorinated aromatics which potentially could bioaccumulate (see Chapter 4). Leuenberger et al. (1985) also reported the presence of a number of chlorinated and non-chlorinated neutral terpenoids in untreated BSME, without determining their concentration.

1.2.3 Mechanical Pulping Effluent. Mechanical pulping commonly produces pulp yields in the range of 90% (McCubbin, 1983). Appreciable degradation of the lignin does not occur as in the kraft and sulphite processes and most of the lignin remains with the pulp. Wood extractives are removed, however; hence the high concentrations of resin acids found in the studies reported in Table 1.1. Levels range from below 100 µg/L in some instances for levopimaric, neoabietic and pimaric/sandaracopimaric acid to over 15 000 µg/L for abietic, dehydroabietic and levopimaric acid. Levels in final biotreated effluent from these mills also can be high, with concentrations up to 7900 µg/L in the case of isopimaric acid. Information on levels in thermomechanical (TMP) or chemi-thermomechanical (CTMP) effluents could not be found in the published literature. Because TMP and CTMP processes employ heat and/or chemical treatment of wood chips prior to refining, the solubilization of wood extractives such as resin acids could be expected to be greater. Dellinger (1980; Appendix A) reported the following levels of resin acids in untreated effluent from groundwood - fine paper mills: abietic (11-600 µg/L), dehydroabietic (28-360 µg/L), isopimaric (0-110 µg/L), pimaric (31-150 µg/L). The low levels of resin acids found in effluents for this category of mechanical mills are undoubtedly due to the dilution represented by the papermaking effluents from these integrated operations.

Levels of fatty acids in untreated effluents from groundwood and refiner mechanical mills are not dissimilar from those in untreated BKME, and range from < 100 µg/L for linolenic acid to 9000 µg/L for linoleic acid (Table 1.2). Concentrations in biotreated effluent are below the LC_{50} values. Dellinger (1980; Appendix A) reported 17-450 µg/L oleic, 180-620 µg/L linoleic, and 120-480 µg/L linolenic acid in untreated groundwood effluent.

Toxic neutral compounds found in mechanical pulping effluent include pimarol, isopimarol, juvabione, juvabiol (Leach and Thakore, 1976), sandaracopimaradiene, dehydroabietane and 4-ρ-tolyl-1-pentanol (Rogers et al., 1979). Combined levels of juvabione and todomatuic acid which arise from pulping balsam fir (Leach and Thakore,

1976) range from 200 to 1700 µg/L in untreated effluent and from 8 to 1600 µg/L in treated effluent from groundwood mills (Leach and Chung, 1980).

Additional information on levels of resin acids, fatty acid and neutral wood extractives in TMP and CTMP effluents is required, particularly since more mills are now employing these processes. Because mechanical pulp is brightened with hydrosulphite or peroxide there are no noxious bleaching products corresponding to the chlorophenols.

1.2.4 Paper Mill Effluent. Limited information is available concerning toxic constituents and their concentrations in paper mill effluents. Integrated production of pulp and paper, as occurs in most paper mills in Canada (McCubbin, 1984), and internal recycling of washwaters complicate any analysis of available information. Many mills have reduced white water losses to a minimum, and recycle effluent to the white water system. Cooling water from paper machine areas is uncontaminated. However, toxic constituents can originate within the paper mill with the pulp stock/waste paper which constitutes the mill's raw materials. In many instances a mill's end product may be paper, but its process activity would be very predominantly chemical pulping. An example would be the category "unbleached kraft-bag" (Dellinger, 1980; Appendix). Deinking compounds, slimicides or other additives also can represent sources of potentially toxic materials in paper mill effluents.

Keith (1976) reported resin and fatty acids were present in effluent from two unbleached kraft paper mills in the state of Georgia, U.S.A. Untreated effluent contained 420-1900 µg/L abietic, 3600-4000 µg/L dehydroabietic, 770-1200 µg/L isopimaric, 450 µg/L neoabietic, 570-610 µg/L pimaric and 125-275 µg/L sandaracopimaric acid. Treated effluent (3-6 months' lagooning without aeration) contained 50 µg/L abietic, 1000-3900 µg/L dehydroabietic, 780-800 µg/L isopimaric, 500-800 µg/L pimaric and 45-110 µg/L sandaracopimaric acid. Comparable concentrations of 13-abieten-18-oic and 6,8,11,13-abietatetraen-18-oic acid and lower levels of a number of unidentified resin acids were also reported. The fatty acids, linoleic and oleic, were present at 160-230 µg/L and 120-430 µg/L, respectively, in untreated effluent, and at 100 µg/L and 80-400 µg/L in treated effluent. Easty et al. (1978) reported lower levels of resin acids in untreated paper effluent from an unbleached kraft mill. Final treated effluent from a paper mill in Wisconsin, U.S.A., was reported to contain up to 3200 µg/L dehydroabietic acid (Ball et al., 1978). The papermaking activity associated with unbleached kraft mills is usually minimal, producing coarse grades such as bag paper. Although the nature of the papermaking process at the mills involved has not been defined by the respective authors,

it is highly probable that the effluents are more characteristic of those from unbleached kraft mills than otherwise.

The survey by Dellinger (1980; Appendix) also reported levels of resin and fatty acids in a variety of paper mill effluents. Concentrations of 0-14 000 µg/L abietic, 0-6000 µg/L dehydroabietic, 0-3000 µg/L isopimaric, 0-1600 µg/L pimaric, 0-3600 µg/L linoleic, 0-330 µg/L linolenic and 0-3500 µg/L oleic acid were found for various categories of mill discharges. Average levels of individual resin acids in treated effluents were all below 350 µg/L, and fatty acids below 600 µg/L.

Traces of chlorophenols may be found in effluents from paper mills that purchase bleached pulp or use slimicides containing chlorophenols (Ball et al., 1978; Peterman et al., 1980). Tetrachloroguaiacol was reported in one effluent at 14 µg/L. Dellinger (1980; Appendix) reported 0-5 µg/L 2,4-dichlorophenol, 0-420 µg/L 2,4,6-trichlorophenol, 0-28 µg/L trichloroguaiacol and 4-16 µg/L tetrachloroguaiacol in untreated effluents. Treated effluents contained 0-3 µg/L 2,4-dichlorophenol, 0-450 µg/L 2,4,6-trichlorophenol, 10-17 µg/L trichloroguaiacol and 6-13 µg/L tetrachloroguaiacol. Deinking of recycled wastepaper also releases PCBs, which were previously used in printing inks. Levels from this source are decreasing (NCASI, 1982). Additives such as dyes, adhesives and fillers may have some inherent toxicity (Rosehart and Ozburn, 1975) but are used in small enough amounts that concentrations in effluents will be very low.

1.3 Toxic Constituents in Receiving Waters

Environmental research relating to the pulp and paper industry is increasingly concerned with the potential consequences of the discharge of sublethal levels of toxic chemicals. Although concentrations of toxic constituents in final discharged effluent may be evaluated in terms of acutely lethal effects, "safe" levels have long been recognized as those which do not stress the flora and fauna of the receiving ecosystem (see Chapters 2 and 3).

A prerequisite to defining the causative agent(s) for any toxic effect on indigenous organisms attributed to discharged pulp and paper mill effluents is the evaluation of the nature and concentration of the responsible chemicals within the receiving environment. Such determinations may enable appropriate remedial measures to be taken.

Loadings of toxic materials discharged to the environment have been greatly reduced in recent years by tightening up in-mill flows, thus eliminating losses of pulping liquors; and by the introduction, in some instances, of biotreatment systems for whole mill

effluents. Bartsch (1964) and Waldichuk (1962) provide some assessment of industry problems as viewed by investigators 20-25 years ago.

1.3.1 Freshwater.

1.3.1.1 Resin and fatty acids. Maenpaa et al. (1968) analyzed receiving water in the vicinity of kraft and sulphite pulp mills on the shore of Lake Saimaa, Finland. The mills produced spruce sulphite pulp, and pine and birch sulfate pulp. Dehydroabietic acid and small amounts of abietic, pimaric and palustric acids were found up to 6 km from the mill outfall. Details regarding effluent treatment were not given and concentrations of the resin acids in the discharges were not reported. The same geographical area was studied by Oikari et al. (1980) after production of sulphite pulp was discontinued and primary and secondary wastewater treatment were installed. Levels of resin and fatty acids in composite water samples representative of the whole water column (total depth from 3-5 m) were highest near the mill outfall, and close to detection limits 3.5 km away (Tables 1.4 and 1.5). Abietic, dehydroabietic, isopimaric and pimaric were the dominant resin acids present in this receiving water. Unsaturated fatty acids decreased to background levels of a few micrograms per litre within 3.5 km of the outfall (Table 1.5). The preceding data and those presented subsequently in this report for other Scandinavian lakes and for the coastal waters of the Gulf of Bothnia are not necessarily representative of Canadian receiving-water situations, where the industry is much more dispersed and it is rare that two or more major mills discharge concurrently and in proximity into the same receiving waterbody. Indeed, the degree of effluent dilution and flushing for many Scandinavian receiving-water sites is notoriously poor. Attention is given to these overseas studies due to their comprehensive nature and the lack of extensive (similar) receiving-water studies for North American sites.

Fox (1976, 1977) analyzed the levels of resin and fatty acids in the effluent plume from a combined bleached kraft and groundwood mill which discharged clarified (primary-treated) effluent into Nipigon Bay on Lake Superior. Trace levels (usually <10 µg/L) of isopimaric, sandaracopimaric, dehydroabietic, abietic, 6,8,11,13-abietatetraen-18-oic acid and 7-oxodehydroabietic acid were identified in the plume at distances of more than 2 km from the mill. Dehydroabietic acid decreased in a dilution-related manner from an average of 3700 µg/L at the mill outfall to background levels of approximately 40 µg/L or less at a distance of 2 km (Fox, 1976). According to Fox (1976), dehydroabietic acid was "the single major effluent component which shows a tendency to reach an equilibrium concentration in the receiving water at significant distances from

TABLE 1.4 CONCENTRATIONS OF RESIN ACIDS IN FRESHWATER RECEIVING SITES AT VARIOUS DISTANCES FROM MILL OUTFALL(s)

Resin acid	Effluent type(s)	Effluent treatment	Distance from outfall(s) (km)	Receiving-water concentration (µg/L)	Reference
abietic acid	BKME	secondary*	0.1 0.8 3.5 6.0	1-114 2-7 <0.5 <0.5-1	Oikari et al., 1980
dehydroabietic acid	BKME	secondary	0.1 0.8 3.5 6.0	6-600 4-10 <0.5-1 1-3	Oikari et al., 1980
dehydroabietic acid	BKME + mechanical	primary	0.1-0.5 0.6-1.0 1.1-2.0 2.1-3.0	290-1930 1.8-295 12-380 35-40	Fox, 1976
dihydroabietic + sandaraco-pimaric	BKME	secondary	0.1 0.8 3.5 6.0	<0.5-34 <0.5 <0.5 <0.5	Oikari et al., 1980
isopimaric	BKME	secondary	0.1 0.8 3.5 6.0	2-79 2-3 <0.5-1 <0.5-1	Oikari et al., 1980
neoabietic	BKME	secondary	0.1 0.8 3.5 6.0	1-10 <1 <0.5 <0.5	Oikari et al., 1980
pimaric	BKME	secondary	0.1 0.8 3.5 6.0	1-67 2 <0.5 <0.5-2	Oikari et al., 1980

* 24-h retention in aerated lagoon.

TABLE 1.5 CONCENTRATIONS OF FATTY ACIDS IN FRESHWATER RECEIVING SITES AT VARIOUS DISTANCES FROM THE MILL OUTFALL

Resin acid	Effluent type(s)	Effluent treatment	Distance from outfall(s) (km)	Receiving-water concentration (µg/L)	Reference
oleic acid	BKME*	secondary*	0.1 0.8 3.5 6.0	12-114 8-14 2-15 1-6	Oikari et al., 1980
linoleic	BKME	secondary	0.1 0.8 3.5 6.0	2-54 3-10 <0.5-1 <0.5-2	Oikari et al., 1980
linolenic	BKME	secondary	0.1 0.8 3.5 6.0	<3-25 <1-<2 <0.5 <0.5	Oikari et al., 1980

* 24-h retention in aerated lagoon.

the source". Oleic and linoleic acid were also detected in the plumes but at levels equivalent to background. Brownlee and Strachan (1977) found trace levels (0.1-2.2 µg/L) of 7-oxodehydroabietic and sandaracopimaric acid in water samples collected outside the effluent plume from the same mill, up to 4.7 km from the outfall. Similarly, low levels of dehydroabietic acid were found outside the plume.

1.3.1.2 Chlorophenols. Salkinoja-Salonen et al. (1981) reported that chlorophenols were present in surface and bottom waters of a lake receiving effluent from two bleached kraft pulp mills in Finland. Respective ranges of 2,4,6-trichlorophenol, trichloroguaiacols and 2,6-dimethoxy-3,4,5-trichlorophenol were 0.1-13.1, 0.1-3.1, and 0-12.8 µg/L at approximately 1 km distant from the mills; and 0.2-3.0, 0.1-1.0, and 0.02-0.6 µg/L, 4-5 km from the mills (Table 1.6). Chlorocatechols (3,4-dichloro-, 3,4,5-trichloro- and tetrachloro-) and 2,4-dichlorophenol were also identified at the same sites but low recoveries negated quantification.

Chlorophenols were detected by Voss et al. (1981a) in a Canadian river up to 110 km downstream from a softwood bleached kraft pulp mill. More recently, Voss and Yunker (1983) measured the concentrations of various chlorophenols in the Fraser River (B.C.) at a site appproximately 3 km downstream (below the Nechako River confluence) of the nearest of three adjacent mills discharging biotreated BKME, and at a second site 50 km below a fourth mill (farther downstream) also discharging biotreated BKME. Of the chlorophenolic compounds measured, concentrations of trichloroguaiacols were highest (1.0 µg/L at the 3-km site; 0.2 µg/L at 50 km) (Table 1.6). The predominent trichloroguaiacol at each site was the 3,4,5-isomer. Concentrations of tetrachloroguaiacol, trichlorocatechol (3,4,5-) and tetrachlorocatechol at the Fraser River site 3 km downstream were 0.3, 0.4 and 0.8 µg/L, respectively. Lower ($\leq$0.1 µg/L) but detectable concentrations of these three compounds were found at the 50-km downstream site (Table 1.6). Levels of dichlorophenol, trichlorophenol and dichloroguaiacol detected at each site did not exceed 0.1 µg/L (Voss and Yunker, 1983).

1.3.1.3 Other organic constituents. The literature contains almost no information on the concentrations of other mill-derived toxicants in freshwater receiving environments. Trace levels (2-6 µg/L) of chloroform were reported approximately 2.5 km downstream from a bleached kraft pulp mill in Alberta (Anon., 1984). Levels of chloroform are detectable short distances downstream from any pulp mill employing chlorine bleaching and, as will be reported subsequently, can be used as a tracer for studying effluent dispersion patterns. The logical source of other compounds such as the chloromethylsul-

TABLE 1.6 CONCENTRATIONS OF CHLOROPHENOLS IN FRESHWATER RECEIVING SITES AT VARIOUS DISTANCES FROM MILL OUTFALL(s)

Chlorophenol	Effluent		Distance from outfall(s) (km)	Receiving-water concentration (µg/L)	Reference
	type	treatment			
4,5-dichloroguaiacol	BKME	secondary	3[a]	0.08	Voss & Yunker, 1983
4,5-dichloroguaiacol	BKME	secondary	50	ND[b]	Voss & Yunker, 1983
2,4-dichlorophenol	BKME	secondary	3	0.1	Voss & Yunker, 1983
2,4-dichlorophenol	BKME	secondary	50	0.02	Voss & Yunker, 1983
2,6-dimethoxy-3,4,5-trichlorophenol	BKME	-[c]	1	0-12.8	Salkinoja-Salonen et al., 1981
	BKME	-	4-5	0.02-0.6	Salkinoja-Salonen et al., 1981
tetrachlorocatechol	BKME	secondary	3	0.8	Voss & Yunker, 1983
tetrachlorocatechol	BKME	secondary	50	0.02	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	secondary	3	0.3	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	secondary	50	0.09	Voss & Yunker, 1983
trichlorocatechol	BKME	secondary	3	0.4	Voss & Yunker, 1983
trichlorocatechol	BKME	secondary	50	0.009	Voss & Yunker, 1983
trichloroguaiacols	BKME	-	1	0.1-3.1	Salkinoja-Salonen et al., 1981
trichloroguaiacols	BKME	-	4-5	0.1-1.0	Salkinoja-Salonen et al., 1981
trichloroguaiacols	BKME	secondary	3	1.0	Voss & Yunker, 1983
trichloroguaiacols	BKME	secondary	50	0.2	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	-	1	0.1-13.1	Salkinoja-Salonen et al., 1981
	BKME	-	4-5	0.2-3.0	Salkinoja-Salonen et al., 1981
2,4,6-trichlorophenol	BKME	secondary	3	0.09	Voss & Yunker, 1983
	BKME	secondary	50	0.04	Voss & Yunker, 1983

a Below a river junction.
b Not detectable.
c Not indicated.

phones, which have been found in tissues of fish collected near pulp mills (see Chapter 4), are the pulp mills themselves; so presumably these compounds do exist in some concentration in adjacent receiving waters.

1.3.2 Estuarine/Marine Waters.

1.3.2.1 Resin and fatty acids. No information was found on levels of resin and fatty acids in estuarine/marine receiving waters.

1.3.2.2 Chlorophenols. Levels of chlorophenols in estuarine/marine receiving waters near pulp mills have been determined recently by scientists in both Sweden and Canada. The extensive program of environmental research undertaken recently in Sweden (Anon. 1982) determined that chlorophenols were present in an area characterized by brackish water with limited replacement (Table 1.7). Concentrations of 0.12-0.28 µg/L 2,4-dichlorophenol, 0.45-0.90 µg/L 2,4,6-trichlorophenol, 1.04-2.0 µg/L trichloroguaiacols and 0.45-1.3 µg/L tetrachloroguaiacol were present in surface water 2 km from the mill; and 0.04-0.26 µg/L, 0.14-0.36 µg/L, 0.14-0.73 µg/L and 0.06-0.4 µg/L, respectively, at a distance of 6 km (Table 1.7).

Voss and Yunker (1983) reported levels of chlorophenols in receiving waters adjacent to two coastal mills in British Columbia which discharge untreated bleached kraft mill effluent to Howe Sound and Stuart Channel (Table 1.7). Chlorocatechols were present in concentrations up to 0.08 µg/L within 2.6 km of one of the mills, and up to 0.05 µg/L within 4.8 km of the second mill. Beyond these distances, chlorocatechols were not detected. Chloroguaiacols were found in concentrations ranging up to 0.17 µg/L within 12 km of one mill and up to 0.45 µg/L within 7 km of the second mill. Levels of 2,4-dichlorophenol and 2,4,6-trichlorophenol ranged from background levels to 0.07 µg/L over similar distances. The proportion of chlorocatechols relative to other chlorophenols was much lower in the receiving water relative to the mill effluent in both cases, indicating different removal rates for these two groups of phenols. Depth profiles were different at each site and this was attributed to a difference in the location of the diffuser at each mill and to differences in physical oceanography and tidal patterns in each area.

Xie et al. (1984) studied levels of chlorophenols in estuarine waters off the east coast of Sweden. The distribution pattern of the effluent was determined by analyzing chloroform levels in the receiving waters, a technique reported previously by other Swedish researchers for tracking effluent plumes (Fogelqvist et al., 1982). Approximately 2 km from the mill, chlorophenol levels ranged from 0.11-0.12 µg/L for 2,4-

TABLE 1.7 CONCENTRATIONS OF CHLOROPHENOLS IN ESTUARINE/MARINE RECEIVING-WATERS AT VARIOUS DISTANCES FROM MILL OUTFALLS

Chlorophenol	Effluent type	Effluent treatment	Distance from outfall (km)	Receiving-water concentration (µg/L)	Reference
4,5-dichlorocatechol	BKME	untreated	0.25 0.72-7.0	0.006 ND[a]	Voss & Yunker, 1983
4,5-dichloroguaiacol	BKME	untreated	0.16 1.7-12.5	0.05 ND	Voss & Yunker, 1983
4,5-dichloroguaiacol	BKME	untreated	0.25-6.5 6.8-7.0	ND-0.02 ND	Voss & Yunker, 1983
2,4-dichlorophenol	BKME	-[b]	2 6	0.12-0.28 0.04-0.26	Anon., 1982
2,4-dichlorophenol	BKME	untreated	0.16-4.6 8-12.5	0.008-0.04 -[c]	Voss & Yunker, 1983
2,4-dichlorophenol	BKME	untreated	0.25-7.0	0.004-0.05[d]	Voss & Yunker, 1983
2,4-dichlorophenol	BKME	-	2-8	0.002-0.12	Xie et al., 1984
tetrachlorocatechol	BKME	untreated	0.16-2.6 3.2-12.5	0.005-0.08 ND	Voss & Yunker, 1983
tetrachlorocatechol	BKME	untreated	0.25-4.8 5.6-7.0	ND-0.05 ND	Voss & Yunker, 1983
tetrachlorocatechol	BKME	untreated	2-13	<0.001-1.34	Xie et al., 1984
tetrachloroguaiacol	BKME	-	2 6	0.45-1.30 0.06-0.40	Anon., 1982
tetrachloroguaiacol	BKME	untreated	0.16-10 12.0-12.5	0.005-0.05 -[c]	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	untreated	0.25-7.0	0.006-0.35[e]	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	2-15	<0.001-1.3	Xie et al., 1984
trichlorocatechol	BKME	untreated	0.16-2.6 3.2-12.5	ND-0.02 ND	Voss & Yunker, 1983
trichlorocatechol	BKME	untreated	0.25-2.1 2.4-7.0	0.003-0.05 ND	Voss & Yunker, 1983
trichloroguaiacols	BKME	-	2 6	1.04-2.0 0.14-0.73	Anon., 1982
trichloroguaicols	BKME	untreated	0.16-12 12.5	0.004-0.17 -[c]	Voss & Yunker, 1983
trichloroguaiacols	BKME	untreated	0.25-7	0.006-0.45	Voss & Yunker, 1983
trichloroguaiacols	BKME	-	2-15	<0.001-1.77	Xie et al., 1984
2,4,6-trichlorophenol	BKME	-	2 6	0.45-0.90 0.14-0.36	Anon., 1982
2,4,6-trichlorophenol	BKME	untreated	0.16-12 12.5	ND-0.038 -[c]	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	untreated	0.25-7.0	0.003-0.07[f]	Voss & Yunker, 1983

a Not detected in composite sample.
b Not indicated.
c Background levels.
d Background samples contained 0.01 µg/L.
e Background samples contained 0.006 µg/L.
f Background samples contained 0.009-0.01 µg/L.

dichlorophenol, and from 0.93-1.77 µg/L for the trichloroguaiacols. Concentrations of other chlorophenolic compounds determined at this site were intermediate between these ranges. Between 2 and 10 km downstream from the mill, these concentrations decreased sharply; although detectable amounts of some chlorophenols could be found at a distance of 15 km. Xie and co-workers (1984) also determined the "half distances"; that is, the distance down-current within the distribution pattern for each compound, over which the measured concentration was diminished by 50 percent. "Half distances" for 2,4,6-trichlorophenol, 3,4,5-trichloroguaiacol, tetrachloroguaiacol and tetrachlorocatechol were between 0.5 and 1.1 km.

It is evident from the three studies cited above that sublethal concentrations of chlorophenols can be present in receiving water near bleached pulp mills; particularly where effluents are not biotreated. Their slow degradation rates, as presented previously, create a potential for dispersal well beyond the immediate vicinity of the mill outfall.

1.3.2.3 Other organic constituents. As for freshwater situations, limited information exists on levels of other organic constituents in estuarine/marine waters. Chloroform is one of the few compounds for which information is available and, as mentioned above, chloroform concentrations can be used as a means of tracing effluent plumes. Xie et al., (1984) reported that, for the mill they studied, levels of chloroform within receiving waters decreased from 5.4-15 µg/L at approximately 2 km, to 0.02 µg/L at a distance of 15 km. Detection in aquatic organisms of other compounds such as chlorinated cymenes and sulphones is the sole evidence for the presence of these compounds in receiving waters (see Chapter 4). Indeed, where bioaccumulation in the fat tissues in aquatic organisms does occur, this is a considerably more sensitive technique for detection of environmental contaminants. Where it does not occur, their presence at these concentration levels is of no significance.

1.4 Toxic Constituents in Sediments

Organic compounds which have low solubilities in water can be removed by suspended solids or sediment by surface adsorption phenomena. Factors such as surface area and sediment composition affect the adsorption process. While any detailed discussion of the mechanisms of removal of organic material by sediment is beyond the scope of this review, it can be stated that adsorption is generally greater when sediment particles are smaller (i.e., have a large surface area) and have a high organic content, as in the case of pulp mill fibres. Effects such as chelation and pH changes may influence the binding of phenols to sediment (Schellenberg et al., 1984). Most receiving-water

sampling studies now include sediment sampling as an integral part of the program. Sediments serve as repositories for pollutants and the information derived regarding levels of organics in sediment relative to water provides considerable insight with respect to their bioavailability and potential toxicity.

Determining the relative levels of toxic constituents in water and sediment from the same area also permits predictions to be made regarding which biota (i.e., bottom or surface dwelling) will be affected to the greatest extent. The limited information available concerning levels of toxic constituents in sediment collected near pulp and paper mills is summarized here.

1.4.1 Freshwater Sediment.

1.4.1.1 Resin and fatty acids. Dehydroabietic acid is the major resin acid reported in freshwater sediment. Fox (1976) reported levels of 100 µg/g in surface sediment near the outfall from a bleached kraft and groundwood mill discharging untreated effluent into Nipigon Bay (Lake Superior). A study of its distribution pattern showed elevated levels were present along a deep bottom channel, with 10 µg/g or about 10 times background still being present 15 km from the discharge. Brownlee and Strachan (1977) analyzed sediment near the same mill and found levels of 150 µg/g dehydroabietic acid, 1 km from the discharge; and 0.1-2 µg/g (i.e., background levels) at 3-7 km. In a more detailed study of distribution within the sediment, Brownlee et al. (1977) reported that abietic, pimaric, an abietanoic and an abietenoic acid were present in the surficial layer of sediment near the same mill. Abietic acid was suggested as a possible source of the latter two compounds. Levels of fatty acids in sediment were not reported in this or other environmental studies.

1.4.1.2 Chlorophenols. Paasivirta et al. (1980) analyzed levels of chlorophenols in lake sediments near pulp mills in Finland. Tetrachlorocatechol was the main chlorophenol found in sediment collected 5 km downstream from the mill (Table 1.8). The concentration was roughly 10 times that of tetrachloroguaiacol, trichloroguaiacol and 2,4,6-trichlorophenol. Traces of the same compounds (0.003-0.01 µg/g) were present 40 km downstream from the same mill, at a point which was also about 15 km downstream from the city of Jyvaskyla. Levels at the 40-km site were at least a factor of two above background levels in samples collected at a remote site. Based on statistical correlations of the concentrations of each chlorophenol, Paasivirta et al. (1980) concluded that, while tetrachloroguaiacol, trichloroguaiacol and 2,4,6-trichlorophenol clearly originated from

TABLE 1.8 CONCENTRATIONS OF CHLOROPHENOLS IN FRESHWATER SEDIMENT AT VARIOUS DISTANCES FROM PULP AND PAPER MILL OUTFALLS

Chlorophenol	Effluent		Distance from outfall (km)	Concentration (μg/g)	Reference
	type	treatment			
4,5-dichlorocatechol	BKME	secondary	50	ND[a]-0.004	Voss & Yunker, 1983
4,5-dichloroguaiacol	BKME	secondary	50	ND-0.006	Voss & Yunker, 1983
tetrachlorocatechol	-[b]	-	5 40	0.35 0.01	Paasivirta et al., 1980
tetrachlorocatechol	-	-	2-3	2-6	Salkinoja-Salonen et al., 1981
tetrachlorocatechol	BKME	secondary	50	0.004-0.01	Voss & Yunker, 1983
tetrachloroguaiacol	-	-	5 40	0.05 0.006	Paasivirta et al., 1980
tetrachloroguaiacol	BKME	secondary	50	0.0009-0.003	Voss & Yunker, 1983
3,4,5-trichloro-catechol	BKME	secondary	50	0.002	Voss & Yunker, 1983
trichloroguaiacols	-	-	5 40	0.04 0.003	Paasivirta et al., 1980
trichloroguaiacols	BKME	secondary	50	0.0007-0.0008	Voss & Yunker, 1983
2,4,6-trichloro-phenol	-	-	5 40	0.03 0.01	Paasivirta et al., 1980
2,4,6-trichloro-phenol	BKME	secondary	50	ND-0.0007	Voss & Yunker, 1983

a Not detected.
b Not indicated.

the mill, tetrachlorocatechol was probably also a metabolite of pentachlorophenol and tetrachloroguaiacol. No water samples were analyzed in this study.

In another study in Finland, Salkinoja-Salonen et al. (1981) also found that tetrachlorocatechol was the major chlorophenol in freshwater sediment near pulp mills. Combined levels of tri- and tetrachlorocatechol ranged from 6 µg/g sediment in the surface layer of sediment to less than 1 µg/g at depths below 10 cm. Since the levels of tetrachlorocatechol in mill effluent were very low, these researchers suggested that other chlorinated compounds in the sediment were converted to tetrachlorocatechol.

In the study by Voss and Yunker (1983), levels of a variety of chlorophenols in sediment collected 50 km downstream from the nearest mill discharging biotreated BKME to the Fraser River were reported (Table 1.8). Tetrachlorocatechol was present at 0.004-0.01 µg/g sediment, the highest of any of the chlorophenols reported. Total chlorocatechols ranged from 0.01-0.02 µg/g while total chloroguaiacols were approximately 0.01 µg/g, and 2,4,6-trichlorophenol ranged from below the detection limit to 0.0007 µg/g.

1.4.1.3 Other organic constituents. Elevated levels of polynuclear aromatic hydrocarbons, plasticizers and chlorinated organics have been found in sediments in industrialized areas. Polychlorinated biphenyls (PCBs) appear to be the major group of compounds in sediments whose presence could be related to the pulp and paper industry. PCB levels in sediment from the Lower Fox River in Wisconsin (Sullivan et al., 1983), which receives a heavy effluent load from waste paper recycling plants, ranged from 0.1-100 µg/g. Since the background level was <0.1 µg/g, elevated levels of PCBs were clearly present. As mentioned earlier, the PCB content of wastepaper has declined (NCASI, 1982).

1.4.2 Estuarine/Marine Sediment.

1.4.2.1 Resin and fatty acids. Dehydroabietic acid was found in sediment samples collected from the Saint John River estuary near bleached kraft and groundwood pulp mills (Bacon and Silk, 1978). Levels ranged from 7.4-25 µg/g sediment. Details concerning effluent treatment were not reported. Kinae et al. (1981) analyzed sediment collected at three points on the coast of Japan near pulp and paper mills (effluent treatment not indicated). Dehydroabietic acid was identified in sediment at one of the locations but no details were given on the concentration or distance from the mill. Levels of fatty acids have not been reported, mainly because of the natural occurrence of these materials in the environment.

1.4.2.2 Chlorophenols. Kinae et al. (1981) reported that 2,4,6-trichloro-phenol and tetrachloroguaiacol were present in the sediment sample mentioned above. As with dehydroabietic acid, concentrations and sampling details were not given. Swedish scientists measured levels of chlorophenols in estuarine/marine sediment near a number of coastal mills (Anon., 1982). Chloroguaiacols were not detectable in surficial sediment samples collected from one marine area which had good flushing. However, sediment from a bay in the Baltic Sea contained measurable quantities of 3,4,5-trichloroguaiacol and tetrachloroguaiacol. Most samples of surficial (0-4 cm) sediment contained 0.01-0.1 µg/g of each chlorophenol, lower concentrations being found at a depth of 4-8 cm. In these studies, levels of chlorophenols were generally elevated above background levels only within a few kilometres of the mills.

Concentrations of a number of chlorophenolic compounds in estuarine/marine sediments sampled at distances of up to 15 km from mills discharging BKME (untreated or treatment unidentified) have been reported (Table 1.9). For the two B.C. coastal mill sites examined, the highest sediment concentrations found were for the trichloroguaiacols ($\leq$0.01 µg/g) and tetrachlorocatechol (0.007 µg/g). The highest concentration of trichlorocatechol and tetrachloroguaiacol detected in surficial sediments was 0.003 µg/g. Concentrations of these chlorophenolics were not related consistently to distance from either mill outfall. Other chlorophenolic compounds measured were below detection limits or present in trace amounts only (Table 1.9). Voss and Yunker (1983) noted that the chlorinated catechols, often present only in minor amounts in the receiving water samples, were major components of the effluent constituents identified in sediment samples. These researchers speculated that these chlorinated catechols may have been formed by the degradation of other chlorinated organics or they may have preferentially precipitated from the water column. The maximum concentrations of trichlorocatechols (3.0 µg/g), tetrachlorocatechol (0.8 µg/g), trichloroguaiacols (0.3 µg/g) and tetrachloroguaiacol (0.1 µg/g) reported by Swedish investigators for samples of coastal sediments collected within the vicinity of bleached kraft mills were appreciably higher than those found in B.C. coastal waters (Xie, 1983; Xie et al., 1984) (Table 1.9). As with the Canadian studies, the concentrations of other chlorophenolic compounds measured in these sediments were normally below the limit of detection or present in trace amounts only.

1.4.2.3 Other organic constituents. There is very little published information on levels of other pulp mill-derived organic constituents in estuarine/marine sediment.

TABLE 1.9 CONCENTRATIONS OF CHLOROPHENOLS IN ESTUARINE/MARINE SEDIMENT AT VARIOUS DISTANCES FROM PULP AND PAPER MILL OUTFALLS

Chlorophenol	Effluent type	Effluent treatment	Distance from outfall (km)	Concentration (μg/g)	Reference
4,5-dichlorocatechol	BKME	untreated	0.25-2.4	0.0003-0.0004	Voss & Yunker, 1983
	BKME	untreated	3.6-6.8	ND[a]	
4,5-dichloroguaiacol	BKME	untreated	0.16-4.0	ND-0.002	Voss & Yunker, 1983
	BKME	untreated	4.6-12.5	ND	Voss & Yunker, 1983
4,5-dichloroguaiacol	BKME	-[b]	2	0.007	Xie, 1983
			10	ND	Xie, 1983
4,5-dichloroguaiacol	BKME	-[b]	2-5	0.004-0.05	Xie et al., 1984
2,4-dichlorophenol	BKME	-	2	0.0009	Xie, 1983
	BKME	-	10	ND	Xie, 1983
2,4-dichlorophenol	BKME	-	2-10	<0.0002-0.02	Xie et al., 1984
tetrachlorocatechol	BKME	untreated	0.16-12.5	ND-0.003	Voss & Yunker, 1983
tetrachlorocatechol	BKME	untreated	0.25-6.8	0.0009-0.007	Voss & Yunker, 1983
tetrachlorocatechol	BKME	-	2	0.01	Xie, 1983
tetrachlorocatechol	BKME	-	10	0.001	Xie, 1983
tetrachlorocatechol	BKME	untreated	2-15	0.0004-0.77	Xie et al., 1984
tetrachloroguaiacol	BKME	untreated	0.16-12.5	ND-0.002	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	untreated	0.25-6.8	0.0006-0.003	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	2	0.02	Xie, 1983
	BKME	-	10	0.001	Xie, 1983
tetrachlorocatechol	BKME	-	2-15	<0.00005-0.136	Xie et al., 1984
trichlorocatechols	BKME	untreated	0.16-12.5	ND-0.0009	Voss & Yunker, 1983
trichlorocatechols	BKME	untreated	0.25-6.8	0.0002-0.003	Voss & Yunker, 1983
trichlorocatechols	BKME	-	2	0.08	Xie, 1983
trichlorocatechols	BKME	-	10	0.005	Xie, 1983
trichlorocatechols	BKME	-	2-15	0.0009-3.04	Xie et al., 1983
trichloroguaiacols	BKME	untreated	0.16-12.5	0.0009-0.01	Voss & Yunker, 1983
trichloroguaiacols	BKME	untreated	0.25-6.8	0.002-0.007	Voss & Yunker, 1983
trichloroguaiacols	BKME	-	2	0.03	Xie, 1983
	BKME	-	10	0.001	Xie, 1983
trichloroguaiacols	BKME	-	2-15	0.00009-0.31	Xie et al., 1984
2,4,6-trichloro-phenol	BKME	untreated	0.16-12.5	ND-0.001	Voss & Yunker, 1983
	BKME	untreated	0.25-6.8	0.0002-0.0008	Voss & Yunker, 1983
2,4,6-trichloro-phenol	BKME	-	2	0.0004	Xie, 1983
	BKME	-	10	0.0001	Xie, 1983
2,4,6-trichloro-phenol	BKME	-	2-10	<0.00005-0.002	Xie et al., 1984

[a] Not detected.
[b] Not indicated.

Yamaoka (1979) reported diterpenoid hydrocarbons of the abietane type were present in surface sediment near a coastal mill in Japan. Kinae et al. (1981) identified juvabione in sediment near a mill, although no link with the mill was established.

1.5 References

Anon. 1982. Environmentally Harmonized Production of Bleached Pulp. Final Report (in Swedish). Swedish Forest Products Research Laboratory, Stockholm, Sweden.

Anon. 1984. Toxicity and Environmental Chemistry of Wastewater from Proctor and Gamble Cellulose Ltd. (Grande Prairie). Draft report. Alberta Environmental Centre Research Report AECV84-R6. Vegreville, Alberta.

Bacon, G.B. and P.J. Silk. 1978. Bioaccumulation of Toxic Compounds in Pulp-mill Effluents by Aquatic Organisms in Receiving Waters. CPAR Rep. No. 675-1. Environment Canada. Ottawa, Ontario.

Ball, J., F. Priznar and P. Peterman. 1978. Investigation of Chlorinated and Nonchlorinated Compounds in the Lower Fox River Watershed. U.S. Environmental Protection Agency Rep. EPA-905/3-78-004, Chicago, IL.

Bartsch, A.F. 1964. Study of pulp and paper mill pollution in Puget Sound, pp. 43-64. In E.A. Pearson, ed. Advances in Water Pollution Research. Vol. 3. Pergamon Press. New York, NY.

Beeland, G.V., D.K. Whitenight and K.G. Barnhill. 1979. Environmental Impact Assessment Guidelines for New Source Pulp and Paper Mills. U.S. Environmental Protection Agency Rep. EPA-130/6-79-002. Washington, D.C.

Brouzes, R.J.P. 1976. Fish toxicity with specific reference to the pulp and paper industry, pp. 81-124. In Proceedings of Seminars on Water Pollution Abatement Technology in the Pulp and Paper Industry. Environment Canada Rep. EPS-3-WP-76-4. Water Pollution Control Directorate. Ottawa, Ontario.

Brownlee, B. and W.M.J. Strachan. 1977. Distribution of some organic compounds in the receiving waters of a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 830-837.

Brownlee, B., M.E. Fox, W.M.J. Strachan and S.R. Joshi. 1977. Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. J. Fish. Res. Board Can. 34: 838-843.

Casey, J.P. (ed.). 1980. Pulp and Paper Chemistry and Chemical Technology. Third ed. Vol. I - III. John Wiley & Sons. New York, NY.

Chung, L.T.K., H.P. Meier and J.M. Leach. 1979. Can pulp mill effluent toxicity be estimated from chemical analyses? TAPPI 62: 71-74.

Claeys, R.R., L.E. LaFleur and D.L. Borton. 1980. Chlorinated organics in bleach plant effluents of pulp and paper mills, pp. 335-345. In R.J. Jolley, ed. Water Chlorination, Environmental Impact and Health Effects, Vol. 3. Ann Arbor Science Publ. Inc., Ann Arbor, MI.

Coutts, R.T., E.E. Hargesheimer and F.M. Pasutto. 1979. Gas chromatographic analysis of trace phenols by direct acetylation in aqueous solution. J. Chromatog. 179: 291-299.

Davis, J.C. and R.A.W. Hoos. 1975. Use of sodium pentachlorophenate and dehydroabietic acid as reference toxicants for salmonid bioassays. J. Fish. Res. Board Can. 32: 411-416.

Dellinger, R.W. 1980. Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper and Paperboard and the Builders' Paper and Board Mills. U.S. Environmental Protection Agency Rep. EPA-440/1-80/025-b. Washington, D.C.

Easty, D.B., L.G. Borchardt and B.A. Wabers. 1978. Removal of Wood-derived Toxics from Pulping and Bleaching Wastes. U.S. Environmental Protection Agency Rep. EPA-600/2-78-013. Cincinnati, OH.

Fogelqvist, E., B. Josefsson and C. Roos. 1982. Halocarbons as tracer substances in studies of the distribution patterns of chlorinated waters in coastal areas. Environ. Sci. Technol. 16: 479-482.

Fox, M.E. 1976. Fate of selected organic compounds in the discharge of kraft paper mills into Lake Superior, pp. 641-659. In L.H. Keith, ed. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science Publ. Inc. Ann Arbor, MI.

Fox, M.E. 1977. Persistence of dissolved organic compounds in kraft pulp and paper mill effluent plumes. J. Fish. Res. Board Can. 34: 798-804.

Holmbom, B. and K-J. Lehtinen. 1980. Acute toxicity to fish of kraft pulp mill waste waters. Pap. Puu 62: 673-684.

Howard, T.E. and J.M. Leach. 1973. Identification and Treatment of Toxic Materials in Mechanical Pulping Effluents. CPAR Rep. No. 149-1. Environment Canada, Ottawa, Ontario.

Howard, T.E. and J.M. Leach. 1978. Identification of Toxic Materials in Sulphite Pulp Mill Effluents. CPAR Rep. No. 407-3. Environment Canada, Ottawa, Ontario.

Hrutfiord, B.F., T.S. Friberg, D.F. Wilson and J.R. Wilson. 1975. Organic compounds in aerated stabilization basin discharge. TAPPI 58: 98-100.

Hutchins, F.E. 1979. Toxicity of Pulp and Paper Mill Effluent. A Literature Review. U.S. Environmental Protection Agency Rep. EPA-600/3-79-013. Corvallis, OR.

Jones, P.A. 1981. Chlorophenols and Their Impurities in the Canadian Environment. Envir. Canada, Econ. Tech. Rev. Rep. EPS 3-EC-81-2. Ottawa, Ontario.

Jones, P.A. 1984. Chlorophenols and Their Impurities in the Canadian Environment: 1983 Supplement. Envir. Canada, Econ. Tech. Rev. Rep. EPS 3-EP-84-3. Ottawa, Ontario.

Keith, L. 1976. Identification of organic compounds in unbleached treated kraft paper mill wastewaters. Environ. Sci. Technol. 10: 555-564.

Kinae, N., T. Hashizume, T. Makita, I. Tomita, I. Kimura and H. Kanamori. 1981. Studies on the toxicity of pulp and paper mill effluents - I. Mutagenicity of the kraft sediment samples derived from kraft paper mills. Water Res. 15: 17-24.

Kovacs, T.G., R.H. Voss and A. Wong. 1984. Chlorinated phenolics of bleached kraft mill origin. Water Res. 18: 911-916.

Kringstad, K.P. and K. Lindstrom. 1984. Spent liquors from pulp bleaching. Environ. Sci. Technol. 18: 236A-248A.

Kringstad, K.P., L.G. Stockman and L.M. Stromberg. 1984. The nature and environmental significance of spent bleach liquor toxicants: present state of knowledge. J. Wood Chem. Technol. 4: 389-404.

Kutney, G.W., H.H. Holton, D.H. Andrews, J.R. du Manoir and G.P. Donnini. 1984. A review of low versus high ClO_2 substitution in the C stage: Part II: Effluent properties. Pulp Paper Can. 85: T95-102.

Leach, J.M. and L.T.K. Chung. 1980. Development of a Chemical Toxicity Assay for Pulp Mill Effluents. Rep. EPA-600/2-80-206. U.S. Environmental Protection Agency, Cincinnati, OH.

Leach, J.M. and A.N. Thakore. 1975. Isolation and identification of constituents toxic to juvenile rainbow trout (Salmo gairdneri) in caustic extraction effluents from kraft pulp mill bleach plants. J. Fish. Res. Board Can. 32: 1249-1257.

Leach, J.M. and A.N. Thakore. 1976. Toxic constituents in mechanical pulping effluents. TAPPI 59: 129-132.

Leach, J.M. and A.N. Thakore. 1977. Compounds toxic to fish in pulp mill waste streams. Prog. Water Technol. 9: 787-798.

Leach, J.M., J.C. Mueller and C.C. Walden. 1977. Biodegradability of toxic compounds in pulp mill effluents. Trans. Tech. Section Can. Pulp Paper Assoc. 3: 126-130.

Leach, J.M., A.N. Thakore and J.F. Manville. 1975. Acute toxicity to juvenile rainbow trout (Salmo gairdneri) of naturally occurring insect juvenile hormone analogues. J. Fish. Res. Board Can. 32: 2556-2559.

Leuenberger, C., W. Giger, R. Coney, J. Graydon and E. Molnar-Kubica. 1985. Persistent chemicals in pulp mill effluents: occurrence and behaviour in an activated sludge treatment plant. Water Res. 19: 885-894.

Maenpaa, R., P. Hynninen and J. Tikka. 1968. On the occurrence of abietic acid and pimaric type resin acids in the effluents of sulphite and sulphate pulp mills. Pap. Puu 49: 143-150.

McCubbin, N. 1983. The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices. Training Manual EPS 6-EP-83-1. Environment Canada, Ottawa, Ontario.

McCubbin, N. 1984. State-of-the-Art of the Pulp and Paper Industry and its Environmental Protection Practices. Environmental Protection Service Rep. EPS 3-EP-84-2. Environment Canada. Ottawa, Ontario.

McKague, A.B. 1981a. Some toxic constituents of chlorination-stage effluents from bleached kraft pulp mills. Can. J. Fish. Aquat. Sci. 38: 739-743.

McKague, A.B. 1981b. Phenolic constituents in pulp process streams. J. Chromatog. 208: 287-293.

NCASI 1977. Analysis of Volatile Halogenated Organic Compounds in Bleached Pulp Mill Effluent. Tech. Bull. No. 298. Nat. Counc. Air Stream Improvement, Inc. New York, N.Y.

NCASI 1981a. Experience with the Analysis of EPA's Organic Priority Pollutants and Compounds Characteristic of Pulp Mill Effluents. Tech. Bull. No. 343. Nat. Counc. Air Stream Improvement, Inc. New York, N.Y.

NCASI 1981b. Experience with the Analysis of Pulp Mill Effluents for Chlorinated Phenols using an Acetic Anhydride Derivatization Procedure. Tech. Bull. No. 347. Nat. Counc. Air Stream Improvement, Inc. New York, N.Y.

NCASI 1982. Supplemental Data Reflective of Available Technological Capability for Separation of Chlorinated Organics from Pulp and Paper Industry Wastewaters. Special Rep. No. 82-1. Nat. Counc. Air Stream Improvement, Inc. New York, N.Y.

NCASI 1983. A Study of Methods for Reducing Chloroform Concentrations in Bleached Pulp Mill Effluents. Tech. Bull. No. 399. Nat. Counc. Air Stream Improvement, Inc. New York, N.Y.

Nikki, M. and R. Korhonen. 1983. Chlorinated organic compounds in effluents of bleaching with countercurrent washing. J. Pulp Paper Sci. 9: TR123-128.

Oikari, A., B. Holmbom, E. Anas and H. Bister. 1980. Distribution in a recipient lake and bioaccumulation in fish of resin acids from kraft pulp mill waste waters. Pap. Puu 62: 193-202.

Paasivirta, J., J. Sarkka, T. Leskijarvi and A. Roos. 1980. Transportation and enrichment of chlorinated phenolic compounds in different aquatic food chains. Chemosphere 9: 441-456.

Peterman, P.H., J.J. Delfino, D.J. Dube, T.A. Gibson and F.J. Priznar. 1980. Chloro-organic compounds in the Lower Fox River, Wisconsin, pp. 145-160. In D. McKay, ed. Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment. Vol. 16. Environ. Science Res. Ser. Plenum Publ. Corp., New York, N.Y.

Rao, K.R. ed. 1978. Pentachlorophenol: Chemistry, Pharmacology, and Environmental Toxicology. Plenum Press, New York, N.Y.

Richardson, D.E. and H. Bloom. 1983. Chemical composition of treated thermomechanical pulp effluent from an activated sludge plant. Appita 36: 456-460.

Rogers, I.H., J.C. Davis, G.M. Kruzynski, H.W. Mahood, J.A. Servizi and R.W. Gordon. 1975. Fish toxicants in kraft effluents. TAPPI 58: 136-140.

Rogers, I., H. Mahood, J. Servizi and R. Gordon. 1979. Identifying extractives toxic to aquatic life. Pulp Paper Can. 80: T286-290.

Rosehart, R.G. and G.W. Ozburn. 1975. Origins and Reduction of Toxicity from Typical Sulphite Newsprint Mills - Mill Stream and Additive Study. CPAR Rep. No. 261-1. Environment Canada. Ottawa, Ontario.

Salkinoja-Salonen, M., M.-L. Saxelin and J. Pere. 1981. Analysis of toxicity and biodegradability of organochlorine compounds released into the environment in bleaching effluents of kraft pulping, pp. 1131-1163. In L.H. Keith, ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Vol. 2. Ann Arbor Science Publ. Inc. Ann Arbor, MI.

Schellenberg, K., C. Leuenberger and R.P. Schwarzenbach. 1984. Sorption of chlorinated phenols by natural sediments and aquifer materials. Environ. Sci. Technol. 18: 652-657.

Sullivan, J.R., J.J. Delfino, C.R. Buelow and T.B. Sheffy. 1983. Polychlorinated biphenyls in the fish and sediment of the Lower Fox River, Wisconsin. Bull. Environ. Contam. Toxicol. 30: 58-64.

Voss, R.H. 1983. Chlorinated neutral organics in biologically treated kraft mill effluents. Environ. Sci. Technol. 17: 530-537.

Voss, R.H. and M.B. Yunker. 1983. A Study of Chlorinated Phenolics Discharged into Kraft Mill Receiving Waters. Project report prepared for the Council of Forest Industries (B.C.) by the Pulp and Paper Research Institute of Canada and Dobrocky Seatech Ltd., Vancouver, B.C.

Voss, R.H., J.T. Wearing, R.D. Mortimer, T. Kovacs and A. Wong. 1980. Chlorinated organics in kraft bleaching effluents. Pap. Puu 62: 809-814.

Voss, R.H., J.T. Wearing and A. Wong. 1981a. A novel gas chromatographic method for the analysis of chlorinated phenolics in pulp mill effluents, pp. 1059-1095. In L.H. Keith, ed. Advances in the Identification and Analysis of Organic Pollutants in Water. Vol. 2. Ann Arbor Science Publ. Inc. Ann Arbor, MI.

Voss, R.H., J.T. Wearing and A. Wong. 1981b. Effect of softwood chlorination conditions on the formation of toxic chlorinated compounds. Pulp Pap. Can. 82: T65-T71.

Voss, R.H., J.T. Wearing and A. Wong. 1981c. Effect of hardwood chlorination conditions on the formation of toxic chlorinated compounds. TAPPI 64: 167-170.

Walden, C.C. 1976. The toxicity of pulp and paper mill effluents and corresponding measurement procedures. Water Res. 10: 639-664.

Walden, C.C. and T.E. Howard. 1974. Identification and Treatment of Toxic Materials in Mechanical Pulping Effluents. CPAR Rep. No. 149-2. Environment Canada. Ottawa, Ontario.

Walden, C.C. and T.E. Howard. 1981. Toxicity of pulp and paper mill effluents - a review. Pulp Paper Can. 82: T143-148.

Walden, C.C. and J.M. Leach. 1975. Identification and Treatment of Toxic Materials in Mechanical Pulping Effluents. CPAR Rep. No. 149-3. Environment Canada. Ottawa, Ontario.

Walden, C.C., R.W. Lockhart and J.M. Leach. 1976. Identification of the Toxic Materials in Sulphite Pulp Mill Effluents. CPAR Rep. No. 407-1. Environment Canada. Ottawa, Ontario.

Waldichuk, M. 1962. Some water pollution problems connected with the disposal of pulp mill wastes. Can. Fish. Cult. 31: 3-34.

Willard, H.K. 1983. Toxicity Reduction of Pulp and Paper Mill Wastewater. Contract Rep. 68-03-3028, WA 20. U.S. Environmental Protection Agency. Cincinnati, OH.

Wong, A., M. LeBourhis, R. Wostradowski and S. Prahacs. 1978. Toxicity, BOD and color of effluents from novel bleaching processes. Pulp Paper Can. 79: T235-241.

Xie, T-M. 1983. Determination of trace amounts of chlorophenols and chloroguaiacols in sediment. Chemosphere 12: 1183-1191.

Xie, T-M., K. Abrahamsson, E. Fogelqvist and B. Josefsson. 1984. The distribution of chlorophenolics in a marine recipient. Appendix report. In Xie, T-M. Investigation of Chlorophenolic Compounds From the Paper and Pulp Industries. Ph.D. Thesis. University of Goteborg. Goteborg, Sweden.

Yamaoka. 1979. Identification of terpenoid compounds in the sediment in Hiro Bay by gas chromatography-mass spectrometry. Agric. Biol. Chem. 43: 1143-1144.

2 LABORATORY MONITORING FOR TOXICITY OF MILL EFFLUENTS

2.1 Introduction

Our knowledge of the toxicity of pulp and paper mill effluents to aquatic life is based primarily on bioassay tests performed under controlled laboratory conditions. Findings from acute (short-term) lethal bioassays with fish and other aquatic organisms are used for varied purposes including the intercomparison of toxic loadings and emission rates for various types of pulp and paper mill discharges, identification and control of in-plant sources of toxicity and of specific toxic constituents, assessment of the efficacy of effluent treatment in removing toxicity, and the routine monitoring of mill discharges for quality control and compliance with respect to federal and provincial governmental regulatory requirements. Studies which have examined sublethal responses of aquatic life, including determinations of lowest concentration(s) of effluent that elicit a response, have been undertaken primarily to assess "safe" effluent concentrations in receiving waters, below which no environmental impact occurs. Results from these studies have been applied in the design and construction of effluent diffusers in receiving waters. Some of the more sensitive, rapid and reliable sublethal bioassay procedures have been used for laboratory or on-site monitoring of residual toxicity in treated mill effluents.

This review describes the proven and more promising bioassay tests now available and/or in common use for monitoring lethal and sublethal toxicity of pulp and paper mill effluents and effluent constituents. Besides the conventional acute lethal bioassay with fish (rainbow trout), other tests (i.e., daphnia, oyster larval, algal and Microtox assay), which are useful in quantifying the toxicity of pulp mill effluents, are described. These bioassays have received various degrees of national and international acceptance for use with pulp and paper mill effluents, and are applicable to differing orders of both freshwater and estuarine/marine organisms.

Sublethal effects of brief (hours, days) and more prolonged exposure of freshwater and estuarine/marine organisms to pulp mill effluent are reviewed here under separate headings. Sublethal effects attributable to specific effluent constituents are also described. Threshold concentrations of whole mill effluent evoking various diverse sublethal responses are summarized in terms of both percentage concentration and fraction of the 96-h LC_{50} value. The extent to which secondary (biological) treatment of effluent modifies these responses is indicated.

Although our current understanding is far from complete, we now know that a number of natural environmental variables (i.e., dissolved oxygen, temperature, pH, salinity) acting alone or in concert can modify the toxicity (and thus the potential environmental impact) of pulp mill effluents. Present-day knowledge with respect to the modifying influence of these variables is reviewed and discussed.

2.2 Short-Term Bioassay Tests in Common Use

By definition, acute toxic effects are those which occur within a relatively short period of time (conventionally within four days). These effects may be lethal (death with short-term exposure) or sublethal, depending on the strength of the toxicant and on the tolerance of the test organism (Sprague, 1969; Anon., 1980a). This distinction is emphasized here inasmuch as the literature not uncommonly but also incorrectly equates the terms "acute toxicity" or "acutely toxic" as synonymous with acute lethal toxicity, ignoring acute sublethal toxic effects.

2.2.1 LC_{50} Bioassays with Fish. Laboratory methods for measuring the acute lethal toxicity of effluents to fish or other aquatic organisms have been established and have been in common use since the 1950s. Specific procedural details for conducting these laboratory bioassays, together with more recent improvements, have been published elsewhere (Sprague, 1969; EIFAC, 1975; Peltier, 1978; Anon., 1980a). In Canada, bioassay procedures for determining the acute lethal toxicity of pulp mill and other liquid effluents to fish under controlled laboratory conditions have also been specified (Anon., 1972a; Anon., 1980b; Anon., 1982a). The present review considers these test procedures only insofar as their relevance for evaluating the toxic effects of pulp and paper mill effluents within receiving waters and the manner in which environmental variables may modify the test results.

In Canada and elsewhere, the standard laboratory test for evaluating the acute lethal toxicity of pulp and paper mill effluents is the 96-h LC_{50} (median lethal concentration) fish bioassay. Rainbow trout (Salmo gairdneri) are used routinely as a test fish in Canada, Scandinavian countries and northern U.S. states where waters receiving effluent discharges are cool. In warmer climates, warmwater fish species (i.e., fathead minnows, Pimephales promelas; golden shiners, Notemigonus crysoleucas; bluegill sunfish, Lepomis macrochirus) are employed. Other species of freshwater, estuarine and marine fish suitable for laboratory bioassay tests with effluents or chemicals have been identified (Peltier, 1978; Anon., 1980a; Parker, 1984).

The LC_{50} bioassay involves placing groups of fish (usually ten per concentration) in a range of concentrations of effluent, diluted with freshwater (to which the fish are acclimated), and observing their survival throughout a 96-h test period. Based on the percentage survival of fish at various effluent concentrations, the median lethal concentration is calculated. Since effluent dilutions are normally on a volume-to-volume basis, LC_{50} values are expressed as percentage effluent by volume (% v/v). The term "LC_{50}" is synonymous with TL_m and TL_{50} (median tolerance limit), used in the earlier literature.

The higher the LC_{50} value, the less its toxicity, i.e., the higher the concentration the fish or other aquatic organism can tolerate. Samples of effluent identified as "non-toxic" are those in which more than half (50%) of the test fish exposed to full-strength effluent for 96-h survived. "Non-toxicity" does not distinguish toxic levels causing less than 50% deaths of test fish in full-strength effluent, nor any unmeasured sublethal toxic effects.

In the LC_{50} fish bioassay it is not common to record behaviour such as loss of equilibrium or immobilization of surviving fish at various test concentrations. However, concurrent assessment of the median effective concentration (EC_{50}) causing these sublethal responses has been recommended, as an expression of "functional death" (Stephan, 1982).

A number of test variables, controlled or uncontrolled, can influence (often markedly) LC_{50} values. For instance, untreated or clarified pulp mill effluent samples appear to be two to four times more toxic if test solutions are renewed (semi-static or continuous-flow tests) during the bioassay (Loch and MacLeod, 1974; Walden et al., 1975). Inter-and intra-laboratory LC_{50} or other lethal bioassay results for samples of pulp mill effluents may also differ due to variations in the overall condition and tolerance of fish stocks, differing fish-loading densities and/or aeration rates, and sample pH. Additionally, the chemical characteristics of the diluent water can cause up to four-fold variations in the LC_{50} values derived with primary-treated (clarified) bleached kraft whole mill effluent (McLeay et al., 1979a). The use of replicate (duplicate or triplicate) bioassay tests with the same effluent sample enables an understanding of the validity and reproducibility of the intra-laboratory test results (Sprague and Fogels, 1977); however, as a "cost-saving" measure, bioassays conducted for routine monitoring or even legal purposes are often not replicated.

The acute lethal toxicity of various types of pulp and paper mill effluents to freshwater fish and invertebrates, as determined under controlled laboratory conditions, has been reviewed extensively (Brouzes, 1976; Walden, 1976; Walden and Howard, 1977,

1981; Poole et al., 1978; Hutchins, 1979; Willard, 1983). These summary documents indicate that most untreated or primary-treated (clarified) pulp and paper whole mill effluents are acutely lethal to fish or aquatic invertebrates. The LC_{50} values derived for these effluents do not differ markedly due to process type, and are in most instances greater than 5%. Compared to effluents from other industries, particularly those processing chemicals, pulp and paper mill effluents are only marginally lethal (Brouzes, 1976; Poole et al., 1978). The concerns with respect to environmental impact stem from the point discharge of large volumes of mildly toxic effluent (Poole et al., 1978) and the resulting potential for adverse sublethal effects where dilution is minimal (Walden, 1976). Bioassay results for all pulp and paper mill effluents that have received effective secondary (biological) treatment indicate no acute lethal toxicity to salmonid fish or other aquatic organisms when tested at full strength (Walden et al., 1972; Walden and Howard, 1974; Anon., 1979; Willard, 1983).

Some of the 96-h LC_{50} values reported for a single sensitive salmonid fish species (rainbow trout) exposed to various types of whole mill effluents are presented in Table 2.1, together with information concerning the type of mill process, bioassay type and the type of effluent treatment. Inasmuch as these tests were conducted at a number of facilities using somewhat differing test conditions (i.e., fish loading densities, temperature, pH, solution replacement or not, fish stocks and diluent waters), the values are not directly comparable. However, these data generally support the conclusions reached in previous reviews, and delineate the efficacy of treatment in reducing or removing the acute lethal toxicity of whole mill effluents of various types.

The data in Table 2.1 indicate a range of 96-h LC_{50} values for all types of kraft effluents, from 3 to 100%. No obvious differences in toxicity are due to bleaching or to primary clarification. Various authors have noted that primary treatment of kraft whole mill effluent does not reduce the concentrations of known toxic constituents (Easty et al., 1978; Wallin and Condrin, 1981; Willard, 1983). The species of wood pulped can affect the acute lethal toxicity of kraft whole mill effluents (Holmbom and Lehtinen, 1980; Leach and Chung, 1980; Anon., 1982b) and, in general, effluents produced from softwood furnishes are more toxic than those from hardwood. In-plant modifications involving the substitution of chlorine dioxide for chlorine in the bleach plant (Rapson et al., 1977; Donnini, 1983; Kutney et al., 1983, 1984) and the possible treatment of acid bleach effluent with sulphur dioxide (Donnini, 1981; Donnini et al., 1984) can reduce the acute lethal toxicity of kraft bleach plant process effluents. The extent to which chlorine

TABLE 2.1 ACUTE LETHAL TOXICITY OF UNTREATED AND TREATED PULP AND PAPER MILL EFFLUENTS TO RAINBOW TROUT

Type of process		Effluent treatment: untreated	primary	secondary	Bioassay type	No. of samples	96-h LC_{50} (% v/v)	References
unbleached kraft		X			Static	5	7-14	Fisher, 1982
		X			Static	5	15-58	Fisher, 1982
		X			Static	5	65-100	Fisher, 1982
			X		Continuous flow	1	3	Loch & Macleod, 1973
			X		Static	7	3-19	Leach & Chung, 1980
				X	Static	2	>100	Leach & Chung, 1980
				AL	Static	15	80->100	Fisher, 1982
bleached kraft		X			Static	2	14-17	Holmbom & Lehtinen, 1980
		X			Static	15	5-74	Fisher, 1982
		X			Semi-static	1	20	Miettinen et al., 1982
		X			Semi-static	2	9-15	Nikunen, 1983
			X		Static	2	20-40	Fahmy & Lush, 1974
			X		Static	29	5-87	Leach & Chung, 1980
				AL	Static, Continuous flow	1	>100	Loch & MacLeod, 1973
				AL	Static	1	>100	Fahmy & Lush, 1974
				AL	Static	2	42-44	Holmbom & Lehtinen, 1980
				X	Static	44	13->100	Leach & Chung, 1980
				AL	Static	15	15->100	Fisher, 1982
				AS	Semi-static	1	98	Miettinen et al., 1982
				AL	Semi-static	1	37	Nikunen, 1983
unbleached sulphite	(Na)	X			Static	1	8	Leach & Howard, 1978
	(Na)		X		Static	3	8-95	Leach & Chung, 1980
bleached sulphite	(NH_3, Ca/Mg)	X			Static	2	10-50	Leach & Howard, 1978
	-	X			Static	10	4-100	Fisher, 1982
	(Ca)	X			Static	4	22-29	Anon., 1979
	(Na)		X		Static	4	4-19	Anon., 1979
	(Mg)		X		Static	4	2-7	Anon., 1979
	(NH_3)		X		Static	4	40-68	Anon., 1979
	(NH_3)		X		Static	3	9-76	Leach & Chung, 1980
	(Ca)			AL	Static	4	21->100	Anon., 1979
	(Na)			AS	Static	4	>100	Anon., 1979
	(Mg)			AL	Static	4	16->100	Anon., 1979
	(NH_3)			AL	Static	4	>100	Anon., 1979
	-			AL	Static	10	72->100	Fisher, 1982
	(NH_3)			X	Static	2	45->100	Leach & Chung, 1980
groundwood		X			Static	3	4-10	Leach & Howard, 1973
		X			Static	4	3-12	Leach & Howard, 1975
		X			Semi-static	1	9	Nikunen, 1983
			X		Static	6	1-100	Leach & Chung, 1980
				AL*, AS*	Static	3	>100, >65	Leach & Chung, 1973
				X	Static	4	3->100	Leach & Chung, 1980
thermo-mechanical (TMP)		X			Semi-static	1	7	Buckney, 1978
				AS*	Semi-static	1	>100	Buckney, 1978
chemi-mechanical		X			Static	5	28-46	Fisher, 1982
				X	Static	5	85->100	Fisher, 1982

TABLE 2.1 ACUTE LETHAL TOXICITY OF UNTREATED AND TREATED PULP AND PAPER MILL EFFLUENTS TO RAINBOW TROUT (Cont'd)

Type of process	Effluent treatment			Bioassay type	No. of samples	96-h LC_{50} (% v/v)	References
	untreated	primary	secondary				
newsprint (kraft/ground-wood)	X			Static	2	25-26	Dumouchel et al., 1975
			AS*	Static	2	>100	
newsprint (Na) (unbleached sulphite/ groundwood)		X		Static	1	16	Loch & MacLeod, 1973
fine paper	X			Semi-static	4	55-65	Wilson et al., 1975
	X			Static	5	29-100	Fisher, 1982
		X		Static	5	82->100	Fisher, 1982
NSSC	X			Static	4	10-28	Wilson & Chappel, 1974
		X		Static	2	18-48	Leach & Chung, 1980
NSSC/ unbleached kraft		X		Static	4	16-56	Willard, 1983
			X	Static	4	>100	Willard, 1983
bleached sulphite and (Mg) kraft		X		Static	2	25-65	Leach & Chung, 1980
			X	Static	1	>100	
unbleached sulphite/ (Mg) groundwood		X		Static	4	20-43	Anon., 1979
		X		Static	1	32	Leach & Chung, 1980
			AL	Static	4	19->100	Anon., 1979
			X	Static	1	>100	Leach & Chung, 1980
unbleached (Mg) sulphite/TMP/ groundwood		X		Static	8	6-25	Anon., 1979
			AL	Static	8	>100	Anon., 1979

* Bench-scale (laboratory) treatment.

dioxide substitution and treatment of C-stage effluent with sulphur dioxide can reduce the toxicity of whole bleach plant effluent and of BKME is unknown.

Untreated or primary-treated unbleached and bleached sulphite whole mill effluents show a similar range of LC_{50} values for rainbow trout as does kraft whole mill effluent (Table 2.1). The toxicity of these effluents is not affected by the pulping base (Na, Ca, Mg or NH_3). The lack of difference in LC_{50} values between unbleached and bleached effluents indicates that the process streams involved are of approximately equivalent toxicity (Rosehart et al., 1974; Hutchins, 1979; Table 2.1). Available LC_{50} values for untreated or primary-treated NSSC effluent are similar to the above.

It is difficult to secure representative LC_{50} values for untreated or primary-treated groundwood (stone or refiner) or TMP effluent, since the toxicity of the effluent depends greatly on the internal water recycle within the mill. However, generally, these effluents are somewhat more toxic than untreated kraft or sulphite whole mill effluent (Table 2.1). Although published information with respect to the acute lethal toxicity of thermomechanical pulping (TMP) effluent is scarce, its toxicity is thought to be somewhat greater than that of groundwood effluent (McCubbin, 1984a).

The LC_{50} (rainbow trout) values for untreated or clarified final effluents from newsprint, fine paper or integrated mills varied from 6 to 65%, i.e., the toxicity of these effluents was similar to untreated kraft or sulphite whole mill effluents (Table 2.1).

Conventional (aerated lagoon or activated sludge) full-scale secondary treatment does effectively remove acute lethal toxicity to fish (LC_{50} >100%) from all types of pulp and paper mill effluents. Failures to detoxify (Table 2.1) are usually attributable to improper design (short-circuiting), to inadequate operation of the biobasin, or to in-plant spills. In North America the "typical" biotreated effluent discharged by modern pulp and paper mills does not kill rainbow trout or other fish when tested at full strength in 96-h laboratory or on-site bioassays (Walden and Howard, 1974; Anon., 1979; Schneiderman and Allard, 1979; Fisher, 1982; Willard, 1983).

2.2.2 Toxic Unit Concept. "Toxic units" were originally proposed as a method for expressing the toxicity of chemicals or effluents to fish in terms related directly to the concentration of toxicants (Sprague and Ramsay, 1965; Sprague, 1971). According to this concept, one toxic unit (TU) corresponds to the concentration of chemical(s) or effluent which kills 50% of the test fish within 96 h, i.e., 1 TU = 96-h LC_{50}. Using this approach, the "amount of toxicity" in a particular effluent is expressed in terms of toxic units, as follows:

$$TU = \frac{100\%}{96\text{-h } LC_{50}\ (\%)}$$

For example, an effluent with a 96-h LC_{50} value of 20% (v/v) contains 5 TU, whereas a more toxic sample would contain a correspondingly higher number of toxic units (i.e., for a 96-h LC_{50} of 4%, TU = 100/4 or 25). The advantage of this approach is that toxic values increase directly and linearly with toxicant concentration -- known or otherwise -- whereas this is not so for other bioassay values.

The toxic unit concept is useful to assess the quantity of toxicity discharged daily by a particular pulp mill or other industrial/municipal plant (Wilson et al., 1975b; Metikosh, 1979), where toxicity emission rate (TER) is:

TU x daily discharge volume.

The discharge volume is normally expressed as cubic metres per day (m^3/d). This approach is also useful for comparing the relative quantities of toxic material (sometimes referred to as toxic loading) discharged daily to the environment by various industries or mills with differing processes/treatment systems, etc. TER calculations provide a means to compare and assess relative differences in toxic loadings discharged daily to the environment by one or more mills. Such comparisons are not possible where discharge volumes are ignored and implications of the potential environmental impact of these discharges are restricted to a consideration of the effluent samples' LC_{50} values. Additionally, monitoring or regulatory guidelines based on TER values (Anon., 1972b) vitiate any attempt to meet discharge requirements merely by effluent dilution (Brouzes, 1976).

For the process engineer, the quantity of toxicity generated per unit of production frequently is important in evaluating mill operation and/or process design modifications. These data are derived by dividing toxicity emission rates by the daily tonnage (ADt) to yield a toxicity emission factor (TEF) (Wong et al., 1978, 1981; Holmbom and Lehtinen, 1980; Voss et al., 1981; Anon., 1982b; Nikunen, 1983). However, these TEF values are not directly relevant to effluent quality per se.

The toxic unit concept has been used to assess the relative contributions of in-plant process streams to the overall toxicity of the final mill discharge. This approach assumes that the toxic contributions of individual process streams are additive when the streams are combined. Toxicity-balance studies have demonstrated that this has not always been the case (Bruynesteyn, 1977; Metikosh, 1979).

Toxic units have also been used in attempts to develop a chemical approach for predicting the acute lethal toxicity (to fish) of pulp mill effluents (Leach et al., 1979; Holmbom and Lehtinen, 1980; Leach and Chung, 1980). According to this approach, the concentration of each individual toxicant in the effluent is determined by chemical means. Then the toxic contribution (TU) of each of these toxicants is calculated as follows (Leach et al., 1979):

$$TU = \frac{\text{concentration of constituent in effluent}}{\text{96-h } LC_{50} \text{ of constituent}}$$

The sum of the toxic unit contributions of the various individual toxicants is taken as the overall toxicity of the solution.

For 113 samples of primary- or secondary-treated kraft or sulphite whole mill effluents and groundwood effluent, measured and calculated toxicities were in close agreement. However, variation exceeded 30% for 27% of the samples (Leach and Chung, 1980). These investigators concluded that "the (chemical) analysis method should be used to augment information from conventional bioassay and not as a replacement for such tests". Using a similar approach with kraft bleach plant effluents, Holmbom and Lehtinen (1980) determined that, for 7 of the 12 samples examined, more than half of the toxicity of kraft bleach plant effluents was unaccounted for by chemical assay. Thus the general applicability (and cost effectiveness) of this approach has yet to be realized, and bioassay tests "remain the standard toxicity measurement technique" (Willard, 1983).

Inasmuch as TU and TER values are derived from the results of LC_{50} bioassays, these values are <u>not</u> absolute measures of toxicity. Rather, they are relative values, and are subject to the effects of those same controlled or uncontrolled test variables that influence the LC_{50}. The LC_{50} bioassay's inability to demonstrate acute or chronic sublethal toxic effects is also integral in toxic unit and toxicity emission rate values.

In summary, the LC_{50} value and the toxic unit are quantitative yet relative (test-dependent) measures of the concentration and amount of toxicity, respectively, which do not require that the makeup of the responsible chemical constituents is known. Additional information is required before the biological impact of a particular discharge on receiving waters can be assessed. This includes an understanding of water chemistry, differing sensitivities of indigenous fish or other aquatic biota, and sublethal toxic effects caused by their acute or chonic exposure. Unless these variables are considered, LC_{50}, TU, TER or TEF values derived by bioassay tests with rainbow trout or other aquatic

species (Voss et al., 1981) are subject to misinterpretation if used to assess the likelihood of lethal toxic effects within the environment. Further, in reporting LC_{50} values or toxic units, it still remains necessary to qualify the results with respect to the test conditions and procedures employed.

2.2.3 Bioassays with Daphnia. Daphnia are freshwater micro-crustaceans (zooplankton) commonly occur in cool or warmwater lakes and streams. These organisms often comprise a major source of food for juvenile salmonid and other small resident freshwater fish species. Daphnia are easily cultured under laboratory conditions, and are now used routinely in Canada and other countries for evaluating the aquatic toxicity of effluents and chemicals (OECD, 1984; Van Coillie et al., 1984).

Standardized laboratory procedures and guidelines for measuring the acute toxicity of effluents or chemicals to daphnia are available (Anon., 1980a, 1982b; OECD, 1984). All these procedures are similar, except for some pertinent differences such as the source and characteristics of the diluent water and culturing media. The Daphnia bioassay has two specific advantages. It evaluates the tolerance of a sensitive fish-food organism to an effluent or discharge. Also, it is simple and low cost, requires a minimum effluent sample, and is suitable for on-site evaluations of in-plant toxicity or the efficacy of effluent treatment (Tunstall and Solinas, 1977; Schmaltz, 1979; Cary and Barrows, 1981; Donnini, 1981, 1983; Voss et al., 1981). Two daphnid species (Daphnia pulex and D. magna) have been used routinely for laboratory bioassays, although the latter is now the accepted test species due to its larger size. Basic test procedures are similar to those for the LC_{50} fish bioassay, except that bioassay solutions are not aerated and exposures normally are for 48 hours. More extended exposures result in deaths due to starvation (Zanella and Berben, 1980). Since death is difficult to discern for such small organisms (particularly in a coloured effluent), the bioassay determines the median effective concentration (EC_{50}) of effluent which causes complete immobilization of 50% of the exposed organisms.

A number of researchers have compared bioassay results obtained for identical samples of pulp and paper mill effluents, using both daphnia and rainbow trout as the test organisms (Table 2.2). According to two studies, no differences in sensitivity were observed between these two species for the majority of effluent samples examined (Tunstall and Solinas, 1977; Schmaltz, 1979). However, other investigators (Brouzes and Naish, 1975; Nikunen, 1983) found that rainbow trout were appreciably more sensitive than daphnia (higher EC_{50} values for daphnia). Based on similar findings of lesser

TABLE 2.2 RELATIVE SENSITIVITY OF Daphnia sp. AND RAINBOW TROUT TO SHORT-TERM EXPOSURE TO PULP AND PAPER MILL EFFLUENTS

Effluent		Number of bioassays (each species)	Number of tests showing greater sensitivity for:			Reference
type(s)	treatment		daphnia	rainbow	no difference	
BKME + process streams	untreated	18	1	14	3	Brouzes & Naish, 1975
newsprint	untreated	2	2			Dumouchel et al., 1975
newsprint	secondary	2			2	Dumouchel et al., 1975
BKME, chemi-mechanical groundwood, newsprint	untreated	23	2	2	19	Tunstall & Solinas, 1977
TMP	untreated	1		1		Buckney, 1978
BKME	untreated	26	2	6	18	Schmaltz, 1979
BKME + process streams	untreated	4		4		Nikunen, 1983
	treated	1		1		Nikunen, 1983
groundwood, debarking	untreated	3		3		Nikunen, 1983
kraft bleach plant	untreated	2			2	Donnini et al., 1984
	treated	2	1		1	

sensitivity for daphnia, Swedish scientists have excluded daphnia bioassays from their battery of biological procedures used to evaluate the aquatic toxicity of kraft bleach plant effluents (Anon., 1982a). In the 84 comparative bioassay results summarized in Table 2.2, daphnia were more sensitive than rainbow trout in 9 instances (11%) and as sensitive as rainbow trout in 45 cases (54%).

The differing conditions and procedures (i.e., test duration, replacement or non-replacement of test solutions, etc.) employed in these comparative bioassays by the different investigators may be responsible, in part, for the variation in results. For example, ambient test temperatures should be optimal for the test species involved. The range of temperatures (6-15°C) used by Brouzes and Naish (1975) for their daphnia tests may be responsible for the reduced sensitivity encountered. The findings of Dumouchel et al. (1975) suggest that higher temperatures (20°C) should have been employed for maximum sensitivity with Daphnia magna. The significantly lesser sensitivity of daphnia to pulp and paper mill effluents found by Nikunen (1983) may, on the other hand, be attributable to his reported preparation of synthetic diluent water for this test according to the ISO standard recommendation (Anon., 1982c). This document specifies a diluent water with a pH of 7.8 and a hardness of 250±25 mg $CaCO_3$/L.

Based on our present knowledge of the degree to which diluent-water pH and hardness may alter the observed toxicity of pulp mill effluent (McLeay et al., 1979a), it is likely that the use of this diluent water in daphnia bioassays with pulp and paper mill effluents would decrease their apparent sensitivity, relative to that if softer, more acidic waters were used (as was the case for the comparative fish bioassays performed by Nikunen (1983)). Dumouchel et al. (1975) reported a three-fold increase in the EC_{50} concentrations for daphnia exposed to a sample of newsprint mill effluent diluted with a 50 mg/L hardness water, compared with that using a softer (25 mg/L) diluent water and otherwise identical test conditions.

2.2.4 Oyster Larval Bioassays. A short-term (48-h) marine bioassay using fertilized eggs of the Pacific oyster (Crassostrea gigas) was developed during the late 1950s for measuring toxic concentrations of sulphite pulp mill waste liquor in seawater, and for evaluating the toxicity to oysters of receiving waters containing dilute concentrations of whole mill effluents (Woelke, 1962). Procedures for conducting this test have since been optimized (Woelke, 1967, 1972) and are reported in Standard Methods (Anon., 1980a) as an accepted bioassay protocol. The oyster larval bioassay has also been used to evaluate the toxicity of chemicals released from contaminated marine sediments (Chapman et al.,

1983). Besides evaluating the toxic response to pulp mill effluent for commercially relevant marine species, this test has other desirable attributes: it is simple; it is short-term; it is highly sensitive to pulp mill effluent; and it is applicable to the early life stages of the test organisms (Woelke, 1967; Woelke et al., 1972).

The test involves exposing freshly fertilized oyster eggs under controlled conditions (20-25°C) for 48 hours to a range of effluent concentrations diluted with seawater (26-30 °/oo salinity). The percentage of embryos failing to develop into free-swimming, fully-shelled veliger larvae are recorded. Where the range of effluent concentrations under examination is sufficiently broad, 48-h LC_{50} and EC_{50} (for developmental anomalies) values can be determined concurrently. Although the oyster larvae bioassay was developed over 25 years ago, it appears to have fallen into disuse, at least for pulp mill effluents.

The following EC_{20} (concentration causing 20% abnormal larvae) and EC_{50} values have been reported (Woelke, 1967; Woelke et al., 1972):

Effluent			
type	treatment	EC_{20} (% v/v)	EC_{50} (% v/v)
sulphite (NH_3) whole mill	primary	0.3	0.3
sulphite (NH_3) whole mill	secondary	0.2	0.3
sulphite (Mg) whole mill	primary	0.08	0.09
sulphite (Mg) whole mill	secondary	0.13	0.15
BKME	primary	1.8	2.0
BKME	secondary	1.3	1.5
groundwood (refiner)	untreated	1.7	-[a]
debarking	untreated	1.6	-
debarking	untreated	4.5	-
paper mill	untreated	>10[b]	-

a Not determined.
b Highest concentration examined.

The reason(s) for the atypically poor performance of these treatment systems was not apparent (Woelke et al., 1972) and no comparative data for fish bioassay tests were provided. Although these results suggest a greater sensitivity to pulp and paper mill

effluents for this bioassay than the 96-h LC_{50} test with rainbow trout (see Table 2.1), the evidence is inconclusive.

Because low-salinity waters can adversely affect the development of oyster larvae (Woelke, 1968; Cardwell et al., 1979), any non-toxic freshwater effluent (or natural freshwater runoff) could cause a "toxic" finding in this test. The degree to which reduction in salinity can affect test results with toxic effluents is not known. Accordingly, caution in the use and interpretation of findings for this bioassay procedure are merited in instances where the salinity of test solutions is lowered appreciably. A salinity of 20 °/oo has been suggested as the minimum level acceptable for the normal development and survival of Pacific oyster larvae, although salinity was judged to have a slight negative effect on larval development at 24 °/oo (Cardwell et al., 1979).

2.2.5 Microtox Assay. A number of bioassay tests using bacteria have been developed for rapid screening of the toxicity of aquatic contaminants (Dutka and Kwan, 1981; Williamson and Johnson, 1981; OECD, 1984; Van Coillie et al., 1984). One of these assays, known as "Microtox" (Beckman Instruments Inc.), has been examined with various chemicals and industrial effluents including pulp and paper mill effluents (vanAggelen, 1982; Blaise, 1984a; McCubbin, 1984b). This test determines the median effective concentration of effluent or chemical which inhibits light production by the luminescent marine bacterium Photobacterium phosphoreum. The concentration-dependent extinction of light output is thought to reflect the effluent's effect on cellular respiration, although the exact mechanism(s) is not understood (Chang et al., 1981). The principal desirable attributes of the Microtox asssay are its rapidity (< 1 h) and small (< 5 mL) effluent volume requirements.

Some instances of large intra- and inter-laboratory errors in reproducibility for Microtox assays with chemicals have been reported by Dutka and Kwan (1981). The quality of the bacterial cell suspensions was implicated. However, replicate tests with the same bacterial culture normally provide EC_{50} values which deviate by no more than 10% (de Zwart and Sloof, 1983).

A number of investigators (Chang et al., 1981; Dutka and Kwan, 1981; vanAggelen, 1982; de Zwart and Sloof, 1983; Blaise, 1984a) have compared the Microtox assay with LC_{50} fish bioassays or EC_{50} tests with daphnia or algae, using various diverse aquatic contaminants. In comparative bioassays with 15 chemicals, de Zwart and Sloof (1983) determined that, despite various inconsistencies, rainbow trout and Daphnia magna were, on average, 2.0 and 2.5 times (respectively) more sensitive than Microtox. Similar-

ly, the U.S. Environmental Protection Agency reported that the Microtox test identified only 81% of effluent samples shown to be toxic to fish (fathead minnows; Pimephales promelas) and only 62% of those samples toxic to daphnia (cited in Dutka and Kwan, 1981). Notwithstanding, correlation coefficients for Microtox vs. fish LC_{50} results as high as 0.88 have been reported (Samak and Noiseux, 1981; vanAggelen, 1982.)

Few results have been reported for Microtox assays with pulp and paper mill effluents. Effluent colour is not a problem, since a correction is made for its absorbance (vanAggelen, 1982). Comparative Microtox EC_{50} and rainbow trout static 96-h LC_{50} assays with 15 samples of untreated BKME and mechanical pulping whole mill effluents showed similar values for seven samples (47%) (vanAggelen, 1982). Of the remainder, the sensitivity of the Microtox assay was greater in six instances (40%) and less in two (13%). For 49 samples of untreated or treated pulp and paper whole mill effluents (kraft, chemi-mechanical, TMP, fine paper), Blaise (1984a) determined that the EC_{50}/LC_{50} values derived for Microtox and rainbow trout static bioassays were the same in four instances (8%), whereas Microtox was the more sensitive assay for 37 (76%) and less sensitive for eight (16%) of these comparisons. His lack of correction for effluent colour in the Microtox assay may have accounted in part for the generally greater sensitivity of this test. All effluent samples receiving secondary treatment were relatively non-toxic (mean rainbow LC_{50} 100%; Microtox EC_{50} 91%) according to both bioassay procedures.

As the sensitivity and stability of the Microtox procedure is reportedly optimum at pH 6.7 (Dutka and Kwan, 1981), the efficacy of the test may be affected where the pH of the effluent (or receiving water) deviates markedly from this value. Chang et al. (1981) reported that different freshwater sources also affect the bioluminescence of the test bacteria.

2.3 Sublethal Responses to Acute Exposure

2.3.1 Histological/Morphological Changes. Studies examining the effects of acute (hours or few days) exposure to pulp mill effluent on the structure of tissues or organs of aquatic species are limited. Light microscopic examination of gill, thyroid, spleen, kidney, interrenal and epithelial tissues of juvenile coho salmon held in 30% neutralized unbleached kraft mill effluent (a concentration equivalent to 0.5 of the 96-h LC_{50} value) for 12 hours revealed no pathological changes (McLeay, 1973) (Table 2.3). Using scanning electron microscopy, Howard and Monteith (1977) observed damage to the fine-ridged structure of gill lamellae for rainbow trout exposed for 12 to 96 hours to dehydroabietic acid at concentrations as low as 70 µg/L (the lowest strength examined). Regeneration of

TABLE 2.3 SUBLETHAL RESPONSES OF AQUATIC LIFE TO ACUTE EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS

Function or system affected	Effluent		Test species	Diluent water	Nature of response measured	Duration of exposure (h)	Median effective concentration		Reference
	type	treatment					% (v/v)	Fraction of 96-h LC_{50} (% v/v)	
Histology/ Morphology	UKME	untreated	coho salmon	FW	histology of gill, thyroid, spleen, interrenal, kidney	12	>30[b]	>0.5[b]	McLeay, 1973
	SME (Mg)	primary	Pacific oyster larvae	SW	abnormal development	48	0.08	-[a]	Woelke et al., 1972
		secondary	Pacific oyster larvae	SW	abnormal development	48	0.13	-[a]	Woelke et al., 1972
	SME (NH_3)	primary	Pacific oyster larvae	SW	abnormal development	48	0.3	-[a]	Woelke et al., 1972
		secondary	Pacific oyster larvae	SW	abnormal development	48	0.2	-[a]	Woelke et al., 1972
	BKME	primary	Pacific oyster larvae	SW	abnormal development	48	1.8	-[a]	Woelke et al., 1972
		secondary	Pacific oyster larvae	SW	abnormal development	48	1.3	-[a]	Woelke et al., 1972
	paper mill	-[a]	Pacific oyster larvae	SW	abnormal development	48	>10[b]	-[a]	Woelke, 1967
	groundwood (refiner)	-[a]	Pacific oyster larvae	SW	abnormal development	48	1.7	-[a]	Woelke, 1967
Metabolism/ Stress	BKME	primary	coho salmon	FW	decreased liver glycogen stores	16-96	<40	<0.7	McLeay & Brown, 1975
	BKME	primary	coho salmon	FW	elevated blood lactate	3-96	<44	<0.8	McLeay & Brown, 1975
	BKME	primary	coho salmon	FW	elevated blood sugar	4	0.6	0.04	McLeay, 1977
	BKME	primary	coho salmon	FW	elevated blood sugar	4	<3	<0.2	McLeay & Gordon, 1978
	BKME	primary	coho salmon	FW	decreased white blood cells	24	5	0.3	McLeay & Gordon, 1977
	BKME	secondary	coho salmon	FW	decreased white blood cells	24	>90[b]	-[c]	McLeay & Gordon, 1977
	BKME	primary	rainbow trout	FW	decreased white blood cells	24	3	0.2	McLeay & Gordon, 1977
	BKME	secondary	rainbow trout	FW	decreased white blood cells	24	>90[b]	-[c]	McLeay & Gordon, 1977
	BKME	primary	coho salmon	FW	decreased white blood cells	24	1.5	0.1	McLeay & Howard, 1977
	UKME	untreated	rainbow trout	FW	decreased white blood cells	24	1-5	0.1-0.4	Fisher, 1982
	UKME	secondary	rainbow trout	FW	decreased white blood cells	24	60	-[c]	Fisher, 1982
	BSME	untreated	rainbow trout	FW	decreased white blood cells	24	2-6	0.5	Fisher, 1982
	BSME	secondary	rainbow trout	FW	decreased white blood cells	24	56-72	-[c]	Fisher, 1982
	chemi-mechanical	untreated	rainbow trout	FW	decreased white blood cells	24	2	0.1-0.2	Fisher, 1982
	chemi-mechanical	secondary	rainbow trout	FW	decreased white blood cells	24	5	0.1-0.2	Fisher, 1982

TABLE 2.3 SUBLETHAL RESPONSES OF AQUATIC LIFE TO ACUTE EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS (Cont'd)

Function or system affected	Effluent		Test species	Diluent water	Nature of response measured	Duration of exposure (h)	Median effective concentration		Reference
	type	treatment					% (v/v)	Fraction of 96-h LC_{50} (% v/v)	
Respiration/ Circulation	BKME	primary	rainbow trout	FW	increased cough frequency	3-12	20	0.2	Walden et al., 1970
	BKME	primary	sockeye salmon	FW	increased cough frequency	<1-2	11	0.2	Davis, 1973
	BKME	primary	sockeye salmon	FW	increased ventilatory volume	2	-[a]	0.2	Davis, 1973
	BKME	primary	sockeye salmon	FW	increased oxygen uptake rate	2	-[a]	0.2	Davis, 1973
	BKME	primary	sockeye salmon	FW	decreased blood oxygen	1-24	-[a]	0.3	Davis, 1973
Stamina/ Performance	BKME	primary	coho salmon	FW	reduced swimming performance	1	-[a]	<0.4	Howard, 1975
	BKME	primary	coho salmon	FW	reduced swimming performance	18-96	-[a]	0.2	Howard, 1975
	BKME	secondary	coho salmon	FW	reduced swimming performance	18	65->100	-[a]	Howard, 1975
	BKME	primary	coho salmon	FW	reduced swimming performance	27	8	0.5	McLeay & Howard, 1977
	BKME	primary	coho salmon	FW	reduced temperature tolerance	19	8	0.3	Howard & Walden, 1974
	BKME	secondary	coho salmon	FW	reduced temperature tolerance	19	>25	-[c]	Howard & Walden, 1974
	BKME	primary	coho salmon	FW	reduced temperature tolerance	19	5	0.3	McLeay & Howard, 1977
	BKME	primary	rainbow trout	FW	reduced temperature tolerance	19	7	0.4	McLeay & Gordon, 1978
	BKME	primary	rainbow trout	FW	reduced tolerance to hypoxia	12	6	0.4	McLeay & Howard, 1977
Behaviour	KME	untreated	chinook salmon	FW	avoidance	1	<2.5	-[a]	Jones et al., 1956
	BKME	primary	Atlantic salmon	FW	avoidance	0.2	0.001	0.0001	Sprague & Drury, 1969
	KME	untreated	coho salmon	FW	avoidance	1	>10[b]	-[a]	Jones et al., 1956
	BKME	untreated	coho salmon, rainbow trout	FW	avoidance	0.2-1	14-28	0.7-2.7	Gordon & McLeay, 1978
	BKME	secondary	rainbow trout	FW	avoidance	0.2-1	32	-[c]	Gordon & McLeay, 1978
	BKME	untreated	coho salmon, rainbow trout	FW	attraction	0.2-1	0.1	0.003	Gordon & McLeay, 1978
	BKME	secondary	rainbow trout	FW	attraction	0.2-1	0.5-1	-[a]	Gordon & McLeay, 1978
	BKME	primary	pinfish, killifish	SW	avoidance	1	0.06	0.006	Lewis & Livingston, 1977
	BKME	primary	lobster	SW	avoidance	0.2	>20[b]	-	McLeese, 1970
	BKME	primary	amphipod	SW	precopulation	96	20	0.5	Davis, 1978

TABLE 2.3 SUBLETHAL RESPONSES OF AQUATIC LIFE TO ACUTE EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS (Cont'd)

Function or system affected	Effluent type	Effluent treatment	Test species	Diluent water	Nature of response measured	Duration of exposure (h)	Median effective concentration % (v/v)	Median effective concentration Fraction of 96-h LC_{50} (% v/v)	Reference
Primary Productivity	BKME	primary	Selenastrum sp.	FW	decreased C-14 uptake	5	7	-[a]	Eloranta et al., 1985
	BKME	primary	Selenastrum sp.	FW	decreased C-14 uptake	96	3	-[a]	Eloranta et al., 1985
	BKME	primary	indigenous phytoplankton	FW	decreased C-14 uptake	5	9	-[a]	Eloranta et al., 1985
	BKME	primary	indigenous phytoplankton	FW	decreased C-14 uptake	96	10	-[a]	Eloranta et al., 1985
	BKME	primary	Selenastrum sp.	FW	decreased photosynthesis	120	5	-[a]	Nikunen, 1983
	BKME	primary	blue-green alga	BW	decreased biomass	5	4-9	-[a]	Rainville et al., 1975
	BKME	secondary	blue-green alga	BW	decreased biomass	5	>100	-[a]	Rainville et al., 1975
	KME	secondary	periphyton	FW	decreased biomass	96	5	-[a]	Bothwell & Stockner, 1980
	BKME	secondary	Selenastrum sp.	FW	increased photosynthesis	120	0.1	-[a]	Nikunen, 1983
	BKME	secondary	indigenous phytoplankton	BW	decreased CO_2 assimilation	72	1	-[a]	Anon., 1982b

a Not determined/not indicated.
b Highest concentration examined.
c 96-h $LC_{50} \geq 100\%$.

this structure during a 20-day recovery of fish in freshwater was minor. More recently, Tuurala and Soivio (1982) exposed rainbow trout to a high but sublethal concentration of this resin acid for 96 hours and also reported structural and circulatory damage to the secondary gill lamellae. The histological effects of dilute strengths of dehydroabietic acid were not examined. Oikari et al. (1983) found that the relative weight of liver tissue in rainbow trout decreased markedly during their 96-h exposure to a high (1.2 mg/L) concentration of this resin acid.

Developing oyster larvae appear to be particularly susceptible to dilute pulp and paper mill effluents. Exposure of developing embryos for 48 hours to effluent concentrations as low as 0.08% (SME) or 1.3% (BKME) can cause deformities (Woelke et al., 1972) (Table 2.3). Kinae et al. (1981) reported that ether extracts derived from kraft pulp mill effluent (type and treatment undefined) caused impaired fertilization success, retarded development, atypical morphology and cellular lysis for exposed sea urchin (Anthocidaris crassipina) eggs during a 24-h incubation. Any effects attributable to the unextracted effluent were not determined.

2.3.2 Metabolic/Stress Effects. Published studies examining metabolic changes in aquatic life due to acute exposure to pulp mill effluent have been restricted to freshwater fish. Exposure of juvenile coho salmon (Oncorhynchus kisutch) to primary-treated BKME for periods as brief as three hours is known to affect their carbohydrate metabolism. High (0.7 LC_{50}) sublethal concentrations of effluent can cause depletion of liver glycogen energy reserves and elevated plasma lactic acid levels (McLeay and Brown, 1975; McLeay, 1977). These responses are indicative of acute stress (McLeay and Brown, 1975; Wedemeyer and McLeay, 1981) due, in these instances, to effluent exposure. Similar metabolic changes in fish have been found during their acute exposure to resin acids.

Short-term (three days) exposure of rainbow trout to a sublethal concentration of a mixture of resin acids, equivalent to 0.3 of its 96-h LC_{50} value, has been shown to deplete liver glycogen reserves and to inhibit the liver enzyme, UDP-glucuronyltransferase (Oikari and Nakari, 1982). A four-day exposure of trout to 20 µg/L dehydroabietic acid also diminished UDP-glucuronyltransferase activities of both liver and kidney tissues (Oikari et al., 1983). This enzyme is believed to be responsible for the conjugation (detoxification) of certain effluent constituents (resin acids, chlorophenolic compounds) known to bioaccumulate in effluent-exposed fish (see Chapter 4), prior to their excretion in the bile (Oikari, 1984; Oikari et al., 1984a,b). The enzyme also serves to conjugate bilirubin.

Nikinmaa and Oikari (1982) observed a marked elevation in plasma bilirubin concentration for rainbow trout held in a high sublethal concentration of a resin acid mixture for 24 h. Blood bilirubin levels continued to increase during a subsequent 48-h recovery of fish in freshwater; whereas other metabolic changes (elevated plasma lactate and decreased plasma chloride concentrations) rapidly returned to normal. Similar metabolic dysfunctions have been found previously in juvenile sockeye salmon (Oncorhynchus nerka) acutely exposed to a high sublethal concentration of dehydroabietic acid (Kruzynski, 1979).

Salmonids exposed to untreated or primary-treated pulp mill effluents (UKME, BKME, BSME, mechanical) for 4 to 24 hours exhibit specific changes in certain blood constituents (elevated plasma glucose, decreased leucocrit or numbers of circulating white blood cells), which are characteristic of stressed fish. Standardized test procedures for measuring the median effective concentrations of pulp mill effluent that cause stress in fish (McLeay, 1977; McLeay and Gordon, 1977) have proven useful in on-site monitoring of untreated and treated whole mill effluents (Fisher, 1982). The lowest concentration of untreated or primary-treated whole mill effluent reported to cause acute stress in fish was 0.6% (0.04 of the effluent's 96-h LC_{50} value), and median effective concentrations of 1-5% were common (Table 2.3). Conventional bio-treatment of effluent normally increased these EC_{50} values to 32% or higher (McLeay and Gordon, 1977; Fisher, 1982), although some exceptions were evident. Among samples of secondary-treated pulp mill effluent that permitted survival of all fish at full strength, the occasional sample caused an acute stress response at concentrations as low as 10% (Leach and Meier, 1978).

Metabolic effects of pulp mill effluents on aquatic invertebrates have, to our knowledge, not been examined. This is somewhat surprising since general biochemical indices of sublethal stress responses in marine invertebrates have been used for a number of years for evaluating the potential biological effects of other aquatic contaminants (Bayne et al., 1976; Livingstone, 1982).

2.3.3 Respiratory/Circulatory Effects. Laboratory studies conducted more than 10 years ago with juvenile salmonid fish exposed to neutralized primary-treated (filtered) BKME demonstrated that effluent concentrations equivalent to 0.2 of the 96-h LC_{50} value and higher caused a rapid (within one to three hours) increase in their "cough" frequency (frequency of gill clearing) (Walden et al., 1970; Davis, 1973). This effect was transient, and dissipated on prolonged exposure. Howard and Walden (1974) determined that this response disappeared if the BKME received secondary treatment.

Primary-treated pulp mill effluent also increased ventilatory volume (i.e., the volume of water moved across fish gills per unit time) and oxygen uptake rate (Davis, 1973; 1976), at a median effective concentration equivalent to 0.2 LC_{50} (Table 2.3). As with cough frequencies, these responses were also transient.

Davis (1973) measured the arterial oxygen tensions (the amount of oxygen carried in the blood) for rainbow trout and coho salmon exposed acutely to neutralized untreated (filtered) BKME. Values declined by approximately 50% within 1 h of exposure to effluent strengths as low as 0.3 LC_{50}, and remained depressed throughout a 24-h test period. The recovery of arterial oxygen tension following the return of fish to fresh water was not examined.

Early laboratory studies by Servizi et al. (1968) indicated that brief (5-h) exposures of Pacific salmon alevins or young fry to sublethal concentrations of chlorinated catechols caused increased respiration. Threshold strengths of tetrachlorocatechol which effected this response were equivalent to 0.1-0.3 (sockeye salmon) or 0.5 (pink salmon; Oncorhynchus gorbuscha) of the respective 96-h LC_{50} values. Effects of acute exposure to sublethal concentrations of resin acids on the respiration of fish (rainbow trout) have been reported more recently. The responses observed (increased oxygen uptake rates, decreased arterial oxygen tension) were consistent with those caused by pulp mill effluent (Nikinmaa and Oikari, 1982; Oikari, 1983). Arterial oxygen tensions remained depressed during the 48-h observation period in freshwater which followed a 24-h exposure (Nikinmaa and Oikari, 1982). However, the concentrations of resin acids utilized in these experiments approached lethal levels.

2.3.4 Effects on Stamina/Performance of Fish. A number of laboratory studies have assessed the threshold concentrations of pulp mill effluent that acutely affect the stamina or adaptive capabilities of salmonid fish (Table 2.3). Untreated (filtered) BKME in freshwater has been shown to impair the swimming stamina (critical swimming speed) of juvenile coho salmon (Oncorhynchus kisutch) at median effective concentrations equivalent to 0.2-0.5 of the effluent's 96-h LC_{50} values (Howard, 1975; McLeay and Howard, 1977). However, biotreated (activated sludge or aerated lagoon) BKME samples did not affect the swimming performance of fish until test concentrations were 65% or higher (Howard, 1975). Other studies have shown that short-term exposure of salmonid fish to primary-treated BKME impairs their tolerance of upper lethal temperatures (Howard and Walden, 1974; McLeay and Howard, 1977; McLeay and Gordon, 1978) and hypoxia (oxygen-deficient water) (McLeay and Howard, 1977) at median effective

concentrations equivalent to 0.3-0.4 of the 96-h LC_{50} (5-8% by volume). Biotreated effluent at strengths of up to 25% did not affect temperature tolerance (Table 2.3). No similar studies have been reported for other types of pulp mill effluents or for seawater-acclimated fish species.

2.3.5 Behavioural Effects. Short-term controlled behavioural studies with pulp mill effluents have focussed primarily on their ability to cause avoidance responses for salmonid and other fish species. Jones et al. (1956) showed that juvenile chinook salmon (Oncorhynchus tshawytscha) avoided untreated KME concentrations in freshwater as low as 2.5%, whereas coho salmon were unresponsive to all strengths tested including 10%. Chinook salmon also displayed avoidance reactions to dilute strengths of sulphite waste liquor. Using a sharp-gradient test apparatus, Sprague and Drury (1969) found that Atlantic salmon (Salmo salar) showed a weak but consistent avoidance response within 0.2 h exposure to neutralized primary-treated BKME at concentrations as low as 0.001% (Table 2.3). The median effective concentration for this response was only 0.0001 of the reported 96-h LC_{50} value of 15%. These results are substantially different from those of Gordon and McLeay (1978) who, using a similar test apparatus, were unable to detect avoidance responses to untreated BKME by either coho salmon or rainbow trout, until concentrations were 0.7-2.7 LC_{50} (Table 2.3). Biotreated BKME did not cause avoidance until effluent strengths were 32% or higher. More dilute concentrations of untreated effluent (0.1-8%) or treated effluent (0.5-24%) attracted these fish species, although these responses were not consistent for all samples or concentrations (Gordon and McLeay, 1978). Laboratory tests with two marine fish species (pinfish, Lagodon rhomboides; gulf killifish, Fundulus grandis) demonstrated significant avoidance reactions to primary-treated BKME concentrations of 0.06% (0.006 LC_{50}) and higher (Lewis and Livingston, 1977). Greer and Kosakoski (1978) reported that seawater-acclimated pink salmon (Oncorhynchus gorbuscha) fry avoided untreated BKME in a concentration range of 0.8-16%. However, they similarly avoided the same range of concentrations of freshwater in seawater. Accordingly, in this instance the avoidance reactions were not attributed to the BKME.

Wildish et al. (1977) determined that herring (Clupea harengus) avoided sodium lignosulphonate (a component of sulphite whole mill effluent) at concentrations as low as 0.3 mg/L. Separate bioassays with 1.0 mg/L concentrations of abietic and dehydroabietic acid failed to demonstrate any avoidance reactions. Behavioural responses of other fish species to constituents of pulp mill effluent have not been reported.

Only two reports pertain to behavioural effects caused by short-term exposure of aquatic invertebrates to pulp mill effluent. McLeese (1970) found that lobsters (Homarus americanus) did not avoid bleached kraft mill effluent at concentrations up to and including 20%. Davis (1978) noted that neutralized untreated (filtered), salinity-adjusted BKME concentrations of 20% or higher disrupted precopulatory behaviour of marine amphipods.

2.3.6 Effects on Primary Productivity. Diverse bioassays have been conducted to ascertain the effects of pulp and paper mill effluent on freshwater algae (i.e., aquatic organisms at the bottom of the food chain). Studies reported include bioassays with the green algae Selenastrum capricornutum (Dumouchel et al., 1975; Soniassy et al., 1977; Eloranta and Eloranta, 1980; Eloranta and Laitinen, 1981, 1982; Blaise, 1984a; Van Coillie et al., 1984), Ankistrodesmus falcatus (Eloranta, 1976a+b, 1978a); and Scenedesmus sp. (Dumouchel et al., 1975; Anon., 1982b; Rowe et al., 1982). Freshwater species of blue-green algae (Anaboena cyclindrica and Synechococcus cedrorum) were found to be unaffected by high concentrations of untreated newsprint mill effluents (Dumouchel et al., 1975) and subsequent tests with freshwater blue-green algae have not been reported.

The short-term exposure of freshwater species of phytoplankton or periphyton to dilute concentrations of pulp mill effluent can affect their productivity. Nikunen (1983) determined that sub-acute (5-11 day) exposure of Selenastrum sp. to untreated BKME inhibited photosynthesis at concentrations of 5% (v/v) or higher; whereas 0.5% effluent caused slight stimulation of algal growth. Similar results pertained to a mill-treated (two-week aeration lagoon) sample of this effluent. Untreated newsprint whole mill effluent caused no effects at 0.1% concentration, although higher strengths (0.5% and 2%) impaired photosynthesis (Nikunen, 1983). Eloranta et al. (1985) reported that primary-treated BKME inhibited the productivity of Selenastrum sp. and indigenous lacustrine phytoplankton, with median effective concentrations of 3-10% (Table 2.3). This inhibition was attributed in large part to the attenuation of light caused by the effluent's colour. Bothwell and Stockner (1980) determined that secondary-treated kraft mill effluent concentrations of 5% and higher initially (within five to six days) inhibited the productivity of attached freshwater algae; whereas a stimulatory effect occurred on a more prolonged (8-28 day) exposure of these periphyton to treated effluent strengths of 0.5-25%.

Studies with diverse species of estuarine/marine phytoplankton or periphyton exposed experimentally to pulp mill effluents have also shown differing responses and

levels of sensitivity. Rainville et al. (1975) reported decreased productivity for the estuarine blue-green alga Coccochloris elebans during a 5-h exposure to primary-treated BKME concentrations of 4-9% or higher. On the other hand, full strength BKME samples from mills practising secondary treatment did not affect the production of this organism. However, productivity of mixed cultures of indigenous brackish-water algae exposed to secondary-treated BKME concentrations of 1% or higher for three days was inhibited, a response attributed to the effluent's colour (Anon., 1982b). Productivity of three species of marine phytoplankton (Skeletonema costatum, Dunaliella tertiolecta and Amphidinium carteri) cultured in primary-treated BKME or combined BKME/newsprint effluent was not affected until effluent concentrations exceeded 10% (Stockner and Costella, 1976). Four-day bioassay tests by Walsh et al. (1982) with the marine alga Skeletonema costatum and four samples of pulp and paper mill effluents (treatment not identified) indicated enhanced growth at concentrations of 0.02-0.9% and growth inhibition at 14-62%.

The U.S. Environmental Protection Agency has examined a marine algal bioassay method for the screening of industrial effluents for stimulatory or toxic effects (EPA, 1977; Walsh and Alexander, 1980; Walsh et al., 1982). Preliminary comparative four-day bioassays with Skeletonema costatum and the freshwater Selenastrum capricornutum exposed to pulp and paper mill effluents suggest a somewhat lesser sensitivity for this marine organism to stimulatory or inhibitory effects, although equivalent responses were found in some instances.

Apart from their potential toxic effects, dilute strengths of pulp and paper mill effluents within receiving waters may inhibit the productivity of phytoplankton or periphyton by light attentuation, or enhance productivity through nutrient enrichment. These differing effects make the design and interpretation of algal bioassays difficult. The biological relevance of the test results is also confounded by the variety of pretreatment procedures used for sample preparation (i.e., filtration, autoclaving, pH adjustment) and for monitoring algal survival and biomass (cell numbers, volume, turbidity, chlorophyll, C-14 incorporation) (Eloranta, 1978b; Eloranta and Laitinen, 1981, 1982).

Standardized procedures and guidelines for the use of the freshwater green alga, Selenastrum capricornutum, with chemicals and effluents have been proposed (Miller et al., 1978; Joubert, 1980; OECD, 1984). An "Algal Assay Bottle Test" (AABT), developed initially by the U.S. Environmental Protection Agency (Miller et al., 1978), has proven useful in assessing nutrient effects of pulp and paper mill effluents within receiving streams (Tesmer and Joyce, 1980; Mischuk, 1983). However, this test takes

14 days. Joubert (1980) enriched the test media with nutrients, reducing the test period to eight days. Blaise (1984a) found this modified technique useful for assessing the toxic effects of dilute concentrations of pulp and paper mill effluents. Further modifications of the AABT by Eloranta and Laitinen (1982) have permitted measurements of the percentage inhibition of algal growth in lacustrine samples receiving pulp and paper mill effluents within 96 hours and with increased sensitivity relative to the original (14-day) procedure. Short-term (24-h) procedures for evaluating the inhibiting effects of dilute concentrations of pulp mill effluents on algal production are presently under development (Eloranta et al., 1985). In Canada, modified algal toxicity tests requiring only four hours also show promise for the routine monitoring of effluents or receiving waters (Blaise, 1984b).

Blaise (1984a) compared 96-h LC_{50} fish (static rainbow trout) bioassays with eight-day Algal Assay Bottle Tests for 53 separate samples of pulp and paper whole mill effluents. The algal assay was the more sensitive (lower EC_{50} values) for 49 (92%) of the samples, with a lesser sensitivity for only 3 (6%). On average, the EC_{50} values for these effluents were 0.1 of the LC_{50} values derived for rainbow trout, i.e., the samples inhibited algal productivity at concentrations appreciably lower than those which killed fish. Mill effluents which had received secondary treatment did not inhibit algal productivity at effluent concentrations up to 40% v/v (Blaise, 1984a).

Using a short-term (96-h) modified AABT procedure, Kuivasniemi et al. (1985) determined EC_{50} values for a number of chlorinated phenolic compounds, known to be present in pulp and paper mill effluents. The EC_{50} values derived for di-, tri- and tetrachloroguaiacol were similar to respective LC_{50} values reported for Daphnia sp. and rainbow trout, whereas those for di-, tri- and tetrachlorocatechol were 3-10 times lower (Kuivasniemi et al., 1985). Thus this algal species (Selenastrum capricornutum) is highly susceptible to chlorocatechols. In preliminary assays, these authors found that the tolerance of mixed cultures of indigenous lacustrine phytoplankton to the same chlorophenolic compounds was 1.2-4 times higher than that for Selenastrum capricornutum.

2.4 Effects of Prolonged Exposure

2.4.1 Survival. A review of published information concerning the effects of prolonged (weeks or months) exposure of aquatic organisms to pulp mill effluents under controlled conditions indicates that pertinent studies have dealt primarily with salmonid fish exposed to kraft whole mill effluent diluted with freshwater. As shown in Table 2.4, sustained (up to 200 days) exposure of juvenile fish to untreated or primary-treated BKME

concentrations of 8-25% under otherwise optimum or near-optimum conditions normally does not affect survival. This appears to be true even when the effluent concentrations to which they are exposed are equivalent to 0.2-0.5 of the samples' 96-h LC_{50} values (McLeay and Brown, 1974, 1979). Although one on-site investigation (Whittle and Flood, 1977) reported significant deaths of rainbow trout after 16 days' exposure to 10% untreated BKME, periodic problems (toxic spills, low dissolved oxygen) may have been responsible.

Generally, biotreatment of BKME enhanced survival of freshwater fish and invertebrates to prolonged (15-200 day) exposure (Table 2.4). Juvenile coho salmon exposed to laboratory-treated BKME at mean concentrations of 27 or 5% for 95 or 200 days, respectively, showed no appreciable mortalities (McLeay and Brown, 1979). Similarly, exposure of free-swimming underyearling rainbow trout in outdoor experimental channels to 1% secondary-treated BKME for 300 days (NCASI, 1982) did not affect fish survival (NCASI, 1984a). However, separate studies with fish held for 270-300 days in biotreated BKME strengths averaging 2% (NCASI, 1983a) or 5% (NCASI, 1984a) showed fewer surviving fish compared to corresponding control groups (NCASI, 1984a).

Graves et al. (1980) found that crayfish (Procambrus clarki) and three species of fish (green sunfish, Lepomis cyanella; hybrid bream, Lepomis sp.; channel catfish, Ictalurus punctatus) survived for 30 days in continuous-flow bioassays with fresh mill-treated BKME even when the concentration was 100% (undiluted). Similarly, Weinbauer and Somers (1982) determined that the first and second generations of Daphnia magna held in biologically treated effluent (BKME plus effluent from a fine paper mill) at concentrations ranging from 1 to 100%, survived a 21-day test period.

The effects of prolonged exposure to biotreated (14-day retention) BKME on the survival and growth of salmonid fish in their early life stages have been reported recently (NCASI, 1982, 1983a). Rainbow and steelhead trout (Salmo gairdneri), as freshly fertilized or eyed eggs, alevins or fry, were exposed in continuous-flow bioassays to a range of concentrations of freshly treated BKME for 4-62 days over two years. The median lethal concentrations corresponding to the various life stages of these fish species ranged from 16 to 91% when exposures were 16 days or more (Table 2.4). No-effect effluent concentrations (i.e., strengths where mortalities did not differ from controls) were consistently 10% or higher. The life stage most sensitive to BKME appeared to be the early embryonic development prior to the eyed egg (NCASI 1982). In comparison, trout exposed to treated BKME as free-swimming fry were relatively tolerant (LC_{50} values 42->100%) (NCASI, 1982, 1983a).

TABLE 2.4 EFFECTS ON AQUATIC LIFE OF PROLONGED EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS

Function or system affected	Effluent		Test species	Diluent water	Nature of response measured	Duration of exposure (days)	Median effective concentration		Reference
	type	treatment					% (v/v)	Fraction of 96-h LC_{50} (% v/v)	
Survival	BKME	primary	chinook salmon	FW	survival	56	>25[a]	>0.5[a]	Webb & Brett, 1972
	BKME	primary	coho salmon	FW	survival	200	>10[a]	>0.25[a]	McLeay & Brown, 1974
	BKME	untreated	rainbow trout	FW	survival	18	>6<10	>0.2<0.4	Whittle & Flood, 1977
	BKME	primary	coho salmon	FW	survival	140	>14[a]	>0.5[a]	McLeay & Brown, 1979
	BKME	primary	coho salmon	FW	survival	200	>8[a]	>0.3[a]	McLeay & Brown, 1979
	BKME	secondary	coho salmon	FW	survival	95	>27[a]	-[b]	McLeay & Brown, 1979
	BKME	secondary	coho salmon	FW	survival	200	>5[a]	-[b]	McLeay & Brown, 1979
	BKME	secondary	catfish, bream, sunfish, crayfish	FW	survival	30	>100	-[b]	Graves et al., 1980
	BKME/fine paper	secondary	Daphnia magna	FW	survival	21	>100	-[b]	Weinbauer & Somers, 1982
	BKME	secondary	rainbow/ steelhead trout	FW	survival	15-62	25-91	-[c]	NCASI, 1982
	BKME	secondary	rainbow/ steelhead trout	FW	survival	15-38	16-68	-[c]	NCASI, 1983a
	BKME	secondary	rainbow trout	FW	survival	270-300	>1<5[a]	-[c]	NCASI, 1984a
Metabolism/ Stress	BKME	primary	coho salmon	FW	altered white blood counts	200	>5<12	>0.1<0.25	McLeay & Brown, 1974
	BKME	primary	coho salmon	FW	elevated blood sugar	200	<5	<0.1	McLeay & Brown, 1974
	BKME	primary	coho salmon	FW	elevated blood lactate: pyruvate	200	<5	<0.1	McLeay & Brown, 1974
	BKME	primary	coho salmon	FW	elevated blood sugar	200	<1	<0.05	McLeay & Brown, 1979
	BKME	secondary	coho salmon	FW	elevated blood sugar	200	<5	-[b]	McLeay & Brown, 1979
	BKME	primary	coho salmon	FW	elevated blood lactate	200	<1	<0.05	McLeay & Brown, 1979
	BKME	secondary	coho salmon	FW	elevated blood lactate	200	<5	-[b]	McLeay & Brown, 1979
	BKME	primary	pinfish	SW	decreased body lipid	28	>0.1<1	<0.1	Stoner & Livingston, 1978
	BKME	primary	pinfish	SW	increased body protein	28	>0.1<1	<0.1	Stoner & Livingston, 1978

TABLE 2.4 EFFECTS ON AQUATIC LIFE OF PROLONGED EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS (Cont'd)

Function or system affected	Effluent		Test species	Diluent water	Nature of response measured	Duration of exposure (days)	Median effective concentration		Reference
	type	treatment					% (v/v)	Fraction of 96-h LC_{50} (% v/v)	
Respiration/ Circulation	BKME	primary	pinfish	SW	increased gill ventilation rate	28	>0.1-<1	<0.1	Stoner & Livingston, 1978
	UKME	primary	coho salmon	FW	increased number immature erythrocytes	25	<30	<0.3	McLeay, 1973
	BKME	primary	coho salmon	FW	increased number immature erythrocytes	200	>20[a]	>0.25[a]	McLeay & Brown, 1974
	BKME	secondary	rainbow trout	FW	increased hematocrit	300	>1-<2	-[c]	MCASI, 1984a, b
	BKME	secondary	rainbow trout	FW	increased leucocrit	300	>2[a]	-[c]	MCASI, 1984a, b
	BKME	secondary	bass, bluegill	FW	hematocrit	365	>10[a]	-[c]	NCASI, 1984b
	BKME	secondary	bass, bluegill	FW	leucocrit	365	>10[a]	-[c]	NCASI, 1984b
Stamina/ Performance	UKME	primary	chinook salmon	FW	swimming performance	12	>[a]	-[c]	NCASI, 1968
	BKME	primary	coho salmon	FW	swimming performance	90	>14[a]	>0.5[a]	McLeay & Brown, 1979
	BKME	secondary	coho salmon	FW	swimming performance	90	>28[a]	-[b]	McLeay & Brown, 1979
	BKME	secondary[d]	perch	BW	torque compensation	14	>1-<2	-[c]	Lehtinen & Oikari, 1980
Behaviour	UKME	primary	chinook salmon	FW	rate of food consumption	16	>1[a]	-[c]	NCASI, 1968
	UKME	secondary	chinook salmon	FW	rate of food consumption	16	>5[a]	-[b]	NCASI, 1968
Histology	UKME	primary	coho salmon	FW	gill, thyroid, spleen, interrenal, kidney	25	>30[a]	>0.3[a]	McLeay, 1973
	BKME	secondary[d]	perch	BW	liver	14	1	-[c]	Lehtinen & Oikari, 1980
	BKME	secondary[d]	perch	BW	gill	14	>4[a]	-[c]	Lehtinen & Oikari, 1980
	BKME	primary	pinfish	SW	gill	28	>1[a]	>0.1[b]	Stoner & Livingston, 1978
	BKME	secondary	rainbow trout	FW	gill, liver, spleen, gonad, heart, pancreas, kidney, muscle, brain	300	>2[a]	-[c]	NCASI, 1984a
	UKME	-[c]	flounder	BW	gill, liver	60	<2.5	-[c]	Lehtinen et al., 1984
	BKME	-[c]	flounder	BW	liver	60	<1	<0.03	Lehtinen et al., 1984

TABLE 2.4 EFFECTS ON AQUATIC LIFE OF PROLONGED EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS (Cont'd)

Function or system affected	Effluent		Test species	Diluent water	Nature of response measured	Duration of exposure (days)	Median effective concentration		Reference
	type	treatment					% (v/v)	Fraction of 96-h LC_{50} (% v/v)	
Growth/ Development	BPE	neutralized	pink, sockeye salmon	FW	decreased growth of alevins	-[c]	1-2	0.1	Servizi et al., 1966
	UKME	primary	chinook salmon	FW	decreased growth of juvenile fish	16	1	0.2	NCASI, 1968
	BKME	primary	sockeye salmon	FW	decreased growth of juvenile fish	56	>10<25	>0.2<0.5	Webb & Brett, 1972
	UKME	primary	coho salmon	FW	abnormal growth of juvenile fish	25	>30[a]	>0.3[a]	McLeay, 1973
	BKME	primary	rainbow trout	FW	decreased growth of juvenile fish	18	>-<6	>0.1<0.2	Whittle & Flood, 1977
	BKME	primary	pinfish	SW	decreased growth of juvenile fish	28	>1[a]	>0.1[a]	Stoner & Livingston, 1978
	BKME	primary	coho salmon	FW	increased growth of juvenile fish	50-200	>5<12	>0.1<0.25	McLeay & Brown, 1974
	BKME	primary	coho salmon	FW	increased growth of juvenile fish	200	>14[a]	>0.5[a]	McLeay & Brown, 1979
	UKME	secondary	chinook salmon	FW	decreased growth of juvenile fish	30	5[a]	-[c]	Warren et al., 1974
	BKME	secondary	coho salmon	FW	abnormal growth of juvenile fish	200	>5	-[b]	McLeay & Brown, 1979
	BKME	secondary	rainbow trout	FW	decreased growth (larval to fry)	62	10	-[c]	NCASI, 1982
	BKME	secondary	rainbow trout	FW	decreased growth of juvenile fish	18	10	-[c]	NCASI, 1982
	UKME	secondary	steelhead trout	FW	development (fertilized eggs to alevins)	25	>4[a]	-[c]	NCASI, 1977a
	BKME	secondary	steelhead trout	FW	abnormal development (to eyed egg)	22	32	-[c]	NCASI, 1982
	BKME	secondary	Daphnia magna	FW	abnormal development or growth	21	>100	-[b]	Weinbauer & Somers, 1982

TABLE 2.4 EFFECTS ON AQUATIC LIFE OF PROLONGED EXPOSURE TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS (Cont'd)

Function or system affected	Effluent type	Effluent treatment	Test species	Diluent water	Nature of response measured	Duration of exposure (days)	Median effective concentration % (v/v)	Median effective concentration Fraction of 96-h LC_{50} (% v/v)	Reference
Reproduction	UKME	secondary	brown, cut-throat trout	FW	spawning success affected	-[c]	<4	-[c]	NCASI, 1977a
	BKME	secondary	bass, sunfish	FW	spawning success	-[c]	>7[a]	-[b]	NCASI, 1978
	BPE	untreated	zebra fish	FW	effects on second generation	13-14	1-2	0.03-0.1	Anon., 1982b
	BKME	secondary	Daphnia magna	FW	reproduction	21	>100	-[b]	Weinbauer & Somers, 1982
Disease Resistance	UKME	secondary[d]	perch	BW	proliferation of gill parasites	14	<1	-[c]	Lehtinen & Oikari, 1980
	UKME	-[c]	flounder	BW	proliferation of gill parasites	60	<2.5	-[c]	Lehtinen et al., 1984
	BKME	-[c]	flounder	BW	proliferation of gill parasites	60	<1	-[c]	Lehtinen et al., 1984
	BKME	secondary	rainbow trout	FW	incidence of parasites and other lesions	300	>2[a]	-[c]	NCASI, 1984
Productivity	UKME	primary	chinook salmon	FW	enhanced production in laboratory streams	90	≤1.5	≤0.06	Warren et al., 1974
	UKME	primary	chinook salmon	FW	reduced production in laboratory streams	30	>0.5-<1.5	>0.06-<0.2	Seim et al., 1977
	UKME	secondary	chinook salmon	FW	enhanced production in laboratory streams	30	≤4	-[b]	Seim et al., 1977
	UKME	secondary	chinook salmon	FW	reduced production in laboratory streams	30	1.5	-[b]	Seim et al., 1977
	BKME	secondary	rainbow trout	FW	enhanced production in outdoor streams	300	>2-<5	-[c]	NCASI, 1983a, 1984a
	BKME	-[c]	Fucus sp.	BW	reduced productivity in model ecosystem	60	1	-[c]	Anon., 1982b

a Highest concentration examined.
b 96-h LC_{50} >100%.
c Not determined/not indicated.
d Unfiltered whole mill effluent from an aeration lagoon.

2.4.2 Metabolic/Stress Effects. Chonic exposure to primary-treated BKME concentrations of 1% and higher (concentrations equal to 0.05-0.1 of the samples' 96-h LC_{50} values) causes a number of metabolic disturbances in freshwater and marine fish (Table 2.4). Effects noted include altered carbohydrate metabolism (decreased liver glycogen energy reserves at 30 days; increased liver:muscle glycogen ratio and plasma glucose concentrations at 200 days) and elevated concentrations of lactic acid (or increased lactate:pyruvate ratios) in fish blood (McLeay and Brown, 1974, 1979). Changes in differential white blood cell counts (increased numbers of neutrophils) have also been reported following 30 or 200 days' exposure to somewhat higher concentrations of neutralized, filtered BKME (McLeay, 1973; McLeay and Brown, 1974). These responses are consistent with our current understanding of the generalized stress responses of fish which may result from their prolonged exposure to adverse concentrations of aquatic contaminants or other environmental stressors (Mazeaud et al., 1977; Passino, 1984; Wedemeyer et al., 1984). However, this interpretation remains tenuous because of inadequacies in our knowledge. Significant changes in lipid and protein metabolism of the marine pinfish Lagodon rhomboides exposed to 1% primary-treated BKME for 28 days have also been reported (Stoner and Livingston, 1978).

Only limited data are available concerning the metabolic effects of prolonged exposure of fish to dilute concentrations of biotreated pulp mill effluent. Biochemical changes displayed by juvenile coho salmon held for 30 or 200 days in laboratory-fermented BKME at an average strength of 5% included decreased liver glycogen content and elevated plasma glucose and lactate concentrations, interpreted as a state of chonic stress (McLeay and Brown, 1979).

The metabolic effects of prolonged exposure of rainbow trout to some of the toxic constituents of pulp and paper mill effluents have received some attention. Fish exposed for 11 days to a resin acid mixture at a concentration equivalent to 0.15 of its 96-h LC_{50} suffered markedly depleted liver glycogen and a pronounced inhibition of liver UDP-glucuronyl-transferase enzyme activity (Oikari and Nakari, 1982). A similar response was noted for rainbow trout that were held in a mixture of resin acids and chlorophenolic compounds (0.08 of the 96-h LC_{50}) (Oikari et al., 1984a) or 2% BKME (Castren and Oikari, 1979) for 30 days. Inhibition of this enzyme is considered relevant, because UDP-glucuronyl-transferase acts to conjugate (detoxify) accumulated resin acids and chlorophenolic compounds prior to their excretion (Oikari, 1984; Oikari et al., 1984a,b).

2.4.3 Respiratory/Circulatory Effects. Respiratory/circulatory responses of fish or aquatic invertebrates resulting from prolonged exposure to pulp mill effluent have been largely ignored; possibly because short-term exposures have been reported to result in only transient changes (Walden et al., 1970; Davis, 1973). Stoner and Livingston (1978) found that the gill ventilation rates for marine pinfish held in 1% primary-treated BKME for 28 days declined from initially high values within three days of exposure; however, values remained significantly elevated thoughout the test period. The numbers of circulating immature red blood cells in juvenile coho salmon increased when fish were held in 30% unbleached kraft mill effluent (0.3 of the 96-h LC_{50}) for 25 days (McLeay, 1973), although this response did not occur in fish exposed for a more prolonged period (McLeay and Brown, 1974) (Table 2.4). Underyearling rainbow trout held for periods of 270-300 days in outdoor experimental streams receiving biotreated BKME concentrations of (approximately) 1, 2 or 5% showed slight but significant changes in hematocrit values at the two higher strengths only (NCASI, 1984a, b). However, all mean hematocrit values were within the range considered normal for this fish species (NCASI, 1984a). Leucocrit values for these fish were unchanged by any effluent treatment (NCASI, 1984a, b) (Table 2.4). Similar studies with bluegill sunfish (Lepomis macrochirus) and largemouth bass (Micropterus salmoides) held for approximately one year in experimental warmwater streams containing, on average, 10% biotreated BKME showed no significant changes (from freshwater control fish) in hematocrit or leucocrit values (NCASI, 1984b). These findings are consistent with previous findings that total numbers of circulating white blood cells in salmonid fish recovered from initially depressed values when exposure to pulp mill effluent was prolonged (McLeay, 1973; McLeay and Brown, 1974).

Oikari et al. (1983) found that the relative weights of spleens for rainbow trout held in 20 µg/L dehydroabietic acid for 30 days were increased, a response which may be attributable to either increased erythocyte production or storage. Leucocrit values for rainbow trout exposed to a resin acid mixture (0.15 of 96-h LC_{50}) for 11 days were also elevated, although not in trout exposed for 30 days (Oikari et al., 1984a).

2.4.4 Effects on Stamina/Performance. Only a limited number of studies have examined the stamina of fish following their prolonged exposure to pulp mill effluent (Table 2.4). The swimming performance of juvenile chinook salmon, determined as maximum sustainable swimming speed in freshwater, was found to be unaffected by their prior exposure to 1% primary-treated unbleached kraft mill effluent for 12 days (NCASI, 1968). The swimming stamina of juvenile coho salmon following a 90-day exposure to

primary- or secondary-treated BKME concentrations in experimental streams was examined by McLeay and Brown (1974). Critical swimming speeds (Brett, 1964; Howard, 1975) for groups of fish chronically exposed to primary-treated effluent concentrations averaging 14% (0.5 of 96-h LC_{50}) or less, or to concentrations for secondary-treated effluent of 6 or 28%, did not differ significantly from the performance of control fish reared in freshwater (McLeay and Brown, 1974). Equivalent or superior short-term stamina of fish exposed for prolonged periods to low levels of other aquatic contaminants has been found in numerous instances, even where damage to fish gills and other tissues has been evident (Lemke and Mount, 1963; Larmoyeux and Piper, 1973; Waiwood and Beamish, 1978).

Lehtinen and Oikari (1980) found that perch (Perca fluviatilis) could compensate for torque when tested in a rotary-flow swimming apparatus, following 14 days' exposure to 1% secondary-treated BKME, but not when the concentration was 2% or 4%. The effluent to which these fish were exposed was unfiltered, so the response could have been due to suspended fibres or to dissolved toxic constituents. A similar test, following exposure of perch to 1% or 2.5% BKME (treatment unidentified) for two months, showed no decreased performance (Anon., 1982b).

2.4.5 Behavioural Effects. No reports have been encountered in the literature relating to behavioural changes due to the prolonged exposure of fish or aquatic invertebrates to pulp mill effluent. However, a related study showed that the daily rates of consumption of live tubifex worms (Tubifex sp.) by juvenile chinook salmon held in unbleached kraft pulp mill effluent for 16 days were unaffected by primary-treated effluent concentrations of 1%, or 1-5% biotreated effluent (NCASI, 1968), regardless of the ration level.

2.4.6 Histological Effects. Inconsistent results are reported following light microscopic examination of numerous tissues of fish exposed for extended periods to kraft mill effluent. No pathological changes attributable to a 25-day exposure of juvenile coho salmon to 30% unbleached filtered kraft pulping effluent (0.3 of 96-h LC_{50}) were discerned by McLeay (1973) for any of the tissues examined (Table 2.4). Lehtinen and Oikari (1980) reported hepatocellular changes in livers of perch held in 1-4% unfiltered, aerated BKME for 14 days, whereas gill histology appeared normal. More recently, Lehtinen et al. (1984) reported gill epithelial damage for flounders (Platichtys flesus) held in brackish water containing 2.5% unbleached kraft whole mill effluent (treatment not specified) for 60 days. The liver tissue from these flounders and from those held in 1% or

2.5% BKME for this period also appeared atypical, with cytoplasmic vacuolization and a significantly greater number of shrunken nuclei. The 1% concentration of this effluent was equivalent to 0.03-0.04 of its average 96-h LC_{50} value.

Stoner and Livingston (1978) found that the gill tissue of marine pinfish held in 1% primary-treated BKME for 28 days appeared normal, although excessive mucous was evident on the gill filaments. Detailed histopathological examination of rainbow trout exposed for 270-300 days in experimental streams containing biotreated BKME concentrations of 1%, 2% or 5% revealed no adverse changes (NCASI, 1984a,b). Similar studies of largemouth bass and bluegill sunfish held for approximately one year in warmwater streams containing 10% biotreated BKME also showed no increased incidences of histopathologies relative to corresponding samples of control fish (NCASI, 1984b).

2.4.7 Effects on Growth and Development of Fish and Invertebrates. The effect of prolonged exposure to pulp mill effluent on the development and growth of the early life stages of fish has received considerable attention. Most reported studies have been conducted with juvenile salmonid fish exposed to primary- or secondary-treated bleached or unbleached kraft whole mill effluent diluted with freshwater (Table 2.4). These investigations indicate that extended (16-200 days) exposure to effluent concentrations equivalent to 0.1 of the 96-h LC_{50} value or less does not affect fish growth. Higher strengths (0.2->0.5 LC_{50}) may impair growth (NCASI, 1968; Webb and Brett, 1972; Whittle and Flood, 1977), whereas growth enhancement occurred in some instances (McLeay and Brown, 1974; Davis, 1976). The various authors have offered plausible explanations for their own data, but no reason(s) for the dissimilar response is evident. The concentrations of primary-treated kraft mill effluent affecting the growth of fish under controlled conditions are in most instances greater than 3-10% (Table 2.4). One study (NCASI, 1968) reported a median effective concentration of 1% for unbleached effluent; however, the acute lethal toxicity of this effluent was atypically high (mean 96-h LC_{50}, 5%).

Servizi et al. (1966) incubated newly hatched pink and sockeye salmon alevins in dilute (1-2%) concentrations of neutralized bleach plant effluent until yolk absorption was complete. These researchers found that for each fish species, alevin growth (measured as dry weight) was reduced significantly relative to corresponding groups of fish incubated in freshwater only. The effluent strengths were equivalent to 0.05-0.1 of the 96-h LC_{50} value derived for this bleach plant effluent using sockeye salmon fingerlings.

Where concentrations of biotreated unbleached or bleached kraft whole mill effluent have been less than 5%, fish growth under laboratory conditions has not been affected (Table 2.4). Decreased growth has been found for fish chonically exposed to 5% (Warren et al., 1974) or 10% (NCASI, 1982) secondary-treated effluent.

When rainbow trout were exposed throughout the alevin and fry stages (62 days) to a range of concentrations of biotreated (14-day aerated lagoon) BKME with a 96-h LC_{50} value of 28%, growth was unaffected at 5.6%, but reduced at 10% (NCASI, 1982). No embryonic abnormalities were observed when freshly fertilized eggs of steelhead trout were exposed until hatched, 31 days later, to 5.6-18% concentrations of this stabilized effluent (NCASI, 1982). A variety of abnormalities occurred at higher ($\geq$32%) effluent concentrations, including malformed embryos and altered developmental schedules. Previous studies (NCASI, 1977a) with freshly fertilized steelhead trout eggs incubated for 25 days in outdoor experimental streams receiving 4% biotreated unbleached kraft mill effluent also showed no effects on the survival or development of embryos and alevins. More prolonged studies have not been reported. Limited evidence (NCASI, 1982, 1983a) suggests that the early (fertilization to eyed-egg stage) life stages of developing fish may be appreciably more sensitive to pulp mill effluent than the later stages.

Burton et al. (1984) exposed striped bass (Morone saxatilis) larvae for 20 days to a range of concentrations of biotreated BKME in brackish (5 °/oo salinity) water. All effluent strengths examined ($\geq$20%) did not affect fish survival, growth or metamorphosis to the juvenile stage.

Weinbauer and Somers (1982) determined that the growth and development of two generations of Daphnia magna chronically (21 days) held in biotreated BKME (48-h renewal of test solutions) concentrations of 100% or less did not differ from controls in freshwater. Similar studies with other types of pulp and paper mill effluents have not been reported.

2.4.8 Effects on Reproduction. Scant attention has been given to the possible effects of dilute concentrations of pulp and paper mill effluents on the reproductive activities of fish or aquatic invertebrates and on the subsequent survival and well-being of their offspring (Table 2.4). Attempts to induce the spawning of adult brown trout (Salmo trutta) and cutthroat trout (Salmo clarki) in outdoor experimental spawning channels receiving 4% biotreated unbleached kraft whole mill effluent proved unsuccessful (NCASI, 1977a). No other attempts with salmonid fish have been reported. However, warmwater

warmwater fish species (largemouth bass, Micropterus salmoides; bluegill sunfish, Lepomis macrochirus) have spawned in outdoor experimental channels containing approximately 7% biotreated BKME (NCASI, 1978).

Swedish scientists have exposed the zebra fish (Brachydanio rerio), a freshwater fish species with a rapid reproductive cycle, to bleach plant effluents or effluent constituents to determine the delayed (second generation) effects (Anon., 1982b). The procedure for this bioassay has recently been reported (Landner et al., 1985). Exposure of adult fish to 1-2% kraft bleach plant effluent (0.03-0.1 of the 96-h LC_{50}) for 13 or 14 days, prior to spawning, significantly increased mortalities and developmental anomalies of the offspring, relative to those from unexposed parents (Anon., 1982b). The concentrations of effluent or chemicals (i.e., tetrachloroveratrole) found to induce "delayed" (second generation) effects in zebra fish were at least five times lower than the median effective concentration found for the direct exposure of eggs or larvae (Neilson et al., 1984; Landner et al., 1985). Whole mill effluents have not yet been evaluated according to this test procedure.

The absence of any effect of undiluted (100%) biotreated BKME on the reproduction of Daphnia magna and on the subsequent survival and development of their offspring has been reported (Weinbauer and Somers, 1982). These organisms reproduced parthenogenetically (asexually) under the bioassay conditions employed.

Renberg et al. (1980) reported that tetrachloroguaiacol decreased the fecundity of the estuarine copepod (crustacean) Nitocra spinipes at median effective concentrations of 37-54 µg/L. These concentrations were 0.01 of the 96-h LC_{50} value determined for these organisms. Similar reproductive tests with this or other estuarine/marine species have not been reported.

2.4.9 Effects on Disease Resistance. Many examples in the literature indicate that the resistance of fish to disease is diminished by their exposure to environmental stressors including sublethal concentrations of aquatic contaminants. The interactions between stress and the resistance of fish to disease are complex and little understood (Ellis, 1981). However, if the degree of stress is sufficiently strong or prolonged, their ability to withstand the myriad of viral, bacterial or parasitic organisms to which they are routinely exposed is often lowered sufficiently to allow the proliferation of these pathogens and the manifestation of disease symptoms (Snieszko, 1974; Wedemeyer and McLeay, 1981; Wedemeyer et al., 1976, 1984). Dilute concentrations of chemicals shown to be mutagenic or carcinogenic to mammals can also induce neoplasms (tumours) in livers and other

tissues of exposed fish (Sinnhuber et al., 1977; Grieco et al., 1978; Sonstegard and Leatherland, 1984).

As with other types of effluent discharges, the extent to which pulp and paper mill effluents may alter the disease resistance of fish and other aquatic organisms has received little attention and is not understood. Concerns regarding potential mutagenic/carcinogenic risk associated with these effluents have been raised since Hoglund et al. (1979) showed that chlorination stage effluents possess mutagenic activity. However, an extensive number of mutagenicity screening assays conducted with whole mill effluents indicate that this risk is minimal at most (Hoglund et al., 1979; Anon., 1982b).

Only limited information has been derived regarding the incidence of disease attributable to the exposure involved in the controlled growth/productivity/histology studies reported above (Table 2.4). In most instances, no specific examinations for lesions or infections were made. During a histological examination of gill specimens from perch (Perca fluviatilis) experimentally exposed in brackish water to unfiltered, secondary-treated BKME concentrations of 1%, 2% or 4% for 14 days, Lehtinen and Oikari (1980) noted parasitic cysts, identified as Oodinium sp., between the secondary lamellae in all effluent-exposed fish but not in the controls. Subsequent studies conducted by Lehtinen and co-workers with flounder (Platichtys flesus) and other estuarine organisms exposed in model ecosystems for two months, to 2.5% (unbleached) or 1% and/or 2.5% (bleached) kraft whole mill effluents from three separate mills, revealed that the gills of all effluent-exposed fish (but not controls) were infested with Tricodina sp. (Anon., 1982b; Lehtinen et al., 1984). No information was provided concerning any treatment of these effluents. The biological (respiratory) relevance of these attached ciliates was not investigated.

A detailed analysis was made on rainbow trout introduced initially as 1-g fry into outdoor experimental streams receiving a continuous supply of freshly biotreated BKME at average concentrations of 1%, 2% or 5%, and held for 270-300 days (NCASI, 1984a,b). Numerous tissue types (gill, liver, kidney, intestine, pancreas, skin, nares, brain, heart, muscle) showed no differences in incidences of parasites between the freshwater controls and effluent-exposed fish. With the exception of the gill tissues (high incidence of lesions in both controls and effluent-exposed fish, attributed primarily to the blood parasite Sanguinicola), tissue parasites were uncommon. No incidences of neoplastic lesions in fish livers or other tissues were observed. Similar findings were also reported for warmwater fish species receiving prolonged exposure to biotreated BKME in southern experimental streams (NCASI, 1984b). However, the greatest risk of induction of tumours

in fish, due to their exposure to mutagenic/carcinogenic chemicals, is during their early stages of embryonic development (although the tumours may not be manifested until many months later) (Sinnhuber et al., 1977; Grieco et al., 1978). More information relating to the prolonged observation of organisms exposed during early embryonic development is required.

2.4.10 Effects on Productivity. The effects of primary- and secondary-treated kraft whole mill effluents on cold and warmwater stream communities has been the subject of extensive investigative research by the National Council of Air and Stream Improvement Inc. (New York) during the past 18 years. Early studies in cooperation with scientists at the Oregon State University (NCASI, 1968, 1977a; Warren et al., 1974; Seim et al., 1977) examined the effects of unbleached kraft whole mill effluent on the production of juvenile salmon in laboratory streams or experimental channels containing diverse communities of freshwater algae and invertebrates. Subsequent studies have examined the effects of secondary-treated (12-14 day aerated lagoon) BKME on cold (NCASI, 1982, 1983a) and warmwater (NCASI, 1977b, 1978, 1983b) stream productivity using large (100 m) outdoor experimental channels with alternating riffles and pools.

The production of a population is the sum of the growth of all individuals in the population (Warren et al., 1974). In the initial studies with laboratory streams colonized by stocking with algae, insect larvae and invertebrates from natural streams, the production of juvenile chinook salmon was calculated as the daily change in fish weight per unit area of stream bottom, under differing conditions of exposure to UKME. Primary-treated UKME from one mill enhanced fish production at concentrations of 0.8 and 1.5% (equivalent to 0.03-0.06 of the 96-h LC_{50}) whereas a somewhat more toxic UKME source caused decreased production at 1.5% (Warren et al., 1974; Seim et al., 1977). When examined during spring and fall, secondary-treated UKME again reduced fish production at a 1.5% concentration but production of fish exposed to the same effluent source was enhanced during summer experiments at concentrations up to 4% (Seim et al., 1977; Table 2.4). On the other hand, experiments with naturally colonized outdoor channels stocked with young rainbow trout have failed to demonstrate any effects on fish productivity throughout extended (300-day) exposures to biotreated BKME concentrations averaging 1 or 2% (NCASI, 1982, 1983a); whereas prolonged (270-day) exposure of rainbow trout to 5% biotreated BKME significantly enhanced fish production (NCASI, 1984a). A number of factors including season, the specific characteristics of the stream habitat and community, together with the type, source, concentration, nutrient content and degree of treatment of the effluent, may modify the effluent's ability to influence fish production.

Concurrent measurements of periphyton productivity in the outdoor channels during the fish production studies showed no significant differences between the control streams and those receiving 1% or 2% biotreated BKME (NCASI, 1982, 1983a). Mean monthly benthic macroinvertebrate density and biomass were significantly greater (relative to corresponding control streams) in streams receiving 1% effluent, and the same as controls at 2%. No differences were evident in species diversity of the macroinvertebrate communities reared in freshwater and in 2% biotreated BKME (NCASI, 1983a).

Model ecosystem (microcosm) studies have been conducted recently with communities of estuarine organisms exposed experimentally to dilute concentrations of bleach plant effluent and to unbleached and bleached kraft whole mill effluents (Anon., 1982b). Circular 7.5 m^3 tanks with sand bottoms were stocked with seaweed (Fucus sp.), shrimp (Neomysis sp.), flounder (Platichtys flesus) and perch (Perca fluviatilis), and allowed to stabilize for one month prior to the introduction of effluents. Significant declines in the productivity of periphyton (seaweed) and phytoplankton were noted within two months for tanks receiving 1% and 2.5% BKME. Data relating to fish or shrimp productivity were not reported.

2.5 Environmental Variables Modifying Toxicity

2.5.1 General. Procedural and sampling variables which affect the quantitative assay of the acute lethal toxicity of pulp and paper mill effluents, have been elucidated to a large degree. These include effluent sample pre-treatment (i.e., conditions of collection, storage and preparation) and variables such as solution pH, rate of replacement, test organism:effluent volume ratio, and aeration rates for test solutions (Walden et al., 1972, 1975; Davis and Mason, 1973; Loch and MacLeod, 1974; Walden and McLeay, 1974). Moreover, recent standardization incorporates most of these experimental findings into bioassay procedures (Anon., 1980b, 1982), resulting in reduced intra- and inter-laboratory errors for bioassay determinations. Nonetheless the gap between the controlled laboratory environment and the continually changing real world situation remains huge. Some understanding of the manner in which variables that are controlled in the laboratory bioassay actually affect toxicity is essential to any appreciation of real environmental impact of the toxic constituents. Some of these modifying variables are considered briefly here.

2.5.2 Dissolved Oxygen. The oxygen demand of pulp and paper mill effluents, its environmental consequences and the capacities of differing receiving environments to

assimilate oxygen-deficient effluents or those with a high oxygen-consuming potential are discussed in detail by Poole et al. (1978). According to these authors and, more recently, Waldichuk (1983), one of the main ecological problems associated with the disposal of pulp and paper mill effluent continues to be low dissolved oxygen. However, this is not universally so and, at least for numerous B.C. fresh and marine waters receiving these discharges, significant oxygen depletion is not apparent (Anon., 1976).

Davis (1975) reviewed the dissolved oxygen requirements of freshwater and marine organisms with emphasis on Canadian species, and indicated examples where the deleterious effects of toxic effluents and oxygen-deficient waters can be additive. Alderdice and Brett (1957) first suggested that pulp mill effluent was more toxic when test solutions (or receiving waters) were oxygen-deficient. Subsequent laboratory studies by Hicks and DeWitt (1971) determined that, for juvenile coho salmon exposed to primary-treated BKME, the lower the dissolved oxygen values the greater the toxicity, within the limitations of oxygen solubility in water. Graves et al. (1981) demonstrated that the acute lethal toxicity of biotreated BKME to juvenile sheepshead minnow (Cyprinodon variegatus) increased markedly at lower dissolved oxygen concentrations, although differing responses were found for other life stages.

2.5.3 Temperature. The modifying influence of environmental temperature on the toxic responses of aquatic life to pulp and paper mill effluents has received little attention. Whereas almost all laboratory bioassays with Canadian fish and aquatic invertebrate species have been conducted at 10-15°C, seasonal extremes in the temperature of the receiving waters can differ markedly from this range. For instance, water temperatures in Canada during winter months are often 5°C or less. No toxicity data exist for such low temperatures despite the fact that such water temperatures may prevail for up to six months out of the year.

After acclimating juvenile rainbow trout to temperatures of 8, 10, 15 and 20°C for 30 days, Loch and MacLeod (1974) measured their acute time to median survival for a single sample of pulp mill effluent (type unidentified) at each of these temperatures. Tolerance decreased (i.e., toxicity increased) with increasing temperature, i.e., the higher the test temperature the shorter the survival time. Gordon and McLeay (1977) acclimated groups of juvenile rainbow trout and coho salmon for six weeks to 10 or 15°C and then exposed them to differing concentrations of primary-treated BKME at these temperatures under otherwise identical conditions. Although differences were minor, toxicity was greater (lower 96-h LC_{50} values) for each species at the higher temperature.

Insofar as we can elucidate, no studies have been undertaken of the influence of temperature on long-term survival or well-being of effluent-exposed fish or other aquatic organisms. The combined influence of differing (controlled) temperature and dissolved oxygen regimes on the acute or chonic toxicity to aquatic life of pulp and paper mill effluent also has not been studied. Such studies would be prerequisite to any understanding of how fluctuating versus stable temperature (or dissolved oxygen) may influence fish tolerance to these discharges.

2.5.4 Photoperiod. Seasonal variations in photoperiod (day length) have been reported to cause changes in fish respiration rates and perhaps in their tolerance to aquatic contaminants even when temperatures are held constant (Spieler et al., 1977; Zitko and Carson, 1977). In a controlled study, a population of juvenile rainbow trout was acclimated for 18 weeks to either summer or winter photoperiods under otherwise identical conditions. These two groups showed no appreciable differences in their acute lethal (LC_{50}) and sublethal (stress, temperature and hypoxic tolerances) responses to a single sample of primary-treated BKME (McLeay and Gordon, 1978). The degree to which seasonal photoperiod may modify toxic responses to pulp mill effluent for other cultured or indigenous aquatic species is unknown.

2.5.5 pH. For many years it has been known that pH extremes will significantly enhance the toxic effects of untreated or clarified pulp and paper mill effluents; however, within Canada most whole mill effluents are now neutralized prior to discharge to freshwater or rapidly become so upon their mixing with seawater. Less well recognized is that the pH of diluent and receiving waters affects bioassay results and toxic effects within the environment, respectively.

A number of reports show that pH changes within the range of values characteristic of natural waterbodies (i.e., pH 6.0-9.5) significantly affect the acute lethal toxicity of untreated or primary-treated pulp mill effluent (Ladd, 1969; McLeay and Walden, 1976; McLeay et al., 1979a,b) and certain effluent constituents. Results from LC_{50} bioassays with salmonid fish exposed to a range of freshwater concentrations of untreated or clarified kraft whole mill effluents held at differing pH values indicate that these effluents are considerably less toxic at pH 9 than at neutrality; and that LC_{50} values decrease progressively with decreasing pH values thoughout the pH range of 5 to 9 (Ladd, 1969; McLeay et al., 1979b). In a separate study, the LC_{50} values for a single primary-treated BKME sample were found to vary appreciably when tested with differing natural freshwater sources (pH 6.4-8.4) as diluent water, whereas differences were

minimal when all solutions were adjusted to the same pH prior to fish (rainbow trout) exposure (McLeay et al., 1979a). The influence of effluent- or diluent water-pH on the toxicity of secondary-treated pulp and paper mill effluents has not been reported.

Consistent with the above findings, various resin acids have been shown to be substantially more toxic at pH 6.4 than at pH 7.0 (Leach and Thakore, 1974); and dehydroabietic acid has been demonstrated to be least toxic at pH 9.5 (McLeay et al., 1979b). Zanella (1983) recently reported that the LC_{50} value for dehydroabietic acid was nine times greater for Daphnia magna and seven times greater for fathead minnows, when tested at pH 8.0 and 6.5, respectively. Similar differences due to pH were found for mono-and dichlorodehydroabietic acid (Zanella, 1983).

The toxicity of certain chlorophenolic compounds has been shown to be significantly greater when tested at lower pH values. For instance, the LC_{50} value for 2,4,6-trichlorophenol was four times greater (less toxic) for guppies (Poecilia reticulata) when tested in freshwater at pH 8 than in solutions at pH 6 (Saarikoski and Viluksela, 1981). Similarly, Voss et al. (1980) found that both 2,4,6-trichlorophenol and tetrachloroguaiacol were appreciably more toxic to rainbow trout when LC_{50} bioassays were performed at pH 6.4-7.0 than at pH 7.3-8.1. Swedish investigators have reported that the LC_{50} value for tetrachloroguaiacol was four times greater for Daphnia magna when tested at pH 7.4-8.1, than in solutions at pH 6.0-7.1 (Anon., 1982b).

2.5.6 Alkalinity. In natural freshwaters, alkalinity values are positively correlated with pH. Thus reported observations of decreasing toxicity of sulphite waste liquor (Grande, 1964) or BKME (McLeay et al., 1979a) for concurrent fish bioassays using natural diluent waters with increasing pH may involve some interaction with water alkalinity or even hardness.

A series of fish (rainbow trout) bioassays, conducted by Middelraad and Wilson (1975), involved filtered mechanical pulping effluent diluted with different volumes of a hard (350 mg $CaCO_3$/L) wellwater mixed with de-ionized water to provide resultant hardness values of 40 mg/L, 100 mg/L or 150 mg/L. Although 96-h LC_{50} values increased from 25% to 59% with increases in hardness from 40 to 150 mg/L, pH values were not controlled. Accordingly, pH may also have been implicated.

As part of the LC_{50} bioassays undertaken by McLeay et al. (1979a) using a primary-treated BKME sample diluted with each of ten natural freshwaters, one series of tests was conducted whereby the pH of all test solutions was held constant. The range of LC_{50} values derived was narrowed appreciably by this pH adjustment, albeit decreases in

effluent toxicity were still positively correlated with increasing alkalinity and hardness. The degree to which alkalinity and hardness modify the toxicity of secondary-treated mill effluents has not been reported.

2.5.7 Salinity. A clear understanding of the effect of seawater chemistry on the toxicity of pulp and paper mill effluents is difficult to obtain. Differences in sensitivity of biological species (if fresh- vs. seawater organisms are compared) or their overall health and condition (if a single euryhaline species is acclimated to fresh, brackish and/or seawater prior to testing) may mask the effects of chemical speciation in seawater.

Seawater has been diversely reported to increase (Anon., 1975; Rogers et al., 1975), decrease (Waldichuk, 1962, 1983) or not appreciably alter (McLeay et al., 1979b) the toxicity of pulp mill effluent, relative to its toxic effect in freshwater. Experimental artifacts due to fish condition and lack of pH control in comparative bioassays using fresh- or seawater may have been responsible for these differing conclusions. Comparative LC_{50} tests performed with a single population of juvenile coho salmon acclimated to fresh- or seawater for five months produced equivalent values when test pH was the same (7.5) (McLeay et al., 1979b).

Preliminary studies with perch exposed to 2,4,6-trichlorophenol or a resin acid mixture dissolved in brackish (7 o/oo) or freshwater indicated that the acute lethal toxicity of trichlorophenol increased and that of resin acids decreased in brackish water, compared to their toxicities in freshwater (Lindgren and Oikari, 1982).

2.6 References

Alderdice, D.F. and J.R. Brett. 1957. Some effects of kraft mill effluent on young Pacific salmon. J. Fish. Res. Board Can. 14: 783-795.

Anon., 1972a. Guidelines for the Pulp and Paper Effluent Regulations Promulgated Under the Fisheries Act. Regulations, Codes and Protocols, Report 2. Water Pollution Control Directorate, Environment Canada. Ottawa, Ontario.

Anon., 1972b. Water Quality Control Plan for Ocean Waters of California. State Water Resources Control Board. July 6, 1972.

Anon., 1975. Brief Presented to the Pollution Control Board Inquiry into the Pollution Control Objectives for the Forest Products Industry of British Columbia. Environment Canada. West Vancouver, B.C.

Anon., 1976. Brief presented at the Public Inquiry into the Pollution Control Objectives for the Forest Products Industry of British Columbia, by the B.C. Council of Forest Industries. Exhibit 1. B.C. Dept. Lands, Forests and Water Resources. Victoria, B.C.

Anon., 1979. Toxicity of Effluents from Sulphite Pulping Operations Practising Recovery and Biological treatment. Environment Canada Report No. EPS 3-WP-79-9. Water Polution Control Directorate, Environment Canada. Ottawa, Ontario.

Anon., 1980a. Part 800 bioassay methods for aquatic organisms. Standard Methods for the Examination of Water and Wastewater. 15th ed. American Public Health Assoc., Washington, D.C.

Anon., 1980b. Standard Procedure for Testing the Acute Lethality of Liquid Effluents. Report No. EPS 1-WP-80-1. Water Pollution Control Directorate, Environment Canada. Ottawa, Ontario.

Anon., 1982a. Provincial Guidelines and Laboratory Procedures for Measuring Acute Lethal Toxicity of Liquid Effluents to Fish. November, 1982. B.C. Ministry of Environment. Victoria, B.C.

Anon., 1982b. Environmentally Harmonized Production of Bleached Pulp. Final report (in Swedish). Swedish Forest Products Research Laboratory, Stockholm, Sweden.

Anon., 1982c. Water quality - Determination of the Inhibition of the Mobility of Daphnia magna Straus (Cladocera, Crustacea). International Organization for Standardization. Geneva, Switzerland.

Bayne, B.L., D.R. Livingstone, M.N. Moore and J. Widdows. 1976. A cytochemical and biochemical index of stress in Mytilus edulis L. Mar. Poll. Bull. 7: 221-224.

Blaise, C. 1984a. Développement de bioessais sublétaux pour les évaluations écotoxicologiques des effluents. Thèse de doctorat, Université de Metz (France), 172 pp.

Blaise, C. 1984b. Personal communication.

Bothwell, M.L. and J.G. Stockner. 1980. Influence of secondarily treated kraft mill effluent on the accumulation rate of attached algae in experimental continuous-flow troughs. Can. J. Fish. Aquat. Sci. 37: 248-254.

Brett, J.R. 1964. The respiratory metabolism and swimming performance of young sockeye salmon. J. Fish Res. Board Can. 21: 1183-1226.

Brouzes, R.J.P. 1976. Fish toxicity with specific reference to the pulp and paper industry. pp. 81-124. In Proceedings of Seminars on Water Pollution Abatement Technology in the Pulp and Paper Industry. Envir. Canada Rep. EPS 3-WP-76-4. March 1976. Water Pollution Control Directorate. Ottawa, Ontario.

Brouzes, R.J.P. and V.A. Naish. 1975. Acute toxicity of pulp and paper mill effluents using daphnia and rainbow trout as test animals. pp. 54-66. In Proc. Second Ann. Aquat. Tox. Workshop. November 4 & 5, 1975. Ontario Ministry of the Environment. Toronto, Ontario.

Bruynesteyn, A. 1977. Determination of the Practical Value of Toxic Loadings. CPAR Rep. No. 588-1. Environmental Protection Service. Ottawa, Ontario.

Buckney, R.T. 1978. Toxicity of treated and untreated P. radiata TMP effluents on a number of organisms. Appita 32: 129-133.

Burton, D.T., R.J. Klauda, L.W. Hall and M.A. Jepson. 1984. An evaluation of the potential toxicity of treated bleached kraft mill effluent to striped bass (Morone saxatilis Walbaum) larvae exposed through metamorphosis to the juvenile stage. Water Res. 18: 1365-1376.

Cardwell, R.C., S. Olsen, M.I. Carr and E.W. Sanborn. 1979. Causes of Oyster Larvae Mortality in South Puget Sound. NOAA Tech. Memo. ERL MESA-39. National Oceanic and Atmospheric Administration. Boulder, CO.

Cary, G.A. and M.E. Barrows. 1981. Reduction of Toxicity to Aquatic Organisms by Industrial Wastewater Treatment. Rep. EPA-600/3-81-043. U.S. Environmental Protection Agency. Springfield, VA.

Castren, M. and A. Oikari. 1979. The use of detoxification reactions (glucuronidation) in evaluating the water toxicity to fishes. p. 84. Abstract from the 2nd Symposium on Fish Physiology. Goteborg, Sweden. June 8-10, 1979.

Chang, J.C., P.B. Taylor and F.R. Leach. 1981. Use of the Microtox assay system for environmental samples. Bull. Environ. Contam. Toxicol. 26: 150-156.

Chapman, P.M., D.R. Munday, J.R. Morgan, R. Fink, R.M. Kocan, M.L. Landolt and R.N. Dexter. 1983. Survey of Biological Effects of Toxicants Upon Puget Sound Biota. II. Tests of Reproductive Impairment. NOAA Tech. Rep. NOS 102 OMS 1. National Oceanic and Atmospheric Administration. Rockville, MD.

Davis, J.C. 1973. Sublethal effects of bleached kraft pulp mill effluent on respiration and circulation in sockeye salmon (Oncorhynchus nerka). J. Fish. Res. Board Can. 30: 369-377.

Davis, J.C. 1975. Minimal dissolved oxygen requirements of aquatic life with emphasis on Canadian species: A review. J. Fish. Res. Board Can. 32: 2295-2332.

Davis, J.C. 1976. Progress in sublethal studies with kraft pulp mill effluent and salmonids. J. Fish Res. Board Can. 33: 2031-2035.

Davis, J.C. 1978. Disruption of precopulatory behavior in the amphipod Anisogammarus pugattensis upon exposure to bleached kraft pulp mill effluent. Water Res. 12: 273-275.

Davis, J.C. and B.J. Mason. 1973. Bioassay procedures to evaluate acute toxicity of neutralized bleached kraft pulp mill effluent to Pacific salmon. J. Fish. Res. Board Can. 30: 1565-1573.

deZwart, D. and W. Sloof. 1983. The Microtox as an alternative assay in the acute toxicity assessment of water pollutants. Aquatic Toxicol. 4: 129-138.

Donnini, G.P. 1981. Reduction of toxicity and mutagenicity of chlorination effluents with sulphur dioxide. Pulp Paper Can. 82: T373-378.

Donnini, G.P. 1983. Bleach plant effluents: chemical control of some environmental problems. Pulp Paper Can. 84: T93-98.

Donnini, G.P., S.C. Mosher and R.P. Scroggins. 1984. Mill scale application of sulphur dioxide to reduce bleaching effluent toxicity. pp. B195-B201. In Proc. 70th Ann. Meeting, Tech. Sect., CPPA. February 2 & 3, 1984. Montreal, Quebec.

Dumouchel, A., T. Matula, J. Reed and M.A. Wilson. 1975. Assessment of the Sensitivity of Major Aquatic Food Chain Organisms to Newsprint Mill Effluents. CPAR Rep. No. 328-1. Environmental Protection Service. Ottawa, Ontario.

Dutka, B.J. and K.K. Kwan. 1981. Comparison of three microbial toxicity screening tests with the Microtox test. Bull. Environ. Contam. Toxicol. 27: 753-757.

Easty, D.B., L.G. Borchardt and B.A. Wabers. 1978. Removal of Wood-derived Toxics from Pulping and Bleaching Wastes. Rep. EPA-600/2-78-031. U.S. Environmental Protection Agency. Cincinnati, OH.

EIFAC 1975. Report on Fish Toxicity Testing Procedures. EIFAC Tech. Paper No. 24. European Inland Fisheries Advisory Commission. FAO, Rome.

Ellis, A.E. 1981. Stress and the modulation of defense mechanisms in fish. pp. 147-169. In Stress and Fish. A.D. Pickering, ed. Academic Press, London, Eng.

Eloranta, V. 1976a. The influence of sulphate cellulose effluents on the growth of green algae (Ankistrodesmus falcatus). Vatten 32: 20-37.

Eloranta, V. 1976b. Effects of different process wastes and main sewer effluents from pulp mills on the growth and production of Ankistrodesmus falcatus var. acicularis (Chlorophyta). Biol. Res. Rep. Univ. Jyvaskyla 2: 3-33.

Eloranta, V. 1978a. Effects of different process wastes and main sewer effluents from pulp mills on the growth and production of Ankistrodesmus falcatus var. acicularis (Chlorophyta). Mitt. Internat. Verein. Limnol. 21: 342-351.

Eloranta, V. 1978b. On biomass monitoring methods in toxic assays of algae. pp. 147-156. In Nordforsk Miljovardssekretariatet Publikation 1978: 2. Fjortonde Nordiska Symposiet om Vattenforskning, April 25-27, 1978. Alborg, Denmark.

Eloranta, V. and P. Eloranta. 1980. Algal assays on waters receiving sulphite and sulphate cellulose effluents. Ann. Bot. Fennici 17: 26-34.

Eloranta, V. and O. Laitinen. 1981. Evaluation of sample preparation for algal assays on waters receiving cellulose effluents. Verh. Internat. Verein. Limnol. 21: 770-775.

Eloranta, V. and O. Laitinen. 1982. The usefulness of the Selenastrum capricornutum algal assay to evaluate the toxic effects of pulp and paper mill effluents in lake water. Vatten 38: 317-331.

Eloranta, V., L. Halttunen-Keyrilainen and K. Kuivasniemi. 1985. The acute toxicity of spent bleaching liquors and bleached kraft mill effluent studied by the Selenastrum algal test and indigenous phytoplankton bioassays. Sciences et Techniques de L'eau. In Press.

EPA 1977. Draft Final Report: Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. U.S. Environmental Protection Agency, Cincinnati, OH.

Fahmy, F.K. and D.L. Lush. 1974. Sensitivity of Major Aquatic Food Chain Organisms to Treated Kraft Mill Effluents. CPAR Rep. No. 356-1. Environmental Protection Service, Ottawa, Ontario.

Fisher, J.N. 1982. Employing acute and subacute toxicity measurements in on-site biomonitoring studies. TAPPI J. 65: 89-91.

Gordon, M.R. and D.J. McLeay. 1977. Sealed-jar bioassays for pulp mill effluent toxicity: effects of fish species and temperature. J. Fish. Res. Board Can. 34: 1389-1396.

Gordon, M.R. and D.J. McLeay. 1978. Avoidance reactions of salmonids to pulp mill effluents. CPAR Rep. No. 688. Environmental Protection Service. Ottawa, Ontario.

Grande, M. 1964. Water pollution studies in the River Otra, Norway: Effects of pulp and paper mill wastes on fish. Int. J. Air Wat. Poll. 8: 77-88.

Graves, W.C., D.T. Burton and L.B. Richardson. 1980. Effect of 20- to 30-day continuous exposure of treated bleached kraft mill effluent on selected freshwater species. Bull. Environ. Contam. Toxicol. 25: 651-657.

Graves, W.C., D.T. Burton, L.B. Richardson and S.L. Margrey. 1981. The interaction of treated bleached kraft mill effluent and dissolved oxygen concentration on the survival of the developmental stages of the sheepshead minnow (Cyprinodon variegatus). Water Res. 15: 1005-1011.

Greer, G.L. and G.T. Kosakoski. 1978. Avoidance of seawater dilutions of kraft pulp mill effluent by seawater acclimated pink salmon fry. Fish. Mar. Serv. Tech. Rep. No. 831. Fisheries and Environment Canada. West Vancouver, B.C.

Grieco, M.P., J.D. Hendricks, R.A. Scanian, R.O. Sinnhuber and D.A. Pierce. 1978. Carcinogenicity and acute toxicity of dimethyl nitrosamine in rainbow trout (Salmo gairdneri). J. Natn. Cancer Inst. 60: 1127-1130.

Hicks, D.B. and J.W. DeWitt. 1971. Effects of dissolved oxygen on kraft pulp mill effluent toxicity. Water Res. 5: 693-701.

Hoglund, C., A.-S. Allard, A.H. Neilson and L. Landner. 1979. Is the mutagenic activity of bleach plant effluents persistent in the environment? Svensk Papperstidning 15: 447-449.

Holmbom, B. and K.-J. Lehtinen. 1980. Acute toxicity to fish of kraft pulp mill wastewaters. Pap. Puu 62: 673-684.

Howard, T.E. 1975. Swimming performance of juvenile coho salmon (Oncorhynchus kisutch) exposed to bleached kraft pulp mill effluent. J. Fish. Res. Board Can. 32: 789-793.

Howard, T.E. and C.C. Walden. 1974. Measuring stress in fish exposed to pulp mill effluents. TAPPI 57: 133-135.

Howard, T.E. and D.D. Monteith. 1977. Site of Action of Chemicals from Pulp Mill Effluent That are Toxic to Fish. CPAR Rep. No. 488-1. Environmental Protection Service, Ottawa, Ontario.

Hutchins, F.E. 1979. Toxicity of Pulp and Paper Mill Effluent. A Literature Review. Rep. EPA-600/3-79-013. U.S. Environmental Protection Agency. Corvallis, OR.

Jones, B.F., C.E. Warren, C.E. Bond and P. Doudoroff. 1956. Avoidance reactions of salmonid fishes to pulp mill effluents. Sewage Ind. Wastes 28: 1403-1413.

Joubert, G. 1980. A bioassay application for quantitative toxicity measurements, using the green algae Selenastrum capriocornutum. Water Res. 14: 1759-1763.

Kinae, N., T. Hashsizume, T. Makita, I. Tomita and I. Kimura. 1981. Kraft pulp mill effluent and sediment can retard development and lyse sea urchin eggs. Bull. Environ. Contam. Toxicol. 27: 616-623.

Kruzynski, G.M. 1979. Some effects of dehydroabietic acid (DHA) on hydro-mineral balance and other physiological parameters in juvenile sockeye salmon Oncorhynchus nerka. Ph.D. thesis. 187 pp. Univ. British Columbia, Vancouver, B.C.

Kuivasniemi, K., V. Eloranta and J. Knuutinen. 1985. Acute toxicity of some chlorinated phenolic compounds to Selenastrum capricornutum and phytoplankton. Arch. Environ. Contam. Toxicol. 14: 43-49.

Kutney, G.W., T.S. Macas and G.P. Donnini. 1983. The C stage for the 1980's. pp. A11-A18. In Proc. 69th Ann. Meeting, Tech. Sect., CPPA. February 1 & 2, 1983. Montreal, Quebec.

Kutney, G.W., H.H. Holton, D.H. Andrews, J.R. duManoir and G.P. Donnini. 1984. A review of low versus high ClO_2 substitution in the C stage: part II - Effluent properties. Pulp Paper Can. 85: T95-102.

Ladd, J.M. 1969. The Effects of pH on the Acute Toxicity of Kraft Pulp Mill Effluent to Juvenile Coho Salmon, Oncorhynchus kisutch. M.Sc. Thesis. Humboldt State Coll., Ancata, CA.

Landner, L., A.H. Neilson, L. Sorensen, A. Tarnholm and T. Viktor. 1985. Short-term test for predicting the potential of xenobiotics to impair reproduction success in fish. Ecotoxicol. Environ. Safety 9: 282-293.

Larmoyeux, J.D. and R.G. Piper. 1973. Effects of water reuse on rainbow trout in hatcheries. Prog. Fish-Cult. 35: 2-8.

Leach, J.M. and L.T.K. Chung. 1980. Development of a Chemical Toxicity Assay for Pulp Mill Effluents. Rep. EPA-600/2-80-206. U.S. Environmental Protection Agency. Cincinnati, OH.

Leach, J.M. and T.E. Howard. 1973. Identification and Treatment of Toxic Materials in Mechanical Pulping Effluents. CPAR Rep. No. 149-1. Environmental Protection Service. Ottawa, Ontario.

Leach, J.M. and T.E. Howard. 1975. Identification and Treatment of Toxic Materials in Mechanical Pulping Effluents. CPAR Rep. No. 149-3. Environmental Protection Service. Ottawa, Ontario.

Leach, J.M. and T.E. Howard. 1978. Identification of the Toxic Materials in Sulphite Pulp Mill Effluents. CPAR Rep. No. 407-3. Environmental Protection Service. Ottawa, Ontario.

Leach, J.M. and H.-P. Meier. 1978. Biodegradability of Various Toxic Compounds in Pulp Mill Effluents. CPAR Rep. No. 408-3. Environmental Protection Service. Ottawa, Ontario.

Leach, J.M. and A.N. Thakore. 1974. Isolation of the Toxic Constituents of Kraft Pulp Mill Effluent. CPAR Rep. No. 11-4. Can. For. Serv. Ottawa, Ontario.

Leach, J.M., L.T.K. Chung and H.-P. Meier. 1979. Can pulp mill effluent toxicity be estimated from chemical analyses? pp. 141-145. In Proc. TAPPI Environm. Conf., Houston, Texas.

Lehtinen, K.-J. and A. Oikari. 1980. Sublethal effects of kraft pulp mill waste water on the perch, Perca fluviatilis, studied by rotary-flow and histological techniques. Ann. Zool. Fennici 17: 255-259.

Lehtinen, K.-J., M. Notini and L. Landner. 1984. Tissue damage and parasite frequency in flounders, Platichtys flesus (L) chronically exposed to bleached kraft pulp mill effluents. Ann. Zool. Fennici 21: 23-28.

Lemke, A.E. and D.I. Mount. 1963. Some effects of alkyl benzene sulfonate on the bluegill, Lepomis macrochirus. Trans. Amer. Fish. Soc. 92: 372-378.

Lewis, F.G. and R.J. Livingston. 1977. Avoidance of bleached kraft pulp mill effluent by pinfish (Lagogon rhomboides) and gulf killifish (Fundulus grandis). J. Fish. Res. Board Can. 34: 568-570.

Lindgren, S. and A. Oikari. 1982. The toxicity of resin acids and 2,4,6-trichlorophenol to perch (Perca fluviatilis L.) in fresh and brackish water. p. 23. In Tvarminne Studies 2. Research Activities in 1981. Tvarminne Zoological Station, University of Helsinki. Helsinki, Finland.

Livingstone, D.R. 1982. General biochemical indices of sublethal stress. Mar. Poll. Bull. 13: 261-263.

Loch, J.S. and J.C. MacLeod. 1973. Fish Toxicity Survey of Four Prairie Province Pulp Mill Effluents. Fish. Mar. Serv. Tech. Rep. CEN/T-73-4. Environment Canada. Winnipeg, Manitoba.

Loch, J.S. and J.C. MacLeod. 1974. Factors Affecting Acute Toxicity Bioassays With Pulp Mill Effluent. Fish. Mar. Serv. Tech. Rep. CEN/T-74-2. Environment Canada. Winnipeg, Manitoba.

McCubbin, N. 1984a. State-of-the-Art of the Pulp and Paper Industry and its Environmental Protection Practices. Environmental Protection Service Rep. EPS 3-EP-84-2. Environment Canada. Ottawa, Ontario.

McCubbin, N. 1984b. Quick new toxicity test simplifies procedures, cuts costs. Pulp Paper Can. 85: 10-11.

McLeay, D.J. 1973. Effects of a 12-h and 25-day exposure to kraft pulp mill effluent on the blood and tissues of juvenile coho salmon (Oncorhynchus). J. Fish. Res. Board Can. 30: 395-400.

McLeay, D.J. 1977. Development of a blood sugar bioassay for rapidly measuring stressful levels of pulp mill effluent to salmonid fish. J. Fish. Res. Board Can. 34: 477-485.

McLeay, D.J. and D.A. Brown. 1974. Growth stimulation and biochemical changes in juvenile coho salmon (Oncorhynchus kisutch) exposed to bleached kraft pulp mill effluent for 200 days. J. Fish. Res. Board Can. 31: 1043-1049.

McLeay, D.J. and D.A. Brown. 1975. Effects of acute exposure to bleached kraft pulp mill effluent on carbohydrate metabolism of juvenile coho salmon (Oncorhynchus kisutch) during rest and exercise. J. Fish. Res. Board Can. 32: 753-760.

McLeay, D.J. and D.A. Brown. 1979. Stress and chronic effects of untreated and treated beached kraft pulp mill effluent on the biochemistry and stamina of juvenile coho salmon (Oncorhynchus kisutch). J. Fish. Res. Board Can. 36: 1049-1059.

McLeay, D.J. and M.R. Gordon. 1977. Leucocrit: a simple method for measuring acute stress in salmonid fish including stressful concentrations of pulp mill effluent. J. Fish. Res. Board Can. 34: 2164-2175.

McLeay, D.J. and M.R. Gordon. 1978. Effect of seasonal photoperiod on acute toxic responses of juvenile rainbow trout (Salmo gairdneri) to pulp mill effluent. J. Fish. Res. Board Can. 35: 1388-1392.

McLeay, D.J. and T.E. Howard. 1977. Comparison of rapid bioassay procedures for measuring toxic effects of bleached kraft mill effluents to fish. pp. 141-155. Proc. Third Aquatic Toxicity Workshop Conference, Halifax, N.S., November 2-3, 1976. Tech. Rep. EPS-5-AR-77-1. Environmental Protection Service, Halifax, N.S.

McLeay, D.J. and C.C. Walden. 1976. Effect of pH on Bioassays in Fresh and Seawater. CPAR Rep. No. 402-1. Canadian Forestry Service, Ottawa, Ontario.

McLeay, D.J., C.C. Walden and J.R. Munro. 1979a. Influence of dilution water on the toxicity of kraft pulp and paper mill effluent, including mechanisms of effect. Water Res. 13: 151-158.

McLeay, D.J., C.C. Walden and J.R. Munro. 1979b. Effect of pH on toxicity of kraft pulp and paper mill effluent in fresh and seawater. Water Res. 13: 249-254.

McLeese, D.W. 1970. Behaviour of lobsters exposed to bleached kraft mill effluent. J. Fish. Res. Board Can. 27: 731-736.

Mazeaud, M.M., F. Mazeaud and E.M. Donaldson. 1977. Primary and secondary effects of stress in fish: Some new data with a general review. Trans. Amer. Fish. Soc. 106: 201-212.

Metikosh, S. 1979. Industrial application of the toxic unit concept. pp. 63-79. In Proc. Fifth Ann. Aquat. Tox. Workshop. November 7-9, 1978. Hamilton, Ontario. Fish. Mar. Serv. Tech. Rep. No. 862. Environment Canada. Ottawa, Ontario.

Middelraad, I. and M.A. Wilson. 1975. The Effect of Hardness on the Toxicity to Fish of Pulp Mill Effluents. CPAR Rep. No. 330-1. Canadian Forestry Service. Ottawa, Ontario.

Miettinen, V., B.-E. Lonn and A. Oikari. 1982. Effects of biological treatment on the toxicity for fish of combined debarking and kraft pulp bleaching effluent. Pap. Puu SN4: 251-254.

Miller, W.E., J.C. Green and T. Shiroyama. 1978. The Selenastrum capricornutum Printz Algal Assay Bottle Test Report EPA-600/9-78-018. U.S. Environmental Protection Agency. Corvallis, OR.

Mischuk, M.W. 1983. Use of the algal assay bottle test in assessing nutrient effects of pulp and paper effluents on receiving streams. pp. 1-4. In Proc. TAPPI 1983 Environ. Conf. Atlanta, GA.

NCASI 1968. The Effects of Unbleached Kraft Mill Effluents on Salmon. I. Growth, Food Consumption and Swimming Ability of Juvenile Chinook Salmon. Tech. Bull. No. 217. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1977a. Effects of Unbleached Kraft Mill Effluents on Growth and Production of Fish in Experimental Stream Channels. Tech. Bull. No. 290. Nat. Counc. Air Steam Improvement, Inc. New York, NY.

NCASI 1977b. Effects of Bleached Kraft Mill Effluent on Growth and Production of Fish in Experimental Stream Channels. Tech. Bull. No. 292. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1978. Effects of Bleached Kraft Mill Effluent on Growth and Production of Fish in Experimental Stream Channels. 2nd Progress Report. Tech. Bull. No. 301. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1982. Effects of Biologically Stabilized Bleached Kraft Mill Effluent on Cold Water Stream Productivity as Determined in Experimental Streams - First Progress Report. Tech. Bull. No. 368. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1983a. Effects of Biologically Stabilized Bleached Kraft Mill Effluent on Cold Water Stream Productivity in Experimental Streams - Second Progress Report. Tech. Bull. No. 413. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1983b. Effects of Biologically Stabilized Bleached Kraft Effluent on Warm Water Stream Productivity in Experimental Streams - Third Progress Report. Tech. Bull. No. 414. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1984a. Effects of Biologically Treated Bleached Kraft Mill Effluent on Cold Water Stream Productivity in Experimental Stream Channels - Third Progress Report. Tech. Bull. No. 445. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1984b. Observations of the Condition of Organs and Tissues of Fish Exposed to Biologically Treated Bleached Kraft Mill Effluent. Tech. Bull. No. 419. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

Neilson, A.H., A.S. Allard, S. Reiland, M. Remberger, A. Tarnholm, T. Viktor and L. Landner. 1984. Tri- and tetrachloroveratrole, metabolites produced by bacterial O-methylation of tri- and tetrachloroguaiacol: an assessment of their bioconcentration potential and their effects on fish reproduction. Can. J. Fish. Aquat. Sci. 41: 1502-1512.

Nikinmaa, M. and A.O.J. Oikari. 1982. Physiological changes in trout (Salmo gairdneri) during a short-term exposure to resin acids and during recovery. Toxicology Letters 14: 103-110.

Nikunen, E. 1983. The acute toxicity of some Finnish pulp and paper mill effluents and comparison of three measurement methods. Pap. Puu 11: 726-730.

OECD 1984. Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). Organization for Economic Co-operation and Development Workshop held September 10-14, 1984. Duluth, Minnesota.

Oikari, A.O.J. 1983. Development of physiological fish tests for assessment of toxic pollution from the pulp and paper industry. pp. 241-248. In Chemicals in the Environment. K. Christiansen et al., eds. Proc. Int. Symp. October 18-20, 1982. Copenhagen, Denmark.

Oikari, A. 1984. On the metabolism of chlorinated phenolics and resin acids in rainbow trout (Salmo gairdneri). p. III 2. In Environmental Changes and Adaptions (April 24-25, 1984). Nat. Sci. Publ. Univ. Kuopio. Kuopio, Finland.

Oikari, A.O.J. and T. Nakari. 1982. Kraft pulp mill effluent components cause liver dysfunction in trout. Bull. Environ. Contam. Toxicol. 28: 266-270.

Oikari, A., B.-E. Lonn, M. Castren, T. Nakari, B. Snickars-Nikinmaa, H. Bister and E. Virtanen. 1983. Toxicological effects of dehydroabietic acid (DHAA) on the trout, Salmo gairdneri Richardson, in freshwater. Water Res. 17: 81-89.

Oikari, A., T. Nakari and B. Holmbom. 1984a. Sublethal actions of simulated kraft pulp mill effluents (KME) in Salmo gairdneri: residues of toxicants, and effects on blood and liver. Ann. Zool. Fennici 21: 45-53.

Oikari, A., E. Anas, G. Kruzynski and B. Holmbom. 1984b. Free and conjugated resin acids in the bile of rainbow trout, Salmo gairdneri. Bull. Environ. Contam. Toxicol. 33: 233-240.

Parker, W.R. 1984. The use of marine bioassays in hazard assessment. pp. 111-123. In R. Van Coillie, N. Bermingham and C. Blaise, eds. Biological Testing and Hazard Assessment. Proc. Conf. October 20-21, 1982. Environment Canada. Montreal, Quebec.

Passino, D.R.M. 1984. Biochemical indicators of stress in fishes: an overview. pp. 37-50. In V.W. Cairns et al. (eds.). Contaminant Effects on Fisheries. Wiley & Sons. New York, N.Y.

Peltier, W. 1978. Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms. Rep. EPA-600/4-78-012. U.S. Environmental Protection Agency. Cincinnati, OH.

Poole, N.J., D.J. Wildish and D.D. Kristmanson. 1978. The effects of the pulp and paper industry on the aquatic environment. CRC Crit. Rev. Environ. Control 8: 153-195.

Rainville, R.P., B.J. Copeland and W.T. McKean. 1975. Toxicity of kraft mill wastes to an estuarine phytoplankter. J. Water Poll. Control Fed. 47: 487-503.

Rapson, H., C.B. Anderson and D. Reeve. 1977. The effluent-free bleached kraft pulp mill. Part VI - substantial substitution of chlorine dioxide for chlorine in the first stage of bleaching. Pulp Paper Can. 78: T137-T148.

Renberg, L., O. Svanberg, B.E. Bengtsson and G. Sundstrom. 1980. Chlorinated guaiacols and catechols: bio-accumulation potential in bleaks (Alburnus alburnus, Pisces) and reproductive and toxic effects on the harpacticoid Nitrocra spinipes (Crustacea). Chemosphere 9: 143-150.

Rogers, I.H., J.C. Davis, G.M. Kruzynski, H.W. Mahood, J.A. Servizi and R.W. Gordon. 1975. Fish toxicants in kraft effluents. TAPPI 48: 136-140.

Rosehart, R.G., G.W. Ozburn and R. Mettinen. 1974. Origins of toxicity in sulphite pulping. Pulp Paper Can. 75: T215-218.

Rowe, E.L., R.J. Ziobro, C.J.K. Wang and C.W. Dance. 1982. The use of an alga Chlorella pyrenoidosa and a duckweed Lemna perpusilla as test organisms for toxicity bioassays of spent bleaching liquors and their components. Environ. Poll. (Ser. A.) 27: 289-296.

Saarikoski, J. and M. Viluksela. 1981. Influence of pH on the toxicity of substituted phenols to fish. Arch. Environm. Contam. Toxicol. 10: 747-753.

Samak, Q.M. and R. Noiseux. 1981. Acute aquatic toxicity measurement by the Beckman Microtox. pp. 290-308. In Proc. Seventh Ann. Aquat. Tox. Workshop. November 5-7, 1980. Montreal, Quebec. Can. Tech. Rep. Fish. Aquat. Sci. No. 990. Fisheries and Oceans Canada. Ottawa, Ontario.

Schmaltz, J.F. 1979. Can Daphnia replace fish for bioassays? Pulp Paper Can. 80: T224-228.

Scheiderman, S. and G.A. Allard. 1979. Bio-treatment detoxifies spent sulphite effluents. Pulp Paper Can. 80 (10): T310-314.

Seim, W.K., J.A. Lichatowich, R.H. Ellis and G.E. Davis. 1977. Effects of kraft mill effluents on juvenile salmon production in laboratory streams. Water Res. 11: 189-196.

Servizi, J.A., E.T. Stone and R.W. Gordon. 1966. Toxicity and Treatment of Kraft Pulp Bleach Plant Waste. Int. Pacific Salmon Fish. Comm. Progr. Rep. No. 13. New Westminster, B.C.

Servizi, J.A., R.W. Gordon and D.W. Martens. 1968. Toxicity of two chlorinated catechols, possible components of kraft pulp mill bleach waste. Int. Pacific Salmon Fish. Comm. Progr. Rep. No. 17. New Westminster, B.C.

Sinnhuber, R.O., J.D. Hendrix, J.H. Wales and G.B. Putman. 1977. Neoplasms in rainbow trout, a sensitive model for environmental carcinogenesis. Ann. N.Y. Acad. Sci. 298: 389-408.

Snieszko, S.F. 1974. The effects of environmental stress on outbreaks of infectious diseases of fishes. J. Fish Biol. 6: 197-208.

Soniassy, R.N., J.C. Mueller and C. Walden. 1977. The effects of BKME color and toxic constituents on algal growth. Pulp Paper Can. 78: T179-184.

Sonstegard, R.A. and J.F. Leatherland. 1984. Comparative epidemiology: the use of fishes in assessing carcinogenic contaminants. pp. 223-231. In V.W. Cairns et al. (eds.). Contaminant Effects on Fisheries. Wiley & Sons. New York, N.Y.

Spieler, R.E., T.A. Noeske and G.L. Seegert. 1977. Diel variations in sensitivity of fishes to potentially lethal stimuli. Progr. Fish-Cult. 39: 144-147.

Sprague, J.B. 1969. Measurement of pollutant toxicity to fish. I Bioassay methods for acute toxicity. Water Res. 3: 793-821.

Sprague, J.B. 1971. Measurement of pollutant toxicity to fish. III Sublethal effects and "safe" concentrations. Water Res. 5: 245-266.

Sprague, J.B. and D.E. Drury. 1969. Avoidance reactions of salmonid fish to representative pollutants. pp. 169-179. In Advances in Water Pollution Research. S.H. Jenkins, ed. Pergamon Press, New York, N.Y.

Sprague, J.B. and A. Fogels. 1977. Watch the Y in bioassay. pp. 107-118. In Proc. Third Ann. Aquat. Tox. Workshop. November 2-3, 1976. Halifax, N.S. Tech. Rep. EPS-5-AR-77-1. Environmental Protection Service, Halifax.

Sprague, J.B. and A.D. Ramsay. 1965. Lethal mixtures of mixed copper-zinc solutions for juvenile fish. J. Fish. Res. Board Can. 22: 425-432.

Stephan, C.E. 1982. Increasing the usefulness of acute toxicity tests. pp. 69-81. In J.G. Pearson et al., eds. Aquatic Toxicology and Hazard Assessment: Fifth Conference. ASTM STP 766. American Society for Testing and Materials. Philadelphia, PA.

Stockner, J.G. and A.C. Costella. 1976. Marine phytoplankton growth in high concentrations of pulp mill effluent. J. Fisheries Res. Board of Canada 33: 2758-2765.

Stoner, A.W. and R.J. Livingston. 1978. Respiration, growth and food conversion efficiency of pinfish (Lagodon rhomboides) exposed to sublethal concentrations of bleached kraft mill effluent. Environ. Poll. 17: 207-217.

Tesmer, M.G. and T.W. Joyce. 1980. Algal assay bottle test response to pulp and paper mill effluents. TAPPI 63: 105-108.

Tunstall, E.W. and M. Solinas. 1977. Daphnia pulex pulls its weight in pulp mill toxicity tests. Pulp Paper Can. 78: T93-98.

Tuurala, H. and A. Soivio. 1982. Structural and circulatory changes in the secondary lamellae of Salmo gairdneri gills after sublethal exposures to dehydroabietic acid and zinc. Aquatic Toxicol. 2: 21-29.

vanAggelen, G. 1982. Comparison of Microtox EC_{50} bioassay against static 96-h LC_{50} rainbow trout bioassay using selected industrial effluents. Paper presented at B.C. Ministry of the Environment Biologists' Meeting. November 1982. Environ. Lab., B.C. Ministry of the Environment. Vancouver, B.C.

Van Coillie, R., N. Birmingham and C. Blaise. 1984. eds. Proceedings of the Conference "Biological Testing and Hazard Assessment". Environment Protection Service, Environment Canada. Montreal, Canada.

Voss, R.H., J.T. Wearing, R.D. Mortimer, T. Kovacs and A. Wong. 1980. Chlorinated organics in kraft bleachery effluents. Paperi ja Puu 12: 809-814.

Voss, R.H., J.T. Wearing and A. Wong. 1981. Effect of softwood chlorination conditions on the formation of toxic chlorinated compounds. Pulp Paper Can. 82: T65-71.

Waiwood, K.G. and F.W.H. Beamish. 1978. Effects of copper, pH and hardness on the critical swimming performance of rainbow trout (Salmo gairdneri Richardson). Water Res. 12: 611-619.

Walden, C.C. 1976. The toxicity of pulp and paper mill effluents and corresponding measurement procedures. Water Res. 10: 639-664.

Walden, C.C. and T.E. Howard. 1974. Effluent toxicity removal on the West Coast. Pulp Paper Can. 75: T370-374.

Walden, C.C. and T.E. Howard. 1977. Toxicity of pulp and paper mill effluents. A review of regulations and research. TAPPI 60: 122-125.

Walden, C.C. and T.E. Howard. 1981. Toxicity of pulp and paper mill effluents - a review. Pulp Paper Can. 82: T143-T148.

Walden, C.C. and D.J. McLeay. 1974. Interrelationships of Various Bioassay Procedures for Pulp and Paper Mill Effluents. CPAR Rep. No. 165-1. Canadian Forestry Service. Ottawa, Ontario.

Walden, C.C., T.E. Howard and G.C. Froud. 1970. A quantitative assay of the minimum concentrations of kraft mill effluents which affect fish respiration. Water Res. 4: 61-68.

Walden, C.C., D.J. McLeay and T.E. Howard. 1972. An Examination of the Efficacy of Waste Treatment Systems at Pacific Coast Pulp and Paper Mills in Removing Effluent Toxicity Together with Pertinent Regulations and Bioassay Procedures. Report prepared by B.C. Research for the Environmental Protection Service. Ottawa, Ontario.
Waldichuk, M. 1962. Some water pollution problems connected with the disposal of pulp mill wastes. Can. Fish Cult. 31: 3-34.

Walden, C.C., D.J. McLeay and D.D. Monteith. 1975. Comparing bioassay procedures for pulp and paper effluents. Pulp Paper Can. 76: T130-T134.

Waldichuk, M. 1962. Some water pollution problems connected with the disposal of pulp mill wastes. Can. Fish. Cult. 31: 3-34.

Waldichuk, M. 1983. Water pollution from pulp mill effluent in British Columbia: a general overview. pp. 1-60. In W.M. Pomeroy, ed. Proceedings of Pulp Mill Effluent Monitoring. Environmental Protection Service Regional Program Report 83-15. Environment Canada. West Vancouver, B.C.

Wallin, B.K. and A.J. Condrin. 1981. Fate of Toxic and Nonconventional Pollutants in Wastewater Treatment Systems Within the Pulp, Paper, and Paperboard Industry. EPA 600/52-81-158. U.S. Environmental Protection Agency Rep. Cincinnati, OH.

Walsh, G.E. and S.V. Alexander. 1980. A marine algal bioassay method results with pesticides and industrial wastes. Wat. Air Soil Poll. 13: 45-55.

Walsh, G.E., K.M. Duke and R.B. Foster. 1982. Algae and crustaceans as indicators of bioactivity of industrial wastes. Water Res. 16: 879-883.

Warren, C.E., W.K. Seim, R.O. Blosser, A.L. Caron and E.L. Owens. 1974. Effect of kraft effluent on the growth and production of salmonid fish. TAPPI 57: 127-132.

Webb, P.W. and J. R. Brett. 1972. The effects of sublethal concentrations of whole bleached kraftmill effluent on the growth and food conversion efficiency of underyearling sockeye salmon (Oncorhynchus nerka). J. Fish. Res. Board Can. 29: 1555-1563.

Wedemeyer, G.A. and D.J. McLeay. 1981. Methods for determining the tolerance of fishes to environmental stressors. pp. 247-275. In Stress and Fish. A.D. Pickering, ed. Academic Press. London, England.

Wedemeyer, G.A., F.P. Meyer and L. Smith. 1976. Environmental stress and fish diseases, Book 5. pp. 1-192. In Diseases of Fishes. S.F. Snieszko and H.R. Axelrod, eds. T.F.H. Publ. Inc., Neptune City, NJ.

Wedemeyer, G.A., D.J. McLeay and C.P. Goodyear. 1984. Assessing the tolerance of fish and fish populations to environmental stress: the problems and methods of monitoring. pp. 163-195. In V.W. Cairns et al. (eds.). Contaminant Effects on Fisheries. Wiley & Sons. New York, N.Y.

Weinbauer, J.D. and L.S. Somers. 1982. Chronic toxicity testing of treated pulp and paper mill effluent. pp. 1-7. In Proc. TAPPI Environ. Conf., Minneapolis, MN.

Whittle, D.M. and K.W. Flood. 1977. Assessment of the acute toxicity, growth impairment and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (Salmo gairdneri). J. Fish. Res. Board Can. 34: 869-878.

Wildish, D.J., H. Akagi and N. J. Poole. 1977. Avoidance by herring of dissolved components in pulp mill effluents. Bull. Environ. Contam. Toxicol. 18: 521-525.

Willard, H.K. 1983. Toxicity Production of Pulp and Paper Mill Wastewater. Contract No. 68-03-3028, WA 20. February 1983. U.S. Environment Protection Agency. Cincinatti, Ohio.

Wilson, M.A. and C.I. Chappel. 1974. Reduction of Toxicity of Sulphite Mill Effluents. CPAR Rep. No. 49-3. Environmental Protection Service. Ottawa, Ontario.

Wilson, M.A., R. LeBlanc, I. Middelraad and P.J. LeBlanc. 1975a. Reduction of the Toxicity to Fish of Effluents from Paper Mills. CPAR Rep. No. 329-1. Environmental Protection Service. Ottawa, Ontario.

Wilson, R.C.H., R.H. Cook and E. Pessah. 1975b. Practical application of the toxicity emission rate concept in a survey of maritime pulp and paper mills. In Proc. Environm. Improv. Conf., Tech. Sect., CPPA. Vancouver, B.C.

Williamson, K.J. and D.G. Johnson. 1981. A bacterial bioassay for assessment of wastewater toxicity. Water Res. 15: 383-390.

Woelke, C.E. 1962. Bioassays of pulp mill wastes with oysters. pp. 67-77. In Biological Problems in Water Pollution. Third Seminar, Tech. Rep. 999-WP-25. USPHS, Cincinnati, Ohio.

Woelke, C.E. 1967. Measurement of water quality with the Pacific oyster embryo bioassay. pp. 112-120. In ASTM STP 416. Amer. Soc. Testing Materials. Philadelphia, PA.

Woelke, C.E. 1968. Application of shellfish bioassay results to the Puget Sound pulp mill pollution problem. Northwest 42: 125-133.

Woelke, C.E. 1972. Development of a Receiving Water Quality Bioassay Criterion Based on the 48-h Pacific Oyster, Crassostrea gigas Embryo. Wash. Dept. Fish. Tech. Rep. No. 9. Olympia, WA.

Woelke, C.E., T. Schink and E. Sanborn. 1972. Effect of Biological Treatment on the Toxicity of Three Types of Pulping Wastes to Pacific Oyster Embryos. U.S. Environmental Protection Agency Contract No. 68-01-377. State of Washington Dept. of Fisheries. Olympia, WA.

Wong, A., M. LeBourhis, R.A. Wostradowski and S. Prahacs. 1978. Toxicity, BOD and color of effluents from novel bleaching processes. Pulp Paper Can. 79: T235-241.

Wong, A., D. Breck, J. Constantino, J. Wearing and D.A. Holder. 1981. A method for the evaluation of effluent quality of various mechanical pulping processes. Pulp Paper Can. 2: T331-336.

Zanella, E. 1983. Effect of pH on acute toxicity of dehydroabietic acid and chlorinated dehydroabietic acid to fish and daphnia. Bull. Environ. Contam. Toxicol. 30: 133-140.

Zanella, E.F. and S.A. Berben. 1980. Evaluation of methodologies for the determination of acute toxicity in pulp and paper effluents. TAPPI 63: 77-82.

Zitko, V. and W.G. Carson. 1977. Seasonal and developmental variation in the lethality of zinc to juvenile Atlantic salmon (Salmo salar). J. Fish. Res. Board Can. 34: 139-141.

3 TOXIC EFFECTS OF MILL EFFLUENTS WITHIN RECEIVING WATERS

3.1 Introduction

The impact of pulp and paper mill effluents on the aquatic life in receiving waters is not limited to the effects of toxic constituents. Other effluent parameters (colour, pH, oxygen demand, suspended and settleable solids content, nutrient constituents) may, alone or in conjunction with toxic chemicals present in lethal or sublethal concentrations, cause a number of diverse biological effects. Any change is usually considered harmful unless it is proven otherwise. However, specific responses of individual organisms may not be significant or detrimental to higher food-chain organisms or at the level of organization of populations and communities of aquatic organisms. Actually, some effects may prove to be beneficial. For example, enhanced microbial growth and increased primary productivity due to organic enrichment of the receiving waters may, in some (but certainly not all) waterbodies, provide larger quantities of a valuable food source.

The potential for seasonal changes in site-specific environmental variables modifying the toxic impact of mill effluents on receiving waters has been discussed in Chapter 2. Other environmental conditions, including the degree of dilution, aeration and flushing of these effluents, also can affect their impact on receiving waters (Poole et al., 1978; Anon., 1982; Waldichuk, 1983). Thus these and other variables (e.g., the presence of other aquatic contaminants within the receiving waters, rates of degradation/adsorption of toxic constituents, biological effects of metabolites formed) will dictate the extent to which a particular discharge may affect sensitive life stages of fish and other aquatic organisms indigenous to the region.

This review of the literature is concerned with the toxic effects of pulp and paper mill effluents on organisms inhabiting or frequenting natural waterbodies receiving these wastes. Studies reviewed relate to the effects of untreated or treated whole mill discharges on aquatic life within the freshwater, estuarine or marine environment. Many of the changes reported may reflect responses to effluent characteristics (e.g., temperature, salinity, colour, nutrients) other than toxicity, and a distinction as to cause(s) is often unclear.

Environmental impact assessments and in situ studies of receiving waters adjacent to pulp and paper mill outfalls are reviewed here to provide information on the nature of the response, relative to the distance from the mill outfall. Particular attention

has been given to studies that are relevant to Canadian receiving waters and to the well-being of our fishery resources.

The present review provides some understanding of the real or potential biological impact of discharged untreated and treated pulp mill wastes. The reader wishing a historical review of past incidences and studies of environmental impacts of these effluents is referred to Willard (1983).

3.2 Freshwater Sites

3.2.1 Fish.

3.2.1.1 Survival. Published reports of fish kills associated with the discharge of pulp and paper mill effluents to the freshwater environment are few. Some investigators have reported decreased survival of indigenous fish species or those held captive in freshwaters receiving untreated or primary-treated effluent, relative to fish at downstream or upstream sites (Table 3.1). However, most of these findings are historical or deal with older mills not practising containment of spills or (in the case of sulphite mills) recovery of toxic chemicals. Some (EPA, 1972; Oikari et al., 1980) but not all (Whitney and Spindler 1959; Hasselrot, 1964) of the short-term fish mortalities reported could be attributed at least in part to low dissolved oxygen and/or elevated temperatures within the receiving waters, associated with the effluent discharges. Other contributing factors may have been domestic sewage discharged to the same receiving waters (EPA, 1972), supersaturation of dissolved gases in downstream waters due to damming and waterfalls (Grande, 1964), stresses due to capture and caging of test fish, and the presence of other unidentified contaminants. On occasion, lethal conditions in certain stretches of Canadian (Maritime) freshwaters have been attributed to the discharge of untreated pulp mill effluents (Sprague and Ruggles, 1966, cited in Poole et al., 1978). Poor mixing and inadequate dilution within receiving waters may have compounded the reported toxic effects.

In reviewing the toxicity reduction of pulp and paper mill effluents due to biological treatment, Willard (1983) noted 14 incidents of fish kills in the U.S. between 1977 and 1981. Most of these incidents were due to spills of pulping chemicals. No details were provided regarding the type of effluent process/treatment, the nature of the receiving environment or the magnitude of the effect (although the incidents were described as "dramatic").

No reports have been found of fish kills caused by the discharge of typical biotreated pulp and paper mill effluent to freshwater. This is not surprising since

TABLE 3.1 RECEIVING-WATER STUDIES EXAMINING CHANGES IN FRESHWATER ORGANISMS IN THE VICINITY OF PULP AND PAPER MILL EFFLUENT DISCHARGES

Class of organisms	Function or system affected	Effluent		Receiving water	Organism(s)	Distance from discharge(s) (km)	Duration of exposure (days)	Nature of response measured	Response attributed[a] to effluent			Reference
		type	treatment						yes	no	maybe	
Fish	Survival	KME	untreated	Clark Fork River (MO)	mixed fish species	≤3	1	survival of indigenous /caged fish	X			Whitney & Spindler, 1959
		SME/MPE	untreated	River Otra (Norway)	Atlantic salmon	proximate	6-10	survival of caged/ captive fish	X			Grande, 1964
		BKME	primary	lake (Sweden)	Atlantic salmon	≤4	5	survival of caged fish	X			Hasselrot, 1964
		BKME/MPE/paper	primary	St. Croix River (NB)	Atlantic salmon	≤13	4	survival of caged fish	X			EPA, 1972
		PME	untreated	- (Maritime Prov.)	Atlantic salmon	-	-	survival	X			Poole et al., 1978
		BKME	partial secondary	Lake Saimaa (Finland)	rainbow trout	≤4	10	survival of caged fish			X	Oikari et al., 1980
		BKME	secondary	Thompson River (BC)	rainbow trout	proximate	3	survival of caged fish		X		Langer & Nassichuk, 1975
		BKME	secondary	Fraser River (BC)	salmonid + other spp.	proximate	-	survival of indigenous fish		X		Anon., 1976
	Histology/ Morphology	BKME/MPE/paper	primary	St. Croix River (NB)	Atlantic salmon	≤13	0.5-4	olfactory tissue	X			EPA, 1972
		BKME	secondary	Wapiti River (Alta.)	lake chub, suckers	0.01-2.5	-	liver tissue			X	Anon., 1984
		paper	-[b]	Florida streams	mosquito fish	≤10	-	secondary sexual characteristics	X			Howell et al., 1980
	Biochemistry/ Physiology	BKME	secondary	Lake Saimaa (Finland)	rainbow trout	≤6	2-10	decreased liver enzyme	X			Oikari, 1983
	Behaviour	KME	primary	Snake River (WA)	steelhead trout	0.2-11	15-42	upstream migration		X		Falter & Ringe, 1974
		BKME/MPE	primary	Nipigon Bay (Ont.)	white sucker	≤2	0.3	avoidance	X			Kelso, 1977
		paper	-	Florida stream	mosquito fish	-	-	reproductive behaviour	X			Howell et al., 1980
		BKME/MPE	primary	Nipigon Bay (Ont.)	larval smelt	proximate	-	feeding behaviour		X		Leslie & Kelso, 1977
		pulp + paper	secondary	Wisconsin River (WI)	walleye pike	-	-	feeding behaviour		X		Weinbauer et al., 1980
	Distribution/ Abundance	BKME/MPE	primary	Nipigon Bay (Ont.)	fish species (7)	≤1	-	density, distribution	X			Kelso, 1977
		BKME/MPE	primary	Nipigon Bay (Ont.)	larval smelt	≤1	-	density, distribution		X		Leslie & Kelso, 1977
		pulp + paper	-	Lake Paijanne (Finland)	fish species (7)	≤20	-	density, distribution	X			Nyronen, 1978
		BKME	secondary	Wapiti River (Alta.)	fish species (8-9)	0.01-2.5	-	density, distribution		X		Anon., 1984
Macro-Invertebrates	Diversity/ Abundance	KME	untreated	Clark Fork River (MO)	benthic invertebrates	-	-	relative abundance	X			Whitney & Spindler, 1959
		SME/MPE	untreated	River Otra (Norway)	benthic invertebrates	proximate	-	relative abundance	X			Grande, 1964
		MPE/SME/KME	primary	Winnipeg River (Man.)	benthic invertebrates	≤6	-	species diversity	X			Gregory & Loch, 1973a
		BKME/MPE	primary	Nipigon Bay (Ont.)	benthic invertebrates	≤10	-	relative abundance	X			Vander Wal, 1977
		KME/MPE	primary	St. Francis R. (Que.)	benthic invertebrates	-	-	diversity, abundance	X			Hilton, 1980
		pulp + paper	secondary	Wisconsin River (WI)	benthic invertebrates	-	-	diversity, abundance		X		Weinbauer et al., 1980;
		pulp + paper	secondary	Fox River (WI)	benthic invertebrates	-	-	relative abundance		X		Markert, 1981
		BKME	secondary	Sacramento River (CA)	benthic invertebrates	≤50	-	diversity, abundance		X		Zanella & Weber, 1981
		BKME	secondary	Kootenay River (BC)	benthic invertebrates	≤2	-	relative abundance	X			Derkson & Lashmar, 1981
		UKME	secondary	Kitimat River (BC)	benthic invertebrates	-	-	relative abundance			X	Derkson, 1981
		BKME	secondary	Fraser River (BC)	benthic invertebrates	proximate	-	diversity, abundance		X		Stone et al., 1974;
Zooplankton	Diversity/ Abundance	SME	untreated	lake (Finland)	mixed species	≤15	-	diversity, abundance	X			Eloranta, 1980
Phytoplankton/ Periphyton	Diversity/ Abundance	SME	untreated	lake 1 (Finland)	indigenous phyto-plankton	≤15	-	inhibited productivity	X			Eloranta & Kettunen, 1979
		SME	untreated	lake 1 (Finland)	Selenastrum sp.	7	-	inhibited growth	X			Eloranta & Eloranta, 1980
		SME/paper	-	lake 2 (Finland)	Selenastrum sp.	≤15	-	inhibited growth	X			Eloranta & Laitinen, 1982
		KME	-	lake 3 (Finland)	Selenastrum sp.	35	-	growth stimulation	X			Eloranta & Eloranta, 1980
		KME	-	lake 3 (Finland)	Selenastrum sp.	8	-	inhibited growth	X			Eloranta & Laitinen, 1982
		BKME	secondary	Kootenay River (BC)	periphyton	≤15	-	decreased diversity, increased biomass	X			Derkson & Lashmar, 1981

a By the investigator(s).
b Not indicated/not determined.

laboratory bioassays routinely demonstrate 100% survival of fish exposed to full-strength treated effluent (see Chapter 2). The survival of caged rainbow trout held for three days in an interior B.C. river immediately downstream from a kraft mill discharging biotreated BKME (Langer and Nassichuk, 1975) is one example.

3.2.1.2 Histology/morphology. Few published studies have examined indigenous or caged freshwater fish within the vicinity of pulp and paper mill discharges for histological changes. Dead or moribund juvenile Atlantic salmon (Salmo salar) which had been held in cages in the St. Croix River up to 13 km downstream from a Maritime integrated pulp and paper mill were reported to have histological alterations in their olfactory (smell) organs, which were attributed to the mill discharge (EPA, 1972). However, these changes were observed in only 3 of 49 downstream fish and were no more prevalent for fish held at 0.4 km than for those held further downstream. The authors also reported some difficulty with techniques. The claims made in this study cannot be considered proven.

A recent study of indigenous fish species captured from the Wapiti River (Alberta) within the vicinity of a mill discharging biotreated BKME included a histological examination of tissues from lake chub (Couesius plumbeus) and longnose suckers (Catostomus catostomus) taken 30 km upstream and up to 2.5 km downstream (Anon., 1984). Decreased amounts of liver glycogen were noted in both downstream species, relative to upstream fish; however, the degree of liver pathology was described as minor. No changes in other tissues were reported. The investigators concluded that no cause-effect relationship had been demonstrated.

Howell et al. (1980) reported that a population of resident mosquitofish (Gambusia affinis) in a Florida stream was masculinized downstream of a site where paper mill effluent (nature, treatment unidentified) was discharged. Of the 500 specimens examined, all of the 350 female fish captured downstream possessed a male-like gonopodium, and downstream males exhibited precocious sexual development, whereas over 3000 individuals collected upstream or from adjacent streams appeared normal. These researchers reported similar findings for a few individuals of this species captured 5 km downstream from a second Florida paper mill. No other studies relating to masculinization of fish downstream of pulp or paper mill discharges have been reported.

3.2.1.3 Biochemistry/physiology. Oikari (1983) recently reported reduced liver enzyme (UDP-glucuronyltransferase) activity in rainbow trout held in cages at distances of 0.8 to 6 km from a mill discharging biotreated BKME into Lake Saimaa, Finland. This enzyme system is responsible for detoxification of toxic chemical constituents contained

in pulp and paper mill effluents (Chapter 2). However other details which might assist in assessing the relevance of the findings, such as the conditions to which the reference fish were exposed, effectiveness of mill treatment in detoxification, and receiving-water concentrations of this effluent, were not provided. No other reports of biochemical or physiological changes in freshwater fish inhabiting inland waters receiving pulp and paper mill effluents, or exposed experimentally, were located.

3.2.1.4 Behaviour. The upstream migration of adult steelhead trout (Salmo gairdneri) within a 25 km stretch of the Snake River (Washington-Idaho border) was studied for three years by the U.S. Environmental Protection Agency (Falter and Ringe, 1974). Sonic-tagged fish moved normally through waters containing up to 3% primary-treated kraft mill effluent. Kelso (1977) reported that sonic-tagged white suckers (Catostomus commersoni) released in Nipigon Bay (Lake Superior) near a mill discharging primary-treated BKME/MPE showed a general tendency to avoid waters containing this discharge. Two tagged fish released into water containing >15% effluent concentration showed localized, erratic bursts of activity within the effluent plume, but little evidence of avoidance. The two fish released into <15% effluent concentrations within the effluent plume did show some downstream movement (i.e., a tendency to avoid the effluent plume). However, the observed behaviour may have been a temperature response, since temperatures within the discharge plume were significantly higher than in the surrounding water. The brief tracking period (3-7 h) and the small number of fish (four) prevent any meaningful conclusions.

Howell et al. (1980) observed male-like reproductive behavioural patterns for masculinized female mosquitofish captured downstream of a paper mill. However, these behavioural studies were preliminary only and restricted to a few fish.

An examination of the gut contents of larval smelt (Osmerus mordax) captured adjacent to waters receiving primary-treated BKME/MPE showed no differences in the types of prey items with increasing distance from the mill outfall (Leslie and Kelso, 1977). Accordingly, these investigators were unable to demonstrate that the feeding habits of these fish were influenced by the mill effluent.

Based upon an examination of the gut contents of walleye pike (Stizostedion vitreum) captured within a 110 km stretch of the Wisconsin River receiving secondary-treated effluents from eight pulp and paper mills, Weinbauer et al. (1980) concluded that these fish were feeding normally in terms of both apparent prey preference patterns and prey availability. The condition factors and growth rates for these fish also appeared

to be normal. However, no comparisons were made with fish captured upstream of these mills.

No other reports concerning the behaviour of fish in freshwaters receiving pulp and paper mill discharges were found. Additionally, no studies dealing with effects on reproduction, development or disease resistance were found, either for indigenous freshwater fish or those exposed experimentally to receiving waters.

3.2.1.5 Distribution/abundance. The few attempts to discern the influence of pulp and paper mill effluents on the distribution and abundance of freshwater or anadromous fish species in the receiving waters include some reports testifying only to changes which have occurred without any data linking the changes to specific mill discharges. For instance, Ryder (1968) speculated that the elimination of the walleye fishery in Nipigon Bay, Lake Superior, was "most likely attributable to industrial (pulp mill) pollution". He concluded that the evidence for primary-treated effluent (discharged from an integrated pulp and paper mill into Nipigon Bay) affecting the walleye population was obvious but largely circumstantial. Dominy (1973) ascribed the declines over the past two decades in Atlantic salmon (Salmo salar) stocks frequenting the Saint John River to a number of factors including the discharge of untreated pulp and paper mill effluents. Similarly, Elson (1974) attributed the historical declines of the Atlantic salmon runs in the Northwest Miramichi River (New Brunswick) in part to the discharge of primary-treated kraft and groundwood effluents. In this instance, increased fishing pressures, urbanization and other contributing aquatic contaminants (runoff from pesticide spraying, mining effluent, wood preservatives) were also cited. A trend to recovering fish populations within this river system occurred, coincident with the combined advent of secondary treatment of pulp mill discharges, decreased fishing pressures and improved effluent/pesticide control practices. For its own part, industry has cited examples of thriving populations of commercial fish runs (e.g., the annual Adams River, B.C., sockeye salmon spawning run) which pass successfully through lakes and rivers receiving (treated) pulp and paper mill discharges (Anon., 1976).

The density and distribution of a number of freshwater nektonic fish species within Nipigon Bay were examined by Kelso (1977) with respect to the possible influence of a pulp mill discharging primary-treated BKME/MPE. Despite considerable variation, white suckers were dominant adjacent to the mill outfall, whereas elsewhere yellow perch (Perca flavescens) predominated at similar nearshore areas. Although the percentage distribution of other fish species (smelt, Osmerus mordax; alewife, Alosa pseudoharengus)

was similar at both locales, absolute numbers, as determined by electro-acoustic techniques, were greatest within 1 km of the mill's discharge (Kelso, 1977). Net tows within the effluent plume, close to the mill, also revealed an increased abundance of larval smelt, relative to deeper water (Leslie and Kelso, 1977). It is clear that these fish populations did not avoid these receiving waters.

Nyronen (1978) reported that between 1969 and 1975 the abundance of Lake Paijanne (Finland) fish stocks within 20 km of a number of pulp and paper mills (effluent type and treatment not identified) varied directly according to the effluent loading. That is, during periods of high effluent loading, numbers of fish caught in test catches were low, whereas during periods of decreased loading the abundance of young fish (particularly perch and bream) at these test sites was increased. Other aquatic contaminants (e.g., domestic sewage) were involved and lake waters were oxygen-deficient. These other loadings were not quantified nor related to fish-catch data.

Studies of fish communities at a number of U.S. freshwater (riverine) sites receiving biotreated pulp and paper mill effluents reported that fish populations "are generally not affected by the pulp mill effluents", although some reduction in fish diversity and abundance was evident at one location (Thut et al., 1980). Technical data to substantiate these findings were not provided.

A recent survey by the Alberta Environmental Centre identified eight fish species inhabiting a river receiving biotreated BKME, immediately below the mill's discharge point. These same (and one additional) species were evident at an upstream (30 km) "control" site (Anon., 1984). Population numbers were not estimated although age distributions were similar. Based on the presence of young-of-the-year fish at the downstream site, these investigators suggested that at least five species may reproduce "in the vicinity of the plant". Nonetheless fish movements were unrestricted and the young fish found at the downstream site may have emigrated from upstream or tributary waters. Certainly the resident fish did not avoid river water receiving biotreated BKME. The range of effluent concentrations within these waters was not indicated.

3.2.2 Benthic Macroinvertebrates.

3.2.2.1 Sites receiving untreated effluent. Published reports concerning the effects of untreated pulp and paper mill effluents on freshwater invertebrate communities do not pertain to many current situations because primary or secondary treatment of effluent is now common. Pre-and post-operational studies of a Montana stream by Whitney and Spindler (1959) indicated a shift in the relative abundance of benthic invertebrates

towards pollutant-tolerant organisms within seven months following the start-up of a kraft paper mill (Table 3.1). In a survey of the River Otra downstream of untreated (acidic) SME/MPE discharges, Grande (1964) noted a predominance of pollutant-tolerant chironomid larvae. The upstream invertebrate community was not described. Both studies noted extensive blanketing of the downstream river bottom by cellulose fibres.

3.2.2.2 Sites receiving primary-treated effluent. A two-year species diversity study of benthic invertebrates in the Winnipeg River revealed that pollutant-tolerant organisms (in particular, Chironomus sp. and Tribelos sp.) predominated up to 6 km downstream from an integrated newsprint mill, whereas the upstream community was more diverse (Gregory and Loch, 1973a). Significant deposits of wood fibre were evident at all downstream sites (mill clarifier only removed bark fines).

A survey of the benthic macroinvertebrate community in Nipigon Bay (Ontario) indicated changes in organismic abundance downstream of a pulp and paper mill, whereas species diversity was not greatly influenced (Vander Wal, 1977). Benthic organisms were absent within the immediate zone of influence, and numbers of worms (Pontoporeia affinis), considered to be pollutant-intolerant, were depressed up to 10 km from the mill's discharge.

Hilton (1980) reported significant reductions in the number of families, genera and individuals of benthic invertebrates inhabiting a Quebec river, downstream from a kraft paper mill. The river bottom downstream was reportedly blanketed by fibre deposits.

3.2.2.3 Sites receiving secondary-treated effluent. A number of U.S. studies have examined benthic invertebrate communities in freshwaters receiving pulp and paper mill effluents, before and after installation of secondary treatment facilities. In the Wisconsin River, the abundance of pollutant-intolerant organisms (i.e., mayfly nymphs) increased and pollutant-tolerant organisms decreased at a number of downstream sites shortly after the commencement of secondary treatment (Weinbauer et al., 1980; Rades, 1982). Similarly, following the advent of secondary treatment of effluent at a number of pulp and paper mills discharging to the Fox River (Wisconsin), Markert (1981) observed the downstream recovery of pollutant-intolerant species (i.e., caddisfly larvae) and the disappearance of pollutant-tolerant species (i.e., naidid worms). It should be noted that the Fox and Wisconsin Rivers are not representative of Canadian rivers receiving pulp and paper mill effluents, inasmuch as these two U.S. rivers each receive discharges from numerous mills in close proximity.

A 16-year (2 pre-, 14 post-operational) study of the macroinvertebrate community in the Sacramento River, upstream and downstream of a mill discharging biotreated BKME since start-up, showed no changes in species diversity or abundance (Zanella and Weber, 1981; Table 3.1). Laboratory rainbow trout bioassay tests conducted routinely with this effluent indicated that, for 93% of the time during a six-year period, the undiluted mill discharge was not acutely lethal to fish. Benthic invertebrate surveys at a number of U.S. freshwater sites receiving biotreated pulp and paper mill effluents showed that effects were restricted to the areas immediately below the outfalls (Thut et al., 1980). In some instances, numbers of organisms were enhanced.

A number of macroinvertebrate studies within Canadian freshwaters receiving secondary-treated pulp and paper mill effluents have been reported. Gregory and Loch (1973b) surveyed species diversity for benthic invertebrates within the North Saskatchewan River above and below a bleached kraft mill which had recently installed a five-day aerated lagoon. However, populations were so small that the results were inconclusive. Surveys at this site prior to biotreatment of mill effluents (Royer et al., 1971, cited in Gregory and Loch, 1973b) noted a decreased abundance of pollutant-sensitive organisms up to 50 km downstream. Prior to the installation of a rapid infiltration system for removal of colour from mill effluent, macroinvertebrate surveys of the Kootenay River (B.C.) upstream and downstream of a mill discharging biotreated BKME found decreased numbers of pollutant-intolerant organisms (mayfly/stonefly larvae) downstream (Derkson and Lashmar, 1981). Similarly, benthic invertebrate surveys of the Kitimat River (B.C.) above and below a kraft mill discharging biotreated UKME indicated some disruption of community structure attributable to this effluent (Derkson, 1981). Routine laboratory bioassays with discharge samples from these two mills indicated that toxicity removal was substandard. Effluent concentrations as high as 3% (Kootenay River) or 5% (Kitimat River) could exist in these receiving waters during seasonal periods of low river flow, after complete mixing (Derkson, 1981; Derkson and Lashmar, 1981).

Extensive pre- and post-operational surveys of benthic invertebrate communities in the upper Fraser River, above and below sites receiving biotreated BKME from three pulp and paper mills, have shown no evidence of effect attributable to these discharges (Stone et al., 1974; Derkson, 1982). Pollutant-intolerant macroinvertebrate species predominated at both upstream and downstream sites in most instances. The lack of any effect was despite seasonal periods of minimal (i.e., 30:1) effluent dilution and aperiodic toxic (lethal bioassays with rainbow trout) discharges from two of the three mills prior to the upgrading of their treatment facilities (Derkson, 1982).

3.2.3 Zooplankton. The abundance and species diversity of freshwater zooplankton in relation to discharges from pulp and paper mills have not been examined to any significant extent. Eloranta (1980) reported a diminution in the biomass and species diversity for zooplankton communities within Finnish lakewaters receiving untreated (acidic) SME. A significant depletion of dissolved oxygen was also apparent. Studies on zooplankton communities in freshwater sites adjacent to Canadian pulp mill discharges have not been found.

3.2.4 Phytoplankton/periphyton. A number of studies by Finnish investigators have demonstrated the potential effects on phytoplankton of pulp and paper mill effluents within the freshwater (lacustrine) environment. During a five-year study, Eloranta and Ketunnen (1979) reported that the indigenous phytoplankton biomass in a central Finland lake receiving untreated (acidic) SME was markedly depressed within a zone extending 15 km downstream from the mill. Effluent concentrations within 10 km of this sulphite mill were estimated to be 10% or greater; whereas concentrations at distances of 20-45 km were between 2 and 7%. Beyond the 15 km region, a 10 km zone existed where algal biomass was appreciably higher than at reference sites outside this zone of influence. Laboratory algal (Selenastrum capricornutum) bioassays with samples of filtered lakewater showed similar results: growth inhibition where effluent concentrations were higher and enhanced growth where greater dilution had occurred (Eloranta and Eloranta, 1980). The pH and dissolved oxygen values within the initial (15 km) zone were markedly depressed. Indeed, it would be difficult to ascribe any of the observed effects as due to factors other than abnormal pH and dissolved oxygen values. Algal bioassays with samples of lakewater from a separate Finnish lake receiving discharges from a paper mill and a number of sulphite mills also showed a significant inhibition of algal growth for waters within 15 km of the nearest discharge (Eloranta and Laitinen, 1982). Neutralization of sample pH prior to bioassays decreased the growth inhibition, although effects still remained which the authors ascribed to toxicity (Eloranta and Laitinen, 1982). Lack of definition of the types of processes and effluent treatment vitiate the usefulness of these data for application to other discharge situations.

Water samples from a Finnish lake receiving effluent from a kraft mill (type, treatment not specified) were examined for effects on algal (Selenastrum capricornutum) growth in two separate studies (Eloranta and Eloranta, 1980; Eloranta and Laitinen, 1982). In the initial survey, seasonal sampling showed greater algal growth in lakewater 35 km downstream than in lakewater from a reference site (Table 3.1). In a subsequent year,

algal growth inhibition occurred for water samples collected within 8 km of this discharge (Eloranta and Laitinen, 1982). The pH of all these test waters did not differ appreciably.

The influence of pulp and paper mill discharges on freshwater phytoplankton or periphyton communities within Canadian waters has not been examined intensively. Routine periphyton monitoring studies in the Kootenay River upstream and downstream of a mill discharging poorly biotreated BKME (prior to upgrading of secondary treatment and the installation of a rapid infiltration system) indicated a decreased diversity and increased biomass of phytoplankton up to 15 km downstream (Derkson and Lashmar, 1981). As this region of river received nutrient loadings from other sources (e.g., sewage), the mill discharge was not confirmed to be the sole causative agent. In a study downstream of a B.C. interior mill discharging biotreated UKME into the Kitimat River, the attached periphyton were generally too sparse to warrant quantitative sampling (Derkson, 1981). On the Thompson River, downstream of a mill discharging biotreated BKME, changes could not be distinguished from possible effects due to sewage inputs (Langer and Nassichuk, 1975). Subsequent laboratory bioassays with benthic algae and samples of sewage and treated BKME collected from this (Thompson River) study site indicated that the sewage was the primary (if not sole) cause of these changes (Stockner and Costella, 1978).

3.3 Estuarine/Marine Studies

3.3.1 Fish.

3.3.1.1 Survival. With the exception of Livingston (1975), published reports of fish kills in estuarine or marine waters receiving pulp and paper mill discharges are limited to mortalities reported in caged-fish studies (Table 3.2). Studies conducted in Puget Sound (Washington State) during the 1960's found acute mortalities for juvenile fish caged in near-shore regions adjacent to pulp mill outfalls (type, treatment undefined) (Bartsch, 1964). These occurrences were sometimes coincident with elevated sulphide or free chlorine concentrations, or severely depressed dissolved oxygen concentrations. Thick fibre deposits were also noted at stations where deaths of caged fish occurred.

Using downstream migrant chinook salmon (Oncorhynchus tshawytscha) as test fish, similar studies were conducted during 1974 in the Grays Harbor (Washington State) estuary adjacent to two pulp mills. Greater numbers of caged fish died during three- or four-day in situ bioassays when the mills were operating than when they weren't (Jeanne, 1975). However, inasmuch as some mortalities occurred at all sites whether the mills were operating or not, and because cage design affected fish survival, these results may

TABLE 3.2 RECEIVING-WATER STUDIES EXAMINING CHANGES IN ESTUARINE/MARINE ORGANISMS IN THE VICINITY OF PULP AND PAPER MILL EFFLUENT DISCHARGES

Class of organisms	Function or system affected	Effluent		Receiving water	Organism(s)	Distance from discharge(s) (km)	Duration of exposure (days)	Nature of response measured	Response attributed[a] to effluent			Reference
		type	treatment						yes	no	maybe	
Fish	Survival	SME/BKME/MPE	-[b]	Puget Sound (WA)	juvenile salmon	≤2	1	survival of caged fish	X			Bartsch, 1964
		pulp + paper	-	Grays Harbor (WA)	salmon, trout	0.6	4	receiving-water bioassays		X		Hermann, 1975
		pulp + paper	-	Grays Harbor (WA)	chinook salmon	≤1	3-4	survival of caged fish			X	Jeane, 1975
		UKME/BKME/MPE	secondary	Alberni Inlet (BC)	chinook salmon	≤1	14	survival of caged fish		X		Birtwell, 1978; Birtwell & Harbo, 1980
		BKME	untreated	Howe Sound (BC)	salmon, herring	≤0.4	-	survival of caged fish	X			Birtwell & Harbo, 1980
		SME	primary	Neroutsos Inlet (BC)	coho, sockeye salmon	≤5	1-2	survival of caged fish			X	Davis et al., 1978
		SME	primary	Neroutsos Inlet (BC)	chum salmon	≤1.5	1	survival of caged fish	X			McGreer & Vigers, 1983
	Histology/ Morphology	PME	-	bay (Japan)	Sparus macrocephalus	≤0.3	0.5-1	liver, intestine	X			Fujiya, 1961
	Biochemistry/ Physiology	paper/PME	-	Grays Harbor (WA)	chinook salmon	0.6	<0.1	swimming stamina			X	Dunn & Brix, 1975
		BKME/MPE/paper	primary	Stuart Channel (BC)	coho salmon	0.2	≤0.5	swimming stamina		X		Davis et al., 1976
		BKME/MPE/paper	untreated	Stuart Channel (BC)	coho salmon	0.2	≤0.5	oxygen uptake rate			X	Davis et al., 1976
		SME	primary	Neroutsos Inlet (BC)	coho, sockeye salmon	≤10	1-2	blood clotting time, hematocrit			X	Davis et al., 1978
	Disease Resistance	pulp + paper	-	Port Gardner (WA)	English sole	-	-	skin lesions		X		English, 1967
		pulp + paper	-	Port Gardner (WA)	English sole	proximate	-	liver lesions			X	Malins et al., 1983
		pulp + paper	-	estuary (Japan)	croaker nibe	proximate	-	skin lesions			X	Kimura et al., 1984
		BKME	-	Baltic Sea (Sweden)	flounder	proximate	-	frequency of gill parasites			X	Lehtinen et al., 1984
	Behaviour	pulp + paper	-	Miramichi estuary (NB)	Atlantic salmon	proximate	1-2	upstream migration			X	Elson et al., 1972
		BKME/MPE/paper	untreated	Stuart Channel (BC)	coho salmon	0.2	<0.1	avoidance			X	Greer, 1976
		BKME	untreated	Howe Sound (BC)	Pacific salmon	≤0.4	0.1	avoidance	X			Birtwell, 1977; Birtwell & Harbo, 1980
		BKME	untreated	Howe Sound (BC)	herring	≤0.4	0.1	avoidance		X		Birtwell, 1977
		UKME/BKME/MPE	secondary	Alberni Inlet (BC)	chinook salmon	0.3-1.5	0.1	avoidance/perference		X		Birtwell, 1978; Birtwell & Harbo, 1980
		SME	primary	Neroutsos Inlet (BC)	chum salmon	≤10	≤0.2	avoidance	X			McGreer & Vigers, 1980
		SME	primary	Neroutsos Inlet (BC)	chum salmon	≤1.3	0.05	avoidance	X			McGreer et al., 1982
		SME	primary	Neroutsos Inlet (BC)	chum salmon	-	-	seaward migration		X		Poulin & Oguss, 1982
		SME	primary	Neroutsos Inlet (BC)	chum salmon	≤2.5	1-4	food consumption	X			Poulin & Oguss, 1982
		UKME/BKME/MPE	secondary	Alberni Inlet (BC)	chinook salmon	≤1	-	food consumption		X		Birtwell, 1978; Birtwell & Harbo, 1980
	Distribution/ Abundance	pulp + paper	-	Port Gardner (WA)	English sole	-	-	relative abundance		X		English, 1967
		KME	untreated	Apalachee Bay (FL)	mixed species	≤30	-	diversity, abundance	X			Livingston, 1975
		BKME	untreated	Howe Sound (BC)	salmonids +	≤0.4	-	diversity, abundance		X		Birtwell & Harbo, 1980
		UKME/BKME/MPE	secondary	Alberni Inlet (BC)	salmonids	0.3-1.5	-	relative abundance		X		Birtwell, 1978; Birtwell et al., 1983
		SME	primary	Neroutsos Inlet (BC)	chum salmon	≤2	-	distribution	X			Davis et al., 1978; Poulin & Oguss, 1982
Macro-Invertebrates	Survival	BKME	primary	Northumberland Channel (BC)	Pacific oyster	<0.1-0.3	365	survival of transplants		X		Quayle, 1964
		BKME	untreated	Stuart Channel (BC)	Pacific oyster	<0.1-2	380	survival of transplants		X		Quayle, 1964
		BKME	untreated	Howe Sound (BC)	Pacific oyster	<0.1-0.2	365	survival of transplants	X			Pedlow, 1974
		BKME	untreated	Howe Sound (BC)	barnacle	proximate	120	survival of transplants		X		Wu & Levings, 1980
		BKME	untreated	Howe Sound (BC)	mussel	proximate	120	survival of transplants	X			Wu & Levings, 1980
	Development/ Condition	BKME	untreated	Stuart Channel (BC)	Pacific oyster	<0.1	380	condition factor	X			Quayle, 1964
		BKME	untreated	Northumberland Channel (BC)	Pacific oyster	<0.1-0.3	365	condition factor	X			Quayle, 1964
		BKME	untreated	Howe Sound (BC)	Pacific oyster	<0.1-0.5	365	condition factor	X			Pedlow, 1974
		BKME/MPE/paper	untreated	Stuart Channel (BC)	Pacific oyster	≤1.9	-	condition factor	X			Davis et al., 1976
		SME	-	Bellingham Bay (WA)	Pacific oyster	≤7	2	abnormal larvae	X			Bartsch, 1964
		BKME	untreated	Howe Sound (BC)	mussel, barnacle	proximate	120	growth, fecundity	X			Wu & Levings, 1980

TABLE 3.2 RECEIVING-WATER STUDIES EXAMINING CHANGES IN ESTUARINE/MARINE ORGANISMS IN THE VICINITY OF PULP AND PAPER MILL EFFLUENT DISCHARGES (Cont'd)

Class of organisms	Function or system affected	Effluent		Receiving water	Organism(s)	Distance from discharge(s) (km)	Duration of exposure (days)	Nature of response measured	Response attributed[a] to effluent			Reference
		type	treatment						yes	no	maybe	
	Diversity/ Abundance	BKME	primary	Northumberland Strait (NS)	benthic invertebrates	<0.1-3	-	diversity, abundance		X		Rades, 1976
		SME	secondary	L'Etang estuary (NB)	benthic invertebrates	≤6	-	diversity, abundance	X			Wildish et al., 1977, 1979
		BKME	untreated	Howe Sound (BC)	benthic invertebrates	≤1	-	diversity, abundance	X			Nelson, 1979b
		BKME	untreated	upper Howe Sound (BC)	benthic invertebrates	≤0.4	-	diversity, abundance	X			Nelson, 1979c
		BKME/MPE/TMP	untreated	Malaspina Strait (BC)	benthic invertebrates	≤1	-	diversity, abundance	X			Nelson, 1979d
		BKME	untreated	Northumberland Channel (BC)	benthic invertebrates	-	-	relative abundance	X			Packman, 1979
		BKME/MPE/paper	untreated	Stuart Channel (BC)	benthic invertebrates	≤2	-	diversity, abundance	X			Nelson, 1979a
		BKME	untreated	Muchalat Inlet (BC)	benthic invertebrates	proximate	-	relative abundance	X			Sullivan & Nelson, 1979
		UKME	secondary	Kitimat R. estuary (BC)	benthic invertebrates	3.2	-	diversity, abundance		X		Derkson, 1981
		UKME/BKME/MPE	secondary	Alberni Inlet (BC)	benthic invertebrates	≤2	-	diversity, abundance	X			Nelson, 1979e
		BKME	untreated	Porpoise Harbour (BC)	benthic invertebrates	proximate	-	diversity, abundance	X			Pomeroy, 1983
		SME	primary	Neroutsos Inlet (BC)	benthic invertebrates	≤8	-	diversity, abundance	X			Cross, 1982

a By the investigator(s).
b Not indicated/not determined.

be artifacts of the test procedures. On-site continuous-flow bioassays conducted during the same test periods with surficial and near-bottom water samples, taken from the same region, demonstrated that these waters were not acutely lethal to three species of salmonid fish (including chinook salmon) (Herrman, 1975).

In situ studies undertaken in Howe Sound (B.C.) showed that the surface waters within 350 m of a mill discharging untreated BKME to surface waters were often acutely lethal to herring (Clupea harengus pallasii) and juvenile chinook, chum (Oncorhynchus keta) and coho (O. kisutch) salmon (Birtwell and Harbo, 1980). However these researchers described their findings for fish held at these or more distant sites as "variable". Similar studies conducted within Alberni Inlet (B.C.) showed that survival of juvenile chinook salmon held in surface waters in cages at a site adjacent to the outfall of an integrated pulp and paper mill discharging secondary-treated effluent was equivalent to that for fish held at more distant stations (Birtwell, 1978; Birtwell and Harbo, 1980). However, marked differences were found in fish survival between surface waters and those at depth, regardless of distance from the mill outfall; with mean survivals of 75% and 17% after 14-days, for fish held at depths of 0.5 or 4 m, respectively. In this stratified inlet, where mill effluent is surficially discharged, the effluent "plume" is confined primarily to surface waters (Parker et al., 1972). During the 14-day test period, dissolved oxygen values at depth within the inlet were frequently lowered to "highly stressful" levels (i.e., 5% of the saturation value) (Birtwell and Harbo, 1980).

A number of studies have examined the survival of fish held briefly (one or two days) in surficial waters of Neroutsos Inlet. This inlet is approximately 20 km long and 1.5 km wide, and receives primary-treated sulphite mill effluent (ammonium base with recovery) near its head end. In situ bioassays conducted during, 1973 with caged juvenile coho and sockeye (O. nerka) salmon demonstrated fish mortalities for a site adjacent to the mill and, on one of two occasions, at a site 4.7 km from the outfall (Davis et al., 1978). All fish survived at the more distant sites. Dissolved oxygen levels were low (<3 mg/L) in waters where fish deaths occurred, and undoubtedly were a major factor in these deaths. Similar studies conducted during, 1980 (subsequent to improved in-plant recovery of spent sulphite liquor) with caged chum salmon demonstrated fish survival at all distances greater than 0.5 km from the mill's outfall, whereas earlier (1978, 1979) in situ bioassays showed mortalities within 1.5 km from the mill (McGreer and Vigers, 1983). This improved survival of caged fish within receiving waters was also coincident with a reduction in toxicity of the mill effluent according to routine 96-h LC_{50} bioassays with rainbow trout (McGreer and Vigers, 1983).

3.3.1.2 Histology/morphology. No histological or morphological studies of indigenous fish frequenting estuarine or marine waters receiving pulp and paper mill effluents have been reported in the literature. The findings by Fujiya (1961) of histological changes in the liver (glycogen and RNA depletion, vascular anomalies), pancreas (RNA depletion) and intestine (epithelial necrosis) for fish (Sparus macrocephalus) held for 12 or 24 h in a bay within 300 m of a kraft mill outfall remain the only published report of fish histopathologies associated with estuarine or marine receiving waters. Tissues of fish held at more distant (500 or 800 m) locations appeared normal. The type (bleached or unbleached) and treatment of the effluent discharged to this bay were not indicated, although it has been calculated (Walden, 1976) that the toxicity of this (untreated) effluent was atypically high.

3.3.1.3 Biochemistry/physiology. Few studies have examined fish within estuarine/marine receiving waters for biochemical or physiological effects associated with pulp mill discharges. As part of the 1974 Grays Harbor fish toxicity studies, Dunn and Brix (1975) measured the swimming stamina of juvenile chinook salmon exposed for short periods to surficial harbour waters taken from within 0.6 km of the nearest pulp mill (type and treatment of effluent not indicated). Swimming performance was superior when the nearby pulp mills were not operating. However, water quality conditions other than the presence or absence of mill effluent (salinity, temperature, dissolved oxygen) differed between tests and some of the fish may have been infected with Vibrio anguillarum (Dunn and Brix, 1975). Variations in performance were also attributed to fish length. Consequently these investigators concluded that these other causative factors may also have been implicated in the test results.

Davis et al. (1976) examined the swimming stamina and oxygen uptake rates for laboratory-reared salmon (coho smolts) exposed within a floating research barge to seawater pumped from various depths within 0.2 or 0.8 km of the outfalls of a mill discharging untreated BKME, MPE and newsprint mill effluent into Stuart Channel (B.C.). Although their swimming stamina was not affected, the oxygen uptake rates for fish held in waters taken adjacent to the outfalls were significantly lower than those for fish exposed to water taken from the more distant site. However, the researchers concluded that this difference may have been caused by deterioration in the condition of the fish stock, observed by the time that the bioassays were performed adjacent to the outfalls (Davis et al., 1976).

In conjunction with the in situ fish survival bioassays undertaken in Neroutsos Inlet by Davis et al. (1978), these investigators measured hematocrit values and blood clotting times for laboratory-reared salmon following their being caged for one or two days in receiving waters downstream of a mill discharging primary-treated SME. Results were equivocal; values for fish caged at each station were variable and showed no consistent trend with increasing distance from the mill's outfall. Some indications of increased hematocrit and blood clotting times were evident for fish held closer to the outfall; however, the cause(s) of the inconsistent findings could not be ascertained.

3.3.1.4 Disease resistance. Reported investigations of the incidence of disease in fish populations captured in estuarine or marine waters, adjacent to pulp and paper mill discharges, are rare. A four-year survey of English sole (Paraphrys vetulus) captured by bottom trawl in marine waters of Port Gardner (northern Puget Sound, WA), adjacent to a deep-water diffuser discharging SME and paper mill effluent from two mills, found no increase in skin lesions or parasitised fish, compared to sole from waters of southern Puget Sound (English, 1967). A more recent (1982) survey of English sole from Port Gardner found an increased incidence (70%) of liver lesions in fish captured adjacent to the mill outfall compared to those (17-23%) in fish captured at more distant sites (Malins et al., 1983). A significant proportion (29%) of the liver lesions in fish captured adjacent to this outfall were identified as neoplastic or pre-neoplastic.

Japanese investigators recently reported high incidences of skin tumours (chromatophoromas) in a teleost fish species (croaker nibe; Nibea mitsukurii) from a single coastal marine site receiving effluents (type, treatment undefined) from three large pulp and paper mills (Kimura et al., 1984). Over a nine-year period, between 30 and 80% of this species of fish captured at this site had tumours, whereas from numerous other sites only 0-5% of this species had tumours. Additionally, ether extracts of livers from croaker nibe captured from these receiving waters were demonstrated to cause mutations in Ames microsomal assays (Kinae et al., 1981). However, chemical analysis of these extracts by Kinae et al. (1981) revealed many compounds not known to be present in pulp and paper mill effluents. Kimura et al. (1984) also noted that the frequency of skin tumours for croakers captured from four separate sites receiving effluents from other pulp and paper mills was low (0-5%). Accordingly, the high level of effects reported for this one site are most likely attributable to some cause other than typical pulp and paper mill effluent.

Swedish scientists recently noted a high prevalance of gill parasites in a single group of flounders (Platichtys flesus) captured from estuarine waters adjacent to a mill

discharging BKME (Anon., 1982; Lehtinen et al., 1984). Controlled BKME exposure studies (Lehtinen et al., 1984) conducted with this fish species also showed that effluent strengths less than 1% could cause a proliferation of these parasites if exposures were sustained (see Chapter 2). This study did not include any report on incidence of gill parasites in field specimens outside the influence of the pulp and paper mill discharges.

Other studies by Swedish investigators have reportedly found an increase in bacteria (Alteromonas putrefaciens, Aeromonas hydrophila, Pseudomonas fluorescens, Vibrionaceae) in the skin mucosa of fish caught in receiving waters adjacent to pulp mill outfalls (Anon., 1982). Data linking bacterial numbers and the proximity of fish to mill discharges were not provided.

3.3.1.5 Behaviour. Preliminary studies in the Miramichi River (New Brunswick) with sonic-tagged migrant adult Atlantic salmon suggested that they avoided estuarine waters receiving pulp and paper mill effluent (type, treatment undefined) or ascended them more slowly than an adjacent clean-water tributary (Elson et al., 1972). However, other factors including the presence of other industrial effluents identified in these waters, and the fishes' innate preference for the tributary waters of origin, may have accounted for the patterns of movement observed.

Preliminary avoidance/preference studies with three seawater-acclimated juvenile coho salmon were performed by Greer (1976) on board a research barge in Stuart Channel (B.C.) within 0.2 km of the outfall of a coastal mill discharging untreated BKME, MPE and newsprint mill effluent. Fish offered a choice between surface and deep waters consistently preferred the deep water when the surficial waters (sampled under an ebbing tide) contained effluent, but didn't when effluent was absent (sampled under flood tide conditions). Although the results suggested that the laboratory-reared fish avoided surface waters containing mill effluent, the condition of the fish employed for these tests was suspect, and differences in temperature and salinity for waters drawn from these depths may have confounded the results. Control tests were not performed with surface and deep waters from sites removed from the influence of this mill discharge.

Birtwell (1977) constructed a 6 m vertical apparatus for studying the avoidance or preference behaviour of fish exposed to pulp mill effluent in shallow, stratified estuarine waters. Hatchery-reared juvenile chum, chinook and coho salmon, acclimated previously to seawater and held in this test chamber for 3-h at various locations within 1.8 km of a mill discharging untreated BKME to the surface waters of Howe Sound all showed a distinct avoidance of the surficial 1 m layer within 350 m of the outfall. At

greater distances, these fish preferred the surface waters (Birtwell, 1977; Birtwell and Harbo, 1980) (Table 3.2). Similar in situ behavioural studies conducted at three sites within Alberni Inlet using groups of hatchery-reared juvenile chinook salmon showed that these fish in all instances preferred the surface waters (Birtwell, 1978; Birtwell and Harbo, 1980). The only avoidance reaction displayed was for subsurface waters, which were oxygen-deficient.

Hatchery seawater-acclimated juvenile chum salmon held in Birtwell's (1977) vertical chambers within the surface waters of Neroutsos Inlet, downstream of a mill discharging primary-treated SME to surface waters, were studied during two consecutive years (McGreer and Vigers, 1980; McGreer et al., 1982). Initial (1979) tests showed that, at sites up to 10 km seaward from the mill, fish avoided surface (0-1 m) waters, whereas these waters were preferred by fish held at a more distant (20 km) site (McGreer and Vigers, 1980). This response was attributed to decreased pH and dissolved oxygen associated with dilute (unquantified) concentrations of mill effluent in upper waters, predominantly evident under ebb tidal conditions. Tests conducted during, 1980 (after improved in-plant recovery of spent sulphite liquors) showed a less-pronounced avoidance of surface waters within 1.3 km of the mill outfall, dependent on tidal cycle, a finding considered to reflect improved receiving-water quality (McGreer et al., 1982). Behavioural studies were not conducted at more distant downstream sites.

A mark-recapture study undertaken in Neroutsos Inlet during, 1980 demonstrated that dye-tagged chum salmon fry released at the head of the inlet moved freely and rapidly past the waters receiving primary-treated SME (Poulin and Oguss, 1982). Migrants apparently avoided the effluent plume within 2 km downstream of the point of discharge, an observation consistent with beach-seining surveys in previous years (Poulin and Rosberg, 1978, 1980). The tagged-fish data indicated that fish released on the side of the inlet above the mill migrated seaward slower than those released on the opposite side. The cause and significance of this observation was not understood by the investigators. An analysis of the stomach contents of chum fry recaptured in the above study showed that the quantity of food consumed by fish recaptured from nearshore waters within 2.5 km downcurrent of the mill was reduced relative to that for more distant migrants or those seined on the opposite shore in waters removed from the normal pattern of effluent dispersal (Poulin and Oguss, 1982). Diet for fish captured within this zone of mill influence was predominantly gammarid amphipods, unlike the more diverse diet for those recaptured at other sites.

As part of the fisheries investigations undertaken within Alberni Inlet, Birtwell (1978) examined the stomach contents of indigenous juvenile chinook salmon captured by beach seine at various distances within 1 km of the discharge of secondary-treated effluent from an integrated pulp and paper mill. Fish were found to be feeding at all sites. However, the nature of the diet consumed by fish differed for the various collection sites, presumably due to both fish feeding preference and the relative abundance of prey types (Birtwell, 1978; Birtwell and Harbo, 1980). Differences in diet appeared to be related to the proximity of fish to the discharged effluent together with the flow from the Somass River. No other studies relating to the feeding or other behaviour of fish inhabiting estuarine or marine waters receiving pulp and paper mill effluents have been found in the published literature.

3.3.1.6 Distribution/abundance. Few attempts have been made to quantify the influence of pulp and paper mill discharges on the size and distribution of fish populations frequenting adjacent marine or estuarine waters. Based upon a four-year survey of trawl catches of English sole from Port Gardner and adjacent waters of Puget Sound, English (1967) concluded that this commercial fishery was highly productive and apparently not affected by the effluent discharged by the two nearby pulp and paper mills. Life stages of English sole found near the (jointly used) deep-diffuser outfall included planktonic eggs, young-of-the-year and adults in spawning condition. Growth of young-of-the-year was reported to be similar to that for fish taken at sites distant from the mill discharge, although no data were provided. In another U.S. study, Livingston (1975) compared the diversity and abundance of estuarine fish species within two neighbouring shallow-water marsh regions, one of which received untreated effluent from a kraft pulp mill located approximately 25 km upriver. Numbers and species of estuarine fishes within approximately 5 km of this latter river mouth were severely reduced compared with the (similar) marsh area receiving uncontaminated river-water. Several fish kills were also observed at the mouth of the river into which the untreated wastes were discharged. Levels of dissolved oxygen within these estuarine waters were not depressed. No estimates were made of effluent concentration within the shallow water marsh.

Investigations of fish distribution and abundance have included B.C. coastal sites receiving discharges of untreated BKME (Howe Sound), biotreated kraft/mechanical pulping effluent (Alberni Inlet) and clarified SME (Neroutsos Inlet). Numbers and species of Pacific salmon, trout and other fish captured by beach seine in Howe Sound adjacent to the outfall area were low compared to more distant sites; however, differences were not

significant. Gill net sets demonstrated that juvenile salmonid fish did not continually avoid the (often) acutely toxic surface waters within 0.4 km of the outfall (Birtwell and Harbo, 1980).

Experimental beach-seine catches within Alberni Inlet showed that the total numbers of salmonid fish captured at each of a number of sites were not dependent on distance from the mill outfall (Birtwell, 1977; Birtwell et al., 1983). Gill-net data derived concurrently confirmed the in situ vertical avoidance/preference studies showing that salmonid fish preferred the surface waters (containing, in some instances, biotreated effluent) over the oxygen-deficient (effluent-free) subsurface waters below the halocline. This oxygen deficiency has been attributed in part to the presence of mill effluent in the surface layers of the inlet (Parker et al., 1972; Birtwell and Harbo, 1980).

An examination of catch and escape statistics for Alberni Inlet between 1950 and 1970 led Parker et al. (1972) to conclude that the pulp mill's effluent discharge has had no adverse effect on the viability of sockeye salmon and other salmonid fish stocks within the region. These data showed that indigenous salmon populations in this region had increased since the mill was constructed.

Changes in the vertical distribution of adult pink salmon (Oncorhynchus gorbuscha) migrating through Muchalat Inlet (B.C.) have been reported following the discharge of untreated BKME to this deep-water fjord. Test fishing indicated that fish that frequented surface waters in pre-operational years had moved to the deeper waters of the inlet (Sullivan and Nelson, 1979). Adult chinook migrations were also reportedly delayed, although no substantiating data were provided. Escapement records showed that the number of returning pink and sockeye salmon that passed through Muchalat Inlet was, on average, twice that recorded prior to the opening of the mill.

Beach-seine surveys conducted in Neroutsos Inlet from, 1976 to, 1979 indicated that outbound migrant chum salmon fry avoided the nearshore waters within a region approximately 2 km seaward of the sulphite mill discharge (Davis et al., 1978; Poulin and Rosberg, 1978, 1980). Similar surveys undertaken subsequent to the improved in-plant recovery of spent sulphite liquor found that this zone was diminished to 1 km (Poulin and Oguss, 1982). A summary of the four-year environmental impact study conducted in Neroutsos Inlet concluded that fish populations, in general, were normal within the inlet. An area near the mill constituting about 5% of the inlet was without doubt unsuitable for chum salmon; however, this region was avoided by fish (Tollefson, 1982).

3.3.2 Macroinvertebrates.

3.3.2.1 Survival of transplants. In situ studies with Pacific oysters (Crassostrea gigas) transplanted to estuarine/marine waters receiving untreated BKME have been conducted at three B.C. sites. The survival (97-99%) of oysters held for one year in surface and subsurface waters adjacent to the outfalls of two coastal kraft mills was not affected by mill effluent (Quayle, 1964; Table 3.2). Similar transplant studies with oysters held intertidally in Howe Sound for a two-year period showed mortalities within the immediate vicinity ($\leq$0.2 km) of the mill outfall but not at more distant stations (Pedlow, 1974). Mussels (Mytilus edulis) held adjacent to this outfall for four months also showed decreased survival relative to a reference group, whereas the survival of transplanted barnacles (Balanus glandula) held concurrently at this site was unaffected (Wu and Levings, 1980).

3.3.2.2 Development/condition. The condition factors (i.e., plumpness) for Pacific oysters held by Quayle (1964) in waters adjacent to the outfalls of two B.C. coastal mills discharging untreated BKME declined relative to groups held concurrently at distant reference sites with similar water quality (Table 3.2). The number of stations (two or three) at which oysters were held was insufficient to define the zone of influence. The condition factors for oysters held for a prolonged period within the intertidal waters of Howe Sound were also decreased within a zone up to approximately 0.5 km from the mill outfall. However after eight months' exposure, differences were not observed at distances greater than 0.2 km (Pedlow, 1974).

Prior to the establishment of a bleached kraft pulp mill, the nearshore waters of Stuart Channel supported a commercial oyster fishery (Quayle, 1964). However, within six years following mill start-up, the condition of the oysters reportedly deteriorated to the point where they could not be marketed commercially (Nelson, 1979a). Condition factors were determined for indigenous Pacific oysters collected from Stuart Channel at differing distances from the outfalls of an integrated kraft pulp and paper mill (Davis et al., 1976). Values were lowest adjacent to the outfalls, intermediate within an area 1.1 km southeast or 1.9 km northwest, and highest 2.4 km northwest of the outfalls. These values were not compared statistically, although noted differences were substantial. Condition factors for oysters from more distant sites were not determined. Appreciable accumulations of zinc metal were reported for whole-body tissues of oysters taken from distances of up to 11 km from the mill (Nelson, 1979a). The zinc undoubtedly originated from mill use of zinc hydrosulphite for brightening groundwood pulp, which was

subsequently discontinued. The extent to which this prior use may have contributed to diminished condition of oysters is not known.

The results of a six-year survey (1961-1966) of the quality of estuarine/marine coastal waters of Washington State, based upon receiving-water bioassays with developing Pacific oyster larvae, have been summarized (Woelke, 1968). Samples collected from waterbodies receiving (untreated) pulp and paper mill effluents (e.g., Grays Harbor and waters near Bellingham and Everett) had a high incidence of abnormal larvae, relative to sites removed from these (or other) industrial discharges. Developmental anomalies for waters near Seattle were surprisingly low. Woelke (1968) concluded that the results from this survey indicated "(other than temperature), low salinity and pulp and paper mill wastes are the two principal factors in the field which adversely affect oyster embryo development". A similar six-month survey of the waters from 60 stations within Puget Sound (Washington State) showed that receiving-water samples containing a relatively high concentration of sulphite waste liquor (as determined by a modified Pearl-Benson technique) were associated with a high incidence of abnormal development in oyster larvae (Bartsch, 1964). These samples were obtained at distances of up to 7 km from a mill discharging SME. The contribution of salinity or other effluent discharges (e.g., sewage) to these findings was not discussed.

Wu and Levings (1980) determined that the growth of mussels held within 50 m of the outfall of a mill discharging untreated BKME to the waters of Howe Sound (B.C.) was impaired. Barnacles held at this site also showed decreased soft-tissue weights and reduced fecundity, relative to those held concurrently at a distant (reference) station. These investigators suggested various possible causes, including low dissolved oxygen and salinity, reduced primary productivity and the presence of toxic constituents. No observations were made at stations removed from the outfall area.

3.3.2.3 Diversity/abundance. Numerous publications report changes in benthic estuarine or marine invertebrate communities attributed to pulp and paper mill discharges (Poole et al., 1978; Pearson, 1980). Benthic macroinvertebrate surveys along the Swedish Baltic coast (Landner et al., 1977) and, more recently, at Loch Eil on the west coast of Scotland (Pearson, 1981; Pearson et al., 1982) are particularly noteworthy. The present summary is restricted to the findings of Canadian surveys.

Results of surveys of the benthic invertebrates within Pictou Harbour and Northumberland Strait (Nova Scotia) were performed by Rades (1976) for one year prior to and six years following the start-up of a bleached kraft mill discharging lagooned

effluent. A moderately diverse community was evident throughout this seven-year period at each of the 60 sampling stations. A significant increase in the density of infaunal forms within Northumberland Strait was apparent post-operationally, although unrelated to distance from the mill outfall. It was concluded that no significant degradation of environmental quality had occurred. No data were provided on water quality or effluent concentrations in these receiving waters.

A five-year survey of the macrofauna within the L'Etang Estuary (New Brunswick) was initiated upon start-up of a sulphite mill discharging effluent to the upper end of the estuary (Wildish et al., 1979). Although this effluent passes through settling and aeration lagoons prior to discharge, treatment efficiency and in-plant recovery of spent chemicals have been historically poor, resulting in the discharge of an effluent with a high oxygen demand and suspended solids content. The residence time of effluent in the surficial waters of this shallow (4 m) narrow estuary has been estimated to be 5-10 days (Kristmanson et al., 1976). Changes reported in L'Etang following mill start-up included the development of anoxic or hypoxic bottom waters, hydrogen sulphide production and the elimination of macrofauna within 4 km downstream of the mill discharge. At greater distances downstream a gradual disappearance of indigenous species and repopulation by benthic organisms tolerant of oxygen-deficient conditions was observed (Wildish et al., 1977, 1979).

Changes in the diversity and abundance of benthic invertebrates in B.C. coastal waters receiving pulp and paper mill effluents, derived from Environment Canada assessments of environmental impact, are summarized in Table 3.2. Surveys in Howe Sound waters receiving untreated discharges of BKME from two mills showed that areas immediately adjacent to these outfalls were covered by fibre and devoid of benthic life. Within a zone extending approximately 0.4 km seaward from the outfalls, fewer numbers of species and organisms were present than in areas well removed from the mills' environs (Nelson, 1979b, 1979c). The areas affected were covered with varying amounts of fibre, described for one site (Nelson, 1979b) as gasiferous (hydrogen sulphide). Intertidal biota had been adversely affected 1-2 km south of the outfalls.

Benthic surveys were conducted in Malaspina Strait to obtain baseline data prior to the installation of the deep-water diffuser and fibre removal facilities at an integrated kraft/MPE/TMP/paper mill. Results showed a reduction in numbers of species and an increase in numbers of pollutant-tolerant organisms within 1 km of the outfall, an area of high fibre deposition (Nelson, 1979d). Intertidal communities adjacent to the outfall were also affected. However, intertidal surveys conducted after the installation

of the diffuser indicated that the impacts on these communities were "alleviated" (Sullivan, 1982).

Surveys of intertidal invertebrates on the shore of Northumberland Channel in the vicinity of a mill discharging untreated BKME were conducted prior and subsequent to the installation of a deep-water diffuser (Packman, 1979). Pre-diffuser studies indicated that the effluent appeared to exert its greatest effect on the larval and juvenile life stages of intertidal fauna. Post-diffuser studies found a definite increase in speciation and numbers of animals within the previous zone of influence. Subtidal surveys showed a shift in benthic communities from infaunal to epifaunal, associated with fibre and bark deposits. Diversity indices showed little effect (Packman, 1979).

Surveys of benthic invertebrate communities in Stuart Channel indicated reduced abundance and species diversity for waters immediately adjacent to the marine outfalls of an integrated BKME/MPE/paper mill. Beyond this region, a transition zone (up to 2 km from the outfalls) existed where an enhanced abundance of polychaete worms and two species of amphipods was evident (Nelson, 1979a).

Biological surveys in Muchalat Inlet indicate that untreated BKME discharged at depth to this deep-water fjord has had only minimal impact on the benthos (Sullivan and Nelson, 1979). Some reduction of intertidal organisms was apparent near the effluent discharge. Reduced subtidal benthos was also evident at the head of the inlet, which was attributed to the naturally occurring hypoxic conditions of bottom waters within this fjord, compounded by a build-up of fibre deposits (Sullivan and Nelson, 1979). No depletion of dissolved oxygen levels in surface waters attributable to mill effluent was evident.

Although survey data are limited, examinations of benthos in the Kitimat River estuary before and after start-up of a mill discharging biotreated UKME to river water at a point 3.2 km upstream of the estuary showed no significant changes (Derkson, 1981).

Benthic surveys within Alberni Inlet have reported significant changes in the abundance and diversity of invertebrate species for an area extending approximately 2 km seaward of the point of discharge of biotreated effluent to surface waters (Nelson, 1979e). Fibre deposition and light extinction associated with mill discharge have been suggested as being responsible for these changes (Morris and Leaney, 1980). The light extinction effect is undoubtedly due to the surface discharge of mill effluent.

Surveys in Porpoise Harbour have indicated an abundance of only one invertebrate species (Capitella capitata) within the region adjacent to a diffuser discharging untreated BKME (Pomeroy, 1983). The dissolved oxygen concentrations of surface waters

immediately adjacent to the outfall were somewhat depressed. Species diversity increased with greater distance from the mill outfall.

Intertidal surveys performed in Neroutsos Inlet during 1980 indicated zones of biological change which were attributed to SME discharged at the head of the inlet (Cross, 1982). Benthic invertebrates within the immediate region of this outfall were restricted to sparse numbers of pollutant-tolerant species (e.g., oligochaetes). A gradient of decreasing effect was reported up to 8 km from the outfall.

3.3.3 Zooplankton. Although some evidence suggests that certain zooplankton species common to estuarine/marine waters may be sensitive to dilute concentrations of pulp and paper mill effluents (Anderson, 1983), few surveys of zooplankton productivity in these receiving waters have been reported. A number of surveys of zooplankton diversity and abundance in the waters of Neroutsos Inlet failed to show any significant differences between stations or effects due to discharge of sulphite mill effluent to surface waters, even before chemical recovery was installed (Pennimpede and Corbett, 1982; Tollefson, 1982). This is surprising in view of the substantial changes in phytoplankton and macroinvertebrate communities noted at this site.

3.3.4 Phytoplankton. Using C-14 assimilation studies with surface and subsurface water samples collected adjacent to outfalls of two B.C. (Howe Sound) mills discharging untreated BKME, Stockner and Cliff (1976) determined that primary productivity was inhibited by the effluent. The authors estimated that the overall primary production in Howe Sound was decreased by up to 4% due to these discharges, with losses of up to 26% immediately adjacent to the outfalls. Tests performed when the mills were not operating showed no effect. Samples collected from receiving waters adjacent to the outfalls of six other B.C. coastal mills inhibited algal productivity only where circulation and flushing of these waters was considered to be poor (Stockner and Cliff, 1976). Attenuation of light caused by mill effluent, as opposed to toxic substances in the effluent, was considered to be the major cause of the reduced primary productivity.

Although algal photosynthesis was diminished in coastal waters near pulp mill outfalls, Stockner and Cliff (1976) noted that phytoplankton biomass and chlorophyll values were unaffected. Similarly, Swedish investigators (Lyden and Landner, 1979; Anon., 1982) found that light-dependent primary production (based on C-14 assimilation) was markedly reduced in estuarine waters within a 6 km^2 area next to a BKME outfall, although biomass and chlorophyll concentration were unchanged. These researchers concluded that blockage of new algal biomass production by photosynthesis may, in the

environment, be partially or fully compensated for by heterotrophic algal production, i.e., the algae utilize dissolved organic matter directly to create new cells. If operative, this response may compensate for any effects on more normal primary productivity, i.e., photosynthesis.

Carbon-assimilation studies conducted with receiving waters taken from near the outfalls of mills discharging untreated kraft/mechanical effluent (Stuart Channel) or secondary-treated BKME (Alberni Inlet) also showed evidence of decreased algal productivity (Table 3.2), attributed to effluent colour. However, chlorophyll levels (and phytoplankton populations) in Alberni Inlet during the period of investigation (1974-1976) were similar to those at distant reference sites (Nelson, 1979e). The results of a phytoplankton survey within Muchalat Inlet indicated little if any impact on the phytoplankton community from the discharge of untreated BKME (Sullivan and Nelson, 1979). A five-year survey of algal productivity within Neroutsos Inlet indicated inhibited C-14 uptake (i.e., impaired light-dependent photosynthesis) for a considerable distance from the SME outfall, although a decreased zone of influence was apparent after in-plant spent liquor recovery was instigated (Pennimpede and Corbett, 1982; Tollefson, 1982). Estimates of the phytoplankton standing crop within these waters showed considerable variation with respect to season, depth and proximity to the outfall (Pennimpede and Corbett, 1982).

3.4 References

Anderson, E. 1983. Effects of kraft mill effluent on phytoplankton and zooplankton. pp. 125-128. In W.M. Pomeroy, ed. Proceedings of Pulp Mill Effluent Monitoring. Environmental Protection Service Regional Program Rep. 83-15. Environment Canada. West Vancouver, B.C.

Anon. 1976. Brief presented at the Public Inquiry into the Pollution Control Objectives for the Forest Products Industry of British Columbia, by the B.C. Council of Forest Industries. Exhibit 1. B.C. Dept. Lands, Forests and Water Resources. Victoria, B.C.

Anon. 1982. Environmentally Harmonized Production of Bleached Pulp. Final report (in Swedish). Swedish Forest Products Research Laboratory, Stockholm, Sweden.

Anon. 1984. Toxicity and Environmental Chemistry of Wastewater from Proctor and Gamble Cellulose Ltd. (Grande Prairie). Draft report. Research Rep. AECV84-R6. Alberta Environmental Centre. Vegreville, Alberta.

Bartsch, A.F. 1964. Study of pulp and paper mill pollution in Puget Sound. pp. 43-64. In E.A. Pearson, ed. Advances in Water Pollution Research. Pergamon Press. New York, N.Y.

Birtwell, I.K. 1977. A field technique for studying the avoidance of fish to pollutants. pp. 69-86. In Proc. 3rd Aquatic Toxicity Workshop, Halifax, N.S., November 2-3, 1976. Technical Rep. No. EPS-5-AR-77-1. Environmental Protection Service. Halifax.

Birtwell, I.K. 1978. Studies on the relationship between juvenile chinook salmon and water quality in the industrialized estuary of the Somass River. pp. 57-78. In B.C. Sheppard and R.M.J. Ginetz, eds. Proc. 1977 Northwest Pacific Chinook and Coho Workshop. Fish. Mar. Serv. Tech. Rep. 759. Fisheries and Environment Canada. Vancouver, B.C.

Birtwell, I.K. and R.M. Harbo. 1980. Pulp mill impact studies at Port Alberni and Port Mellon, B.C. Trans. Tech. Sect. Canad. Pulp Paper Assoc. 81 (12): 85-89.

Birtwell, I.K., S. Nelles and R.M. Harbo. 1983. A Brief Investigation of Fish in the Surface Waters of the Somass River Estuary, Port Alberni, British Columbia. Can. MS Rep. Fish Aquat. Sci. 1744. Fisheries and Oceans Canada. West Vancouver, B.C.

Cross, S. 1982. Assessment of Shoreline Rehabilitation at the Port Alice Pulp Mill: 1978-1980 Review. Volume 3. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Davis, J.C., I.G. Shand and B.J. Mason. 1976. Biological and oceanographic studies at a kraft pulp and paper mill outfall at Crofton, B.C. 1974. Fish. Mar. Serv. Tech. Rep. 652. Fisheries and Oceans Canada. West Vancouver, B.C.

Davis, J.C., I.G. Shand, G. Christie and G. Kosakoski. 1978. Biological and Oceanographic Observations in the Neroutsos Inlet Area with Emphasis on the Effect of Sulphite Pulp Mill Waste on Pacific Salmon. 1973-1977. Fish. Mar. Serv. MS Rep. 1447. Fisheries and Oceans Canada. West Vancouver, B.C.

Derkson, G. 1981. Environmental Review of the Eurocan Pulp Mill at Kitimat, B.C. EPS Regional Program Rep. No. 81-27. Environmental Protection Service. West Vancouver, B.C.

Derkson, G. 1982. Environmental Review of the Northwood, Intercontinental and Prince George Pulp Mills at Prince George, B.C. EPS Regional Program Rep. No. 82-4. Environmental Protection Service. West Vancouver, B.C.

Derkson, G. and M. Lashmar. 1981. Environmental Review of the Crestbrook Pulp Mill at Skookumchuck, British Columbia. EPS Regional Program Rep. No. 81-24. Environmental Protection Service. West Vancouver, B.C.

Dominy, C.L. 1973. Recent changes in Atlantic salmon (Salmo salar) runs in the light of environmental changes in the Saint John River, New Brunswick, Canada. Biol. Conserv. 5: 105-113.

Dunn, C. and R. Brix. 1975. Stamina testing on chinook salmon (Oncorhynchus tshawytscha) in upper Grays Harbour during 1974. pp. 132-168. In Grays Harbour Fish Toxicity Studies 1974. Wash. State Dept. Ecol. Rep. 75-16. Washington State Department of Ecology. Olympia, WA.

Eloranta, P. 1980. Zooplankton in a watercourse polluted by a sulphite pulp mill. Ann. Zool. Fennici 17: 261-267.

Eloranta, P. and R. Kettunen. 1979. Phytoplankton in a watercourse polluted by a sulphite cellulose factory. Ann. Bot. Fennici 16: 338-350.

Eloranta, V. and P. Eloranta. 1980. Algal assays on waters receiving sulphite and sulphate cellulose effluents. Ann. Bot. Fennici 17: 26-34.

Eloranta, V. and O. Laitinen. 1982. The usefulness of the Selenastrum capricornutum algal assay to evaluate the toxic effects of pulp and paper mill effluents in lake water. Vatten 38: 317-331.

Elson, P.F. 1974. Impact of recent economic growth and industrial development on the ecology of Northwest Miramichi Atlantic salmon (Salmo salar). J. Fish. Res. Board Can. 31: 521-544.

Elson, P.F., L.N. Lauzier and V. Zitko. 1972. A preliminary study of salmon movements in a polluted estuary. pp. 325-330. In Marine Pollution and Sea Life. Fishing News Books, United Kingdom.

English, T.J. 1967. Preliminary assessment of the English sole in Port Gardner, Washington. J. Water Poll. Control Fed. 39: 1337-1350.

EPA 1972. A Study of Water Quality and Benthic Conditions in the St. Croix River Grand Falls to Milltown, Maine and New Brunswick. U.S. Environmental Protection Agency Report. Boston, MS.

Falter, C.M. and R.R. Ringe. 1974. Pollution Effects on Adult Steelhead Migration in the Snake River. Rep. EPA-660/3-73-017. U.S. Environmental Protection Agency. Washington, D.C.

Fujiya, M. 1961. Effects of kraft pulp mill wastes on fish. J. Water Poll. Control Fed. 33: 968-977.

Grande, M. 1964. Water pollution studies in the River Otra, Norway: Effects of pulp and paper mill wastes on fish. Int. J. Air Wat. Poll. 8: 77-88.

Greer, G.L. 1976. Avoidance by Juvenile Coho Salmon of Effluent Contaminated Surface Waters in the Vicinity of a Coastal Pulp Mill in British Columbia. Fish. Mar. Serv. Tech. Rep. 666. Environment Canada. West Vancouver, B.C.

Gregory, L.A. and J.S. Loch. 1973a. Benthos studies (1971 and, 1972) on the Winnipeg River in the vicinity of the Abitibi Manitoba Paper Company, Pine Falls, Manitoba. Fish. Mar. Serv. Tech. Rep. CEN T-73-3. Environment Canada. Winnipeg, Manitoba.

Gregory, L.A. and J.S. Loch. 1973b. A benthos survey (1972) in the North Saskatchewan River in the vicinity of the Prince Albert Pulp Company, Prince Albert, Saskatchewan. Fish. Mar. Serv. Tech. Rep. CEN T-73-2. Environment Canada. Winnipeg, Manitoba.

Hasselrot, T.B. 1964. Investigations with caged fish as an indication of pollution from kraft pulp mills. Vattenhygien 20: 74-83.

Hermann, R.B. 1975. Continuous flow bioassay studies in upper Grays Harbor, 1974. pp. 14-92. In Grays Harbor Fish Toxicity Studies 1974. Rep. 75-16. Washington State Department of Ecology. Olympia, WA.

Hilton, D.F.J. 1980. The effect of kraft paper mill effluents on insects inhabiting the St. Francis River near East Angus, Quebec. Ann. Soc. ent. Quebec 25: 179-189.

Howell, W.M., D.A. Black and S.A. Bortone. 1980. Abnormal expression of secondary sex characters in a population of mosquitofish, Gambusi affinis holbrooki: evidence for environmentally-induced masculinization. Copeia 1980: 676-681.

Jeanne, G.S. 1975. In situ bioassay study in upper Grays Harbor estuary. pp. 93-131. In Grays Harbor Fish Toxicity Studies, 1974. Rep. 75-16. Washington State Department of Ecology. Olympia, WA.

Kelso, J.R.M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish. Res. Board Can. 34: 879-885.

Kimura, I., N. Taniguchi, H. Kumai, I. Tomita, N. Kinae, K. Yoshizaki, M. Ito and T. Ishikawa. 1984. Correlation of epizootiological observations with experimental data: chemical induction of chromatophoromas in the croaker, Nibea mitsukurii. Nat. Cancer Inst. Monogr. 65: 139-154.

Kinae, N., T. Hashizume, T. Makita, I. Tomita, I. Kimura and H. Kanamori., 1981. Studies on the toxicity of pulp and paper mill effluents - II. Mutagenicity of the extracts of the liver from spotted sea trout (Nibea mitsukurii). Water Res. 15: 25-30.

Kristmanson, D.D., D.J. Wildish and N.J. Poole. 1976. Mixing of Pulp Mill Effluents in the Upper L'Etang. Fish. Res. Board Can. MS Rep. Ser. No. 1416. Department of the Environment. St. Andrews, N.B.

Landner, L., K. Nilsson and R. Rosenberg. 1977. Assessment of industrial pollution by means of benthic macrofauna surveys along the Swedish Baltic Coast. Vatten 3: 324-379.

Langer, O.E. and M.D. Nassichuk. 1975. Selected Biological Studies of the Thompson River System. Tech. Rep. Ser. No. PAC/T-75-22. Environment Canada. Vancouver, B.C.

Lehtinen, K.-J., M. Notini and L. Landner. 1984. Tissue damage and parasite frequency in flounders, Platichtys flesus (L) chronically exposed to bleached kraft pulp mill effluents. Ann. Zool. Fennici 21: 23-28.

Leslie, J.K. and J.R.M. Kelso. 1977. Influence of a pulp and paper mill effluent on aspects of distribution, survival and feeding of Nipigon Bay, Lake Superior, larval fish. Bull. Environ. Contam. Toxicol. 18: 602-610.

Livingston, R.J. 1975. Impact of kraft pulp mill effluents on estuarine and coastal fishes in Apalachee Bay, Florida, USA. Marine Biol. 32: 19-48.

Lyden, A. and L. Landner. 1979. Inverkan av skogsindustriella utslapp pa vaxtplanktons fotosyntes och tillvaxt. Svensk Papperstidning 16: 473-476.

McGreer, E.R. and G.A. Vigers. 1980. The use of in situ preference/avoidance studies with fish in monitoring sulphite mill effluent. Can. Tech. Rep. Fish. Aquat. Sc. 975: 152-161.

McGreer, E.R. and G.A. Vigers. 1983. Development and validation of an in situ fish preference-avoidance technique for environmental monitoring of pulp mill effluents. In W.E. Bishop et al., eds. Aquatic Toxicology and Hazard Assessment: Sixth Symposium. ASTM STP 802. American Society for Testing and Materials. Philadelphia, PA. pp. 519-529.

McGreer, E.R., D.R. Munday and G.A. Vigers. 1982. Acute Toxicity and Fish Avoidance Behaviour Studies in Neroutsos Inlet - 1980. Volume 6. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Malins, D.C., B.B. McCain, M.S. Myers, D.W. Brown and S-L Cham. 1983. Liver diseases of bottom fish from Everett Harbour, Washington. Coastal Ocean Pollution Assessment News 2: 41-42.

Markert, B.E. 1981. Water quality improvements in the Lower Fox River, Wisconsin, 1970-1980: an historical perspective. pp. 269-277. In Proc. TAPPI Environ. Conf., New Orleans, LA.

Morris, S. and A.J. Leaney. 1980. The Somass River Estuary: Status of Environmental Knowledge to 1980. Special Estuary Ser. No. 9. Fisheries & Oceans Canada and Environment Canada. West Vancouver, B.C.

Nelson, H. 1979a. Pulp Mill Environmental Impact Assessment British Columbia Forest Products, Crofton Pulp and Paper Division. EPS Regional Program Rep. No. 79-5. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979b. Pulp Mill Environmental Impact Assessment. Canadian Forest Products Ltd., Howe Sound Pulp Division. EPS Regional Program Rep. No. 79-2. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979c. Pulp Mill Environmental Impact Assessment. Rayonier Canada Limited, Woodfibre Division. EPS Regional Program Rep. No. 79-3. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979d. Pulp Mill Environmental Impact Assessment. MacMillan Bloedel Limited, Powell River Division. EPS Regional Program Rep. No. 79-14. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979e. Pulp Mill Environmental Impact Assessment. MacMillan Bloedel Ltd. Alberni Pulp and Paper Division. EPS Regional Program Rep. No. 79-11. Environmental Protection Service. West Vancouver, B.C.

Nyronen, J. 1978. Effects of pulp mill effluents on the changes of fish stocks in Lake Paijanne. Verh. Internat. Verein. Limnol. 20: 910-913.

Oikari, A.O.J. 1983. Development of physiological fish tests for assessment of toxic pollution from the pulp and paper industry. pp. 241-248. In Chemicals in The

Environment. K. Christansen et al., eds. Proc. Int. Symp. October 18-20, 1982. Copenhagen, Denmark.

Oikari, A.O.J., B. Holmbom, E. Anas and H. Bister. 1980. Distribution in a recipient lake and bioaccumulation in fish of resin acids from kraft pulp mill waste waters. Pap. Puu 62: 193-196.

Packman, G.A. 1979. Pulp Mill Environmental Assessment. MacMillan Bloedel Co. Ltd. Harmac Pulp Division. EPS Regional Program Rep. No. 79-8. Environmental Protection Service. West Vancouver, B.C.

Parker, R.R., D.H. Heller, C.R. Horwood and J.G. Sanderson. 1972. Some facets of the impact of pulp mill effluent on the Alberni Inlet. Pulp Paper Can. 73: T289-299.

Pearson, T.H. 1980. Marine pollution effects of pulp and paper industry wastes. Helgolander Meeresunters 33: 340-365.

Pearson, T.H. 1981. The Loch Eil project: introduction and rationale. J. exp. mar. Biol. Ecol. 55: 93-102.

Pearson, T.H., G. Duncan and J. Nuttall. 1982. The Loch Eil project: population fluctuations in the macrobenthos. J. exp. mar. Biol. Ecol. 56: 305-321.

Pedlow, J.C. 1974. Kraft Mill Effluent and the Pacific Oyster. M.Sc. thesis. 120 pp. Univ. British Columbia. Vancouver, B.C.

Pennimpede, W.J. and P.G. Corbett. 1982. An Assessment of the Impact of Sulphite Mill Effluent on Neroutsos Inlet. Volume 1. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Pomeroy, W.M. 1983. B.C. Timber Pulp Mill, Porpoise Harbour. An Assessment of Mill Impact on the Receiving Environment (1979 to 1982). EPS Regional Program Rep. 83-09. Environmental Protection Service. West Vancouver, B.C.

Poole, N.J., D.J. Wildish and D.D. Kristmanson. 1978. The effects of the pulp and paper industry on the aquatic environment. CRC Crit. Rev. Environ. Control 8: 153-195.

Poulin, V.A. and E. Oguss. 1982. Migration Characteristics of Juvenile Chum Salmon in Neroutsos Inlet with Particular Emphasis on the Effects of Sulphite Mill Effluent on Migratory Behaviour, 1980. Vol. 4. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Poulin, V.A. and G.E. Rosberg. 1978. Migratory Studies of Juvenile Salmonids in Upper Neroutsos Inlet, 1978. Vol. 5. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Poulin, V.A. and G.E. Rosberg. 1980. Migratory Studies of Juvenile Salmonids in Neroutsos Inlet, 1979. Volume 5. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Quayle, D.B. 1964. The Effect of Kraft Mill Effluent on the Pacific Oyster (Crassostrea gigas) with Particular Reference to Crofton, B.C. Fish. Res. Board Can. MS Rep. Ser. No. 765. Department of Fisheries. Nanaimo, B.C.

Rades, D.L. 1976. The benthos of Pictou Harbour and Northumberland Strait. Pulp Paper Can. 77: T69-74.

Rades, D.L. 1982. Biological water quality investigations of the Wisconsin River: pre and post BPT. pp. 29-36. In Proc. TAPPI Environ. Conf. Minneapolis, MN.

Ryder, R.A. 1968. Dynamics and exploitation of mature walleyes, Stizostedion vitreum vitreum, in the Nipigon Bay region of Lake Superior. J. Fish. Res. Board Can. 25: 1347-1376.

Stockner, J.G. and D.G. Cliff. 1976. Effects of pulp mill effluent on phytoplankton production in coastal marine waters of British Columbia. J. Fish. Res. Board Can. 33: 2433-2442.

Stockner, J.G. and A.C. Costella. 1978. Benthic Algae in the Thompson River, British Columbia: Their Response to Pulp Mill and Sewage Effluent. Fish Mar. Serv. Tech. Rep. 758. Fisheries and Environment Canada. West Vancouver, B.C.

Stone, D., T.C. Griffing and M.C. Knight. 1974. Biological monitoring of the Fraser River near Prince George, B.C. Pulp Paper Can. 75: T110-116.

Sullivan, D.L. 1982. Marine Environmental Surveillance Monitoring at B.C. South Coast Pulpmills 1981-1982. EPS Regional Program Rep. No. 83-17. Environmental Protection Service. West Vancouver, B.C.

Sullivan, D.L. and H. Nelson. 1979. Pulp Mill Environmental Impact Assessment. Tahsis Company Ltd. Gold River, B.C. EPS Regional Program Rep. No. 79-4. Environmental Protection Service. West Vancouver, B.C.

Thut, R.N., R.B. Herrman and J.N. Fisher. 1980. Monitoring the treated effluent and receiving waters of pulp and paper mills. TAPPI 63: 43-46.

Tollefson, R. 1982. Summary Report. Environmental Improvement at Neroutsos Inlet, B.C. Western Forest Products Ltd. Vancouver, B.C.

Vander Wal, J. 1977. Relations between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34: 824-829.

Walden, C.C. 1976. The toxicity of pulp and paper mill effluents and corresponding measurement procedures. Water Res. 10: 639-664.

Waldichuk, M. 1983. Water pollution from pulp mill effluent in British Columbia: a general overview. pp. 1-60. In W.M. Pomeroy, ed. Proceedings of Pulp Mill Effluent Monitoring. Environmental Protection Service Regional Program Rep. 83-15. Environment Canada. West Vancouver, B.C.

Weinbauer, J.D., D.A. Thiel, V.W. Kaczynski and C.S. Martin. 1980. Receiving stream fisheries studies relative to secondary treated pulp and paper mill effluents. TAPPI 63: 121-125.

Whitney, A.N. and J.C. Spindler. 1959. Effects of kraft paper wastes on a Montana stream. Trans. Amer. Fish. Soc. 88: 153.

Wildish, D.J., N.J. Poole and D.D. Kristmanson. 1977. Temporal Changes of Sublittoral Macrofauna in L'Etang Inlet Caused by Sulphite Pulp Mill Pollution. Fish. Mar. Serv. Tech. Rep. No. 718. Fisheries and Environment Canada. St. Andrews, N.B.

Wildish, D.J., N.J. Poole and D.D. Kristmanson. 1979. Pulp Mill Pollution in L'Etang Estuary, A Case History and Clean-Up Alternatives. Fish. Mar. Serv. Tech. Rep. No. 884. Fisheries and Environment Canada. St. Andrews, N.B.

Willard, H.K. 1983. Toxicity Production of Pulp and Paper Mill Wastewater. 76 pp. Contract No. 68-03-3028, WA 20. February 1983. U.S. Environment Protection Agency. Cincinnati, OH.

Woelke, C.E. 1968. Application of shellfish bioassay results to the Puget Sound pulp mill pollution problem. Northwest Science 42(4): 125-133.

Wu, R.S.S. and C.D. Levings. 1980. Mortality, growth and fecundity of transplanted mussel and barnacle populations near a pulp mill outfall. Mar. Poll. Bull. 11: 11-15.

Zanella, E.F. and J.R. Weber. 1981. Monitoring the ecological impact of kraft mill effluents on the Sacramento River. pp. 261-267. In Proc. TAPPI Environ. Conf., New Orleans, LA.

4 BIOACCUMULATION AND ELIMINATION OF ORGANIC CONSTITUENTS OF MILL EFFLUENTS

4.1 Introduction

A comprehensive evaluation of the risks associated with releasing chemicals to the aquatic environment embraces the extent to which they may bioaccumulate in aquatic organisms. The uptake and storage of certain chemicals or their metabolites in commercially-important species of exposed fish or shellfish may render them unfit for human consumption. Exposure may also overload the normal capability of the organism to cope with other chemicals to which they are already being exposed.

Certain chemicals are known to bioconcentrate in fish or other aquatic organisms as a result of their direct uptake from water. Some of these chemicals are biomagnified through the food chain, as the predators in the chain feed on prey organisms which have already accumulated significant concentrations of these chemicals. Bioconcentration factors indicate the degree to which specific chemicals accumulate in aquatic life during direct exposure. Many factors affect the rate and extent of bioconcentration: the duration and conditions (pH, temperature, dissolved oxygen, etc.) of exposure; the chemical concentration and speciation; the species of the organism, its overall state of health and, in particular, its metabolic (respiratory) rate. In addition, the relative solubility of the chemical in the fatty or parenchymatous tissues of an organism strongly influences its bioaccumulation potential (Neely et al., 1974; Mackay, 1982).

The insertion of chlorine into organic molecules increases their fat solubility, and thereby enhances their bioaccumulation in aquatic organisms. Thus the potential for bioconcentration of the more environmentally persistent chlorinated organic chemicals formed during the bleaching of kraft or sulphite pulp deserves greater attention than that for the constituents of unchlorinated effluents which are more readily biodegraded and have a lesser fat solubility.

This chapter summarizes present knowledge concerning bioaccumulation of chemicals in pulp and paper mill effluents, together with available information regarding bioconcentration factors and rates, and modes for their elimination by aquatic life. Data relating to the uptake and elimination of specific effluent constituents during controlled (laboratory) exposure of aquatic organisms are also reviewed. Finally, information on bioaccumulation of effluent constituents in freshwater or estuarine/marine organisms collected from natural waters receiving discharges of pulp and paper mill effluents is summarized and assessed.

No attempt has been made here to distinguish the biological relevance of accumulated effluent constituents; correlations between tissue concentrations and toxic effects have yet to be established/reported. A review of the known sublethal and lethal responses of aquatic life to exposure to many of these effluent constituents is included in Chapter 2.

Certain chemical constituents of pulp and paper mill effluents which readily bioaccumulate in aquatic species can cause off-flavours in edible tissues. These off-flavours, although perhaps not deleterious to the organism or to man as a consumer, can significantly reduce the value of a sports or commercial fishery. The present review summarizes current knowledge on the occurrence and significance of off-flavours in aquatic life attributable to pulp and paper mill effluents and delineates the threshold concentrations of pulp and paper mill effluents, in-plant process effluents and effluent constituents, that cause significant tainting of fish flesh.

4.2 Exposure to Effluent Constituents

4.2.1 Resin and Fatty Acids. Because fatty acids occur naturally in all aquatic biota, their bioaccumulation has received limited attention. Howard and Monteith (1977) examined the uptake and elimination of radioactively-labelled linolenic acid (one of the major fatty acids contributing to the acute lethal toxicity of unbleached pulp mill effluents; Leach and Thakore, 1977) by juvenile rainbow trout. The greatest uptake of radioactivity was found in gill tissue, with lesser but appreciable amounts in the blood and viscera. Little, if any, uptake was evident in muscle tissue. The concentration of accumulated linolenic acid in specific tissues or whole-fish preparations reached a maximum within 12 to 24 h and declined fairly rapidly thereafter (presumably due to metabolism of the linolenic acid and excretion of the metabolites), or when fish were transferred to freshwater (Howard and Monteith, 1977). The bioaccumulation and retention of chlorinated fatty acids in fish or other aquatic life has not been reported.

Bioaccumulation of the toxic and environmentally-persistent resin acid, dehydroabietic acid (DHA), has been studied by a number of researchers. Mahood and Rogers (1975) found DHA (unquantified) in whole-body tissue of sockeye salmon exposed to a lethal concentration of this resin acid. Kruzynski (1979) determined the concentration of DHA in liver bile and various tissues of sockeye salmon smolts held in a high (650 µg/L) sublethal DHA concentration for five days. His results (Table 4.1) showed the highest concentration of this resin acid in the brain, with lesser but significant concentrations in kidney and liver. The carcass (muscle, bone, skin) contained a relatively small amount of

TABLE 4.1 CHEMICAL BIOACCUMULATION IN AQUATIC ORGANISMS EXPOSED TO SPECIFIC CONSTITUENTS OF PULP AND PAPER MILL EFFLUENTS

Chemical	Test concentration (µg/L)	Diluent water	Exposure (days)	Organism	Tissue	Tissue concentration[a] (µg/g)	BCF[b]	Reference
dehydroabietic acid	650	FW[c]	5	sockeye salmon	whole-body	19	30	Kruzynski, 1979
					bile	647	996	Kruzynski, 1979
					brain	620	954	Kruzynski, 1979
					kidney	278	428	Kruzynski, 1979
					liver	263	404	Kruzynski, 1979
					carcass	8	12	Kruzynski, 1979
dehydroabietic acid	400	BW[d]	5	amphipods	whole-body	8	20	Kruzynski, 1979
dehydroabietic acid	1 200	FW	4	rainbow trout	plasma	237	198	Oikari et al., 1982
					liver	101	84	Oikari et al., 1982
					kidney	83	69	Oikari et al., 1982
					brain	37	31	Oikari et al., 1982
					muscle	16	13	Oikari et al., 1982
resin acid mixture	1 400	FW	2	rainbow trout	liver	273	195	Oikari et al., 1982
					kidney	88	63	Oikari et al., 1982
					brain	82	59	Oikari et al., 1982
					muscle	24	17	Oikari et al., 1982
2,4-dichlorophenol	1 700	FW	1	brown trout	whole-body	18	10	Hattula et al., 1981
trichlorophenol	800	FW	1	brown trout	whole-body	6	12	Hattula et al., 1981
tetrachlorophenol[g]	500	FW	1	brown trout	whole-body	210	450	Hattula et al., 1981
pentachlorophenol[g]	200	FW	1	brown trout	whole-body	200	100	Hattula et al., 1981
4,5-dichlorocatechol	2 300	FW	1	brown trout	whole-body	10	4	Hattula et al., 1981
tetrachlorocatechol	1 100	FW	1	brown trout	whole-body	6	6	Hattula et al., 1981
3,4,5-trichloroveratrole[e]	10	FW	28	zebra fish	whole-body	350[f]	3 200	Neilson et al., 1984
tetrachloroveratrole[e]	20	FW	56	zebra fish	whole-body	2 300[f]	25 000	Neilson et al., 1984

a Determined on a wet weight basis except where indicated.
b Bioconcentration factor. Most values presented are "apparent" rather than "true" BCF's since studies did not determine that a state of equilibrium had been attained and water concentrations were monitored infrequently or not at all.
c Freshwater.
d Brackish water (salinity 10-15 °/oo).
e Not found in effluent; but formed by bacterial methylation of tri- or tetrachloroguaiacol.
f Values expressed as µg/g fat.
g Present if used as slimicide in paper mill effluents.

DHA. Bioconcentration factors were 996, 954 and 12 for bile, brain and carcass, respectively. The appreciable bioconcentration of this resin acid in bile suggested a hepatobiliary route for elimination. Kruzynski (1979) also found that dehydroabietic acid was bioconcentrated in estuarine amphipods after a five-day exposure to a high (400 µg/L) DHA concentration (Table 4.1).

Oikari et al. (1982) determined that fish exposed for four days to purified DHA showed the highest accumulation of this resin acid in the blood plasma (Table 4.1). Liver, kidney and brain showed appreciable accumulations of DHA, with lower levels in fish muscle tissue. Rainbow trout exposed to a mixture of resin acids for two days provided similar results (Table 4.1; Oikari et al., 1982). Besides DHA, bioaccumulation in liver of the resin acids abietic, neo-abietic, pimaric, sandaracopimaric, isopimaric, levopimaric and palustric was also noted. The likely role of the liver in the detoxification and elimination of accumulated resin acids was discussed by these authors.

When rainbow trout were held for 30 days in a resin acid mixture at a strength equivalent to 0.08 of the 96-h LC_{50} value, total resin acid concentrations determined for bile, plasma and brain were similar (Oikari et al., 1984a). Certain resin acids (neobietic, dehydroabietic) were detected in appreciable quantities in plasma and in the bile, where the bioconcentration factor for resin acids was high (800-1000). Other resin acids (pimaric, abietic) were concentrated in the brain (9400 and 5200, respectively). The lowest resin acid concentration was found in fish gills. These fish also showed impaired liver UDP-glucuronyltransferase activity and a significant decline in plasma protein content (Oikari et al., 1984a).

Oikari et al. (1984b) demonstrated that more than 99% of the dehydroabietic acid in the bile of rainbow trout exposed to DHA for three days was conjugated, almost exclusively as glucuronides. Separate studies with rainbow trout injected intraperitoneally with labelled DHA demonstrated the highest radioactivity in the bile and feces, an order of magnitude greater than in the kidney and gills (Oikari, 1984). Together, these studies indicate that resin acids accumulated in fish are excreted predominantly via the hepatobiliary route in a conjugated (detoxified) form.

4.2.2 Chlorinated Phenolics. The bioaccumulation in aquatic organisms of the various chlorophenols associated with effluents from pulp and paper manufacture and from wood preservation plants has been reviewed by Jones (1981, 1984). This subject has also been addressed in an extensive Swedish report on the production of "environmentally harmonized" bleached pulp (Anon., 1982). In general, the studies conducted indicate that

the degree of bioaccumulation of specific chemicals is a function of the extent of chlorine substitution. Differing test conditions, including aquatic species, nature of diluent water, duration of exposure and chemical strength prevent firm conclusions from being reached in this respect.

Of the various chlorinated derivatives of simple phenol (C_6H_5OH) derived during pulp bleaching, di- and trichlorophenol are the only ones normally found in substantial (µg/L) quantities in final effluents discharged from pulp mills (see Chapter 1). However, due to the use of tetra- and pentachlorophenol as slimicides in certain paper mills, and for the purpose of comparison, the degree of bioaccumulation of these more-highly chlorinated phenols is also reported here.

Hattula et al. (1981) compared the bioconcentration of chlorinated phenols and catechols by brown trout (Salmo trutta) under identical exposure conditions. The apparent bioconcentration factors (BCFs) for di- and trichlorophenol were low (10-12), as were those for di- and tetrachlorocatechol (2-6). These authors found a greater uptake of the slimicides tetra-and pentachlorophenol (BCFs 100-450). Unfortunately these studies involved unrealistically high concentrations of chemicals and exposures restricted to 24 h (Table 4.1).

Renberg et al. (1980) exposed fish (Alburnus alburnus) for 14 days to a brackish water mixture containing approximately 8 µg/L 4,5,6-trichloroguaiacol and 10 µg/L tetrachloroguaiacol. Both chemicals were taken up rapidly during the first 24 h. The whole-body tissue concentration of these chlorinated phenolics increased markedly between 7 and 14 days, i.e., no steady state was attained during the exposure. Bioconcentration of both chemicals was in the order of 400 (Table 4.1). Approximately 75% of these accumulated chlorinated organics were eliminated during the first day after transfer of fish to uncontaminated water; and concentrations of both chemicals in fish had dropped to the limit of detection after two weeks (Renberg et al., 1980).

The bioaccumulation of chlorophenols in plasma, bile, gill and brain of rainbow trout exposed for 30 days to a freshwater solution containing resin acids and four chlorophenols was determined by Oikari et al. (1984a). The total concentration of chlorophenols in this mixture was low (23 µg/L), and the toxicity of the mixture was equivalent to 0.08 of the 96-h LC_{50}. As the concentrations of individual chlorophenols in solution were not monitored throughout the exposure, no tissue BCFs were derived. Tissue analyses showed a greater accumulation of tetra- and pentachlorophenol in gill and bile samples than of di- or trichlorophenol. Unlike the resin acids examined, negligible amounts of any chlorophenol were found in the brain tissue.

The method of excretion of accumulated chlorophenols by fish has not been examined in detail. Kobayashi (1978) reported that pentachlorophenol is conjugated to glucuronides and sulphates in the liver, for subsequent biliary and branchial (respectively) excretion; and that only a small portion (10%) is excreted in the unconjugated form. The pattern with the other chlorophenols is thought to be similar (Oikari et al., 1984a). Oikari (1984) reported that, as with the resin acids, more than 99% of the chlorophenolics in fish bile (including 2,4,6-trichlorophenol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol) are conjugated. These conjugates were present almost exclusively as glucuronides.

In a recent laboratory study, Neilson et al. (1984) examined the bioconcentration potential for tri- and tetrachloroveratrole, two metabolites which are produced by bacterial methylation of tri- and tetrachloroguaiacol (Neilson et al., 1983). Zebra fish (Brachydanio rerio) exposed for four weeks to 10 µg/L trichloroveratrole accumulated this chemical in whole-body extracts, reaching an apparent steady-state concentration of 350 µg/g wet weight (bioconcentration factor, 3200 based on total wet weight). Approximately 80% of this chemical was lost from fish within three days following their transfer to uncontaminated freshwater, although low tissue concentrations were still evident 12 days after transfer (Neilson et al., 1984). Fish exposed for eight weeks to 20 µg/L tetrachloroveratrole showed an even greater accumulation of this metabolite (BCF, 25 000; Table 4.1). As with trichloroveratrole, the concentration of this chemical in exposed fish fell rapidly (80% loss within three days) when fish were transferred to uncontaminated water.

4.2.3 Other Organic Constituents. Bioaccumulation of volatile halogenated organic constituents of pulp and paper mill effluents has not been studied in detail. Neely et al. (1974) determined that tetrachloroethylene did not accumulate to a large extent (BCF 40) in muscle tissue of exposed rainbow trout. Studies with fish exposed to chloroform for 14 days suggest that this volatile effluent constituent also does not bioaccumulate appreciably (BCF 6; Anon., 1980).

Environmentally-persistent chlorinated sulphones (di-, tri- and tetrachlorodimethyl sulphone) are present in appreciable quantities in treated or untreated bleached kraft whole mill effluent (BKME). Utilizing the octanol-water partition coefficients of these compounds as indices of their bioaccumulation potential, as per Neely et al. (1974) and Mackay (1982), Voss (1983) concluded that the potential for bioconcentration of these chlorinated sulphones was very low. No experimental studies were undertaken.

4.3 Controlled Effluent Exposure

4.3.1 Bioaccumulation of Resin Acids. On-site flowthrough exposure of rainbow trout to 3-18% (v/v) untreated (clarified) BKME for two or six days resulted in whole-fish DHA concentrations of 2-9 µg/g (Table 4.2) (Fox et al., 1977). Based on the concentrations of DHA in solution (0.1-0.7 mg/L), apparent BCF's were 13-30. The authors concluded that dehydroabietic acid accumulated to a level "which is likely to result in sublethal toxic effects"; however, no supporting evidence was presented.

Oikari et al. (1984b) determined the concentrations of total and individual resin acids accumulated in the bile of rainbow trout exposed in the flowthrough mode to 0.5 or 1% (v/v) treated BKME for 10 and 30 days, respectively. Significant quantities of each of the 5-8 resin acids measured were evident, with total resin acid concentrations of 196 (10 days) or 311 (30 days) µg/mL (Table 4.2). More than 99% of each resin acid examined was conjugated; predominantly as glucuronides. These data demonstrate conjugation in the liver of exposed fish as a mechanism for detoxification of resin acids prior to their excretion.

For rainbow trout exposed to 0-13% treated BKME for 10 to 30 days, Oikari (1984) reported that the amounts of conjugated resin acids in bile extracts were linearly related to the effluent concentration, and that several days were required to "turn on" the mechanism of hepatobiliary elimination. In these studies, the majority of bile conjugates were eliminated within five days following the transfer of fish to fresh water.

4.3.2 Bioaccumulation of Chlorinated Phenolics. The uptake and elimination of chlorinated phenolics by fish or other aquatic life during controlled (laboratory) exposure to bleached pulp mill effluent has not been studied in detail. Landner et al. (1977) measured the amounts of 2,4,6-trichlorophenol (Cl_3P), trichloroguaiacol (Cl_3G) and tetrachloroguaiacol (Cl_4G) taken up in rainbow trout exposed to 2.5% (v/v) kraft chlorination (C-stage) or caustic extraction (E-stage) effluent, diluted with brackish seawater (salinity 7 °/oo). Bioaccumulation of Cl_3P, Cl_3G, and Cl_4G in fish livers after a two-week exposure to either type of effluent could be detected, with greater amounts attributable to the caustic extraction effluent (Table 4.2). The concentrations detected were not large; a maximum of 3 µg/g of Cl_3G in the liver tissue, with lesser concentrations of Cl_3P and Cl_4G. It should be pointed out that concentrations in the liver would be expected to be higher than in the bulk of other tissues; that the in-process streams selected for evaluation would contain the highest concentration of the chemicals under examination; and that these in-process streams had not been subjected to

TABLE 4.2 BIOACCUMULATION OF RESIN ACIDS AND CHLORINATED PHENOLICS IN FISH EXPOSED TO PULP AND PAPER MILL EFFLUENTS UNDER CONTROLLED CONDITIONS

Chemical constituent	Effluent (diluent water)	Effluent concentration (% v/v)	Chemical concentration (µg/L)	Exposure (days)	Organism	Tissue	Tissue concentration[a] (µg/g)	BCF[b]	Reference
dehydroabietic acid	untreated BKME[c] (FW)[d]	18	700	2	rainbow trout	whole-body	9	13	Fox et al., 1977
		10	400	2			8	20	
		6	200	2			6	30	
		3	100	6			2	20	
total resin acids	treated BKME (FW)	1	-[e]	30	rainbow trout	bile	311[f]	-	Oikari et al., 1984b
		0.5	-	10	rainbow trout	bile	196[f]	-	
2,4,6-tri-chlorophenol	kraft C[g] (BW)[h]	2.5	-	14	rainbow trout	liver	0.4	-	Landner et al., 1977
2,4,6-tri-chlorophenol	kraft E[i] (BW)	2.5	-	14	rainbow trout	liver	0.8	-	Landner et al., 1977
trichloro-guaiacol	kraft C (BW)	2.5	-	14	rainbow trout	liver	0.4	-	Landner et al., 1977
trichloro-guaiacol	kraft E (BW)	2.5	-	14	rainbow trout	liver	3	-	Landner et al., 1977
tetrachloro-guaiacol	kraft C (BW)	2.5	-	14	rainbow trout	liver	0.07	-	Landner et al., 1977
tetrachloro-guaiacol	kraft E (BW)	2.5	-	14	rainbow trout	liver	0.8	-	Landner et al., 1977
2,4,6-tri-chlorophenol	kraft BPE[j] (FW)	2	-	56	fish	whole-body	-	210	Anon., 1982
3,4,5-tri-chloroguaia-col	kraft BPE (FW)	2	-	56	fish	whole-body	-	1800	Anon., 1982
tetrachloro-guaiacol	kraft BPE (FW)	2	-	56	fish	whole-body	-	280	Anon., 1982

a Wet weight basis.
b Apparent bioconcentration factor.
c Bleached kraft whole mill effluent.
d Freshwater.
e Not determined.
f Values are µg/mL.
g Kraft chlorination (C-stage) bleach plant effluent.
h Brackish water (salinity 7 °/oo).
i Kraft caustic extraction (E-stage) bleach plant effluent.
j Combined bleach plant effluent.

biooxidation. Chlorinated catechols were not detected in the liver extracts. An additional three weeks of exposure to either the chlorination or caustic extraction effluent did not result in any increased uptake of the three chlorinated phenolics by liver tissue (Landner et al., 1977). All traces of Cl_3P and Cl_3G in the liver were lost within three weeks following the transfer of fish to uncontaminated water (Landner et al., 1977). Data regarding clearance of Cl_4G were indeterminate. Since concentrations of specific chlorinated phenolics in the test solutions were not measured, bioconcentration factors could not be determined.

Swedish scientists (Anon., 1982) reported bioaccumulation of 2,4,6-Cl_3P, 3,4,5-Cl_3G and Cl_4G in whole body tissues of freshwater fish held in 2% combined kraft bleach plant effluent, within one week. Steady-state concentrations were not attained during an additional seven weeks of exposure; however, the apparent bioconcentration factors for the eight-week period were 210, 1800 and 280 for Cl_3P, Cl_3G and Cl_4G, respectively.

Finnish studies cited recently by Oikari (1984) and Kunnamo and Oikari (1984) suggest that chlorinated phenolics accumulated in fish are conjugated and eliminated in a manner similar to that reported for resin acids (Oikari et al., 1984b). Concentrations of conjugated chlorinated phenolics in bile samples from rainbow trout exposed for 10 to 30-days to different concentrations (0-13% v/v) of treated BKME were closely related to effluent strength (Kunnamo and Oikari, 1984). As with the resin acids, the majority of these conjugated phenolics were in the form of glucuronides (Oikari, 1984).

No data were found related to the uptake and retention of chlorinated phenolics by fish or other aquatic life when exposed under controlled conditions to BSME. Nor were any comparable data located pertaining to lower forms of aquatic life (invertebrates, phytoplankton).

4.4 Receiving-Water Studies

4.4.1 Freshwater.

4.4.1.1 Resin acids. Kaiser (1977) captured three species of freshwater fish from Nipigon Bay, Lake Superior, at up to 8 km from the outfall of a bleached kraft pulp and paper mill practising primary clarification only. Qualitative measurements indicated that dehydroabietic acid was present in whole-body tissues of fish captured within 3 km of the outfall, but absent for fish taken 8 km away.

Holmbom (1980) and Oikari et al. (1980) reported the concentrations of dehydroabietic and other resin acids in samples of blood plasma and bile from rainbow trout caught at varying distances from a bleached kraft pulp mill lacustrine outfall. Prior

to discharge the effluent was clarified and biotreated in an aerated lagoon for 24 h. Accumulation of pimaric, isopimaric, dehydroabietic and, to a lesser extent, neoabietic acid in plasma and bile samples from caged fish was evident at stations 0.1-0.8 km from the mills' outfall, although only dehydroabietic acid was found in bile samples from fish held at greater distances (3.5-6.0 km) (Oikari et al., 1980). Extension of exposure times beyond two days did not increase the concentration of resin acids in plasma or bile samples. Resin acid concentrations were generally higher in the bile than in the plasma.

The concentration of total resin acids in receiving waters at stations 0.1-0.8 km from the mill's outfall range from 10 to 30 µg/L, whereas at more distant stations it was less than 5 µg/L (Holmbom, 1980). The bioconcentration factors for total resin acids accumulated in fish held within 0.8 km of the outfall were 40-60 in plasma, and 70-130 in bile (Oikari et al., 1980). Despite the authors' conclusion that resin acids were accumulated in fish "to such an extent that various metabolic sublethal effects of resin acids could be expected", no direct supporting evidence was developed. The findings of this study may have been affected by the concurrent persistence of low dissolved oxygen concentrations (3-6 mg O_2/L) at all stations within 3.5 km of the mill's outfall.

Oikari et al. (1980) reported the concentrations of five resin acids (pimaric, palustric, isopimaric, abietic, dehydroabietic) in perch (Perca fluviatilis) captured within 0.9 km of the mill outfall during the above caged fish studies. Levels of each resin acid in plasma and bile samples were the same or higher than corresponding values found for rainbow trout held in cages at the same location.

4.4.1.2 Chlorinated phenolics. Landner et al. (1977) determined that livers of indigeneous perch (Perca fluviatilis) and northern pike (Esox lucius) caught near a mill producing full bleached kraft pulp, contained 2,4,6-Cl_3P, Cl_3G, Cl_4G and, to a lesser extent, chlorocatechols. Concentrations within and between fish species varied appreciably, and were expressed only as micrograms per gram liver fat (<11.5 µg/g). Conversion of these values to micrograms per gram wet liver weight by Voss and Yunker (1983) showed comparable liver concentrations of 0.03-0.06 µg/g Cl_3P, 0.08-0.3 µg/g Cl_3G and 0.05-0.2 µg/g Cl_4G for these fish species.

Bjorseth et al. (1981) reported the total organochlorine content in four species of fish captured where a river containing BSME (presumably untreated) discharged into a lake. The total organochlorine concentration varied nine-fold between the different fish species. Additionally, these concentrations were 3 (perch) to 11 (roach) times higher than corresponding values for the same species collected from an "uncontaminated" area of the

same lake. Individual organochlorine compounds were not identified, although the data suggested the presence of chlorinated phenols and guaiacols.

The bioaccumulation of chlorophenolic compounds in the muscle tissue of northern pike captured from a large Finnish lake receiving untreated effluent from numerous kraft and sulphite mills was studied by Paasivirta et al. (1981). Tissue concentrations of 2,4,6-Cl_3P, Cl_4C and Cl_4G in fish taken from waters adjacent to pulp and paper mills were clearly higher than those for fish captured approximately 40 km from the nearest mill, although all values were low (1-37 ng/g wet weight) (Table 4.3).

Swedish researchers (Anon., 1982) reported the concentrations of chlorophenolics in liver and muscle tissues of fish captured adjacent to two freshwater sites receiving effluent from Swedish mills manufacturing bleached kraft pulp. No information was provided as to whether these effluents were treated prior to discharge. Chloroguaiacols were detected in the muscle tissue of pike captured at each site, although concentrations were low (<0.008 µg/g 3,4,5-Cl_3G, <0.015 µg/g Cl_4G). No chloroguaiacols were detected in muscle samples from perch or whitefish. Liver tissue showed a greater accumulation of chloroguaiacols, with maximum values of 1.8 (3,4,5-Cl_3G), 0.36 (4,5,6-Cl_3G) and 0.57 (Cl_4G) µg/g wet weight (Table 4.3). The degree of accumulation of chlorocatechols was not reported.

The concentration of chlorinated phenolics in muscle and liver tissues of fish caught in the Fraser River downstream of four kraft mills discharging treated BKME was studied recently (Voss and Yunker, 1983). Mountain whitefish and large scale suckers captured 50 km below the nearest pulp mill showed accumulations of chloroguaiacols (particularly 3,4,5-Cl_3G) and, to a lesser extent, trichlorophenol in liver tissue (Table 4.3). Concentrations of Cl_3P, Cl_3G or Cl_3G), in muscle tissue from these fish were below detection limits or present in trace (<5 ng/g) amounts. The estimated concentration of treated effluent at this downstream site was approximately 0.4% (v/v), and riverwater concentrations of Cl_3P, Cl_3G and Cl_4G determined on one occasion were 0.035 µg/L, 0.023-0.153 µg/L, and 0.087 µg/L, respectively. No fish upstream of the pulp mills were examined. No attempt was made to assess what contribution, if any, municipal sewage discharged upstream from two medium-sized cities contributed to the loading of chlorinated phenolics.

Assorted species of fish captured upstream and downstream (within 2.5 km) of a pulp mill discharging treated BKME into a river were examined for whole-body concentrations of a number of effluent constituents including chlorinated phenolics (Anon., 1984). Trace amounts (0.001-0.004 µg/g) of Cl_3P and Cl_3G were found in the

TABLE 4.3 BIOACCUMULATION OF ORGANIC CONSTITUENTS OF PULP AND PAPER MILL EFFLUENTS IN FRESHWATER ORGANISMS TAKEN FROM OR HELD IN THE RECEIVING WATERS

Chemical	Effluent[a] type(s)	Effluent[a] treatment	Receiving water concentration (µg/L)	Distance from outfall(s) (km)	Organism(s)	Tissue	Tissue concentration[b] (µg/g)	Reference
total resin acids	BKME[c]	24-h aeration	10-30	0.8	rainbow trout	plasma	20-30[e]	Oikari et al., 1980
total resin acids	BKME	24-h aeration	2-5	3.5-6	rainbow trout	plasma	<3[e]	Oikari et al., 1980
total resin acids	BKME	24-h aeration	10-30	0.8	rainbow trout	bile	45-60[e]	Oikari et al., 1980
total resin acids	BKME	24-h aeration	2-5	3.5-6	rainbow trout	bile	2-5	Oikari et al., 1980
2,4,6-Cl_3P	BKME	-	-	-	pike, perch	liver	≤0.06	Landner et al., 1977
Cl_3G	BKME	-	-	-	pike, perch	liver	≤0.3	Landner et al., 1977
Cl_4G	BKME	-	-	-	pike, perch	liver	≤0.2	Landner et al., 1977
2,4,6-Cl_3P	-	-	-	5	roach	muscle	0.056	Paasivirta et al., 1980
4,5,6-Cl_3G	-	-	-	5	roach	muscle	0.047	Paasivirta et al., 1980
Cl_4G	-	-	-	5	pike	muscle	0.19	Paasivirta et al., 1980
Cl_4G	-	-	-	5	phytoplankton	whole-body	0.11	Paasivirta et al., 1980
2,4,6-Cl_3P	BKME, BSME[f]	-[d]	-[d]	<5	northern pike	muscle	0.037	Paasivirta et al., 1981
2,4,6-Cl_3P	BKME, BSME[f]	-	-	40	northern pike	muscle	0.001-0.002	Paasivirta et al., 1981
Cl_4C	BKME, BSME[f]	-	-	<5	northern pike	muscle	0.006	Paasivirta et al., 1981
Cl_4C	BKME, BSME[f]	-	-	40	northern pike	muscle	<0.001	Paasivirta et al., 1981
Cl_4G	BKME, BSME[f]	-	-	<5	northern pike	muscle	0.007	Paasivirta et al., 1981
Cl_4G	BKME, BSME[f]	-	-	40	northern pike	muscle	<0.001	Paasivirta et al., 1981
3,4,5-Cl_3G	BKME	-	-	-	pike	muscle	≤0.008	Anon., 1982
3,4,5-Cl_3G	BKME	-	-	-	pike	liver	≤1.8	Anon., 1982
3,4,5-Cl_3G	BKME	-	-	-	perch, whitefish	liver	≤0.11	Anon., 1982
4,5,6-Cl_3G	BKME	-	-	-	pike	liver	≤0.14	Anon., 1982
4,5,6-Cl_3G	BKME	-	-	-	perch, whitefish	liver	≤0.36	Anon., 1982
Cl_4G	BKME	-	-	-	pike	muscle	≤0.015	Anon., 1982
Cl_4G	BKME	-	-	-	pike	liver	≤0.57	Anon., 1982
2,4,6-Cl_3P	BKME	aeration	0.035	50	sucker, whitefish	liver	0.015, 0.033	Voss & Yunker, 1983
3,4,5-Cl_3G	BKME	aeration	0.153	50	sucker, whitefish	liver	0.12, 0.30	Voss & Yunker, 1983
4,5,6-Cl_3G	BKME	aeration	0.027	50	sucker, whitefish	liver	0.013, 0.062	Voss & Yunker, 1983
Cl_4G	BKME	aeration	0.086	50	sucker, whitefish	liver	0.027, 0.118	Voss & Yunker, 1983
Cl_3P	BKME	aeration	-	≤2.5	fish	whole-body	0.004	Anon., 1984
Cl_4P	BKME	aeration	-	≤2.5	fish	whole-body	0.002	Anon., 1984
Cl_3G	BKME	aeration	-	≤2.5	fish	whole-body	0.001	Anon., 1984
chlorobenzene (tri-, tetra-, hexa-)	BKME	-	-	≤3	perch, sucker	whole-body	-	Kaiser, 1977
hexachloro-benzene	BKME, BSME	-	-	5-40	pike	muscle	≤0.001	Paasivirta et al., 1981
chloroform	BKME	aeration	2-6	≤2.5	fish	whole-body	<0.001	Anon., 1984
dichlorodimethyl	BKME	aeration	<1	≤2.5	fish	whole-body	0.026	Anon., 1984

a Characteristics of effluent discharged to the receiving-waters.
b Determined on a wet weight basis except where indicated.
c Bleached kraft whole mill effluent.
d Not determined/not indicated.
e Dry weight basis.
f Bleached sulphite whole mill effluent.

downstream fish only. Concentrations of these constituents in the treated whole mill effluent were 1-15 µg/L, whereas those in samples of downstream water were below the limit of detection. Tissue concentrations of Cl_4G were not determined.

Paasivirta et al. (1980) examined the concentrations of chlorophenolic compounds in fish and lower food-chain organisms inhabiting a number of lakes in central Finland which receive differing inputs of these compounds from effluents discharged from bleached pulp mills and wood-preservation plants. Concentrations of Cl_3P, Cl_3G, Cl_4G and tetrachlorocatechol (Cl_4C) in phytoplankton, zooplankton, freshwater mussels (Anodonta piscinalis) and muscle samples from two fish species (roach, Rutilus sp; pike, Esox lucius) were appreciably higher in specimens collected 5 km downstream from a bleached pulp mill (type and effluent treatment undefined) than in control samples from a lake free from pulp bleaching residues. Concentrations of trichlorophenol and tetrachloroguaiacol were highest in the fish species, suggesting biomagnification through the food chain. However, concentrations of tetrachlorocatechol were highest in the plankton. The highest (mean) tissue concentration reported for each of these chlorophenolic compounds is given in Table 4.3.

When Paasivirta et al. (1983a) subsequently examined muscle tissue of pike collected from this same site, concentrations of trichlorophenol and tetrachloroguaiacol were below the limit of detection (0.2 ng/g, wet weight). These researchers attributed this decline to atypically high seasonal precipitation, and perhaps also to changes in the bleaching process (more use of hypochlorite) between the two studies. The concentrations of chlorophenolics in the receiving waters were not determined in either study.

4.4.1.3 Other organic constituents. The bioaccumulation of other specific organic constituents in freshwater organisms exposed to dilute concentrations of pulp and paper mill effluents within receiving waters has not been studied in any detail. Indeed, the evidence that some of these organic compounds even originate from a pulp mill discharge might be considered questionable. Chlorobenzenes (tri-, tetra-and hexa-) were identified by Kaiser (1977) in extracts from a number of fish species from Nipigon Bay, Lake Superior within 3 km of a kraft mill discharging untreated BKME. No effluent or receiving-water concentrations of these chemicals were determined, however, and the source(s) of these chemicals was not identified. Hexachlorobenzene in fish tissue was reported "in comparable quantities in many samples from all areas" (Kaiser, 1977). Paasivirta et al. (1981, 1983a) found low but detectable concentrations of hexachlorobenzene (<0.001 µg/g) in muscle tissue of pike and in lower food-chain organisms captured

from waters receiving bleached pulp mill wastes. However no relationship could be established between their concentration in tissue and the distance from any pulp mill.

Polychlorinated biphenyls (PCBs) have been identified in freshwater organisms inhabiting waters receiving chlorinated pulp mill effluent (Kaiser, 1977; Paasivirta et al., 1981, 1983a). However, PCBs are not a constituent of either BKME or BSME. In this instance, it is not surprising that levels of PCBs in tissue samples were unrelated to the proximity of pulp mill discharges -- as was the case with hexachlorobenzene. An exception is reported by Sullivan et al. (1983), who attributed the bioaccumulation of PCBs in fish tissues to previous discharges of de-inking wastewaters from paper recycling mills.

Chlorinated cymenes have been identified in whole-body tissue of freshwater fish captured from waters receiving untreated bleached sulphite and/or kraft mill effluents (Bjorseth et al., 1981; Paasivirta et al., 1983a). Bjorseth et al. (1981) reported concentrations of 5 (monochlorocymene) µg/g and 3.6 (dichlorocymene) µg/g in oil extracts of fish caught in a river receiving BSME and BKME discharges. Paasivirta et al. (1983a) reported the presence of chlorinated cymenes in samples of pike and roach. However, the levels reported were near the limit of detection (0.2 ng/g), and were also present in one fish species (pike) taken from a location where the origin of the chemical could not have been a pulp mill.

Ofstad et al. (1981) identified chloroform and smaller quantities of trichloroethylene and tetrachloroethylene in fat extracts from perch and roach, taken from a lake receiving effluent from an unidentified pulp and paper mill. These chemicals could not be detected in extracts from salmon taken from a river below another mill. Other researchers (Paasivirta et al., 1983a; Anon., 1984) have been unable to detect chloroform in exposed fish. Paasivirta et al. (1983a) found trace quantities of tetrachloroethylene in fish muscle tissue. However, the concentrations were independent of their proximity to pulp mill effluent discharges.

Bioaccumulation in fish of the persistent chemical dichlorodimethyl sulphone (DDMS) has been reported recently (Anon., 1984). Although whole-body tissue of fish captured from a river within 2.5 km downstream of a kraft mill discharging biologically-treated BKME contained 0.026 µg DDMS/g, the control sample contained 0.010 µg/g.

4.4.2 Estuarine/Marine Waters.

4.4.2.1 Chlorinated phenolics. Bacon and Silk (1978) examined a number of estuarine species collected from waters receiving untreated discharges from a bleached kraft mill

and a groundwood mill. The chlorinated phenolics Cl_3P, Cl_3G and Cl_4G were detected in muscle, liver and whole-body tissues of clams (Mya arenaria), sturgeon (Acipenser sp.), winter flounder (Pseudopleuronects americanus), tomcod (Microgadus tomcod) and smelt (Osmerus mordax). Concentrations of Cl_2P were at or below the limit of detection. Values for all chemicals measured were presented only as micrograms per gram lipid; however, Voss and Yunker (1983) expressed these as micrograms per gram wet weight. Accordingly, concentrations of Cl_3P, Cl_3G and Cl_4G in fish muscle were $\leq$0.01 µg/g. Those in fish liver were similarly low except for tomcod, with 0.1 µg/g Cl_3P and 0.05 µg/g Cl_3G. Homogenates of clam and sandshrimp showed chlorophenolic concentrations of 0.05 µg/g (Cl_3G; clam) or less (Table 4.4). The same chemicals could not be detected in the receiving waters.

Measurements of chlorinated phenolics in estuarine/marine organisms from five sites receiving discharges from separate Swedish bleached kraft mills are summarized in Table 4.4 (Anon., 1982). At all sites, concentrations of chlorophenols or chloroguaiacols in shellfish or fish muscle were below the limits of detection or only trace amounts (<0.02 µg/g). However, significant accumulations of these compounds were found in fish livers collected from a few sites with poor flushing (Table 4.4).

Voss and Yunker (1983) conducted a similar survey of chlorophenolic compounds in fish and shellfish in the vicinity of two British Columbia coastal bleached kraft mills practising primary clarification only. As was found in the Swedish surveys, the concentrations of chlorophenols or chloroguaiacols in fish muscle tissue or shellfish (mussels, shrimps, crabs) whole-body tissue were, with the exception of mussel Cl_3P and Cl_3G concentrations, low and often below detection limits (Table 4.4). On the other hand, livers of chum salmon (Oncorhynchus keta) captured within 3 km of each mill outfall showed an appreciable accumulation of 3,4,5-Cl_3G (0.03-0.06 µg/g wet weight). The concentration of other chlorophenolic compounds measured in salmon livers did not exceed 0.02 µg/g, and all chlorophenolics (including Cl_3G) in livers of rockfish were <0.006 µg/g.

Neilson et al. (1984) identified tri- and tetrachloroveratrole, metabolites formed by the bacterial methylation of tri- and tetrachloroguaiacol, in liver and muscle tissue of three species of estuarine fish captured from three localities receiving unidentified types of bleached pulp mill effluent. Neither of these chemicals was present in tissues of fish collected from remote sites. The authors concluded that these chemicals were formed in the receiving waters by the methylation of the corresponding chloroguaiacols or high molecular weight chlorinated lignin derived from pulp mill bleachery effluent.

TABLE 4.4 BIOACCUMULATION OF ORGANIC CONSTITUENTS OF PULP AND PAPER MILL EFFLUENTS IN ESTUARINE/MARINE ORGANISMS TAKEN FROM THE RECEIVING WATERS

Chemicals	Effluent[a] type(s)	Effluent[a] treatment	Receiving water type	Receiving water chemical concentration (µg/L)	Distance from outfall(s) (km)	Organism(s)	Tissue	Tissue concentration[b] (µg/g)	Reference
2,4-dichlorophenol	BKME,[c] MPE[d]	-[e]	SW[f], BW[g]	BLD[h]	-[e]	sturgeon, tomcod	muscle	≤0.01[i]	Bacon & Silk, 1978
2,4,6-trichlorophenol						flounder, smelt	liver	≤0.1[i]	Bacon & Silk, 1978
trichloroguaiacol						shrimp, clam	whole-body	≤0.05[i]	Bacon & Silk, 1978
tetrachloroguaiacol									Bacon & Silk, 1978
chloroguaiacols	BKME	-	SW	≤0.06	-	fish,	liver	BLD	Anon., 1982
						mussels	muscle	BLD	Anon., 1982
							whole-body	BLD	Anon., 1982
2,4-dichlorophenol	BKME	-	BW	0.1-0.3	2-6			BLD-<0.02	Anon., 1982
2,4,6-trichlorophenol	BKME	-	BW	0.1-0.9	2-6	bivalves,	liver,	BLD-<0.02	Anon., 1982
3,4,5-trichloroguaiacol	BKME	-	BW	0.1-1.4	2-6	sculpin	muscle,	BLD	Anon., 1982
4,5,6-trichloroguaiacol	BKME	-	BW	0.1-0.6	2-6		whole-body	BLD	Anon., 1982
tetrachloroguaiacol	BKME	-	BW	0.1-0.4	2-6			BLD	Anon., 1982
chlorophenols	BKME	-	BW	-	-	bivalves	whole-body	<0.02	Anon., 1982
chlorophenols	BKME	-	BW	-	-	herring	muscle	≤0.006	Anon., 1982
3,4,5-trichloroguaiacol	BKME	-	BW	-	-	herring	muscle	≤0.01	Anon., 1982
tetrachloroguaiacol	BKME	-	BW	-	-	herring	muscle	≤0.002	Anon., 1982
3,4,5-trichloroguaiacol	BKME	-	BW	-	-	perch, whitefish	liver	≤1	Anon., 1982
2,4,5-trichlorophenol	BKME	-	BW	-	-	flounder	liver	<0.54	Anon., 1982
chloroguaiacols	BKME	-	BW	-	-	flounder, pike	liver	≤0.055	Anon., 1982
chloroguaiacols	BKME	-	BW	-	-	mussels	whole-body	≤0.02	Anon., 1982
2,4,6-trichlorophenol	BKME	-	SW	0.01	3	salmon	liver	0.01-0.02	Voss & Yunker, 1983
3,4,5-trichloroguaiacol	BKME	-	SW	0.004-0.07	3	salmon	liver	0.03-0.06	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	SW	0.01-0.03	3	salmon	liver	0.01-0.02	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	-	SW	0.01	3	salmon	muscle	0.003	Voss & Yunker, 1983
chloroguaiacols	BKME	-	SW	0.004-0.07	3	salmon	muscle	BLD-0.011	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	-	SW	0.005-0.01	2.5-10	rockfish	liver	BLD-0.003	Voss & Yunker, 1983
chloroguaiacols	BKME	-	SW	0.003-0.01	2.5-10	rockfish	liver	BLD-0.006	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	-	SW	0.005-0.01	3.5-10	mussels	whole-body	0.01-0.02	Voss & Yunker, 1983
3,4,5-trichloroguaiacol	BKME	-	SW	0.003-0.007	3.5-10	mussels	whole-body	0.02-0.04	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	SW	0.008-0.01	3.5-10	mussels	whole-body	BLD-0.008	Voss & Yunker, 1983

TABLE 4.4 BIOACCUMULATION OF ORGANIC CONSTITUENTS OF PULP AND PAPER MILL EFFLUENTS IN ESTUARINE/MARINE ORGANISMS TAKEN FROM THE RECEIVING WATERS (Cont'd)

Chemicals	Effluent[a]		Receiving water		Distance from outfall(s) (km)	Organism(s)	Tissue	Tissue concentration[b] (µg/g)	Reference
	type(s)	treatment	type	chemical concentration (µg/L)					
2,4,6-trichlorophenol	BKME	-	SW	0.01	2	shrimp	whole-body	BLD-0.005	Voss & Yunker, 1983
3,4,5-trichloroguaiacol	BKME	-	SW	0.007-0.07	2	shrimp	whole-body	BLD-0.005	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	SW	0.01-0.03	2	shrimp	whole-body	0.002-0.004	Voss & Yunker, 1983
2,4,6-trichlorophenol	BKME	-	SW	0.01	2-3.5	crab	whole-body	BLD-0.005	Voss & Yunker, 1983
3,4,5-trichloroguaiacol	BKME	-	SW	0.007-0.07	2-3.5	crab	whole-body	BLD	Voss & Yunker, 1983
tetrachloroguaiacol	BKME	-	SW	0.01-0.03	2-3.5	crab	whole-body	BLD	Voss & Yunker, 1983
dehydroabietic acid	BKME, MPE	-	BW	-	-	clam tomcod	whole-body muscle	0.3 0.3	Bacon & Silk, 1978 Bacon & Silk, 1978

a Characteristics of effluent discharged to the receiving-waters.
b Determined on a wet weight basis.
c Bleached kraft whole mill effluent.
d Mechanical pulping effluent.
e Not determined/not indicated.
f Sea water.
g Brackish water (salinity $\leq$20 °/oo).
h Below the limit of detection for the analytical technique employed.
i Values for Cl_3P, Cl_3G and Cl_4G as calculated by Voss and Yunker, 1983.

4.4.2.2 Other organic constituents. Limited information is available with respect to the accumulation of resin or fatty acids in estuarine/marine organisms inhabiting waters receiving pulp and paper mill effluents. Bacon and Silk (1978) found 0.3 µg/g (wet weight) dehydroabietic acid in clams (Mya arenaria) and muscle tissue of tomcod collected from an estuary receiving untreated effluents from a bleached kraft mill and a groundwood mill. No other reports relevant to estuarine/marine biota are available.

No reports of chlorobenzene accumulation in estuarine/marine life associated with pulp mill discharges have been found. Bjorseth et al. (1981) identified dichlorocymene and terpenes in fat extracts from a single sample of codfish caught within 0.5 km of kraft and sulphite pulp mills. The concentrations of these constituents in the pulp mill discharge were not determined.

Ofstad et al. (1981) found higher values for chloroform and trichloroethylene in fish captured in the immediate proximity of a pulp and paper mill. Although these results were attributed to chlorinated discharges, the species of fish collected at various sites were not directly comparable.

Lindstrom and Schubert (1984) recently examined mussels and the livers of flounders caught in the vicinity of a pulp mill (undefined) for the presence of the slowly-degradable effluent constituent 1,1-dichlorodimethyl sulphone (DDMS). Concentrations of DDMS found in extracts of fish liver and mussel fat were 1 µg/g and 0.5 µg/g, respectively.

4.5 Off-Flavours in Fish

4.5.1 Receiving-Water Studies. Reports of off-flavours in fish or shellfish from North American waters receiving discharges from pulp and paper mills have been restricted primarily to freshwater fish. This may be due in large measure to the greater dilution of effluent in estuarine/marine waters.

Off-flavours in fish and shellfish can be caused by natural chemical compounds occurring in the environment as well as by ingestion of naturally-occurring bacteria and algal blooms (Persson et al., 1983). Results from any field studies which attribute a loss of palatability of indigenous fish or shellfish to a particular effluent discharge must also consider natural factors, and other point and non-point discharges to receiving waters in the vicinity. Migratory species of fish may have acquired off-flavours from a distant (unknown) source. Off-flavours may also result from improper carcass storage subsequent to capture (Reineccius, 1979), or may be attributed to what is simply the differing flavours of particular aquatic species.

Kuusi and Suihko (1983) recently reviewed the occurrence of various off-flavours in fish from Finnish waters. A trained taste panel assessed the occurrence of off-flavours in brackish-water (Baltic Sea) fish, attributable to kraft effluent, as being limited. Nonetheless of all off-flavours encountered in both freshwater and brackish water species, 41% were ascribed to kraft pulp mill effluent.

Within North American waters, tainting of eulachon fish (Thaleichthys pacificus) in estuarine waters was reported in conjunction with the start-up of a coastal mill discharging treated unbleached kraft effluent, but no factual evidence was developed to support these allegations (Bell and Kallman, 1976). Other reports of off-flavours in edible estuarine/marine species associated with discharges from pulp and paper mills have not been encountered.

Reports of off-flavours in fish in freshwaters receiving pulp and paper mill effluents are listed in Table 4.5, together with available information concerning effluent type and treatment, type of receiving water, species of fish, and the presence or absence of off-flavours. The estimated concentration of mill effluents within the receiving waters was only provided in one instance. The distance from the mill outfall(s) at which the fish were taken was indicated in only four of the ten studies reviewed.

In the only study reviewed involving BSME, Berg (1983) positively correlated the intensity of off-flavour in Atlantic salmon (Salmo salar), as determined by a taste panel, with the concentrations of objectionable volatiles (terpenes, cymene, alkylbenzenes) present in the fish flesh. Off-flavours could not be detected in fish residing downstream of conventional bleached kraft or integrated bleached kraft/groundwood mills discharging untreated effluent into larger rivers (Liem et al., 1977; Anon., 1979), whereas off-flavours were found in fish from smaller rivers (Swabey, 1965) and from a freshwater bay (Wells, 1967) close to this type of discharge (Table 4.5).

In response to complaints by sports fishermen of off-flavours in fish captured from a small river downstream of a kraft mill dicharging treated BKME, a number of controlled flavour-evaluation studies were conducted on upstream and downstream fish (Langford, 1974). Despite the conclusion that the mill effluent significantly affected the taste and odour of downstream fish, the data did not provide a significant level of proof. Fish collected upstream and downstream were of different species; fish of the same species did not differ significantly in all instances; or comparisons within a single species involved control fish from another river. Nonetheless, the consistently low flavour ratings for downstream fish did support the hypothesis that the BKME discharge was the causative agent.

TABLE 4.5 REPORTS OF OFF-FLAVOURS IN FISH ASSOCIATED WITH DISCHARGES FROM PULP AND PAPER MILLS

Effluent		Receiving water					
type(s)	treatment[a]	type	effluent concentration (% v/v)	Fish species	Distance from outfall(s) (km)	Significant off-flavour	Reference
BSME[b]	-[f]	river	-	Atlantic salmon	-	yes	Berg, 1983
KME[c]	-	lake, river, brackish sea	-	herring, salmonids, pike, cod, perch	-	yes[g]	Kuusi & Suihko, 1983
BKME[d]	no	river	-	perch	-	no	Liem et al., 1977
BKME/MPE[e]	no	lake	-	whitefish whitefish	1.5 10	yes no	Wells, 1967 Wells, 1967
BKME/MPE	no	river	-	pike, pickerel	-	yes	Swabey, 1965
BKME/MPE	no	river	-	kokanee, trout, suckers	2	no	Anon., 1979
BKME	yes	river	-	trout, whitefish	-	yes[g]	Langford, 1974
BKME/BSME/MPE	yes	river	-	walleye pike	-	yes[g]	Weinbauer et al., 1980
BKME	yes	river	-	rainbow trout	<1	yes[g]	Langer & Nassichuk, 1975
BKME	yes	river	0.5-1	whitefish	-	yes[g]	Kovacs, 1982

a Refers to presence or absence of secondary (aerated microbiological) effluent treatment. Primary clarification of effluent may be practised where "no" is indicated.
b Bleached sulphite whole mill effluent.
c Kraft pulp mill effluent.
d Bleached kraft whole mill effluent.
e Mechanical pulping effluent.
f Not indicated/not determined.
g Off-flavour not attributable/not demonstrated to be attributable to discharge(s) of pulp and paper mill effluents.

Two separate studies have investigated off-flavours in fish species inhabiting a river receiving biologically-treated effluent from a bleached kraft pulp mill. In the first study, where rainbow trout were caged for up to 13-days, fish held immediately downstream of the mill diffuser had the poorest flavour. However, flavour scores for all of the caged fish, regardless of cage location, were low (poor) compared to controls held in a separate water supply (Langer and Nassichuk, 1975). Moreover, the descriptive terms for fish flavour (i.e., bitter, sour, stale, metallic) applied to all samples by the taste panel were not those terms normally used to describe fish tainting caused by pulp and paper mill effluents (Kuusi and Suihko, 1983). A subsequent study compared the flavour of native mountain whitefish (Prosopium williamsoni) captured concurrently from each of the two major upstream tributaries of this river and from a location several kilometres downstream of the mill. Flavour evaluations of the fish by trained panelists rated the downstream fish and fish from one of the upstream tributaries, equally poorly; whereas fish from the other upstream tributary had an acceptable flavour (Kovacs, 1982).

Weinbauer et al. (1980) examined the palatibility of fish (walleye pike; Stizostedion vitreum) captured at five separate locations from a 70-mile stretch of river receiving treated pulp and paper mill effluents. Fish captured upstream of all discharges had significantly poorer flavour than any captured in the immediate vicinity of the mills. No explanation was given for this finding. Additionally, no effort was made to restrict fish movements. Walleye captured from an adjacent waterbody had consistently better flavour than any fish from the river under study.

4.5.2 Controlled Exposure to Mill Effluents. Flavour impairment in commercially-valuable freshwater species due to exposure to pulp and paper mill effluents has been studied under controlled conditions. The tainting propensities and estimated threshold concentrations of pulp and paper whole mill effluents reported to cause off-flavours in fish under defined laboratory conditions are summarized in Table 4.6. Most of the studies have dealt with bleached kraft mill effluent, alone or mixed with bleached sulphite or mechanical pulping effluents (Table 4.6). No studies with mechanical pulping effluents were located, and only one with sulphite whole mill effluent was found. Although these studies are not directly comparable, since test procedures, species of fish, and conditions of exposure varied from test to test, a number of general observations can be made.

Shumway and Chadwick (1971) reported that untreated unbleached kraft whole mill effluent caused significant off-flavours in coho salmon (Oncorhynchus kisutch) held for three or four days in effluent strengths of 1.5% (v/v) and higher. No tainting occurred

TABLE 4.6 INDUCTION OF OFF-FLAVOURS IN FISH BY CONTROLLED EXPOSURE TO PULP AND PAPER WHOLE MILL EFFLUENTS

Effluent		Concentration		Exposure time	Significant	ETTC[b]	Flavour evaluation	
type	treatment[a]	(% v/v)	Fish species	(days)	off-flavour	(% v/v)	test	Reference
UKME[c]	no	0.2-2.6	coho salmon	3-4	yes	1.5	hedonic	Shumway & Chadwick, 1971
UKME	yes	0.7-2.9	coho salmon	4	no	>2.9	hedonic	Shumway & Chadwick, 1971
BKME/BSME[d]	no	0.3	perch	44	no	>0.3	triangle	Cook et al., 1971, 1973
BKME/BSME	no	5-10	perch	7	yes	>5<10	triangle	Cook et al., 1971, 1973
KME[e]	yes	1.4-100	rainbow trout	2	yes	>8<20	hedonic	Shumway & Palensky, 1973
SME[f]	yes	1-67	rainbow trout	2	yes	>34<51	hedonic	Shumway & Palensky, 1973
BKME/MPE[g]	no	3-18	rainbow trout	2	yes	3	hedonic	Whittle & Flood, 1977
BKME/MPE	no	2-3	rainbow trout	6	yes	3	hedonic	Whittle & Flood, 1977
BKME[h]	no	0.3-80	rainbow trout	4	yes	5	triangle	Liem et al., 1977
BKME	no	0.1-10	rainbow trout	4	yes	1	triangle	Liem et al., 1977
BKME	no	0.1-10	perch	4	yes	5	triangle	Liem et al., 1977
BKME	yes	0.5-4	rainbow trout	0.3-2	no	>4	hedonic	Langer & Nassichuk, 1975
BKME	no	0.1-4	rainbow trout	0.2-1	yes	0.2-0.8	triangle	Gordon et al., 1980
BKME	yes	0.7-10	rainbow trout	0.2-1	yes	2.0-2.9	triangle	Gordon et al., 1980

a Refers to presence or absence of secondary (aerated microbiological) mill treatment. Primary clarification of effluent may be practised where "no" is indicated.
b Estimated threshold tainting concentration. Lowest concentration at which significant off-flavour of fish was noted.
c Unbleached kraft whole mill effluent.
d Bleached sulphite whole mill effluent.
e Kraft whole mill effluent (not indicated if bleached or not).
f Ammonia-based sulphite whole mill effluent (not indicated if bleached or not).
g Mechanical pulping effluent.
h Bleached kraft whole mill effluent.

when fish were exposed for four days to 2.9% unbleached effluent which had been previously treated for seven to eight days in a laboratory fermenter.

Rainbow trout exposed to untreated bleached kraft whole mill effluents (BKME) developed significant off-flavours at effluent strengths as low as 0.2-0.8% (greater than 100-fold dilution with freshwater) and exposures limited to 4 h (Gordon et al., 1980). These same authors showed that when the BKME from two mills was treated in conventional aerated lagoons, the flavour impairment within 4 h did not occur until effluent concentrations were 2.0-2.9% and higher. Other studies with this species have reported significant flavour impairment at untreated BKME concentrations of 1-5%, but none at lower concentrations. In specific instances treated BKME concentrations as high as 4% did not cause significant off-flavours in rainbow trout exposed for 8 or 48 h (Langer and Nassichuk, 1975; Table 4.6). These differing values for threshold concentrations of untreated or treated BKME are undoubtedly attributable to variations in test procedures and conditions.

Of the numerous types of sensory tests available for evaluating off-flavour in food, two (triangle and hedonic) have been used for examining the tainting propensity of pulp and paper mill effluents (Table 4.6). In the triangle test, trained taste panelists are asked to distinguish between three offerings (two of which are identical), and to indicate which of these numbered samples has any undesirable flavour. The panelists are then asked to describe this flavour. In the hedonic scale test, six samples (one identified and one unidentified control, four treatment samples) are presented and the panelist is asked to assign each a value of from 1 to 8; "one" being the worst possible score and "eight" the best. The identified control is arbitrarily assigned a "seven" (Farmer et al., 1973). Flavour evaluations with BKME-exposed rainbow trout and perch performed according to each of these test procedures indicated that the triangle test gave reliable quantitative results, whereas those determined according to the hedonic rating were subjective and inconsistent (Liem et al., 1977; Brouzes et al., 1978). These differences in test protocol undoubtedly account for some of the reported variations in threshold-effect concentrations of pulp and paper mill effluents, and may explain, at least in part, the anomalously high threshold tainting concentrations reported for kraft and sulphite whole mill effluents by Shumway and Palensky (1973) (Table 4.6).

A number of laboratory studies have examined the effect of duration of effluent exposure on fish tainting propensity. Early studies by Cook et al. (1971, 1973) indicated that the off-flavours that developed within three to four days in perch exposed to untreated bleached kraft/sulphite whole mill effluent did not occur when the

concentration was reduced to 0.3%, even over a 44-day exposure. Whittle and Flood (1977) showed that the estimated threshold concentration that caused tainting within two-days (3%) for rainbow trout exposed to untreated BKME/groundwood effluent was unchanged when the exposure was extended to six days. In a similar study, Brouzes et al. (1978) concluded that extending the effluent exposure time beyond 24 h did not affect the taste of fish significantly. More recently Gordon et al. (1980) demonstrated that exposure of fish to dilute (0.5-1.4% untreated; 3-8% treated) BKME for only 1 h caused a significant flavour impairment, although the estimated threshold concentrations causing tainting were lowered somewhat when exposures were continued for 4 h. No significant reduction in tainting thresholds for respective samples of untreated or treated BKME were evident when exposure times were increased to 24 h (Gordon et al., 1980).

Limited information is available concerning the rate with which off-flavour in fish attributable to pulp and paper mill effluents, is lost upon their transfer to fresh water. One to three days was found to be required before off-flavours in coho salmon previously exposed experimentally to pulp mill effluent was purged (Shumway, 1966; cited in Persson, 1984). Brouzes et al. (1978) showed that tainting in rainbow trout exposed to foul condensate for two days cleared between four and seven days after transfer to uncontaminated water. Thus purging of off-flavours would appear to require only a matter of days, albeit tainting can occur in a few hours.

A flavour-impairment study conducted with rainbow trout and perch exposed simultaneously to a range of BKME concentrations showed a lower threshold tainting concentration for trout (Liem et al., 1977) (Table 4.6). Subsequent evaluations with these fish species and with walleye (Stizostedion vitreum) confirmed that rainbow trout were a more sensitive fish species for off-flavour appraisals (Brouzes et al., 1978).

A number of untreated in-plant process effluents have been examined for their ability to cause off-flavours in fish. Sulphite waste liquor diluted to 0.7% (v/v) with freshwater resulted in a significant off-flavour for perch exposed for seven days (Cook et al., 1971, 1973). Kraft foul condensates caused tainting in rainbow trout at strengths as low as 0.05% (Brouzes et al., 1978). Reported threshold-effect concentrations for steam-stripped foul condensates or evaporator condensates are somewhat higher (0.7-2%) (Cook et al., 1971; Liem et al., 1977).

The fish-tainting threshold concentrations for a number of major kraft mill process effluents were examined by Findlay and Naish (1979). Their findings were as follows:

Effluent Source	% (v/v) of Whole Mill Effluent	Threshold Tainting Concentration (%)
recovery (condensates & scrubber effluent)	8	0.007-1
paper machine effluent (includes slimicides, defoaming agents)	24	>20
bleach plant effluent (CEDED)	37	>1
whole mill effluent	100	0.1

These results indicate that the bleach plant and paper machine effluents were not major contributors to the tainting propensity of the whole mill effluent. The recovery effluent, although a minor component (8%) of the final volume of whole mill effluent, contributed significantly to the tainting propensity of the combined effluent discharge.

The limited available data derived for the same effluent samples using the same fish species, indicate no obvious relationship between effluent toxicity (96-h LC_{50} values) and its ability to cause off-flavour in fish (Liem et al., 1977; Findlay and Naish, 1979). This is not surprising inasmuch as some of the effluent constituents which contribute appreciably to the acute lethal toxicity of pulp mill effluents (i.e., fatty and resin acids) (Chapter 1) may not cause tainting at low concentrations, and other constituents with high LC_{50} values (i.e., DDMS) may bioaccumulate and taint at very low strengths (McKague, 1981; Voss, 1983; Anon., 1984).

4.5.3 Effluent Constituents Causing Off-Flavours. Threshold concentrations of chemicals causing tainting of fish flesh have been reviewed by Persson (1984) and, in an earlier publication, by Thomas (1973). The chemicals listed by these authors that are reported to be present in certain pulp and paper mill effluents are listed in Table 4.7. Information concerning test conditions (fish species, duration(s) of exposure) and the threshold concentration(s) for each chemical reported to impart off-flavour in fish flesh is also summarized. Chlorophenol, benzene, naphthalene, pentachlorophenol, phenol and toluene are normally present in treated or untreated whole mill effluents in trace amounts only or below the limit of detection. As the concentrations at which these chemicals cause tainting in fish exceed effluent concentrations by several orders of magnitude, their

TABLE 4.7 CONSTITUENTS IN PULP AND PAPER MILL EFFLUENTS KNOWN TO CAUSE OFF-FLAVOURS IN FISH

Chemical	Fish species	Exposure time (days)	ETTC[a] (µg/L)	No-effect concentration[b] (µg/L)	Reference
chlorophenol	trout, perch, carp	2-7	24-60	20-1 000	Persson, 1984
2,4-dichlorophenol	trout, perch, bass	2-7	0.4-14	0.01-10	Persson, 1984
2,4-dichlorophenol	rainbow trout	4	0.1	0.01	Shumway & Palensky, 1973
2,4,6-trichlorophenol	rainbow trout	2	1-52	10	Persson, 1984
benzene	rainbow trout	2	-[c]	5 600	Persson, 1984
naphthalene	roach, carp	0.8	1 000-3 400	-	Persson, 1984
pentachlorophenol	rainbow trout	2	-	20	Persson, 1984
phenol	eel, carp, trout	2-28	20-25 000	5 600-25 000	Thomas, 1973; Persson, 1984
toluene	yellow perch	5-7	250-50 000	-	Persson, 1984

a Estimated threshold tainting concentration. Lowest concentration at which significant off-flavour fish was noted.
b Concentration reported to not impair the flavour of fish.
c Not determined.

contribution to off-flavours in effluent-exposed fish is extremely minor. Off-flavours in rainbow trout have been attributed to concentrations of 2,4-Cl_2P as low as 0.1 µg/L, although other data indicate concentrations as high as 10 µg/L having no effect, under other conditions (Persson, 1984; Table 4.7). This range virtually blankets the concentrations of this chemical found in effluents from nine Canadian bleached kraft mills, i.e., 1.7 to 15.0 µg/L (Kovacs et al., 1984). The chlorophenolic chemical 2,4,6-Cl_3P, reported to cause off-flavours in fish at strengths as low as 1 µg/L, has been shown to be present in treated BKME at an average concentration of 9.5 µg/L (Kovacs et al., 1984). However, the range of threshold concentrations of 2,4,6-Cl_3P reported to impart off-flavours in fish is also wide (1-52 µg/L; Table 4.7). The potential contribution of either of these chlorophenolic compounds to off-flavours in fish or other edible aquatic species exposed to dilute concentrations of pulp and paper mill effluents is unclear.

Various authors (Blackwell et al., 1979; Findlay and Naish, 1979; Gordon et al., 1980; Paasivirta et al., 1983b) have implicated phenolics as major contributors to the off-flavours in fish; however, proof is lacking. Based on taste, odour and phenolic evaluations of various pulp mill effluents before and after primary and secondary treatment, it was concluded that both chlorination and biological treatment of sulphite and kraft mill effluents would reduce their odour and flavour-impairment potential and that chlorination did not impart a chlorophenolic flavour or odour to the effluent samples examined (NCASI, 1973). However, this study related to potable water supplies and no fish-flavour evaluations were conducted. Paasivirta et al. (1983b) cited chlorinated phenols and anisoles (microbial metabolites of the former) as potential off-flavour compounds from the chlorine-bleaching of pulp.

A number of chlorophenolic compounds have been identified in the present review as having some potential to bioaccumulate in the edible tissues of aquatic animals. No information is available in the literature to indicate the contribution, if any, of chloroguaiacols or chlorocatechols to off-flavours in fish.

Resin acids have been suggested as potential off-flavour sources in pulp and paper mill effluents (Findlay and Naish, 1979), although no information concerning their tainting propensity is readily available. Organosulphur compounds and monoterpenes (other known effluent constituents) have also been proposed as potential tainting agents (Rogers, 1978; Findlay and Naish, 1979), but no analytical proof is available and no relevant studies have been reported.

Initial efforts to correlate the fish-tainting propensity of pulp mill effluents with specific chemicals accumulated in the muscle tissue of exposed fish have been

largely unsuccessful, primarily due to analytical difficulties (Findlay and Naish, 1979). However Berg (1983) recently reported that concentrations of certain off-flavour volatiles present in different samples of Atlantic salmon (Salmo salar) captured from a river receiving sulphite mill effluent showed good correlations with their degree of off-taste. These researchers identified terpenes and their derivatives, together with chlorinated compounds and transformation products such as cymene and alkylbenzenes. Paasivirta et al. (1983b) also employed taste panel experiments together with trace organic analyses of muscle tissue from fish captured at various locales adjacent to or distant from pulp mills. Despite the logic of the approach, results were inconclusive.

4.6 References

Anon., 1979. Kootenay Air and Water Quality Study Phase II. Water Quality in the Lower Columbia River Basin. Water Investigations Branch, B.C. Ministry of Environment. Victoria, B.C.

Anon., 1980. Ambient Water Quality Criteria for Chloroform. U.S. Environmental Protection Agency Report EPA-440/5-80-030. Washington, D.C.

Anon., 1982. Environmentally Harmonized Production of Bleached Pulp. Final Report (in Swedish). Swedish Forest Products Research Laboratory, Stockholm, Sweden.

Anon., 1984. Toxicity and Environmental Chemistry of Wastewater from Proctor and Gamble Cellulose Ltd. (Grande Prairie). Draft Report. Alberta Environmental Centre Research Report AECV84-R6. Vegreville, Alberta.

Bacon, G.B. and P.J. Silk. 1978. Bioaccumulation of Toxic Compounds in Pulp Mill Effluents by Aquatic Organisms in Receiving Waters. CPAR Rep. No. 675-1. Environmental Protection Service, Ottawa, Ontario.

Bell, L.M. and R.J. Kallman. 1976. The Kitimat River Estuary. Status of Environmental Knowledge to 1976. Special Estuary Series No. 6. Fisheries and Marine Service, Environment Canada. West Vancouver, B.C.

Berg, N. 1983. Chemical and sensory analysis of off-flavours in fish from polluted rivers in Norway. Wat. Sci. Tech. 15: 59-65.

Bjorseth, A., G.E. Carlberg, N. Gjos, M. Moller and G. Tveten. 1981. Halogenated organic compounds in spent bleach liquors: Determination of mutagenicity, testing and bioaccumulation. pp. 1115-1130. In L.H. Keith, ed., Advances in the Identification and Analysis of Organic Pollutants in Water. Vol. 2. Ann Arbor Sci. Publ., Ann Arbor, MI.

Blackwell, B.R., W.B. MacKay, F.E. Murray and W.K. Oldham. 1979. Review of kraft foul condensates. Sources, quantities, chemical composition, and environmental effects. TAPPI 62: 33-37.

Brouzes, R.J.P., A.J. Liem and V.A. Naish. 1978. Protocol for Fish Tainting Bioassay. CPAR Rep. No. 775-1. Environmental Protection Service, Ottawa, Ontario.

Cook, W.H., F.A. Farmer, O.E. Kristiansen, K. Reid, J. Reid, and R. Rowbottom. 1971. Effect of Pulp and Paper Mill Effluents on the Taste and Odour of Water and Fish. CPAR Rep. No. 12-1. Environmental Protection Service, Ottawa, Ontario.

Cook, W.H., F.A. Farmer, O.E. Kristiansen, K. Reid, J. Reid and R. Rowbottom. 1973. The effect of pulp and paper mill effluents on the taste and odour of the receiving water and the fish therein. Pulp Paper Can. 113: T97-106.

Farmer, F.A., H.R. Neilson and D. Esar. 1973. Flavor evaluation by triangle and hedonic scale tests of fish exposed to pulp mill effluents. Can. Inst. Food Sci. Technol. J. 6: 12-16.

Findlay, D.M. and V.A. Naish. 1979. Nature and Sources of Tainting in a Kraft Mill. CPAR Rep. No. 775-2. Environmental Protection Service, Ottawa, Ontario.

Fox, M.E., D.M. Whittle and K.L.E. Kaiser. 1977. Dehydroabietic acid accumulation by rainbow trout (Salmo gairdneri) exposed to kraft mill effluent. J. Great Lakes Res. 3(1-2): 155-158.

Gordon, M.R., J.C. Mueller and C.C. Walden. 1980. Effect of biotreatment on fish tainting propensity of bleached kraft whole mill effluent. Trans. Tech. Sect. Canad. Pulp Paper Assoc., Vol. 6. TR 2-8. March, 1980.

Hattula, M.L., V.M. Wasenius, H. Reunanen and A.U. Arstila. 1981. Acute toxicity of some chlorinated phenols, catechols and cresols to trout. Bull. Environ. Contam. Toxicol. 26: 295-298.

Holmbom, B.R. 1980. Studies on resin acids and chlorinated phenolics in Finnish pulp mill effluents and on their bioaccumulation in fish. Paper presented at the 89th National AIChE Meeting, Portland, Oregon, August 17-20, 1980.

Howard, T.E. and D.D. Monteith. 1977. Site of Action of Chemicals from Pulp Mill Effluent that are Toxic to Fish. CPAR Rep. No. 488-1. Environmental Protection Service, Ottawa, Ontario.

Jones, P.A. 1981. Chlorophenols and Their Impurities in the Canadian Environment. Envir. Canada, Econ. Tech. Rev. Rep. EPS 3-EC-81-2. Ottawa, Ontario.

Jones, P.A. 1984. Chlorophenols and Their Impurities in the Canadian Environment: 1983 Supplement. Envir. Canada, Econ. Tech. Rev. Rep. EPS 3-EP-84-3. Ottawa, Ontario.

Kaiser, K.L.E. 1977. Organic contaminant residues in fishes from Nipigon Bay, Lake Superior. J. Fish Res. Board Can. 34: 850-855.

Kobayashi, K. 1978. Metabolism of Pentachlorophenol in Fishes, pp. 89-105. In K.R. Rao (ed.). Pentachlorophenol. Plenum Press, New York, NY.

Kovacs, T.G. 1982. The Effect of Bleached Kraft Effluent on the Aquatic Environment. Report prepared for Weyerhaeuser Canada Ltd. Kamloops, B.C., by Pulp Pap. Res. Inst. Can., Pte. Claire, PQ.

Kovacs, T.G., R.H. Voss and A. Wong. 1984. Chlorinated phenolics of bleached kraft mill origin. An olfactory evaluation. Water Res. 18: 911-916.

Kruzynski, G.M. 1979. Some effects of dehydroabietic acid (DHA) on hydro-mineral balance and other physiological parameters in juvenile sockeye salmon Oncorhynchus nerka. Ph.D. thesis. 187 pp. Univ. British Columbia, Vancouver, B.C.

Kunnamo, T. and A. Oikari. 1984. Analysis of conjugated xenobiotics in fish bile: a new tool to quantify contamination of recipient waters downstream to pulp and paper industry. p. 84. In H. Tahti et al., eds. Proc. Symposium on Toxicity and Pharmacology. May 18-19, 1984. Tampere, Finland.

Kuusi, T. and M. Suihko. 1983. Occurrence of various off-flavours in fish in Finland from 1969 to 1981. Wat. Sci. Tech. 15: 47-58.

Landner, L., K. Lindstrom, M. Karlsson, J. Nordin and L. Sorensen. 1977. Bioaccumulation in fish of chlorinated phenols from kraft pulp mill bleachery effluents. Bull. Environ. Contam. Toxicol. 18: 663-673.

Langford, R.W. 1974. Data Review of Biological and Chemical Effects of the Crestbrook Pulp Mill Effluent on the Kootenay River. Fish and Wildlife Branch, B.C. Ministry of Environment. Victoria, B.C.

Langer, O.E. and M.D. Nassichuk. 1975. Selected Biological Studies of the Thompson River System. Environment Canada Tech. Rep. Ser. No. PAC/T-75-22. Vancouver, B.C.

Leach, J.M. and A.N. Thakore. 1977. Compounds toxic to fish in pulp mill waste streams. Progr. Water Technol. 9: 787-798.

Liem, A.J., V.A. Naish and R.S. Rowbottom. 1977. An Evaluation of the Effect of Inplant Treatment Studies on the Abatement of Air and Water Pollution from a Hardwood Kraft Pulp Mill. CPAR Rep. No. 484-1. Environmental Protection Service, Ottawa, Ontario.

Lindstrom, K. and R. Schubert. 1984. Determination by MS-MS of 1,1 di-chlorodimethyl sulphone from pulp mill bleach plant effluents in aquatic organisms. J. High Res. Chromat. Chromat. Commmun. 7: 68-73.

McKague, A.B. 1981. Some toxic constituents of chlorination-stage effluents from bleached kraft pulp mills. Can. J. Fish. Aquat. Sci. 38: 739-743.

Mackay, D. 1982. Correlation of bioconcentration factors. Environ. Sci. Technol. 16: 274-278.

Mahood, H.W. and I.H. Rogers. 1975. Separation of resin acids from fatty acids in relation to environmental studies. J. Chromat. 109: 281-286.

NCASI 1973. The Measurement of Phenolic Substances and the Significance of Their Presence in Pulp Mill Effluents on Taste and Odor in Receiving Waters. Tech. Bull. No. 268. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficients to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

Neilson, A.H., A.S. Allard, P.A. Hynning, M. Remberger and L. Landner. 1983. Bacterial methylation of chlorinated phenols and guaiacols: formation of veratroles from guaiacols and high-molecular-weight chlorinated lignin. Appl. Environ. Microbiol. 45: 774-783.

Neilson, A.H., A.S. Allard, S. Reiland, M. Remberger, A. Tarnholm, T. Viktor and L. Landner. 1984. Tri- and tetrachloroveratrole, metabolites produced by bacterial O-methylation of tri- and tetrachloroguaiacol: an assessment of their bioconcentration potential and their effects on fish reproduction. Can. J. Fish. Aquat. Sci. 41: 1502-1512.

Ofstad, E.B., H. Drangsholt and G.E. Carlberg. 1981. Analysis of volatile halogenated organic compounds in fish. Sci. Total Environ. 20: 205-215.

Oikari, A. 1984. On the metabolism of chlorinated phenolics and resin acids in rainbow trout (Salmo gairdneri). p. III 2. In Environmental Changes and Adaptions (April 24-25, 1984). Nat. Sci. Publ. Univ. Kuopio. Kuopio, Finland.

Oikari, A., B. Holmbom, E. Anas and H. Bister. 1980. Distribution in a recipient lake and bioaccumulation in fish of resin acids from kraft pulp mill waste waters. Pap. Puu 62: 193-196.

Oikari, A., B. Holmbom and H. Bister. 1982. Uptake of resin acids into tissues of trout (Salmo gairdneri Richardson). Ann. Zool. Fennici 19: 61-64.

Oikari, A., T. Nakari and B. Holmbom. 1984a. Sublethal actions of simulated kraft pulp mill effluents (KME) in Salmo gairdneri: residues of toxicants, and effects on blood and liver. Ann. Zool. Fennici 21: 45-53.

Oikari, A., E. Anas, G. Kruzynski and B. Holmbom. 1984b. Free and conjugated resin acids in the bile of rainbow trout, Salmo gairdneri Bull. Environ. Contam. Toxicol. 33: 233-240.

Paasivirta, J., J. Sarkka, T. Leskijarvi and A. Roos. 1980. Transportation and enrichment of chlorinated phenolic compounds in different aquatic food chains. Chemosphere 9: 441-456.

Paasivirta, J., J. Sarkka, M. Aho, K. Suma-Aho, J. Tarhanen and A. Roos. 1981. Recent trends of biocides in pikes of the Lake Paijanne. Chemosphere 10: 405-414.

Paasivirta, J., J. Sarkka, K. Surma-Aho, T. Humppi, T. Kuokkanen and M. Marttinen. 1983a. Food chain enrichment of organochlorine compounds and mercury in clean and polluted lakes of Finland. Chemosphere 12: 239-252.

Paasivirta, J., J. Knuutinen, J. Tarhanen, T. Kuokkanen, K. Surma-Aho, R. Paukku, H. Kaariainen, M. Lahtipera and A. Veijanen. 1983b. Potential off-flavour compounds from chloro-bleaching of pulp and chlorodisinfection of water. Wat. Sci. Tech. 15: 97-104.

Persson, P.E. 1984. Uptake and release of environmentally occurring odorous compounds by fish. A review. Water Res. 18: 1263-1271.

Persson, P.E., M. Yurkowski and E. Marshall. 1983. Taste and odour in waters and aquatic organisms. Wat. Sci. Tech. 15: 1-333.

Reineccius, G.A. 1979. Off-flavours in meat and fish - a review. J. Food Sci. 44: 12-21.

Renberg, L., O. Svanberg, B.E. Bengtsson and G. Sundstrom. 1980. Chlorinated guaiacols and catechols bioaccumulation potential in bleaks (Alburnus alburnus, Pisces) and reproductive and toxic effects on the harpacticoid Nitrocra spinipes (Crustacea). Chemosphere 9: 143-150.

Rogers, I.H. 1978. Environmental effects of terpenoid chemicals: a review. J. Amer. Oil Chem. Soc. 55: 113A-118A.

Shumway, D.L. 1966. Effects of Effluents on Flavor of Salmon Flesh. Research Report of the Agricultural Experimental Station. Oregon State University. Corvallis, OR.

Shumway, D.L. and G.G. Chadwick. 1971. Influence of kraft mill effluent on the flavor of salmon flesh. Water Res. 5: 997-1003.

Shumway, D.L. and J.R. Palensky. 1973. Impairment of the Flavour of Fish by Water Pollutants. U.S. Environmental Protection Agency Report EPA-R3-73-010. Washington, D.C.

Sullivan, J.R., J.J. Delfino, C.R. Buelow and T.B. Sheffy. 1983. Polychlorinated biphenyls in the fish and sediment of the Lower Fox River, Wisconsin. Bull. Environ. Contam. Toxicol. 30: 58-64.

Swabey, Y.H. 1965. Report on a Study of the Flavour of Fish from the Spanish River and Adjacent North Channel. Ontario Wat. Res. Comm. Toronto, Ontario.

Thomas, N.A. 1973. Assessment of fish flesh tainting substances. pp. 178-193. In J. Cairns and K.L. Dickson, eds. Biological Methods for the Assessment of Water quality. ASTM STP 528. American Society for Testing and Materials. Philadelphia, PA.

Voss, R.H. 1983. Chlorinated neutral organics in biologically treated bleached kraft mill effluents. Environ. Sci. Technol 17: 530-537.

Voss, R.H. and M.B. Yunker. 1983. A Study of Chlorinated Phenolics Dicharged into Kraft Mill Receiving Waters. Project report prepared for the Council of Forest Industries (B.C.) by the Pulp and Paper Research Institute of Canada and Dobrocky Seatech Ltd. Vancouver, B.C.

Wells, D.L. 1967. Report on the Flavour of Whitefish from Nipigon Bay 1967. Ontario Wat. Res. Comm. Toronto, Ontario.

Weinbauer, J.D., D.A. Thiel, V.M. Kacynski and C.S. Martin. 1980. Receiving stream fisheries studies relative to secondary treated pulp and paper mill effluents. TAPPI 63: 121-125.

Whittle, D.M. and K.W. Flood. 1977. Assessment of the acute toxicity, growth impairment and flesh tainting potential of a bleached kraft mill effluent on rainbow trout (Salmo gairdneri). J. Fish. Res. Board Can. 34: 869-878.

5 BIOASSAYS FOR PREDICTING THE TOXICITY OF MILL EFFLUENTS IN THE AQUATIC ENVIRONMENT

5.1 Introduction

During about the last 10 years, aquatic toxicology has shown significant changes in both attitudes and methodology. The reader wishing to review these developments is referred to the annual Proceedings of the Canadian Aquatic Toxicity Workshop since 1975 (Gilbertson, 1985) and to the following publications: Davis 1977; Mayer and Hamelink, 1977; Butler, 1978; Cairns et al., 1978; Dickson et al., 1979, 1982; Marking and Kimerle, 1979; Hocutt and Stauffer, 1980; Maki et al., 1980; Mount, 1980; Bates and Weber, 1981; Buikema et al., 1982; Nriagu, 1983; Cairns et al., 1984; Persoone et al., 1984).

One attitudinal change has been the realization that, despite the many advantages of chemical analyses, "...toxicity is a property that can be measured only by an organism's response" (Mount, 1980). Another is an emergence from the science of aquatic toxicology (a study of the effects of toxicants on aquatic species) of a discipline referred to as "ecotoxicology", i.e., the science of the integrated assessment of toxic aggression on all biological communities of the environment (Blaise, 1984). This change in attitude, reflecting a greater emphasis on the environmental consequences of aquatic contaminants than was evident before, is now apparent throughout the international scientific community. Whereas early efforts and approaches were concerned primarily with the toxic effects of specific chemical contaminants and the derivation of water quality criteria, biological testing of effluents and receiving waters for toxic effects is now accorded a predominating role in assessing environmental impacts. The recently published Proceedings of the (OECD) International Workshop on Biological Testing of Effluents (and related receiving waters) (Anon., 1984) attests to current and future international endeavours in this respect.

Toxicity tests (bioassays) with effluents or receiving waters may be used for a variety of purposes, including the following:

- to regulate effluent discharges;
- to define the need for control/treatment;
- to monitor the effectiveness of controls;
- to compare the relative toxicity of in-plant and external-to-plant effluents, processes and treatments;

- to compare the sensitivities of different aquatic species and trophic levels;
- to examine the influences of differing environmental and test variables on one or more toxic responses; and
- to predict the toxic environmental consequences of an existing or planned effluent discharge.

One toxicity test or group of tests does not necessarily serve each purpose equally well.

The present discussion is limited to the capability of the various bioassay tests reviewed previously (Chapters 2-4) to predict the toxic effects of pulp and paper mill effluents in the aquatic (freshwater, estuarine or marine) environment. The predictive capabilities of bioassay tests may be applicable at differing levels of organization. For instance, appropriate laboratory bioassays with effluents might permit some assessment of the toxic effects of these discharges on the test species and related aquatic species indigenous to the receiving waters. In combination with information concerning effluent concentration and dispersal in receiving waters, the same bioassay data can provide some estimate of the spatial zone affected. The same bioassay procedures, applied to receiving water samples either in situ or on-site, can provide confirmatory evidence concerning the toxic zone of influence for these biota. However, these data do not necessarily permit valid predictions of the toxic effects and zones of influence of the discharged effluent towards all populations and communities of individual species inhabiting these waters. Particularly, bioassays which provide valid information for specific test species may not provide worthwhile estimates of the biological consequences of the effluent on our fisheries resources.

Inasmuch as the Federal Fisheries Act (Anon., 1970) prohibits the discharge to Canadian waters of effluents toxic or otherwise deleterious to fish, fish habitat or man's use of fish, the various bioassay test procedures and approaches for predicting the impact of pulp and paper mill effluents towards the fisheries resource will be considered in these terms. Promising approaches now being applied or considered in Canada and abroad for predicting the toxic impact of pulp mill and other effluents within the aquatic environment will also be reviewed briefly in this chapter.

5.2 Predictive Capability of Bioassays

5.2.1 Fish. For the purposes of this discussion, "fish" includes shellfish, crustaceans, marine animals and the eggs, spawn, spat and juvenile stages of fish, shellfish, crustaceans and marine animals (Anon., 1970).

5.2.1.1 Acute lethal bioassays. In general terms, acute lethal bioassays performed in the laboratory with fish or other aquatic organisms exposed to a range of concentrations of pulp and paper mill effluents have predictive value. Effluents that consistently are not lethal at full strength are unlikely to cause any immediate mortalities for organisms frequenting the receiving waters. On the other hand, effluents that are acutely toxic with substantial dilution (low LC_{50} values) would pose a toxic threat unless their degree of dilution and dispersal was adequate (i.e., dilute receiving-water concentrations). Without site-specific estimates of receiving-water concentrations, LC_{50} values are of limited predictive value. Even with valid information, the acute lethality data derived in the laboratory may not allow valid predictions of the ability of indigenous organisms to survive in proximate waters. For instance, the sensitivity of the test organism to effluent exposure may be different from that of the species inhabiting these waters; receiving-water chemistry may differ substantially from the bioassay diluent water; or other environmental or genetic variables may modify the tolerance of native organisms to the effluent (Chapter 2). These organisms may have acclimated (increased their tolerance) to pulp mill effluent due to previous exposure, or they may show increased sensitivity due to previous/simultaneous exposure to sublethal concentrations of other aquatic contaminants.

Acute lethal bioassays per se do not provide any basis for meaningfully predicting the toxic effects towards aquatic organisms caused by their prolonged exposure to sublethal effluent concentrations. Likewise, acute lethal bioassays cannot predict any acute sublethal effects (e.g., stress, behavioural) caused by the discharge of biotreated or other mill effluents which are not lethal at full strength. Nor can such tests be used to predict toxic effects caused by environmentally persistent effluent constituents which are slowly bioaccumulated (Chapter 4), or by toxic metabolites formed within receiving waters during effluent biodegradation (Neilson et al., 1983, 1984). Self-evidently, lethal conditions which might develop within receiving waters adjacent to pulp mill outfalls due to oxygen deficiency and the highly toxic hydrogen sulphide (Smith and Oseid, 1972, 1975; Reynolds and Haines, 1980), produced by decomposing bottom fibre deposits (Chapter 3) would not be predicted from any lethal or sublethal laboratory bioassays with mill effluents.

As seawater chemistry can modify the form, bioavailability and toxicity of the toxic constituents in pulp and paper mill effluents, toxic effects on estuarine or marine organisms predicted from acutely lethal laboratory toxicity tests with freshwater

organisms (and freshwater as the diluent) may be invalid. Appropriate estuarine and marine species are now available for laboratory bioassays (Chapter 2), and should be employed where one wishes to predict (by laboratory techniques) the toxic effects of coastal mill discharges. Although less satisfactory, bioassays with freshwater organisms might still be useful if their relationship with corresponding seawater bioassays is evaluated and thoroughly understood.

Numerous examples can be cited where the LC_{50} fish (rainbow trout) bioassay has demonstrated a predictive value with respect to the ecological consequences of mill discharges. For instance, while in-plant recovery of spent sulphite liquor by the mill on Neroutsos Inlet resulted in an appreciable increase in LC_{50} values (decreased toxicity), a concurrent environmental improvement within the inlet was also evident (McGreer and Vigers, 1983). Similarly, LC_{50} fish bioassays for a mill discharging biotreated BKME into the Sacramento River, showing an absence of toxicity, were consistent with the apparent absence of any environmental effects in the river (Zanella and Weber, 1981). Other examples where LC_{50} data have corroborated environmental findings are presented in Chapter 3.

Bioassays utilizing samples of receiving waters collected at various distances from an effluent source enhance the capability of these tests to predict environmental toxicity and zones of influence. Misinterpretations attributable to the differing chemistry of the different diluent waters are avoided. In situ survival tests with caged fish or other test organisms held at various distances (and depths) upstream and downstream of a mill outfall are also useful and appropriate in certain situations for deriving information concerning lethal zones of impact. However, difficulties (and erroneous results) may ensue due to the stress associated with fish handling and confinement (Pickering, 1981; Wedemeyer et al., 1984). For instance, fish might be held in waters (that they might otherwise avoid) that are either periodically supersaturated with oxygen or oxygen deficient, resulting in sublethal stress or, in extreme situations, short-term deaths.

Not surprisingly, the predictive value of acute toxicity tests has been shown to increase with increasing numbers of test species employed (Blanck, 1984; Blanck et al., 1984). The sensitivity of test organisms to effluents or chemicals may vary by more than three orders of magnitude, although reported differences are usually one order or less (Klapow and Lewis, 1979; Franklin, 1980; Blanck, 1984). Since no species is generally sensitive to all chemicals or effluent types, it is argued that a number of different species, selected for their general susceptibility to aquatic contaminants and their ability to represent differing trophic (food chain) levels of organisms within the receiving

environment, should be used to evaluate the toxic impact of effluent discharges (Anon., 1984; Blanck, 1984).

A substantial data base concerning threshold concentrations of untreated or primary-treated BKME or UKME which cause acute sublethal effects (e.g., stress and other metabolic changes, impaired swimming, respiratory responses and decreased tolerance to environmental extremes) has been derived in the laboratory for freshwater-acclimated salmonid fish species (Walden, 1976; McLeay and Howard, 1977). Effluent strengths causing these responses have been calculated and expressed as a fraction of the sample's 96-h LC_{50} value (Chapter 2). From this information, it is evident that acute sublethal effects on these organisms rarely occur at concentrations below 0.05 LC_{50}. Criteria for effluent dilutions of 0.02 (Davis, 1976) or 0.05 LC_{50} (Walden, 1976) in the waters immediately adjacent to kraft mills have been recommended to protect pollutant-sensitive salmonid fish and, hopefully, other commercially-viable species which comprise our fisheries resource. While acute lethal bioassay data may be applied in this manner, their predictive use has limitations because of the source from which they were derived (i.e., juvenile freshwater-acclimated laboratory-reared salmonid fish exposed to kraft pulp mill effluent under controlled laboratory conditions). Application of LC_{50} data requires interpretation and extrapolation of the relationships and interactions pertinent to real environmental situations.

5.2.1.2 Acute sublethal bioassays. The Microtox assay, an automated bioassay procedure which determines the median effective concentration of effluent that inhibits light production under defined conditions by a luminescent marine bacterium, is no more sensitive to pulp and paper mill effluents than the acute lethal fish bioassay. Further, the ecological relevance of this test is presently unclear. For instance, some comparative bioassays have reported a good correlation between Microtox assay results and LC_{50} values for fish or other aquatic species (Chapter 2), whereas other (unpublished results for certain B.C. kraft mills) studies have found poor correlations. Other limitations of the Microtox assay are described in Chapter 2.

The principal advantages of the Microtox test are its extremely rapid response time (less than 1 h for result), small effluent volume requirements, and adaptability for toxicity evaluations by mill personnel. In closely controlled comparative situations, this test can indicate effluents that, due to in-plant or treatment modifications, may be more or less toxic than usual when discharged. When considered together with effluent and receiving-water flow data, the extent to which a spill or otherwise atypical effluent may

pose a toxic threat if discharged can be assessed using this bioassay, and remedial measures instigated.

The capability and limitations of the oyster larval assay (Woelke, 1972) for estimating the toxic zone of influence within receiving waters for discharged pulp and paper mill effluents have already been discussed (Chapters 2 and 3). The apparently high susceptibility of oyster larvae to pulp mill effluent and the economic relevance of these shellfish encourage the use of this seawater bioassay for on-site and laboratory evaluations. However, the effective performance of this test with a variety of pulp mill effluent types and receiving-water samples requires confirmation, and the seasonal or year-round availability of test organisms must be demonstrated, before this test can be accepted for common use. Reports of declining populations of viable oysters in marine waters receiving pulp mill discharges (Quayle, 1964) may be associated, in part, with effects on this early life stage, although substantive evidence is lacking.

Acute sublethal bioassays measuring toxic responses of fish or other aquatic organisms exposed to sublethal concentrations of pulp mill effluents (Chapter 2) or receiving waters (Chapter 3) show considerable promise as predictive tools for assessing environmental impact. By and large, these tests are 6 to 10 times more sensitive than acute lethal bioassays. Appropriate laboratory or on-site tests with samples of whole mill effluents and receiving waters are able to discern the degree of dilution required to eliminate these responses, and to define the limits of any demonstrable toxic zone of influence (Davis, 1977; McLeay and Gordon, 1978; Fisher, 1982; Oikari, 1983). These tests can also be employed to determine the effectiveness of effluent treatment in removing residual (sublethal) toxicity (Leach and Meier, 1978; McLeay and Gordon, 1978). In contrast, the relative insensitivity of acute lethal (or Microtox) bioassays renders them of little value in assessing residual toxicity for samples of receiving waters or biotreated ("detoxified") effluents.

Behavioural studies with fish and aquatic invertebrates can provide useful clues concerning the environmental consequences of effluent discharges. Limitations of such tests include their complexity (in some instances) and difficulties in interpreting the relevance of responses. In addition, it is often difficult to differentiate between a response due to toxic constituents and those caused by other water quality variables (e.g., colour, salinity, temperature, etc.). Despite these difficulties, appropriate behavioural tests may provide a much-needed link between effects measured for individual organisms and those acting upon indigenous populations.

In situ avoidance/preference bioassays with vertical chambers have proven useful for distinguishing the selective responses of fish frequenting stratified waters where dispersed effluent is restricted to certain depths (Birtwell, 1977; Birtwell and Harbo, 1980; McGreer and Vigers, 1983). Receiving-water studies of movement patterns and rates for sonic-tagged fish (Elson et al., 1972; Falter and Ringe, 1974; Kelso, 1977) (Chapter 3) also show promise in predicting any influence of mill effluents on fish migratory runs, distribution and abundance. However, these studies are expensive and (to date) many have been preliminary and restricted to too few fish, test stations or concurrent water quality data to permit meaningful conclusions. The predictive worth of such behavioural investigations can best be appraised when performed in conjunction with ongoing assessments of fish populations within receiving and adjacent waters (Birtwell, 1978).

On-line, fully-automated biological monitoring systems have been developed for the continuous assessment of effluent toxicity (Morgan, 1977; Gruber et al., 1981; Gruber and Miller, 1982). These computerized systems continuously record fish respiration or activity rates using external sensors, and automatically sound alarms if abnormal responses occur. Atypically toxic effluents can be immediately detected in-plant or external-to-plant (within treatment systems), and appropriate remedial measures taken should toxic spills occur or treatment efficiency decline.

Morgan et al. (1982) reported the environmental and industrial benefits gained from the installation of an automated fish biomonitoring system recently installed at an integrated pulp and paper mill in South Africa. Improved effluent quality and public relations were evident following installation, and operating costs were less than those normally incurred for the routine chemical/physical analyses of the effluent. Automated biomonitoring systems based upon acute sublethal toxic responses appear to be sensitive and reliable indicators for early warning of effluent toxicity. Such systems could also be designed for the on-site continuous monitoring of receiving waters, although associated costs might prove prohibitive.

5.2.1.3 Chronic sublethal bioassays. Various life stages of fish and other aquatic life inhabiting receiving waters may be exposed to dilute concentrations of pulp and paper mill effluents for extended periods of time. Even when their exposure is transient, the risk exists that delayed toxic effects may become subsequently apparent. Accordingly, efforts to understand the chronic effects of effluent exposure on sensitive organisms are justified.

Numerous chronic-effect research studies with differing life stages of salmonid fish exposed to untreated and treated whole mill effluents have been conducted in the laboratory and in experimental outdoor streams (Chapter 2). Such research efforts permit assessments of the threshold concentrations of various effluent types and treatments that may adversely affect the long-term well-being of this valuable fisheries resource, and the nature of responses which might be anticipated in the environment. Because of their duration and cost, these studies are not suitable for routine application. More rapid life-cycle or partial life-cycle bioassays using sensitive species of fish (e.g., Brachydanio rerio, Pimephales promelas) or invertebrates (e.g., Daphnia magna, Nitocra spinipes) amenable to laboratory culturing and evaluations have been developed to permit their regular use (Anon., 1982; Anon., 1984; Landner et al., 1985) (Chapter 2). Such tests are useful in defining potential chronic toxic effects (e.g., development, growth, reproduction, disease resistance, long-term survival) of specific effluent constituents or whole mill effluents to which other sensitive aquatic species may be exposed in the environment. These comparatively more rapid chronic-effect bioassays could also be applied to receiving waters sampled at various distances from mill outfalls. Notwithstanding, corroborative field surveys and monitoring receiving-water studies with appropriate organisms indigenous to these waters are required before the ecological relevance of these predictive tests is confirmed. The development and use of life-cycle bioassays with temperate or coldwater fish and other aquatic species is to be encouraged because the results would be more directly applicable to our receiving environment than those derived with warmwater species (e.g., tropical fish).

Sublethal studies with oysters, mussels or other shellfish species transplanted to marine or estuarine coastal receiving waters offer a promising approach for assessing the chronic toxic effects of pulp mill discharges towards this fisheries resource. Decreased condition factors have been reported for Pacific oysters held for extended periods in waters receiving untreated pulp and paper mill wastes (Quayle, 1964; Pedlow, 1974) (Chapter 3). No other (metabolic) assessments of the physiological condition of shellfish have been reported, despite the availability of proven biochemical and functional assays for determining their health when exposed to other environmental contaminants (Bayne et al., 1976; Livingstone, 1982; Johnson et al., 1984).

Multiple-species bioassay tests which attempt to simulate microcosms of the environment (i.e., model ecosystems) have been employed in a few instances to examine the toxic effects of pulp mill effluents or receiving waters on communities of organisms (Anon., 1982; NCASI, 1982, 1983; Lehtinen et al., 1984) (Chapters 2 and 3). These chronic

bioassays normally include natural bottom substrates, and a variety of food-chain organisms, permitting chemical interactions/transformations of effluent constituents which might not occur in single-species bioassays. Additionally, multiple-species tests allow some of the natural predator-prey and other community interactions. A strong argument can be made that single-species tests alone are inadequate for predicting effluent concentrations in the environment that will not cause harm at all levels of biological organization (Cairns, 1983). However, microcosm tests are complex and create difficulties in experimental control and interpretation. Mount (1980) comments on microcosm bioassays as follows: "There certainly is no a priori reason that data from these tests should be able to be extrapolated to field communities any more than those from single-species tests, but there are reasons to expect them to lead to a better appreciation of environmental pathways, aqueous chemistry and biochemical behaviour than will single-species tests." Multiple-species bioassays with pulp mill effluents and receiving waters, although still research tools and necessarily expensive, offer the possibility of assessing the broad spectrum impacts of a specific mill discharge.

5.2.2 Fish Habitat. "Fish habitat" means spawning grounds and nursery, rearing, food supply and migration areas on which fish depend directly or indirectly in order to carry out their life processes (Anon., 1970). Numerous studies have reported fibre deposits in bottom substrates immediately downstream from pulp and paper mills discharging untreated or primary-treated effluent (Vander Wal, 1977; Nelson, 1979a,b; Wildish et al., 1979; Hilton, 1980). Field surveys at other mill sites discharging non-biotreated effluents have found a decreased abundance of benthic organisms (usually restricted to pollutant-tolerant species) in proximate waters or those beyond abiotic zones (Gregory and Loch, 1973; Packman, 1977; Nelson, 1979a,b,c) (Chapter 3). Fibre deposits have also been noted in these bottom regions. These findings represent a loss of food supply for demersal fish species and epibenthic invertebrates, i.e., a loss of fish habitat. The cause of this loss could be a number of conditions, including the blanketing of natural bottom sediment/substrate with fibre, ensuing hypoxic or anoxic conditions concomitant with the production of toxic hydrogen sulphide gas (in estuarine/marine situations only), or the adsorption to substrate material of toxic effluent constituents (transformed or otherwise). No battery of toxicity bioassays with pulp mill effluents or receiving-water samples can be expected to predict these conditions.

Methods are available to assess the degree of risk posed to the fisheries resource where varying degrees of habitat loss are apparent, and to distinguish the

causative agent(s). Vertical profiles of dissolved oxygen and oxidation-reduction potential are useful in mapping receiving waters for regions of likely biological effect (and for indicating the extent of significant fibre deposits) (Pearson and Stanley, 1979; Pearson, 1980). Sediment core sampling and analysis for fibre content is worthwhile. Sediment samples can also be analysed for concentrations of organic carbon and other chemical constituents (e.g., resin acids, chlorophenolic compounds) (Chapter 1). Additionally, artifical plates or boxes containing natural substrate can be positioned on the sea bed or on the bottom of rivers or lakes at differing distances from the pulp mill outfall to examine the degree of settlement for larval organisms and their subsequent survival and growth (Ellis, 1977). Sediment samples can also be taken and analysed in the laboratory for toxic effects, using a variety of bioassay tests now available for evaluating contaminated or uncontaminated sediment (Chapman et al., 1982; Pierson et al., 1983).

The definition of "fish habitat" (Anon., 1970) is construed here to include the food supply upon which fish depend either directly or indirectly. Effects of effluent discharges on phytoplankton and zooplankton are considered to be effects on fish food supply. Changes in primary productivity have direct consequences to oysters, mussels and other filter-feeding organisms. As indicated previously (Chapters 2 and 3), algal bioassays conducted with samples of whole mill effluents and receiving waters can predict the responses of indigenous populations of phytoplankton. However, other effluent characteristics (i.e., colour, nutrients) are also known to influence (often markedly) algal productivity, either decreasing or increasing primary productivity within proximate waters or at greater distances. Prediction of the environmental effects of pulp mill discharges on primary producers in the receiving waters may be misleading if restricted to toxicity bioassays.

5.2.3 Man's Use of Fish. Although the term "man's use of fish" is not defined in the Fisheries Act, it undoubtedly encompasses concerns with respect to the bioaccumulation of effluent constituents and associated tainting (off-flavour) problems in fish or shellfish. Our knowledge of this subject has been reviewed in Chapter 4.

Laboratory bioassays with fish exposed to specific effluent constituents or effluent samples have demonstrated that certain chemicals (e.g., resin acids, chlorophenolic compounds) can bioaccumulate in whole-body or specific tissues. Receiving-water studies with caged organisms and indigenous fish or shellfish have confirmed that these substances can also bioaccumulate in field specimens (Chapter 4), demonstrating the predictive capability of these tests. However, with respect to human health concerns, no

risks for consumers have been demonstrated. The majority of data on concentrations of specific chemicals in exposed fish are restricted to analyses of whole-body or liver tissues. The meagre analytical results for muscle samples from fish exposed experimentally to mill effluent/effluent constituents show no evidence for chemical bioaccumulation in this (edible) tissue (Chapter 4). Where the concentrations of suspect chemicals in fish muscle tissue or in whole-body (edible) shellfish tissues of organisms held in or captured from receiving waters were determined, these values were routinely low or below detection limits.

Field and laboratory studies involving bioaccumulation of effluent constituents in edible fish and shellfish species have not been adequate to enable any meaningful prediction of the degree of risk (if any) posed to human consumers. Valid laboratory and field data need to be assessed together with corresponding data derived from appropriate mammalian (e.g., rats, mice) toxicity studies (Sonstegard and Leatherland, 1979; Leatherland and Sonstegard, 1980) and human epidemiological and clinical data.

Off-flavours in fish can result from their short-term exposure to dilute concentrations of pulp and paper mill effluent in the laboratory and in receiving waters (Chapter 4). Regardless of whether the tainting compounds pose any risk to human health, obvious off-flavours in fish or shellfish make them unmarketable. However, in many instances, the real cause of reported off-flavours has not been adequately assessed. Naturally occurring contaminants or contaminants other than of pulp and paper mill origin are frequently indicated. Some reports of tainted fish by local fishermen or the public are also unsubstantiated. An important requirement for any predictive test is that it must identify the causative agent/source.

Since studies have not yet identified the effluent constituents that contribute to off-flavours in fish, chemical analysis of edible products presently will not provide meaningful predictions of the extent to which mill effluents may have contributed to tainting. Controlled laboratory or in situ exposures of fish (or shellfish), combined with taste panel flavour evaluations (Brouzes et al., 1978; Gordon et al., 1980; Kovacs, 1982) (Chapter 4) can predict the extent to which specific mill discharges may cause off-flavours. Where possible, results for laboratory exposures should be confirmed by in situ studies and field samplings of indigenous fish or shellfish for taste panel evaluations. Nonetheless this approach is unwieldy, time consuming, and usually produces data only well after the fact.

5.3 International Approaches to Monitoring Toxicity of Effluents and Receiving Waters

5.3.1 Sweden. Landner (1979) outlined the biological methods and strategies employed since 1978 by Swedish investigators for evaluating the ecological effects of pulp mill discharges as part of a four-year research project entitled "Environmentally Harmonized Production of Bleached Pulp" (Anon., 1982). Swedish approaches towards the monitoring of effluents and receiving waters for toxic impacts have been summarized by Lindestrom et al. (1981) and, more recently, by Bengtsson (1984) and Renberg (1984).

For their four-year (1978-1981) research program, Swedish scientists selected a battery of relatively simple tests which included:

- acute lethal bioassays with rainbow trout and zebra fish;
- bioaccumulation studies with fish;
- chronic bioassays with fish (zebra fish; Baltic herring) to determine reproductive effects including those on second generations;
- acute bioassays with freshwater and estuarine algae; and,
- bioassays with model ecosystems (microcosms).

These tests enabled a comparison of the relative toxic hazard posed by BKME produced from soft- or hardwood using conventional and non-conventional bleaching techniques, and of the degree of effluent dilution required to eliminate any responses. Receiving-water surveys of indigenous fish species confirmed the bioaccumulation of certain chlorophenolic compounds found in laboratory studies with mill effluents (Anon., 1982). Additional receiving-water evaluations were not performed in sufficient detail to assess the utility of the other bioassay tests for predicting toxic effects within the environment.

The strategy presently being used by Swedish scientists to characterize the environmental hazard of a particular effluent source incorporates similar screening and more comprehensive biological and chemical tests (Renberg, 1984). Biological screening assays include acute lethal and reproductive tests with fish and crustaceans, tests for disturbances to primary production (algae and higher plants), and genotoxic assays (i.e., Ames bacterial tests). The comprehensive biological tests determine effluent effects on physiology, behaviour, growth, reproduction and diversity. Organisms used for such evaluations are chosen as those most representative of the particular receiving water into which the effluent is discharged (i.e., freshwater, estuarine or marine species).

The National Swedish Environment Protection Board commenced in 1982 a new five-year project "Environment/Cellulose" to clarify the effects of bleached pulp and paper mill effluents on the aquatic environment (Sodergren et al., 1984). Their research strategy is designed to answer the following questions:

a) To what extent are the receiving body of water and remote areas exposed to emissions?
b) What biological effects have been observed in the receiving body of water?
c) What part of the ecosystem is most sensitive to impact?
d) What substances in the effluent are responsible for the biological effects?
e) What are the ecological consequences of the biological effects that have been observed?

Among the sub-projects associated with this project are field trials intended to gain an understanding of the ecological relevance of the various laboratory-developed bioassays. Field studies with fish will include a number of biochemical determinations of condition (e.g., liver glycogen and blood lactate concentrations, blood cell counts), embryonic and histological examinations, examinations for incidence of parasites and tumours, and tests for physiological capabilities. Results from these field trials and from the laboratory bioassays with mill effluents will be compared. In addition, field surveys within receiving waters will examine the abundance and diversity of indigenous fish species and their state of health (histopathologies, parasite frequencies). Field surveys will attempt to determine if fish production is reduced or enhanced due to the effluent discharges.

5.3.2 Finland. Finnish scientists now employ a battery of routine bioassays tests, each reflecting different trophic levels (e.g., fish, daphnia, algae, bacteria), in order to predict the environmental toxicity of pulp and paper mill effluents (Nikunen, 1983; Miettinen et al., 1984). Field and laboratory investigations have incorporated both pure algal cultures and indigenous mixed algal populations to predict and confirm the toxic zone of influence (for phytoplankton) of pulp and paper mill effluents discharged to lakes. Results with indigenous cultures, although more variable, have a greater ecological relevance (Miettinen et al., 1984; Eloranta et al., 1985). A variety of sublethal (metabolic, physiological) tests with rainbow trout, optimized for laboratory and field purposes, are now being applied with receiving waters in order to assess their predictive capabilities. These tests include studies of effluent and receiving-water effects on respiration and energetics, osmoregulation (hydromineral balance) and liver metabolism

(including detoxification mechanisms and capabilities) (Oikari, 1983). Attempts are being made to clarify the overall relevance of observed responses to the fishes' well-being. Research efforts, involving both laboratory and receiving water studies, are continuing to assess the ecological relevance of effluent constituents which may bioaccumulate and cause fish flesh-tainting problems.

Miettinen et al. (1984) recently reported the findings of the National Board of Waters (Finland) for detailed bioassay tests with a number of biotreated and untreated kraft, sulphite, mechanical, thermomechanical and paper mill effluents. These authors concluded "The results of this study clearly show that (an) ecotoxicological approach, where different tests with many organisms complete each other, is necessary to get sufficient information on the effects of industrial effluents to aquatic biota".

5.3.3 U.S.A. Past and present policies of the U.S. Environmental Protection Agency (EPA) for monitoring and controlling effluent discharges and for predicting effluent toxicity were outlined recently (Hanmer and Newton, 1984; Mount, 1984).

During the 1970s, EPA scientists undertook an intensive analysis program to identify priority contaminants and, based on pertinent water quality criteria and on the chemical analysis of their concentrations in effluent, to establish upper limits for the discharge of these substances. However, this approach could not begin to assess the large number of potentially toxic contaminants in complex effluents, nor their toxic interactions. "One thing we have learned using toxicity tests is that effluent toxicity is not predictable by looking at commonly considered factors such as industry type or effluent chemistry" (Hanmer and Newton, 1984). The U.S. has now begun to use toxicity bioassays to measure and predict whole effluent effects as a supplement to chemical-specific regulation (Hanmer and Newton, 1984).

Ecological surveys for biological effects, although of recognized value in discerning environmental change, are presently considered by EPA scientists to be inappropriate for the routine prediction and monitoring of toxic effluent effects. Reasons tendered for this decision included their high cost ("The cost of a good biological survey is at least two and probably more than three orders of magnitude greater than toxicity tests in all but the simplest situations and smallest receiving waters"); their inability to provide worthwhile conclusions with respect to cause and effect ("...in the U.S. there is considerable reluctance to use field surveys because results are often ambiguous and subject to argument...if there are multiple dischargers, there is no chance to determine which discharge is causing how much effect except in rare instances"); and their

retrospective nature ("...field surveys require that the adverse impacts have occurred in order to measure them and therefore are not useful for treatment decisions on new discharges") (Mount, 1984; Hanmer and Newton, 1984).

The EPA's Environmental Research Laboratory (Duluth, MN) recently initiated a multi-year research program, "Complex Effluent Toxicity Testing Program". One of the major objectives of this program is to investigate the validity of effluent toxicity tests to predict and quantify adverse impact to receiving waters caused by the discharge of toxic industrial (and municipal) effluents. A number of freshwater and estuarine sites receiving single or multiple effluent discharges are being currently assessed as part of this project. The experimental approach taken involves concurrent laboratory bioassays with effluent and receiving-water samples, in situ caged fish bioassays, dye injection studies for determination of ambient effluent concentrations, and field sampling for assessments of biological impact. The measured impact is compared with the predictions to see if the effluent toxicity tests are valid predictors. The laboratory bioassays with effluents and receiving-water samples include (for freshwater discharges) a seven-day larval fish (fathead minnows; Pimephales promelas) bioassay and a seven-day life cycle test with Ceriodaphnia sp. (a freshwater daphnid invertebrate). The diluent water used for all effluent bioassays is collected just upstream of the discharge point. Effluent, diluent and receiving-water (upstream and downstream) samples used in these and concurrent acute lethal bioassays are fresh samples, renewed daily (Mount, 1984).

Results for the first site investigation (Ottawa River; Lima, Ohio) have been reported (Mount et al., 1984). The stretch of river studied received discharges from a municipal sewage treatment plant, a refinery and a chemical company. Findings for the study showed that the effluent bioassays were good predictors of the toxic responses found for receiving-water samples, and that the effluent and receiving-water bioassays both predicted accurately the receiving-water impact shown by surveys of indigenous organisms. A similar predictability has been found for other sites investigated to date, although some instances were seen where the toxic impact was less than anticipated (Mount, 1984). No mention was made of comparable studies with pulp and paper mill effluents.

5.3.4 Canada. The limitations of end-of-pipe acute lethal bioassay tests for predicting and monitoring the toxic impact of effluents within receiving waters are now well recognized by Canadian scientists and regulatory personnel. Some of the limitations of the acute lethal rainbow trout bioassay (Anon., 1980) as used routinely in Canada for

measuring the toxicity of pulp mill and other effluent discharges have been delineated previously (Chapter 2). In referring to this test, Pessah and Cornwall (1980) (as representatives of the Canadian Environmental Protection Service) commented "It is important at this time to restate that the test is designed to test for compliance with a regulation and not to investigate the biological effects of industrial wastes on fish. It is clear that the existing test does not take into account ecologically significant sublethal effects...It is also recognized that a mortality test will not indicate the variety of chemical species that can bioaccumulate in the environment...The relationship between toxicity at the end of the industrial pipe and the state of the environment beyond the pipe will only be understood when the results of long-term trend studies of the aquatic systems affected by effluents and effluent regulations are undertaken and analyzed...There is an immediate need for more rapid, more sensitive toxicity tests to increase the efficiency of spot-check and monitoring activities". Informed representatives of the Canadian pulp and paper industry have, on occasion, expressed a similar viewpoint. As an example, Paavila (1982) commented "At least in Canada, we do not have a quantifiable measure of the impact of the pulp and paper industry on the environment, except in certain isolated instances...A strong case can be made for directing more scientific effort to document environmental cause/effect relationships before implementing further arbitrary industrial pollution control programs...There is no single set of emissions standards for any industrial sector that adequately harmonizes industrial activity and environmental protection. Environmental control must be based on site-specific conditions and parameters". Scientists in the Federal Department of Fisheries and Oceans have also voiced this opinion. Based upon his experiences with L'Etang Estuary, Wildish (1983) concluded "...pulp mill effluents should be assessed on a site-specific basis. Effluent control measures could then take into account the assimilatory capacity of a specific recipient water".

Consistent with the present international evolution of ecotoxicological tests for predicting and monitoring the toxic environmental impact of effluent discharges (Anon., 1984), Canadian researchers and regulatory personnel are proposing that a similar approach be applied here on a routine basis (Blaise et al., 1984; Dafoe et al., 1984). The October, 1982 conference "Biological Testing and Hazard Assessment" organized by Environment Canada (Van Coillie et al., 1984) included a number of presentations concerning ecotoxicological tests and their potential applications. Testing capabilities now available at certain Environment Canada laboratories include acute lethal and sublethal bioassay tests with a variety of freshwater and estuarine/marine organisms

besides rainbow trout (e.g., Daphnia sp., Homarus sp., Selenastrum sp., Microtox), and chronic sublethal bioassays with Daphnia sp. (for reproductive and other life-cycle responses) and shellfish (for bioaccumulation) (MacGregor and Wells, 1984). Numerous provincial government scientists and independent environmental consultants in Canada are familiar with these and other ecotoxicological tests, although their application is sporadic and mainly associated with specific research studies.

Environment Canada scientists in the Quebec region are currently developing and evaluating an integrated ecotoxicological approach for assessing the environmental hazards posed by specific effluents (Blaise et al., 1984). This approach incorporates the use of a battery of simple and relatively inexpensive diverse bioassays for measuring the lethal and sublethal (acute and chronic) toxic effects of effluents.

Environment Canada recently reviewed a number of Canadian experiences in the application of biological tests for controlling and monitoring effluents and receiving waters, and in setting water quality objectives (Dafoe et al., 1984). The limitations of solely using "end-of-pipe" tests for detecting potential environmental problems and the worth of acute and chronic sublethal bioassays with diverse organisms were emphasized. These authors concluded that "The trout test is used frequently in Canada; nevertheless, short-term, sensitive and predictive biological tests should now be applied more frequently to non-lethal effluents at source and in situ...There should be a continued effort to correlate effluent biomonitoring tests with those useful for monitoring and predicting contaminants effects in situ".

5.4 References

Anon., 1970. Fisheries Act. R.S.C., 1970, C. F-14. Amendment List May 4, 1981. Fisheries & Oceans Canada. Ottawa, Ontario.

Anon., 1980. Standard Procedure for Testing the Acute Lethality of Liquid Effluents. Report No. EPS 1-WP-80-1. Water Pollution Control Directorate, Environment Canada. Ottawa, Ontario.

Anon., 1982. Environmentally Harmonized Production of Bleached Pulp. Final Report (in Swedish). Swedish Forest Products Research Laboratory, Stockholm, Sweden.

Anon., 1984. OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Bates, J.M. and C.I. Weber (eds.). 1981. Ecological Assessments of Effluent Impacts on Communities of Indigenous Aquatic Organisms. ASTM STP 730. American Society for Testing and Materials. Philadelphia, PA.

Bayne, B.L., D.R. Livingstone, M.N. Moore and J. Widdows. 1976. A cytochemical and biochemical index of stress in Mytilus edulis L. Mar. Poll. Bull. 7: 221-224.

Bengtsson, B-E. 1984. Some experience from combined biological and chemical testing of complex effluents. pp. 323-336. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Birtwell, I.K. 1977. A field technique for studying the avoidance of fish to pollutants. pp. 69-86. In Proc. 3rd Aquatic Toxicity Workshop, Halifax, N.S., November 2-3, 1976. Technical Report No. EPS-5-AR-77-1. Environmental Protection Service. Halifax, Nova Scotia.

Birtwell, I.K. 1978. Studies on the relationship between juvenile chinook salmon and water quality in the industrialized estuary of the Somass River. pp. 57-78. In B.C. Sheppard and R.M.J. Ginetz, eds. Proc. 1977 Northwest Pacific Chinook and Coho Workshop. Fish. Mar. Serv. Tech. Rep. 759. Fisheries & Environment Canada. Vancouver, B.C.

Birtwell, I.K. and R.M. Harbo. 1980. Pulp mill impact studies at Port Alberni and Port Mellon, B.C. Trans. Tech. Sect. Can. Pulp Paper Assoc. 81 (12): 85-89.

Blaise, C. 1984. Introduction to ecotoxicological concepts. pp. 11-47. In R. Van Coillie, N. Bermingham and C. Blaise, eds. Biological Testing and Hazard Assessment. Proc. Conf. October 20-21, 1982. Environment Canada. Montreal, Quebec.

Blaise, C., N. Bermingham and R. Van Coillie. 1984. An integrated approach to assess ecotoxicity. pp. 215-244. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Blanck, H. 1984. Species dependent variation among aquatic organisms in their sensitivity to chemicals. Ecol. Bull. 36: 107-119.

Blanck, H., G. Wallin and S-A. Wangberg. 1984. Species-dependent variation in algal sensitivity to chemical compounds. Ecotoxicol. Environ. Safety 8: 339-351.

Brouzes, R.J.P., A.J. Liem and V.A. Naish. 1978. Protocol for Fish Tainting Bioassay. CPAR Rep. No. 775-1. Environmental Protection Service. Ottawa, Ontario.

Buikema, A.L. Jr., B.R. Niederlehner and J. Cairns Jr. 1982. Biological monitoring. Part IV-toxicity testing. Water Res. 16: 239-262.

Butler, G.C. (ed.). 1978. Principles of Ecotoxicology: Scope 12. Wiley & Sons, Inc. New York, NY.

Cairns, J. Jr. 1983. Are single species toxicity tests alone adequate for estimating environmental hazard? Hydrobiologia 100: 47-57.

Cairns, J. Jr., K.L. Dickson and A. Maki (eds.). 1978. Estimating The Hazard of Chemical Substances to Aquatic Life. American Society for Testing and Materials. Philadelphia, PA.

Cairns, V.W., P.V. Hodson and J.O. Nriagu. (eds.). 1984. Contaminant Effects on Fisheries. Vol. 16, Adv. Sci. Technol. Wiley & Sons, Inc. New York, NY.

Chapman, P.M., G.A. Vigers, M.A. Farrell, R.N. Dexter, E.A. Quinlan, R.M. Kocan and M. Landolt. 1982. Survey of Biological Effects of Toxicants Upon Puget Sound Biota. I. Broad-Scale Toxicity Survey. NOAA Tech. Mem. OMPA-25. National Oceanic and Atmospheric Administration. Boulder, CO.

Dafoe, T., J.H. Carey, S.H. McCrindle, P.G. Wells and R.C.H. Wilson. 1984. Relationships between the biological testing of industrial effluents and the quality of receiving waters-Canadian approaches and examples. pp. 245-287. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environment Protection Agency and Environment Canada. Ottawa, Ontario.

Davis, J.C. 1976. Progress in sublethal studies with kraft pulp mill effluent and salmonids. J. Fish. Res. Board Can. 33: 2031-2035.

Davis, J.C. 1977. Standardization and protocols of bioassays-their role and significance for monitoring research and regulatory usage. pp. 1-14. In W.R. Parker et al., eds. Proceedings of the 3rd Aquatic Toxicity Workshop. Environmental Protection Service Report EPS-5-AR-77-1. Environment Canada. Halifax, Nova Scotia.

Dickson, K.L., J. Cairns Jr. and A. Maki (eds.). 1979. Analyzing The Hazard Evaluation Process. Am. Fish. Society. Washington, D.C.

Dickson, K.L., A.W. Maki and J. Cairns, Jr. (eds.). 1982. Modeling for Estimating The Fate of Chemicals in Aquatic Environments. Ann Arbor Sci. Publ., Inc. Ann Arbor, MI.

Ellis, D.V. 1977. Pollution control regulations and monitoring technology: a review of research and development from the pulp and paper industry. Prog. Wat. Tech. 9: 673-682.

Eloranta, V., L. Halttunen-Keyrilainen and K. Kuivasniemi. 1985. The acute toxicity of spent bleaching liquors and bleached kraft mill effluent studied by the Selenastrum algal test and indigenous phytoplankton bioassays. Sciences et Techniques de L'eau. In Press.

Elson, P.F., L.N. Lauzier and V. Zitko. 1972. A preliminary study of salmon movements in a polluted estuary. pp. 325-330. In Marine Pollution and Sea Life. Fishing News Books, United Kingdom.

Falter, C.M. and R.R. Ringe. 1974. Pollution Effects on Adult Steelhead Migration in the Snake River. Rep. EPA-660/3-73-017. U.S. Environmental Protection Agency. Washington, D.C.

Fisher, J.N. 1982. Employing acute and subacute toxicity measurements in on-site biomonitoring studies. TAPPI J. 65: 89-91.

Franklin, F.L. 1980. Assessing the Toxicity of Industrial Wastes, with Particular Reference to Variations in Sensitivity of Test Animals. Fish. Res. Tech. Rep. No. 61. Ministry of Agriculture, Fisheries and Food Directorate of Fisheries Research. Lowestoft, U.K.

Gilbertson, M. 1985. Continuity Chairman for the Annual Aquatic Toxicity Workshop (contact for Proceedings). Fish Habitat Management Branch, Fisheries & Oceans Canada. Ottawa, Ontario.

Gordon, M.R., J.C. Mueller and C.C. Walden. 1980. Effect of biotreatment on fish tainting propensity of bleached kraft whole mill effluent. Trans. Tech. Sect. Can. Pulp Paper Assoc., 6(1): TR 2-8.

Gregory, L.A. and J.S. Loch. 1973. A benthos survey (1972) in the North Saskatchewan River in the vicinity of the Prince Albert Pulp Company, Prince Albert, Saskatchewan. Fish. Mar. Serv. Tech. Rep. CEN T-73-2. Environment Canada. Winnipeg, Manitoba.

Gruber, D. and W.R. Miller III. 1982. Assessing industrial wastewater with a continuous and automated on-line toxicity monitoring system. Can. Tech. Rep. Fish. Aquat. Sci. No. 1163. pp. 57-68.

Gruber, D., J. Cairns, Jr. and A.C. Hendricks. 1981. Computerized biological monitoring for demonstrating wastewater discharge. J. Water Poll. Control Fed. 53: 505-511.

Hanmer, R.W. and B.J. Newton. 1984. Utility of effluent toxicity tests from the U.S. regulatory perspective. pp. 353-367. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Hilton, D.F.J. 1980. The effect of kraft paper mill effluents on insects inhabiting the St. Francis River near East Angus, Quebec. Ann. Soc. ent. Quebec 25: 179-189.

Hocutt, C.H. and J.R. Stauffer, Jr. (eds.). 1980. Biological Monitoring of Fish. Lexington Books. Toronto, Ontario.

Johnson, D., T.J. Lack and R.D. Davis. 1984. Biological monitoring of the marine environment in relation to the disposal of sewage sludge. pp. 289-295. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Kelso, J.R.M. 1977. Density, distribution, and movement of Nipigon Bay fishes in relation to a pulp and paper mill effluent. J. Fish. Res. Board Can. 34: 879-885.

Klapow, L.A. and R.H. Lewis. 1979. Analysis of toxicity data for California marine water quality standards. J. Water Poll. Control Fed. 51: 2054-2070.

Kovacs, T.G. 1982. The Effect of Bleached Kraft Effluent on the Aquatic Environment. Report prepared for Weyerhaeuser Canada Ltd., Kamloops, B.C. Pulp Pap. Res. Inst. Can. Pte. Claire, PQ.

Landner, L. 1979. Methods and strategies in evaluating ecological effects of pulp mill discharges. Svensk Papperstidning 15: 444-446.

Landner, L., A.H. Neilson, L. Sorensen, A. Tarnholm and T. Viktor. 1985. Short-term test for predicting the potential of xenobiotics to impair reproduction success in fish. Ecotoxicol. Environ. Safety 9: 282-293.

Leach, J.M. and H.-P. Meier. 1978. Biodegradability of Various Toxic Compounds in Pulp Mill Effluents. CPAR Rep. No. 408-3. Environmental Protection Service. Ottawa, Ontario.

Leatherland, J.F. and R.A. Sonstegard. 1980. Structure of the thyroid and adrenal glands in rats fed diets of Great Lakes coho salmon. Environ. Res. 23: 77-86.

Lehtinen, K.-J., M. Notini and L. Landner. 1984. Tissue damage and parasite frequency in flounders, Platichtys flesus (L) chronically exposed to bleached kraft pulp mill effluents. Ann. Zool. Fennici 21: 23-28.

Lindestrom, L., H. Hultberg, K. Beijer and L. Landner. 1981. Traditional and New Methods for Investigation of Impact in Aquatic Ecosystems by Effluents from Pulp and Paper Mills. IVL Swedish Water and Air Pollution Research Institute. Stockholm, Sweden.

Livingstone, D.R. 1982. General biochemical indices of sublethal stress. Mar. Poll. Bull. 13: 261-263.

McGreer, E.R. and G.A. Vigers. 1983. Development and validation of an in situ fish preference-avoidance technique for environmental monitoring of pulp mill effluents. pp. 519-529. In W.E. Bishop et al., eds. Aquatic Toxicology and Hazard Assessment: Sixth Symposium. ASTM STP 802. American Society for Testing and Materials. Philadelphia, PA.

MacGregor, D.J. and P.W. Wells. 1984. The Role of Ecotoxicological Testing of Effluents and Chemicals in the Environmental Protection Service. EPS Tech. Rep. Environmental Protection Service. Ottawa, Ont.

McLeay, D.J. and M.R. Gordon. 1978. Unpublished receiving-water study.

McLeay, D.J. and T.E. Howard. 1977. Comparison of rapid bioassay procedures for measuring toxic effects of bleached kraft mill effluents to fish. pp. 141-155. Proc. Third Aquatic Toxicity Workshop Conference, November 2-3, 1976. EPS-5-AR-77-1. Environment Canada. Halifax, Nova Scotia.

Maki, A.W., K.L. Dickson and J. Cairns Jr. (eds.). 1980. Biotransformation and Fate of Chemicals in the Aquatic Environment. Am. Society Microbiol. Washington, D.C.

Marking, L.L. and R.A. Kimerle (eds.). 1979. Aquatic Toxicology. American Society for Testing and Materials. Philadelphia, PA.

Mayer, F.L. and J.L. Hamelink (eds.). 1977. Aquatic Toxicology and Hazard Evaluation. American Society for Testing and Materials. Philadelphia, PA.

Miettinen, V., R. Aaltonen, I. Taipalinen and P. Shemeikka. 1984. On the application of tests with algae, bacteria and fish in the assessment of the effects of pulp and paper mill effluents. Rep. No. 237. Vesihallitus - National Board of Waters. Helsinki, Finland.

Morgan, W.S.G. 1977. An electronic system to monitor the effects of changes in water quality on fish opercular rhythms. pp. 38-55. In J. Cairns et al., eds. Biological Monitoring of Water and Effluent Quality. ASTM STP 607. American Society for Testing and Materials. Philadelphia, PA.

Morgan, W.S.G., P.C. Kuhn, B. Allais and G. Wallis. 1982. An appraisal of performance of a continuous automatic fish biomonitoring system at an industrial site. Wat. Sci. Tech. 14: 151-161.

Mount, D.I. 1980. Needs of toxicity tests to meet specific regulations. pp. 33-41. In C.H. Hocutt and J.R. Stauffer Jr., eds. Biological Monitoring of Fish. Lexington Books. Toronto, Ont.

Mount, D.I. 1984. The role of biological assessment in effluent control. pp. 15-30. In OECD Proceedings of the International Workshop on Biological Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Mount, D.I., N.A. Thomas, T.J. Norberg, M.T. Barbour, T.H. Roush and W.F. Brandes. 1984. Effluent and Ambient Toxicity Testing and Instream Community Response on the Ottawa River, Lima, Ohio. Rep. EPA-600/3-84-080. U.S. Environmental Protection Agency. Duluth, MN.

NCASI 1982. Effects of Biologically Stabilized Bleached Kraft Mill Effluent on Cold Water Stream Productivity as Determined in Experimental Streams - First Progress Report. Tech. Bull. No. 368. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

NCASI 1983. Effects of Biologically Stabilized Bleached Kraft Mill Effluent on Cold Water Stream Productivity in Experimental Streams-Second Progress Report. Tech. Bull. No. 413. Nat. Counc. Air Stream Improvement, Inc. New York, NY.

Neilson, A.H., A.S. Allard, P.A. Hynning, M. Remberger and L. Landner. 1983. Bacterial methylation of chlorinated phenols and guaiacols: formation of veratroles from guaiacols and high-molecular-weight chlorinated lignin. Appl. Environ. Microbiol. 45: 774-783.

Neilson, A.H., A.S. Allard, S. Reiland, M. Remberger, A. Tarnholm, T. Viktor and L. Landner. 1984. Tri- and tetrachloroveratrole, metabolites produced by bacterial O-methylation of tri- and tetrachloroguaiacol: an assessment of their bioconcentration potential and their effects on fish reproduction. Can. J. Fish Aquat. Sci. 41: 1502-1512.

Nelson, H. 1979a. Pulp Mill Environmental Impact Assessment. Canadian Forest Products Ltd., Howe Sound Pulp Division. EPS Regional Program Rep. No. 79-2. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979b. Pulp Mill Environmental Impact Assessment. Rayonier Canada Ltd., Woodfibre Division. EPS Regional Program Rep. No. 79-3. Environmental Protection Service. West Vancouver, B.C.

Nelson, H. 1979c. Pulp Mill Environmental Impact Assessment. British Columbia Forest Products Ltd., Crofton Pulp and Paper Division. EPS Regional Program Rep. No. 79-5. Environmental Protection Service. West Vancouver, B.C.

Nikunen, E. 1983. The acute toxicity of some Finnish pulp and paper mill effluents and comparison of three measurement methods. Pap. Puu 11: 726-730.

Nriagu, J.O. (ed.). 1983. Aquatic Toxicology. Vol. 13, Adv. Sci. Technol. Wiley & Sons, Inc. New York, NY.

Oikari, A.O.J. 1983. Development of physiological fish tests for assessment of toxic pollution from the pulp and paper industry. pp. 241-248. In Chemicals in K. Christiansen et al., eds. the Environment. Proc. Int. Symp. October 18-20, 1982. Copenhagen, Denmark.

Paavila, H.D. 1982. Environmental control in the Canadian pulp and paper industry. Pulp Paper Can. 83 (12): 36-38.

Packman, G.A. 1977. Environmental Surveillance in the Vicinity of the Canadian Cellulose Co. Ltd. Pulp mill at Prince Rupert, British Columbia. EPS Regional Rep. No. EPS 5-PR-77-8. Environmental Protection Service. West Vancouver, B.C.

Pearson, T.H. 1980. Marine pollution effects of pulp and paper industry wastes. Helgolander Meeresunters 33: 340-365.

Pearson, T.H. and S.O. Stanley. 1979. Comparative measurement of the redox potential of marine sediments as a rapid means of assessing the effect of organic pollution. Mar. Biol. 53: 371-379.

Pedlow, J.C. 1974. Kraft Mill Effluent and the Pacific Oyster. M.Sc. thesis. 120 pp. Univ. British Columbia. Vancouver, B.C.

Persoone, G., E. Jaspers and C. Claus (eds.). 1984. Ecotoxicological Testing for the Marine Environment. State University of Ghent. Ghent, Belgium.

Pessah, E. and G.M. Cornwall. 1980. Use of toxicity tests in regulating the quality of industrial wastes in Canada. pp. 130-141. In J.G. Eaton et al., eds. Aquatic Toxicology. ASTM STP 707. American Society for Testing and Materials. Philadelphia, PA.

Pickering, A.D. (ed.). 1981. Stress and Fish. Academic Press. London, England.

Pierson, K.B., J.W. Nichols, G.C. McDowell and R.E. Nakatani. 1983. Grays Harbor, Washington, Dredged Sediments: An Assessment of Potential Chemical Toxicity and Bioaccumulation. U.S. Army Corps of Engineers. Seattle, WA.

Quayle, D.B. 1964. The Effect of Kraft Mill Effluent on the Pacific Oyster (Crassostrea gigas) with Particular Reference to Crofton, B.C. Fish. Res. Board Can. MS Rep. Ser. No. 765. Department of Fisheries. Nanaimo, B.C.

Renberg, L. 1984. Principles for composing biological-chemical test systems for complex effluents. pp. 337-352. In OECD Proceedings of the International Workshop on Biological

Testing of Effluents (and related receiving waters). September 10-14, 1984. Duluth, MN. U.S. Environmental Protection Agency and Environment Canada. Ottawa, Ontario.

Reynolds, F.A. and T.A. Haines. 1980. Effects of chronic exposure to hydrogen sulphide on newly hatched brown trout Salmo trutta L. Environ. Pollut. (Series A) 22: 11-17.

Smith, L.L. and D.M. Oseid. 1972. Effects of hydrogen sulphide on fish eggs and fry. Water Res. 6: 711-720.

Smith, L.L. Jr. and D.M. Oseid. 1975. Chronic effects of low levels of hydrogen sulphide on freshwater fish. Prog. Water Technol. 7: 599-605.

Sodergren, A., P. Jonsson, K. Kringstad, S. Lagergren and M. Olsson. 1984. Research Programme for the Project Field, Environment/Cellulose - Biological Effects of Effluents from Pulp Industries. National Swedish Environment Protection Board Bulletin SNV PM 1793. Solna, Sweden.

Sonstegard, R.A. and J.F. Leatherland. 1979. Growth retardation in rats fed coho salmon collected from the Great Lakes of North America. Chemosphere 7: 903-910.

Van Coillie, R., N. Bermingham and C. Blaise, eds. 1984. Proceedings of the Conference "Biological Testing and Hazard Assessment". Environmental Protection Service, Environment Canada. Montreal, Quebec.

Vander Wal, J. 1977. Relations between Nipigon Bay benthic macroinvertebrates and selected aspects of their habitat. J. Fish. Res. Board Can. 34: 824-829.

Walden, C.C. 1976. The toxicity of pulp and paper mill effluents and corresponding measurement procedures. Water Res. 10: 639-664.

Wedemeyer, G.A., D.J. McLeay and C.P. Goodyear. 1984. Assessing the tolerance of fish and fish populations to environmental stress: the problems and methods of monitoring. pp. 163-195. In V.W. Cairns et al., eds. Contaminant Effects on Fisheries. Vol. 16, Adv. Sci. Technol. Wiley & Sons, Inc. New York, NY.

Wildish, D.J. 1983. Coastal zone management and the pulp and paper industry. Pulp Paper Can. 84: T145-148.

Wildish, D.J., N.J. Poole and D.D. Kristmanson. 1979. Pulp Mill Pollution in L'Etang Estuary, A Case History and Clean-Up Alternatives. Fish. Mar. Serv. Tech. Rep. No. 884. Fisheries and Environment Canada. St. Andrews, N.B.

Woelke, C.E. 1972. Development of a Receiving Water Quality Bioassay Criterion Based on the 48-h Pacific Oyster, Crassostrea gigas Embryo. Wash. Dept. Fish. Tech. Rep. No. 9. Olympia, WA.

Zanella, E.F. and J.R. Weber. 1981. Monitoring the ecological impact of kraft mill effluents on the Sacramento River. pp. 261-267. In Proc. Environ. Conf., TAPPI. New Orleans, LA.

APPENDIX

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
130. Abietic Acid									
Dissolving Kraft	3	3	3	3	8 600-18 000	100-2 500	11 800	1 467	Biological Treatment
Market Bleached Kraft	6	6	5	3	0-390	0-1 800	177	767	Biological Treatment
BCT Bleached Kraft	9	9	7	6	0-2 700	15-520	1 043	119	Biological Treatment
Alkaline-Fine	9	9	6	3	190-1 100	0-11	470	3	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	2	350-1 200	0-21	753	10	Biological Treatment
Bag	6	6	6	6	3 700-12 000	30-250	6 983	165	Biological Treatment
Semi-Chemical	6	6	3	3	220-290	35-43	257	39	Biological Treatment
Unbleached Kraft and									
Semi-Chemical	6	6	6	6	650-2 000	580-1 000	1 392	710	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	3	94-5 200	0-940	1 949	383	Biological Treatment
Papergrade Sulphite	12	12	8	9	0-490	8-340	137	76	Biological Treatment
Groundwood-Fine Papers	6	6	6	4	11-600	0-26	182	7	Biological Treatment
Deink									
Fine Papers	3	3	3	2	700-990	0-31	837	12	Biological Treatment
Newsprint	3	--	3	--	2 300-4 100	-- - --	3 467	--	POTW
Tissue Papers	3	3	3	3	370-680	50-140	557	97	Partial Final Effluent
	3	3	3	3	330-740	40-90	513	72	Biological Treatment
Tissue from Wastepaper	6	6	4	0	0-150	0 - --	54	0	Biological Treatment
	3	3	3	3	120-260	35-140	203	84	Primary Treatment
Paperboard from Wastepaper	15	15	15	6	18-1 900	0-96	651	19	Biological Treatment
	3	3	3	0	120-710	0 - --	407	0	Primary Treatment
Wastepaper-Molded Products	3	3	3	1	190-250	0-21	210	7	Biological Treatment
	3	--	3	--	540-680	-- - --	633	--	POTW*
Builders' Paper and	9	--	9	--	930-14 000	-- - --	7 559	--	POTW
Roofing Felt	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	5	2	0-660	0-18	207	6	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Tissue Papers	6	6	3	0	39-75	0 - --	53	0	Biological Treatment
Non-integrated-Paperboard	6	6	5	0	0-1 800	0 - --	748	0	Biological Treatment
Integrated-Miscellaneous	12	12	8	6	0-4 100	0-160	1 029	61	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	1	140-240	0-24	177	8	Primary Treatment
	3	3	0	0	0 - --	0 - --	0	--	Primary w/Holding Pond
131. Dehydroabietic Acid									
Dissolving Kraft	3	3	3	2	300-5 200	0-800	3 500	520	Biological Treatment
Market Bleached Kraft	6	6	6	4	10-560	0-1 000	232	430	Biological Treatment
BCT Bleached Kraft	9	9	9	9	280-1 400	48-310	861	123	Biological Treatment
Alkaline-Fine	9	9	6	6	140-430	3-7	273	5	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	3	330-640	6-15	470	11	Biological Treatment
Bag	6	6	6	6	950-27 600	30-200	7 142	85	Biological Treatment
Semi-Chemical	6	6	6	4	79-230	0-27	168	14	Biological Treatment
Unbleached Kraft and									
Semi-Chemical	6	6	6	6	230-1 000	200-330	607	235	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, *1980*) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
131. Dehydroabietic Acid (Cont'd)									
Dissolving Sulphite Pulp	4	4	4	4	190-1870	6-400	1000	171	Biological Treatment
Papergrade Sulphite	12	12	12	9	2-1300	0-950	464	246	Biological Treatment
Groundwood-Fine Papers	6	6	6	6	28-360	10-50	148	26	Biological Treatment
Deink									
Fine Papers	3	3	3	3	1400-2900	42-62	2267	49	Biological Treatment
Newsprint	3	--	3	--	2600-4800	-- - --	3700	--	POTW
Tissue Papers	3	3	3	3	2200-4700	130-630	3267	343	Partial Final Effluent
	3	3	3	3	1400-2400	180-300	1833	253	Biological Treatment
Tissue from Wastepaper	6	6	6	4	150-840	0-37	372	20	Biological Treatment
	3	3	3	3	220-650	160-300	417	250	Primary Treatment
Paperboard from Wastepaper	15	15	15	12	130-920	15-140	479	55	Biological Treatment
	3	3	3	3	410-530	59-120	467	96	Primary Treatment
Wastepaper-Molded Products	3	3	3	3	340-530	2-170	453	61	Biological Treatment
	3	--	3	--	550-620	-- - --	573	--	POTW
Builders' Paper and	9	--	9	--	670-6000	-- - --	2199	--	POTW
Roofing Felt	3	3	3	3	110-170	60-200	143	117	Primary Treatment
Non-integrated-Fine Papers	6	6	6	6	58-720	17-66	433	45	Biological Treatment
	3	3	3	3	160-660	49-150	483	93	Primary Treatment
Non-integrated-Tissue Papers	6	6	3	3	190-230	85-112	213	98	Biological Treatment
Non-integrated-Filter and	3	3	2	0	0-50	0 - --	33	0	Biological Treatment
Non-woven Papers	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Paperboard	6	6	6	4	110-780	0-180	413	64	Biological Treatment
Integrated-Miscellaneous	12	12	10	9	0-2000	0-310	585	96	Biological Treatment
Non-integrated-Miscellaneous	6	6	6	4	2-400	0-220	174	67	Primary Treatment
	3	3	3	3	10-16	160-270	14	200	Primary w/Holding Pond
132. Isopimaric Acid									
Dissolving Kraft	3	3	3	3	660-1300	160-590	887	380	Biological Treatment
Market Bleached Kraft	6	6	3	3	66-180	230-500	115	407	Biological Treatment
BCT Bleached Kraft	9	9	8	7	0-250	0-86	107	21	Biological Treatment
Alkaline-Fine	9	9	6	3	54-110	0-3	74	1	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	2	78-450	0-10	283	6	Biological Treatment
Bag	6	6	6	3	380-1600	0-32	770	15	Biological Treatment
Semi-Chemical	6	6	6	3	23-48	0-16	34	7	Biological Treatment
Unbleached Kraft and									
Semi-Chemical	6	6	6	6	260-850	140-260	547	187	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	3	15-1760	0-230	774	115	Biological Treatment
Papergrade Sulphite	12	12	6	7	0-230	0-84	62	17	Biological Treatment
Groundwood-Fine Papers	6	6	4	5	0-110	0-6	29	3	Biological Treatment
Deink									
Fine Papers	3	3	3	3	420-900	1-9	587	5	Biological Treatment
Newsprint	3	--	3	--	240-690	-- - --	510	--	POTW
Tissue Papers	3	3	3	3	110-180	14-24	150	18	Partial Final Effluent
	3	3	3	3	120-270	1-20	193	13	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
132. Isopimaric Acid (Cont'd)									
Tissue from Wastepaper	6	6	3	0	21-43	0 - --	32	0	Biological Treatment
	3	3	3	0	13-45	0 - --	28	0	Primary Treatment
Paperboard from Wastepaper	15	15	15	4	12-600	0-15	128	3	Biological Treatment
	3	3	3	1	65-100	0-23	84	8	Primary Treatment
Wastepaper-Molded Products	3	3	3	0	41-56	0 - --	48	0	Biological Treatment
	3	--	3	--	80-120	-- - --	94	--	POTW
Builders' Paper and	9	--	9	--	160-3000	-- - --	1 164	--	POTW
Roofing Felt	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	6	0	8-140	0 - --	39	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Tissue Papers	6	6	3	1	23-46	0-6	37	2	Biological Treatment
Non-integrated-Paperboard	6	6	6	0	8-190	0 - --	62	0	Biological Treatment
Integrated-Miscellaneous	12	12	8	6	0-1400	0-77	374	31	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	2	69-110	0-22	84	11	Primary Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary w/Holding Pond
133. Pimaric Acid									
Dissolving Kraft	3	3	3	3	970-1900	620-790	1 357	710	Biological Treatment
Market Bleached Kraft	6	6	3	3	120-200	320-530	157	430	Biological Treatment
BCT Bleached Kraft	9	9	7	6	0-350	0-74	115	22	Biological Treatment
Alkaline-Fine	9	9	6	0	20-93	0 - --	63	0	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	1	38-51	0-3	43	1	Biological Treatment
Bag	6	6	6	6	420-2500	10-60	1 168	32	Biological Treatment
Semi-Chemical	6	6	4	2	0-130	0-13	36	4	Biological Treatment
Unbleached Kraft and									
Semi-Chemical	6	6	6	6	37-370	39-190	152	106	Biological Treatment
Dissolving Sulphite Pulp	4	4	3	3	180-450	20-38	277	31	Biological Treatment
Papergrade Sulphite	12	12	2	1	0-64	0-52	25	17	Biological Treatment
Groundwood-Fine Papers	6	6	3	1	31-150	0-15	76	5	Biological Treatment
Deink									
Fine Papers	3	3	3	0	92-160	0 - --	127	0	Biological Treatment
Newsprint	3	--	3	--	220-310	-- - --	257	--	POTW
Tissue Papers	3	3	3	0	31-52	0 - --	39	0	Partial Final Effluent
	3	3	3	0	36-160	0 - --	80	0	Biological Treatment
Tissue from Wastepaper	6	6	3	0	2-18	0 - --	12	0	Biological Treatment
	3	3	3	0	19-78	0 - --	43	0	Primary Treatment
Paperboard from Wastepaper	15	15	11	0	0-210	0 - --	78	0	Biological Treatment
	3	3	3	0	35-48	0 - --	41	0	Primary Treatment
Wastepaper-Molded Products	3	3	3	0	48-64	0 - --	57	0	Biological Treatment
	3	--	0	--	0 - --	-- - --	0	--	POTW
Builders' Paper and	9	--	9	--	130-1600	-- - --	576	--	POTW
Roofing Felt	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	5	0	0-40	0 - --	19	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
133. Pimaric Acid (Cont'd)									
Non-integrated-Tissue Papers	6	6	2	0	0-15	0 - --	10	0	Biological Treatment
Non-integrated-Paperboard	6	6	3	0	22-29	0 - --	25	0	Biological Treatment
Integrated-Miscellaneous	12	12	4	4	0-1 300	0-48	384	25	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	0	40-65	0 - --	54	0	Primary Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary w/Holding Pond
134. Oleic Acid									
Dissolving Kraft	3	3	3	2	3 000-4 500	0-810	3 667	333	Biological Treatment
Market Bleached Kraft	6	6	6	6	250-520	22-250	345	153	Biological Treatment
BCT Bleached Kraft	9	9	7	4	0-2 900	0-92	1 084	17	Biological Treatment
Alkaline-Fine	9	9	6	6	16-970	15-130	276	41	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	3	160-500	4-65	337	38	Biological Treatment
Bag	6	6	6	3	1 700-6 700	0-150	3 133	70	Biological Treatment
Semi-Chemical	6	6	6	4	21-200	0-56	115	33	Biological Treatment
Unbleached Kraft and Semi-Chemical	6	6	6	6	210-1 200	130-800	618	407	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	4	28-1 860	31-120	1 157	81	Biological Treatment
Papergrade Sulphite	12	12	12	12	14-330	13-220	130	76	Biological Treatment
Groundwood-Fine Papers	6	6	6	4	17-450	0-46	174	23	Biological Treatment
Deink									
Fine Papers	3	3	3	3	500-1 200	30-75	967	49	Biological Treatment
Newsprint	3	--	3	--	1 300-1 500	-- - --	1 367	--	POTW
Tissue Papers	3	3	3	3	190-710	470-750	400	590	Partial Final Effluent
	3	3	3	3	310-560	220-280	410	243	Biological Treatment
Tissue from Wastepaper	6	6	6	5	98-270	0-310	183	193	Biological Treatment
	3	3	3	1	81-200	0-74	147	25	Primary Treatment
Paperboard from Wastepaper	15	15	15	10	34-940	0-310	339	78	Biological Treatment
	3	3	3	0	180-450	0 - --	290	0	Primary Treatment
Wastepaper-Molded Products	3	3	3	3	460-540	5-80	493	48	Biological Treatment
	3	--	3	--	340-360	-- - --	353	--	POTW
Builders' Paper and Roofing Felt	9	--	9	--	830-3 500	-- - --	2 237	--	POTW
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	3	0	55-80	0 - --	65	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Tissue Papers	6	6	6	4	4-290	0-61	136	27	Biological Treatment
Non-integrated-Paperboard	6	6	3	0	250-270	0 - --	260	0	Biological Treatment
Integrated-Miscellaneous	12	12	11	5	0-1 900	0-230	450	38	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	2	48-68	0-13	55	8	Primary Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary w/Holding Pond
135. Linoleic Acid									
Dissolving Kraft	3	3	3	1	2 200-3 900	0-510	2 900	170	Biological Treatment
Market Bleached Kraft	6	6	6	4	220-2 300	0-100	792	53	Biological Treatment
BCT Bleached Kraft	9	9	6	0	180-1 300	0 - --	762	0	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
135. Linoleic Acid (Cont'd)									
Alkaline-Fine	9	9	3	3	170-470	2-7	283	4	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	0	150-270	0 - --	203	0	Biological Treatment
Bag	6	6	6	0	610-1 700	0 - --	958	0	Biological Treatment
Semi-Chemical	6	6	3	3	66-160	13-17	122	14	Biological Treatment
Unbleached Kraft and Semi-Chemical	6	6	6	3	98-820	0-170	441	59	Biological Treatment
Dissolving Sulphite Pulp	4	4	3	1	240-1 000	0-25	510	8	Biological Treatment
Papergrade Sulphite	12	12	9	4	8-270	0-160	63	34	Biological Treatment
Groundwood-Fine Papers	6	6	3	3	180-620	11-150	337	72	Biological Treatment
Deink									
Fine Papers	3	3	3	0	260-650	0 - --	470	0	Biological Treatment
Newsprint	3	--	3	--	160-1 200	-- - --	750	--	POTW
Tissue Papers	3	3	3	0	38-86	0 - --	55	0	Partial Final Effluent
	3	3	3	0	74-320	0 - --	178	0	Biological Treatment
Paperboard from Wastepaper	15	15	5	0	0-87	0 - --	63	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Wastepaper-Molded Products	3	3	3	0	170-240	0 - --	207	0	Biological Treatment
	3	--	3	--	110-150	-- - --	123	--	POTW
Builders' Paper and	9	--	8	--	0-3 600	-- - --	897	--	POTW
Roofing Felt	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	1	0	0-200	0 - --	67	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Non-integrated-Filter									
Non-woven Papers	3	3	0	1	0 - --	0-9	0	3	Biological Treatment
Integrated-Miscellaneous	12	12	7	1	0-830	0-6	290	1	Biological Treatment
Non-integrated-Miscellaneous	6	6	2	0	0-77	0 - --	33	0	Primary Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary w/Holding Pond
136. Linolenic Acid									
Market Bleached Kraft	6	6	1	0	0-210	0 - --	70	0	Biological Treatment
Alkaline-Fine	9	9	3	0	42-93	0 - --	71	0	Biological Treatment
Unbleached Kraft									
Bag	6	6	3	0	670-3 170	0 - --	1 543	0	Biological Treatment
Semi-Chemical	6	6	3	3	54-140	31-39	98	35	Biological Treatment
Papergrade Sulphite	12	12	5	0	0-130	0 - --	58	0	Biological Treatment
Groundwood-Fine Papers	6	6	3	0	120-480	0 - --	250	0	Biological Treatment
Deink									
Fine Papers	3	3	3	3	85-330	79-120	212	99	Biological Treatment
Newsprint	3	--	3	--	< 100-< 200	-- - --	167	--	POTW
Paperboard from Wastepaper	15	15	3	1	55-83	0-14	69	5	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
Builders' Paper and	9	--	3	--	84-170	-- - --	138	--	POTW
Roofing Felt	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
137. Epoxystearic Acid									
Dissolving Sulphite Pulp	3	3	3	0	800-850	0 - --	817	0	Biological Treatment
Unbleached Kraft and Semi-Chemical	6	6	3	2	99-380	0-190	266	113	Biological Treatment
Papergrade Sulphite	12	12	1	1	0-120	0-20	40	7	Biological Treatment
Paperboard from Wastepaper	15	15	3	0	310-490	0 - --	413	0	Biological Treatment
	3	3	0	0	0 - --	0 - --	0	0	Primary Treatment
139. Chlorodehydroabietic Acid									
Dissolving Kraft	3	3	3	3	1 300-1 600	330-700	1 433	473	Biological Treatment
Market Bleached Kraft	6	6	4	3	0-120	0-140	50	42	Biological Treatment
BCT Bleached Kraft	9	9	5	5	0-190	0-31	78	11	Biological Treatment
Alkaline-Fine	9	9	9	0	2-240	0 - --	44	0	Biological Treatment
Semi-Chemical	6	6	0	3	0 - --	4-18	0	9	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	3	45-360	0-241	161	108	Biological Treatment
Papergrade Sulphite	12	12	6	3	8-340	0-93	123	39	Biological Treatment
Deink Fine Papers	3	3	3	0	330-730	0 - --	467	0	Biological Treatment
Tissue Papers	3	3	3	2	18-28	0-26	24	14	Partial Final Effluent
	6	6	0	3	0 - --	0 - --	0	0	Biological Treatment
Integrated-Miscellaneous	12	12	4	1	0-84	0-3	33	1	Biological Treatment
140. Dichlorodehydroabietic Acid									
Market Bleached Kraft	6	6	3	3	30-86	11-65	57	39	Biological Treatment
BCT Bleached Kraft	9	9	2	1	0-15	0-4	3	1	Biological Treatment
Alkaline-Fine	9	9	2	0	0-32	0 - --	6	0	Biological Treatment
Semi-Chemical	6	6	0	2	0 - --	0-30	0	13	Biological Treatment
Dissolving Sulphite Pulp	4	4	1	0	0-280	0 - --	93	0	Biological Treatment
Papergrade Sulphite	12	12	3	1	0-5	0-3	2	1	Biological Treatment
Deink Fine Papers	3	3	2	0	0-12	0 - --	6	0	Biological Treatment
Integrated-Miscellaneous	12	12	1	0	0-5	0 - --	2	0	Biological Treatment
141. Trichloroguaiacol									
Market Bleached Kraft	6	6	3	0	15-21	0 - --	18	0	Biological Treatment
BCT Bleached Kraft	9	9	1	0	0-1	0 - --	1	0	Biological Treatment
Alkaline-Fine	9	9	4	1	0-9	0-2	4	1	Biological Treatment
Dissolving Sulphite Pulp	4	4	1	0	6 - --	0 - --	6	0	Biological Treatment
Papergrade Sulphite	12	12	3	2	2-6	0-2	4	1	Biological Treatment
Deink Fine Papers	3	3	2	3	0-28	10-17	14	14	Biological Treatment
142. Tetrachloroguaiacol									
Market Bleached Kraft	6	6	6	0	4-23	0 - --	11	0	Biological Treatment
BCT Bleached Kraft	9	9	6	1	2-17	0-1	8	1	Biological Treatment
Alkaline-Fine	9	9	9	5	4-17	0-8	7	3	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
142. Tetrachloroguaiacol (Cont'd)									
Dissolving Sulphite Pulp	4	4	1	1	4 - --	2 - --	4	2	Biological Treatment
Papergrade Sulphite	12	12	1	0	0-2	0 - --	1	0	Biological Treatment
Deink									
Fine Papers	3	3	3	3	4-16	6-13	8	9	Biological Treatment
143. Xylenes									
Alkaline-Fine	9	9	2	0	0-8	0 - --	4	0	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	0	22-44	0 - --	33	0	Biological Treatment
Bag	6	6	3	0	8-10	0 - --	9	0	Biological Treatment
Semi-Chemical	6	6	2	3	0-4	1-3	2	2	Biological Treatment
13. 1,1-Dichloroethane									
Papergrade Sulphite	12	12	3	0	5-22	0	12	0	Biological Treatment
21. 2,4,6-Trichlorophenol									
Market Bleached Kraft	6	6	6	6	1-26	3-6	11	5	Biological Treatment
BCT Bleached Kraft	9	9	8	1	0-21	0-2	8	1	Biological Treatment
Alkaline-Fine	9	9	9	7	3-23	0-8	11	3	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	4	7-15	1-7	11	5	Biological Treatment
Papergrade Sulphite	12	12	6	6	10-370	2-270	181	106	Biological Treatment
Deink									
Fine Papers	3	3	2	1	0-16	0-21	7	7	Biological Treatment
Tissue Papers	3	3	3	3	29-65	39-43	48	41	Partial Final Effluent
	3	3	0	0	0	0	0	0	Biological Treatment
Paperboard from Wastepaper	15	15	5	2	0-5	0-6	2	1	Biological Treatment
	3	3	3	3	270-420	420-450	360	430	Primary Treatment
Integrated-Miscellaneous	12	12	1	1	0-18	0-3	6	1	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	3	6-30	6-28	18	19	Primary Treatment
	3	3	0	0	0	0	0	0	Primary w/Holding Pond
23. Chloroform									
Dissolving Kraft	3	3	3	3	360-900	40-86	647	67	Biological Treatment
Market Bleached Kraft	6	6	6	6	830-2 200	6-20	1 405	12	Biological Treatment
BCT Bleached Kraft	9	9	9	8	580-4 000	0-11	1 550	6	Biological Treatment
Alkaline-Fine	9	9	9	9	43-1 800	2-110	1 148	52	Biological Treatment
Unbleached Kraft									
Linerboard	3	3	3	0	1-2	0	1	0	Biological Treatment
Semi-Chemical	6	6	3	0	1-4	0	2	0	Biological Treatment
Unbleached Kraft and									
Semi-Chemical	6	6	2	0	0-6	0	3	0	Biological Treatment
Dissolving Sulphite Pulp	4	4	4	4	110-360	1-42	268	13	Biological Treatment
Papergrade Sulphite	12	12	12	12	62-8 600	120-1 200	2 677	433	Biological Treatment
Groundwood-Fine Papers	6	6	6	6	17-240	4-36	99	15	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
23. Chloroform (Cont'd)									
Deink									
Fine Papers	3	3	3	3	670-9 700	95-240	4 190	145	Biological Treatment
Tissue Papers	3	3	3	3	1 000-1 800	48-61	1 367	55	Partial Final Effluent
Newsprint	3	--	3	--	1	--	1	--	POTW
	3	3	3	3	12-46	2-10	25	5	Biological Treatment
Tissue from Wastepaper	6	6	1	0	0-9	0	3	0	Biological Treatment
	3	3	0	1	0	0-1	0	1	Primary Treatment
Paperboard from Wastepaper	15	15	11	3	0-40	0-20	15	4	Biological Treatment
	3	3	0	0	0	0	0	0	Primary Treatment
Builders' Paper and	9	--	3	--	2-21	--	10	--	POTW
Roofing Felt	3	3	0	0	0	0	0	0	Primary Treatment
Non-integrated-Fine Papers	6	6	3	3	0-26	0-6	6	3	Biological Treatment
	3	3	3	3	4-9	4-6	7	5	Primary Treatment
Non-integrated-Tissue Papers	6	6	3	3	2-4	4	3	4	Biological Treatment
Non-integrated-Lightweight Papers	3	3	3	3	15-51	2-3	27	3	Biological Treatment
Integrated-Miscellaneous	12	12	4	3	0-1 100	0-14	417	5	Biological Treatment
Non-integrated-Miscellaneous	6	6	3	3	3-15	2-6	8	4	Primary Treatment
	3	3	0	0	0	0	0	0	Primary w/Holding Pond
24. 2-Chlorophenol									
Papergrade Sulphite	12	12	2	3	0-120	21-50	65	27	Biological Treatment
Deink									
Fine Papers	3	3	1	0	0-2	0	1	0	Biological Treatment
31. 2,4-Dichlorophenol									
Market Bleached Kraft	6	6	4	4	0-8	0-8	4	4	Biological Treatment
BCT Bleached Kraft	9	9	4	2	0-4	0-1	2	1	Biological Treatment
Alkaline-Fine	9	9	2	1	0-6	0-5	3	2	Biological Treatment
Dissolving Sulphite Pulp	4	4	2	7	0-4	0-1	2	1	Biological Treatment
Papergrade Sulphite	12	12	6	3	2-220	0-130	103	53	Biological Treatment
Deink									
Fine Papers	3	3	1	1	0-5	0-3	2	1	Biological Treatment
Tissue Papers	3	3	3	2	1-5	0-2	4	1	Partial Final Effluent
	3	3	0	0	0	0	0	0	Biological Treatment
38. Ethylbenzene									
Market Bleached Kraft	6	6	1	0	0-82	0	27	0	Biological Treatment
BCT Bleached Kraft	9	9	0	1	0	0-3	0	1	Biological Treatment
Unbleached Kraft Bag	6	6	3	0	1-2	0	2	0	Biological Treatment
Semi-Chemical	6	6	2	2	0-2	0-2	1	1	Biological Treatment
Groundwood-Fine Papers	6	6	1	0	0-3	0	1	0	Biological Treatment

APPENDIX RANGE OF CONCENTRATIONS OF RESIN ACIDS, FATTY ACIDS AND CHLOROPHENOLS IN UNTREATED AND TREATED WHOLE MILL EFFLUENTS FROM VARIOUS PROCESSES (Dellinger, 1980) (Cont'd)

Toxic Pollutant/Subcategory	Total Number of Samples		Total Number of Detected Analyses		Concentration Range (µg/L)		Average Concentration (µg/L)		Comments
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
38. Ethylbenzene (Cont'd)									
Deink									
Newsprint	3	--	2	--	0-4	--	2	--	POTW
Tissue Papers	3	3	3	0	27-45	0	33	0	Partial Final Effluent
	3	3	0	0	0	0	0	0	Biological Treatment
Tissue from Wastepaper	6	6	3	0	2-74	0	27	0	Biological Treatment
	3	3	1	0	0-5	0	2	0	Primary Treatment
Builders' Paper and	9	--	3	--	1-11	--	5	--	POTW
Roofing Felt	3	3	0	0	0	0	0	0	Primary Treatment
Non-integrated-Tissue Papers	6	6	3	3	54-39 000	36-300	13 081	149	Biological Treatment
Non-integrated-Filter	3	3	1	0	0-2	0	1	0	Biological Treatment
and Non-woven Papers	3	3	0	0	0	0	0	0	Primary Treatment
Non-integrated-Paperboard	6	6	3	2	2-6	0-2	3	1	Biological Treatment
Integrated-Miscellaneous	12	12	1	0	0-2	0	1	0	Biological Treatment
Non-integrated-Miscellaneous	6	6	0	2	0	0-32	0	13	Primary Treatment
	3	3	0	0	0	0	0	0	Primary w/Holding Pond
39. Fluoranthene									
Dissolving Kraft	3	3	1	0	0-7	0	2	0	Biological Treatment
Dissolving Sulphite Pulp	4	4	1	1	0-4	0-1	1	1	Biological Treatment

* POTW = Publicly Owned Treatment Works

Reference

Dellinger, R.W. 1980. Development Document for Effluent Limitations, Guidelines and Standards for the Pulp, Paper and Paperboard and the Builders' Paper and Board Mills. U.S. Environmental Protection Agency Rep. EPA-440/1-80/025-b. Washington, D.C.