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CHARACTERISATION AND FATE OF BLEACHED KRAFT MILL EFFLUENTS FROM A NEW ZEALAND PULP AND PAPER MILL

A thesis submitted in fulfilment
of the requirements for the degree
of

Doctor of Philosophy

at the
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1990

To Meghan

ABSTRACT

The wastewater discharges from the Kinleith mill, a New Zealand integrated bleached kraft pulp and paper mill, were characterised and their treatability assessed.

The chlorination stage bleaching effluents from the mill's second bleach plant [(C30D70)EoDED sequence] contained a group of novel chlorinated compounds. Fourteen compounds were isolated from the effluents by a combination of liquid-liquid extraction, column chromatography, and preparative gas chromatography. Mass spectral and ^{1}H and ^{13}C NMR data showed these compounds to be hydroxylated and/or chlorinated derivatives of *Pinus radiata* monoterpenes. The major compounds were a dichlorobornane and four dichloro-*p*-menthane-1,8-diols. The chlorinated monoterpenes were detected in total concentrations of 1400-12 300 μg L^{-1} [70-600 g air-dried tonne^{-1} (ADT) bleached pulp] and they were the major class of low molecular weight extractable organic compounds present in the chlorination stage effluent. The principal factor determining their formation appeared to be the high concentration of monoterpenes remaining in the *Pinus radiata* brown stock produced in the mill's continuous digester.

The biological activity of the chlorinated monoterpenes was assessed. The chlorinated monoterpene alcohols were base labile with a 94% decrease in concentration being observed within 4 hours at pH 12. The chlorinated monoterpene hydrocarbons exhibited a lesser degree of alkaline lability. Acute toxicity tests on the monoterpene alcohols gave EC_{50} concentrations of 60-200 mg L^{-1}, indicating that these compounds display relatively little toxicity. The monoterpene alcohols were also tested for mutagenicity and genotoxicity. Some of these compounds produced mutagenic and genotoxic responses. An assessment of the bioaccumulation potential of the chlorinated monoterpene alcohols showed them to have log K_{ow} values of 1.37-2.1. Therefore, these compounds are unlikely to exhibit a significant bioaccumulation propensity.

Treatment of the chlorination stage effluents in an aerated lagoon treatment system removed 80% of the chlorinated monoterpene alcohols but only a small fraction of the monoterpene hydrocarbons. It was concluded that these compounds were unlikely to produce significant environmental effects in the recipient.

The mill has two secondary treatment systems. The relative effectiveness of each of these was assessed. The two systems operate in different configurations. Treatment system A, which receives general mill wastewaters and chlorination stage bleaching discharges utilises deep, aerated lagoons and has a 4.5 day retention time. Treatment system B, which receives alkali extraction bleaching wastewaters and foul condensates, uses a lagoon system with a retention time of 51 days.

Detailed chemical analyses of the untreated and treated wastewaters were made. Mass balances were calculated for a range of physical parameters and for specific chlorinated and non-chlorinated organic constituents. Significant differences in the treatability of various constituents were found. In particular, while system A was able to reduce levels of adsorbable organic halide (AOX) by 65%, no significant reduction in AOX occurred in system B. In contrast, system B reduced levels of chloroacetic acids by 84% while system A did not achieve any statistically significant removal of these compounds. The treatablility of chlorophenolic compounds also differed. System A was unable to remove chlorophenols and chloroguaiacols while system B did not reduce levels of chlorocatechols.

The removal of AOX from effluents treated in system A was high compared to published data and an assessment was made of possible mechanisms for the observed AOX removal. Much of this removal took place in a short section (3.3 hr residence time) of the system's main lagoon. The initial AOX decrease in the aqueous phase could be achieved in part by settling of AOX-containing suspended solids from the influent wastewaters. In addition, lime and bacterial solids present in the treatment system were able to adsorb AOX from the influent wastewaters. Only a small proportion of the organic chlorine removed was found in sludges. A mass balance of aqueous and solid phases indicated that over 99% of the removed AOX was mineralised.

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LIST OF ABBREVIATIONS

ADT	air-dried tonne
AOX	adsorbable organic halide
amu	atomic mass unit
BKME	bleached kraft mill effluents
BOD	biological oxygen demand
BP	bleach plant
CI-MS	chemical ionisation mass spectrometry
COD	chemical oxygen demand
CPU	chloroplatinate units
EC_{50}	median effective concentration -c oncentration at which an effect, lethal or sub-lethal, is observed
ECD	electron capture detector
EI-MS	electron impact mass spectrometry
EOX	extractable organic halide
FID	flame ionisation detector
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
ITDS	ion trap detection system
LC_{50}	median lethal concentration - concentration required to cause mortality in half a group of organisms
MS	mass spectrometry/mass spectrum
MW	molecular weight
MWCO	molecular weight cut-off
NMR	nuclear magnetic resonance spectrometry
P no.	Kappa number - measure of amount of lignin in pulp
SD	standard deviation

Chapter One

INTRODUCTION

INTRODUCTION

INTRODUCTION

Ferguson (1990) recently stated:

> "The early 1990s will certainly be a time for emphasis on the environment. With federal and state governments feeling the pressure of growing public concern, stricter legislation will result for most industries. The pulp and paper industry is already being pressed for changes in processes and controls to reduce pollutants to minute levels..."

The pulp and paper industry produces substantial quantities of wastewater. Extensive research over the past twenty years has firmly established that these discharges are capable of causing substantial harmful effects to the environment. The increased environmental awareness of the past decade has forced the pulp and paper industry to initiate further measures to control the quality and quantity of its wastewaters to the recipient. This can be achieved in two ways: a) changes can be made to the processes used to produce pulp and paper and b) external treatment of the wastewaters can be improved. It is clear that a combination of both of these approaches is required. An important prerequisite to making changes of these types is to gain a clear understanding of the current production processes and effluent treatment systems. In this way, improvements in their operation can be quantitatively measured.

The aim of this study was to characterise the discharges from a New Zealand pulp and paper mill and to determine the fate of wastewater constituents in the mill's effluent treatment system. In this chapter the characteristics of the mill are described and the objectives of this study are outlined.

NEW ZEALAND PULP AND PAPER INDUSTRY

The manufacture of pulp and paper is one of New Zealand's largest industries. The production of pulp and paper products has increased from 36 757 tonnes in 1945 to 1 994 213 tonnes in 1989 (Department of Statistics, 1990). In 1989, exports of pulp and paper products were valued at approximately $NZ700 million. Due to a rapid expansion in plantings in the 1960's, increasing quantities of the major pulp wood species, *Pinus radiata*, will become available for use in the 1990s. The country currently has seven pulp and paper mills in operation (Figure 1.1). These mills produce over 1.5 million air-dried tonnes (ADT) of pulp per year (Table 1.1).

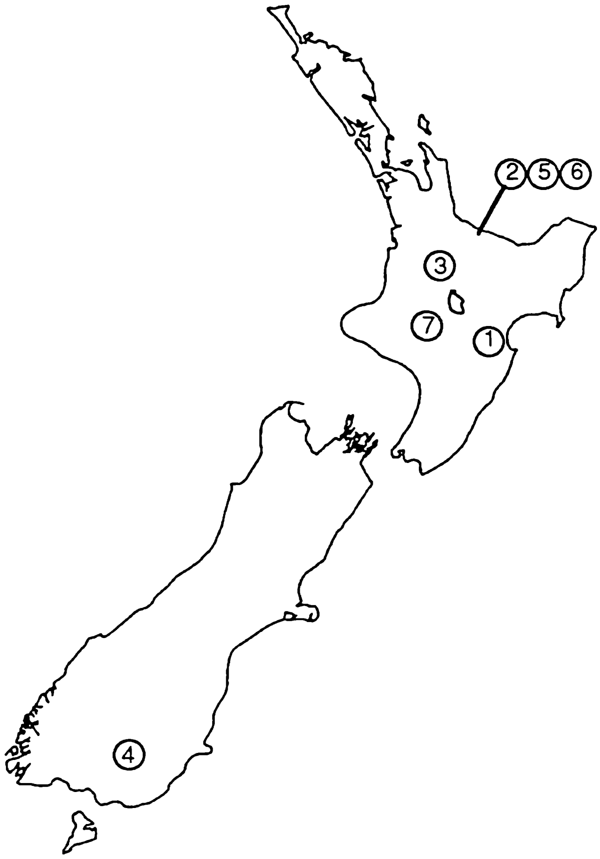

Figure 1.1: Locations of New Zealand pulp and paper mills (see Table 1.1 for identification)

TABLE 1.1: 1990 Pulp Production in New Zealand (PPI, 1990)

company	mill type	processes	total production ADT yr^{-1}
1. Carter Oji Kokusaku Pan Pacific Ltd, Napier	pulp	TMP	215 000
2. Caxton Paper Ltd., Kawerau	pulp and paper	CTMP	72 500
3. NZFP Pulp and Paper Ltd, Kinleith	pulp and paper	kraft, NSSC	420 000
4. NZFP Pulp and Paper Ltd, Mataura	paper	-	24 000
5. NZFP Pulp and Paper Ltd, Whakatane	pulp and paperboard	GW, NSSC, RFP	65 000
6. Tasman Pulp and Paper Co. Ltd., Kawerau	pulp and paper	GW, RMP, kraft	600 000
7. Winstone Pulp International Ltd., Ohakune	pulp	CTMP	125 000
	total pulp production		1 521 500

CTMP - chemi-thermomechanical, GW - groundwood, NSSC - neutral sulphite semi-chemical, RFP - recycled fibre processing, RMP - refiner mechanical pulp, TMP - thermomechanical

KINLEITH PULP AND PAPER MILL

The mill under study in this research, the Kinleith mill of NZFP Pulp and Paper Ltd., was established in 1953. This integrated pulp and paper mill is situated in the centre of the North Island of New Zealand (Figure 1.1). A paper-reprocessing facility and chemical plant are also on site. The mill currently utilises approximately two million cubic metres of wood annually from its own *Pinus radiata* plantations plus small quantities of native hardwood (*Beilschmeldia tawa*).

Three pulp lines operate at the Kinleith mill to produce kraft pulp and a smaller amount of semi-chemical pulp. The No.1 pulp mill has six kraft batch digesters producing approximately 600 ADT d^{-1}. The No.2 pulp mill is a Kamyr kraft continuous digester with a capacity of 650 ADT d^{-1}. The No.3 pulp mill is a continuous digester using neutral sulphite, semi-chemical pulping to produce approximately 200 ADT d^{-1}.

Approximately 40% of the kraft pulp produced at the Kinleith mill is bleached in the mill's two bleach plants. The chemicals necessary for bleaching are produced on site in chlorine, chlorine dioxide and chlorate plants. The No.1 bleach plant bleaches a mixture of batch-digested softwood (*Pinus radiata*) and hardwood (*Beilschmeldia tawa*) pulps (typically 25% hardwood). It uses a CEHDP bleaching sequence and drum pulp washers. Production for this bleach plant is 100-150 ADT d^{-1}. Water use is approximately 90 m^3 ADT^{-1} and 55 m^3 ADT^{-1} for the chlorination and alkaline extraction stages respectively.

Continuously-digested softwood kraft pulp from the No.2 pulp mill is bleached in the mill's No.2 bleach plant. This plant has a (C70D30)E_ODED bleaching sequence with counter-current washing. Diffuser washers are used in all post-chlorination stages. Production for this bleach plant is 160-300 ADT d^{-1}. Water use is approximately 48 m^3 ADT^{-1} and 12 m^3 ADT^{-1} for the chlorination and alkaline extraction stages respectively. Oxygen delignification will soon be added to this bleach plant.

Effluent Treatment

The Kinleith pulp and paper mill produces up to 180 ML d^{-1} of effluent. This arises from process discharges such as debarking, pulp washing and screening, bleaching, paper-making and cooling waters. Non-process discharges such as pulp mill spills and stormwater can also be major contributors to mill discharges. Three wastewater streams are discharged from the mill for treatment in two separate biological treatment systems (Figure 1.2).

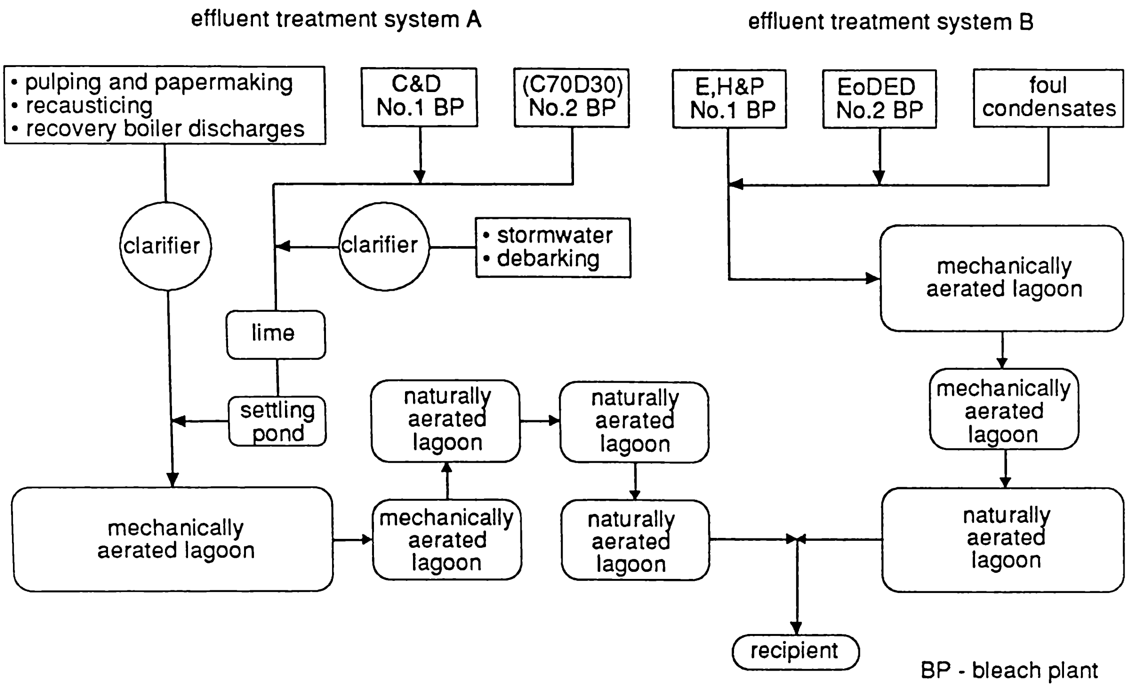

Figure 1.2: Schematic of Kinleith pulp and paper mill effluent treatment systems

Treatment System A

General mill wastewaters, with a flow rate of approximately 120 ML d^{-1}, are discharged via the No.1 sewer where they undergo primary screening and clarification prior to treatment in system A. Sludge removed at the clarifier is sent to one of two sludge ponds and then, after drying, to landfill. Leachate from the landfill also enters system A. This system consists of a 540 ML, mechanically-aerated, 20 m deep lagoon and four smaller lagoons aerated in series. The main lagoon has an average retention time of 3.4 days and receives 510 kW of aeration and mixing from fifteen fixed and floating mechanical aerators. Details of this lagoon are given in Table 1.2. The remaining lagoons have a total retention time of approximately one day. The first of these lagoons has 32 kW of mechanical aeration, whilst the others rely on natural re-aeration from spillways. From the mill site to the receiving waters, the effluent travels over 15 km and drops almost 200 m in elevation. Treated effluent from this system flows into a natural stream and is then discharged into a freshwater hydro-electric lake.

Chlorination stage bleaching effluents and settled stormwater and debarking effluents, with a combined flow rate of 45 ML d^{-1}, are discharged via the No.3 acid sewer. They are partially neutralised by passage over a bed of limerock fines before joining the general mill wastewaters at the head of treatment system A (Figure 1.2).

TABLE 1.2: Comparison of Main Lagoons in Kinleith Treatment Systems

parameter	system A	system B	
		AL*	SL*
volume, ML	550	277	230
depth, m	16	3	3
hydraulic retention time, d	3.4	28	23
mechanical aeration, kW	510	260	0
volatile suspended solids, mg L^{-1}	57	50	50
dissolved oxygen content, mg L^{-1}	0.4	1.2	0.2
BOD$_5$ removal, tonne d^{-1}	7.5	2.6	1.6
BOD$_5$ removal, %	70	45	12.5
COD removal, %	49	25	
temperature (Winter-Summer), °C	26-31	11-20	
pH	7.4	8.2	
effluent origin	pulp and paper mill, debarking, stormwater, chlorination stage	extraction stage, foul condensates	

* AL, SL - aerated lagoons and storage lagoon respectively.

Treatment System B

Alkali extraction stage bleaching effluents, total flow 9 ML d^{-1}, and foul condensates, 2 ML d^{-1}, are segregated from the other mill wastewaters and discharged via the No.2 alkali sewer. These wastewaters are treated in treatment system B (Figure 1.2). This system consists of two lagoons, which receive a total of 260 kW mechanical aeration, and a naturally-aerated storage lagoon giving a total retention time of approximately 51 days. Details of these lagoons are given in Table 1.2. Effluent from this system joins that from system A prior to discharge to the recipient.

A ground seepage treatment system was previously operated as part of system B. This system received approximately half of the No.2 alkali sewer effluents. Use of the ground seepage system was discontinued several years ago.

Mill Recipient

Treated effluents, total volume approximately 180 ML, combine with the Kopakorahi Stream to give a total mill discharge to the recipient of approximately 300 ML d^{-1}. The effluents enter Lake Maraetai via the Kopakarahi Arm where an additional 185 kW of mechanical aeration is supplied (Figure 1.3). Lake Maraetai is a hydro-electric lake on the Waikato River. It is 12 km long, with a volume of 68 000 000 m^3 and has a mean annual flow of 207 $m^3 s^{-1}$ (Zuur, 1989a). The lake is considered to be eutrophic (Scrimgeour, 1989). Discharges from the Kinleith mill undergo a 100-fold dilution when mixed in this recipient. Density differences due to salt concentrations and effluent temperature lead to stratification of the discharged mill wastewaters within the lake (Zuur, 1989b). In winter, the wastewater plume enters the lake at the surface whereas in summer it is found at a lower depth.

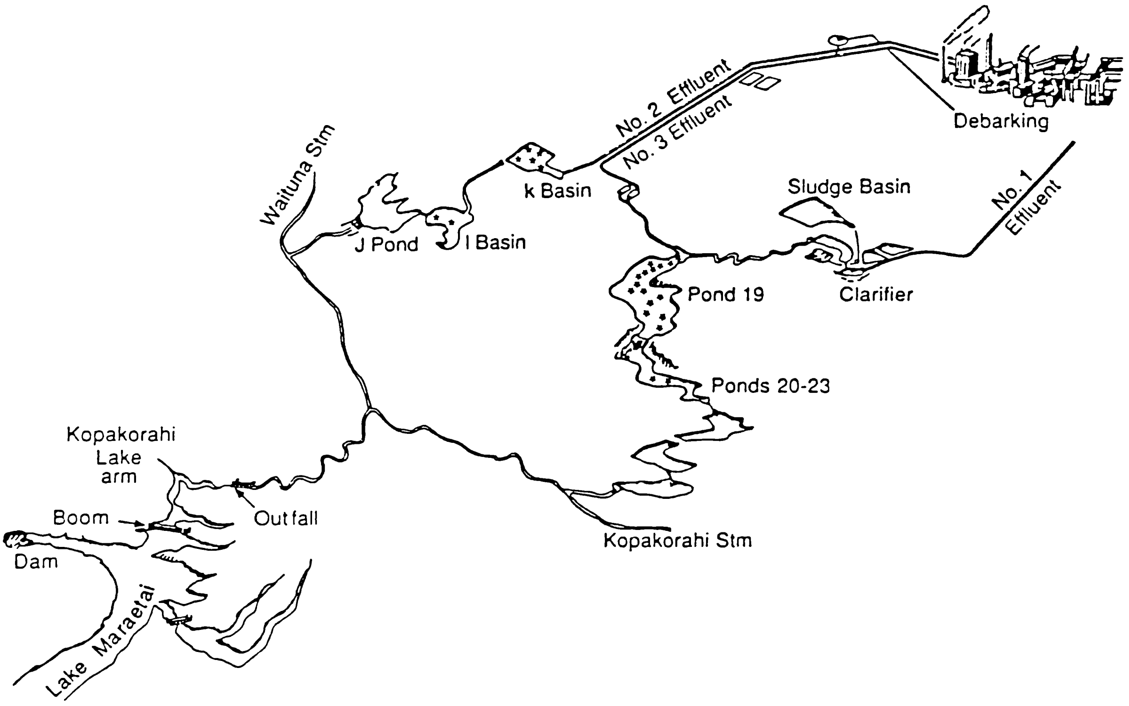

Figure 1.3: Kinleith treatment systems and the recipient

Discharges from the Kinleith mill to Lake Maraetai are regulated by a discharge permit issued in 1971 (WPCC, 1971). The official point of discharge is the Boom situated at the point where the Kopakarahi Arm enters the main body of Lake Maraetai (Figure 1.3). The required standards of purity for wastewaters discharged from the mill into Lake Maraetai are:

i) total ex-site volume of discharge should not exceed 165 ML d^{-1}.
ii) dissolved oxygen should not be less than 5 mg L^{-1}.
iii) pH of wastewaters should be in the range 6.0-8.5.
iv) temperature of recipient waters should not be raised above 24°C.
v) the recipient waters shall not have their colour affected to a conspicuous extent nor shall they be unpalatable or toxic.

The mill has generally complied with the standards controlling dissolved oxygen, pH and temperature (Hoare, 1985). The restrictions on discharge volumes are regularly exceeded (Zuur, 1988). Studies have also shown that the mill effluent produces a conspicuous change in water colour after mixing has occurred in the lake (Zuur, 1989a). A three-fold increase in colour is observed downstream of the Boom and it has been estimated that half of the dissolved colour in the middle Waikato River is derived from Kinleith mill effluent (Zuur, 1989a). Prior to 1982, fish kills occurred approximately once a year in the Kopakorahi Arm and it's vicinity. These events were mostly the result of low dissolved oxygen concentrations in the Arm. Improved management of the system has virtually eliminated this problem. Recent research has shown that the treated effluents exhibit low acute toxicity (McFarlane and Gifford, 1990).

It is expected that the mill's existing water right will be reviewed in the near future. It can be anticipated that the emphasis of the legislation will expanded from the traditional demands on colour, biological oxygen demand (BOD) and pH, and will take into consideration such parameters as AOX, bioaccumulative organics and sub-lethal toxic effects.

OUTLINE OF CURRENT STUDY

Previous Mill Studies

Until recently, the majority of studies concerned with the environmental effects of New Zealand pulp and paper mill effluents, including those of the Kinleith pulp and paper mill, have dealt with the parameters of traditional concern such as oxygen demand, suspended solids, colour and foam (Hoare, 1985; Timperley 1975, 1985; Zuur, 1988, 1989a, 1989b).

A regular monitoring program of the effluent discharges from the Kinleith mill has been undertaken by New Zealand Forest Products Ltd. The effluents are analysed for oxygen demand, solids and sodium losses, and colour. More recent studies have dealt with dioxin emissions from the mill (Campin *et al.*, 1990). The mill has also begun studies to model the performance of Pond 19, the main lagoon in treatment system A (Figure 1.3, Leonard, 1990). The development of a model will allow the mill to optimise and evaluate the performance of the current system, as well as predicting treatment performance under different loadings and configurations.

Studies by Meredith and Davenport (1988), Meredith *et al.* (1988), and Scrimgeour (1989) have examined the effects of the Kinleith pulp and paper mill discharges on the invertebrate and fish communities in the mill recipient. The discharge into Lake Maraetai of treated bleached kraft mill effluent from the Kinleith mill resulted in reduced diversity and altered taxonomic compositions of the macroinvertebrate and fish communities. Fish numbers were 1.5-2.8 times higher in unpolluted sites. Pollution tolerant organisms such as midge larvae, worms, goldfish and rudd dominated in effluent affected sites. The effluent affected regions were considered to be characteristic of heavily polluted sites.

Current Study

In 1987, the author completed a study concerned with Kinleith pulp and paper mill bleaching effluents (Stuthridge, 1987). This research was part of an on-going program begun in 1983 by the Chemistry Department of the University of Waikato. The aim of the research program was to characterise the source effluents from New Zealand kraft pulp and paper mills, determine the fate of effluent constituents in secondary treatment systems, and assess the likely impacts of the treated effluents in the recipient.

Although a great deal of overseas research has been published, it was considered important that this program be undertaken from a New Zealand perspective for the following reasons:

1) The major wood species utilised in the production of pulp and paper in the Northern Hemisphere are Douglas Fir, Western Hemlock, Larch, Spruce and various pines. The predominant pulping species in New Zealand is the softwood, *Pinus radiata*. This species reaches maturity in only 25-30 years - considerably faster than in the Northern Hemisphere. Although overseas studies provide an indication of the likely composition of New Zealand pulp and paper effluents, differences resulting from tree species, growth conditions and process technologies could be expected.

2) The treatability and environmental impacts of bleached kraft mill effluents are very site and system specific. It is not possible to accurately and confidently extrapolate the results from one mill situation to another.

3) Past criteria on the quality of treated effluents have been primarily based on physicochemical parameters, such as BOD, suspended solids and colour. It is becoming increasingly clear that future regulations on the control of pulp and paper discharges would include restrictions on, for example, chlorinated organic compounds, and acute and chronic toxicity. A database on the composition, treatability and impact of these effluents would aid the compliance by the mill to any future legislation. In addition, this information could be used to assess the effects on effluent quality of process modifications and modernisation.

Initial studies of the Kinleith mill undertook to characterise the low molecular weight extractable organic compounds of the mill's pulping effluents (Stuthridge, 1984). Other research sought to determine the fate of resin and fatty acids in effluents discharged to the mill's former ground seepage treatment system (Mills, 1990; Wilkins *et al.*, 1990; Williams, 1986).

Stuthridge (1987) determined the composition of the low molecular weight extractable organic compounds present in the bleaching effluents discharged from the Kinleith pulp and paper mill. Mass spectra were obtained for 276 compounds extracted from chlorination and extraction stage effluents. One hundred and sixty-five of these compounds were positively identified. A comparison of effluents from the mill's two bleach plants showed them to be substantially different in their composition and yields. For example, chlorination and extraction stage effluents from the mill's No.1 bleach plant (CEHDP sequence) had very low levels of chlorophenolic and aromatic compounds. The compositions of the No.2 bleach plant effluents were in accordance with literature reports with one major difference. The effluents contained a series of very high concentration, unidentified, chlorinated organic compounds. These compounds constituted approximately 80% of the total concentration of low molecular extractable organic compounds in the chlorination stage effluents of the No.2 bleach plant.

The current study was instigated as part of the on-going investigation to determine the environmental effects of discharges from a New Zealand integrated pulp and paper mill. The specific aims of this project were:

1) to identify the novel group of chlorinated organic compounds found in the chlorination stage effluents of the mill's second bleach plant.

2) to determine the potential biological effects of these compounds.

3) to undertake a detailed survey of wastewaters entering, within, and leaving the mill's two treatment systems. Data from this survey would be used to determine the treatability of bleached kraft mill effluent constituents in the treatment systems.

4) to examine the mechanisms responsible for the removal of effluent constituents within the treatment systems.

Each of these topics will be addressed in Chapters 4-7 of this thesis. Chapter 2 presents a review of the nature and environmental impacts of bleached kraft mill effluents and Chapter 3 provides general information on methodology. The results obtained during the synoptic survey are presented as an appendix.

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Chapter Two

BLEACHED KRAFT MILL EFFLUENTS AND THE ENVIRONMENT

BLEACHED KRAFT MILL EFFLUENTS AND THE ENVIRONMENT

INTRODUCTION

Papyrus sheets were the most widely used writing material in ancient times. Documents date back to 3600 B.C. Papermaking as we know it was first developed in 105 A.D. by Ts'ai Lun of China, but it did not reach Europe until the twelfth century. Early paper was made from rags, bark fibre and bamboo and paper continued to be produced from rags until the nineteenth century. Wood was not used for the production of paper until 1844 when groundwood pulping was developed. Chemical wood pulping was developed soon after in 1854.

Today, the production of pulp and paper is a major global industry with world pulp production in 1988 estimated to be approximately 161 million tonnes (Uprichard, 1990). As average wastewater discharge volumes range between 80 and 150 m^3 $tonne^{-1}$ of product (Sierra-Alverez, 1990), it is clear that the manufacture of pulp and paper is an important source of pollution.

In this chapter, the nature and environmental impacts of pulp and paper effluents are discussed. Steps which can be taken to minimise these impacts are outlined. A brief discussion on international trends in the legislative controls of pulp and paper industry wastewater discharges is also presented.

WOOD PULPING

Wood Composition

Wood is the major raw material of the pulp and paper industry. It is a complex plant tissue composed of several distinct types of cells. In softwoods, which are coniferous gymnosperms, 90-95 % of the wood volume is composed of highly elongated fibres. In hardwoods, which are woody, dicotyledenous angiosperms, 50 % of the wood is composed of short fibres and the remaining volume consists largely of wider cells called vessel elements. Softwoods, which generally produce higher strength pulps than hardwoods, are the predominant material used in the world pulping industry. In New Zealand the softwood *Pinus radiata* predominates.

Chemically, wood tissue is a composite material constructed from a variety of organic polymers. The four major components are cellulose, hemicelluloses, lignin and extractives (Table 2.1).

TABLE 2.1: Chemical Composition of New Zealand *Pinus radiata* (Uprichard and Lloyd, 1980)

component	% composition
cellulose	42
hemicelluloses	29
lignin	26
extractives	3

Cellulose is the basic skeletal material of all wood fibre cell walls. It is a homopolysaccharide consisting of at least 10,000 1,4-β-linked glucose units. Hemicelluloses serve as matrix substances for the cellulose superstructure. These compounds are heteropolysaccharides which are branched and contain approximately 200 saccharide units. The main hemicelluloses in *Pinus radiata* and other softwoods are galactomannans and arabinoglucuronoxylans (Uprichard and Lloyd, 1980).

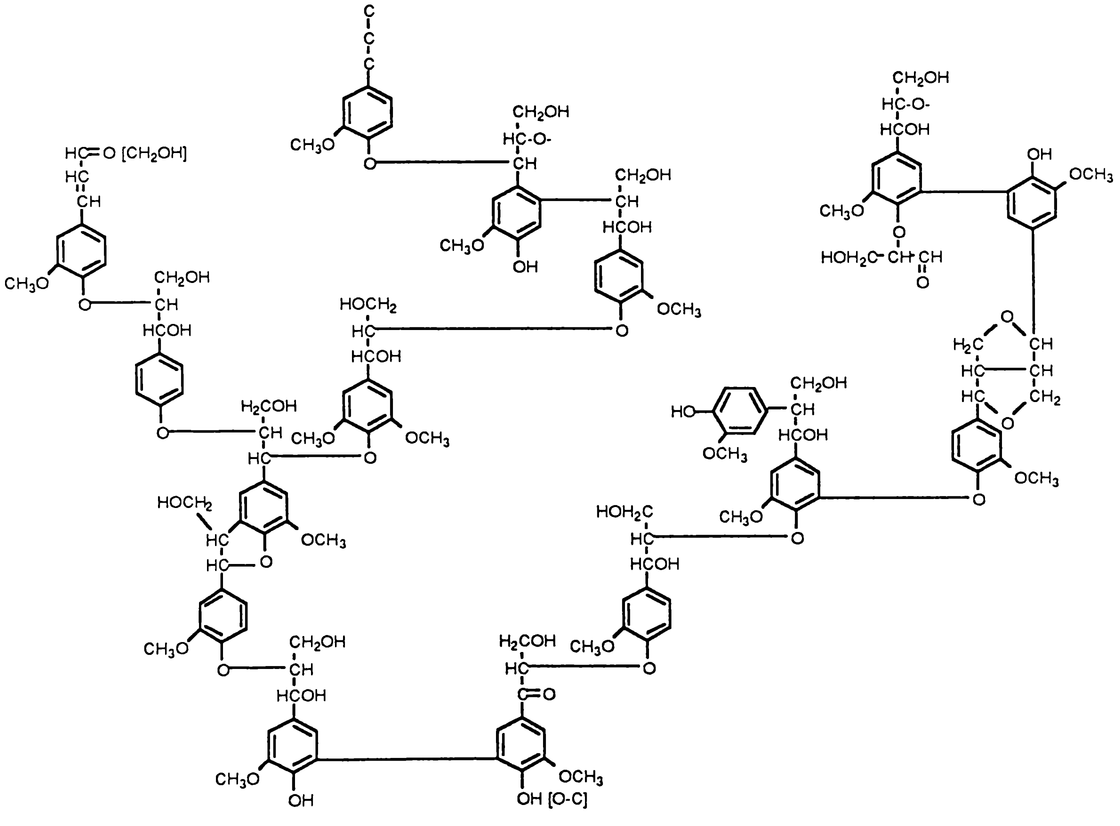


Figure 2.1: Representative structure of softwood lignin (Adler, 1977)

The third major constituent of wood is lignin, an ubiquitous, incrustant substance which permeates both the cell walls and intercellular regions to give wood its structural rigidity. Lignin is a three-dimensional, highly branched aromatic polymer of complex structure and very high molecular weight. In softwoods it is formed by enzyme-initiated polymerisation of coniferyl alcohol and, to a lesser extent, *p*-hydroxycinnamyl alcohol. Guaiacyl groups are the major aromatic units in softwood lignin (Figure 2.1). Hardwood lignin is formed by co-polymerisation of coniferyl and sinapyl alcohols and thus has a significant content of syringyl groups.

Wood extractives are a diverse range of extracellular, low molecular weight, neutral-solvent-extractable organic compounds. Some of the major constituents are fatty acids, fatty acid esters, high molecular weight phenolics, resin acids and monoterpenes. The amount of extractives in the wood plays an important role in the pulping process as they consume pulping chemicals and affect the final quality of the paper. The extractives composition of *Pinus radiata* has been determined by Uprichard and Lloyd (1980). Resin acids and fatty acid esters predominate (Table 2.2). The predominant fatty acids (free and esters) are oleic and linoleic acids (Figure 2.2). Levopimaric acid is the chief resin acid in *Pinus radiata* but a range of other isomers are also found (Figure 2.2). Monoterpenes make up about 0.4% of the wood, the major constituents being α-pinene and β-pinene (Figure 2.2).

TABLE 2.2: Extractives in *Pinus radiata*, % total extractives (Uprichard and Lloyd, 1980)

compounds	heartwood	sapwood
fatty acids (free)	2	1
fatty acids (esters)	11	41
resin acids	71	41
phenols	6	3
unsaponifiables (neutrals)	10	14

Kraft Pulping Processes

The purpose of wood pulping processes is to break down the wood tissue matrix in order to separate the wood fibres. The separated fibre, termed wood pulp, can be used to produce paper and paper-related products. Wood pulping can be achieved in two ways. Firstly, the wood can be disintegrated by the physical action of rotating groundstones or refiners. This process is termed mechanical pulping. Alternatively, chemical pulping uses chemicals to break down the wood matrix. Because it is the predominant pulping process, this review will concentrate upon chemical pulping and its effluents.

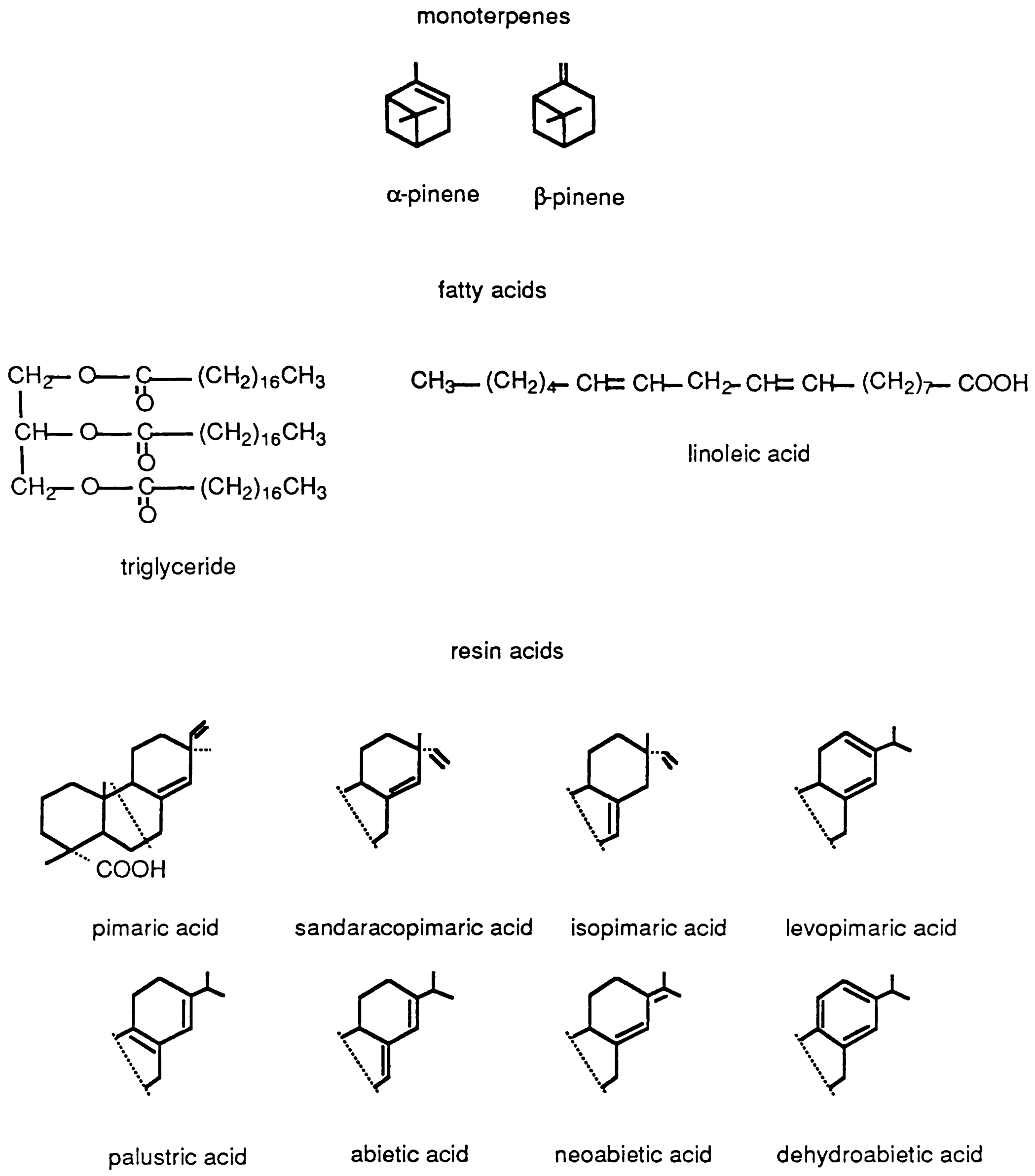


Figure 2.2: Examples of softwood extractives

Chemical pulping aims to selectively remove lignin from the wood matrix with a minimum dissolution of the hemicelluloses and cellulose. Its removal leads to the disintegration of the wood to give free fibres. The two principal chemical pulping processes are sulphite pulping and alkaline pulping. The sulphite process was once a major contributor to chemical pulp production but its use has since declined. The major factors for this decline have been a) pine species cannot be pulped, b) pulp strengths are usually inferior to kraft pulping and c) recovery of spent cooking liquors has been difficult (Jaakko Pöyry, 1989). In New Zealand and throughout the world the predominant chemical wood-pulping method is the kraft or sulphate process (Sierra-Alverez, 1990).

In the kraft process wood chips and the white liquor (typically a 3:1 solution of sodium hydroxide and sodium sulphide) are introduced to a digester (batch or continuous) and cooked at high temperature and pressure (170°C, 800 kPa) (Figure 2.3). After digestion the chips are released to atmospheric pressure whereupon they disintegrate into pulp. The spent cooking solution, named black liquor, contains dissolved organic wood constituents and spent reactant chemicals . The spent black liquor is washed from the pulp and sent through a recovery cycle to regenerate the white liquor (Figure 2.3).

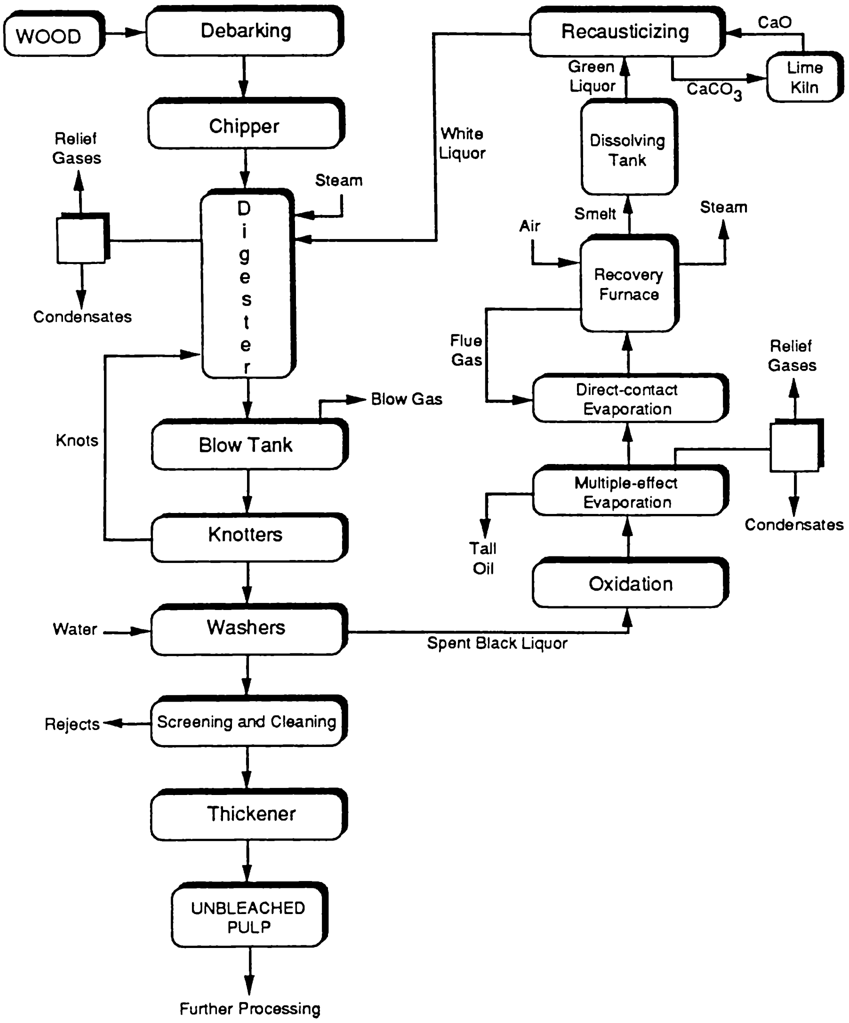


Figure 2.3: Schematic of batch kraft pulping process (adapted from Casey, 1980)

Delignification occurs mainly via the cleavage of alkyl aryl ether bonds in the lignin molecule (Figure 2.1), assisted by neighbouring groups which may be originally present in the native lignin (e.g. phenolic and aliphatic hydroxyl groups) or which are introduced during pulping (e.g. aliphatic thiol and sulphonic acid groups) (Gierer, 1986). These reactions liberate phenolic and glycolic groups, resulting in complete separation of the neighbouring units in the lignin structure and the formation of alkali-soluble, lower-molecular-weight fragments. Although the goal of kraft pulping is to degrade the lignin polymer selectively, alkaline degradation of cellulose and hemicelluloses also occurs leading to the liberation of low molecular weight carbohydrate degradation products (Casey, 1980). In addition, the majority of the wood extractives are removed from the wood matrix during digestion.

Kraft Pulping Effluents

The production of bleached kraft pulp and paper generates large volumes of waste effluents (Figure 2.4). The high efficiency of the kraft recovery process limits discharges from pulping operations to mill spills, condensate losses and debarking wastewaters. Despite this, kraft pulping wastewaters contain a vast range of chemical and physical constituents. They have a substantial BOD and suspended solids content (Figure 2.4). In addition, the wastewaters are generally acutely toxic (McLeay, 1987). Much of this toxicity can be attributed to resin and fatty acids present in the effluents (Leach and Thakore, 1973; McLeay, 1987).

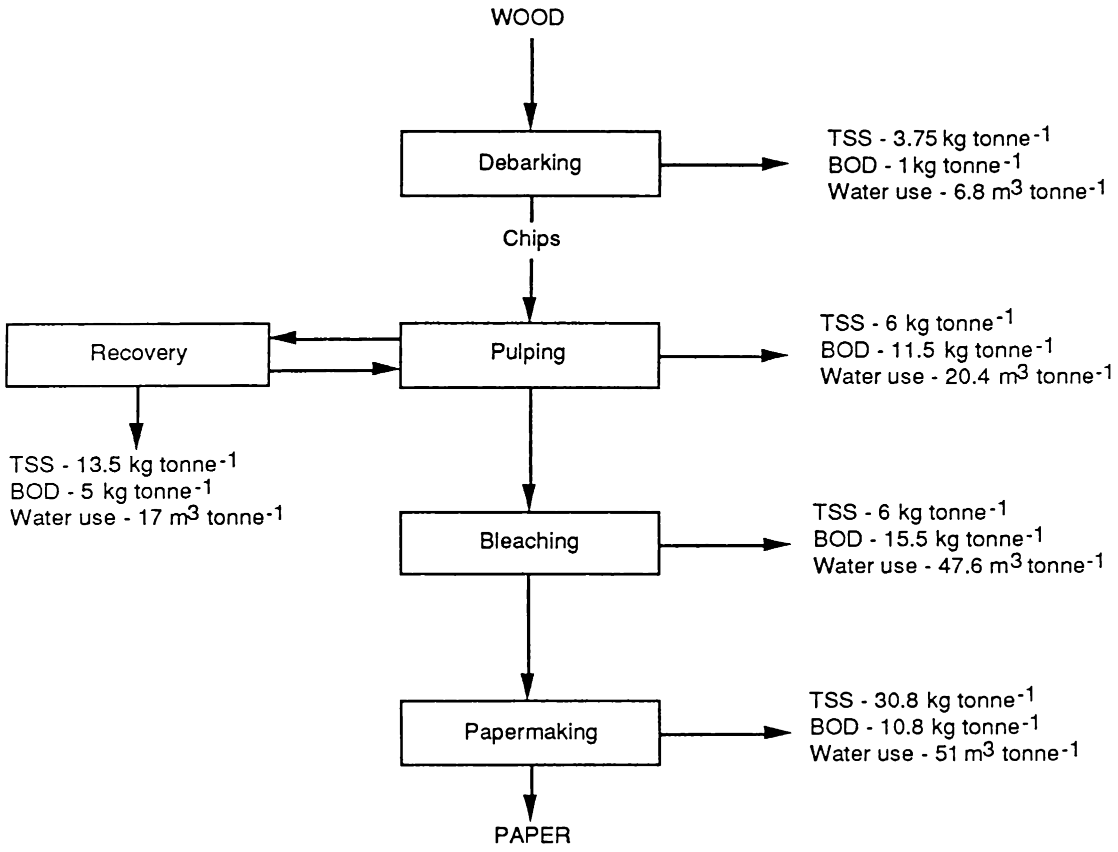


Figure 2.4: Process discharges from kraft pulp and paper production (Springer, 1986)

Kraft pulping effluents contain a wide spectrum of low molecular weight extractable organic compounds. Because of the effects of wood species, pulping and washing conditions, these constituents are found over a broad range of concentrations. Wood extractives, such as monoterpenes and their hydration and isomerisation products (Keranen, 1978), and resin and fatty acids, constitute a major low molecular weight organic component of the wastewaters. These compounds are typically found at mg L^{-1} concentrations (Table 2.3).

TABLE 2.3: Major Extractives in Kraft Pulping Effluents

compound	concentration range, μg L^{-1}	reference
α-pinene	140-6440	a, b, c
β-pinene	10-9060	a, b, c
camphor	60-220	a, b, c, d
isoborneol	60-3070	b, c, d
terpinen-4-ol	80-1650	a, b, c
α-terpineol	50-15 980	a, b, c, d, e
palmitic acid	200-1100	c, e, f
linoleic acid	<20-9300	c, f, g, h
oleic acid	20-7750	c, e, f, g, h
stearic acid	340	f
seco-1-dehydroabietic acid	40	f
seco-2-dehydroabietic acid	18	f
pimaric acid	<20-1010	f, g, h
sandaracopimaric acid	10-320	f, g
isopimaric acid	<20-4800	c, f, g, h
palustric acid	65-1510	f, g, h
dehydroabietic acid	<30-4580	c, f, g, h
abietic acid	<20-4800	c, f, g, h
neoabietic acid	<10-1300	f, g, h

a (Hrutfiord *et al.*, 1975) b (Wilson and Hrutfiord, 1975) c (Stuthridge, 1987)
d (Voss, 1984) e (Turoski *et al.*, 1983) f (Wilkins *et al.*, 1989)
g (Voss, 1987) h (McLeay, 1987)

Degradation of the polymeric lignin to monomeric phenols during pulping produces low molecular weight, lignin-derived phenolic compounds, such as guaiacol, vanillin and 4-hydroxy-3-methoxyacetophenone (Table 2.4).

Many carbohydrate degradation products, such as methanol, sugar acids, and methyl- and hydroxycyclopentenones, are also found in pulping wastewaters (Alén *et al.*, 1985; Blackwell *et al.*, 1979; Niemelä, 1988a; Niemelä, 1988b; Voss, 1984). In addition, the reactions of sulphide ions in the pulping liquor lead to the formation and discharge of significant quantities of sulphur compounds such as methylmercaptans, methylsulphones and thiophenes (Blackwell *et al.*, 1979; Hrutfiord and McCarthy, 1967; Wilson and Hrutfiord, 1971). Inorganic constituents of kraft pulping effluents include high concentrations of sodium and sulphate, and nutrients, such as nitrogen and phosphorus, from wood bark.

TABLE 2.4: Major Phenolic Compounds in Kraft Pulping Effluents

compound	concentration range, $\mu g\ L^{-1}$	reference
guaiacol	100-7350	a, b, c
vanillin	230-670	a, c
acetovanillone	34-320	a, b, c
propiovanillone	60-120	a
vanillic acid	77	b

a (McKague, 1981)
b (Turoski *et al.*, 1983)
c (Stuthridge, 1987)

KRAFT PULP BLEACHING

Bleaching Processes

A small portion of cell wall lignin (5-10%) is retained in the pulp fibres after kraft pulping. It is not possible to remove this by further cooking of the pulp as this results in carbohydrate degradation and consequent losses in pulp yield. As the residual lignin contains chromophores formed during the pulping process, it is necessary to bleach the kraft pulp for its use in high brightness pulp products.

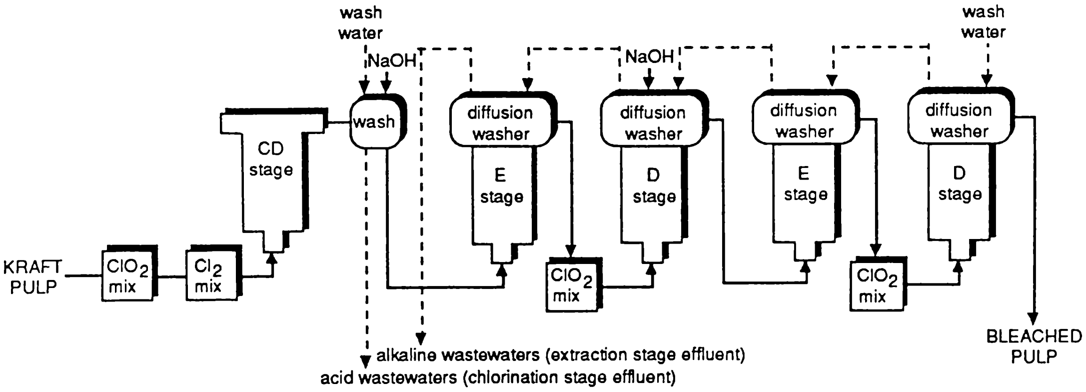


Figure 2.5: Schematic diagram of a typical bleach plant

Currently, the predominant bleaching agent is chlorine. A series of pre-bleaching and bleaching stages are carried out in consecutive steps with an alternation of bleaching (i.e. oxidation) and alkaline extraction steps (Figure 2.5, Table 2.5). Common bleaching sequences are (CD)EHDED, (CD)EDED and (CD)EHD (Sjöström, 1981). The first chlorination and alkaline extraction stages (pre-bleaching stages) remove most of the lignin from the pulp. Subsequent steps in the bleaching process (bleaching stages) bleach residual lignin and carbohydrate chromophores. The bleaching reactions are greatly influenced by the temperature, time of reaction, pH and concentration of reactants. Typical bleaching conditions are given in Table 2.6.

TABLE 2.5: Common Kraft Pulp Bleaching Stages (Casey, 1980)

stage	symbol	description
chlorination	C	chlorine gas or chlorine water
chlorine/chlorine dioxide	(CD)	chlorine + chlorine dioxide, chlorine predominant
chlorine dioxide/chlorine	(DC)	chlorine + chlorine dioxide, chlorine dioxide predominant
alkaline extraction	E	sodium hydroxide solution
oxidative extraction	E_O	inclusion of oxygen in E stage
hypochlorite bleaching	H	sodium or calcium hypochlorite
peroxide bleaching	P	hydrogen peroxide (50% weight solution)
chlorine dioxide bleaching	D	aqueous chlorine dioxide

Pre-bleaching with chlorine depolymerises the residual lignin and makes it more hydrophilic by the introduction of ionisable functional groups such as carboxylic and phenolic groups. The chlorine reacts either as a molecular species or as a radical. As the radicals can lead to significant decomposition of the cellulose, it is common to add chlorine dioxide to the chlorination stage. The chlorine dioxide acts as a radical scavenger and is itself a more selective oxidiser of lignin than chlorine (Hardell and de Sousa, 1977b).

TABLE 2.6: Typical Softwood Kraft Pulp Bleaching Conditions

parameter	C stage	E stage	D stage	H stage
slurry consistency, %	3	10	10-20	10-11
dosage, kg tonne^{-1}	60-70	35-40	3-12	9-11
temperature, °C	15-30	55-70	60-80	30-45
final pH	1.5-2.0	11	3.5-5.0	8-10

Depolymerisation of the lignin takes place primarily by substitution and oxidation (Figure 2.6). Substitution of chlorine onto the aromatic moiety leads to the formation of chlorinated phenolic groups. Oxidation of the aliphatic and aromatic portions of the lignin structure produce water-soluble fragments such as chlorinated acids. Substitution of chlorine into the aliphatic side chain is responsible for the formation of many neutral, chlorinated compounds. In addition, low molecular weight material carried over from the pulping process, such as extractives and black liquor constituents, may also be chlorinated. Under the alkaline conditions of the extraction stage the phenolic hydroxyl and carboxyl groups formed in the chlorination stage are converted to the more soluble hydrophilic salts thereby increasing the solubility of the residual lignin. Over 70% of the substituted chlorine is removed in the extraction stage to give phenolic hydroxyl groups (Figure 2.6).

The organic content of spent bleaching liquors is relatively low (Casey, 1980). This, in combination with their high chloride content, makes recovery of the chemicals in spent bleaching liquors infeasible using current recovery technology.

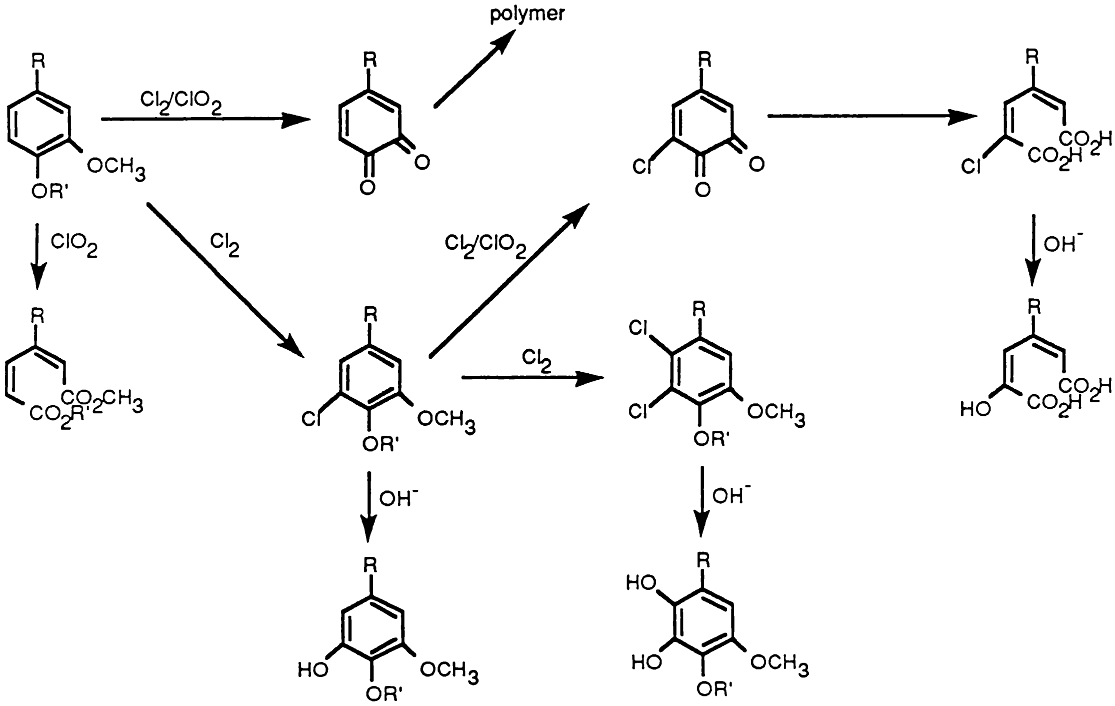


Figure 2.6: Reactions of lignin during bleaching (adapted from Hardell *et al.*, 1977a)

Bleaching Effluents

The organic constituents of bleached kraft mill effluents (BKME) are dominated by chlorinated lignin degradation products (Table 2.7). Extensive demethylation and decarboxylation of guaiacyl units in the residual lignin also produces considerable amounts of methanol and carbon dioxide in the chlorination and extraction stages respectively. The molecular weight distributions of the dissolved organic constituents are markedly different for each bleaching stage (Table 2.7). In chlorination stage effluents 60% of the material is of low molecular weight (MW < 1000). Over 80% of the organic material in extraction stage effluents is of high molecular weight (MW > 10 000).

Because hardwood kraft pulps have a considerably lower lignin content than softwood pulp samples, effluents from hardwood pulp bleaching generally have lower yields of chlorinated organic material (Voss, 1987).

TABLE 2.7: Composition of Organic Material in Chlorination and Extraction Stage Bleached Kraft Mill Effluents (Pfister and Sjöström, 1978; Sjöström, 1981)

component	chlorination stage	extraction stage
total organic material, kg tonne^{-1} pulp	22-24	47-52
chlorinated lignin products, %	67	75
carbohydrates, %	1	5
nonvolatile acids, %	2	4
volatile acids, %	3	3
methanol, %	27	1
carbon dioxide, %	-	12
organic material, MW < 1000, %	60	8-25
organic material, MW > 1000, %	40	75-92
organic material, MW > 10 000, %	<10	80-90

Approximately 10% of the chlorine applied to the pulp in the first bleaching stage is bound to organic matter in the spent bleaching liquors (Table 2.8). A small amount of the applied chlorine is organically bound to the pulp itself and is not removed during the bleaching process. Most of the applied chlorine is discharged as chloride. The use of chlorine dioxide substitution results in high levels of chlorate in the effluents (Germgård, 1989).

TABLE 2.8: Distribution of Applied Chlorine in Bleaching Effluents and Pulp (Pfister and Sjöström, 1979a; Pfister and Sjöström, 1979b)

parameter	chlorination stage		extraction stage	
	kg tonne^{-1}	% in stage	kg tonne^{-1}	% in stage
applied chlorine	64.6	-	-	-
residual chlorine	3.1	5	-	-
chloride in effluent	43.1	67	9.6	64
organically bound chlorine in effluent	3.2	5	3.4	23
organically bound chlorine in pulp	15.2	23	2.0	13

High Molecular Weight Compounds

Chlorination stage and extraction stage effluents differ greatly in the molecular weight distribution of their chlorinated organic material (Lindström and Österberg, 1984; Österberg and Lindström, 1985). In chlorination stage effluents 30% of the organochlorine is found in the low molecular weight organic fraction (MW < 1000) (Figure 2.7). The major portion of organochlorine in extraction stage effluents is found in high molecular weight material (MW > 25 000). Overall, about 80% of the chlorinated organic material present in bleaching effluents is of high molecular weight (i.e. MW > 1000).

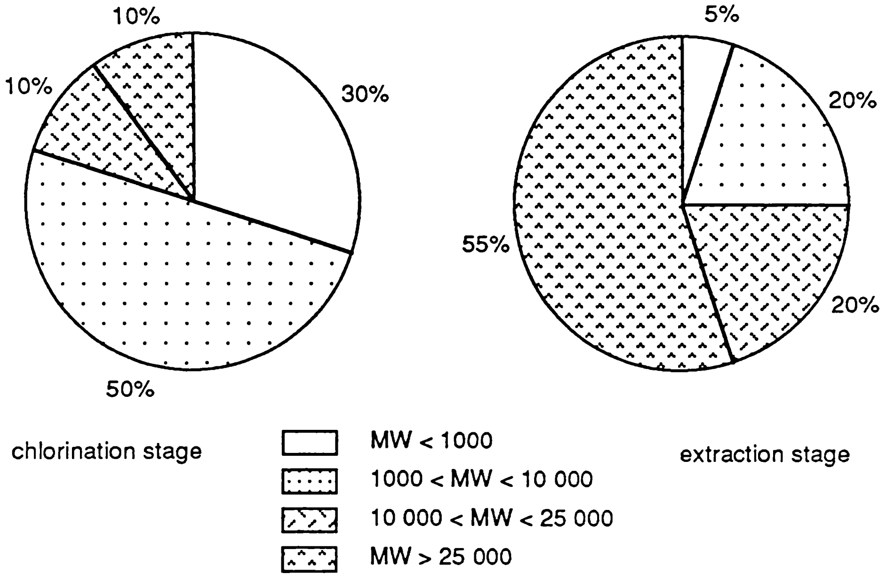


Figure 2.7: Molecular weight distribution of chlorinated material in bleaching effluents (Kringstad, 1984)

The structure of the high molecular weight chlorinated organic constituents in bleaching effluents is still poorly characterised. Much of our current information is based on studies by Lindström and Österberg (1984) and Österberg and Lindström (1985). The material has high carbonyl and carboxyl contents and low methoxyl and phenolic hydroxyl contents relative to that found in unchlorinated lignin. Carbonyl groups conjugated to double bonds and hydroxyl groups attached to aliphatic material are common. Less than 5% of the structure is aromatic with catechol units predominating. Indeed, there is almost a total absence of structures common to native lignin. Chlorine makes up only a small fraction, approximately 10% in both chlorination and extraction stage effluents, of the total mass of high molecular weight material. It appears that the major part of the high molecular weight chlorinated organic material consists of highly cross-linked, unsaturated aliphatic carboxylic acids produced by the oxidative breakdown of lignin phenolic groups during chlorination.

Low Molecular Weight Compounds

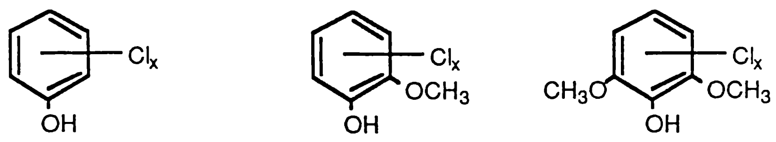
Over the past 20 years the major emphasis of bleach plant effluent characterisation has been focussed on low molecular weight compounds. To date over 300 compounds have been identified. These can be divided into three classes: acids, phenolic compounds, and neutrals. A brief summary of these compounds is given below. A comprehensive tabulation of all compounds identified in bleaching effluents has been compiled by McKague *et al.* (1989).

Over 50% of the organically bound chlorine in the low molecular weight extractable organic fraction of bleaching effluents is associated with acidic compounds (Lindström and Österberg, 1986). Forty five low molecular weight chlorinated and non-chlorinated acidic compounds have been identified (McKague *et al.*, 1989). These cover a broad range of classes including simple aliphatic acids, aromatic acids, dicarboxylic acids, resin and fatty acids, and sugar acids. Examples of these compounds are given in Table 2.9.

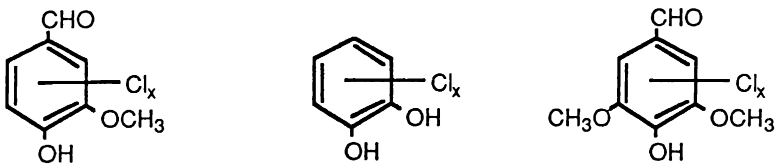
TABLE 2.9: Yields of Selected Chlorinated Acids Formed During Kraft Softwood Pulp Bleaching, (McKague *et al.*, 1989)

compound	chlorination stage g ADT^{-1}	extraction stage g ADT^{-1}
chloroacetic acid	0.3-1	4
dichloroacetic acid	0.2-12	20
trichloroacetic acid	88	5
9,10-epoxystearic acid	-	2-180
dichlorostearic acid	-	0.5-190
chlorodehydroabietic acid (2 isomers)	+	3-70
dichlorodehydroabietic acid	+	3-40

Chlorination of phenolic units in the residual lignin yields chlorophenolic compounds (Figure 2.8). Chlorinated catechols occur primarily in spent chlorination stage effluents, whilst chlorinated phenols, guaiacols and vanillins are found in extraction stage wastewaters (Table 2.10). Chlorophenolic compounds are of particular interest as they are responsible for much of the acute toxicity of softwood bleaching effluents.



chlorophenols chloroguaiacols chlorosyringols



chlorovanillins chlorocatechols chlorosyringaldehydes

Figure 2.8: Major classes of chlorinated phenolic compounds in BKME

Yields of chlorinated phenolic compounds in effluents from the hardwood bleaching are about 20% of those for softwood (Voss *et al.*, 1981a). In addition, the nature of hardwood lignin leads to the formation of chlorinated syringyl derivatives (Figure 2.8)

TABLE 2.10: Yields of Chlorophenolic Compounds Formed During Kraft Softwood Pulp Bleaching, (McKague *et al.*, 1989)

compound	chlorination stage g ADT^{-1}	extraction stage g ADT^{-1}
2,4-dichlorophenol	0.3-1.2	0.4-2.0
2,4,6-trichlorophenol	0.03-1.2	0.5-4
2,3,4,6-tetrachlorophenol	0.03-0.7	0.03-2.3
4,5-dichloroguaiacol	0.5-9	1.0-9.7
3,4,5-trichloroguaiacol	0.02-0.5	0.8-19
4,5,6-trichloroguaiacol	0.04-0.3	0.4-3.7
tetrachloroguaiacol	0.03-8	0.1-40
chlorovanillin (2 isomers)	0.2	2-5.5
5,6-dichlorovanillin	-	1.2-7.1
dichlorocatechol	0.8-17	0.7-2.7
trichlorocatechol (2 isomers)	0.5-16	0.3-3
tetrachlorocatechol	0.2-9.3	0.3-3.1

The dominant neutral constituents of BKME are methanol and hemicelluloses. Chlorinated neutrals are found at lower concentrations and consist of a wide spectrum of compounds such as aldehydes, ketones, and chlorinated sulphur compounds (Table 2.11). Most of the mutagenicity of BKME is due to neutral compounds (Priha and Talka, 1986). As many of the neutral compounds are alkaline labile (Kringstad *et al.*, 1983), substantially lower concentrations of neutral compounds are found in extraction stage effluents.

The neutral compounds of greatest current interest and environmental concern have been the chlorinated dibenzodioxins and dibenzofurans. The polychlorinated dioxins and furans are predominantly formed in the chlorination stage of softwood kraft pulp bleach plants and the most significant factor determining their production is the chlorine charge used (Rappe *et al.*, 1989). The furans are typically found at levels 5-10 times higher than the dioxins (Table 2.11).

TABLE 2.11: Yields of Selected Chlorinated Neutral Compounds Formed During Kraft Softwood Pulp Bleaching, (McKague *et al.*, 1989)

compound	chlorination stage g ADT^{-1}	extraction stage g ADT^{-1}
2-chloropropenal	<0.1-1.9	-
1,1,3-trichloroacetone	0.1-84	-
1,1,3,3-tetrachloroacetone	0.8-96	-
pentachloroacetone	0.3-208	-
hexachloroacetone	0.2-44	-
3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	0.2-0.4	-
3,4-dichloro-5-(dichloromethyl)-5-hydroxy-2(5H)-furanone	5-10	-
1,1-dichlorodimethylsulphone	10-50	-
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	0.24-9.6*	0.06-36*
2,3,7,8-tetrachlorodibenzofuran	2.7-152*	0.56-140*

* µg ADT^{-1}, data converted from Amendola *et al.* (1989) using conversion factors of McKague *et al.* (1989)

ENVIRONMENTAL EFFECTS OF BLEACHED KRAFT MILL EFFLUENTS

The discharge of industrial wastewaters to the recipient can cause environmental stress in two ways. The effluents can cause direct harm to recipient flora and fauna by inducing toxic or mutagenic responses. Alternatively, indirect impacts can arise when the organism's habitat is adversely altered. In this section the properties of BKME which can produce environmental effects are briefly discussed.

Oxygen Demand

The most widely employed measure of the environmental impact of wastewaters has been biochemical oxygen demand (BOD). This is defined as the amount of free oxygen consumed by aerobic microorganisms under specific conditions and over a defined period of time (usually 5 or 7 days, hence BOD_5 and BOD_7) and is a measure of the readily biodegradable material in a wastewater. Discharge of high BOD effluents to the recipient can lead to oxygen depletion with subsequent effects on flora and fauna. Improvements in internal process control have produced a steady decrease in discharges of BOD from bleached kraft pulp and paper mills (Bothnia, 1990). The use of secondary treatment systems has generally lead to the removal of most of the BOD from these wastewaters (Hrutfiord *et al.*, 1975; Skogman and Lammi, 1988).

Suspended Solids

Suspended solids in BKME comprise fibre fragments and other organic and inorganic particles, such as lime and papermaking additives. The discharge of settleable solids into the recipient can lead to the formation of sludge beds on the recipient floor (Springer, 1986). The formation of a sludge layer can alter the composition of benthic life, exert a long term oxygen demand and, as the sludge layer decomposes anaerobically, odour problems and the flotation of sludge can also become a problem.

Recent studies have shown that bleached softwood kraft pulps contain organically bound chlorine at an average concentration of 400 μg Cl g^{-1} (Reeve and Weishar, 1989). Much of this material is highly lipophilic (log $K_{ow} > 4$) and has an average molecular weight of 300-1000 (McKague and Reeve, 1990; Reeve and McKague, 1990). Therefore, bleached pulp fibre losses can contribute recalcitrant, bioaccumulative chlorinated organics to the recipient. Suspended and settleable solids may also adsorb and transport toxic and bioaccumulative organic compounds, such as resin acids and chlorophenolic compounds.

The production of bleached kraft pulp and paper leads to the discharge of significant quantities of suspended solids (Figure 2.4). However, modern mills are able to effectively remove this material from the wastewaters by primary treatment. The two predominant methods are sedimentation and dissolved air flotation.

Colour

Spent bleaching effluents are responsible for much of the colour discharged from kraft pulp mills (Pfister and Sjöström, 1978). Most of the colour is produced in the extraction stages (Table 2.12). The chromophoric material in BKME is principally of high molecular weight. 60-75% and 84-98% of colour has a molecular weight greater than 1000 in the chlorination and extraction stages respectively (Pfister and Sjöström, 1978). For this reason, the colour of BKME has a high degree of chemical and biological stability and persists in secondary treatment systems and the recipient.

Colour discharged into the recipient might produce the following effects (Ramanathan, 1989): i) reduced light penetration and photosynthetic activity, ii) reduced oxygen capacity, iii) accumulation of precipitated coloured bodies in lower-velocity regions causing benthic inhibition, iv) alteration of fish movement and productivity, and v) reduction in aesthetic appeal and increased costs of municipal water treatment.

TABLE 2.12: Colour Formation in Bleaching Effluents (Sjöström, 1981)

bleaching stage	colour kg CPU $tonne^{-1}$
chlorination	7
extraction	138
final bleaching	9
total	154

Colour production during bleaching can be reduced by modifying bleaching processes to use a high percentage of chlorine dioxide substitution, peroxide and ozone or by the introduction of an oxygen delignification stage (Ramanathan, 1989). Physico-chemical treatment of BKME can also be effective in removing colour. Colour removal processes include lime treatment, acid precipitation, adsorption, ion exchange and ultrafiltration (Fitch, 1985; Hynninen and Gullichsen, 1985; Jonsson, 1987; Wagner, 1982). Over 90% of the colour can be removed by these treatments. However, general use of these technologies has not been economically feasible to date.

Toxicity

The toxicity of bleached kraft mill effluents has been the subject of substantial research over the past twenty years. Details of this work are covered extensively in recent reviews (Andersson, 1987; Kovacs, 1988; McLeay, 1987). Toxicity can be defined as any harmful effect to an organism or organisms caused by an effluent. The degree and type of toxicity depends on the concentration of the effluent, the time of exposure and the extent of the elicited response (Kovacs, 1988). Acute and chronic toxicities reflect the exposure time of a toxic effluent to an organism. Acute toxicity is observed over a short-term exposure time lasting 96 hours or less. Chronic toxicity is exhibited over a longer-term exposure time of at least 10% of the organism's life span. Responses to toxicity are usually divided into lethal and sub-lethal effects. Lethal effects lead to the death of the organism whereas sub-lethal effects are more subtle physiological, behavioural and biochemical effects which do not result in immediate mortality but may reduce the organisms ability for long-term survival (Kovacs, 1988). Toxicities of bleached kraft mill effluents are usually determined on the basis of acute lethal and chronic sub-lethal effects.

Acute Lethal Toxicity

Many studies have demonstrated the acute toxicity of untreated bleached and unbleached kraft mill effluents (Holmbom and Lehtinen, 1980; McLeay, 1987; Priha and Talka, 1986; Zanella and Berben, 1980). A wide range of acute lethal toxicities have been reported for these effluents (Table 2.13). Black liquor evaporation and debarking effluents are the major non-bleaching sources of toxicity. In bleaching processes, the greatest contributors of toxicity are the chlorination stage effluents (Holmbom and Lehtinen, 1980; Priha and Talka, 1986).

TABLE 2.13: Typical Ranges of Acute Lethal Toxicities of Kraft Pulp Effluents to Rainbow Trout (Kovacs, 1988)

effluent	96-hour LC_{50}, % v/v	
	untreated	biologically treated
unbleached kraft mill effluents	5 - 100	80 - >100
bleached kraft mill effluents	5 - 75	10 - > 100

The principal acute toxicants in BKME are the resin acids and chlorinated phenolic compounds. Chlorate discharged from pulp bleaching plants utilising chlorine dioxide may also exert a significant toxicity on brown algae in the recipient (Germgård, 1989; Lehtinen *et al.*, 1988; Rosemarin *et al.*, 1986). Of the organic compounds, only the resin acids are usually found at concentrations at or above their acutely toxic levels in untreated effluent (Table 2.14). However, subsequent biological treatment of BKME is also usually able to reduce the concentrations of these compounds to sub-lethal levels. The relative removal of toxicants in aerated lagoons is in the order unsaturated fatty acids > resin acids > chlorinated resin acids > chlorinated phenolics (Chung *et al.*, 1979). The recalcitrance of the chlorophenolic compounds can make their discharge to the recipient of greater concern than the more biologically degradable resin acids. The high molecular weight chlorinated material in BKME is not toxic (Sagfors and Starck, 1988) but its degradation in the recipient may release toxic chlorophenolics (Neilson *et al.*, 1984).

TABLE 2.14: Acute Toxicity of Effluent Constituents to Rainbow Trout (Voss, 1987)

compound	96-hour LC_{50}, mg L^{-1}	concentration in untreated effluent, mg L^{-1}
resin acids	0.5 - 1.5	1 - 5
saturated fatty acids	>20	<1
unsaturated fatty acids	2 - 8	1 - 2
chlorinated resin acids	0.6 - 1.2	< 2
chlorinated phenolics	0.5 - 2.0	< 0.05

Sub-lethal Toxicity

As acute lethal toxicity is in almost all cases removed by effective secondary treatment, much attention has recently been focussed on assessing the longer term chronic sub-lethal toxicity of discharged bleached kraft mill effluents (Andersson, 1987; Kovacs, 1986). Sub-lethal effects may manifest themselves in two ways. The toxicity may exert sub-organism effects which give rise to changes in, for example, blood chemistry, histopathology, respiration, circulation and food chemistry. Alternatively, whole organism changes, such as growth, early life development, reproduction, swimming performance, and avoidance behaviour may be observed. These effects may be observed over a very broad range of threshold concentrations which makes it difficult to ascertain a safe concentration for the discharge of bleached kraft mill effluents (Table 2.15).

TABLE 2.15: Typical Ranges of Sub-lethal Toxicities of Bleached Kraft Pulp Effluents to Freshwater Fish (Kovacs, 1988)

	acute threshold, % v/v		long-term threshold, % v/v	
	whole organism effects	sub-organism effects	whole organism effects	sub-organism effects
untreated BKME	2-32	1.8-47	1- >50	0.65- >28.5
secondary treated BKME	10- >100	32- >100	1-100	1- >57

Significant differences exist in the literature with regard to the sub-lethal effects observed in the recipients of treated BKME. Studies from Canada and the United States have concluded that no serious sub-lethal toxic effects can be expected when treated BKME at concentrations of up to 5-10% volume/volume is discharged to a North American recipient (Burton *et al.*, 1984; Byrd *et al.*, 1986; Davis *et al.*, 1988; Kovacs, 1986). The only anticipated sub-lethal effect of BKME on fish at the concentrations found in the Canadian recipient is tainting of fish flesh (Kovacs, 1986). Similar studies in Australia have also failed to detect any significant short- or long-term effects (Scarlett *et al.*, 1987).

In contrast, Scandanavian studies have found serious sub-lethal effects, such as skeletal deformations, physiological disorders and diseases (e.g., fin rot) at dilutions of 200-1000 fold and over distances of up to 11 km from the mill discharge point (Bengtsson, 1988; Larsson *et al.*, 1988; Lindesjöö and Thulin, 1990; Oikari *et al.*, 1985).

The discrepancies between the Scandanavian results and those from other countries may be due to differences in effluent quality and of the particular ecosystems studied. A study by Procter and Gamble (1989) lists the following factors which may explain these observations:

1) The Swedish recipient, the Baltic Sea, has received a substantial amount of pulp and paper effluent in the past.

2) The Baltic Sea has many sources of pollution, including industrial, municipal and agricultural wastes. These other hazardous wastes may be acting in concert with those from the pulp and paper industry.

3) The Baltic has almost no tidal exchange and hence a low flushing rate. Most other recipients have a significantly greater dilution and dispersion effect.

4) The Gulf of Bothnia has a brackish salinity but no indigenous brackish fish. Marine and freshwater fish may be near the limits of their adaptive capabilities and be susceptible to the effects of pollution.

5) Compared to other recipients, the temperature of the coastal Baltic waters is lower such that slower degradation and greater persistance of BKME constituents may occur.

6) Most North American studies have dealt with effluents which had undergone secondary treatment. Until recently the use of secondary treatment in Scandanavia was relatively limited.

7) Much of the Scandanavian concern with regard to the effects of bleached kraft mill effluents has arisen from the results of a study of the Norssundet mill in the Gulf of Bothnia (Södergren, 1989). There is evidence that at least some of the findings of this study may be atypical due to the unique conditions present at the time of the study.

Mutagenicity

In recent years many investigations have demonstrated the mutagenic activity of bleached kraft mill effluents. Whilst mutagenicity is generally confined to chlorination stage effluents (Hoglund *et al.*, 1979; Kringstad *et al.*, 1981; Priha and Talka, 1986), some studies have found mutagenic activity in extraction stage effluents and kraft weak black liquors (Langi and Priha, 1988; Lee *et al.*, 1981). In chlorination stage effluents the predominant mutagenic compounds are the chloroacetones, 2-chloropropenal and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (Holmbom *et al.*, 1984; Kringstad *et al.*, 1981; McKague *et al.*, 1981). Increased chlorine dioxide substitution in the chlorination stage reduces the formation of these compounds (Kutney *et al.*, 1984; Møller *et al.*, 1986).

The mutagenicity of BKME is decreased rapidly under neutral and alkaline conditions (Eriksson *et al.*, 1979; Kringstad *et al.*, 1983; Wigilius *et al.*, 1985) and is generally eliminated by secondary treatment (Eriksson *et al.*, 1979; Hoglund *et al.*, 1979; Langi and Priha, 1988; Wigilius *et al.*, 1988).

Bioaccumulation

Although their inherent toxicity is low, treated bleached kraft mill effluents are potentially stressful to the aquatic ecosystem because large volumes are discharged to the recipient. Of particular concern are the low molecular weight organic compounds as these may bioaccumulate in the recipient biota. The bioaccumulation potential of organic compounds is directly proportional to their lipophilicity (Mackay, 1982). The partition coefficient of the *n*-octanol-water system, log K_{OW}, has become a useful chemico-physical parameter for characterising the lipophilicity of organic compounds (Xie *et al.*, 1984). It is generally considered that bioaccumulation is an important factor for those compounds having log K_{OW} values of 3 and above (Kringstad *et al.*, 1984). On this basis, the chlorophenolic compounds and resin acids are the compounds of greatest concern in bleached kraft mill effluents (Figure 2.9).

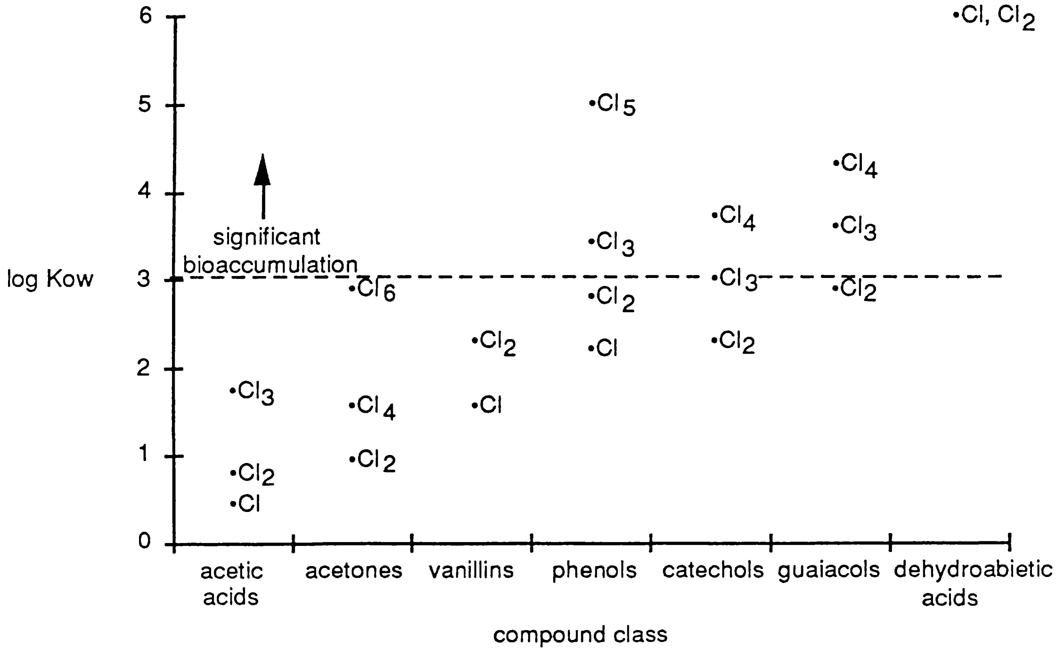


Figure 2.9: Bioaccumulation potentials of selected BKME constituents (data from Bjorndal, 1987)

Bioaccumulation of chlorinated phenolic compounds and resin acids in fish and molluscs has been demonstrated (Landner *et al.*, 1977; Leach *et al.*, 1985; Oikari *et al.*, 1984). The accumulation is greatest in fatty tissues, such as the bile and liver (Landner *et al.*, 1977; Oikari *et al.*, 1984). Analysis of the bile in fish exposed to BKME indicates that the chlorophenolic compounds are metabolised by the liver and stored as bile glucuronic acid conjugates (Oikari *et al.*, 1988). All these compounds show a relatively rapid clearance (days or weeks) from the fish once exposure is ceased (Landner *et al.*, 1977; McLeay, 1987; Seppovaara and Hattula, 1977).

LEGISLATIVE CONTROL OF BLEACHED KRAFT MILL EFFLUENT DISCHARGES

There have historically been three major regulatory strategies for the control of pulp and paper effluent discharges (Gifford and McFarlane, 1990):

1) effluent standards; which specify the end-of-pipe quality of a discharge.

2) receiving water standards; which define quantitative or qualitative minimum standards for the recipient of a discharge.

3) technological standards; which specify a minimum standard of process discharge and wastewater treatment, typically defined by Best Available Technology (BAT).

Each of these strategies has advantages and disadvantages. The use of effluent and technological standards does not take into account the nature and capacity of the recipient into which the effluents are discharged. They are, however, relatively easy to monitor. Receiving water standards are more acceptable as they take into consideration the effects of the effluent on a specific recipient. However, extensive monitoring is required to determine standard compliance. Generally, it is considered desireable to adopt regulations which have a combination of these strategies (Sprague, 1990).

Until the mid 1980s, the emphasis of world-wide BKME discharge legislation was placed on the regulation of conventional pollutants, such as BOD_5 and suspended solids. However, as controls for conventional pollutants have been successfully implemented, for example by the installation of effluent treatment systems, the emphasis of regulation has shifted towards new concerns, such as toxic and chlorinated organic substances in wastewater discharges. A short summary of regulatory controls of toxicity and chlorinated organic compounds is presented below.

Legislative Control of Toxicity

The use of toxicity testing as a control for pulp and paper effluent discharges has developed over the past two decades. Traditionally, toxicity has been regulated on the basis of fish acute lethality. However, there is an increasing awareness of the need for multi-species testing and for the implementation of sub-lethal toxicity controls.

Canadian guidelines for the control of pulp and paper mill effluent toxicity were implemented several decades ago. Currently, Canadian federal toxicity legislation is based upon acute toxicity testing of fish (Sprague, 1990). The regulation specifies that effluent at 65% concentration must not kill more than 20% of the test fish (rainbow trout). This is equivalent to an LC_{50} of >80%.

In Scandanavia, the recent emphasis on regulatory control of BKME has been focussed on controlling the emission of chlorinated organic materials. Sweden and Finland have no toxicity limits for discharges of BKME.

The United States adopted a comprehensive toxicity regulation program in the mid-1980s. These regulations specify both lethal and sub-lethal toxicity requirements (Sprague, 1990). Acute lethal toxicity is controlled by various states in one of three ways : i) the concentration of the effluent at the edge of the mixing zone must not exceed 33% of the LC_{50}, ii) the effluent LC_{50} must be $\geq 100\%$, and iii) mortality must be $\leq 1\%$ in full strength effluent. Effluents are also tested for sub-lethal toxicity using fish, *Daphnia* and algae. The NOEC (no observable effect concentration) of these tests must be higher than the average concentration found at the edge of the mixing zone.

Legislative Control of Organochlorine

In 1986, it was first reported that bleached kraft pulp production could be a significant source of dioxins (Swanson *et al.*, 1988). Since that time the "dioxin problem" has been one of the main driving forces for environmental research in the pulp and paper industry. Much of the progress made in reducing the pollution loadings of bleached kraft mill effluents can be attributed to measures taken to reduce dioxin emissions.

Concerns that other organochlorine compounds might also be of environmental concern has prompted regulatory bodies to seek controls on the discharge of these materials from the pulp and paper industry.

Generic Measurement of Organically Bound Chlorine

As the identification and quantitation of individual chlorinated organic compounds is very time-consuming and complex and because most of the organochlorine material in BKME is of high molecular weight, it has become necessary to obtain a generic measurement of the total chlorinated organic material in wastewaters. Such a parameter can then be used for monitoring and regulatory control of organochlorine discharges.

Three methods have been developed for the generic analysis of chlorinated organic material (Table 2.16). Total Organic Chloride (TOCl) is determined by extracting the organically bound chlorine using XAD resin and ultrafiltration and determining the chlorine content of each recovered fraction by Schöniger combustion and potentiometric titration. This method currently forms the basis for Swedish legislation controlling organochlorine discharges.

The Adsorbable Organic Halide (AOX) procedure mixes granular activated carbon and the sample in a flask to adsorb the chlorinated organic material from the effluent. After washing the carbon with a nitrate solution to displace inorganic chloride, the carbon is pyrolised in

TABLE 2.16: Methods for the Analysis of Organically Bound Chlorine

method	adsorption step	combustion step	detection	reference
TOCl	XAD/ ultrafiltration	Schöniger combustion	potentiometric	Sjöström *et al.* (1981)
AOX	GAC/ shake flask	pyrolysis	microcoulometric	SPPBTC (1989)
TOX	GAC/column	pyrolysis	microcoulometric	APHA (1985)

a furnace and the chloride is determined by microcoulometric titration. The AOX method is rapidly gaining acceptance as a standard method for the analysis of organically bound chlorine and is used in Scandanavia, Europe and Australasia. In Canada and the United States the Total Organic Halogen, or TOX, method is most commonly used. This method is essentially the same as the AOX method with the exception that activated carbon columns are used in the adsorption step.

The advantages of the AOX and TOX methods over the TOCl procedure are i) shorter analysis times, ii) better reproducibilty, iii) lower detection limit and iv) higher recoveries, since the TOCl method loses volatile material and the XAD is a less efficient extractor than GAC (Sjöström *et al.*, 1985).

Current and Future Organochlorine Discharge Regulations

Regulatory controls on chlorinated organic compounds produced during kraft pulp bleaching have been instituted by some countries and are under consideration by others. This trend is prompted by the large variety, toxicity characteristics, and the bioaccumulative nature of many of these compounds. A further concern is the possibility that further undiscovered "dioxin-like" compounds may be present in the effluents. A summary of current and planned organochlorine regulatory limitations is given in Table 2.17.

Although AOX (or TOCl) has been almost universally adopted as a legislative control, some doubts have been raised regarding the applicability of this parameter. The main concerns are:

1) There is no conclusive evidence to link environmental effects to AOX emissions (Department of Ecology, 1990; Fleming *et al.*, 1990; Lehtinen *et al.*, 1990).

2) Only a small proportion of the AOX is of direct environmental significance. Approximately 1% of the total AOX is composed of extractable organic compounds (EOX, Figure 2.10).

TABLE 2.17: Summary of Organochlorine Regulatory Limits (Department of Ecology, 1990; Gifford and McFarlane, 1990)

country	limitation	compliance date
Australia	1.0 kg AOX ADT^{-1} (yearly average)	
Finland	1.5 - 2.0 kg AOX ADT^{-1} (official goal)	
Federal Republic of Germany	1.0 kg AOX ADT^{-1} (bleached sulphite mills)	1990
	(no kraft pulping or elementary chlorine permitted)	
Norway	2 kg AOX ADT^{-1} (bleached kraft mills)	
	1 kg AOX ADT^{-1} (bleached sulphite mills)	
Province of British Columbia,	2.5 kg AOX ADT^{-1}	1991
Canada	1.5 kg AOX ADT^{-1}	1994
Province of Ontario, Canada	$\geq$ 5.0 kg AOX ADT^{-1} (present, without treatment)	
	< 4.5 kg AOX ADT^{-1}(present, with 1° treatment)	
	< 2.5 kg AOX ADT^{-1} (within 1-3 years)	1989-1991
	< 1.5 kg AOX ADT^{-1}	1993
Province of Alberta, Canada	1.5 kg AOX ADT^{-1} (existing bleached kraft mills)	
	1.4 kg AOX ADT^{-1} (new bleached kraft mills)	
	(monthly average values)	
Province of Quebec, Canada	1.5 kg AOX ADT^{-1}	1993
Sweden	1.5 kg TOCl ADT^{-1}	1993
	0.1 kg TOCl ADT^{-1}	2011
United States	1.5 kg AOX ADT^{-1} (proposed limit)	

> This fraction is considered to be representative of the relatively lipophilic, neutral, low molecular weight organic compounds which are of greatest environmental concern. An even smaller fraction of the AOX (0.1 %) is considered to be bioaccumulative. As such, the AOX parameter is "a relatively blunt instrument for monitoring and controlling the discharge of persistant substances that are bioaccumulative and toxic." (Fleming *et al.*, 1990).

Despite these concerns, it is generally agreed that a substantial reduction in the discharge of organically bound chlorine from bleached pulp mills, preferably to the point of zero-emission, must be of benefit to the environment. A large amount of research has been directed towards this aim. Some of the processes developed to reduce the discharge of these constituents are outlined in the following section.

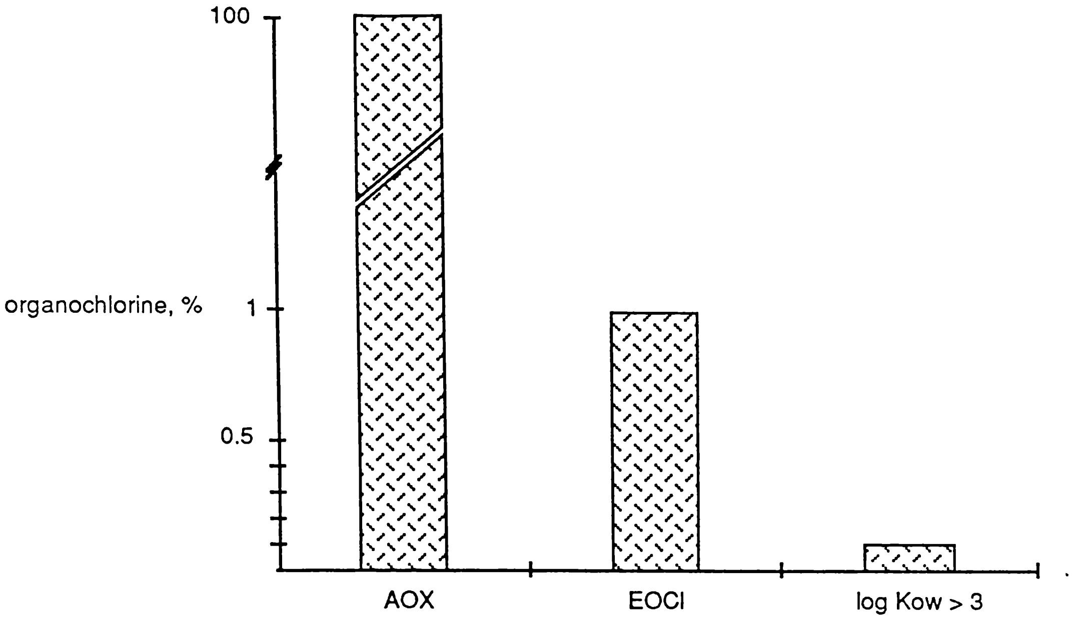


Figure 2.10: Lipophilic fractions of AOX (Martinsen *et al.*, 1988)

REDUCING THE ENVIRONMENTAL IMPACT OF BLEACHED KRAFT MILL EFFLUENTS

Minimisation of Bleaching Effluents at Source

Much of the environmental concern regarding water pollution problems in the pulp industry has focussed on discharges from the chlorine bleaching processes. The ultimate solution to the discharge of bleached kraft mill effluents would be the development of a closed system. Indeed, a closed cycle bleaching process was developed in the 1970s and was tested on an industrial scale in Canada (Teder *et al.*, 1989). Very high operating costs for the process lead to the trial's discontinuation in 1985 (Bothnia, 1990). It is generally agreed that a closed mill capable of meeting the requirements of technical feasibility, pulp quality and production costs is unlikely to be developed before the year 2000 (Teder *et al.*, 1989).

As the formation of chlorinated organic material during pulp bleaching is linearly proportional to the amount of chlorine applied to the pulp (Figure 2.11, Axegård, 1989; Earl and Reeve, 1989), many of the potential environmental effects of BKME could also be greatly reduced if the use of chlorine in bleaching was stopped. However, because of market demands for high brightness papers, it is not yet possible to completely eliminate the use of chlorine in pulp bleaching.

The two most important factors affecting the formation of chlorinated organic material during bleaching are the brownstock kappa number, a measure of the residual lignin content, and chlorine dosage (Heimburger *et al.*, 1988b; McFarlane *et al.*, 1990). The efficiency

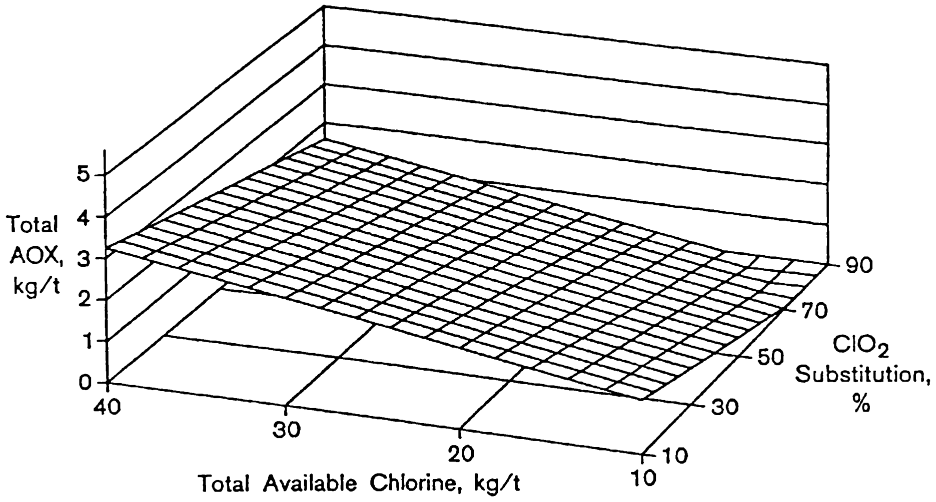


Figure 2.11: Effect of total chlorine dosage and chlorine dioxide substitution on the formation of AOX (Allison *et al.*, 1990)

of brownstock washing also has a major impact on concentrations of chlorinated organics generated in the bleach plant (Nikki and Korhonen, 1983). Implimentation of measures which decrease brownstock kappa number and chlorine dosage can minimise bleaching chemical consumption, decrease bleaching costs and improve bleach plant effluent quality. Examples of these measures are discussed in turn below.

Extended and Oxygen Delignification

Conventional kraft pulping of softwood produces a pulp with a kappa number of 28-32 (Heimburger *et al.*, 1988a). Although the kappa number of the pulps can be further reduced in conventional kraft pulping by longer cooking times or increased chemical doses, excessively poor yields and pulp quality occur. A recent modification to the kraft process, termed extended delignification, has eliminated these restrictions. The two major types of this process are modified continuous cooking (MCC) and rapid displacement heating (RDH). Pulp kappa numbers of 16-18 can be achieved in these processes without significant reductions in pulp quality (Galloway *et al.*, 1989). Presently, these processes are only used in a few mills worldwide.

The process most favoured for enhanced removal of lignin prior to bleaching is oxygen delignification. In this process the pulp is treated with oxygen under alkaline conditions at high temperature and pressure. Using oxygen delignification, it is currently possible to lower kappa numbers to 45-60% of incoming levels (Pulliam, 1989). Subsequent chlorine consumption is reduced by 35% (Ek and Eriksson, 1988). The selectivity of the process can be enhanced by pretreatment of the pulp under acidic conditions with combinations of nitrogen dioxide and oxygen (the Prenox process), ozone, and hydrogen peroxide (Brännland *et al.*, 1986; Simonson *et al.*, 1987).

Introduction of oxygen delignification prior to chlorination of softwood kraft pulp substantially reduces the BOD, COD, colour, AOX, toxicity and low molecular weight chlorinated organics, such as chlorophenolics, in the discharged effluents (Germgård *et al.*, 1985; Idner and Kjellberg, 1989; Soteland and Carlberg, 1987). For example, Tench and Harper (1987) report reductions of 40-55%, 60-75% and 35-50% in oxygen demand, colour and TOCl respectively. Because organic concentrations are higher than those of chlorine bleaching effluents and corrosion problems are minimal, oxygen delignification effluents can be combined with spent kraft cooking liquors and sent through the kraft recovery process. The effectiveness of the subsequent biological treatment of these effluents is also enhanced as a higher percentage of the organic material is of low molecular weight. Until recently, oxygen delignification was practiced primarily in Swedish and Finnish pulp mills (Ek and Eriksson, 1988; Junna and Ruonala, 1990). Its worldwide use has now increased greatly and, by 1988, 47 mills were utilising this technology (Heimburger *et al.*, 1988a).

Chlorine Dioxide Substitution

The increased removal of residual lignin by process modifications prior to bleaching can substantially reduce the amount chlorine required for bleaching. In addition, changes can be made in the bleaching process itself to decrease chlorine consumption. The three process modifications currently in use are 1) high chlorine dioxide substitution, 2) oxidative extraction and 3) use of hydrogen peroxide.

Replacing a high proportion of the chlorine in the chlorination stage with chlorine dioxide (25% or more of the applied chlorine) can achieve substantial reductions in organochlorine (as AOX or TOCl), chlorinated dioxins and furans, and colour (Figure 2.11, Galloway *et al.*, 1989; McFarlane *et al.*, 1990; Pryke, 1989; Voss *et al.*, 1981b). Its effects on other effluent parameters, such as chlorophenolic compounds, oxygen demand, and toxicity are less consistent. Voss *et al.* (1981b) and Axegård (1986) observed an increase in the yield of chlorophenolic compounds as chlorine dioxide substitution was increased to 50% after which production of these compounds decreased. Increases in toxicity and BOD with increased chlorine dioxide substitution have also been noted (Donnini, 1983; Kutney *et al.*, 1985; Pryke, 1989; Voss *et al.*, 1981b). In addition, the potential environmental effects of the increased discharge of chlorate with higher chlorine dioxide use should also be considered (Germgård, 1989). Nevertheless, the economic and pulp quality benefits of chlorine dioxide substitution had lead to the worldwide adoption of this process modification.

Further reductions in the consumption of bleaching chemicals can be achieved by the inclusion of oxygen or hydrogen peroxide in the pre-bleaching extraction stage to give an E_O, E_P or E_{OP} stage. E_O stages are installed in most modern bleach plants.

Treatment of Bleached Kraft Mill Effluents

It can be expected that in the future, modifications to bleaching processes will substantially reduce the discharge of organic pollutants from bleach plants. Nevertheless, a significant discharge of polluting effluents is likely to remain and it will continue to be necessary to supplement internal measures with the external treatment of mill wastewaters. External treatment can be effectively achieved by both physico-chemical and biological means or by a combination of both systems.

Physico-chemical Effluent Treatment

A number of physico-chemical technologies have been developed for the treatment of bleached kraft mill effluents. These processes are technically feasible and capable of achieving high removal efficiencies of BKME constituents. However, the use of physico-chemical processes, with the exception of primary sedimentation, has been limited by the more favourable economics of biological treatment. Interest in physico-chemical treatment methods has been renewed as the emphasis of effluent quality control has shifted from BOD and suspended solids to parameters, such as colour, AOX and COD, which are not efficiently removed in biological treatment systems. The major physico-chemical processes are primary sedimentation, chemical coagulation, and ultrafiltration. All of these processes extract the pollutants from the wastewater rather than degrading them. Adequate disposal of the concentrated wastes, such as sludges or high concentration liquors, continues to be a difficulty.

Primary Sedimentation

Most pulp and paper mills employ primary treatment processes prior to the discharge of wastewaters to the recipient or to secondary treatment systems. Primary sedimentation is carried out in gravity clarifiers, settling basins, or air flotation units and is able to remove 80-95% of the suspended solids in BKME (Bonsor *et al.*, 1988). However, only 10-20% of wastewater BOD is removed by this process (Table 2.18).

Chemical Coagulation

Treatment with lime is the major coagulation process and is particularly effective at removing colour. Over 90% of the effluent colour can be removed in this way (Table 2.18, Bennett *et al.*, 1971; Davis, 1969; Springer, 1986). Lime treatment is also capable of removing 60% of COD and 70-80% of organically bound chlorine from extraction stage effluents (Almemark and Ekengren, 1989). Coagulation of bleaching effluents with aluminium or ferric salts is capable of removing AOX and COD from combined bleaching effluents (50-60% reduction), extraction stage effluents (60-80%), and to a lesser extent, chlorination stage effluents (20-50%) (Almemark and Ekengren, 1989). The lignin removal process (LRP) is another method for the treatment of combined bleaching effluents. This process utilises residual sludges from the pulp and paper mill to precipitate high molecular weight organic material (MW > 2000) and is capable of removing 50-80% and 40-50% of colour and COD respectively (Hynninen and Gullichsen, 1985). In addition, substantial amounts of low molecular weight compounds, such as resin acids and chlorophenolics, are also removed (Hynninen, 1989).

TABLE 2.18: Comparison of Bleached Kraft Mill Effluent Treatment Systems

	physico-chemical treatment, % removal			biological treatment, % removal	
parameter	1° sedimentation	coagulation	ultrafiltration	aerated lagoon	activated sludge
BOD	0-20	n/d	25-45	85-90	90-95
COD	10-30	40-60	50-80	20-50	50-60
suspended solids	80-95	n/d	n/d	n/d	n/d
colour	0-20	50-90	85-90	<10	n/d
toxicity	n/d	n/d	50-80	100	100
resin acids	n/d	75-95	70	80-100	n/d
chlorophenolics	0	40-50	0- >90	20-60	60-95
AOX	n/d	40-80	50-90	25-50	40-65

n/d - no data

Ultrafiltration

Ultrafiltration remains the most promising of the physico-chemical processes. Substantial reductions in AOX, colour and COD can be achieved on a laboratory and pilot scale using ultrafiltration membranes of 5000 to 10 000 molecular weight cut-off (Table 2.18) (Jonsson, 1989; Wagner, 1982). Effective removals of toxicity, resin acids and chlorophenolic compounds can also be achieved using suitable membranes (Ekengren *et al.*, 1990; Jaakko Pöyry, 1989) Although ultrafiltration treatment has previously been restricted to extraction stage wastewaters (due to their low volume and high proportion of high molecular weight material), continuing improvements in membranes, which allow high flow rates and enhanced retention, mean that combined bleaching effluents could now be successfully treated. When used in combination with biological treatment, ultrafiltration is capable of quantitatively removing nearly all environmentally harmful BKME constituents (Boman *et al.*, 1990). Three full-scale installations in Japan and Sweden treat extraction stage effluents by ultrafiltration (Almemark and Ekengren, 1989; Bothnia, 1990).

Biological Effluent Treatment

The traditional emphasis for the treatment of bleached kraft mill effluents has focussed on the removal of biological oxygen demand and suspended solids. Biological treatment systems utilise naturally occurring micro-organisms, principally bacteria, to convert degradable material to water, carbon dioxide and organic solids. Because the organic material must pass through the cell membranes of the micro-organisms, there is a tendency for low molecular weight organic compounds to be preferentially treated. The two predominant biological treatment systems used to treat settled BKME are aerated lagoons and activated sludge plants. Many studies have examined the efficiency of these systems in the removal of BKME constituents. Some of these findings are summarised below and in Table 2.18.

Aerated Lagoons

The aerated lagoon is the most common biological treatment system in the pulp and paper industry. This preference over activated sludge systems can be attributed to a number of factors (Bonsor *et al.*, 1988): i) ability to handle shock loads, ii) little or no nutrient addition during operation, iii) elimination of a sludge disposal problem, iv) lower energy and manpower consumption, v) better toxicity removal and vi) higher reliability due to their simplicity.

A typical aerated lagoon has a 3-10 day retention time. Mechanical aeration is employed to keep the water well oxygenated although an anaerobic layer of anoxic water and sludge is usually present at the bottom of the lagoon. Settled biomass is not recirculated or removed and most aerated lagoons maintain a biomass concentration of 50-100 mg L^{-1} (Boman *et al.*, 1988). Accumulation of biological solids is avoided in well operated lagoons by auto-oxidation reactions.

Aerated lagoons are able to remove 85-90% of effluent BOD (Table 2.18, Gergov *et al.*, 1988; Heimburger *et al.*, 1988a; Lindström and Mohamed, 1988) and eliminate acute toxicity. Non-chlorinated organic compounds such as monoterpenes and resin acids are also effectively removed with typical reductions of 80-100% being reported (Easty *et al.*, 1978; Hrutfiord *et al.*, 1975; Voss, 1984; Voss and Rapsomatiotis, 1985; Wilson and Hrutfiord, 1975). However, aerated lagoons are usually less effective at removing other effluent constituents such as colour, COD and organochlorine compounds. Only 25-50% of the organochlorine (measured as AOX or TOX) is removed during aerated lagoon treatment (Boman *et al.*, 1988; Bryant *et al.*, 1987b; Ek and Eriksson, 1988; Gergov *et al.*, 1988; Heimburger *et al.*, 1988a; Saunamäki, 1989) and increases in the concentrations of chlorinated guaiacols have also be observed after treatment (Bryant *et al.*, 1987a; Chung *et al.*, 1979). Strong indirect evidence has been obtained to attribute much of the observed organochlorine removal in aerated lagoons to biosorptive transport to anaerobic zones with subsequent dehalogenation/mineralisation of this material (Amy *et al.*, 1988; Bryant *et al.*, 1987a, 1987b).

Activated Sludge

High-rate activated sludge plants are becoming more common in the pulp and paper industry. In some countries, such as Finland, they are the preferred biological treatment process (Saunamäki, 1989). The advantages of activated sludge systems over aerated lagoon systems are their compact size and relative insusceptibility to changes in ambient temperature. The major disadvantage of these systems is the formation of large quantities of excess sludge which must be dewatered and disposed of by landfilling or incineration (Almemark *et al.*, 1990). Activated sludge systems operate at high biological solids levels with intensive aeration and recycling of the biomass. Because of this, treatment is usually rapid (2-6 hr). Removal of BOD is comparable to that achieved in aerated lagoons (Table 2.18). However, removal of chlorinated organic materials is substantially higher in these systems. Reported removals of AOX and chlorophenolic compounds are 40-65% and 60-95% respectively (Gergov *et al.*, 1988; Junna and Ruonala, 1990; Skogman and Lammi, 1988)

FATE OF BLEACHED KRAFT MILL EFFLUENT CONSTITUENTS IN THE ENVIRONMENT

The distribution of bleached kraft mill effluent constituents in the recipient will depend on effluent loading, dilution and water movement, partitioning between trophic levels, and removal processes such as biodegradation and sedimentation (Figure 2.12, Folke, 1985).

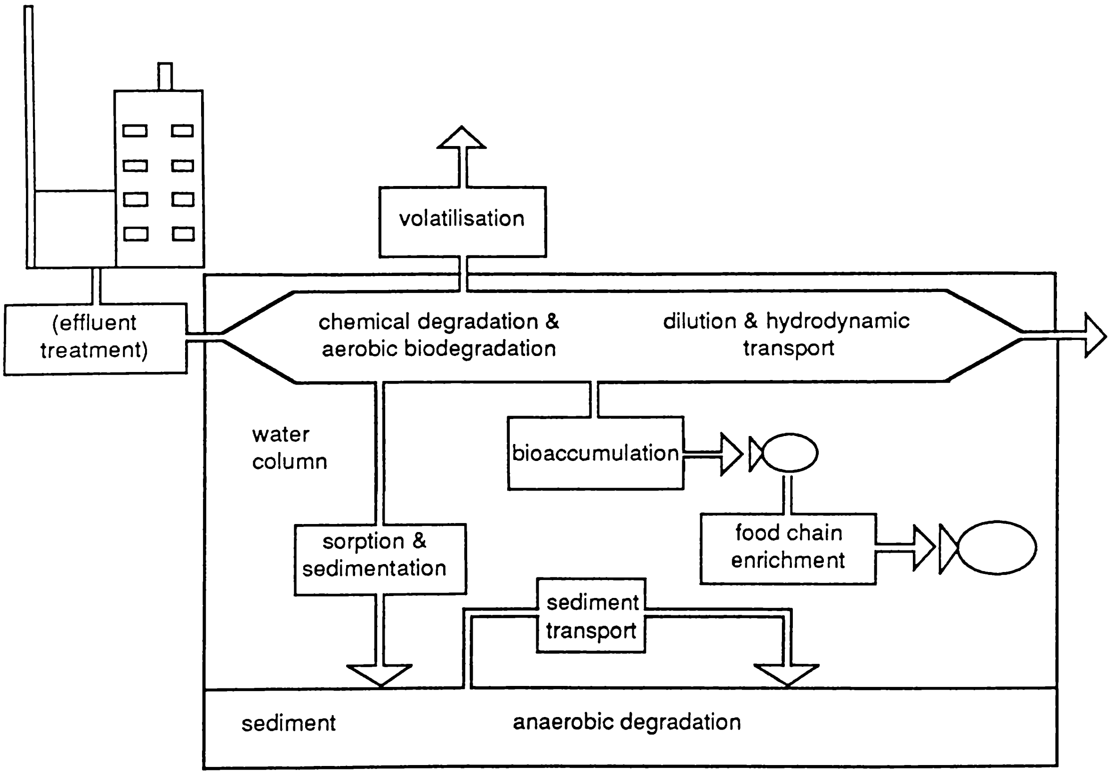


Figure 2.12: Transport mechanisms of BKME constituents in the recipient

Concurrent reductions in resin acid, chlorophenolic and sodium levels indicate that dilution and hydrodynamic transport are the most important mechanisms for the dispersal of BKME constituents (Fox, 1977; Seppala and Kansanen, 1988; Xie *et al.*, 1986). McLeay (1987) has summarised the reported levels of resin acids and chlorophenolic compounds in the aqueous phase of BKME recipients. Concentrations of resin acids in the water column rapidly decrease over a short distance and are generally at trace levels (< 0.5 µg L^{-1}) within 6 km of the point of discharge. Chlorophenolic compounds are significantly more recalcitrant (Oikari *et al.*, 1985). For example, Canadian studies have detected chlorophenolic compounds in river samples taken 50-110 km from the mill discharge point (McLeay, 1987). The chloroguaiacols were the predominant chlorophenolic compounds in the water column.

Adsorption and Sedimentation

Up to 30% of the decrease of BKME constituents in the recipient can be attributed to sedimentation (Kinae *et al.*, 1981a; Paasivirta *et al.*, 1980). The adsorption of organic pollutants is mainly dependent upon the lipophilicity of the compound (Selvakumar and Hsieh, 1988; Xie *et al.*, 1986) and the organic carbon content of the adsorbant (O'Connor and Connolly, 1980; Schellenberg *et al.*, 1984). Sediment transport and continued adsorption mean that contaminated sediments may be found up to 50 km from the point of discharge (McLeay, 1987).

EOX levels for sediments within 10 km of bleached kraft pulp mills have been found in the range 500 - 6000 µg g^{-1} dry weight (Hakanson *et al.*, 1988; Remberger *et al.*, 1990). Attempts to identify the nature of the chlorinated materials in the sediments has so far met with limited success. Remberger *et al.* (1990) and Wesén *et al.* (1990) found that only 5-8% of the organochlorine could be accounted for by known compounds. The identified compounds were principally chlorinated long-chain fatty acids and esters. Chlorinated catechols were the major chlorophenolic compounds found in the sediments (McLeay, 1987). The major part of the chlorinated material differs from that found in BKME suggesting that it is either formed by chemical or biological transformations or originated from another source (de Sousa *et al.*, 1988; Remberger *et al.*, 1990).

Bioaccumulation

Although bioaccumulation and food chain enrichment may have an insignificant role in the total mass balance of BKME constituents in the recipient, they are important mechanisms for the promotion of sub-lethal toxic effects. Bioaccumulation may increase the concentration of biologically active BKME constituents in the biota until a sub-lethal effect threshold is attained.

Enrichment of chlorophenolic compounds, resin acids and extractable organic chlorine in the food chain has been observed in BKME recipients (Hemming and Lehtinen, 1988; Kinae *et al.*, 1981b; Paasivirta *et al.*, 1980; Södergren, 1987). Oikari *et al.* (1985) detected resin acids and chlorophenolics in fish up to 11 km from the point of discharge. The propensity towards bioaccumulation appears to decrease as one moves up the food chain from algae to invertebrates and fish (Wesén and Okla, 1984).

Concentrations of chlorinated organics in biota can be substantial. Neilson *et al.* (1984) and Vuorinen *et al.* (1985) have detected chlorophenolic compounds in fish livers at concentrations of up to 500 $\mu g\,kg^{-1}$ fat. Reported concentrations of EOX in fish and mussels sampled near pulp mill discharges are 120-1990 mg kg^{-1} fat (Leach *et al.*, 1985; Wesén and Okla, 1984). Only 10-15% of the EOX has been identified to date (Wesén *et al.*, 1990). Less than 1% of the EOX is chlorophenolic (Wesén and Okla, 1984) and a major part of the material is made up of high molecular weight compounds ($MW > 500$) (Hemming and Lehtinen, 1988).

As fish may bioaccumulate chlorinated organic material from sediments, it is possible to have continued long-term bioaccumulation once the effluent source is removed (Carlberg *et al.*, 1987).

Biodegradation

It can be expected that after discharge to the recipient aerobic biodegradation processes will continue in a manner analogous to the secondary treatment system. Dilution of biomass and substrate mean that this process will occur more slowly. Persistant BKME constituents such as AOX, chlorophenolics and colour are unlikely to be substantially reduced in this manner. Hardell and de Sousa (1977a) have shown that less than 20% of effluent colour can be expected to break down after five months in the recipient. Similarly, less than 4% of the high molecular weight chlorinated organic material may be mineralised within 3 months (Eriksson and Kolar, 1985).

Transportation of these materials by adsorption and sedimentation to sediment layers means that anaerobic biodegradation might occur. Biodegradation of chlorophenolics has been achieved under anaerobic conditions (Häggblom *et al.*, 1989; Neilson *et al.*, 1987; Sahm *et al.*, 1986; Woods *et al.*, 1989). High molecular weight chlorolignin has also been shown to be partially degraded under anaerobic conditions to form chlorinated veratroles (Eriksson *et al.*, 1985; Neilson *et al.*, 1984). However, the laboratory conditions required for the observed anaerobic biodegradation of chlorolignin (pure bacterial strains, high cell density, no secondary treatment of chlorolignin) are unlikely to be found in the recipient. Fleming *et al.* (1990) conservatively estimated that the upper limit for the formation of low molecular weight chlorinated organic compounds from high molecular weight chlorolignin is unlikely to exceed 5% of that formed in the bleach plant. However, it can be noted that anaerobic mineralisation of high molecular weight chlorinated organic material does appear to take place in aerated lagoon treatment systems (Amy *et al.*, 1988; Bryant *et al.*, 1987a; Bryant *et al.*, 1987b)

SUMMARY

Wastewaters from the production of bleached kraft pulp and paper are a complex mixture of inorganic constituents and low and high molecular weight organic material. The organic material is predominantly lignin degradation products but carbohydrate degradation products and wood extractives are also present.

Untreated bleached kraft mill effluents exert a variety of environmental effects when discharged to the recipient. These include dissolved oxygen deficiency, suspended solids deposition, colour, acute and chronic toxicity, mutagenicity, and bioaccumulation. Primary and secondary treatment are able to effectively reduce the demand for oxygen, the acute toxicity and the concentrations of many of the chlorinated and unchlorinated low molecular weight organic compounds. In order to effectively remove colour and high molecular weight organochlorine, it is generally necessary to employ a physico-chemical process. Of the processes presently available, ultrafiltration offers the most effective means of removing these constituents.

The alternative and complimentary method for reducing the environmental impact of BKME is to modify the bleaching processes. Currently the most effective alternatives for process control of bleaching effluents are extended delignification, oxygen delignification, and substitution of chlorine with chlorine dioxide. These changes provide substantial reductions in AOX, colour and dioxins. Oxygen delignification also reduces oxygen demand and toxicity.

The two major processes by which the concentrations of BKME constituents are lowered in the water column of the recipient are dilution and adsorption onto sediments. Despite the effects of dilution, persistant organic compounds in the wastewaters, such as resin acids and chlorophenolic compounds, can be found at considerable distances from the point of discharge. Transport of sediments containing adsorbed BKME constituents is another means of dispersal. Significant bioaccumulation of resin acids, chlorophenolic compounds and organically bound chlorine also occurs in biota present in BKME recipients. Much of the chlorinated material in sediments and biota is currently uncharacterised.

In Scandanavia, significant sub-lethal toxicity is observed in the biota of recipients receiving BKME. These effects include skeletal malformations, physiological disorders and diseases and and are manifested in effluents diluted from 200 - 1000 times. In contrast, North

American studies detect no significant toxicity effects of BKME at concentrations of 5-10% v/v. It appears that the Scandanavian recipient (i.e. Baltic Sea) has unique features which exacerbate the potential for sub-lethal toxicity.

Overall, it can be seen that the composition of BKME is highly variable both in the nature and concentration/yields of the effluent constituents. There is also a wide range of concentrations and conditions under which environmental effects of discharged BKME are observed.

The wood stock, bleaching processes and recipient of the Kinleith pulp and paper mill are more typical of those found in North America. However, it is clear that it is not possible to extrapolate the results of studies undertaken in North America and apply them to the New Zealand situation. Therefore, the aim of the present study was to determine the specific characteristics and treatability of BKME constituents discharged from the Kinleith pulp and paper mill.

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Chapter Three

METHODOLOGY FOR THE ANALYSIS OF BLEACHED KRAFT MILL EFFLUENTS

METHODOLOGY FOR THE ANALYSIS OF BLEACHED KRAFT MILL EFFLUENTS

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ABSTRACT - An outline is given of analytical methods used in this thesis. The effluent sampling procedure was shown to provide a sample which accurately reflected the average composition of the effluent over the sampling period. The physical and inorganic parameters determined in effluents included chemical oxygen demand (COD), colour, chloride, dissolved and suspended solids, pH and sodium. The reproducibility of these methods was acceptable. Generic analysis of organically-bound chlorine in effluents and sediments was undertaken. Excellent reproducibility was found for both the adsorbable organic halide (AOX) and extractable organic halide (EOX) methods. Low molecular weight organic compounds were analysed using liquid-liquid extraction and subsequent gas chromatographic analysis of the derivatised extracts. Four classes of compounds, chlorinated acetic acids, chlorinated phenolic compounds, resin acids, and neutrals, were determined using specific analytical methods. Satisfactory recoveries and reproducibilities were obtained for each method.

KEYWORDS - Bleached kraft mill effluents, sediments, physical parameters, inorganic constituents, AOX, EOX, low molecular weight compounds, reproducibility

INTRODUCTION

In this section the methods used for the chemical analysis of effluent, sediment and pulp samples are outlined. An assessment has been made of the reproducibility of each method (i.e. % standard deviation) and, for some procedures, recovery figures have been obtained.

SAMPLING

Many factors, such as operating conditions, spills, and production demands, affect both the qualitative and quantitative nature of the effluents discharged from kraft pulp and paper mills. This high variability can make it difficult to obtain a representative effluent sample. In order to minimise the effects of short-term changes in effluent composition, it is preferable to collect composite samples.

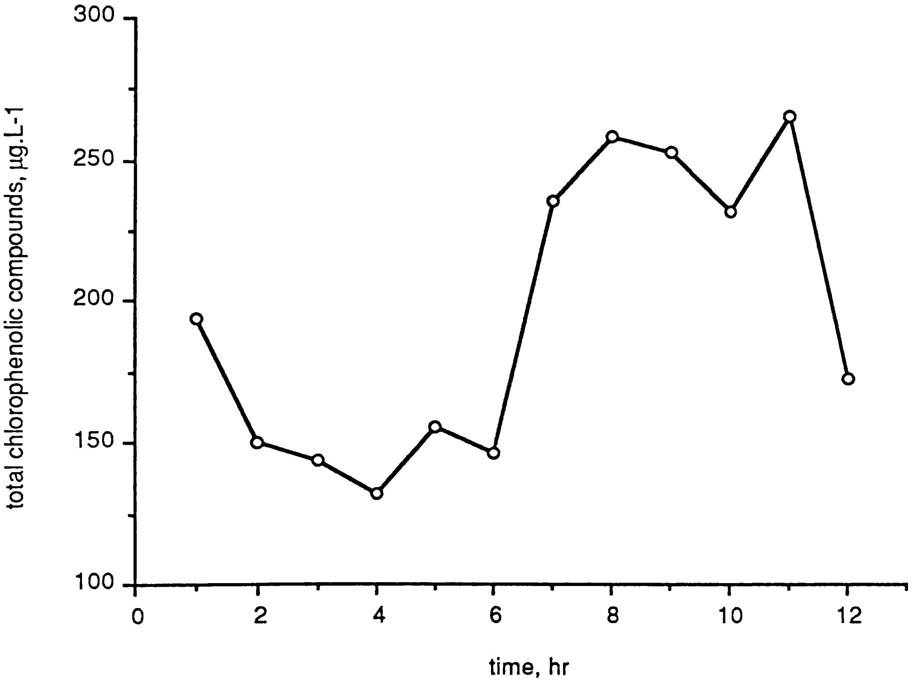

Figure 3.1: Time-variability of acid sewer effluent total chlorophenolic compounds composition

To ascertain whether composite samples would accurately reflect the composition of the discharged effluents, 1 L samples were taken from the No.3 acid sewer on an hourly, 3-hourly composite, 6-hourly composite, and 12-hourly composite basis. Total chlorophenolic compounds in the composite samples were compared with calculated mean concentrations based on the one hourly grab samples (Figure 3.1). It can be seen that the collection of composite samples accurately reflected the mean effluent quality over the sampling period (Table 3.1).

With the exception of the bleach plant stages, 24-hr composite samples were collected from each of the twelve sample sites selected for this study. It was not possible to collect composite samples from the bleach plants themselves. Grab samples were taken from post-washer points of the pre-bleaching chlorination and extraction stages in each bleach plant. Composite sampling was performed with Isco and Manning autosamplers with the exception of the main sewers where permanently installed grab arm composite samplers were used. Samples were taken every 15 min and the samplers were packed with ice to preserve the collected effluents.

Table 3.1: Effects of Composite Sampling on Total Chlorophenolic Content of Acid Sewer Wastewaters

composite	measured chlorophenolics, $\mu g\ L^{-1}$	observed mean chlorophenolics,* $\mu g\ L^{-1}$	ratio measured: calculated
1-3 hours	160	163	0.98
4-6 hours	168	145	1.16
7-9 hours	263	249	1.06
10-12 hours	225	224	1.00
1-6 hours	170	154	1.10
7-12 hours	217	237	0.92
1-12 hours	200	195	1.03

* mean of hourly samples over composite period

Samples were collected within 24 hr of sampling and stored in high density polyethylene (HDPE) containers (1 and 20 L) and 2.5 L amber glass bottles. These containers complied with APHA standards (APHA, 1985). HDPE containers were washed twice with concentrated nitric acid and then rinsed repeatedly with hot water and distilled water. Glass bottles were cleaned with chromic acid and then rinsed repeatedly with hot water and distilled water. Washed containers filled with distilled water for two weeks gave acceptable blanks when analysed for extractable organics. Mill effluent samples were transported in polystyrene boxes containing ice and stored at 4°C until analysis. No further sample preservation was undertaken. All time-sensitive analyses were completed within three days of sample collection.

PHYSICAL AND INORGANIC PARAMETERS

Effluent samples were analysed for chemical oxygen demand (COD), colour, chloride, pH, sodium, and suspended and dissolved solids. With the exception of colour, APHA standards were used (APHA, 1985). Colour was measured spectrometrically at 465 nm after filtering the sample and adjusting the pH to 7.6. Calibration was performed using chloroplatinate standards and the colour was reported as milligrams chloroplatinate (CPU) per litre. Details of these methods and reproducibility determinations for mill effluents are given in Table 3.2.

Table 3.2: Methodology and Reproducibility for Physical and Inorganic Parameters

parameter	analysis	APHA standard	% SD
COD	closed reflux, colourimetric	508 C	2.7
colour	spectrometric	-	2.5
chloride	automated ferricyanide	407 D	5.0
dissolved solids	evaporation at 105°C	209 A	7.2
pH	pH meter	423	-
sodium	atomic adsorption	303	2.7
suspended solids	GF/C filtration, dried at 105°C	209 C	7.0

Molecular Weight Distribution

Mill effluents were fractionated by ultrafiltration. Ultrafiltration was undertaken with an Amicon hollow-fibre cartridge ultrafiltration unit (Model DC2A) using cartridges with nominal molecular weight cut-offs (MWCO) of 3000, 10 000, 30 000 and 100 000 respectively. The pH of a 400 mL filtered sample was adjusted to 7. The sample was ultrafiltered through a 3000 MWCO cartridge with retentate recirculation and the addition of distilled water as a washing solution. Permeate (1000 mL) was collected and the retentate was removed from the unit and made up to 400 mL. Samples of permeate and retentate (2 mL) were removed for analysis before repeating the procedure with each higher MWCO cartridge.

Adsorption Isotherms

AOX adsorption experiments were undertaken at pH 7 and room temperature (22°C). Adsorption equilibrium times were assessed by mixing the wastewaster with the adsorbant (10 g L^{-1} dry weight) and monitoring AOX in the supernatant over time. Isotherms were derived by mixing a constant volume and concentration of wastewater with adsorbant concentrations of approximately 0, 30, 100, 300, 1000, 3000 and 10 000 mg L^{-1}. AOX in the settled wastewater was then determined. Distilled water and adsorbant blanks were also run.

Residual AOX concentrations in the aqueous phase and the mass of adsorbant were used to calculate coefficients for the Freundlich equation:

$$q_e = K_f C^{1/n}$$

where q_e is the solid-phase AOX loading (µg AOX g^{-1} adsorbant), C is the equilibrium liquid-phase concentration (µg L^{-1}) and K_f and 1/n are empirical coefficients. K_f is a constant related to the adsorptive capacity while 1/n is related to adsorption intensity. The constants were determined by regression of the linearised Freundlich equation (log q_e vs log C) where 1/n was the slope and K_f was the y-axis intercept of the regression line. The partition coefficent, K_p, was estimated from the ratio of q_e:C for experiments with the highest adsorbant concentrations.

ORGANICALLY BOUND CHLORINE

Organochlorine in Effluents

Adsorbable organic halide in mill wastewater samples was determined according to SCAN-test Standard SCAN-W 9-89 (SPPBTC, 1989). A Euroglas AOX Analyser with manual boat insertion was used. Because of requirements for other analyses, samples were not preserved by adjusting the pH to 2, but were stored at 4°C. Analyses for AOX were undertaken within 48 hours of sample collection. Source wastewaters, with the exception of No.1 sewer samples, were diluted 1:500. Other samples were diluted 1:100. Recovery of a 50 mg L^{-1} AOX standard was 99.8%. Reproducibility of the method was ± 3.5%

Adsorbable Organic Chlorine in Sludges

AOX determination in sludges was based on the methods of Asplund *et al.* (1989) and Saunamäki *et al.* (1990). 50 mg of wet sludge was suspended in 100 mL of distilled water and thereafter AOX analysis was performed in an analogous manner to wastewater samples. Results were reported as μg AOX g^{-1} dry weight sludge. Reproducibility of the method was ± 5.1%.

Extractable Organic Chloride in Sludges

Despite its widespread use, there is no standard methodology currently available for the analysis of EOX in sludges, sediments and biota (Bethge, 1989). Analyses of sludges for extractable organic chloride in this study were based on the method of Martinsen *et al.*, (1988). The effects of extraction solvent on the recovery of EOX were determined. Three solvent mixtures: hexane/acetone (1:1), cyclohexane/isopropanol (1:1) and cyclohexane/acetone (1:1) gave mean ± 95% C.I. EOX values of 79.4 ± 3.6 μg g^{-1}, 89.9 ± 3.8 μg g^{-1} and 93.7 ± 5.4 μg g^{-1} respectively. Cyclohexane/acetone consistently gave the highest results and suitable reproducibility and was used for all subsequent EOX determinations.

Wet sludge (approximately 25 g) was weighed into a 250 mL centrifuge tube. The sludge was shaken initially with 50 mL acetone prior to the addition of 50 mL cyclohexane. The tube was tightly capped, shaken vigorously on a wrist-shaker for 1 hour, and centrifuged at 2000 rpm for 15 minutes. A 50 mL aliquot of solvent was washed twice with distilled water, dried with anhydrous magnesium sulphate, and a 20 mL aliquot of the washed extract was reduced to 4 mL on a rotary evaporator. The extract was transferred to a 5 mL volumetric flask with 0.5 mL *n*-octanol and made up to the mark with cyclohexane. 10 µL of this solution was manually injected into the boat of a Euroglas AOX analyser and analysed by combustion/microcoulometric titration. Analyses were calibrated using standard solutions of 2,4,6-trichlorophenol in hexane. Reproducibility of the method was ± 5.8%.

LOW MOLECULAR WEIGHT EXTRACTABLE ORGANIC COMPOUNDS

Bleached kraft mill effluents contain many types of low molecular weight extractable organic compounds. Concentrations of these compounds are relatively low, typically ranging from 10 mg L^{-1} to less than 1 µg L^{-1}. The only effective means of determining the nature and quantity of these compounds is to selectively extract them from the wastewater and use gas chromatography and mass spectrometry to identify and quantify them. In this work, liquid-liquid extraction was used for the analysis of low molecular weight extractable organic compounds in bleached kraft mill effluents. The analytical methods for the determination of various classes of low molecular weight extractable organic compounds are given below.

Gas Chromatography and Mass Spectrometry

Effluent extracts were analysed on a Hewlett-Packard 5890 gas chromatograph. The instrument was fitted with a flame ionisation detector (FID) and an electron capture detector (ECD). Instrument operating conditions are given in Table 3.3. A post-column splitter giving a 5 to 1 split of column effluent to the FID and ECD respectively was fitted. Data acquisition was performed using a Delta-Junior PC-based (version 3.03) gas chromatography data acquisition system. The linearity of the FID was determined to ensure that overloading of the detector was avoided (Figure 3.2). The detector gave a linear response up to approximately 350 ng octadecane.

Mass spectrometric data were obtained using a Hewlett-Packard 5985 mass spectrometer or a Hewlett-Packard Mass Selective Detector. Both instruments were interfaced with Hewlett-Packard 5890 gas chromatographs configured as in Table 3.3. EI-MS on the HP-5985 were obtained at 70 eV, 300-µA ionisation energy. Chemical ionisation mass spectra (positive and negative CI) were also obtained on the HP-5985.

TABLE 3.3: Instrument Operating Conditions for Gas Chromatography

instrument	Hewlett-Packard 5890
column	Hewlett-Packard HP-1 fused-silica capillary, length 25 m, bore 0.22 mm, film thickness 20 μm
carrier gas	helium
column pressure	150 kPa (linear velocity 30 cm s^{-1})
injector temperature	225°C
detector temperature	FID 250°C, ECD 300°C
split flow	20 mL min^{-1}
purge flow	5 mL min^{-1}
injection method	Grob splitless
load time	30 s

Chlorinated Acetic Acids

Effluent samples (50 mL) were placed in 250 mL centrifuge tubes and adjusted to pH 0.8 with concentrated sulphuric acid (Lindström and Österberg, 1986). Internal standard solution (250 μL, hexyl trichloroacetate, 5 mg in 50 mL acetone) and 25 mL distilled diethyl ether were added. The tube was capped tightly, shaken vigorously for five minutes and centrifuged to separate the phases. The lower, aqueous layer was carefully removed by

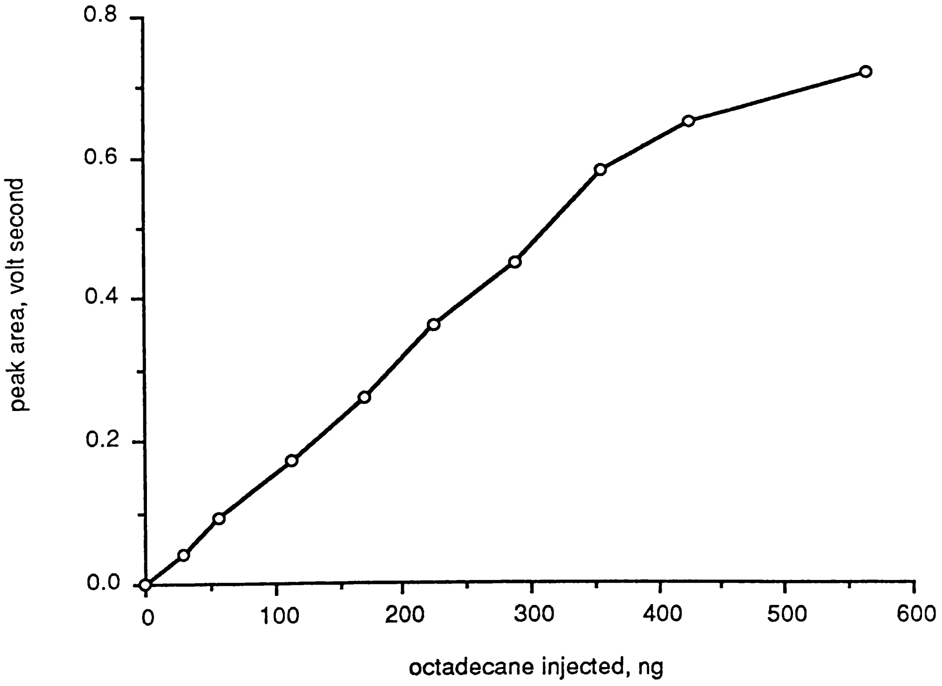

Figure 3.2: Response curve for flame ionisation detector

suction and the diethyl ether dried with anhydrous magnesium sulphate. The solution was filtered and methylated with an ethereal solution of diazomethane. Sufficient methylating reagent was added to maintain an excess of diazomethane. Further concentration of the extract was not required for gas chromatographic analysis. The extracts were analysed on a gas chromatograph using electron capture detection (Table 3.4). Response factors were calculated using a chlorinated acetic acid standard (40 mg chloroacetic acid, 20 mg dichloroacetic acid and 10 mg trichloroacetic acid in 50 mL acetone). No statistical analysis of the recoveries and reproducibility of this method was undertaken.

Table 3.4: Temperature Programmes for Gas Chromatographic Analyses

GC parameter	chloroacetic acids	chlorophenolics	resin and fatty acids	general extractives
inital temperature, °C	40	40	150	40
hold time, min	2	2	1	2
rate 1, °C min^{-1}	5	20	10	5
temperature 1, °C	250	120	200	250
hold time, min	16	0	0	16
rate 2, °C min^{-1}	-	5	2	-
temperature 2, °C	-	250	260	-
hold time, min	-	3	14	-
total run time, min	60	35	50	60
detector	ECD	ECD	FID	ECD/FID

Chlorinated Phenolic Compounds

Chlorophenolic compounds in mill effluents were determined by the *in-situ* acetylation and extraction method of Starck *et al.*, (1985). Extracts were analysed using the gas chromatographic conditions given in Table 3.4. Fifteen standard compounds were used for quantification and identification via retention times (Table 3.5). With one exception, only those peaks corresponding with standards were reported. 3,4-Dichloro-5-(dichloromethyl)-5-hydroxy-2-furanone, a compound co-extracted by this method, was also quantified. In this case, quantification was based on tetrachlorocatechol. A further series of chlorinated phenolic derivatives, such as the chlorinated acetovanillones, propiovanillones and vanillic acids, are not readily analysed by this method (Voss *et al.*, 1980) and were quantified in the general continuous liquid-liquid extractable organics procedure. Recovery and reproducibility data for the analysis of chlorophenolics are given in Table 3.5. Excellent recoveries of chlorophenolic compounds, both at high and low concentrations, and good reproducibility were obtained with this method.

Table 3.5: Recoveries and Reproducibility of Chlorophenolic Method

		recoveries						
		high concentration			low concentration			
		added	recovered		added	recovered		% SD
compound	RRT*	$\mu g\,L^{-1}$	$\mu g\,L^{-1}$	%	$\mu g\,L^{-1}$	$\mu g\,L^{-1}$	%	
2,4-dichlorophenol	0.81	598	533	89	41.9	37.6	90	5.6
2,4,6-trichlorophenol	0.94	144	125	87	10.1	8.3	82	2.7
2,3,6-trichlorophenol (I.S.)	1.00	-	-	-	-	-	-	-
2,3,4,6-tetrachlorophenol	1.22	116	106	92	8.1	6.6	82	4.5
pentachlorophenol	1.47	-	-	-	-	-	-	-
4,5-dichloroguaiacol	1.16	486	415	86	34.0	35.0	103	2.9
3,4,5-trichloroguaiacol	1.33	111	109	98	7.8	6.0	77	4.4
4,5,6-trichloroguaiacol	1.38	110	102	93	7.7	6.7	87	5.0
tetrachloroguaiacol	1.52	90.5	93.3	103	6.3	4.9	77	5.8
4,5-dichlorocatechol	1.30	491	469	96	34.4	29.1	85	7.1
3,4,5-tetrachlorocatechol	1.48	95.3	102	107	6.7	5.8	87	4.4
tetrachlorocatechol	1.65	72.5	67.4	93	5.1	5.1	100	6.0
5-chlorovanillin	1.20	574	530	92	40.1	38.5	96	5.0
6-chlorovanillin	1.23	585	532	91	40.9	36.2	89	7.6
5,6-dichlorovanillin	1.43	565	515	91	39.5	34.9	88	4.4
tetrachlorofuranone	1.05	-	-	-	-	-	-	7.0

* relative retention time

Neutrals, Resin and Fatty Acids

Continuous liquid-liquid extraction with dichloromethane in 125 mL liquid-liquid extractors was the method used for the general analysis of wastewater samples. Verification tests were run using a sample from the No.2 alkali sewer. A 4 hour extraction time at pH 3 was sufficient to quantitatively recover low molecular weight extractable organic compounds (Figure 3.3). Greater than 80% of all compounds were recovered in the first two hours of extraction. In view of the results obtained by Voss and Rapsomatiotis (1985), tests on the effect of extraction pH were also undertaken. It was found that the pH of extraction had a particularly significant effect on the recovery of resin and fatty acids (Figure 3.4). For example, recovery of resin acids was significantly greater at pH 11 than at pH 3. This latter pH had been previously used in studies of New Zealand pulp and paper effluents (Wilkins and Panadam, 1987; Stuthridge, 1987). Unfortunately, a number of the organic compounds

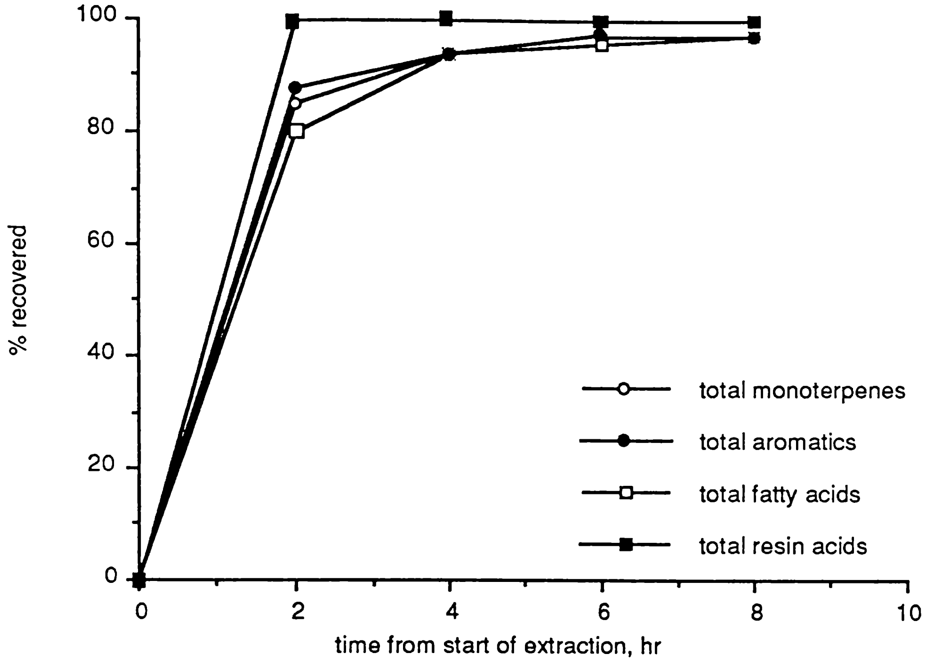

Figure 3.3: Effect of extraction time on recovery of low molecular weight organics

of interest in this study, such as the chlorinated monoterpenes, are labile at alkaline pH. For this reason, it was necessary to use two continuous liquid-liquid extraction analyses. Resin and fatty acids were extracted at pH 9 whilst a general extraction for the quantitation of compounds not determined by other methods was undertaken at pH 3.

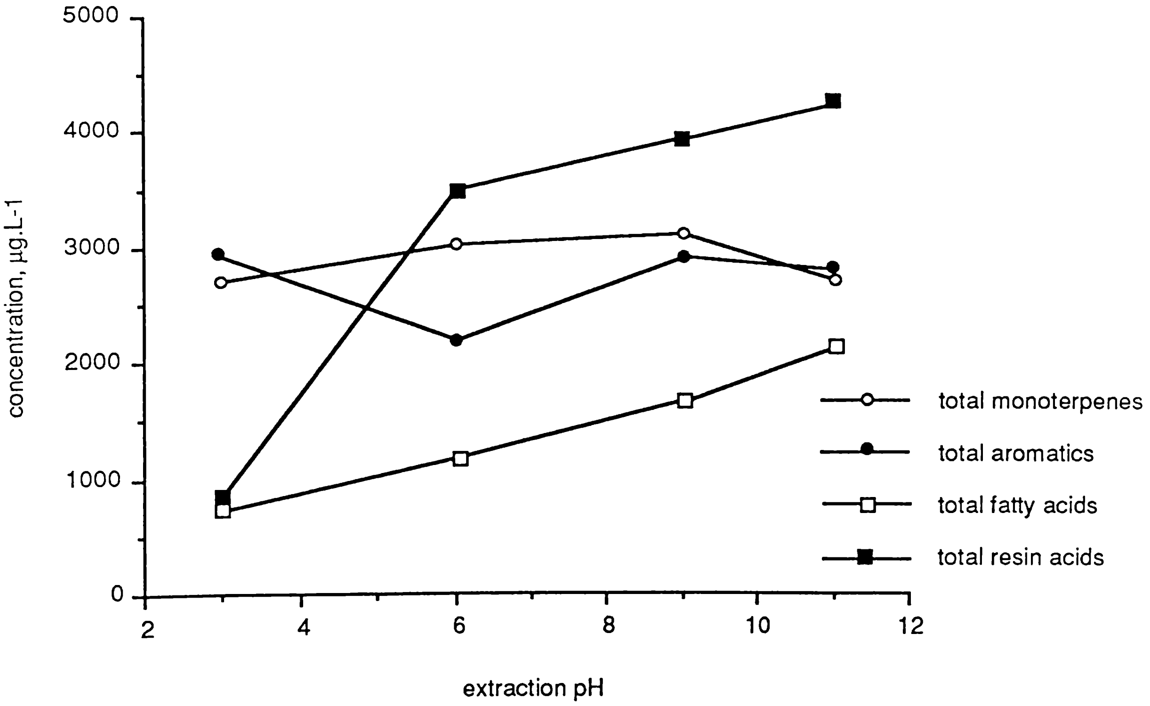

Figure 3.4: Effect of pH on recovery of low molecular weight organic compounds

Resin and Fatty Acids

Wastewater samples (125 mL) were adjusted to a pH of 9 and placed into a 125 mL liquid-liquid extractor containing 80 mL of distilled dichloromethane. The sample was extracted at maximum reflux for four hours and the extract cooled. Internal standard solution (50 µL, octadecane, 50 mg in 50 mL dichloromethane) was added, the extract was dried with anhydrous magnesium sulphate, and filtered. The extract was taken down to 2 mL on a rotary evaporator and methylated with an ethereal solution of diazomethane. Several drops of distilled methanol were added to aid methylation (Turoski, 1981). Sufficient methylating reagent was added to maintain an excess of diazomethane. Extracts were analysed using the gas chromatographic conditions given in Table 3.4. Response factors were determined using a solution of 50 mg each of palmitic acid (for fatty acids), dehydroabietic acid (for resin acids), dichlorostearic acid, chlorodehydroabietic acid (1:1 mixture of 12- and 14-chloro isomers), and dichlorodehydroabietic acid in 50 mL dichloromethane. Recovery and reproducibility data for this method are given in Table 3.6. Excellent recoveries and reproducibilities were obtained for both low and high concentrations of fatty and resin acids. Neoabietic acid was poorly recovered; possibly due to its isomerisation to another resin acid.

Table 3.6: Recovery and Reproducibility of Resin and Fatty Acid Method

		recoveries						
		high concentration			low concentration			
		added	recovered		added	recovered		% SD
compound	RRT*	µg L^{-1}	µg L^{-1}	%	µg L^{-1}	µg L^{-1}	%	
octadecane (I.S.)	1.00	-	-	-	-	-	-	-
palmitic acid	1.18	640	570	89	6.4	5.7	89	4.5
linoleic acid	1.49	723	723	100	7.2	6.2	86	1.5
oleic acid	1.51	736	692	94	7.4	6.3	85	3.4
stearic acid	1.56	-	-	-	-	-	-	9.4
seco-1-dehydroabietic acid	1.65	-	-	-	-	-	-	2.9
seco-2-dehydroabietic acid	1.69	-	-	-	-	-	-	3.9
pimaric acid	1.83	-	-	-	-	-	-	1.6
sandaracopimaric acid	1.86	-	-	-	-	-	-	4.2
isopimaric acid	1.94	883	839	95	8.8	7.6	86	1.9
palustric acid	1.96	-	-	-	-	-	-	2.2
dehydroabietic acid	2.01	1322	1203	91	13.2	11.7	89	3.5
abietic acid	2.13	-	-	-	-	-	-	3.3
neoabietic acid	2.25	659	217	33	6.6	3.5	53	6.4

* relative retention time

General Extraction

Wastewater samples (125 mL) were adjusted to pH 3 and placed into a 125 mL liquid-liquid extractor containing 80 mL of distilled dichloromethane. The sample was extracted at maximum reflux for four hours and the extract cooled. Internal standard solution (50 µL, octadecane, 50 mg, and hexyl trichloroacetate, 50 mg, in 50 mL dichloromethane) was added, the extract was dried with anhydrous magnesium sulphate, and filtered. The extract was evaporated to 2 mL on a rotary evaporator and methylated with a ethereal solution of diazomethane. Several drops of distilled methanol were added to aid methylation. Sufficient methylating reagent was added to maintain an excess of diazomethane. Extracts were analysed using the gas chromatographic conditions given in Table 3.4. Response factors were determined using a solution of 50 mg each of α-terpineol (for monoterpenes), vanillin (for aromatic compounds), and dichlorodimethylsulphone in 50 mL dichloromethane. Chlorinated monoterpenes were quantified by FID using 2α,7-dichloromenthane-1α,8-diol, purified from chlorination stage effluents, as a response factor standard. Recovery and reproducibility data for this method are given in Table 3.7. Recoveries and reproducibility of the more volatile monoterpenes (e.g., α-pinene and limonene) were relatively poor due to losses during the extraction and work-up procedures. Poor recoveries of the aromatic compounds, vanillin and acetovanillone, are likely to be due to difficulties in fully derivatising these compounds.

Table 3.7: Recovery and Reproducibility of General Extraction Method

		recoveries						
		high concentration			low concentration			
		added	recovered		added	recovered		% SD
compound	RRT*	$\mu g\,L^{-1}$	$\mu g\,L^{-1}$	%	$\mu g\,L^{-1}$	$\mu g\,L^{-1}$	%	
α–pinene	0.37	1408	718	51	14.1	13.1	93	28
limonene	0.42	730	548	75	7.3	9.7	133	21
fenchone	0.50	640	544	85	6.4	7.4	116	2.7
α-terpineol	0.59	2083	1812	87	20.8	20.8	100	5.3
vanillin	0.82	787	275	35	7.9	5.9	75	8.9
acetovanillone	0.87	1405	140	10	14.1	5.2	37	8.2
homovanillic acid	0.89	-	-	-	-	-	-	10
chlorinated monoterpene#	0.95	-	-	-	-	-	-	7.8
octadecane (I.S.)	1.0	-	-	-	-	-	-	-

* relative retention time

2α,7-dichloromenthane-1α,8-diol

Monoterpenes in Pulp

A pulp sample (approximately 30 g when filtered) was placed in a 250 mL centrifuge tube. Anhydrous magnesium sulphate (20 g), 50 mL pentane and 500 mL internal standard (octadecane, 50 mg in 50 mL acetone) were added. The tube was capped tightly and shaken on a wrist shaker for one hour. The pentane extract was analysed by gas chromatography without further work-up using the chromatographic conditions of the general extraction method. Monoterpenes in the pulp were reported as g ADT^{-1}. Reproducibility of the method was ± 7%.

CONCLUSIONS

The methods outlined for the analysis of bleached kraft mill effluents have been shown to be adequate for the requirements of this work. In most cases, excellent recovery and reproducibility data were obtained.

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Chapter Four

IDENTIFICATION OF NOVEL CHLORINATED MONOTERPENES FORMED DURING KRAFT PULP BLEACHING OF *PINUS RADIATA*

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IDENTIFICATION OF NOVEL CHLORINATED MONOTERPENES FORMED DURING KRAFT PULP BLEACHING OF *PINUS RADIATA*

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ABSTRACT - The chlorination stage bleaching effluents of a New Zealand kraft pulp and paper mill processing the softwood *Pinus radiata* contained a group of novel chlorinated monoterpenes. Fourteen compounds were isolated from the effluents by a combination of liquid-liquid extraction, column chromatography, and preparative gas chromatography. Mass spectral and ^{1}H and ^{13}C NMR data showed these compounds to be hydroxylated and/or chlorinated derivatives of *Pinus radiata* monoterpenes. The major compounds were a dichlorobornane and four dichloro-*p*-menthane-1,8-diols. The chlorinated monoterpenes were detected in total concentrations of 1400-12 300 μg L^{-1} [70-600 g air-dried tonne^{-1} (ADT) bleached pulp] and they were the major class of low molecular weight extractable organic compounds present in the chlorination stage effluent. The principal factor determining their formation appears to be the high concentration of monoterpenes remaining in the *Pinus radiata* brown stock produced in the mill's continuous digester.

KEYWORDS - Bleaching effluents, chlorinated monoterpenes, *Pinus radiata*

INTRODUCTION

The use of chlorine to bleach kraft pulp leads to the formation of a wide range of high and low molecular weight chlorinated and non-chlorinated organic compounds, many of which are subsequently discharged to the kraft mill effluent treatment system. To date, more than 300 low molecular weight compounds have been identified in bleach plant wastewaters (Kringstad and Lindström, 1984). These low molecular weight chlorinated organic compounds are of particular concern because of their established toxicity, mutagenicity, and potential for bioaccumulation (McLeay, 1987).

As part of an ongoing study at one of New Zealand's two kraft pulp and paper mills we have sought to identify and quantify the low molecular weight extractable organic compounds present in effluents from the mill's two bleach plants. The use of conventional gas chromatography and gas chromatography/mass spectrometry (GC/MS) techniques has lead to the identification of over 200 low molecular weight compounds from chlorination and alkali extraction stage effluents (Stuthridge, 1987). Many of these compounds correspond to those previously detected in the wastewaters from North American or Scandinavian pulp mills. However, high concentrations of a group of chlorinated compounds of unknown structure were also observed. This paper describes the structural characterisation of these compounds.

EXPERIMENTAL

Chlorination Effluent

Effluent was obtained from the chlorination stage of the mill's (C70D30)E_0DED sequence kraft pulp bleaching plant. Typical bleaching conditions during the course of sampling are presented in Table 4.1.

TABLE 4.1: Chlorination Stage Bleaching Conditions

brown stock	kraft *P. radiata*
incoming *P* no.	24
pulp consistency, %	4.3
total applied chlorine (active Cl_2), %	6.67
sequential replacement, %	30.2
reaction time, min.	36
temperature, °C	26.5
final pH	1.6
extracted *P* no.	1.1

Isolation of Compounds

A bulk chlorination stage effluent sample (100 L) was extracted without pH adjustment (pH 1.96) for 48 hr with redistilled dichloromethane in 10 L continuous liquid-liquid extractors. The extracts were dried with anhydrous magnesium sulphate and the solvent was removed on a rotary evaporator; the extracts were combined to afford 6.1 g of extractives.

The combined extract was dissolved in diethyl ether and highly polar material was removed by precipitation/centrifugation following the addition of an equal volume of *n*-hexane. The concentrated supernatant was then introduced onto a 100 cm x 25 mm column of silica gel 60. Thirty 50 mL fractions were collected with hexane/diethyl ether/methanol (50:50:1) and a further 20 fractions (50 mL) were collected with hexane/diethyl ether/methanol (5:5:1) as the eluting solvent. Compound 5, the major chlorinated monoterpene hydrocarbon was present in 95% purity in fraction 8; other chlorinated monoterpene hydrocarbons were present in fractions 4-10. The chlorinated monoterpene alcohols were present in fractions 37-50. Fractions 37-50 were combined and further separated by preparative gas chromatography [10 m x 6 mm column, 5% SE-30 on Chrompak GW, helium carrier gas (400 kPa), temperature programmed from 150 to 222°C at 2°C.min^{-1}]. The preparative GC effluent was split 100:1 to collector and FID detector, respectively. Effluent fractions from 70 injections (5 µL) were combined to variously afford between 0.05 and 2 mg each of compounds 8-14, or their dehydro analogues.

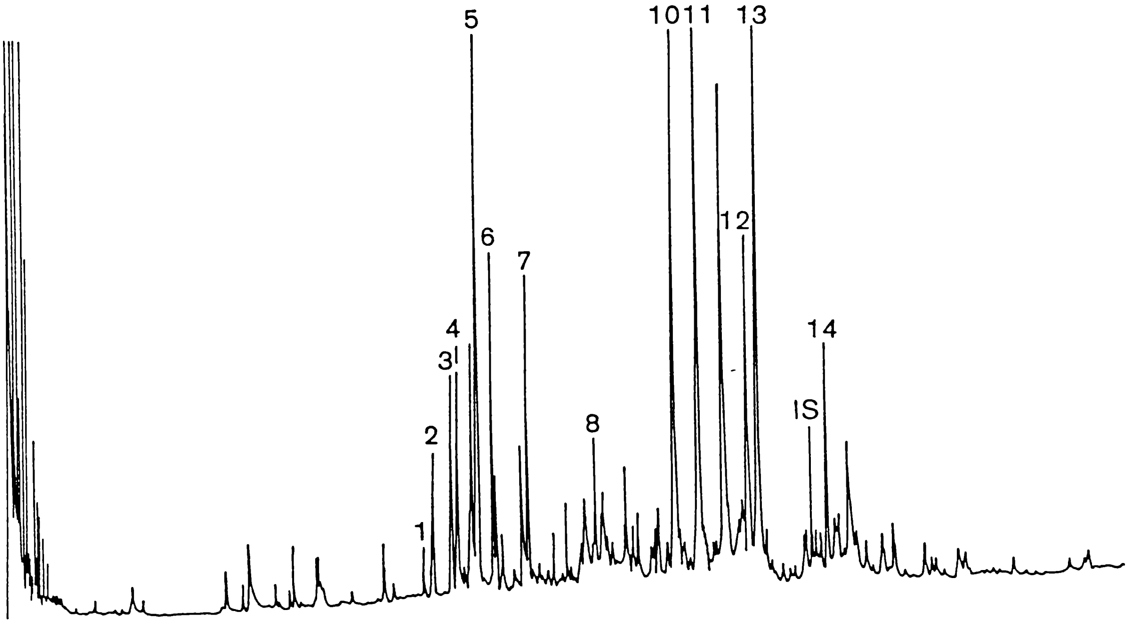


Figure 4.1: Gas chromatogram of chlorination stage effluent extract showing position of compounds 1-14 and octadecane internal standard (IS, 500 µg L^{-1})

Quantitation of Compounds

Effluent samples (125 mL) were acidified to pH 3 and extracted for 4 hr with dichloromethane in 125 mL liquid-liquid extractors using *n*-octadecane as internal standard. Extracts were dried with anhydrous magnesium sulphate and concentrated to ca. 1 mL on a rotary evaporator at 25°C. An ethereal solution of diazomethane was added to the concentrated extracts to derivatise acidic and chlorophenolic compounds present in the extracts. The derivatised samples were analysed on a Hewlett-Packard 5890 gas chromatograph, fitted with a 25 m HP-1 fused-silica capillary column. Helium was employed as carrier gas (linear velocity 30 cm s^{-1}); the injector and flame ionisation detector temperatures were maintained at 225 and 250°C, respectively. After a Grob splitless injection (30 s load), the gas chromatograph was programmed from 40 (2 min hold) to 250°C (16 min hold) at 5°C min^{-1}. Concentrations were calculated from the octadecane internal standard (equivalent to 500 µg L^{-1}) by using purified compound 13 as the response factor standard.

TABLE 4.2: EI Mass Spectral Data for Compounds 1-14

compound	mass fragment *m/z* (relative intensity)
monoterpene hydrocarbons	
1	55 (100), 81 (88.0), 95 (19.6), 105 (21.7), 121 (9.8), 135 (21.7), 171 (18.5)
2	55(100), 67 (80.4), 81 (18.5), 109 (59.2), 121 (16.3), 135 (25.0), 171 (23.9)
3	93 (23.9), 108 (100), 129 (7.6), 135 (23.9), 171 (7.1)
4	81 (100), 93 (38.0), 108 (44.6), 121 (18.5), 135 (53.3), 157 (9.8), 171 (47.3)
5	93 (100), 129 (64.0), 135 (55.9), 170 (13.0), 171 (5.0), 191 (0.5), 206 (0.7)
6	81 (12.0), 95 (15.2), 108 (100), 129 (5.4), 135 (16.8), 171 (16.3)
7	55 (100), 93 (43.5), 107 (50.5), 121 (53.3), 135 (52.2), 170 (8.7), 171 (6.0)
monoterpene alcohols	
8	59 (100), 95 (58.0), 110 (58.2), 135 (3.6), 150 (12.4)
9	69 (43.4), 93 (100), 111 (71.3), 160 (36.9), 207 (7.0), 222 (17.6)
10	59 (100), 93 (26.3), 128 (4.3), 129 (7.1), 171 (1.8), 187 (3.4), 207 (4.3), 225 (1.4)
11	59 (100), 93 (17.6), 128 (8.0), 129 (7.5), 173 (3.4), 187 (1.7), 207 (2.9), 225 (0.8)
12	59 (100), 93 (19.0), 128 (5.7), 129 (5.6), 173 (13.3), 189 (1.9), 207 (2.3), 225 (1.3)
13	59 (100), 93 (15.0), 128 (7.6), 129 (12.7), 171 (2.1), 187 (4.8), 207 (4.0), 225 (1.9)
14	59 (100), 127 (7.0), 177 (2.3), 185 (2.6), 221 (2.9), 241 (5.3), 259 (1.3)

Mass Spectrometry

EI-GC/MS and CI-GC/MS data were obtained on a Hewlett-Packard 5985 mass spectrometer using the GC conditions given above. EI-MS were obtained at 70 eV, 300-µA ionisation energy. CI-MS were obtained by use of hydrogen, ammonia, methane, or isobutane as ionizing gases. Accurate mass data were obtained by GC/MS (EI) on a Kratos MS80 RFA instrument operated at 3000 RP and 1 s $decade^{-1}$ scan rate.

^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM400 NMR spectrometer with deuteriochloroform as solvent and trimethylsilane as reference.

TABLE 4.3: Quantity of Chlorinated Monoterpenes Found in Chlorination Stage Bleaching Effluents[a]

compound	range, g ADT^{-1}	mean, g ADT^{-1}	SD
monoterpene hydrocarbons			
1	0.9-2.3	1.4	0.4
2	1.3-7.1	4.6	1.7
3	0.5-8.5	5.3	2.6
4	0.8-21.0	6.0	4.9
5	4.0-48.5	17.9	14.4
6	3.9-19.8	10.3	5.4
7	8.1-38.3	22.7	10.0
total	28.7-149.1	72.7	39.0
monoterpene alcohols			
8	0.3-10.2	3.3	2.9
9	<0.05[b]		
10	23.7-102.4	55.9	29.7
11	4.7-110.6	71.8	32.7
12	5.9-44.9	27.6	11.7
13	2.3-137.1	79.9	37.0
14	1.1-84.2	45.3	24.5
total	38.5-500.6	283.6	121.5
trichlorocatechol	5-24	16	6

[a] effluent volume for chlorination stage, 48 m^3 ADT^{-1}
[b] trace levels only

RESULTS AND DISCUSSION

GC/MS analysis revealed the presence in chlorination stage effluents of a series of nonaromatic chlorinated monoterpenes (Figure 4.1), the CI-MS and EI-MS of which served to subdivide the substances into two groups; namely, dichlorinated monoterpene hydrocarbons of molecular weight 206 amu (compounds 1-7, Table 4.2) and chlorinated monoterpene alcohols of molecular weight 222 amu and above (compounds 8-14, Table 4.2).

Analysis of chlorination stage effluents collected daily over a 4 week period showed that compounds 1-14 were the dominant low-molecular weight extractable organic compounds occurring in this effluent (Table 4.3; levels of trichlorocatechol are included for comparison).

In order to obtain sufficient quantities of some of the compounds for structural elucidation and biological studies, 100 L of spent chlorination effluent was extracted with dichloromethane. The isolation procedure gave two fractions. The less polar of the two fractions contained the predominant chlorinated monoterpenes hydrocarbon; compound 5, in 95% purity. The second more polar fraction was a dark-brown oil (0.5 g), which contained the chlorinated monoterpene alcohols (i.e., compounds 8-14).

Chlorinated Monoterpene Hydrocarbons (Compounds 1-7)

EI-MS and CI-MS showed that the molecular weight of each of compounds 1-7 was 206 (Table 4.2, Figure 4.2). High-resolution GC/MS analysis of compound 5 established the molecular formula and the identity of mass fragments in the spectra (Table 4.4). This was consistent with a dichlorinated pinane or bornane structure, which might arise from chlorination of *Pinus radiata* monoterpene hydrocarbons such as α-pinene and β-pinene.

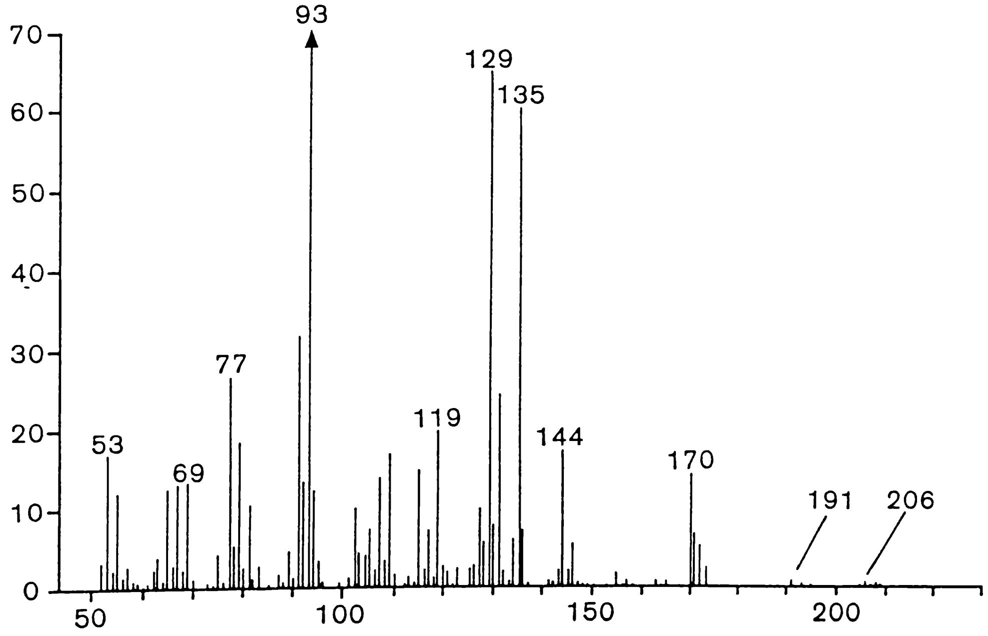


Figure 4.2: EI mass spectrum of compound 5

TABLE 4.4: High-Resolution Mass Spectral Data for Compounds 5 and 11

	m/z				
compound	nominal	exact	Δ (m/z), mmu	ion formula	origin
5	206	206.0559	-7.1	$C_{10}H_{16}Cl_2$	M
	191	191.0299	-9.1	$C_9H_{13}Cl_2$	M - CH_3
	171	171.0924	-1.6	$C_{10}H_{16}Cl$	M - Cl
	170	170.0875	1.5	$C_{10}H_{15}Cl$	M - HCl
	135	135.1158	-1.2	$C_{10}H_{15}$	M - HCl - Cl
	129	129.0453	-1.7	$C_7H_{10}Cl$	M - Cl - C_3H_6
	93	93.0715	1.1	C_7H_9	
11	225	225.0330	-12.0	$C_9H_{15}O_2Cl_2$	M - CH_3
	207	207.0315	-2.5	$C_9H_{13}OCl_2$	M - CH_3 - H_2O
	187	187.0869	-2.1	$C_{10}H_{16}Cl$	M - H_2O - Cl
	173	173.0721	-0.9	$C_9H_{14}OCl$	M - H_2O - CH_2Cl
	129	129.0377	-9.3	$C_7H_{10}Cl$	M - H_2O - Cl - C_3H_6O
	128	128.0323	-6.7	C_7H_9Cl	M - H_2O - HCl - C_3H_6O
	59	59.046	-3.6	C_3H_7O	

The quantity and purity of the fraction containing compound 5 was sufficient for the determination of this substance's ^{1}H and ^{13}C NMR spectra. The spectra (see Table 4.5) corresponded with those previously reported (Parlar *et al.*, 1977) for 2-*endo*-6-*endo*-dichlorobornane, a rearrangement product obtained on chlorination of α-pinene (Figure 4.3).

While the purity and quantities of fractions containing compounds 1-4, 6 and 7 recovered from column chromatography on silica gel were not sufficient for the elucidation of their structures by NMR analysis, their mass spectral features (Table 4.2) were consistent with the view that they were also dichlorinated pinanes or bornanes (Figure 4.3).

Chlorinated Monoterpene Alcohols (Compounds 8-14)

Repeated attempts to further separate compounds 8-14 by column chromatography on silica gel using a variety of solvents were unsuccessful. Separation of these compounds was attempted using a preparative GC system. Ten preparative GC fractions were isolated and were found to be a mixture of the original compounds and dehydrated analogues of some of them. Dehydrated compounds were occasionally also observed when injections were made onto the capillary GC system. The purity and quantity of fractions 4, 6 and 9 were sufficient for the elucidation of the structures of the major substances using one- and two-dimensional NMR techniques.

TABLE 4.5: NMR Assignments for Compounds 5, 11, 13, and 14

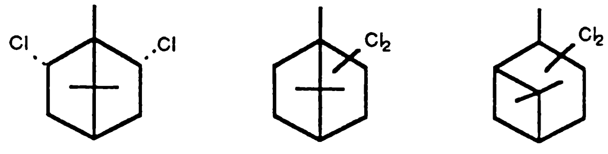
proton position	^1H NMR chemical shifts, ppm			
	5	11[a]	13[a]	14[a]
$H2_{eq}$	4.35 (dd)	4.23 (m)	4.21 (m)	4.62 (m)
$H3_{eq}$	1.5-1.8 (m)	1.94 (m)	1.88 (m)	2.15 (m)
$H3_{ax}$	2.62 (m)	2.17 (m)	2.04 (m)	2.30 (m)
$H4_{ax}$	1.84 (m)	2.43 (m)	2.35 (m)	2.70 (m)
$H5_{eq}$	1.5-1.8 (m)	1.68 (m)	1.75 (m)	1.97 (m)
$H5_{ax}$	2.62 (m)	1.68 (m)	1.75 (m)	1.97 (m)
$H6_{eq}$	4.23 (dd)	1.82 (t)	1.97 (t)	
$H6_{ax}$		1.82 (t)	1.97 (t)	4.20 (m)
$H7_{(1,2,3)}$	1.10 (s)	3.76 (AB q)	3.85 (AB q)	4.25 (AB q)
$H9_{(1,2,3)}$	0.95 (s)	4.74 (s)	4.74 (s)	4.81 (s)
$H10_{(1,2,3)}$	0.95 (s)	1.74 (s)	1.74 (s)	1.78 (s)

carbon position	^{13}C NMR chemical shifts, ppm			
	5	11[a]	13[a]	14[a]
C1	53.1	72.6	75.8	b
C2	64.1	60.5	70.1	60.6
C3	40.2	34.4	33.4	33.3[c]
C4	43.2	37.7	37.5	31.8
C5	40.2	25.8	26.3	34.5[c]
C6	64.1	29.4	32.4	73.2
C7	11.9	53.6	52.9	51.4
C8	49.6	148.6	148.7	b
C9	20.5	109.5	109.4	110.5
C10	20.5	21.0	20.7	20.9

a dehydrated derivatives (at C8) of compounds 11, 13 and 14.
b quaternary carbon atoms saturated, not observed.
c may be assigned either way.

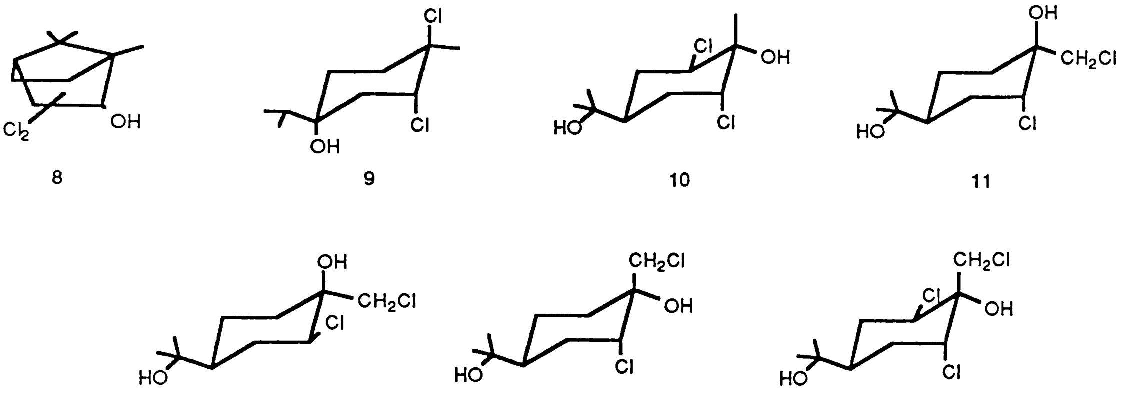
Compounds 11 and 13

EI mass spectra of compounds 11 and 13 (the major constituents of the chlorination stage effluent extracts), while each lacking a molecular ion, included an intense fragment of m/z 59, attributable to a $(CH_3)_2=OH^+$ ion (Table 4.2, Figure 4.4). Such an ion is typical of that displayed by α-terpineol (Swigar and Silverstein, 1981). CI mass spectra established in the molecular weight of these compounds to be 240 amu (Figure 4.5). Under higher source chlorinated monoterpene hydrocarbons



5 1-4, 6, 7

chlorinated monoterpene alcohols



8 9 10 11

12 13 14

Figure 4.3: Proposed structures for compounds 1-14

pressure, such as when using an ion trap detector system (ITDS), (Stuthridge, 1987) or when obtaining CI-MS, compounds 11 and 13 (like compounds 10, 12, and 14) showed a preference for an initial loss of a hydroxyl radical to afford an (M^+ - 17) ion rather than an (M^+ - 15) ion (methyl radical loss). High-resolution EI-MS analysis established the formulas of the principal mass ions (Table 4.4). The foregoing data were consistent with the view that these compounds were dichlorinated derivatives of α-terpineol containing an additional hydroxyl group, but did not establish the sites or stereochemical disposition of the additional substituent groups.

Preparative GC separation of compounds 11 and 13 gave the dehydrated analogues of these compounds as the major products. The ^{1}H NMR spectrum of dehydro-11 included signals attributable to an isopropylidene group [1.74 and 4.75 ppm ($H_3CC{=}CH_2$)], a CH_2Cl group (3.56 and 3.97 ppm, AB q, J = 11.2 Hz) and a CHCl group (4.23 ppm, m, $W_{1/2}$ = 5 Hz) (Table 4.5). The lack of a m/z 59 fragment in the EI mass spectrum of dehydro-11 was consistent with dehydration of the tertiary 2-propanol group. The foregoing observations suggested dehydro-11 to be 2α,7-dichloromenth-8-en-1β-ol or 2α,7-dichloromenth-8-en-1α-ol since the comparatively small line width of the secondary CHCl proton indicates the Cl atom to be axially oriented, while the primary CH_2Cl group's lack of a ^3J coupling requires its attachment to be a quaternary carbon atom.

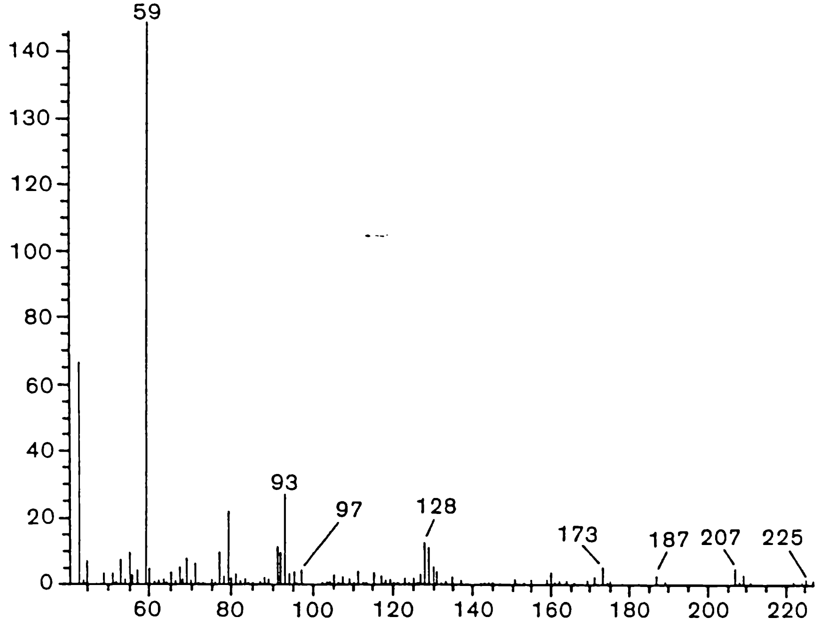


Figure 4.4: EI mass spectrum of compound 11

The 400-MHz two-dimensional ^1H-^1H correlated (COSY) spectrum of dehydro-11 demonstrated that the CHCl proton was ^3J coupled to $H3_{eq}$ (1.94 ppm) and $H3_{ax}$ (2.17 ppm), while $H4_{ax}$ was ^3J coupled with $H3_{ax}$, $H5_{eq}$ and $H5_{ax}$, and ^4J coupled to the protons of the C=CH_2 group. That $H3_{ax}$ experiences two couplings of the order 12 Hz [^2J-($H3_{ax}$-$H3_{eq}$) and ^3J-($H3_{ax}$-$H2_{eq}$)] and one of 3.1 Hz [^3J-($H3_{ax}$-$H2_{eq}$)] confirmed the orientation of the C2 chlorine atom as axial. The ^1H NMR chemical shifts of dehydro-11 were in turn correlated with ^{13}C NMR chemical shift values in a ^{13}C-^1H correlation experiment. This experiment in combination with the COSY experiment, readily distinguished the C3, C5, and C6 methylene carbon signals. Although the chemical shift values of some of the ^1H (and ^{13}C) NMR signals of dehydro-11 differed from those of dehydro-13, the H2, H3, and H4 multiplicities (coupling constants) of these compounds were essentially identical. These compounds were therefore isomers differing only in respect of their Cl configurations.

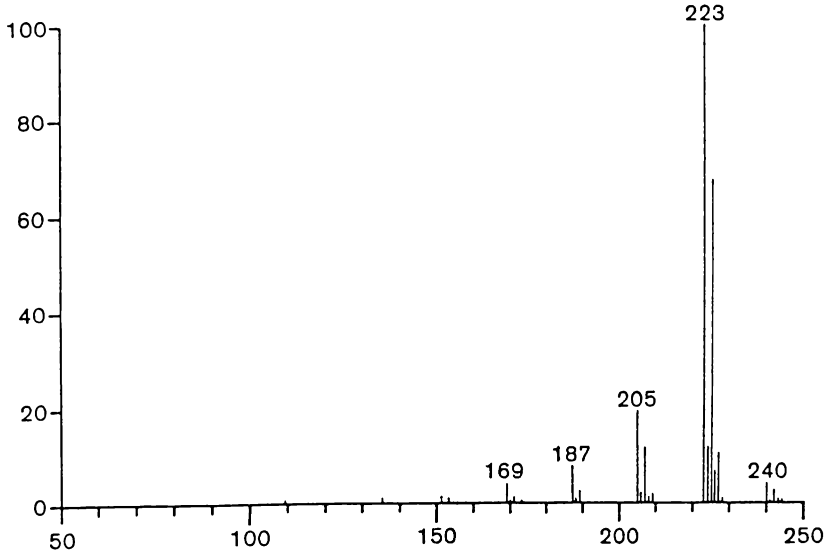


Figure 4.5: CI mass spectrum of compound 11

While the presence of three substituents on two adjacent carbons (C1 and C2) is likely to limit the validity of chemical shift predictions based on substituent group increment values, it can, however, be anticipated that the presence at C1 of an equatorial hydroxyl group will result in C6 and C2 experiencing a greater downfield shift than would be the case for an axial hydroxyl group. Similarly, a difference of approximately 30 ppm in the total ^{13}C NMR shifts of compounds containing axial and equatorial substituents, respectively, could be expected (Breitmaier, 1978). Thus, dehydro-11 (total shift 592.68 ppm) and dehydro-13 (total shift 607.13 ppm) were shown to be 2α,7-dichloromenth-8-en-1β-ol and 2α,7-dichloromenth-8-en-1α-ol, respectively, and therefore it was concluded that compounds 11 and 13 were 2α,7-dichloromenthane-1β,8-diol and 2α,7-dichloromenthane-1α,8-diol, respectively (Figure 4.3).

Compounds 8-10, 12, and 14

The EI mass spectra of compound 8 (Table 4.2, Figure 4.6) did not include a molecular ion. However, its relative retention time was consistent with it being a dichlorinated monoterpene. The presence of strong m/z 95 and 110 fragment ions suggested it was an analogue of borneol (Swigar and Silverstein, 1981) and a structure is tentatively proposed for this compound (see Figure 4.3).

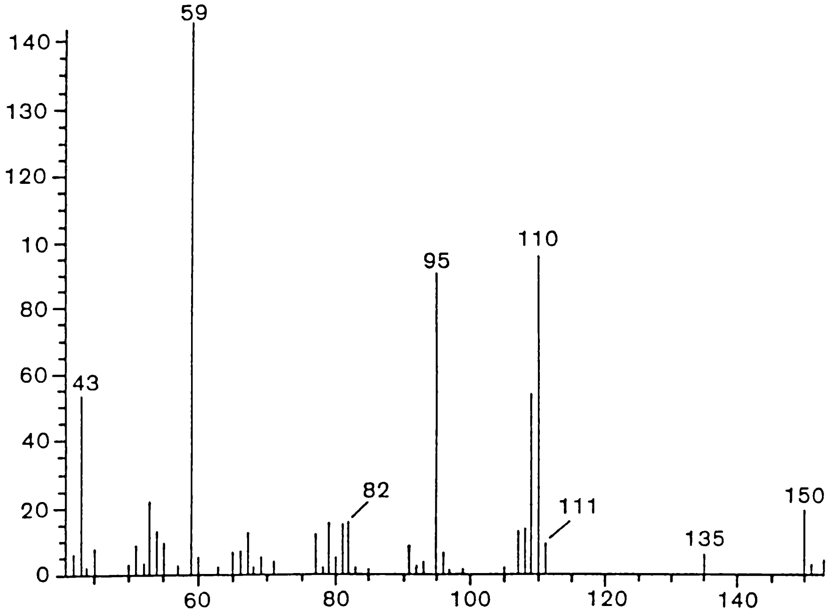


Figure 4.6: EI mass spectrum of compound 8

The EI mass spectrum of compound 9 (Table 4.2, Figure 4.7) included strong m/z 93 and 111 fragment ions reminiscent of the mass spectrum of terpinen-4-ol (Swigar and Silverstein, 1981). The *trans*-diaxial-dichloro adduct is known to be the major product formed during chlorination of terpinen-4-ol (Carman and Venzke, 1973). The prominent fragment at m/z

160, attributable to the retro-Diels-Alder elimination of C_2H_3Cl at C2 and C3 in a six-membered ring, is consistent with this structure (Figure 4.3).

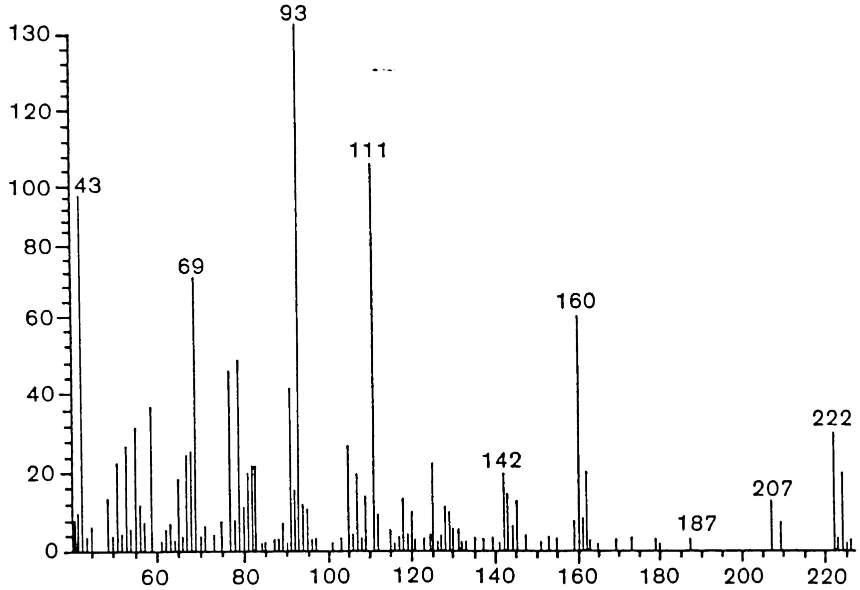


Figure 4.7: EI mass spectrum of compound 9

The EI and CI mass spectra of compound 10 were similar to those of compounds 11 and 13 (Table 4.2). However, the absence of a fragment at m/z 173 in the EI mass spectrum and lack of an AB quartet signal at approximately 4 ppm in this compound's ^1H NMR spectrum indicated that it did not contain a CH_2Cl group. The MS and NMR spectral data were consistent with compound 10 being 2α,6β-dichloro-*p*-menthane-1α,8-diol, a minor component (9% yield) formed during low pH aqueous chlorination of α-terpineol (Kopperman *et al.*, 1976, Figure 4.3).

GC/MS data of compound 12 indicated that it was an isomer of compounds 11 and 13 (Table 4.2). The fragment ion at m/z 173 showed the presence of a CH_2Cl group. It is therefore likely that compound 12 is a C2-epimer of 11 or 13 (Figure 4.3).

CI-MS established the molecular weight of compound 14 to be 274 amu, while mass fragments in the EI-MS (Table 4.2, Figure 4.8), which were m/z 34 higher than those found for compounds 11 and 13, indicated compound 14 to be a trichlorinated analogue of these compounds. GC/MS examination of preparative GC fractions 9 and 10 showed both of them to be dehydrated analogues of compound 14. A sufficient amount of fraction 9 was available for NMR analysis. ^1H and ^{13}C NMR data established that in this fraction the additional chlorine atom was sited at C6 and that the compound had the C1 configuration of dehydro-11 (see Table 4.5). The chemical shifts of the H2 and H6 protons were not equivalent, demonstrating that the C6 chlorine atom is equatorial. This observation is in keeping with Kopperman's observation that aqueous chlorination of α-terpineol affords 2,6-dichlorinated derivatives in which the chlorine atoms are respectively axially and equatorially oriented (Kopperman *et al.*, 1976, Figure 4.3). Since compound 14 gave rise to two preparative GC fractions, it is possible that epimerisation at C1 may have occurred during preparative GC of compound 14. The mass spectra of the two fractions differed in their preference for initial hydroxyl or chlorine loss. This result may be a consequence of the orientation of the C1 hydroxyl group. The C1 stereochemistry of compound 14 was not determined.

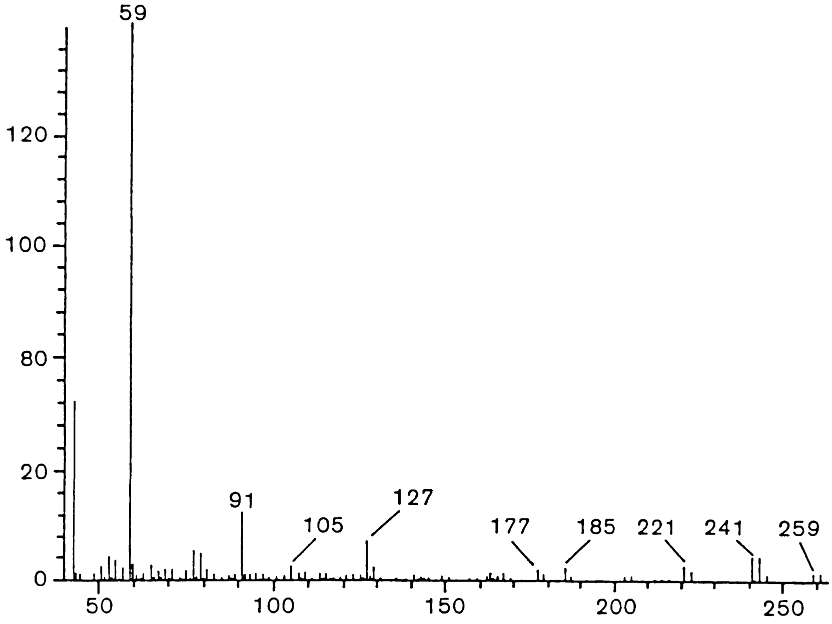


Figure 4.8: EI mass spectrum of compound 14

Formation of Chlorinated Monoterpenes

Compounds 1-14 arise from the chlorination of monoterpenes contained in the brown stock. High concentrations of these chlorinated monoterpenes are found in the wastewaters from one of the mill's two bleach plants. *Pinus radiata* brown stock for this bleach plant is produced in a continuous kraft digester and contains approximately 900 g of pentane-extractable monoterpenes per air-dried tonne of unbleached pulp.

Brown stock for the mill's other bleach plant is supplied from a batch digester kraft pulp mill and contains 20-25% hardwood pulp. The monoterpene content of this brown stock is approximately 80 g ADT^{-1} unbleached pulp and effluents from this bleach plant have substantially lower concentrations ($x10^{-2}$) of chlorinated monoterpenes.

A mill study has shown that a 80% turpentine recovery is achieved by the batch digesters, whereas recoveries of 20% are typical for the continuous digester (Goessens, 1984). Since washing of each of the bleach plant brown stocks utilises fresh water and soda losses for both feeds are approximately 15 kg ADT^{-1}, indicating comparable washing efficiencies (Campin, 1990), it would appear that the formation and high concentration of these chlorinated monoterpenes in the mill's no. 2 bleach plant is due to poor removal of wood extractives during pulping. This is supported by higher levels of other chlorinated extractive products (e.g., chlorinated resin acids) found in wastewaters from this bleach plant.

Chlorinated monoterpenes of this type have also been found in the chlorination stage wastewaters from the other New Zealand kraft mill. This mill also bleaches continuously digested *Pinus radiata* kraft pulp. However, concentrations of the chlorinated monoterpenes are substantially lower than those reported here. It would appear that although chlorine bleaching of pine species pulps should lead to the formation of these chlorine monoterpenes, they will only be readily detectable in bleaching wastewaters when the pulping process leaves a relatively high concentration of extractives in the brown stock.

A previous investigation (Kopperman *et al.*, 1976) of the aqueous chlorination of α-terpineol demonstrated that product distributions were pH sensitive. At low pH the major products were the *cis* and *trans* isomers of the 2-chloro-*p*-menthane-1,8-diols, the formation of which was considered to arise via addition of HOCl. A small amount of compound 10 was also produced but compounds 11 and 13 were not detected. Our results can be accounted for by the proposal that under chlorination stage conditions α-terpineol reacts with chlorine (as Cl_2) to give a chloronium ion species, which can be quenched (neutralised) by the attack of a water molecule to afford a chlorohydrin adduct. The introduction of the second chlorine atom (typically to give a CH_2Cl group) may proceed via dehydration of the initial chlorohydrin to afford a chloroalkene, which may then react in a like manner.

To our knowledge, previous reports of chlorinated monoterpenes in bleaching effluents have been confined to the chlorinated cymenes and cymen-8-ols (Kringstad and Lindström, 1984). Small amounts of these compounds were found in the bleaching effluents of the mill under study. Another group of chlorinated monoterpenes of unknown structure and with molecular masses and formulas different from those reported here have recently been reported (Carlberg *et al.*, 1988). Therefore, it would seem that these chlorinated monoterpene hydrocarbons and alcohols are novel.

CONCLUSIONS

Our work has identified 14 previously unreported compounds present in chlorination stage bleaching effluents from a kraft pulp and paper mill operating on the softwood *Pinus radiata*. The compounds are chlorinated and hydroxylated derivatives of the *Pinus radiata* monoterpenes, α-pinene, β-pinene, borneol, terpinen-4-ol, and α-terpineol. These compounds arise from the chlorination of monoterpenes entering the bleach plant as a result of incomplete removal of wood extractives during pulping in the mill's continuous kraft digester. These chlorinated monoterpenes are the major low molecular weight, chlorinated organic compounds discharged in the mill's bleached plant wastewaters. Studies are underway to determine their toxicity, mutagenicity, and fate in the mill's effluent treatment system.

ACKNOWLEDGEMENTS

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Chapter Five

BIOLOGICAL ACTIVITY OF CHLORINATED MONOTERPENES FORMED DURNG KRAFT PULP BLEACHING OF *PINUS RADIATA*

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Submitted for publication

BIOLOGICAL ACTIVITY OF CHLORINATED MONOTERPENES FORMED DURING KRAFT PULP BLEACHING OF *PINUS RADIATA*

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ABSTRACT - The biological activity of two classes of chlorinated monoterpenes formed during the bleaching of kraft pulped *Pinus radiata* was assessed. The chlorinated monoterpene alcohols were base labile with a 94% decrease in concentration being observed within 4 hours at pH 12. The chlorinated monoterpene hydrocarbons exhibited a lesser degree of alkaline lability. Acute toxicity tests on the monoterpene alcohols gave EC_{50} concentrations of 60-200 mg L^{-1}, indicating that these compounds display relatively little toxicity. The monoterpene alcohols were also tested for mutagenicity and genotoxicity. Some of these compounds produced mutagenic and genotoxic responses. An assessment of the bioaccumulation potential of the chlorinated monoterpene alcohols showed them to have log K_{OW} values of 1.37-2.1. Therefore, these compounds are unlikely to exhibit a significant bioaccumulation propensity.

Treatment of the chlorination stage effluents in an aerated lagoon treatment system removed 80% of the chlorinated monoterpene alcohols but only a small fraction of the monoterpene hydrocarbons. On the basis of these results it is concluded that this class of compounds is unlikely to produce significant environmental effects in the recipient.

KEYWORDS - Bleaching effluents, chlorinated monoterpenes, toxicity, mutagenicity, bioaccumulation, biological effluent treatment

INTRODUCTION

As part of an on-going study on the characteristics and environmental effects of New Zealand bleached kraft mill effluents, the identification of a group of novel chlorinated monoterpenes was recently reported (Stuthridge *et al.*, 1990a). Fourteen chlorinated and hydroxylated derivatives of the major *Pinus radiata* monoterpenes were identified in chlorination stage effluent. Seven compounds were chlorinated monoterpene hydrocarbons and seven were chlorinated monoterpene alcohols (Figure 5.1). These were the predominant low molecular weight extractable organic compounds in this effluent with total concentrations ranging from 1.4-12.3 mg L^{-1}. In this paper, the possible environmental effects of these compounds are assessed. Representative compounds were tested for their stability, toxicity, mutagenicity, genotoxicity, bioaccumulation potential and biodegradability.

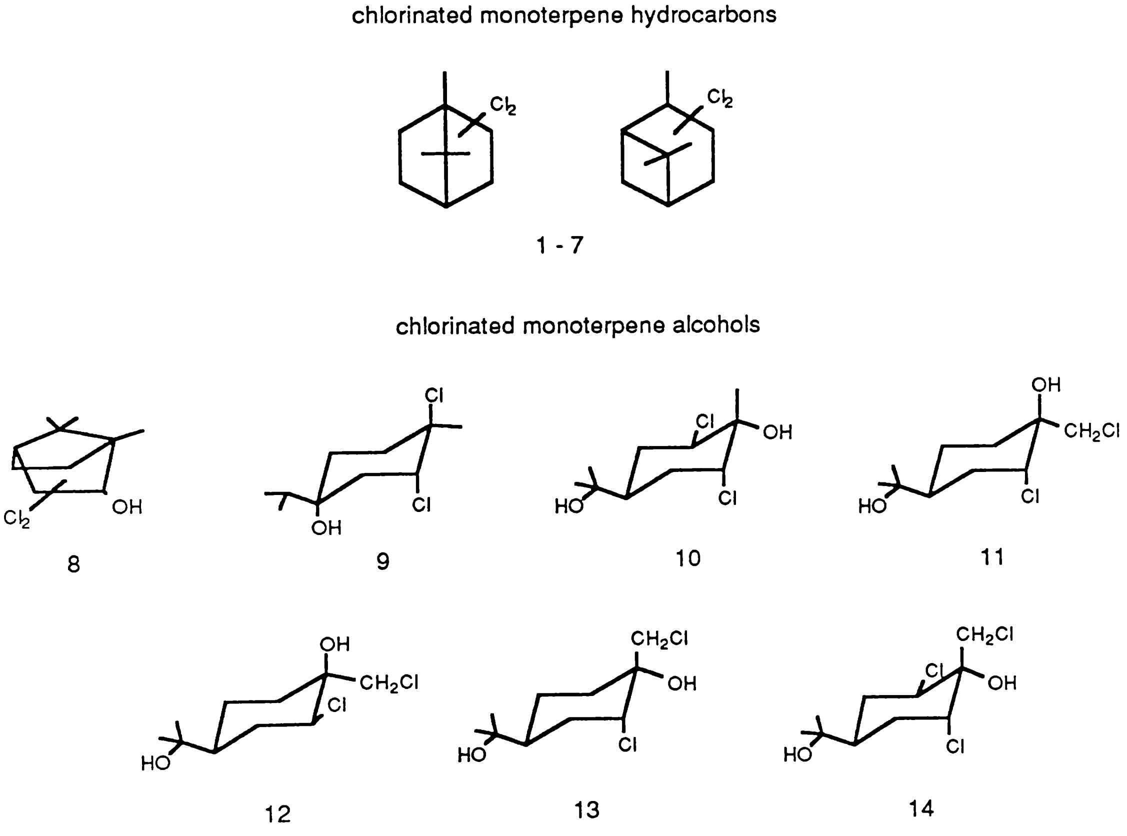

Figure 5.1: Structures of chlorinated monoterpenes

EXPERIMENTAL

Extraction and Isolation

Four samples of effluent were collected over a two week period from the chlorination stage of a New Zealand bleached kraft pulp and paper mill. Details of chlorination stage operating conditions are given in a previous paper (Stuthridge *et al.*, 1990a). Chlorination stage effluent (total volume 1250 L) was extracted for 96 hours immediately after collection without pH adjustment (pH ca. 2) using re-distilled dichloromethane in a 250 L glass liquid-liquid extractor. After drying with anhydrous magnesium sulphate, the solvent was removed to afford a total of 38 g of extractives. A portion of this extract (32 g) was then subjected to the isolation procedures outlined in Figure 5.2.

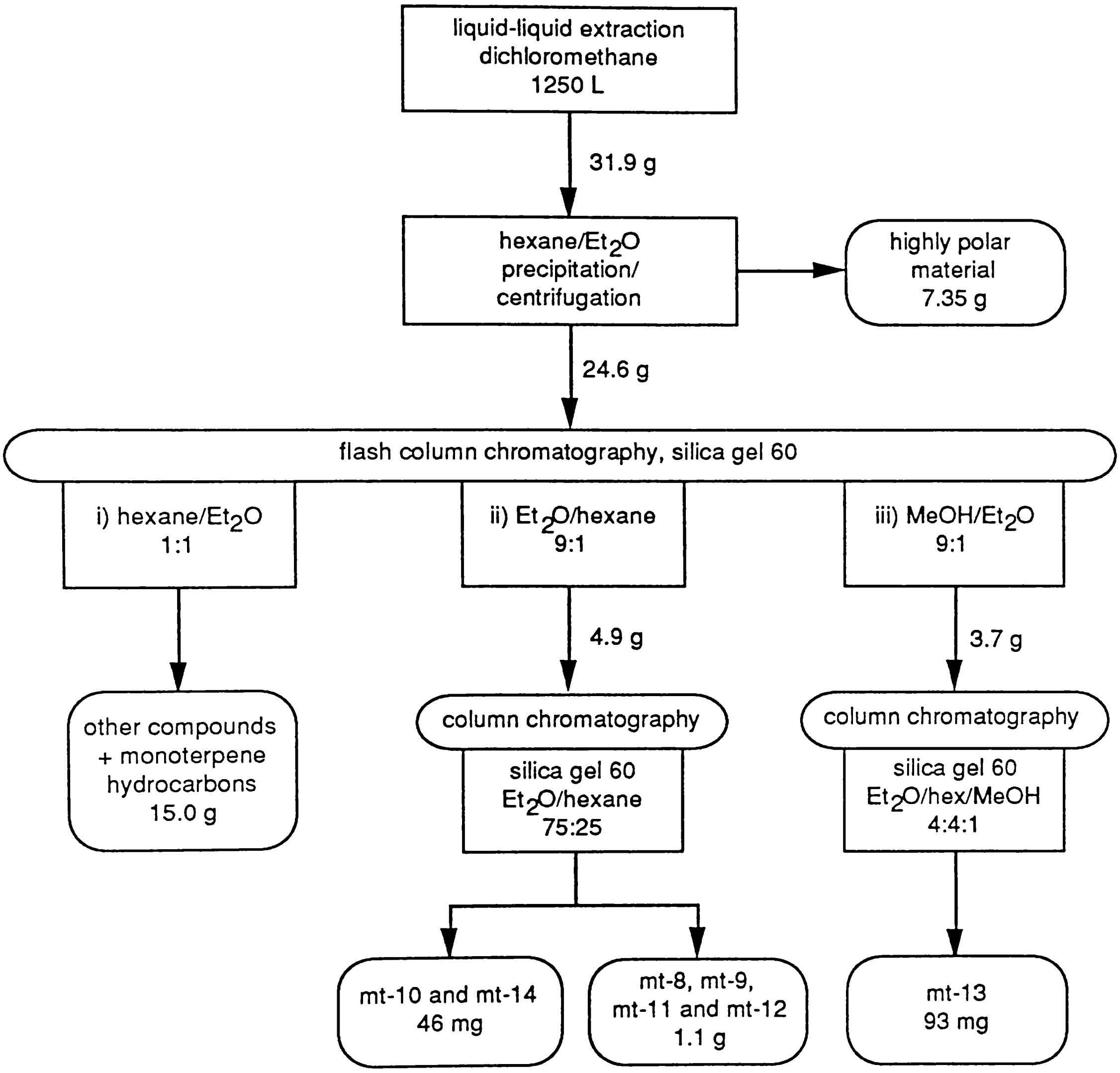

Figure 5.2: Procedure for the isolation of chlorinated monoterpenes

Bioaccumulation Potential

The bioaccumulation potential (log K_{OW}) was determined by reversed-phase HPLC (Xie *et al.*, 1984). A Waters 600 multisolvent pump was used to isocratically pump methanol, in different proportions with 0.05 mol L^{-1} phosphoric acid, at a flow rate of 1.8 mL min^{-1}. All solvents were degassed with helium. A Brownlee MPLC RP-8 Spheri-10 column was used in an oven at 30°C. Detection of eluted compounds was achieved using a Tracor 978 variable wavelength detector. Aromatic compounds were detected at 254 nm, while nitrate, used to determine the retention time of the unretained solute, and the chlorinated monoterpenes were detected at 280 nm.

Capacity factors for each solute were determined at different methanol compositions (65, 75, 80, 85, 90 and 95%) and the log k° value of each compound was calculated by extrapolation to 0% methanol using linear regression analysis. Eight compounds with previously determined log K_{OW} values were chosen to prepare a calibration equation (log k° vs. log K_{OW}, Table 5.1).

TABLE 5.1: Calibration Compounds for Calculation of Partition Coefficients

compound	log K_{OW}	reference
benzoic acid	1.87	Suntio *et al.* (1988)
benzene	2.13	Suntio *et al.* (1988)
2,4-dichlorophenol	2.75	Bjorndal and Solyom (1987)
4,5-dichloroguaiacol	2.89	Bjorndal and Solyom (1987)
2,4,6-trichlorophenol	3.72	Xie *et al.* (1984)
cymene	4.10	Suntio *et al.* (1988)
3,4,5-trichloroguaiacol	4.15	Xie *et al.* (1984)
tetrachloroguaiacol	4.31	Bjorndal and Solyom (1987)

Acute Toxicity

Three assays were used to determine the toxicity of the chlorinated monoterpenes. The toxicity assays are given below. All ethanol concentrations used were tested and shown to exhibit no toxicity in each of the assays.

1. Acute toxicity (EC_{50}, 24 h) with *Daphnia magna*, aged < 24 hours, standard soft dilution water, temperature 20°C (Hickey, 1989). Samples were dissolved in ethanol and the assays undertaken at an ethanol concentration of 0.5%.

2. Algal toxicity (EC_{50}, 96 h) with *Selenastrum capricornutum*, undertaken using the standard assay procedure of Blaise *et al.*, (1986). Samples were dissolved in ethanol and the assays undertaken at an ethanol concentration of 1%.

3. Microtox bioassay (EC_{50}, 15 min) with *Photobacterium phosphoreum*, undertaken using a standard assay procedure (Ribo and Kaiser, 1987). Samples were dissolved in ethanol and the assays undertaken at an ethanol concentration of 5%.

Mutagenicity and Genotoxicity

The chlorinated monoterpenes were tested for mutagenicity with the Ames "pour plate" test (Maron and Ames, 1983). *Salmonella typhimurium* TA-98 and TA-100 were used with and without metabolic activation (±S9). 2-Nitrofluorene, 2-aminoanthracene and sodium azide were used as positive controls.

Genotoxicity assays were performed on the chlorinated monoterpenes using the Orgenics SOS-Chromotest (Quillardet and Hofnung, 1985). Tests were run in duplicate with and without activation mix (±S9). Positive controls were included for validation purposes. Samples were dissolved in 78% DMSO.

Analysis of Effluents

Details of the extraction, gas chromatography and gas chromatography/mass spectrometry methods for the analysis of the chlorinated monoterpenes have been presented elsewhere (Stuthridge *et al.*, 1990a).

RESULTS AND DISCUSSION

Extraction and Isolation

Small amounts (1-5 mg) of each of the chlorinated monoterpenes were previously isolated for the purposes of structural identification (Stuthridge *et al.*, 1990a). These quantities were insufficient for subsequent biochemical analyses. It was not possible to scale up the previous isolation procedure which used preparative gas chromatography. A bulk liquid-liquid extraction of chlorination stage effluent was therefore undertaken.

Following the removal of highly polar material from the extract, it was possible to separate the chlorinated monoterpene alcohols from the remaining low molecular weight organic compounds by flash column chromatography using selected solvent mixtures (Figure 5.2). Further liquid column chromatography of the chlorinated monoterpene extracts led to the isolation of monoterpene 13 as pure crystals (93 mg). Monoterpenes 10 and 14 co-crystallised as a 1:1 mixture (46 mg) and could not be further separated. A pale yellow oil (1.1 g) containing only the remaining chlorinated monoterpene alcohols was also obtained.

Despite rigorous attempts to separate the chlorinated monoterpene hydrocarbons from the remaining low molecular weight compounds, it was not possible to obtain fractions of sufficient purity for the biological activity assessment of these compounds. Therefore, this paper focuses on the biological activity of the chlorinated monoterpene alcohols. However, some inferences on the effects of the monoterpene hydrocarbons can be drawn from the results obtained for the monoterpene alcohols.

pH Stability

Many of the neutral compounds present in chlorination stage effluents are unstable under neutral and alkaline conditions (Holmbom *et al.*, 1984; Kringstad *et al.*, 1983; Odendahl *et al.*, 1989). Storage of the chlorination stage effluents for one month showed that the chlorinated monoterpenes were stable at the discharge pH of these effluents (pH *ca.* 2). To further test the stability of the chlorinated monoterpenes, chlorination stage effluent was adjusted to a range of pH values and mixed for four hours. After mixing, the effluents were readjusted to the initial pH and analyzed. Results of these tests are presented in Figure 5.3. The chlorinated monoterpene alcohols are readily degraded at neutral pH and above with almost complete removal being observed at pH 12 (94% decrease). The monoterpene hydrocarbons show some alkaline lability but are more stable than the alcohols.

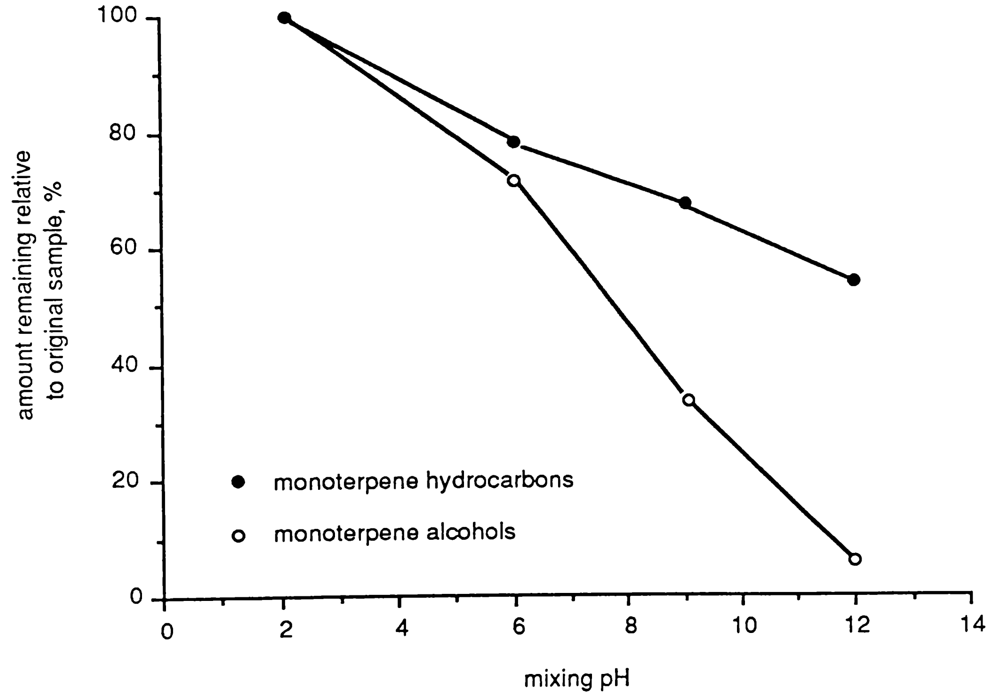

Figure 5.3: Effects of pH on chlorinated monoterpenes

Bioaccumulation Potential

An assessment of the lipophilicity of the chlorinated monoterpene alcohols was made using the HPLC method of Xie *et al.*, (1984). Using compounds of known log K_{OW} values (Table 5.1), an excellent correlation between log k° and log K_{OW} was obtained (Figure 5.4). Monoterpene 13, the only pure chlorinated monoterpene isolated, was analysed and calculated to have a log k° value of 1.325. Using the correlation equation, this compound was found to have a log K_{OW} of 1.37, which is indicative of a low bioaccumulation propensity (Holmbom *et al.*, 1984). The other dichlorinated monoterpene alcohols would be expected to have similar log K_{OW} values.

As a linear correlation exists between the degree of chlorination and log K_{ow} (Kringstad *et al.*, 1984), the lipophilicity of the trichlorinated monoterpene alcohol (monoterpene 14) could also be estimated. Correlations between chlorine number and log K_{ow} were calculated from published data (Suntio *et al.*, 1988). The increase in log k_{ow} per chlorine atom was found to range from 0.55 to 0.72. On this basis, monoterpene 14 would have a greater bioaccumulation potential than the dichlorinated monoterpene alcohols (log K_{ow} *ca.* 1.9-2.1), but would still have a log K_{ow} below 3, the level at which significant bioaccumulation is expected to occur (Hawker and Connell, 1988).

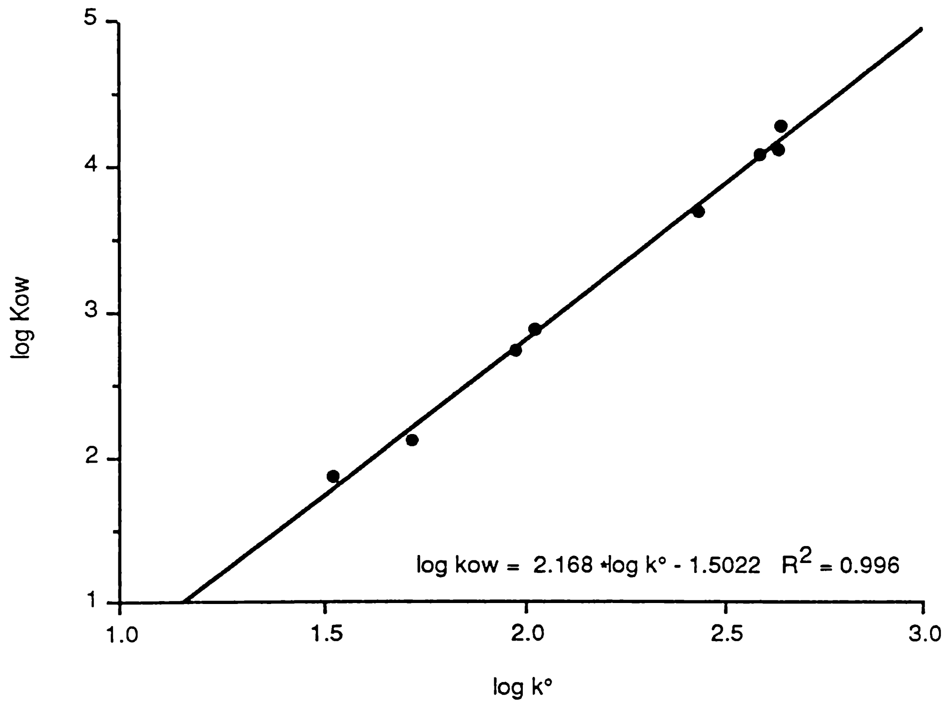

Figure 5.4: Calibration curve for bioaccumulation determination

Acute Toxicity

Assays with *Daphnia magna* confirmed that the chlorination stage effluents discharged from the pulp and paper mill were acutely toxic (24 h EC_{50} = 16% v/v).

Three toxicity bioassays were performed on the isolated chlorinated monoterpene alcohols to determine their contribution to this toxicity. The results of these tests are presented in Table 5.2. The monoterpene alcohols do not exhibit an appreciable acute toxicity and the EC_{50} values for these compounds are greater than the concentrations of these compounds found in the effluents. Previous studies on chlorinated derivatives of monoterpene alcohols have shown them to be of similar toxicity or less than the parent compounds (Kopperman *et al.*, 1976).

TABLE 5.2: Toxicity of Chlorinated Monoterpene Alcohols

compound	toxicity, EC_{50}, mg L^{-1} *D. magna*	algae	Microtox
monoterpene 13	>5.5*	n/d	n/d
monoterpenes 10 & 14	>50*	>50*	232
other monoterpene alcohols	>34*	61	208

* highest concentration available for assay

n/d - not determined

Mutagenicity and Genotoxicity

Chlorination stage effluents are responsible for most of the mutagenic activity found in wastewaters from pulp and paper mills (Priha and Talka, 1986). Mutagenicity and genotoxicity assays of the total chlorination stage effluent extract and the chlorinated monoterpene alcohol fractions were undertaken (Table 5.3). These tests confirmed that the effluent was mutagenic and genotoxic both with and without metabolic activation.

Ames tests indicated that monoterpenes 10, 13 and 14 were not mutagenic. The oil containing the remaining chlorinated monoterpene alcohols was found to be mutagenic without activation (Figure 5.5). Similar results were found for genotoxicity assessments with the exception that monoterpene 13 was also genotoxic without activation.

TABLE 5.3: Mutagenicity and Genotoxicity of Chlorinated Monoterpene Alcohols

	Ames mutagenicity[a]				SOS genotoxicity[b]	
	TA98		TA100			
	-S9	+S9	-S9	+S9	-S9	+S9
total effluent extract	+(3.0)	+(150.3)	+(1.5)	+(15.0)	+(3.5)	+(32.5)
monoterpene 13	-	-	-	-	+(34.8)	-
monoterpenes 10 and 14	-	-	-	-	-	-
other monoterpene alcohols	+(7.6)	-	+(7.6)	-	+(8.4)	-

\- = negative at concentrations tested

a = +, positive response, doubling of mutation rate at concentration in brackets, mg L^{-1}

b = +, positive response, lowest detectable concentration for genotoxicity, mg L^{-1}

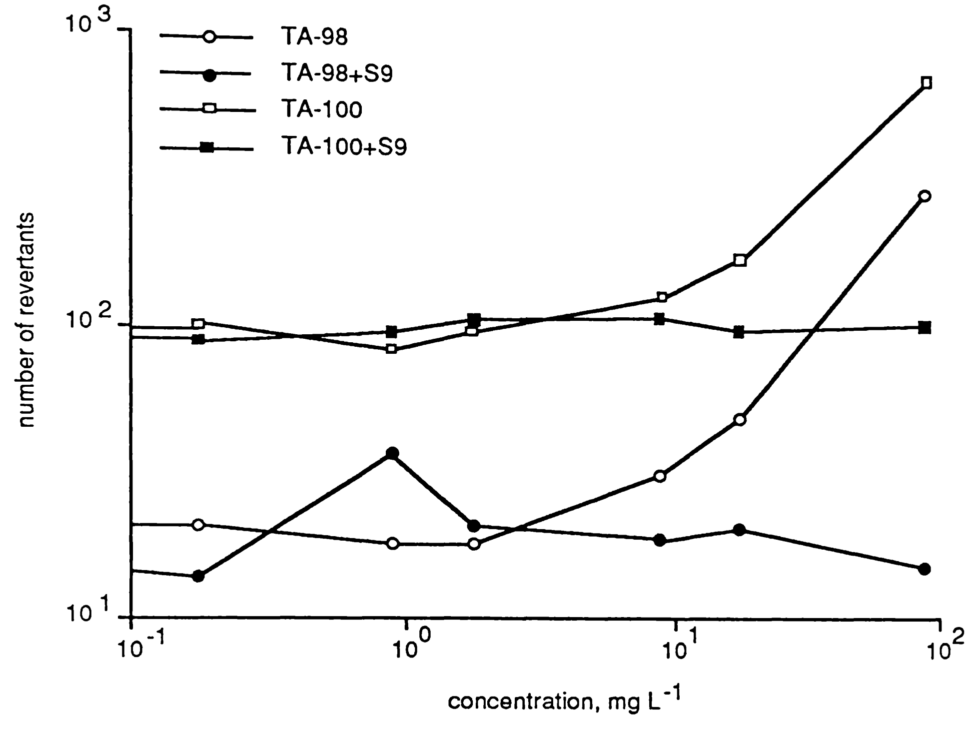

Figure 5.5: Ames mutagenicity dose response curve for the chlorinated monoterpene alcohol oil

Fate in an Effluent Treatment System

Chlorination stage bleaching effluents from the pulp and paper mill under study are segregated from extraction stage bleaching effluents and treated in an aerated lagoon treatment system. Details of this treatment system and its performance have been presented elsewhere (Stuthridge *et al.*, 1990b).

An assessment was made of the fate of the chlorinated monoterpenes upon treatment in this system (Figure 5.6). The chlorinated monoterpene alcohols are extensively degraded in the treatment system. Much of the initial reduction of these compounds can be attributed to pH effects when the chlorination effluents (pH *ca.* 3) are mixed with general pulp and paper wastewaters (pH *ca.* 9) in the mixing zone prior to entering the treatment system. Overall the system removes 80% of the chlorinated monoterpene alcohols. In contrast, only a small removal of the chlorinated monoterpene hydrocarbons takes place in the treatment system. The observed reduction of 17% may be explained solely by the observed increase in pH, implying that these compounds are relatively recalcitrant to biological activity. Previous research has shown that monoterpene hydrocarbons are generally more resistant to biodegradation than monoterpene alcohols (Hrutfiord *et al.*, 1975).

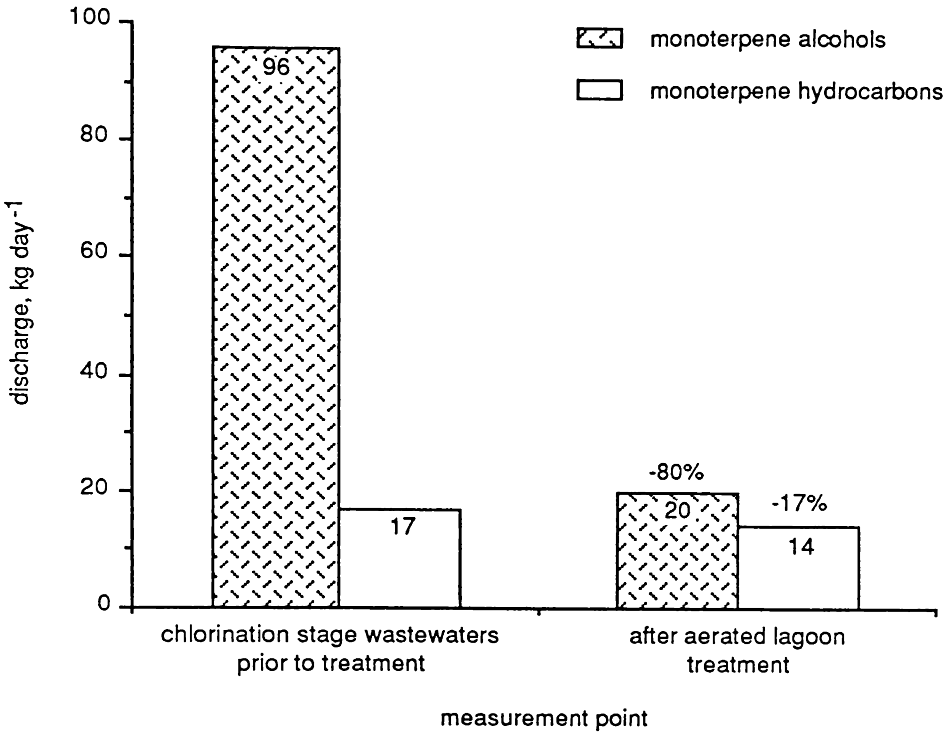

Figure 5.6: Removal of chlorinated monoterpenes in an aerated lagoon treatment system

Environmental Significance of Results

In the chlorination stage effluents of the mill under study, concentrations of chlorinated monoterpene hydrocarbons and alcohols range from 0.6-3.1 mg L^{-1} and 0.8-10.4 mg L^{-1} respectively (Stuthridge *et al.*, 1990a). Treatment of the effluents in the mill's aerated lagoon treatment system reduces the concentrations of the chlorinated monoterpene hydrocarbons and alcohols to 20-117 $\mu g\ L^{-1}$ and 10-487 $\mu g\ L^{-1}$ respectively (Stuthridge *et al.*, 1990b). On the basis of the post-treatment concentrations and the toxicity and mutagenicity results, it would appear that these compounds are unlikely to produce any acute environmental effects once discharged to the recipient. Fish toxicity data and information on the environmental fate of these compounds would be required to confirm this assessment.

CONCLUSIONS

An assessment has been made of the biological activities of the chlorinated monoterpenes found in the chlorination stage bleaching effluents of a New Zealand kraft pulp and paper mill. These studies have shown the following:

- The chlorinated monoterpene alcohols are labile at neutral and alkaline pH's. The chlorinated monoterpene hydrocarbons exhibit some alkaline lability but are more stable than the alcohols.

- The calculated *n*-octanol/water partition coefficients for the chlorinated monoterpene alcohols indicate a low bioaccumulation potential.
- The chlorinated monoterpene alcohols do not exhibit an appreciable acute toxicity to invertebrates, algae or bacteria.
- Some of the chlorinated monoterpene alcohols displayed mutagenic and genotoxic effects.
- The monoterpene alcohols are readily removed during aerated lagoon treatment of the chlorination stage bleaching effluents. In contrast no significant reduction takes place in the levels of the monoterpene hydrocarbons.

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Chapter Six

TREATABILITY OF BLEACHED KRAFT PULP AND PAPER MILL WASTEWATERS IN A NEW ZEALAND AERATED LAGOON TREATMENT SYSTEM

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TREATABILITY OF BLEACHED KRAFT PULP AND PAPER MILL WASTEWATERS IN A NEW ZEALAND AERATED LAGOON TREATMENT SYSTEM

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ABSTRACT - The effectiveness of the two biological treatment systems operating at a New Zealand bleached kraft softwood integrated pulp and paper mill was assessed. The two systems operate in different configurations. Treatment system A, which receives general mill wastewaters and chlorination stage bleaching discharges utilises deep, aerated lagoons and has a 4.5 day retention time. Treatment system B, which receives alkali extraction bleaching wastewaters and foul condensates, uses a lagoon system with a retention time of 51 days.

Detailed chemical analyses of the untreated and treated wastewaters were made. Mass balances were calculated for a range of physical parameters and for specific chlorinated and non-chlorinated organic constituents. Significant differences in the treatability of various constituents were found. In particular, while system A was able to reduce levels of AOX by 65%, no significant reduction in AOX occurred in system B. In contrast, system B reduced levels of chloroacetic acids by 84% while system A did not achieve any statistically significant removal of these compounds. The treatablility of chlorophenolic compounds also differed. System A was unable to remove chlorophenols and chloroguaiacols while system B did not reduce levels of chlorocatechols.

These results confirm that the treatability of bleached kraft pulp and paper mill wastewater constituents is dependent upon the characteristics of the treatment systems and the compositions of the wastewaters.

KEYWORDS - Bleaching effluents, biological effluent treatment, COD, colour, adsorbable organic halide, chlorinated substances, resin acids

INTRODUCTION

Current processes for the production of kraft pulp and paper result in a large volume of wastewater being discharged from the mill and, despite continuing improvements in in-mill process technology and control, it is still necessary to treat pulp and paper mill wastewaters externally. In temperate climates, aerated lagoon systems remain the most frequently used means of biologically treating such wastewaters. These systems are usually able to remove 85-90% of the readily biodegradable fraction of these wastewaters (measured as biological oxygen demand, BOD) (Lindström and Mohamed, 1988; Gergov *et al.*, 1988; Heimburger *et al.*, 1988). However, aerated lagoons are usually less effective at removing other effluent constituents such as colour, COD and organochlorine compounds. Once discharged to the recipient, these constituents may cause detrimental effects in the environment such as toxicity, mutagenicity and reduced light transmission. In addition, many of the compounds in these wastewaters may bioaccumulate. Therefore, when assessing the possible environmental impact of a pulp and paper mill, it is important to determine the effectiveness of the mill's treatment system in removing such constituents.

The results presented in this paper form part of an on-going study of one of New Zealand's kraft pulp and paper mills. Previous work has characterised in detail the composition of the wastewaters produced in the mill, especially those discharged from the bleach plants (Stuthridge, 1987). In this paper the treatability of the wastewater components to the point of discharge into the recipient has been studied and removal effectiveness is related to the wastewater characteristics and the specific operating conditions in the two treatment systems used.

Mill Description

Wastewater samples were collected from a New Zealand integrated kraft pulp and paper mill producing approximately 400 000 ADT yr^{-1} of predominantly softwood pulp of which about 160 000 ADT is bleached. Two bleach plants are operated, the first of which bleaches a mixture of batch-digested softwood (*Pinus radiata*) and hardwood (*Beilschmeldia tawa*) kraft pulps (typically 25% hardwood). It uses a five-stage CEHDP bleaching sequence and drum pulp washers. The second bleach plant has a five-stage (C70D30)E_0DED bleaching sequence with counter-current washing. Feedstock for this bleach plant is softwood (*Pinus radiata*) kraft pulp supplied from a continuous digester.

During the study both pulp production lines were operated with open screening. At present the continuous digester line is being upgraded with a closed screening facility and oxygen delignification.

Treatment system A

Three wastewater streams are discharged from the mill. They are treated in two separate biological treatment systems (Figure 6.1). General mill wastewaters undergo primary screening and sedimentation prior to treatment in system A. This treatment system consists of a 540 ML mechanically-aerated 20 m deep lagoon and four smaller lagoons aerated in series. The main lagoon has an average retention time of 3.4 days and receives 510 kW of aeration and mixing. The remaining lagoons provide a total retention time of approximately one day. The first of these lagoons has 32 kW of mechanical aeration, whilst the others rely on natural re-aeration. From the mill site to the receiving waters, the effluent travels over 15 km and drops almost 200 m in elevation. Treated effluent from this system flows into a natural stream and is then discharged into a freshwater hydro-electric lake. Chlorination stage bleaching effluents and settled stormwater and debarking effluents are partially neutralised by direct contact with limerock fines before joining the general mill wastewaters at the head of treatment system A (Figure 6.1).

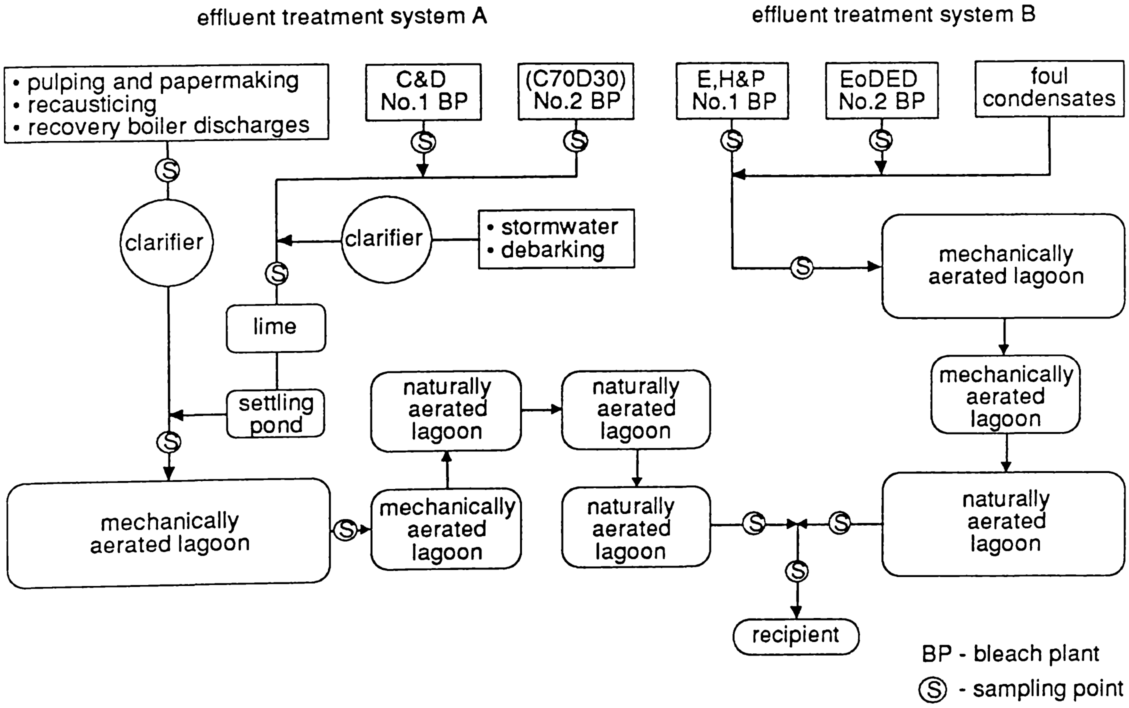

Figure 6.1: Schematic of effluent treatment systems

Treatment system B

Alkali extraction stage bleaching effluents and foul condensates are segregated and treated separately in system B. This system consists of two lagoons receiving a total of 260 kW mechanical aeration and a naturally aerated storage lagoon giving a total retention time of approximately 51 days. Effluent from this system joins that from system A prior to discharge to the recipient (Figure 6.1).

The aims of this study were:

1) to quantify the major physical parameters and organic constituents entering the treatment systems.
2) to determine the quantitative changes in these parameters during and after biological treatment.
3) to assess the contribution of treatment system configuration and influent wastewater source towards the observed treatability of these constituents.

A 30 day survey of wastewaters entering and leaving the treatment system was undertaken for this purpose. In addition, the performance of the combined treatment systems (i.e. measured at the point of discharge into the recipient) was also determined.

EXPERIMENTAL

Analytical Methods

Wastewater samples were analysed for suspended and dissolved solids, chemical oxygen demand (COD), chloride, sodium, colour and pH using APHA standard methods (APHA, 1985). Adsorbable organic halide was determined by SCAN-test Standard SCAN-W 9:89 (SPPBTC, 1989). Ultrafiltration of wastewaters was undertaken at pH 7 with an Amicon hollow-fibre cartridge ultrafiltration unit (Model DC2A) using cartridges with nominal molecular weight cut-offs of 3000, 10 000, 30 000 and 100 000 respectively. Analyses for resin and fatty acids and for neutral extractives were performed by liquid-liquid extraction with dichloromethane, methylation with diazomethane and analysis of the extract by gas chromatography using dual detection (FID/ECD) and mass spectrometry (for chromatography conditions see Stuthridge *et al.*, 1990). Resin and fatty acid extractions were undertaken at pH 9 (Voss and Rapsomatiotis, 1985) whilst neutral compounds were extracted at pH 3 due to the alkaline lability of some neutral constituents. Chlorinated carboxylic acids were analysed using the method of Lindström and Österberg (1986) using hexyl trichloroacetate as the internal standard. Chlorophenolics were determined by the method of Starck *et al.* (1985).

Sampling and Data Analysis

The sampling locations are presented in Figure 6.1. Twenty-four hour composite samples were collected daily from each location over the thirty day period. Samples were analysed for the inorganic and organic parameters outlined in the methods section. Concentration data were converted to yield values (i.e. g ADT^{-1} bleached pulp) for compounds which originated from the bleach plants. All tonnage figures referred to in this paper relate to air-dried tonnes of bleached pulp. Where sources other than bleach plant wastewaters contributed to the parameter value, mass flow values (i.e. kg day^{-1}) were calculated. Data from these analyses were collated for the thirty day period and subjected to statistical analysis to remove outliers and to determine 95% confidence intervals. Removals of specific components in the treatment systems were calculated on the basis of mean influent and effluent parameter values over the sampling period.

This paper will focus on the capability of the two treatment systems to remove important wastewater constituents. Subsequent publications will present results of a survey on the production of wastewater constituents during pulping and bleaching.

TABLE 6.1: Daily Production Rates and Flows Over Survey Period

parameter	mean ± 95% C.I.
total kraft pulp production, ADT day^{-1}	1157.7 ± 15.3
total bleach plant production, ADT day^{-1}	346.5 ± 33.5
No.1 bleach plant - CEHDP sequence	90.3 ± 15.1
No.2 bleach plant - (C70D30)E_ODED sequence	256.2 ± 24.3
treatment system A influent, ML day^{-1}	162.0 ± 7.2
general wastewaters	116.4 ± 8.6
chlorination stage wastewater	45.6 ± 2.2
treatment system B influent, ML day^{-1}	10.7 ± 1.2
extraction stage wastewaters	9.0 ± 1.0
foul condensates	1.7 ± 0.2
discharge to recipient, ML day^{-1}	304.3 ± 11.3

RESULTS AND DISCUSSION

Pulp production and wastewater flow rates during the survey period are summarised in Table 6.1. The survey was undertaken in Summer in mild weather conditions and with little rainfall. Pulp production and bleaching operations were relatively stable over the survey period. The observed changes in selected wastewater parameters within the treatment systems are summarised in Table 6.2. Total chlorine entering and leaving each system was well balanced indicating that adequate flow measurement data was obtained (Table 6.2, Figure 6.2).

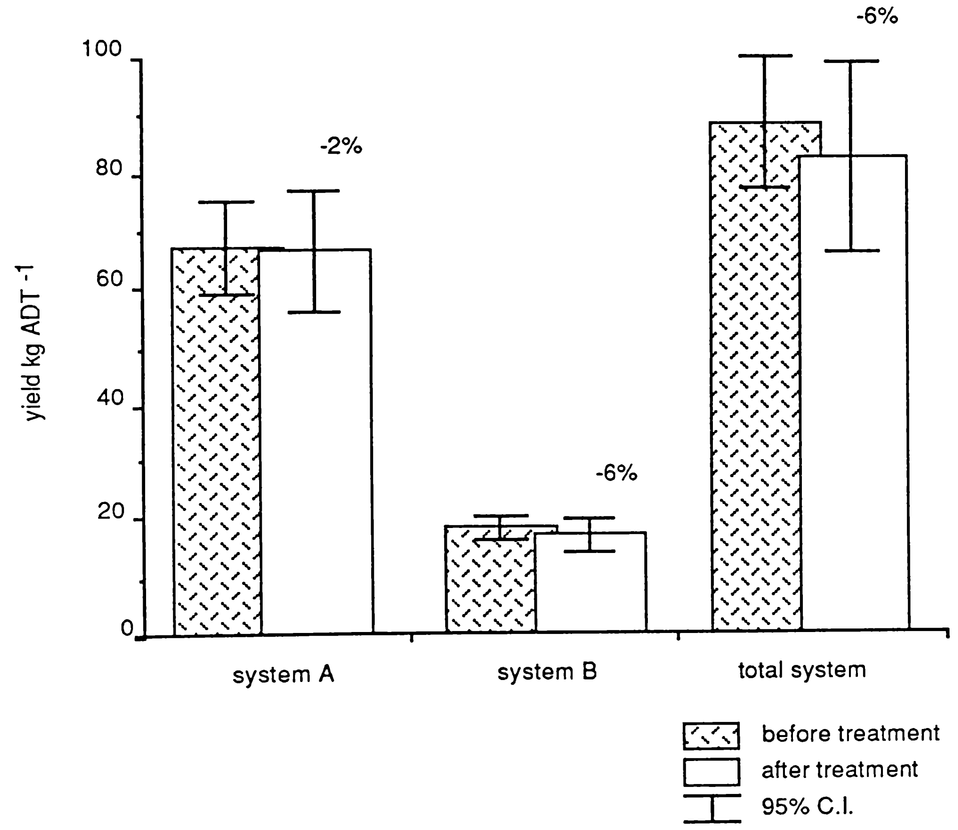

Figure 6.2: Yields of total chlorine in wastewaters discharged to treatment systems

Chemical Oxygen Demand

Treatment systems A and B removed an average of 59% and 36% of the influent chemical oxygen demand (COD) respectively (Table 6.2, Figure 6.3). The total mill effluent treatment system was able to remove 62% of the influent COD. These reductions are comparable with published results where COD removals of 20-50% have been reported for aerated lagoons (Gergov *et al.*, 1988; Heimburger *et al.*, 1988; Yin *et al.*, 1989). Reductions in levels of COD are generally significantly lower than those obtained for biological oxygen demand (BOD_5).

TABLE 6.2: Wastewater Constituents in Aerated Lagoon Treatment Systems (Mean ± 95% C.I.)

parameter	system A			system B			combined system		
	influent	effluent	removal %	influent	effluent	removal %	influent	effluent	removal %
chemical oxygen demand, tonne d^{-1}	74.6 ± 11.8	30.5 ± 3.0	59	28.6 ± 3.6	18.4 ± 1.8	36	104.0 ± 12.3	39.9 ± 5.5	62
colour, tonne chloroplatinate d^{-1}	77.2 ± 6.2	69.0 ± 4.7	11	50.3 ± 8.3	47.4 ± 7.0	6	132.0 ± 7.5	117.3 ± 8.3	11
sodium, tonne d^{-1}	19.9 ± 1.5	17.9 ± 1.6	10	8.8 ± 0.9	8.4 ± 1.0	5	30.0 ± 1.6	25.8 ± 1.4	14
resin acids, kg d^{-1}	1014.0 ± 227.9	51.4 ± 12.1	95	900.9 ± 280.8	504.0 ± 78.4	44	1938.9 ± 337.9	83.2 ± 19.8	96
total chlorine, kg ADT^{-1}	67.5 ± 7.5	66.5 ± 10.3	2	18.0 ± 2.5	16.8 ± 2.7	6	88.7 ± 11.4	83.1 ± 16.1	6
AOX, kg ADT^{-1}	4.2 ± 0.5	1.5 ± 0.2	65	1.5 ± 0.3	1.4 ± 0.3	7	5.7 ± 0.8	2.5 ± 0.3	57
chlorophenolics, g ADT^{-1}	38.5 ± 7.1	13.3 ± 2.5	65	26.0 ± 5.1	6.2 ± 1.4	76	64.5 ± 9.9	19.0 ± 3.5	71
chlorophenols	2.5 ± 1.4	2.5 ± 1.1	-2	3.7 ± 0.9	0.8 ± 0.2	77	5.9 ± 1.7	6.2 ± 2.7	-5
chloroguaiacols	4.2 ± 1.2	5.5 ± 2.0	-32	19.4 ± 5.7	2.9 ± 0.8	85	23.5 ± 6.3	5.0 ± 2.1	79
chlorocatechols	23.3 ± 4.6	4.6 ± 1.3	80	2.6 ± 0.9	2.3 ± 0.4	11	24.3 ± 5.5	6.4 ± 1.5	74
chlorovanillins	4.1 ± 1.2	0.7 ± 0.4	84	2.0 ± 0.4	0.2 ± 0.1	91	6.3 ± 1.4	0.4 ± 0.2	94
tetrachlorofuranone	7.0 ± 1.4	0.5 ± 0.2	93	0.5 ± 0.4	0.0 ± 0.0	92	7.9 ± 1.5	0.3 ± 0.2	96
chloroacetic acids, g ADT^{-1}	468.0 ± 85.0	346.1 ± 59.5	26	165.3 ± 76.5	26.9 ± 8.2	84	646.6 ± 168.5	318.8 ± 80.8	51
dichloroacetic acid	121.1 ± 17.1	83.2 ± 52.2	31	124.5 ± 57.8	23.9 ± 8.7	81	268.4 ± 80.2	110.9 ± 71.4	59
trichloroacetic acid	339.4 ± 83.6	283.8 ± 44.4	16	40.8 ± 19.5	1.5 ± 0.7	96	399.8 ± 102.7	242.3 ± 43.3	39
chlorinated monoterpenes, g ADT^{-1}	358.0 ± 74.4	124.4 ± 50.6	65	29.1 ± 9.6	24.1 ± 8.8	17	380.7 ± 89.6	125.4 ± 63.7	67
monoterpene hydrocarbons	59.6 ± 15.0	36.7 ± 5.1	38	10.0 ± 2.4	11.7 ± 2.4	-16	65.7 ± 21.8	43.9 ± 11.4	33
monoterpene alcohols	276.8 ± 76.8	84.0 ± 42.6	70	15.2 ± 4.4	10.3 ± 4.4	32	305.6 ± 73.9	89.0 ± 64.9	71

Although BOD_5 was not assessed in this survey, the main lagoons in the treatment systems typically show BOD_5 removal efficiencies of 70% and 57.5% for systems A and B respectively (Table 6.3).

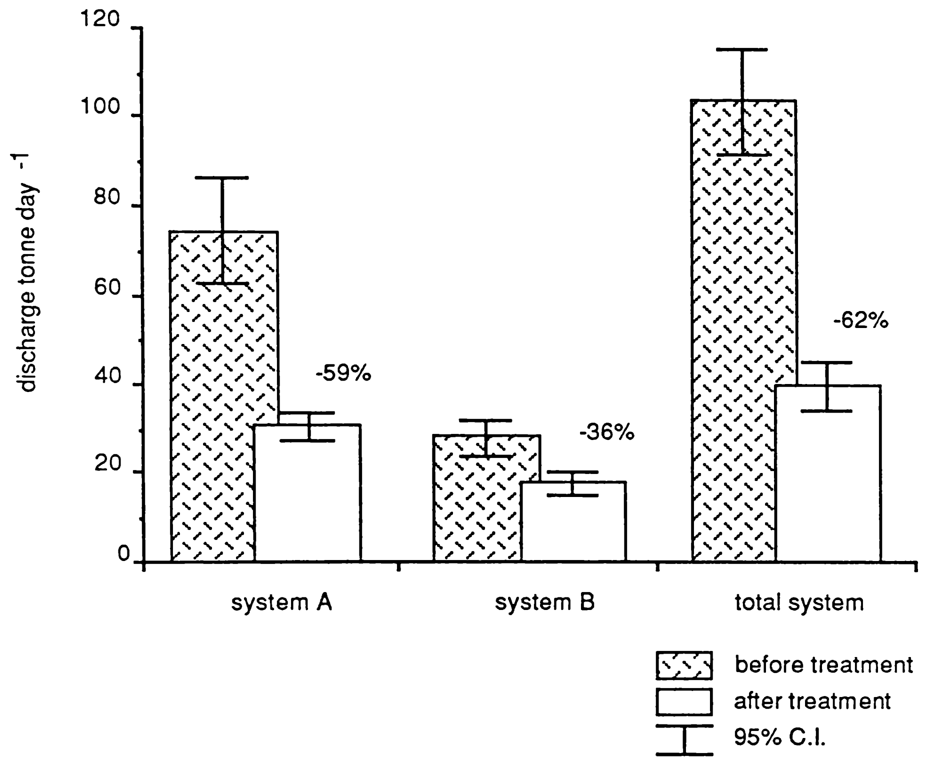

Figure 6.3: Mass flows of chemical oxygen demand in wastewaters discharged to treatment systems

Colour

No significant removal of colour was found in either system or in the system as a whole (Table 6.2, Figure 6.4). The chromophores producing the high colour content of bleached pulp effluents are found in the high molecular weight chlorinated lignin fraction and, as such, they are not readily biodegradable in aerated lagoons (Lindström and Mohamed, 1988; Holmbom and Lehtinen, 1980; Heimburger *et al.*, 1988).

Organic Chlorine

Adsorbable organic chlorine (AOX)

The segregation of the chlorination and extraction wastewaters from the bleach plants and their subsequent passage through treatment systems A and B respectively is an important feature. The molecular weight distributions of the AOX in the wastewaters entering these systems are significantly different (Figure 6.5). In system A, where the characteristics of

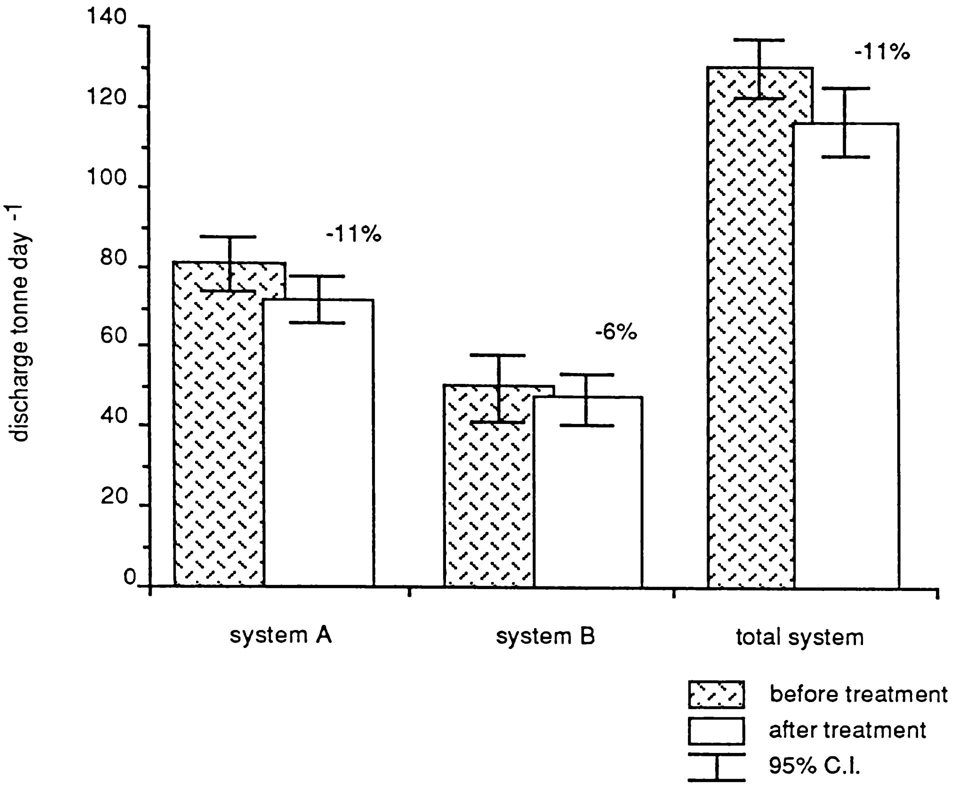

Figure 6.4: Mass flows of colour in wastewaters discharged to treatment systems

the chlorination wastewater predominate, 57% of the AOX is less than 3000 and 7% is greater than 100 000. The characteristics of the extraction stage wastewaters dominate the AOX molecular weight distribution in system B. In this case, 31% of the AOX is less than 3000 and 26% is greater than 100 000. Previous research has indicated that high molecular mass chlorinated material is significantly more recalcitrant than low molecular weight AOX (Ek and Eriksson, 1988). On this basis, system A, which receives chlorination wastewaters, would have been expected to achieve a greater removal of AOX than system B, which treats extraction stage effluents.

During the survey, the pulp and paper mill discharged an average of 5.7 kg AOX ADT^{-1} bleached pulp (equivalent to 1950 kg AOX day^{-1}) to the treatment systems. Treatment system A received 74% of this organic chlorine and achieved an AOX reduction of 65% (Table 6.2, Figure 6.6). In contrast, no statistically significant removal of AOX took place in system B.

An assessment of the molecular weight distributions of AOX entering and leaving each system was undertaken (Figure 6.5). In system A, which achieved 65% AOX removal, no significant change in molecular weight distribution was observed. This indicated that AOX removal was essentially uniform irrespective of molecular weight. Although no significant removal of AOX occurred in system B, substantial changes in the molecular weight distribution of AOX were observed for molecular weights less than 10 000 (Figure 6.5). In particular, the proportion of low molecular weight organic chlorine (i.e. MW less than 3000) was reduced from 31% to 19% of the total AOX.

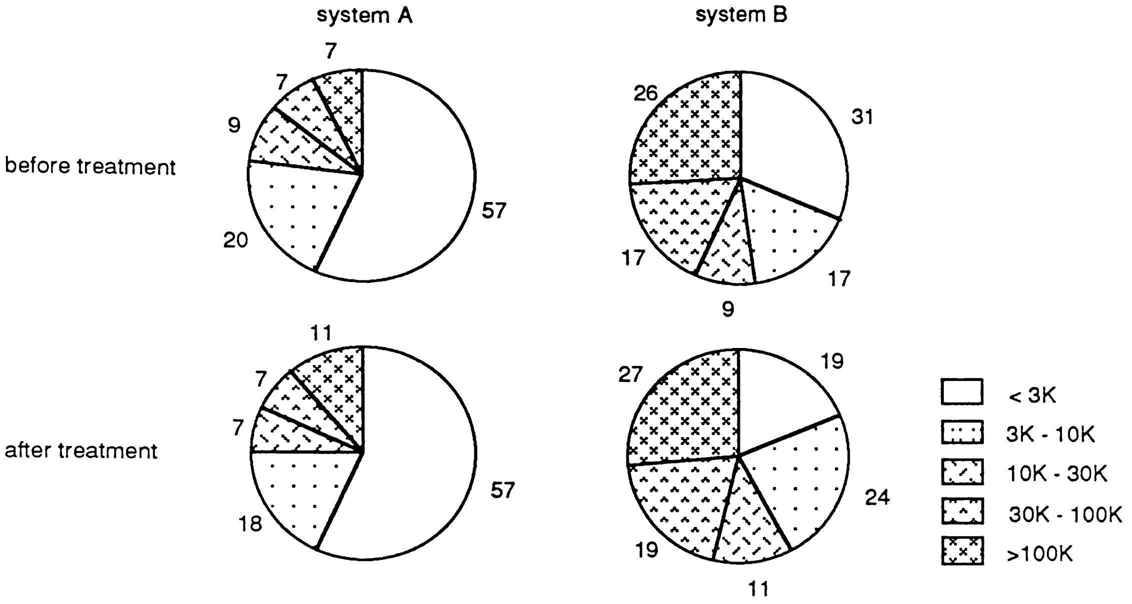

Figure 6.5: Molecular weight distribution of AOX in untreated and treated wastewaters, % total AOX

Overall, the treatment systems were able to reduce AOX by 57% and the discharge to the recipient averaged approximately 800 kg AOX day^{-1}, equivalent to 2.5 kg ADT^{-1}. Other studies have found that approximately 25-50% of the organic chlorine content (as AOX or TOX) of kraft bleaching effluents is removed during aerated lagoon treatment (Boman *et al.*, 1988; Bryant *et al.*, 1987; Cook, 1988; Ek and Eriksson, 1988; Heimburger *et al.*, 1988; Saunamäki, 1989; Yin *et al.*, 1989).

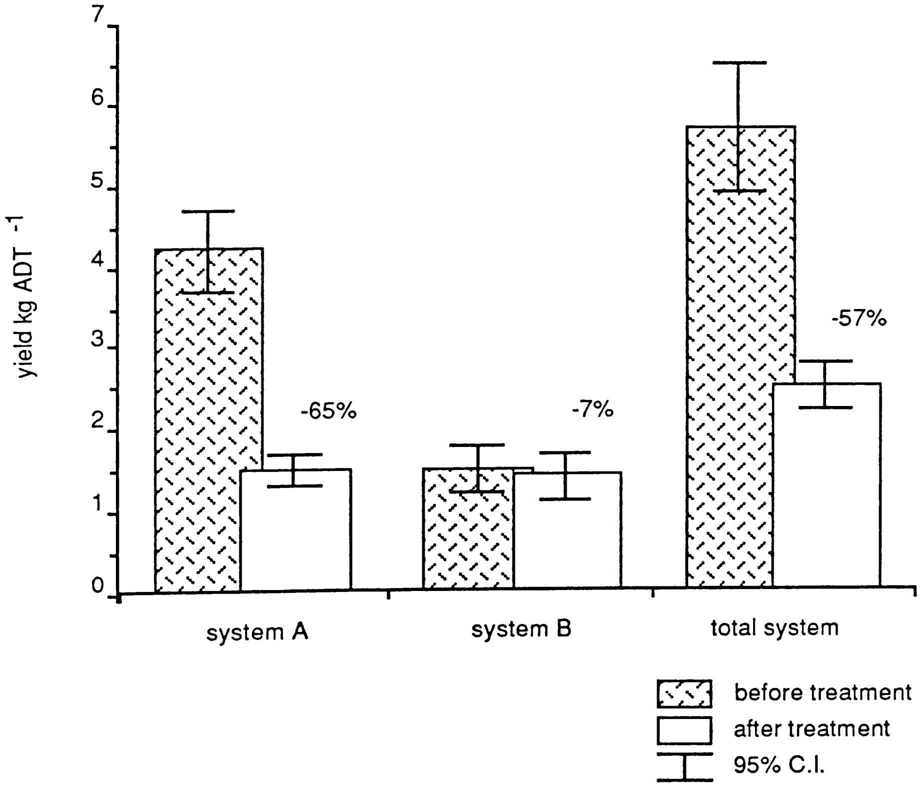

Figure 6.6: Yields of adsorbable organic chlorine in wastewaters discharged to treatment systems

Gas Chromatographic Organic Chlorine (GC-OCl)

The contribution of the low molecular weight chlorinated organic compounds, quantified by gas chromatography, to AOX removal was assessed. The mass of organic chlorine contained in the chlorophenolic, chloroacetic acid and neutral fractions was calculated and the influent and effluent yields (g ADT^{-1}) of gas chromatographically-determined organochlorine (GC-OCl) were quantified.

A comparison was made of the contribution of the GC-OCl to the AOX entering and leaving each treatment system (Figure 6.7). GC-OCl contributed 13% (540 g ADT^{-1}) to the yield of AOX entering system A and 10% (150 g ADT^{-1}) of that entering system B. Following treatment in system A, and 65% removal of total AOX, GC-OCl accounted for 23% (350 g ADT^{-1}) of the AOX. After passage through system B, the GC-OCl was substantially reduced and only accounted for 2% (35 g ADT^{-1}) of the total AOX.

It is clear that different AOX removal mechanisms predominate in each of these treatment systems. Details of these AOX removal mechanisms will be considered in a subsequent publication.

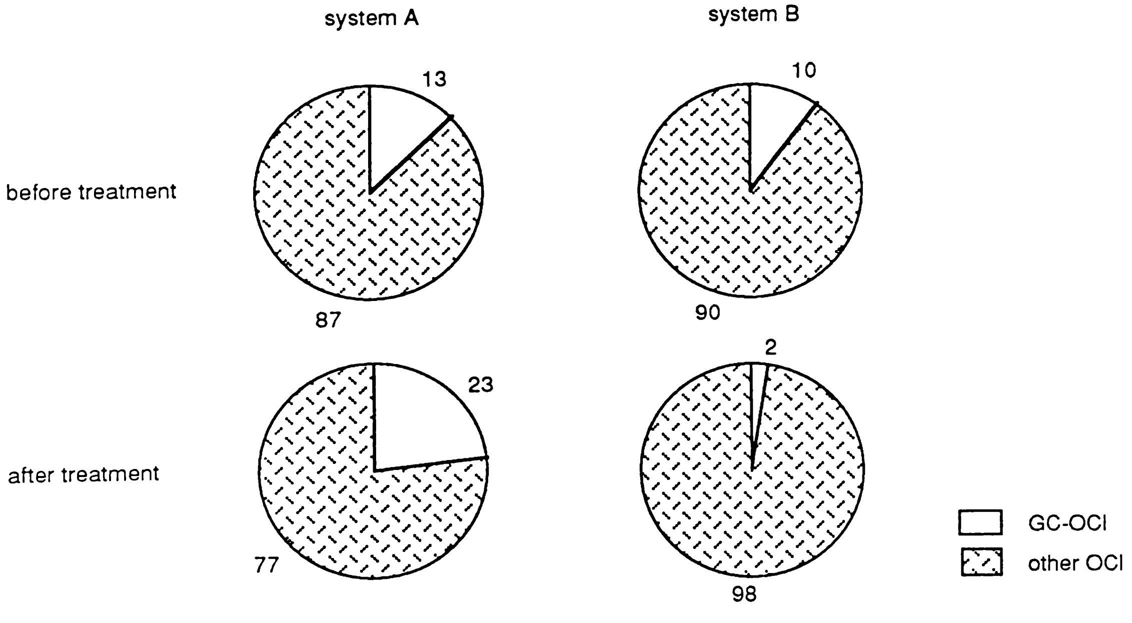

Figure 6.7: Gas chromatographically-determined organic chloride (GC-OCl) in untreated and treated wastewaters, % total AOX

Extractable Organic Compounds

Chlorophenolic Compounds

The characteristics of the chlorophenolic fractions differed for each treatment system. In system A chlorocatechols, the main chlorophenolic compounds discharged from chlorination stages, predominated (Table 6.2). In system B, chloroguaiacols were the major chlorophenolic constituents (Table 6.2). These findings are in agreement with previously published information on the composition of effluents from the bleaching of softwood kraft pulps (Kringstad and Lindström, 1984).

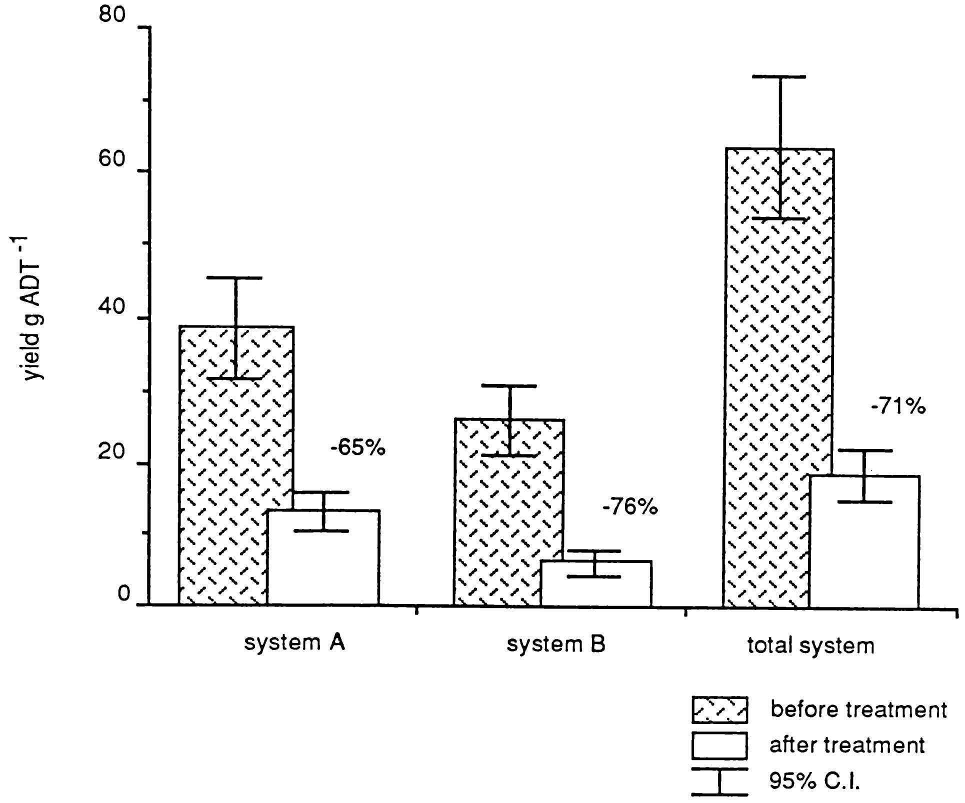

Figure 6.8: Yields of total chlorophenolics in wastewaters discharged to treatment systems

In both treatment systems, chlorinated phenolic compounds were reduced by approximately 70% (Table 6.2, Figure 6.8). However, there were differences in the relative treatability of the individual classes of chlorophenolic compounds. Significant removals of chlorocatechols and chlorovanillins were attained in system A (80% and 84% reductions respectively) but little reduction of chlorophenol and chloroguaiacol yields was observed. There is in fact evidence of a small, but statistically significant, production of chloroguaiacols within system A (Table 6.2). Chlorinated guaiacols have been shown to be produced during the aging of effluents containing chlorolignin (Annergren *et al.*, 1987) and an 88% increase in yield of chlorosyringols has been observed after activated sludge treatment of a combined softwood/ hardwood bleaching wastewater (Gergov *et al.*, 1988). Previous findings have indicated that a significant increase in the removal of chlorophenols and chloroguaiacols is achieved by extending the retention time of an aerated lagoon (Lindström and Mohamed, 1988), which may indicate that the poor removal of these compounds in system A could be due to insufficient treatment time.

In contrast to system A, system B was able to effectively remove chlorophenols, chloroguaiacols and chlorovanillins (77, 85 and 91% reductions respectively) but did not achieve a statistically significant reduction of chlorocatechols.

The treatment system as a whole was able to reduce chlorophenolics by 71%. Previously reported removal efficiencies of chlorinated phenolics in aerated lagoons are 20-60% (Boman *et al.*, 1988; Heimburger *et al.*, 1988; Holmbom and Lehtinen,1980; Lindström and Mohamed, 1988).

The acetylated chlorophenolic extracts of the wastewaters also contained the chlorinated furanone, 3,4-dichloro-5-(dichloromethyl)-5-hydroxy-2-furanone, a mutagen previously identified in chlorination stage effluents by Strömberg *et al.* (1987). This compound was readily removed in both treatment systems (>90% reduction, Table 6.2). The chlorinated furanone was shown by Strömberg *et al.* (1987) to be unstable at the pH of the wastewaters in the treatment systems and readily degraded under ambient conditions.

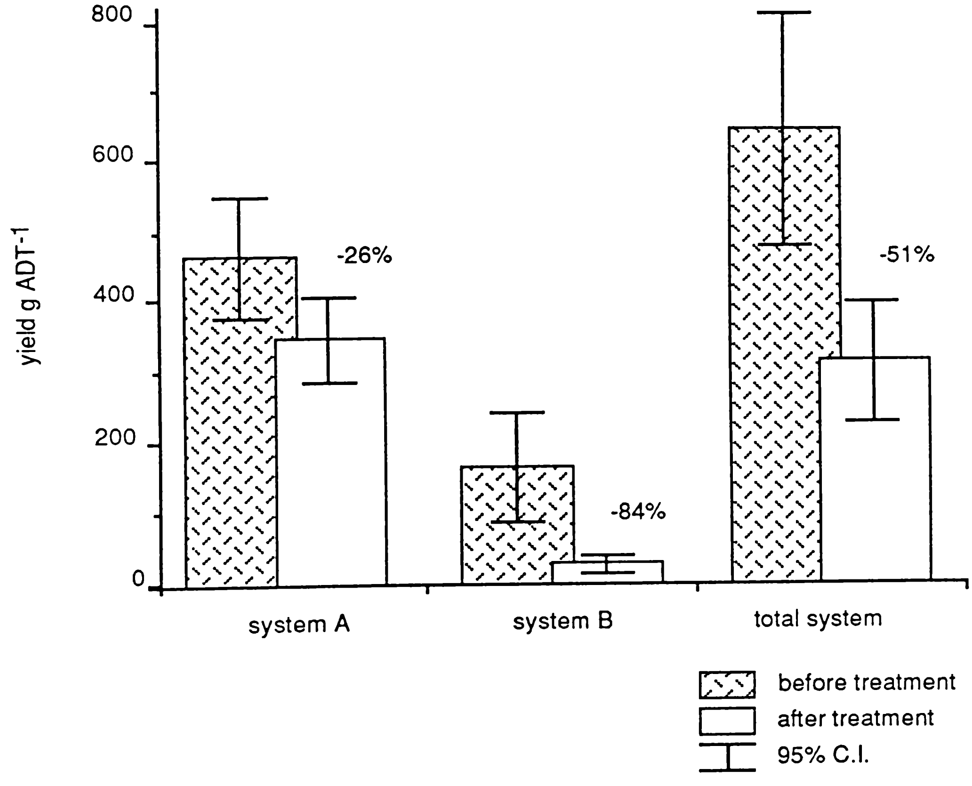

Figure 6.9: Yields of total chloroacetic acids in wastewaters discharged to treatment systems

Chloroacetic Acids

Although similar amounts of dichloroacetic acid were discharged to both systems (approximately 120 g ADT^{-1}), substantially more trichloroacetic acid passed to system A (340 and 40 g ADT^{-1} for systems A and B respectively, Table 6.2). The two treatment systems displayed significant differences in their ability to degrade the chloroacetic acids. System A did not achieve a statistically significant reduction of the chloroacetic acids, while system B was able to remove 84% of these compounds. The mill's total treatment system was able to reduce chloroacetic acids by 51% (Figure 6.9).

Chloroacetic acids have been previously shown to be readily biodegradable in an aerated lagoon treatment system. Reported reductions after treatment are 54-97% and complete removal of dichloroacetic acid has been observed in lagoons with a 2.5 day retention time (Lindström and Mohamed, 1988). Evidence suggests that complete biodegradation of trichloroacetic acid may require an extended period of treatment (Lindström and Mohamed, 1988).

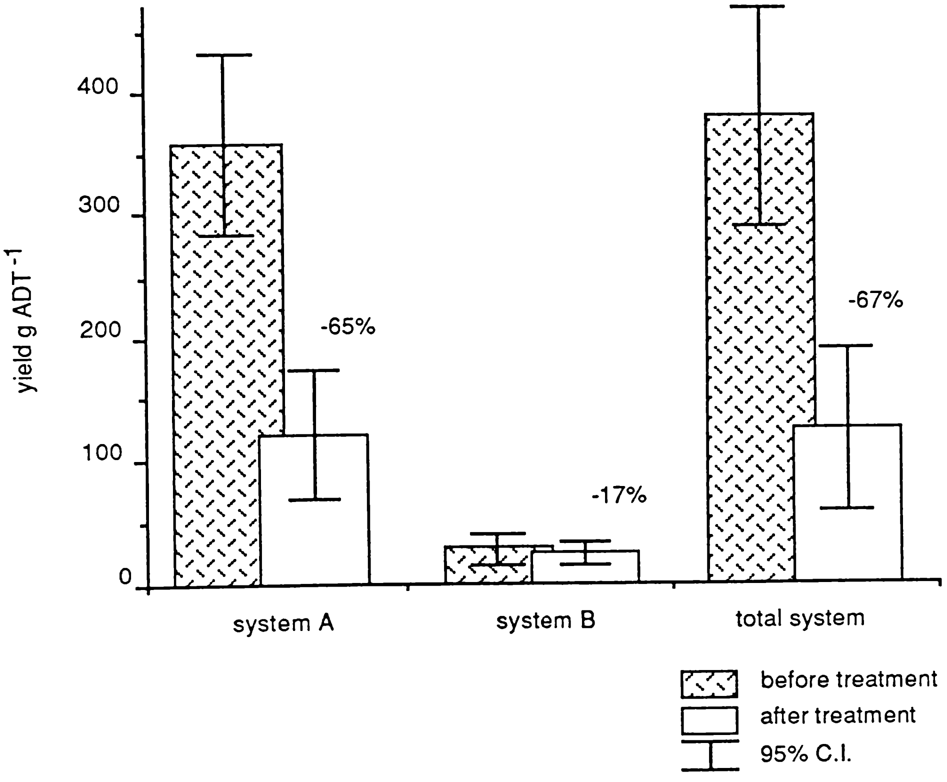

Figure 6.10: Yields of total chlorinated monoterpenes in wastewaters discharged to treatment systems

Chlorinated Monoterpenes

Wastewaters from the chlorination stage of the mill's second bleach plant ((C70D30)E_0DED sequence) contain high concentrations of chlorinated monoterpenes (Table 6.2). Lower concentrations of chlorinated monoterpenes are also found in alkali extraction wastewaters from the same bleach plant. These compounds have been identified as hydroxylated and/or chlorinated derivatives of the major *Pinus radiata* monoterpenes (Stuthridge *et al.*, 1990).

Treatment system A was able to reduce levels of the chlorinated monoterpenes by 65% while system B achieved no statistically significant reduction in these compounds (Table 6.2, Figure 6.10). Unchlorinated monoterpenes are effectively removed in aerated lagoons (Wilson and Hrutfiord, 1975) and reported removals of chlorinated *p*-cymenes in an activated sludge plant are 69-99% (Leuenberger *et al.*, 1985). Monoterpene hydrocarbons are generally more resistant to biodegradation than monoterpene alcohols (Hrutfiord *et al.*, 1975) and the observed reductions of the chlorinated monoterpene hydrocarbons and alcohols in the mill's total treatment system were 33% and 71% respectively (Table 6.2).

Resin Acids.

Resin acids of similar type, and in similar amounts, entered each system (approximately 1000 kg day^{-1}, Table 6.2). System A was efficient at removing resin acids (95% reduction, Figure 6.11). In contrast less than 50% of the influent resin acids were removed by system B. The predominantly anaerobic conditions present in system B lead to the bioconversion of resin acids to saturated and/or hydroxylated derivatives (McFarlane and Clark, 1988). Three resin acids predominated in the discharge from system B. These were dehydroabietic acid, which is relatively resistant to anaerobic biodegradation due to its aromatic nature, abietian-18-oic acid, and 13β-hydroxyabietian-18-oic acid, an hydroxylated anaerobic degradation product of abietic acid (Wilkins *et al.*, 1989). Previous findings have shown that aerated lagoons are able to reduce concentrations of resin acids by 60-100% (Easty *et al.*, 1978; Voss, 1987).

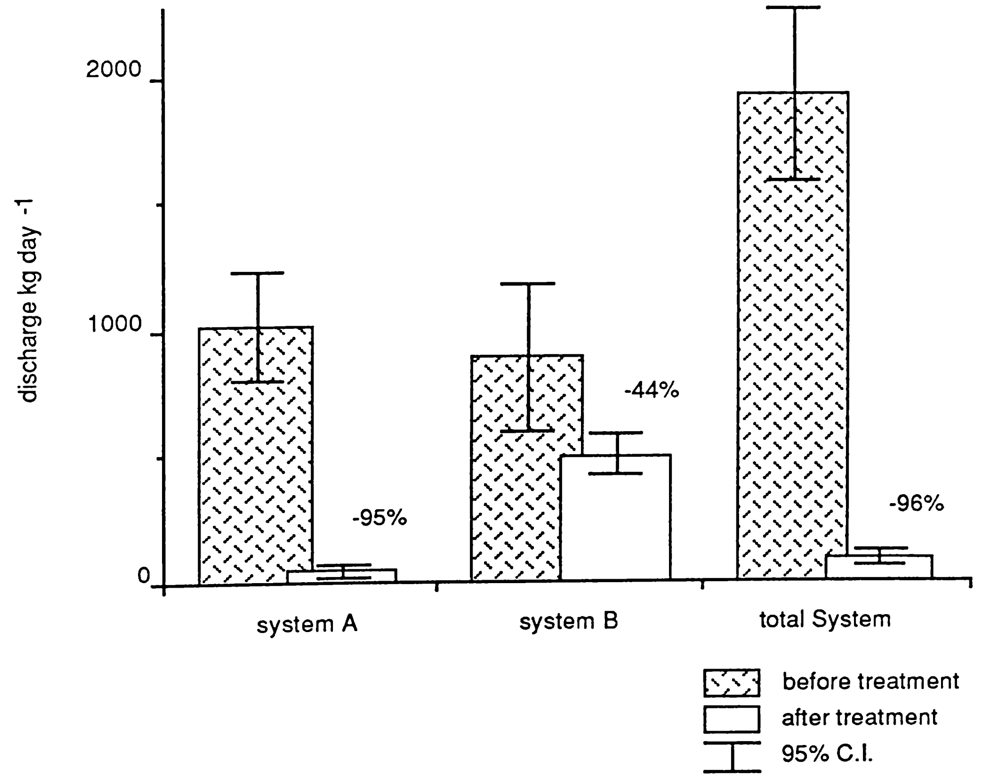

Figure 6.11: Mass flows of total resin acids in wastewaters discharged to treatment systems

System Comparison

System A effectively removed COD and AOX (Table 6.2). In contrast, system B was ineffective at removing total AOX and achieved substantially lower COD removal (Table 6.2). No significant colour removal was attained in either system.

The systems also differed in their ability to remove low molecular weight chlorinated organic compounds. Although system A was able to reduce levels of total chlorophenolic compounds by 65%, it did not remove chlorophenols or chloroguaiacols and may have indeed produced chloroguaiacols during treatment. System B reduced total chlorophenolic yields by 76% but was unable to remove chlorocatechols. Similarly, system A achieved poor reductions in the chloroacetic acids (26%) while system B effectively removed these compounds (84%). Chlorinated monoterpenes were reduced by 65% in system A but only 17% of these compounds were removed in system B. Resin acid removals also differed between systems with a 95% reduction observed in System A and a 44% reduction in system B. Anaerobic conditions in system B lead to the formation and discharge of a range of saturated and/or hydroxylated resin acids.

System configurations and wastewater characteristics both contributed to the differences observed in the treatabilities of the wastewaters in the treatment systems. The characteristics of the major lagoons in the treatment systems have been summarised in Table 6.3. The main lagoon in system A is a deep, but otherwise conventional, aerated lagoon operating at neutral pH and elevated temperature. It has a small surface area to volume ratio which, combined with its extensive foam coverage, minimises surface re-aeration. The lagoon's power to volume ratio of 0.93 W m^{-3} is in the range required to maintain effective suspension of solids (Adams and Eckenfelder, 1974) and results in a moderate dissolved oxygen concentration of 0.4 mg L^{-1}. Approximately 25% of the oxygen demand is stabilised anaerobically. The influents to this lagoon consist of general pulping and papermaking wastewaters and chlorination stage bleach plant discharges (Figure 6.1). The biodegradability of general mill wastewaters and the low molecular weight nature of the organically-bound chlorine in the chlorination stage discharges contribute to the observed high oxygen demand and AOX removals in this lagoon.

Three basins contribute significantly to oxygen demand removal in system B. In combination, these lagoons operate at an alkaline pH with a long hydraulic retention time and a high surface area to volume ratio (Table 6.3). The first two lagoons have a relatively low input of mechanical aeration (0.65 W m^{-3}) and operate with a mean dissolved oxygen concentration of 1.2 mg L^{-1}. The third lagoon is essentially anaerobic with surface re-aeration providing the only oxygen input. Each of these lagoons operates at ambient temperatures. System B treats foul condensates and extraction stage bleach plant discharges. Foul condensates are known to be readily biodegradable under anaerobic conditions and therefore might be expected to be effectively treated in this system (Pipyn *et al.*, 1987). The high molecular weight nature of the organically-bound chlorine in the extraction stage discharges, and its relative recalcitrance, may be the cause of the low observed AOX removal in System B. However, the system B lagoons are very effective at removing many of the gas chromatographically determined organochlorine compounds.

TABLE 6.3: Comparison of Main Lagoons in Treatment Systems

parameter	system A	system B	
		AL*	SL*
volume, ML	550	277	230
depth, m	16	3	3
hydraulic retention time, days	3.4	28	23
mechanical aeration, kW	510	260	0
volatile suspended solids, mg L^{-1}	57	50	50
dissolved oxygen content, mg L^{-1}	0.4	1.2	0.2
BOD$_5$ removal, tonne d^{-1}	7.5	2.6	1.6
BOD$_5$ removal, %	70	45	12.5
COD removal, %	49	25	
temperature (Winter-Summer), °C	26-31	11-20	
pH	7.4	8.2	
effluent origin	pulp and paper mill, debarking, stormwater, chlorination stage	extraction stage, foul condensates	

* AL, SL - aerated lagoons and storage lagoon respectively.

CONCLUSIONS

This study investigated the treatability of bleached kraft mill wastewater constituents in the two effluent treatment systems of a New Zealand integrated kraft pulp and paper mill. The treatability of important wastewater components was dependent upon:

- wastewater composition
- treatment system characteristics

System A, which received general pulp and paper mill wastewaters and chlorination stage bleaching discharges, was effective at removing COD, AOX, chlorinated monoterpenes, resin acids, and some classes of chlorinated phenolic compounds.

System B, which treated foul condensates and alkali extraction bleaching wastewaters, achieved high removals of chloroacetic acids and some classes of chlorophenolic compounds. Little AOX and limited COD removals were achieved.

Neither system was effective at removing colour.

In system A, AOX removal occurred uniformly across the AOX molecular weight range. In system B, reduction of AOX was confined to the low molecular weight AOX region (< 3000) and could be primarily accounted for by the observed reductions in gas chromatographically determined chlorinated organic compounds.

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Chapter Seven

ADSORBABLE ORGANIC HALIDE REMOVAL MECHANISMS IN A PULP AND PAPER MILL AERATED LAGOON TREATMENT SYSTEM

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Submitted for publication

ADSORBABLE ORGANIC HALIDE REMOVAL MECHANISMS IN A PULP AND PAPER MILL AERATED LAGOON TREATMENT SYSTEM

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ABSTRACT - The aerated lagoon treatment system of a New Zealand pulp and paper mill exhibited 65% removal of adsorbable organic chlorine (AOX). This value is high compared to published data and an assessment was made of possible mechanisms for the observed AOX removal. Much of this removal took place in a short section (3.3 hr residence time) of the system's main lagoon. The initial AOX decrease in the aqueous phase could be achieved in part by settling of AOX-containing suspended solids from the influent wastewaters. In addition, lime and bacterial solids present in the treatment system were able to adsorb AOX from the influent wastewaters. Only a small proportion of the organic chlorine removed was found in sludges. A mass balance of aqueous and solid phases indicated that over 99% of the removed AOX was mineralised.

KEYWORDS - AOX, aerated lagoons, pulp and paper, treatment, sediment, adsorption, dehalogenation

INTRODUCTION

In a previous paper an assessment was made of the treatability of bleached kraft pulp and paper wastewaters in the aerated lagoon treatment systems of a New Zealand bleached softwood kraft pulp and paper mill (Stuthridge *et al.*, 1990). Significant differences were found in the ability of the mill's two treatment systems to remove organic constituents from influent wastewaters. Of particular interest were the adsorbable organic halide (AOX) reductions observed in these systems. System A, which received chlorination stage bleaching and general pulping wastewaters, was able to remove 65% of the influent AOX. In contrast, system B, which received extraction stage bleaching wastewaters and foul condensates, achieved no significant removal of this parameter.

Typically, aerated lagoon treatment systems are able to reduce the organic chlorine content (as AOX or TOX) of kraft bleaching effluents by 15-50% (Bryant *et al.*, 1987; Gergov *et al.*, 1988; Lindström and Mohamed, 1988; Saunamäki, 1989). Therefore, the observed AOX removal in system A was significantly higher than in comparable systems and in this paper an assessment is made of possible mechanisms for this high AOX removal.

Mill Description

Details of the mill under study and it's wastewater treatment systems have been given in detail elsewhere (Stuthridge *et al.*, 1990). A brief summary is presented in Table 7.1.

TABLE 7.1: Description of Mill

type	integrated pulp and paper
pulp source	kraft digested softwood (*Pinus radiata*)
total production	400 000 ADT yr^{-1}
bleached production	160 000 ADT yr^{-1}
bleach plants	2
bleaching sequences	CEHDP, (C70D30)E_ODED
AOX production	5.7 kg ADT^{-1} total bleached pulp

An important feature of wastewater treatment at the mill is the segregation of chlorination stage and extraction stage bleaching wastewaters prior to their treatment in the mill's two wastewater treatment systems. In treatment system A, general mill wastewaters undergo screening and sedimentation prior to treatment in a series of aerated lagoons with a total of five days hydraulic retention. Chlorination stage bleaching effluents, settled stormwater and debarking effluents are partially neutralised by direct contact with limerock fines before joining the general mill wastewaters at the head of the aerated lagoon treatment system. The system consists of one major mechanically-aerated lagoon with an influent mixing zone and four smaller lagoons which rely principally upon natural re-aeration (Table 7.2). The system's main lagoon is approximately 20 m deep, elongated and was formed by damming a natural gully. The wastewater mixing zone is a narrow channel following the original stream path into this gully (Figure 7.1).

TABLE 7.2: Description of Treatment System A

parameter	mixing zone	main lagoon	other lagoons
influent flow, ML day^{-1}	162	162	162
pulp and paper wastewater, ML day^{-1}	116	-	-
chlorination stage wastewater, ML day^{-1}	46	-	-
retention time, hr	3.3	80	24
mean dimensions			
length, m	195	515	-
width, m	42	140	-
depth, m	7	20	2-3
total volume, ML	57	648	160
sludge volume, ML	35	107	-
mechanical aeration, kW	32	481	32
dissolved oxygen, mg L^{-1}	2-4.5	0.4	2.2-5
BOD_5 removal, tonne d^{-1}	-	7.5	1

Alkali extraction stage bleaching effluents and foul condensates are segregated and treated separately in the treatment system B; a partially-aerated lagoon system with a retention time of approximately 45 days. Treated effluents from both systems are combined in a natural stream and are then discharged into a freshwater hydro-electric lake (Stuthridge *et al.*, 1990).

EXPERIMENTAL

Sampling

Twenty-four hour composite wastewater samples were collected using autosamplers. Sludge samples were collected using a core sampler. Core depths were approximately 40 cm. Prior to analysis, all samples were stored at 4°C.

Adsorbable Organic Halide

Adsorbable organic halide in wastewater samples was determined by SCAN-test Standard SCAN-W 9:89 (SPPBTC, 1989). Sludges were suspended in distilled water and the AOX content of the diluted suspension determined as for an aqueous sample (Saunamäki *et al.*, 1990).

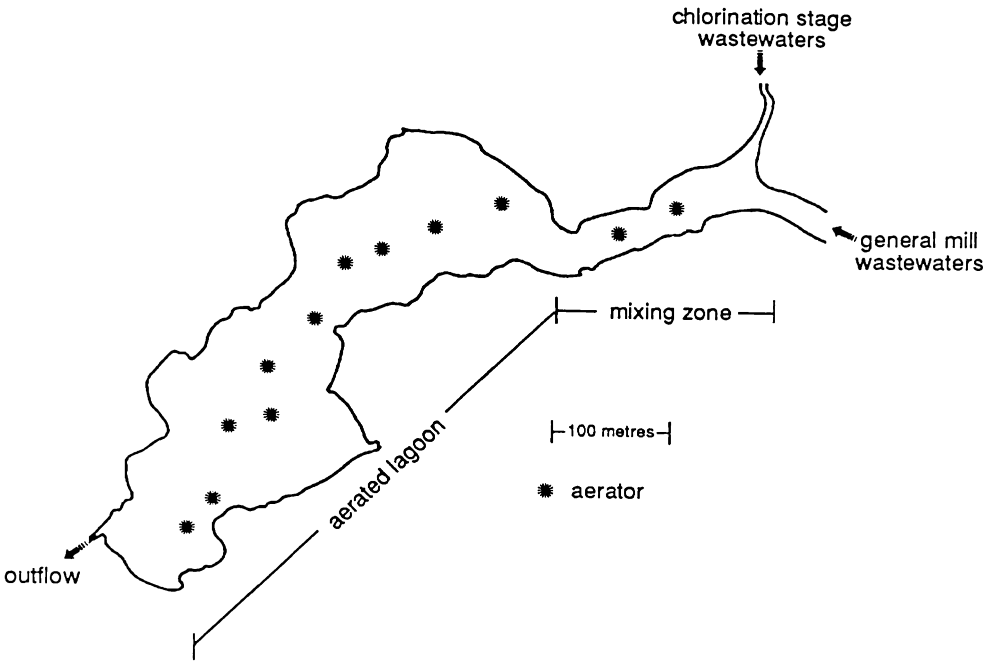

Figure 7.1: Plan view showing influent streams, mixing zone and the main aerated lagoon in treatment system A

Extractable Organic Halide

Analysis of sludges for extractable organic halide was based on the method of Martinsen *et al.* (1988). Initial investigations determined the effect of extraction solvent on the recovery of EOX from an aerated lagoon sludge. Three solvent mixtures: hexane/acetone, cyclohexane/isopropanol and cyclohexane/acetone gave mean ± 95% C.I. EOX values of 79.4 ± 3.6 $\mu g\ g^{-1}$, 89.9 ± 3.8 $\mu g\ g^{-1}$ and 93.7 ± 5.4 $\mu g\ g^{-1}$ respectively. Cyclohexane/acetone gave consistently higher results with an acceptable level of reproducibility and was chosen as the extraction solvent mixture for all work reported here for sludges.

EOX in sludges was determined by placing 25 g sludge (wet weight) into a 250 mL centrifuge tube. The sludge was shaken with 50 mL acetone and then 50 mL cyclohexane was added. The mixture was capped, shaken vigorously on a wrist-shaker for 1 hr and then centrifuged at 2000 rpm for 15 min. A 50 mL aliquot of solvent was washed twice with distilled water and then dried with anhydrous magnesium sulphate. Washed extract (20 mL) was reduced to 4 mL on a rotary evaporator and transferred to a 5 mL volumetric flask. *n*-Octanol (0.5 mL) was added and the solution was made up to mark with cyclohexane. Combustion/microcoulometric titration of a 10 µL injection of the concentrated extract was undertaken with a Euroglas AOX analyser. Results were calculated on a dry weight basis determined by drying sludge to a constant weight at 105°C.

Mixing Tests

Flow proportional volumes of general mill wastewater (post-sedimentation) and acid wastewaters (post-lime treatment) were combined and stirred for 4 hrs. Glass fibre filter paper (GF/C) was used for filtration tests. For the pH mixing tests, the combined effluents were adjusted to the required pH using 0.5 mol L^{-1} NaOH. No significant dilution occurred during pH adjustment.

Adsorption Isotherms

Adsorption experiments were undertaken at pH 7 (the pH of the mixed wastewaters) and at room temperature (22°C). Lime and pulp fibre (mixed in proportion of unbleached and bleached pulp losses) were sampled from their respective process streams. Secondary sludge was obtained from a core taken from the centre of the mixing zone of the aerated lagoon under study. An initial assessment of adsorption equilibrium time was made by mixing the effluent with each adsorbant (10 g L^{-1} dry weight) and monitoring AOX concentrations of the supernatant over time. Freundlich adsorption isotherms were then derived by mixing a constant volume and concentration of the wastewaters with adsorbant concentrations of approximately 0, 30, 100, 300, 1000, 3000 and 10 000 mg L^{-1} and determining AOX levels after settling. Correction for possible addition of AOX from the adsorbant was determined by mixing the adsorptive media with distilled water.

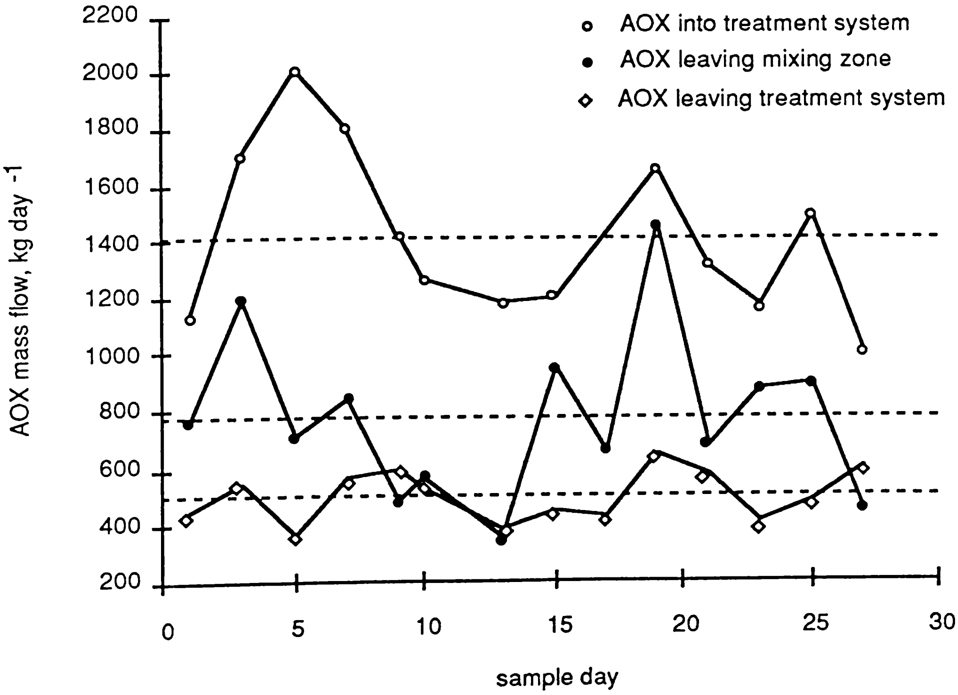

Figure 7.2: AOX mass flows over survey period

RESULTS AND DISCUSSION

Measurements of AOX in wastewaters entering, within, and leaving treatment system A were made over a 30 day period. The system was able to consistently remove a significant amount of AOX (Figure 7.2).

Much of the reduction took place between the sources of the wastewaters and the sample point at the head of the treatment system's main lagoon. More detailed sampling showed that this observed removal occurred in the influent wastewater mixing zone prior to entering the main body of the largest aerated lagoon in the treatment system (Figure 7.1). A mass balance indicated that this short section, which has a mean hydraulic retention time of 3.3 hr (Table 7.2), was responsible for 71% of the total AOX removed in treatment system A (Figure 7.3).

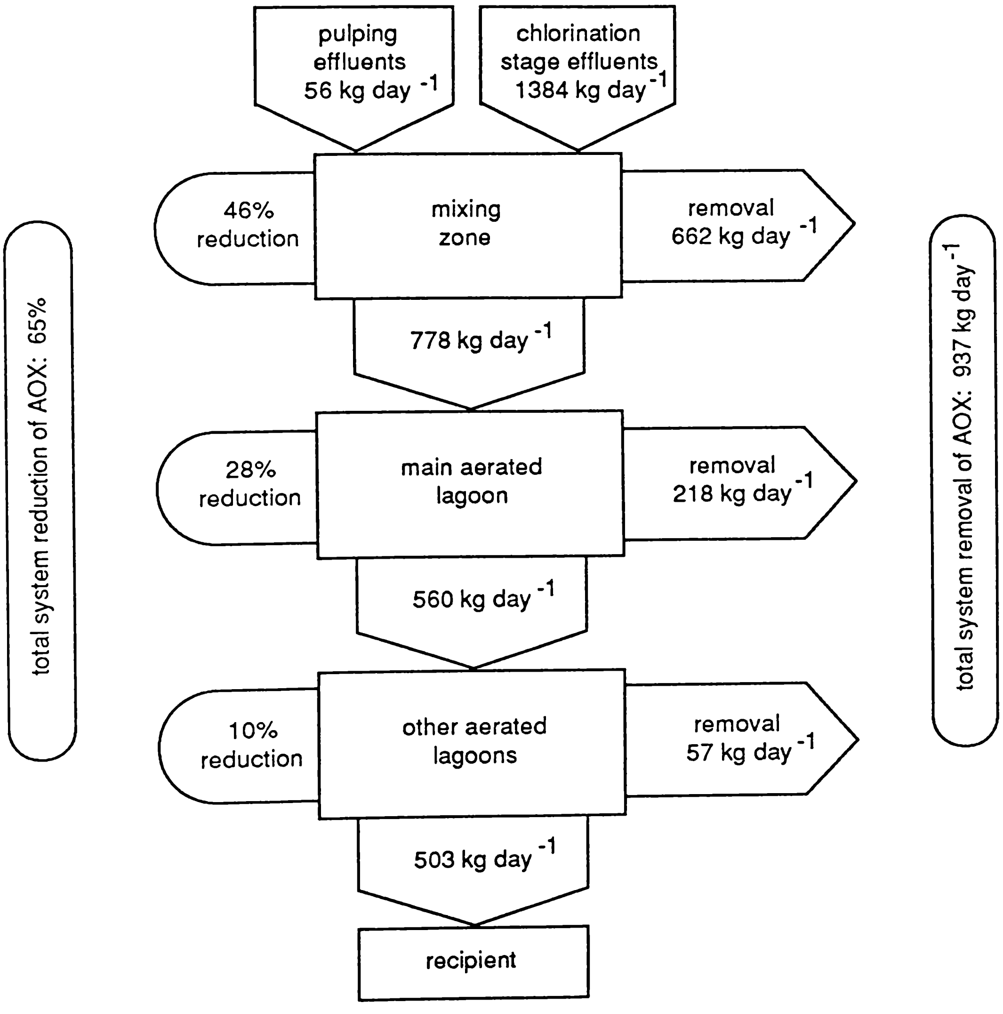

Figure 7.3: AOX mass balance across aerated lagoon treatment system

AOX removal occurred uniformly across the entire molecular weight range (Stuthridge *et al.*, 1990), consistent with previous studies of AOX removal in aerated lagoons (Bryant *et al.*, 1987; Lindström and Mohamed, 1988). This mixing zone was also responsible for much of the observed removal of other wastewater constituents in this treatment system (Table 7.3).

TABLE 7.3: Contribution of Mixing Zone to Observed Reductions of Wastewater Constituents in Treatment System

parameter	total reduction in treatment system, %	proportion of reduction due to mixing zone, %
colour	11	73
AOX	65	71
chlorophenolics	65	97
chloroacetic acids	26	69
chlorinated monoterpenes	65	62
resin acids	95	45

Based upon previous studies, it was hypothesised that the high observed reduction of AOX levels in this mixing zone could be accomplished by a variety of removal mechanisms (Figure 7.4). The very short hydraulic residence time of the wastewater in the mixing zone (3.3 hr) indicated that the initial AOX removal process would probably be physico-chemical rather than biological. An assessment was made of the contribution of each of these removal mechanisms to the observed removal of AOX.

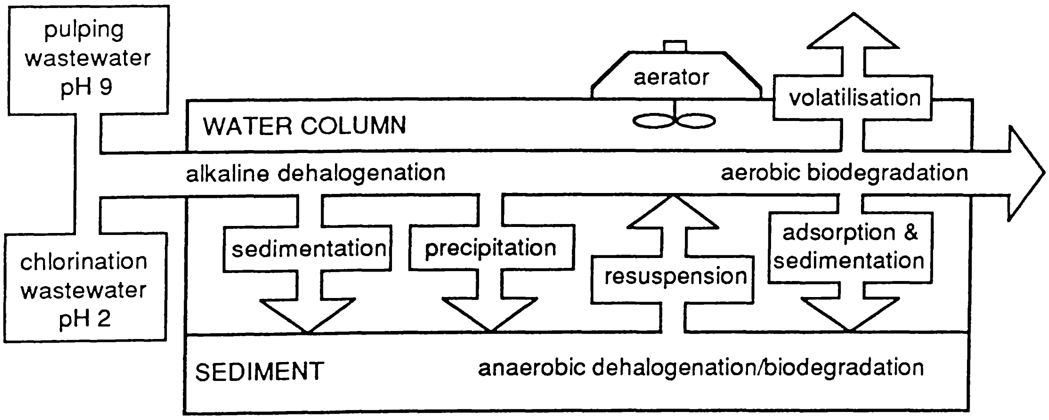

Figure 7.4: AOX removal mechanisms in aerated lagoon treatment system

Volatile Organic Chlorine

Chlorination stage effluents contain volatile chlorinated organic compounds (Talka, 1986). An assessment was made of the possible reduction in AOX due to removal of these compounds via aeration in the mixing zone. Nitrogen gas was passed through chlorination stage wastewater for two hours and the reduction in AOX measured. No significant change in AOX levels was observed with this treatment.

Mixing Tests

Simple mixing tests were performed on system influent to determine if the reduction in AOX was due to degradation via dehalogenation, adsorption onto suspended solids, or precipitation of chlorinated matter from the acid effluent (mean pH 2.6) when mixed with the general mill effluent (mean pH 9.0). In these tests, acid effluent was mixed for four hours with a flow proportional volume of general mill effluent. Pre-mixing and post-mixing treatments were undertaken and mass balances were determined for AOX in the wastewaters. Results of these tests are shown in Figure 7.5.

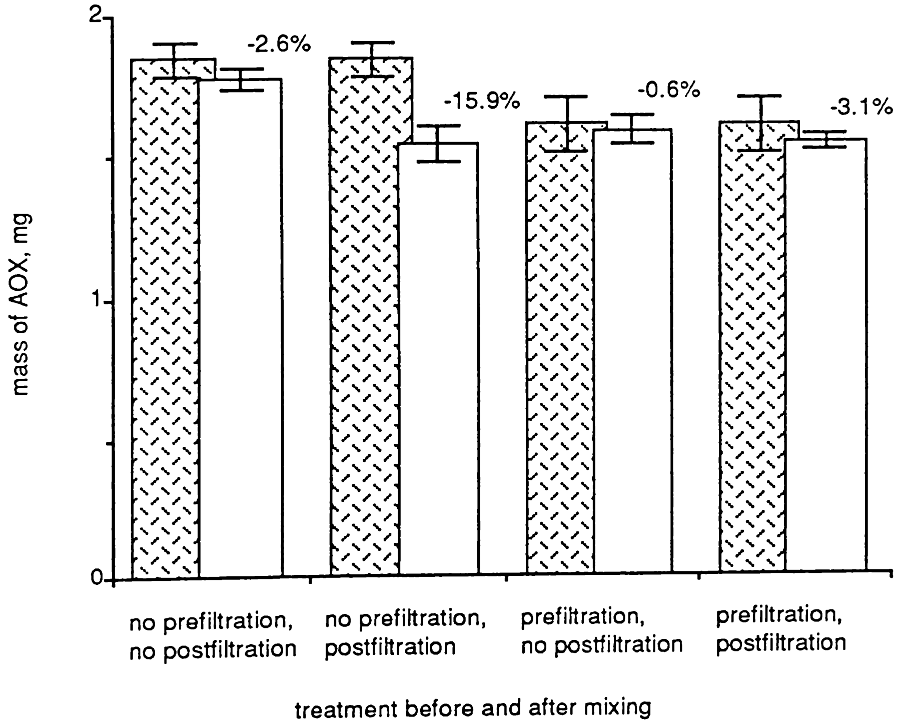

Figure 7.5: Effects of treatment on AOX removal

Simple mixing of the wastewaters led to no significant decrease in AOX despite the increase in pH of the chlorination stage effluent from 2 to 7. A number of the chlorinated constituents of chlorination stage effluents are alkali labile and readily degraded at pH 7 or above

(Eriksson *et al.*, 1982; Gergov *et al.*, 1988). Chemical dehalogenation of chlorination stage organochlorine due to an increase in pH has also been reported previously when these effluents were mixed with extraction stage effluents (Ekengren *et al.*, 1990). The effect of alkali treatment was confirmed by adjusting the mixing pH of the unfiltered combined effluents. A significant, linear decrease in AOX withincreasing pH was observed when the wastewaters were mixed at pH's between 6 and 13 (Figure 7.6). For example, a 60% reduction in AOX occurred when the wastewaters were mixed at pH 13. The average pH of the combined wastewaters in the mixing zone is 7.3. Based upon the regression equation in Figure 7.6, this would lead to only a 4% decrease in AOX.

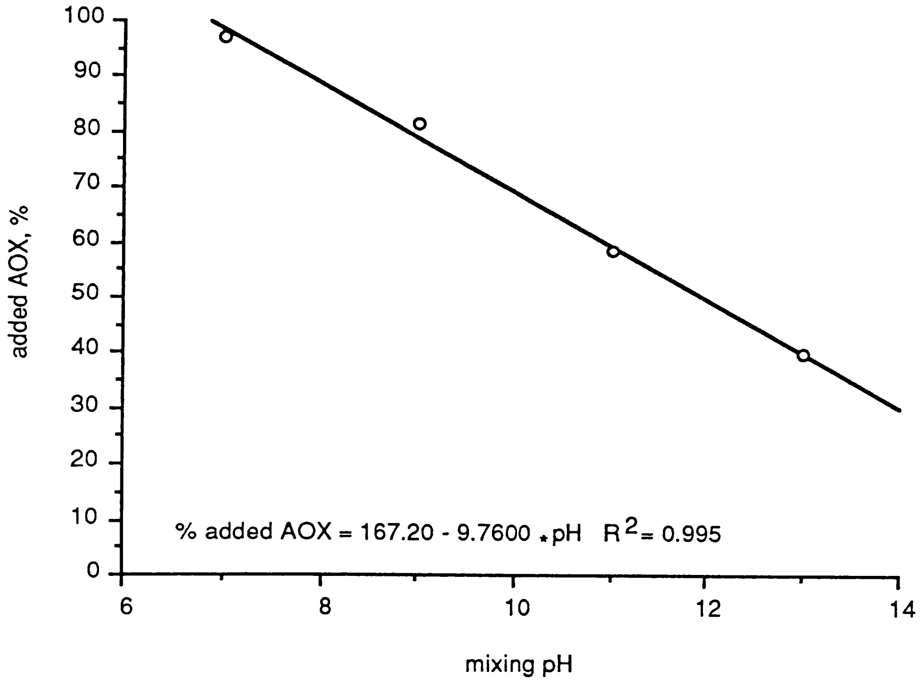

Figure 7.6: Effect of mixing pH on AOX removal

Filtration of the wastewaters after mixing produced a 16% decrease in AOX. A similar reduction was observed when suspended solids were removed by filtration prior to mixing. These results indicate that approximately 16% of the AOX is associated with the suspended solids present in the wastewaters. A reduction in AOX due to removal of suspended solids has been observed previously (Wigilius *et al.*, 1988).

To determine whether mixing of the two wastewaters might lead to precipitation of AOX from the aqueous phase (Bryant and Amy, 1988; Hynninen and Gullichsen, 1985), pre-filtered wastewaters were filtered after mixing. A statistically insignificant reduction in AOX was found suggesting that precipitation was responsible for little of the observed removal in the system.

From these observations it would appear that settling of AOX-containing suspended solids present in the incoming wastewaters may be responsible for some of the observed reduction in AOX. A minor decrease in AOX due to an increase in pH may also occur. Approximately 20% of the incoming AOX could be removed by these mechanisms.

Adsorption Tests

Previous studies have shown that much of the observed removal of AOX in aerated lagoon systems can be attributed to 1), an initial adsorption of the chlorinated organic material onto solids resuspended into the wastewater by mechanical aeration or biogas production, and 2), subsequent transport of adsorbed chlorinated organic material to the benthic layer by settling in quiescent zones (Boman *et al.*, 1988; Bryant *et al.*, 1987; Bryant and Amy, 1988; Ferguson and Jonsson-Dalentoft, 1990).

To determine the role of adsorption as an AOX removal mechanism in the mixing zone, Freundlich adsorption isotherms were derived using likely adsorptive media. The predominant suspended solids present in the influent discharges are lime and pulp fibre. In addition, secondary solids from biological activity are found in the mixing zone. The aqueous phase consisted of the two influent wastewaters made up in proportion to their flows. Initial studies determined that adsorption equilibrium was achieved after 4 hours mixing.

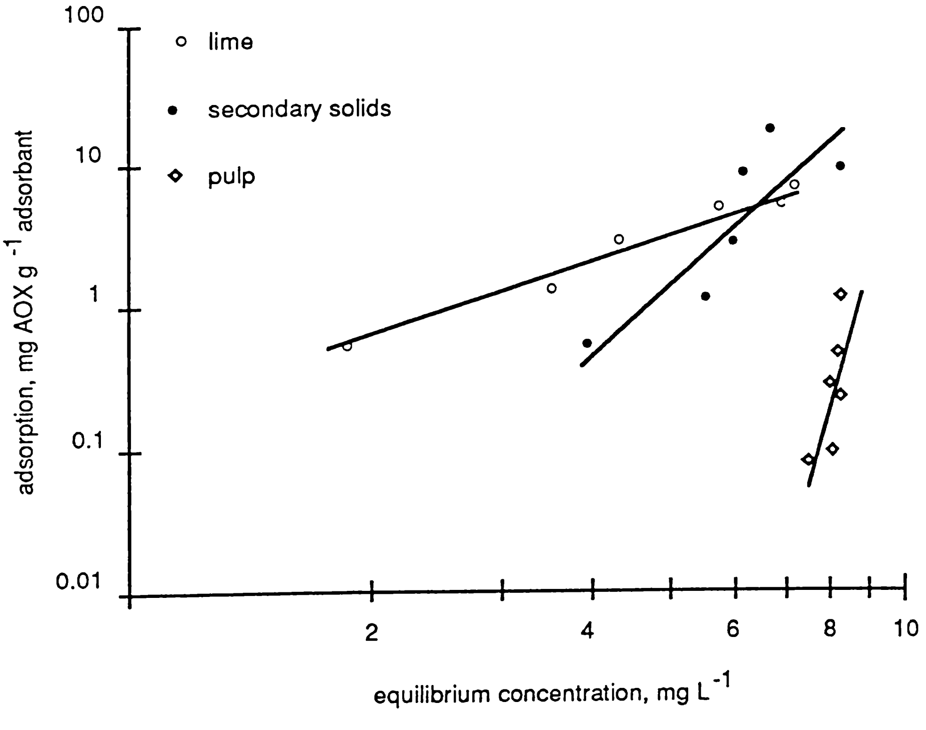

Figure 7.7: Adsorption isotherms for AOX

The results of the adsorption studies are given in Figure 7.7 and Table 7.4. As increasing doses of lime lead to an increase in pH, it was necessary to subtract the effect of mixing pH from the lime adsorption isotherm data using the AOX-pH relationship derived previously (Figure 7.6). The isotherms indicate that lime and secondary sludge will effectively adsorb AOX while pulp adsorbs very little AOX on a weight specific basis.

TABLE 7.4: Calculated Constants for Freundlich Adsorption Isotherms for AOX

adsorbant	log K_F	1/n	R^2	K_p, $cm^3\ g^{-1}$
lime	-1.1	2.21	0.981	330
2° solids	-4.4	5.00	0.759	246
pulp	-22.8	19.49	0.536	21

Previous work has shown that lime readily removes AOX from wastewaters. For example, Haberl *et al.* (1990) was able to remove 50% of the AOX in a bleached kraft mill effluent by treating with 2-3 g L^{-1} lime. However, the isotherm obtained for lime does not necessarily indicate a totally adsorptive phenomenon. It has been shown that lime reacts chemically with the organic matter in the wastewater to produce insoluble precipitates (Bennett *et al.*, 1971).

The Freundlich constants and partition coefficients for the secondary solids match closely those previously reported by Amy *et al.* (1988) for adsorption of AOX onto municipal activated sludge.

Using results obtained from the adsorption isotherms and data regarding the mixing channel, the bioconcentration factor and the effluent AOX in the aqueous phase have been calculated and compared to the observed effluent AOX (Table 7.5).

Based upon these calculations, adsorption onto lime discharged to the mixing zone should be capable of removing a significant proportion of AOX from the aqueous phase. Secondary solids have less capacity to remove AOX at the secondary solids concentration found in the mixing zone. As the mixing tests indicated that little reduction took place when the influent wastewaters were mixed, it would appear that active resuspension and mixing of settled solids is required to achieve the solids concentrations necessary for significant adsorption to occur. This resuspension would occur by the action of mechanical aeration and biogas production. In these circumstances, secondary solids concentrations could be enhanced such that secondary solids adsorption of AOX might have a more important role in removing AOX.

TABLE 7.5: An Assessment of the Significance of Adsorption of AOX onto Secondary Solids and Lime

	secondary solids	lime
bioconcentration factor, K_B	0.021	0.483
settled solids, Sx, kg day^{-1}	623	2845
predicted effluent AOX, C_p, mg L^{-1}	8.8	5.1
measured effluent AOX, mg L^{-1}	4.8	4.8

equations used (Tsezos and Bell, 1988):

$$\text{bioconcentration factor, } K_B = K_F C^{(1/n)-1}$$

$$\text{predicted Effluent AOX, } C_p = \frac{Q_o C_o}{Q_o + S_x K_B}$$

parametric values used:

mean influent flow, $Q_o = 1875$ L s^{-1}
mean influent AOX, $C_o = 8.9$ mg L^{-1}
measured mean effluent AOX, $C = 4.8$ mg L^{-1}

Organic Halide in Sediments

Although the depth to bedrock of the mixing zone channel is approximately 7 m, much of it's volume (62%) is filled with sludge. A small proportion of the total sludge volume (< 5% yearly production) is removed every 1-2 years from the point in the mixing zone where the incoming wastewaters initially combine. The remaining sludge has been accumulating at a rate of 3.5 tonnes dry weight day^{-1} since the aerated lagoon was commissioned 22 years ago.

In order to determine if removed organic halide was accumulating in the sludge after adsorption, samples were taken of sludges from throughout the mixing zone and from the main aerated lagoon. The sludge samples (approximately 25% total solids dry weight, wet density 2.5 tonne m^{-3}) were found to be a mixture of organic solids (pulp fibre and bacterial biomass, 4.5% volatile solids dry weight), sand, and lime mud.

EOX concentrations in the sludges of the mixing zone averaged approximately 90 µg g^{-1} dry weight and were relatively consistent (Figure 7.8). Lowest EOX concentrations were found at the exit of the general mill wastewater inlet (14 mg g^{-1}) whilst the highest levels of EOX were found at the exit of the chlorination stage wastewater inlet (309 µg g^{-1}). Concentrations

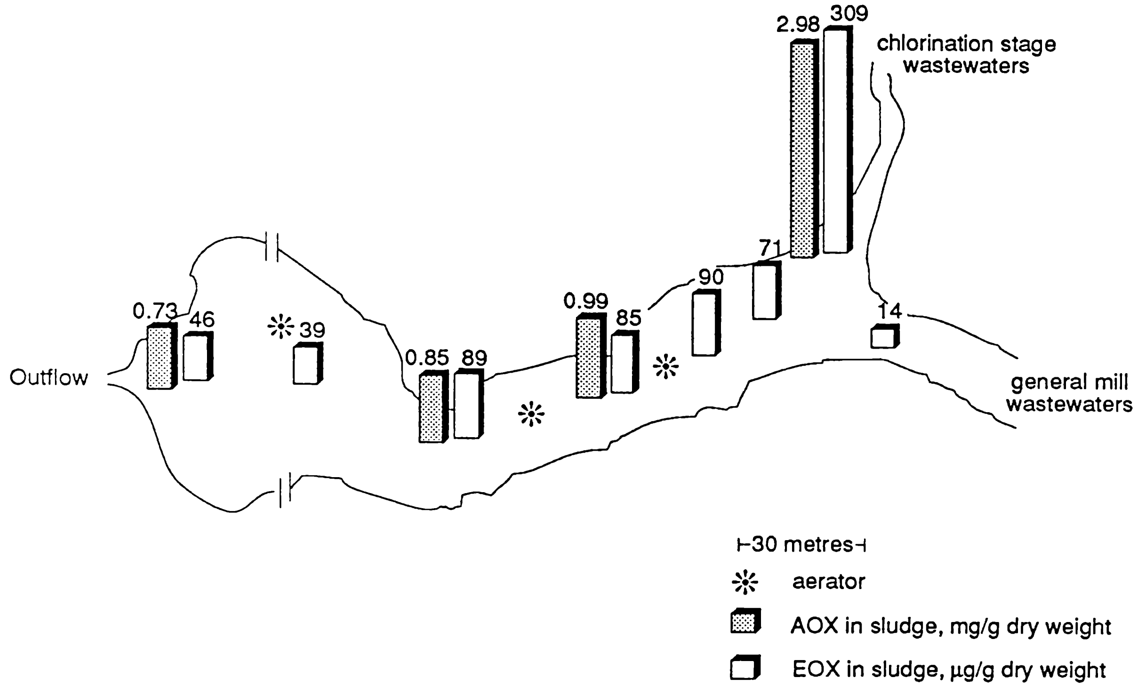

Figure 7.8: Organochlorine concentrations in sludges from mixing zone and aerated lagoon

of EOX in sludges within the main lagoon averaged 40 µg g^{-1}. Previous studies of sludges in aerated lagoons found EOX concentrations of 40-140 µg g^{-1} (Bryant and Amy, 1988; Bryant *et al.*, 1990; Carlberg *et al.*, 1987).

AOX concentrations in mixing zone sludges were found to range from 0.85 - 2.98 mg g^{-1} dry weight (Figure 7.8). Other research has shown aerated lagoon sludge AOX concentrations to be 2-5 mg g^{-1} (Bryant and Amy, 1988; Paasivirta *et al.*, 1988).

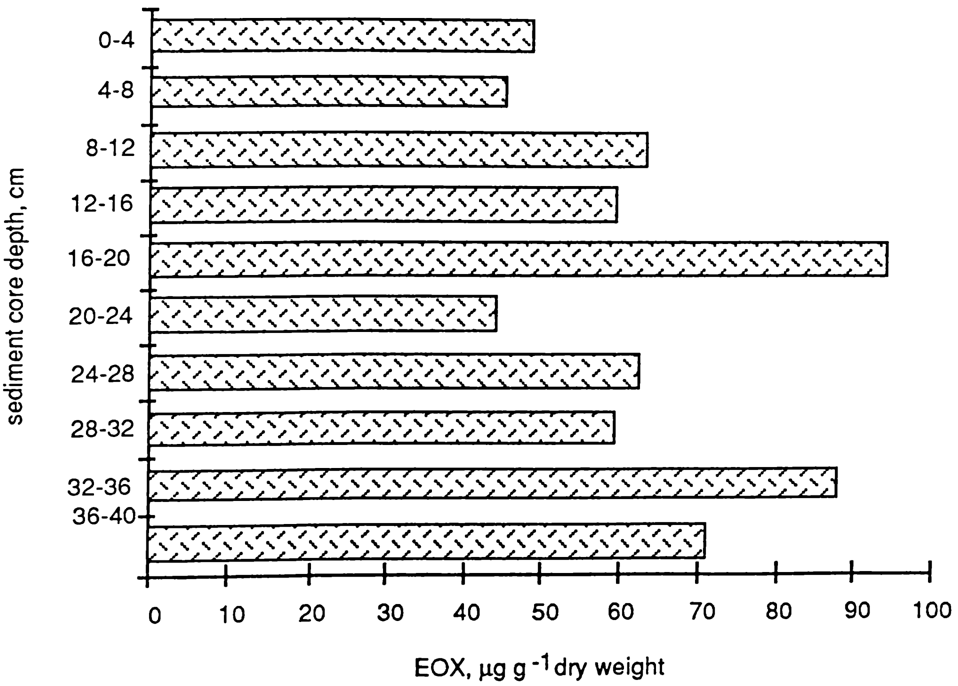

Figure 7.9: EOX in sludge core from mixing zone

A 40 cm sludge core was taken from the middle of the mixing zone. Based on deposition rates, it was estimated that this core had a total age of approximately 585 days. Organochlorine concentrations (measured as EOX) ranged from 43-94 $\mu g\ g^{-1}$ dry weight and were found to be relatively uniform over the depth of the core (Figure 7.9).

Assuming that organochlorine levels were similarly uniform through the remaining depth of the channel sludge, it is possible to determine mass balances for AOX present in sludges in the mixing zone and within the main body of the lagoon (Table 7.6).

TABLE 7.6: Mass balance of AOX in sludges

	mixing zone	main lagoon
sludge volume, m^3	35 500	107 000
dry mass, tonne	22 220	66 875
AOX in sludge, kg $tonne^{-1}$	0.99	0.73
mass AOX, tonne	22	49

From the calculated masses of sludge AOX and the observed daily reduction in AOX during treatment in these sections of the system (Figure 7.3) it is clear that substantial mineralisation of organic chlorine must occur. An assessment was made of the apparent removal of AOX due to dehalogenation of chlorinated organic material upon passage through the mixing zone (Table 7.7). This indicates that over 99% of the AOX removed from the aqueous phase in the mixing zone is mineralised to chloride.

Previous studies have shown dehalogenation/mineralisation to be responsible for 82-100% of the observed removal of AOX in aerated lagoons (Bryant *et al.*, 1987; Dubelsten and Gray, 1990; Ferguson and Jonsson-Dalentoft, 1990; Saunamäki *et al.*, 1990). If mineralisation of AOX is occurring in the mixing zone then it would be expected that increases in inorganic chloride would be observed at the zone's exit. Inorganic chloride discharges entering and leaving the mixing zone were 22 391 ± 2586 and 23 656 ± 3084 kg day^{-1} respectively and, although a mean increase is observed, the difference is not statistically significant.

CONCLUSIONS

Over 70% of the measured removal of AOX in the aerated lagoon treatment system under study can be attributed to a phenomenon occurring in a short residence time section of the treatment system where the chlorination stage effluents are mixed with general mill effluents.

TABLE 7.7: Apparent Dehalogenation in Mixing Zone

	AOX, tonne yr^{-1}
influent wastewater	843
effluent wastewater	455
loss in mixing zone	388
AOX in sludge	2 (0.5%)
apparent dehalogenation	386 (99.5%)

Tests on possible removal mechanisms in this mixing zone have been made. Simple mixing of the incoming wastewaters may be responsible for 20% of the 46% observed removal. Removal of AOX-containing suspended solids from the influent wastewaters is the major cause of this AOX decrease.

Determination of adsorption isotherms with lime, secondary solids and pulp fibre has shown that both lime and secondary solids can adsorb AOX from the aqueous phase. However, only lime was shown to have sufficient adsorptive capacity to account for a significant proportion of the observed AOX decrease in the mixing zone.

EOX concentrations in sludges from the mixing zone were relatively uniform, indicating that the removal phenomenon occurred throughout the mixing zone and not in a specific part of it. Mass balances of total AOX in the sludges of the mixing zone showed that only a small proportion (0.5%) of the observed removal was due to retained AOX on sludges. It appears from these results that a substantial amount of organochlorine dehalogenation/ mineralisation (99.5%) occurs in the mixing zone. Further study is required to elucidate the details of the dehalogenation mechanism.

Based upon our results we consider that the initial removal of AOX in the mixing zone occurs in two ways. Firstly, suspended solids from the chlorination stage settle in the quiescent regions of the mixing zone. Secondly, in regions of the mixing zone where agitation of the bottom sediments takes place, for example, near mechanical aerators and where biogas production is active, a significant amount of adsorption of AOX onto resuspended solids takes place. These solids then settle onto the bottom of the mixing zone. AOX transported to the anaerobic sediments of the mixing zone by these two mechanisms is then rapidly dehalogenated and mineralised by chemical and/or biological degradation processes, such that little accumulation of organically bound chlorine occurs.

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Chapter Eight

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

INTRODUCTION

In this chapter the findings of this study are briefly summarised. Recommendations for further research are also outlined.

CHLORINATED MONOTERPENES

It was found that chlorination stage effluents from the mill's No.2 bleach plant contained high concentrations of a class of chlorinated compounds of unknown structure. The identity and biological activity of these compounds were established in the current study.

Structural Elucidation

The compounds were isolated from chlorination stage effluents using liquid-liquid extraction, column chromatography, and preparative gas chromatography. Sufficient quantities of some of the compounds were obtained (1-5 mg) for their structural elucidation using mass spectrometry and one- and two-dimensional ^{1}H and ^{13}C NMR.

The compounds were found to be previously unreported chlorinated monoterpenes of two types, namely chlorinated monoterpene hydrocarbons and chlorinated monoterpene alcohols. Fourteen compounds were identified and quantified (Table 8.1). These compounds were the dominant low molecular weight extractable organic compounds in No.2 bleach plant chlorination stage effluents. They were also found in effluents from the mill's No.1 bleach plant but at considerably lower concentrations.

The chlorinated monoterpenes are formed by the chlorination of *Pinus radiata* monoterpenes present in unbleached pulp (brownstock) entering the bleach plant. Average monoterpene concentrations in No.1 bleach plant and No.2 bleach plant brownstocks were 80 g ADT^{-1} and 900 g ADT^{-1} respectively. As the unbleached pulps receive comparable washing efficiencies, it appears that the formation and high concentration of these chlorinated monoterpenes in the No.2 bleach plant is due to poor removal of wood extractives during pulping in the mill's continuous digester.

TABLE 8.1: Identities and Concentrations of Chlorinated Monoterpenes in No.2 Bleach Plant Chlorination Stage Effluents.

compound	name	mean concentration* $\mu g\ L^{-1}$
monoterpene hydrocarbons		
1	dichlorobornane or dichloropinane	30
2	dichlorobornane or dichloropinane	96
3	dichlorobornane or dichloropinane	112
4	dichlorobornane or dichloropinane	127
5	2-*endo*-6-*endo*-dichlorobornane	376
6	dichlorobornane or dichloropinane	217
7	dichlorobornane or dichloropinane	476
monoterpene alcohols		
8	dichloro-2-*endo*-hydroxybornane	69
9	1β,2α-dichloro-*p*-menthan-4α-ol	n/d
10	2α,6β-dichloro-*p*-menthane-1α,8-diol	1571
11	2α,7-dichloro-*p*-menthane-1β,8-diol	1506
12	2β,7-dichloro-*p*-menthane-1,8-diol	579
13	2α,7-dichloro-*p*-menthane-1α,8-diol	1676
14	2α,6β,7-trichloro-*p*-menthane-1,8-diol	950

Biological Activity

The biological activities of the two classes of chlorinated monoterpenes were assessed. Despite a scaled-up extraction and isolation procedure, it was not possible to obtain sufficiently pure quantities of the monoterpene hydrocarbons for a full assessment of these compounds.

The stability of the compounds under alkaline conditions was determined. The monoterpene alcohols were readily degraded at neutral pH and above with an almost complete removal at pH 12 (94% decrease). The monoterpene hydrocarbons were more stable than the alcohols but did exhibit some alkaline lability.

The lipophilicity of the monoterpene alcohols was determined using high performance liquid chromatography. Monoterpene 13 was analysed and found to have a log K_{OW} value of 1.37. The other dichlorinated monoterpenes would be expected to have similar values of log K_{OW}.

A linear correlation between log K_{OW} and chlorine substitution was obtained and applied to the trichlorinated monoterpene alcohol 14, to give a log K_{OW} value for this compound of 1.9-2.1. These results indicate that the chlorinated monoterpene alcohols will not readily bioaccumulate in the recipient as the propensity for bioaccumulation is not significant for compounds having log K_{OW} values below 3.

The monoterpene alcohols were assayed for acute toxicity using the *Daphnia magna*, algae, and Microtox tests. The compounds did not exhibit an appreciable toxicity. The calculated EC_{50} values were all significantly higher than the concentrations of these compounds in the effluents.

Mutagenicity (Ames) and genotoxicity (SOS) assays were undertaken on the monoterpene alcohols. Monoterpenes 10, 13 and 14 were not mutagenic. The purified oil containing the remaining monoterpenes induced both mutagenic and genotoxic responses. Monoterpene 13 was also genotoxic.

The biodegradability of the monoterpenes was assessed by monitoring effluents in treatment system A of the Kinleith pulp and paper mill. Overall, the system was able to remove 80% of the chlorinated monoterpene alcohols on a mass flow basis. Only a slight reduction in the discharge of monoterpene hydrocarbons was observed.

In conclusion, the identities of the previously unreported chlorinated monoterpenes have been established. Two classes of compounds, dichlorinated monoterpene hydrocarbons and di- and trichlorinated monoterpene alcohols, are found in the chlorination stage effluents of the Kinleith mill's No.2 bleach plant. An assessment has been made of the biological activity of these compounds. On the basis of the results obtained, it is concluded that these compounds are unlikely to produce any acute environmental effects once discharged to the recipient.

SECONDARY TREATMENT OF BLEACHED KRAFT MILL EFFLUENTS

The Kinleith pulp and paper mill has two effluent treatment systems. General pulping wastewaters, debarking and stormwater discharges, and chlorination stage effluents are treated in system A which has a hydraulic retention time of approximately 5 days. Extraction stage effluents and foul condensates are treated in system B which has a hydraulic retention time of approximately 51 days. The ability of each system to treat bleached kraft mill effluent wastewaters was assessed.

Effluent Treatment

A synoptic survey of the mill's two treatment systems was undertaken. The effluents were analysed for a range of inorganic and organic parameters. Removals in the treatment system of each chemical parameter, calculated on a mean mass flow or yield basis, are summarised in Table 8.2.

TABLE 8.2: Removals of Bleached Kraft Mill Effluent Constituents in Kinleith Treatment Systems

parameter	removal in system A, %	removal in system B, %	removal in combined system, %	literature removal, %
chemical oxygen demand	59	36	62	20-50
colour	11	6	11	<10
sodium	10	5	14	-
total chlorine	2	6	6	-
AOX	65	7	57	25-50
total chlorophenolics	65	76	71	20-60
chlorophenols	-2[a]	77	-5[a]	-
chloroguaiacols	-32[a]	85	79	-
chlorocatechols	80	11	74	-
chlorovanillins	84	91	94	-
total chloroacetic acids	26	84	51	54-97
dichloroacetic acid	31	81	59	-
trichloroacetic acid	16	96	39	-
total chlorinated monoterpenes	65	17	67	69-99
monoterpene hydrocarbons	38	-16	33	-
monoterpene alcohols	70	32	71	-
total resin acids	95	44	96	60-100

[a] indicates increase in constituent after treatment

System A effectively removed COD and AOX. In contrast, system B achieved a substantially lower COD removal and was ineffective at removing AOX. The analysis of the molecular weight distribution of AOX in pre- and post-treatment effluents indicated little change in AOX molecular weight distribution occurred in system A despite a 65% removal of AOX. A decrease in the proportion of low molecular weight AOX (MW < 3 000) occurred in treatment system B. A mass balance of organically bound chlorine in the low molecular weight extractable organic compounds (i.e. analysed on gas chromatograph) confirmed that the AOX reduction in system B was due to the removal of these compounds. Neither system was able to decrease colour discharges.

The systems also differed in their ability to remove low molecular weight chlorinated organic compounds. Both systems were able to remove approximately 70% of the total chlorophenolic compounds. However, system A was unable to remove chlorophenols and chloroguaiacols. System B achieved poor removals of chlorocatechols. Low removals of chloroacetic acids and chlorinated monoterpenes were achieved in system A and system B respectively. While system A was able to effectively remove resin acids, anaerobic conditions in system B lead to the formation and discharge of a range of saturated and/or hydroxylated resin acids.

AOX Removal Mechanisms

Typically, aerated lagoon treatment systems are able to reduce the organically bound chlorine content of BKME by 15-50%. Therefore, the 65% removal of AOX achieved in system A was significantly higher than for comparable systems. An assessment was made of possible mechanisms for this high AOX removal.

An AOX mass balance throughout system A indicated that over 70% of the observed AOX removal was occurring in the wastewater mixing zone prior to entering the main body of the first lagoon in the system. The short hydraulic retention time of this zone (3.3 hr) suggested a physico-chemical removal mechanism.

The effects of effluent mixing (chlorination stage effluent + general pulping effluent) were assessed. Simple mixing of the acidic chlorination stage effluent with the alkaline pulping effluent did not produce a significant decrease in AOX although it was found that a linear decrease in AOX occurred when the pH of the mixed effluent was increased from pH 7 to pH 13. Removal of suspended solids lead to a 16% decrease in AOX indicating that a portion of the AOX was associated with solid material in the effluent.

The role of adsorption of AOX onto solids in the mixing zone was determined. Adsorption isotherms obtained for lime, secondary solids, and pulp indicated that lime and secondary solids were able to adsorb AOX from the effluent. However, calculations based upon physical data from the mixing zone and the isotherms indicated that only lime had sufficient adsorptive capacity to produce the observed AOX removal.

Sludges taken from the mixing zone and the main aerated lagoon were analysed for adsorbable and extractable organic chlorine. The average AOX and EOX concentrations in sludges taken from the mixing zone were 0.99 mg g^{-1} dry weight and 90 $\mu g\ g^{-1}$ dry weight respectively. An organochlorine mass balance based upon measured AOX removals in the mixing zone and the mass of AOX present in the sludges indicated that over 99% of the organically bound chlorine was mineralised.

On the basis of these results it is hypothesised that the high observed removal of AOX in the mixing zone takes place in two steps. Firstly, AOX is transported to the anaerobic sludges at the bottom of the mixing zone. This can be achieved by the settling of AOX-containing suspended solids in quiescent regions of the mixing zone or by adsorption of AOX onto solids resuspended by the action of mechanical aeration or biogas production. The AOX transported to the bottom sediments is then rapidly dehalogenated and mineralised by chemical and/or biological processes.

In conclusion, the Kinleith mill's two effluent treatment systems show significant differences in their ability to treat bleached kraft mill effluents. This reflects the difference in the systems' effluent sources and their operational configuration. The total removal of BKME constituents achieved by the combined systems is generally of comparable standard to or better than aerated lagoon systems reported in the literature. A mechanism has been proposed for the high removal of AOX in the initial section of system A. Knowledge of this mechanism may play an important role in optimising the system to achieve better removals of AOX and other BKME constituents.

RECOMMENDATIONS FOR FURTHER WORK

Based upon the results obtained in this study, the author would recommend that the following research be undertaken:

System Optimisation

Wastewaters entering system B have high resin acid concentrations. The decanter overflow from the mill's tall oil plant is essentially the sole source of these constituents. As treatment system B achieves poor removal efficiencies of these compounds, it is recommended that the decanter overflow be re-directed for discharge to system A which is very effective at removing resin acids.

System B is unable to remove a significant amount of AOX. As system A achieves relatively high AOX removals, it would be of interest to examine the feasibility of sending treated system B effluents through system A.

AOX Removal Processes

Relatively high AOX removals are currently being achieved at the head of system A. This process appears to be fortuitous and is likely to be sub-optimal. In order to gain a better understanding of the mechanisms responsible for this removal, further study should be directed towards laboratory-scale simulations of the mixing zone. Results from such studies may lead to the optimisation of this process and its application as a full-scale effluent treatment system.

Fate and Impacts in the Recipient

As the characteristics and treatability of Kinleith effluents have been examined, it is recommended that research now be directed towards assessing the fate and impacts of post-treatment effluent constituents when discharged to the Kinleith recipient (i.e. Lake Maraetai and the Waikato River). Important aspects of such research would be:

a) distribution of effluent constituents in the recipient water, sediments and biota.
b) chemical and biological transformations of low molecular weight organics in the recipient.
c) long term fate and transformation of the high molecular weight chlorinated organic material.
d) sub-lethal effects of the discharged effluents on recipient flora and fauna.

CONCLUSIONS

This study represents the second stage of the overall program concerning the Kinleith pulp and paper mill. Source effluents have been characterised and the treatability of effluent constituents in the mill's treatment systems has been determined. Data is also presented regarding the nature and quantity of the material being discharged to the recipient.

It is anticipated that the research outlined in this thesis will provide valuable baseline data for the assessment of the Kinleith mill modernisation program and for future environmental impact studies.

Appendix

RESULTS OF SYNOPTIC SURVEY

RESULTS OF SYNOPTIC SURVEY

This appendix provides quantitative data for a selection of BKME constituents analysed for in the synoptic survey. Data are provided for concentrations, mass flows and, where applicable, bleaching production yields. For information on sample sites please refer back to chapter 6. Because J pond in system B is used as a buffer to control discharge rates from this system, the flows entering and leaving the system are often not equal. Therefore for the calculation of mass balances it is necessary to use a correction factor, JFill, to account for accumulation of effluent in the system.

Physical Parameters

Bleach Plant Production

ADT d-1	**No.1 BP C Stage**	**No.1 BP E Stage**	**No.2 BP CD Stage**	**No.2 BP Eo Stage**	**Mill Total**
mean	90	90	256	256	347
95% CI	15	15	24	24	33
min	41	41	200	200	241
max	120	120	301	301	409

Chemical Oxygen Demand

mg L-1	**No.1 BP C Stage**	**No.1 BP E Stage**	**No.2 BP CD Stage**	**No.2 BP Eo Stage**	**No.1 Sewer**	**No.2 Sewer**	**No.3 Sewer**	**Pond 19 Inlet**	**Pond 19 Outlet**	**Pond 23 Outlet**	**Outfall**	**J Pond Outlet**	**J Pond Fill**
mean	289.8	941.3	421.8	3181.7	504.8	3098.3	305.6	328.4	228.6	183.8	124.7	1510.4	1510.4
95% CI	51.8	263.6	59.9	756.0	82.3	873.1	35.0	42.8	26.5	17.9	19.9	216.9	216.9
min	218.0	344.0	275.0	1812.0	338.0	1473.0	234.0	216.0	184.0	133.0	63.0	833.0	833.0
max	420.0	1500.0	589.0	5199.0	747.0	6230.0	417.0	457.0	322.0	250.0	180.0	1909.0	1909.0
tonne d-1													
mean	2.90	5.65	5.29	10.29	58.71	32.01	13.94	53.23	37.22	29.48	38.16	11.00	5.41
95% CI	0.52	1.58	0.94	3.00	11.23	8.18	1.43	7.72	5.51	3.43	6.22	4.05	3.48
min	2.18	2.06	3.11	4.41	38.45	19.37	10.43	34.61	26.54	18.87	19.19	0.00	-2.13
max	4.20	9.00	7.93	18.53	91.21	69.90	18.36	73.03	59.38	38.83	52.36	19.20	12.68
kg ADT-1 bleached pulp													
mean	36.8	70.8	20.3	38.2	-	-	-	-	-	-	-	-	-
95% CI	12.40	24.41	2.9	9.07	-	-	-	-	-	-	-	-	-
min	19.3	17.2	13.2	21.7	-	-	-	-	-	-	-	-	-
max	67.3	126.3	28.3	62.4	-	-	-	-	-	-	-	-	-

Colour

mg L-1	**No.1 BP C Stage**	**No.1 BP E Stage**	**No.2 BP CD Stage**	**No.2 BP Eo Stage**	**No.1 Sewer**	**No.2 Sewer**	**No.3 Sewer**	**Pond 19 Inlet**	**Pond 19 Outlet**	**Pond 23 Outlet**	**Outfall**	**J Pond Outlet**	**J Pond Fill**
mean	399.6	2940.7	603.8	7671.8	579.7	4648.1	360.4	481.4	398.7	420.2	383.4	4364.7	4364.7
95% CI	115.9	460.9	78.4	2081.4	94.7	508.2	35.9	80.1	32.6	24.8	28.9	403.6	403.6
min	76.0	1750.0	325.0	979.0	391.0	2970.0	270.0	307.0	322.0	366.0	279.0	2700.0	2700.0
max	645.0	3635.0	776.0	13154.0	917.0	6340.0	460.0	740.0	487.0	494.0	466.0	5030.0	5030.0
tonne d-1													
mean	4.00	17.64	7.55	24.27	66.34	50.30	16.50	77.00	64.03	67.78	117.07	35.42	11.84
95% CI	1.16	2.77	1.25	7.15	10.06	8.26	1.75	11.19	3.83	3.99	10.65	10.29	9.37
min	0.76	10.50	3.73	2.81	43.91	31.15	12.90	55.52	55.53	55.97	82.44	0.00	-22.32
max	6.45	21.81	11.13	46.88	106.01	71.77	22.05	115.14	73.68	77.55	149.48	52.66	36.16
kg ADT-1 bleached pulp													
mean	51.7	225.5	29.0	92.1	-	-	-	-	-	-	-	-	-
95% CI	21.53	76.71	3.8	25.0	-	-	-	-	-	-	-	-	-
min	7.0	99.1	15.6	11.7	-	-	-	-	-	-	-	-	-
max	107.4	437.3	37.2	157.8	-	-	-	-	-	-	-	-	-

Dissolved Solids

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	425.6	2194.8	724.3	8233.9	674.1	3492.2	872.8	691.3	621.3	626.6	472.1	3006.9	3006.9
95% CI	111.3	311.3	71.6	1242.1	114.7	683.1	115.4	84.4	81.1	49.3	43.1	93.9	93.9
min	278.0	1259.0	516.0	4758.0	472.0	719.0	641.0	514.0	288.0	453.0	361.0	2780.0	2780.0
max	847.0	2748.0	856.0	11564.0	1044.0	4812.0	1205.0	946.0	804.0	732.0	593.0	3228.0	3228.0
tonne d-1													
mean	4.26	13.17	9.14	26.03	77.20	36.59	39.63	111.04	99.07	101.39	141.69	22.42	10.03
95% CI	1.11	1.87	1.38	4.80	11.43	7.27	5.36	12.00	10.45	10.15	14.48	6.42	7.41
min	2.78	7.55	5.90	14.39	51.02	9.20	28.89	80.85	55.09	71.26	105.01	0.00	-15.06
max	8.47	16.49	12.22	35.24	113.69	50.33	55.19	147.20	116.04	126.26	177.90	35.54	23.62
kg ADT-1 bleached pulp													
mean	54.9	176.0	34.8	98.8	-	-	-	-	-	-	-	-	-
95% CI	18.51	62.12	3.4	14.9	-	-	-	-	-	-	-	-	-
min	25.7	71.3	24.8	57.1	-	-	-	-	-	-	-	-	-
max	105.2	351.2	41.1	138.8	-	-	-	-	-	-	-	-	-

Effluent Flows

ML d-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	10.0	6.0	12.3	3.1	116.4	10.7	45.6	162.0	162.0	162.0	304.3	7.8	2.9
95% CI	0.0	0.0	1.2	0.3	8.6	1.2	2.2	7.2	7.2	7.2	11.3	1.9	2.2
min	10.0	6.0	9.6	2.4	92.6	6.8	36.7	141.9	141.9	141.9	281.9	0.0	-5.0
max	10.0	6.0	14.4	3.6	154.6	13.2	50.9	191.3	191.3	191.3	363.7	12.0	8.2

pH

	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	2.6	11.2	2.3	11.0	9.0	10.0	2.6	7.3	7.4	7.5	7.2	8.2	8.2
95% CI	0.1	0.2	0.1	0.4	0.3	0.2	0.1	0.3	0.3	0.3	0.2	0.1	0.1
min	2.4	10.7	2.2	10.1	7.9	9.4	2.5	6.3	6.4	6.4	6.7	8.0	8.0
max	2.7	11.5	2.5	11.8	9.5	10.3	2.8	8.3	8.3	7.8	7.6	8.5	8.5

Sodium

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	28.9	561.6	70.3	2033.9	114.4	841.4	175.6	115.1	110.9	106.3	84.9	781.7	781.7
95% CI	3.5	82.7	8.1	174.9	17.1	114.0	29.8	11.1	6.5	7.3	3.7	16.6	16.6
min	20.0	316.0	50.0	1338.0	84.0	580.0	95.0	90.0	92.0	87.0	75.0	740.0	740.0
max	36.0	744.0	94.0	2416.0	191.0	1382.0	306.0	168.0	131.0	131.0	94.0	830.0	830.0
tonne d-1													
mean	0.29	3.37	0.87	6.31	13.09	8.98	7.96	18.54	17.93	17.26	25.80	6.08	2.29
95% CI	0.03	0.50	0.14	0.94	1.56	1.51	1.32	1.55	1.15	1.58	1.36	1.44	1.73
min	0.20	1.90	0.57	4.05	9.50	4.29	4.75	14.75	15.22	13.91	22.11	0.00	-3.70
max	0.36	4.46	1.31	8.73	20.80	15.51	14.01	26.14	21.23	22.19	29.91	9.17	6.81
kg ADT-1 bleached pulp													
mean	3.6	41.4	3.4	24.4	-	-	-	-	-	-	-	-	-
95% CI	1.2	12.4	0.4	2.1	-	-	-	-	-	-	-	-	-
min	2.1	17.9	2.4	16.1	-	-	-	-	-	-	-	-	-
max	7.2	80.5	4.5	29.0	-	-	-	-	-	-	-	-	-

Suspended Solids

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	129.4	21.5	14.3	46.5	284.7	134.4	133.4	79.8	75.5	63.7	50.8	87.1	87.1
95% CI	94.8	5.7	5.3	7.5	86.5	39.5	32.7	15.3	14.2	12.0	10.1	11.5	11.5
min	22.0	6.0	0.0	34.0	57.0	25.0	72.0	48.0	45.0	40.0	24.0	61.0	61.0
max	482.0	33.0	31.0	68.0	478.0	274.0	252.0	131.0	132.0	118.0	86.0	137.0	137.0
tonne d-1													
mean	1.29	0.13	0.18	0.14	32.95	1.49	6.15	12.91	12.29	10.40	15.68	0.71	0.24
95% CI	0.95	0.03	0.07	0.03	9.94	0.48	1.53	2.55	2.74	2.43	3.70	0.23	0.19
min	0.22	0.04	0.00	0.08	6.49	0.33	3.04	7.30	7.00	6.53	7.31	0.00	-0.39
max	4.82	0.20	0.38	0.24	54.06	3.07	11.13	21.44	25.25	22.57	31.28	1.37	0.70
kg ADT-1 bleached pulp													
mean	14.8	1.6	0.7	0.6	-	-	-	-	-	-	-	-	-
95% CI	9.04	0.64	0.3	0.1	-	-	-	-	-	-	-	-	-
min	2.5	0.4	0.0	0.4	-	-	-	-	-	-	-	-	-
max	44.6	3.4	1.5	0.8	-	-	-	-	-	-	-	-	-

Inorganic and Organic Chlorine

Total Chlorine

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	290.6	394.2	625.2	1302.8	52.3	563.9	378.6	150.6	131.1	134.9	90.8	510.9	510.9
95% CI	35.9	53.2	62.4	143.1	20.9	53.3	54.0	19.1	14.7	20.4	12.7	27.1	27.1
min	197.1	297.4	480.1	767.8	10.9	451.5	233.7	110.0	97.9	103.9	48.2	434.3	434.3
max	352.1	547.6	822.3	1671.0	110.1	744.4	612.5	201.4	173.3	239.9	126.9	584.8	584.8
tonne d-1													
mean	2.9	2.4	7.7	4.0	6.0	6.2	17.2	24.4	21.2	21.8	27.6	4.0	1.5
95% CI	0.36	0.32	1.08	0.66	2.35	0.96	2.49	3.31	2.42	3.31	3.82	0.90	1.17
min	1.97	1.78	4.61	2.32	1.53	3.07	10.91	17.58	14.89	16.08	14.90	0.00	-2.32
max	3.52	3.29	10.93	5.96	12.45	9.42	28.05	37.13	27.26	39.15	37.51	5.76	4.80
kg ADT-1 bleached pulp													
mean	34.5	28.7	30.0	15.6	17.4	18.8	50.7	72.7	63.3	64.5	83.1	12.0	4.5
95% CI	7.5	7.9	3.0	1.7	6.7	4.4	7.9	10.7	10.3	10.3	16.1	3.2	3.5
min	22.1	16.8	23.0	9.2	4.4	8.8	27.3	45.5	36.4	39.3	36.4	0.0	-6.7
max	56.1	57.6	39.5	20.1	35.9	39.1	86.9	106.7	94.6	98.4	135.0	21.8	14.8

Chloride

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	261.7	360.4	555.8	1177.1	52.2	515.8	348.1	145.6	127.6	131.8	88.2	469.1	469.1
95% CI	33.8	48.3	54.4	129.4	19.0	52.4	51.6	18.4	14.8	20.5	12.8	25.2	25.2
min	168.5	266.5	416.2	692.5	10.5	401.4	214.5	104.7	93.4	101.0	45.1	399.9	399.9
max	319.7	506.2	736.9	1498.4	110.0	701.3	580.2	194.9	170.3	237.4	124.6	534.2	534.2
tonne d-1													
mean	2.62	2.16	6.85	3.65	5.98	5.69	15.85	23.66	20.65	21.30	26.79	3.63	1.42
95% CI	0.34	0.29	0.95	0.59	2.13	0.91	2.38	3.21	2.44	3.33	3.85	0.83	1.08
min	1.68	1.60	4.00	2.09	1.47	2.74	10.02	16.73	14.21	15.72	13.93	0.00	-2.11
max	3.20	3.04	9.55	5.34	12.44	8.66	26.57	35.94	26.78	38.74	36.83	5.32	4.38
kg ADT-1 bleached pulp													
mean	31.0	26.2	26.7	14.1	17.3	17.3	46.7	70.5	61.7	63.0	80.7	11.0	4.2
95% CI	6.7	7.2	2.6	1.6	6.1	4.1	7.6	10.4	10.2	10.3	15.9	2.9	3.2
min	18.9	16.0	20.0	8.3	4.2	7.9	25.0	43.3	34.7	38.4	34.1	0.0	-6.1
max	50.5	53.4	35.4	18.0	35.8	35.9	82.3	103.3	92.3	97.3	131.8	20.0	13.6

Adsorbable Organic Halide

mg L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	28.9	33.7	69.4	125.7	0.5	46.4	30.5	4.8	3.5	3.1	2.6	41.8	41.8
95% CI	3.2	7.1	10.1	16.4	0.2	6.0	4.2	1.2	0.4	0.4	0.3	3.4	3.4
min	21.6	15.0	45.4	75.3	0.1	24.3	19.2	2.2	2.2	2.3	1.7	32.7	32.7
max	35.8	52.9	100.1	172.6	1.4	57.9	44.6	10.3	4.8	4.6	3.3	54.4	54.4
tonne d-1													
mean	0.29	0.20	0.85	0.39	0.06	0.50	1.38	0.78	0.56	0.50	0.80	0.32	0.13
95% CI	0.03	0.04	0.15	0.07	0.02	0.10	0.19	0.17	0.07	0.05	0.08	0.07	0.10
min	0.22	0.09	0.57	0.22	0.01	0.18	0.90	0.36	0.37	0.36	0.50	0.00	-0.20
max	0.36	0.32	1.38	0.62	0.15	0.76	1.96	1.47	0.72	0.65	0.99	0.48	0.42
kg ADT-1 bleached pulp													
mean	3.5	2.5	3.3	1.5	0.2	1.5	4.1	2.3	1.7	1.5	2.4	1.0	0.4
95% CI	0.8	0.8	0.5	0.2	0.1	0.4	0.5	0.5	0.3	0.2	0.3	0.3	0.3
min	2.3	0.8	2.2	0.9	0.0	0.4	2.2	1.0	1.0	0.9	1.3	0.0	-0.6
max	5.9	4.7	4.8	2.1	0.4	3.2	5.6	3.6	2.3	2.4	3.2	1.7	1.3

Molecular Weight Distribution of AOX, %

	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
<3K	58	19	65	22	-	31	57	58	54	57	30	19	19
3K-10K	23	15	20	15	-	16	20	32	18	18	19	24	24
10K-30K	6	20	6	4	-	9	9	5	10	7	24	12	12
30K-100	5	15	3	12	-	17	7	0	6	7	7	20	20
>100K	7	31	5	47	-	26	7	4	13	11	21	27	27

Chlorinated Acetic Acids

Chloroacetic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	634	0	1212	0	385	0	0	0	0	0	22	22
95% CI	0	257	0	429	0	267	0	0	0	0	0	17	17
min	0	95	0	161	0	62	0	0	0	0	0	0	0
max	0	1314	0	2944	0	1885	0	0	0	0	0	74	74
kg d-1													
mean	0.00	3.81	0.00	3.79	0.00	4.48	0.00	0.00	0.00	0.00	0.00	0.12	0.11
95% CI	0	2	0	1.52	0	3.53	0.00	0.00	0.00	0.00	0.00	0.10	0.13
min	0.00	0.57	0.00	0.48	0.00	0.58	0.00	0.00	0.00	0.00	0.00	0.00	-0.10
max	0.00	7.88	0.00	10.63	0.00	24.48	0.00	0.00	0.00	0.00	0.00	0.37	0.58
g ADT-1 bleached pulp													
mean	0.0	48.7	0.0	14.5	0.0	12.4	0.0	0.0	0.0	0.0	0.0	0.4	0.3
95% CI	0	34	0	5.1	0	8.6	0.0	0.0	0.0	0.0	0.0	0.3	0.4
min	0.0	11.5	0.0	1.9	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	-0.3
max	0.0	171.4	0.0	35.3	0.0	59.9	0.0	0.0	0.0	0.0	0.0	1.2	1.8

Dichloroacetic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	523	7644	1399	9054	102	3752	639	195	230	178	101	779	779
95% CI	193	3855	978	2543	48	1459	128	86	183	112	74	201	201
min	213	1778	266	1547	28	772	290	41	2	2	0	403	403
max	1045	18244	7121	17130	244	8070	1064	658	823	433	379	1450	1450
kg d-1													
mean	5.23	45.86	17.80	28.06	11.54	41.10	29.22	31.71	36.28	28.37	30.48	5.60	2.95
95% CI	1.93	23	14.34	8.80	5.32	18.77	6.23	14.14	28.91	17.45	22.11	1.76	2.70
min	2.13	10.67	3.82	4.62	3.86	7.10	13.53	6.17	0.38	0.26	0.00	0.00	-2.76
max	10.45	109.46	102.89	61.87	28.15	106.53	50.22	107.35	134.38	66.77	110.28	12.31	11.31
g ADT-1 bleached pulp													
mean	56.2	459.3	67.1	108.6	34.0	124.5	86.0	90.0	95.9	83.2	85.3	17.2	8.6
95% CI	14.4	195	47.0	30.5	13.4	57.7	18.8	35.6	74.0	52.3	60.0	5.3	7.7
min	28.0	170.0	12.8	18.6	11.1	17.7	33.8	25.1	1.0	0.7	0.0	0.0	-7.9
max	96.8	912.2	341.8	205.6	72.9	329.8	158.9	269.7	337.6	206.7	316.9	35.5	30.5

Trichloroacetic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	3037	5096	3077	1296	42	1212	2173	793	568	624	248	32	32
95% CI	991	3248	1030	353	24	497	512	354	64	92	55	20	20
min	595	975	480	286	6	146	702	365	353	455	29	0	0
max	5037	14593	6599	2368	114	2626	3676	2785	712	1060	440	100	100
kg d-1													
mean	30.37	30.57	36.04	3.97	4.61	13.38	99.30	128.78	91.98	101.71	75.51	0.31	0.00
95% CI	10	19	11.01	1.14	2.42	6.12	24.23	58.35	11.22	18.60	16.40	0.22	0.10
min	5.95	5.85	6.89	0.86	0.90	1.08	32.78	56.75	57.58	71.59	8.06	0.00	-0.50
max	50.37	87.56	66.97	7.35	10.51	34.66	164.96	454.56	117.88	195.43	133.99	1.17	0.15
g ADT-1 bleached pulp													
mean	329.5	301.5	147.7	15.5	13.1	40.8	294.6	368.9	277.7	305.1	226.4	1.0	0.0
95% CI	78	172	49.4	4.2	6.7	19.4	76.6	145.0	58.1	61.3	52.4	0.7	0.3
min	145.2	89.2	23.0	3.4	2.6	2.7	81.9	141.9	144.7	199.2	19.7	0.0	-1.4
max	466.4	729.6	316.8	28.4	29.7	107.3	522.0	1142.1	489.1	561.6	353.7	3.4	0.6

Total Chlorinated Acetic Acids

ug L-1	**No.1 BP C Stage**	**No.1 BP E Stage**	**No.2 BP CD Stage**	**No.2 BP Eo Stage**	**No.1 Sewer**	**No.2 Sewer**	**No.3 Sewer**	**Pond 19 Inlet**	**Pond 19 Outlet**	**Pond 23 Outlet**	**Outfall**	**J Pond Outlet**	**J Pond Fill**
mean	3826	15548	4366	11561	144	5233	2873	1050	814	823	328	782	782
95% CI	1029	7306	1609	3282	59	2036	778	504	177	155	89	169	169
min	1892	2853	746	1994	56	1131	992	455	443	533	146	448	448
max	6083	33601	8526	22108	283	11261	4559	3443	1176	1281	571	1315	1315
kg d-1													
mean	38.26	93.29	49.48	35.82	15.81	57.42	134.14	170.61	131.39	133.71	100.86	6.10	2.32
95% CI	10	44	16	11.35	6	26.00	36.07	83.27	26	27.89	27.23	2.08	2.56
min	18.92	17.12	10.71	5.96	6.39	8.76	46.31	70.78	72.44	90.11	41.24	0.00	-3.36
max	60.83	201.61	82.26	79.85	30.92	148.65	215.18	561.91	191.96	236.18	174.05	13.08	10.26
g ADT-1 bleached pulp													
mean	403.8	913.1	209.6	138.7	45.0	174.1	388.4	487.0	380.9	400.8	298.4	19.0	7.2
95% CI	80	373	77	39.4	15	80.2	119.8	204.2	FALSE	82.4	73.7	6.2	7.9
min	221.6	301.7	35.8	23.9	19.8	21.9	115.8	177.0	208.8	225.8	100.8	0.0	-9.7
max	563.2	1680.1	409.2	265.3	75.6	460.2	680.9	1411.8	554.7	678.7	453.8	37.7	32.5

Fatty Acids

Palmitic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	102	261	86	1105	108	2782	75	61	48	41	44	261	261
95% CI	66	73	14	350	26	1312	8	15	7	7	11	136	136
min	19	38	59	536	57	280	54	33	31	12	23	94	94
max	386	420	138	3081	199	8313	101	117	84	58	87	739	739
kg d-1													
mean	1.02	1.57	1.08	3.54	12.46	30.40	3.38	9.85	7.69	6.60	13.46	1.95	1.13
95% CI	0.66	0.44	0.26	1.37	3.07	15.35	0.33	2.28	1.22	1.25	3.35	1.04	1.07
min	0.19	0.23	0.57	1.29	6.53	2.62	2.70	5.54	5.12	1.93	6.97	0.75	-0.62
max	3.86	2.52	1.94	10.98	22.96	93.27	4.73	19.01	13.42	11.11	27.56	7.39	5.10
g ADT-1 bleached pulp													
mean	11.9	20.3	4.1	13.3	-	-	-	-	-	-	-	-	-
95% CI	6.4	9.3	0.7	4.2	-	-	-	-	-	-	-	-	-
min	2.1	2.1	2.8	6.4	-	-	-	-	-	-	-	-	-
max	35.7	50.9	6.6	37.0	-	-	-	-	-	-	-	-	-

anteiso-Heptadecanoic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	8	20	14	171	10	575	6	4	1	0	1	32	32
95% CI	9	7	5	53	5	275	3	2	1	1	1	25	25
min	0	0	9	101	0	37	0	0	0	0	0	0	0
max	45	36	41	478	23	1842	19	14	6	7	5	119	119
kg d-1													
mean	0.08	0.12	0.18	0.54	1.11	6.22	0.25	0.62	0.18	0.09	0.32	0.22	0.17
95% CI	0.09	0.04	0.06	0.21	0.54	3.19	0.13	0.37	0.16	0.20	0.33	0.19	0.17
min	0.00	0.00	0.08	0.24	0.00	0.44	0.00	0.00	0.00	0.00	0.00	0.00	-0.06
max	0.45	0.21	0.47	1.70	2.60	20.66	0.82	2.21	0.81	1.30	1.55	1.19	0.82
g ADT-1 bleached pulp													
mean	0.9	1.6	0.7	2.0	-	-	-	-	-	-	-	-	-
95% CI	0.8	0.9	0.2	0.6	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.4	1.2	-	-	-	-	-	-	-	-	-
max	4.2	4.6	2.0	5.7	-	-	-	-	-	-	-	-	-

Heptadecanoic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	7	17	6	27	5	77	7	6	7	5	17	155	155
95% CI	5	5	5	10	3	42	5	3	4	3	6	68	68
min	0	0	0	11	0	0	0	0	0	0	0	35	35
max	28	27	30	85	13	222	27	14	22	11	43	489	489
kg d-1													
mean	0.07	0.10	0.08	0.09	0.65	0.84	0.30	0.93	1.19	0.73	5.05	1.39	0.31
95% CI	0.05	0.03	0.07	0.04	0.35	0.48	0.21	0.42	0.60	0.45	1.93	0.66	0.27
min	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17	-0.59
max	0.28	0.16	0.42	0.30	1.72	2.49	1.17	2.29	3.53	1.78	13.07	4.40	1.08
g ADT-1 bleached pulp													
mean	0.8	1.3	0.3	0.3	-	-	-	-	-	-	-	-	-
95% CI	0.5	0.4	0.2	0.1	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.1	-	-	-	-	-	-	-	-	-
max	2.6	2.3	1.4	1.0	-	-	-	-	-	-	-	-	-

Linoleic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	3	8	2	23	76	9661	17	10	3	2	4	57	57
95% CI	4	6	2	5	56	4961	9	10	1	2	2	41	41
min	0	0	0	11	8	90	6	0	0	0	0	0	0
max	15	33	10	38	304	33431	61	67	8	8	13	180	180
kg d-1													
mean	0.03	0.05	0.02	0.07	9.20	104.84	0.73	1.55	0.56	0.34	1.19	0.38	0.31
95% CI	0.0	0.04	0.02	0.02	7.07	57.43	0.33	1.49	0.23	0.28	0.75	0.26	0.30
min	0.00	0.00	0.00	0.03	0.90	1.06	0.30	0.00	0.00	0.00	0.00	0.00	-0.09
max	0.15	0.20	0.10	0.14	35.54	375.10	2.25	10.09	1.33	1.40	3.93	1.40	1.40
g ADT-1 bleached pulp													
mean	0.6	0.6	0.1	0.3	-	-	-	-	-	-	-	-	-
95% CI	0.8	0.4	0.1	0.1	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.1	-	-	-	-	-	-	-	-	-
max	3.7	1.9	0.5	0.5	-	-	-	-	-	-	-	-	-

Oleic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	31	19	14	35	155	13808	37	45	14	11	14	367	367
95% CI	47	12	17	10	72	6811	29	27	6	5	8	328	328
min	0	0	0	18	31	356	13	7	6	0	5	18	18
max	240	59	115	70	397	44775	210	148	42	33	50	1502	1502
kg d-1													
mean	0.31	0.12	0.19	0.11	18.33	149.41	1.59	7.19	2.31	1.68	4.29	2.38	2.14
95% CI	0.47	0.07	0.24	0.04	8.82	78.61	1.03	4.26	1.05	0.74	2.35	2.25	2.28
min	0.00	0.00	0.00	0.04	3.39	4.19	0.55	1.09	0.88	0.00	1.57	0.15	-0.15
max	2.40	0.35	1.62	0.25	44.93	502.38	7.70	22.33	7.94	5.32	14.60	12.93	11.72
g ADT-1 bleached pulp													
mean	3.3	1.5	0.7	0.4	-	-	-	-	-	-	-	-	-
95% CI	4.0	1.1	0.8	0.1	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.2	-	-	-	-	-	-	-	-	-
max	20.0	5.7	5.5	0.8	-	-	-	-	-	-	-	-	-

Stearic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	52	148	34	151	36	400	26	29	23	20	21	72	72
95% CI	39	54	9	69	8	181	3	9	4	4	6	25	25
min	10	36	21	51	22	86	19	14	14	5	0	33	33
max	225	271	80	545	74	1222	40	72	38	34	41	171	171
kg d-1													
mean	0.52	0.89	0.44	0.49	4.12	4.34	1.20	4.64	3.78	3.23	6.48	0.59	0.23
95% CI	0.39	0.33	0.15	0.26	0.89	2.12	0.12	1.45	0.68	0.59	1.94	0.25	0.20
min	0.10	0.22	0.20	0.12	2.40	0.64	0.93	2.20	2.32	0.85	0.00	0.26	-0.29
max	2.25	1.62	1.11	1.94	8.57	13.71	1.76	11.80	6.09	5.35	13.08	1.71	0.84
g ADT-1 bleached pulp													
mean	6.5	10.7	1.6	1.8	-	-	-	-	-	-	-	-	-
95% CI	4.2	4.5	0.4	0.8	-	-	-	-	-	-	-	-	-
min	1.1	2.0	1.0	0.6	-	-	-	-	-	-	-	-	-
max	20.8	25.4	3.8	6.5	-	-	-	-	-	-	-	-	-

9,10-Epoxystearic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	148	0	3417	0	630	0	0	1	0	0	62	62
95% CI	0	78	0	609	0	127	0	0	1	0	0	14	14
min	0	34	0	2570	0	357	0	0	0	0	0	42	42
max	0	331	0	6767	0	1067	0	0	7	0	0	119	119

kg d-1													
mean	0.00	0.89	0.00	10.57	0.00	6.72	0.00	0.00	0.07	0.00	0.00	0.50	0.20
95% CI	0.00	0.5	0.00	2.44	0.00	1.52	0.00	0.00	0.15	0.00	0.00	0.14	0.17
min	0.00	0.20	0.00	6.87	0.00	2.71	0.00	0.00	0.00	0.00	0.00	0.26	-0.23
max	0.00	1.99	0.00	24.12	0.00	11.79	0.00	0.00	0.99	0.00	0.00	1.19	0.72

g ADT-1 bleached pulp													
mean	0.0	12.1	0.0	41.0	0.0	20.6	0.0	0.0	0.2	0.0	0.0	1.5	0.6
95% CI	0.0	8.4	0.0	7.3	0.0	6.2	0.0	0.0	0.4	0.0	0.0	0.4	0.5
min	0.0	1.9	0.0	30.8	0.0	6.8	0.0	0.0	0.0	0.0	0.0	0.7	-0.6
max	0.0	43.2	0.0	81.2	0.0	48.9	0.0	0.0	2.4	0.0	0.0	2.9	2.2

9,10-Dichlorostearic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	34	43	897	252	1005	0	0	0	0	0	0	0
S.Dev.	0	12	12	341	133	508	0	0	0	0	0	0	0
min	0	11	22	453	0	0	0	0	0	0	0	0	0
max	0	76	95	2800	0	0	0	0	0	0	0	0	0

kg d-1													
mean	0.00	0.20	0.53	2.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95% CI	0.00	0.1	0.19	1.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
min	0.00	0.07	0.24	1.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.46	1.36	9.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

g ADT-1 bleached pulp													
mean	0.0	2.8	2.1	10.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
95% CI	0.0	1.8	0.6	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
min	0.0	0.6	1.1	5.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	0.0	9.9	4.6	33.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Total Fatty acids

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	180	694	184	5911	390	27932	167	155	97	79	102	1006	1006
95% CI	128	143	36	1598	156	13550	43	57	20	16	23	553	553
min	29	394	120	4488	123	1220	121	61	61	17	36	332	332
max	709	1024	349	13834	917	90391	408	349	180	120	158	2833	2833

kg d-1													
mean	1.80	4.17	2.30	18.62	45.87	302.76	7.45	24.78	15.78	12.67	30.80	7.40	4.49
95% CI	1.3	0.9	0.64	6.38	19.40	156.87	1.46	8.90	3.35	2.51	6.76	4.11	4.26
min	0.29	2.36	1.16	10.93	13.40	13.53	5.25	9.85	9.81	2.78	10.64	2.73	-2.02
max	7.09	6.14	4.98	49.30	109.01	1014.19	14.96	56.97	28.81	19.52	47.86	28.33	20.95

g ADT-1 bleached pulp													
mean	22.7	54.1	8.9	70.9	-	-	-	-	-	-	-	-	-
95% CI	13.6	22.3	1.7	19.2	-	-	-	-	-	-	-	-	-
min	3.2	27.3	5.8	53.9	-	-	-	-	-	-	-	-	-
max	65.6	130.1	16.8	166.0	-	-	-	-	-	-	-	-	-

Resin Acids

Seco-1-dehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	132	2297	14	77	25	14	18	1227	1227
95% CI	0	0	0	0	20	1159	4	17	6	3	6	55	55
min	0	0	0	0	79	169	9	35	14	5	7	1069	1069
max	0	0	0	0	223	8474	36	160	50	22	39	1389	1389
kg d-1													
mean	0.00	0.00	0.00	0.00	15.43	24.66	0.66	12.43	4.12	2.33	5.43	10.34	3.10
95% CI	0.00	0.00	0.00	0.00	2.83	13.27	0.19	2.75	1.02	0.47	1.72	1.93	2.71
min	0.00	0.00	0.00	0.00	8.91	1.99	0.33	5.60	2.25	0.82	2.15	4.91	-5.94
max	0.00	0.00	0.00	0.00	25.79	95.08	1.70	25.50	8.05	3.65	12.54	14.54	10.03
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Seco-2-dehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	90	1221	16	54	16	11	13	683	683
95% CI	0	0	0	0	12	597	5	11	4	3	5	32	32
min	0	0	0	0	52	116	0	23	8	0	0	583	583
max	0	0	0	0	143	4440	43	100	32	18	30	760	760
kg d-1													
mean	0.00	0.00	0.00	0.00	10.57	13.07	0.72	8.81	2.66	1.77	4.03	5.76	1.72
95% CI	0.00	0.00	0.00	0.00	1.84	6.80	0.26	1.77	0.75	0.44	1.55	1.08	1.52
min	0.00	0.00	0.00	0.00	5.87	1.37	0.00	3.68	1.26	0.00	0.00	2.72	-3.35
max	0.00	0.00	0.00	0.00	16.53	49.81	2.00	16.00	5.11	2.84	9.45	8.06	5.64
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Isopimara-8,15-dienoic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	35	135	4	26	6	2	2	474	474
95% CI	0	0	0	0	10	64	4	7	3	2	2	46	46
min	0	0	0	0	14	32	0	9	0	0	0	313	313
max	0	0	0	0	70	423	22	52	17	10	10	586	586
kg d-1													
mean	0.00	0.00	0.00	0.00	4.16	1.40	0.16	4.27	1.02	0.38	0.68	4.11	1.01
95% CI	0.00	0.00	0.00	0.00	1.46	0.68	0.17	1.27	0.52	0.35	0.63	0.93	0.91
min	0.00	0.00	0.00	0.00	1.62	0.35	0.00	1.38	0.00	0.00	0.00	1.36	-2.50
max	0.00	0.00	0.00	0.00	9.14	4.74	0.96	8.15	3.06	1.59	2.80	6.13	3.27
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Pimaric acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	16	686	9643	193	336	43	27	22	4451	4451
95% CI	0	0	0	4	106	4737	60	95	8	8	8	183	183
min	0	0	0	6	417	797	99	87	18	0	10	3821	3821
max	0	0	0	28	1104	35196	494	714	70	62	63	4905	4905
kg d-1													
mean	0.00	0.00	0.00	0.05	80.86	103.64	8.85	54.93	6.91	4.33	6.86	37.57	11.32
95% CI	0.00	0.00	0.00	0.02	16.14	54.24	2.80	16.19	1.42	1.30	2.53	7.08	9.85
min	0.00	0.00	0.00	0.02	45.53	9.40	4.31	13.87	2.95	0.00	2.85	16.88	-20.98
max	0.00	0.00	0.00	0.10	135.48	394.90	23.05	114.02	11.20	9.69	20.11	55.15	35.91
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.2	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.1	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.1	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.3	-	-	-	-	-	-	-	-	-

Sandaracopimaric acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	19	0	33	135	2061	38	64	8	3	2	510	510
95% CI	0	8	0	5	33	966	13	21	3	3	1	81	81
min	0	0	0	23	44	174	18	10	0	0	0	388	388
max	0	42	0	53	241	6399	101	155	16	15	4	798	798
kg d-1													
mean	0.00	0.11	0.00	0.10	16.04	21.59	1.75	10.40	1.25	0.50	0.57	4.15	1.61
95% CI	0.00	0.05	0.00	0.02	4.80	10.39	0.60	3.55	0.48	0.38	0.29	0.85	1.38
min	0.00	0.00	0.00	0.06	4.99	2.05	0.78	1.65	0.00	0.00	0.00	2.64	-1.98
max	0.00	0.25	0.00	0.19	37.30	71.79	4.71	24.83	2.59	2.30	1.33	7.98	5.41
g ADT-1 bleached pulp													
mean	0.0	1.5	0.0	0.4	-	-	-	-	-	-	-	-	-
95% CI	0.0	1.0	0.0	0.1	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.3	-	-	-	-	-	-	-	-	-
max	0.0	5.5	0.0	0.6	-	-	-	-	-	-	-	-	-

Pimarenoic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	0	0	5	153	153
95% CI	0	0	0	0	0	0	0	0	0	0	3	17	17
min	0	0	0	0	0	0	0	0	0	0	0	118	118
max	0	0	0	0	0	0	0	0	0	0	15	215	215
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.60	1.26	0.46
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.21	0.40
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59	-0.64
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.74	1.95	1.76
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

13-Abieten-18-oic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	118	65	44	5214	5214
95% CI	0	0	0	0	0	0	0	0	35	23	10	1046	1046
min	0	0	0	0	0	0	0	0	40	22	20	3938	3938
max	0	0	0	0	0	0	0	0	275	190	87	9756	9756
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	19.12	10.48	13.53	41.33	17.04
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.79	3.64	3.16	6.14	16.76
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.43	3.54	5.73	23.46	-21.42
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	45.64	29.55	27.68	62.35	80.00
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Isopimaric acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	515	6526	126	605	0	0	0	0	0
95% CI	0	0	0	0	109	2945	43	327	0	0	0	0	0
min	0	0	0	0	205	640	63	152	0	0	0	0	0
max	0	0	0	0	884	22740	345	1845	0	0	0	0	0
kg d-1													
mean	0.00	0.00	0.00	0.00	61.30	69.06	5.78	100.67	0.00	0.00	0.00	0.00	0.00
95% CI	0.00	0.00	0.00	0.00	16.36	33.84	2.01	55.68	0.00	0.00	0.00	0.00	0.00
min	0.00	0.00	0.00	0.00	23.33	7.56	2.77	24.12	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	123.45	255.14	16.10	294.83	0.00	0.00	0.00	0.00	0.00
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Palustric acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	1	0	0	0	1356	24023	355	245	19	17	4	5214	5214
95% CI	2	0	0	0	246	12616	209	125	12	7	3	1046	1046
min	0	0	0	0	766	1112	65	5	0	0	0	3938	3938
max	11	0	0	0	2084	88005	1226	627	53	32	11	9756	9756
kg d-1													
mean	0.01	0.00	0.00	0.00	160.55	258.00	16.30	39.99	3.03	2.68	1.12	41.33	17.04
95% CI	0.02	0.00	0.00	0.00	36.48	143.27	9.61	20.70	1.90	1.11	0.90	6.14	16.76
min	0.00	0.00	0.00	0.00	87.27	13.13	2.84	0.86	0.00	0.00	0.00	23.46	-21.42
max	0.11	0.00	0.00	0.00	271.21	987.42	57.24	101.50	8.42	5.14	3.29	62.35	80.00
g ADT-1 bleached pulp													
mean	0.1	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.2	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	1.1	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Abietan-18-oic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	86	54	38	8707	8707
95% CI	0	0	0	0	0	0	0	0	30	15	8	735	735
min	0	0	0	0	0	0	0	0	28	21	12	6629	6629
max	0	0	0	0	0	0	0	0	245	128	61	10761	10761
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.99	8.72	11.65	74.63	20.43
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.88	2.43	2.46	16.14	18.48
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.65	3.45	3.55	26.52	-44.41
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.39	19.92	19.45	109.78	75.15
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Dehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	11	22	8	39	1677	12003	717	1100	105	66	47	10642	10642
95% CI	9	7	7	23	291	5555	213	321	37	19	10	898	898
min	0	5	0	5	954	914	316	228	35	26	15	8102	8102
max	33	44	49	161	2600	42036	1795	2215	299	156	75	13152	13152
kg d-1													
mean	0.11	0.13	0.09	0.13	199.21	127.21	32.91	180.48	17.10	10.66	14.24	91.22	24.97
95% CI	0.09	0.04	0.07	0.08	46.79	62.99	10.12	56.45	5.97	2.97	3.00	19.73	22.59
min	0.00	0.03	0.00	0.02	104.08	10.78	13.82	36.20	5.68	4.21	4.34	32.41	-54.27
max	0.33	0.26	0.47	0.57	401.93	471.65	83.82	369.15	48.14	24.35	23.77	134.17	91.85
g ADT-1 bleached pulp													
mean	1.6	1.6	0.4	0.5	-	-	-	-	-	-	-	-	-
95% CI	1.7	0.5	0.4	0.3	-	-	-	-	-	-	-	-	-
min	0.0	0.3	0.0	0.1	-	-	-	-	-	-	-	-	-
max	8.0	2.5	2.3	1.9	-	-	-	-	-	-	-	-	-

Abietatrienoic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	29	325	0	12	0	0	0	60	60
95% CI	0	0	0	0	6	150	0	4	0	0	0	26	26
min	0	0	0	0	16	22	0	3	0	0	0	0	0
max	0	0	0	0	57	1022	0	24	0	0	0	179	179
kg d-1													
mean	0.00	0.00	0.00	0.00	3.44	3.50	0.00	2.00	0.00	0.00	0.00	0.45	0.23
95% CI	0.00	0.00	0.00	0.00	1.01	1.73	0.00	0.72	0.00	0.00	0.00	0.15	0.26
min	0.00	0.00	0.00	0.00	1.79	0.26	0.00	0.41	0.00	0.00	0.00	0.00	-0.22
max	0.00	0.00	0.00	0.00	8.73	11.47	0.00	4.55	0.00	0.00	0.00	0.95	1.47
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Isopimarenic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	0	0	2	751	751
95% CI	0	0	0	0	0	0	0	0	0	0	3	1115	1115
min	0	0	0	0	0	0	0	0	0	0	0	123	123
max	0	0	0	0	0	0	0	0	0	0	15	6946	6946
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.61	4.64	4.74
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.92	5.44	9.40
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	-1.14
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.87	34.73	56.96
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Abietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	6	4	3	35	2210	36147	161	919	130	70	43	5345	5345
95% CI	7	3	2	13	432	19900	69	284	37	35	16	704	704
min	0	0	0	9	1225	1822	10	195	14	6	5	3514	3514
max	33	12	13	93	3698	146594	501	1870	261	233	90	7049	7049
kg d-1													
mean	0.06	0.02	0.04	0.11	263.76	387.99	7.44	149.37	21.09	11.30	13.25	44.08	15.81
95% CI	0.07	0.0	0.03	0.04	69.40	225.54	3.21	49.28	6.00	5.54	4.95	9.07	14.07
min	0.00	0.00	0.00	0.03	133.68	21.50	0.38	35.81	2.24	0.85	1.35	25.24	-23.11
max	0.33	0.07	0.19	0.23	571.68	1644.79	23.42	320.89	40.61	36.27	26.57	70.49	56.96
g ADT-1 bleached pulp													
mean	1.1	0.2	0.2	0.4	-	-	-	-	-	-	-	-	-
95% CI	1.6	0.2	0.1	0.2	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.1	-	-	-	-	-	-	-	-	-
max	8.1	0.7	0.6	1.1	-	-	-	-	-	-	-	-	-

Hydroxydehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	0	3	5	242	242
95% CI	0	0	0	0	0	0	0	0	0	3	3	75	75
min	0	0	0	0	0	0	0	0	0	0	0	65	65
max	0	0	0	0	0	0	0	0	0	19	17	477	477
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	1.51	2.02	0.73
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.96	0.67	0.65
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.51	-0.33
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.94	5.47	4.40	3.91
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Neoabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	472	11768	103	197	22	6	4	773	773
95% CI	0	0	0	0	138	6737	56	60	8	5	3	259	259
min	0	0	0	0	226	436	18	50	0	0	0	119	119
max	0	0	0	0	972	49589	382	448	51	27	11	1595	1595
kg d-1													
mean	0.00	0.00	0.00	0.00	56.69	125.68	4.71	32.24	3.64	1.04	1.15	6.37	2.40
95% CI	0.00	0.00	0.00	0.00	19.47	76.11	2.61	10.29	1.30	0.76	0.84	2.19	2.42
min	0.00	0.00	0.00	0.00	25.27	5.15	0.82	7.89	0.00	0.00	0.00	0.60	-2.11
max	0.00	0.00	0.00	0.00	115.72	556.39	17.83	71.54	7.86	4.20	3.53	12.73	12.44
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

Hydroxypimaric acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	1	223	1053	80	96	11	9	5	657	657
95% CI	0	0	0	2	106	462	39	35	11	9	6	328	328
min	0	0	0	0	60	96	36	17	0	0	0	228	228
max	0	0	0	15	644	2449	295	205	60	50	33	2348	2348
kg d-1													
mean	0.00	0.00	0.00	0.00	26.04	11.43	3.62	15.63	1.76	1.40	1.37	5.23	2.34
95% CI	0.00	0.00	0.00	0.01	12.19	5.35	1.82	5.87	1.73	1.53	1.70	1.88	3.19
min	0.00	0.00	0.00	0.00	6.88	0.85	1.68	2.70	0.00	0.00	0.00	1.10	-2.60
max	0.00	0.00	0.00	0.05	74.16	32.32	13.80	32.90	9.38	8.29	9.84	11.74	19.26
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.2	-	-	-	-	-	-	-	-	-

13B-Hydroxyabietan-18-oic acid (Kinleithic acid)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	0	0	0	0	0	0	5	2182	2182
95% CI	0	0	0	0	0	0	0	0	0	0	5	737	737
min	0	0	0	0	0	0	0	0	0	0	0	752	752
max	0	0	0	0	0	0	0	0	0	0	27	4619	4619
kg d-1													
mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.50	20.18	2.84
95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.37	8.11	4.58
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.01	-13.02
max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.98	46.19	14.55
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

7-Oxodehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	33	374	111	47	12	4	0	618	618
95% CI	0	0	0	0	13	82	62	21	8	4	0	233	233
min	0	0	0	0	4	154	30	9	0	0	0	202	202
max	0	0	0	0	66	580	375	109	50	22	0	1584	1584
kg d-1													
mean	0.00	0.00	0.00	0.00	4.08	4.01	5.04	7.62	1.91	0.69	0.00	5.35	1.54
95% CI	0.00	0.00	0.00	0.00	1.75	1.15	2.84	3.41	1.32	0.62	0.00	2.27	1.70
min	0.00	0.00	0.00	0.00	0.49	1.36	1.32	1.46	0.00	0.00	0.00	0.81	-2.99
max	0.00	0.00	0.00	0.00	9.25	7.62	17.53	17.60	7.75	3.36	0.00	15.84	8.90
g ADT-1 bleached pulp													
mean	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
95% CI	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
min	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
max	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-

12-Chlorodehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	4	17	8	180	0	0	0	0	0	0	0	0	0
95% CI	4	5	7	61	0	0	0	0	0	0	0	0	0
min	0	7	0	63	0	0	0	0	0	0	0	0	0
max	24	38	44	403	0	0	0	0	0	0	0	0	0
kg d-1													
mean	0.04	0.10	0.10	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95% CI	0.05	0.0	0.08	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
min	0.00	0.04	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.24	0.23	0.53	1.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
g ADT-1 bleached pulp													
mean	0.4	1.3	0.4	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
95% CI	0.5	0.4	0.3	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
min	0.0	0.4	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	2.2	2.5	2.1	4.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

14-Chlorodehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	10	0	471	0	0	0	0	0	0	0	0	0
95% CI	0	11	0	165	0	0	0	0	0	0	0	0	0
min	0	0	0	142	0	0	0	0	0	0	0	0	0
max	0	43	0	1119	0	0	0	0	0	0	0	0	0
kg d-1													
mean	0.00	0.06	0.00	1.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95% CI	0.00	0.07	0.00	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
min	0.00	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.26	0.00	4.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
g ADT-1 bleached pulp													
mean	0.0	0.7	0.0	5.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
95% CI	0.0	0.8	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
min	0.0	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	0.0	2.9	0.0	13.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

12,14-Dichlorodehydroabietic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	28	0	681	0	96	0	0	0	0	0	72	72
95% CI	0	24	0	348	0	72	0	0	0	0	0	30	30
min	0	0	0	99	0	0	0	0	0	0	0	0	0
max	0	125	0	2327	0	343	0	0	0	0	0	166	166
kg d-1													
mean	0.00	0.17	0.00	2.07	0.00	1.07	0.00	0.00	0.00	0.00	0.00	0.62	0.17
95% CI	0.00	0.15	0.00	1.19	0.00	0.83	0.00	0.00	0.00	0.00	0.00	0.26	0.25
min	0.00	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.46
max	0.00	0.75	0.00	8.29	0.00	4.52	0.00	0.00	0.00	0.00	0.00	1.40	1.36
g ADT-1 bleached pulp													
mean	0.0	2.8	0.0	8.2	0.0	3.1	0.0	0.0	0.0	0.0	0.0	1.9	0.5
95% CI	0.0	3.5	0.0	4.2	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.9	0.8
min	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.3
max	0.0	18.3	0.0	27.9	0.0	14.0	0.0	0.0	0.0	0.0	0.0	5.0	4.2

Total Resin acids

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	22	100	19	1517	7834	120964	1916	3809	588	352	259	46214	46214
95% CI	17	38	12	546	1386	59872	734	1370	137	115	60	3692	3692
min	0	34	0	483	4433	29049	818	865	229	147	90	36074	36074
max	66	174	77	3752	12110	406865	5606	7844	964	933	467	57322	57322
kg d-1													
mean	0.22	0.60	0.23	4.72	934.25	1300.78	87.94	630.90	95.39	56.74	79.12	402.79	94.67
95% CI	0.17	0.2	0.13	1.95	221.73	683.23	34.15	239.20	22.67	18.15	18.66	88.97	112.01
min	0.00	0.20	0.00	1.46	504.93	381.99	35.75	137.62	37.12	24.03	26.24	191.96	-222.86
max	0.66	1.04	0.74	13.37	1754.35	4565.02	261.78	1253.41	149.94	145.14	148.54	575.56	374.31
g ADT-1 bleached pulp													
mean	3.2	9.1	0.9	18.2	-	-	-	-	-	-	-	-	-
95% CI	3.3	5.3	0.6	6.5	-	-	-	-	-	-	-	-	-
min	0.0	1.9	0.0	5.8	-	-	-	-	-	-	-	-	-
max	16.1	25.4	3.7	45.0	-	-	-	-	-	-	-	-	-

Unchlorinated Phenolic Compounds

Guaiacol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	349	3696	0	105	8	6	4	116	116
95% CI	0	0	0	0	212	1867	0	71	4	4	2	60	60
min	0	0	0	0	15	862	0	8	0	0	0	0	0
max	0	0	0	0	1147	13599	0	347	15	13	9	220	220
kg d-1													
mean	0.00	0.00	0.00	0.00	40.40	40.38	0.00	16.87	1.21	0.91	1.14	0.87	0.50
95% CI	0.00	0.00	0.00	0.00	25.08	21.85	0.00	11.04	0.61	0.64	0.57	0.46	0.47
min	0.00	0.00	0.00	0.00	1.73	8.06	0.00	1.25	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	132.65	152.58	0.00	56.70	2.40	2.51	2.99	2.20	1.52

Vanillin

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	235	261	45	17	15	9	6	21	21
95% CI	0	0	0	0	92	207	21	9	9	6	4	11	11
min	0	0	0	0	36	0	19	0	6	0	0	0	0
max	0	0	0	0	511	1305	130	47	53	24	21	53	53
kg d-1													
mean	0.00	0.00	0.00	0.00	27.15	2.85	2.04	2.71	2.43	1.52	1.71	0.15	0.09
95% CI	0.00	0.00	0.00	0.00	10.87	2.42	0.85	1.45	1.52	0.96	1.15	0.09	0.09
min	0.00	0.00	0.00	0.00	4.11	0.00	0.94	0.00	0.92	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	59.05	14.64	6.05	7.66	8.40	4.67	6.57	0.53	0.36

Acetovanillone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	308	524	103	88	47	38	36	139	139
95% CI	0	0	0	0	79	411	38	45	26	24	19	96	96
min	0	0	0	0	13	0	4	0	0	4	0	26	26
max	0	0	0	0	488	2432	239	205	115	126	28	453	453
kg d-1													
mean	0.00	0.00	0.00	0.00	35.62	5.73	4.68	14.16	7.58	6.07	10.82	1.04	0.60
95% CI	0.00	0.00	0.00	0.00	9.32	4.81	1.54	6.97	4.27	4.17	5.74	0.73	0.75
min	0.00	0.00	0.00	0.00	1.52	0.00	0.19	0.00	0.00	0.61	0.00	0.21	-0.17
max	0.00	0.00	0.00	0.00	56.45	27.29	11.14	33.41	18.31	24.07	8.96	4.53	3.12

Propiovanillone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	54	180	0	0	0	0	0	9	9
95% CI	0	0	0	0	38	212	0	0	0	0	0	8	8
min	0	0	0	0	0	0	0	0	0	0	0	0	0
max	0	0	0	0	167	1365	0	0	0	0	0	38	38
kg d-1													
mean	0.00	0.00	0.00	0.00	6.30	1.97	0.00	0.00	0.00	0.00	0.00	0.07	0.04
95% CI	0.00	0.00	0.00	0.00	4.44	2.48	0.00	0.00	0.00	0.00	0.00	0.06	0.06
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	19.32	15.32	0.00	0.00	0.00	0.00	0.00	0.38	0.26

Vanillic acid

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	124	282	90	103	9	13	4	43	43
95% CI	0	0	0	0	51	223	30	38	6	2	2	8	8
min	0	0	0	0	0	19	6	0	0	8	0	0	0
max	0	0	0	0	231	1258	193	229	34	17	9	130	130
kg d-1													
mean	0.00	0.00	0.00	0.00	14.34	3.08	4.09	16.57	1.52	2.12	1.14	0.32	0.19
95% CI	0.00	0.00	0.00	0.00	5.99	2.62	1.23	5.81	0.91	0.32	0.57	0.06	0.06
min	0.00	0.00	0.00	0.00	0.00	0.18	0.28	0.00	0.00	1.23	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	26.70	14.12	9.03	37.39	5.40	3.23	2.99	1.30	0.89

Chlorinated Phenolic Compounds

2,4-Dichlorophenol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	2	9	4	63	3	23	3	5	5	5	6	9	9
95% CI	3	6	3	14	3	6	2	2	2	2	3	5	5
min	0	0	0	8	0	8	0	0	0	0	0	0	0
max	13	29	14	106	15	43	9	11	12	10	13	26	26
kg d-1													
mean	0.02	0.05	0.05	0.20	0.41	0.25	0.11	0.88	0.78	0.88	1.79	0.07	0.02
95% CI	0.03	0.04	0.04	0.05	0.38	0.07	0.09	0.37	0.40	0.36	0.82	0.05	0.03
min	0.00	0.00	0.00	0.02	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	-0.10
max	0.13	0.17	0.20	0.33	1.61	0.54	0.38	1.65	1.90	1.62	3.86	0.26	0.11
g ADT-1 bleached pulp													
mean	0.2	0.8	0.2	0.8	1.2	0.8	0.4	2.7	2.6	2.7	5.5	0.2	0.1
95% CI	0.2	0.7	0.2	0.2	1.2	0.3	0.3	1.2	1.4	1.2	2.6	0.1	0.1
min	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	-0.3
max	1.2	3.7	0.7	1.3	6.5	2.3	1.4	5.1	7.1	6.2	12.3	0.8	0.4

2,4,6-Trichlorophenol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	4	26	12	90	0	34	5	0	0	0	0	17	17
95% CI	1	6	9	17	0	5	3	0	0	0	0	1	1
min	0	14	2	36	0	15	0	0	0	0	0	14	14
max	7	37	56	134	1	46	17	1	1	1	1	22	22
kg d-1													
mean	0.04	0.16	0.14	0.28	0.01	0.36	0.23	0.04	0.05	0.05	0.10	0.13	0.05
95% CI	0.01	0.03	0.10	0.06	0.01	0.07	0.12	0.03	0.04	0.04	0.09	0.03	0.04
min	0.00	0.09	0.02	0.11	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	-0.08
max	0.07	0.22	0.64	0.43	0.08	0.55	0.74	0.13	0.19	0.15	0.47	0.20	0.18
g ADT-1 bleached pulp													
mean	0.5	2.0	0.6	1.1	0.0	1.1	0.7	0.1	0.2	0.2	0.3	0.4	0.2
95% CI	0.2	0.8	0.4	0.2	0.0	0.3	0.3	0.1	0.1	0.1	0.3	0.1	0.1
min	0.0	0.7	0.1	0.4	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	-0.2
max	1.1	4.8	2.7	1.6	0.3	2.3	2.1	0.4	0.7	0.5	1.4	0.7	0.6

Tetrachlorophenol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	24	1	324	0	61	0	0	0	0	0	4	4
95% CI	0	14	1	111	0	30	0	0	0	0	0	5	5
min	0	3	0	142	0	6	0	0	0	0	0	1	1
max	2	50	5	785	1	158	0	0	0	0	0	35	35
kg d-1													
mean	0.00	0.14	0.02	1.04	0.01	0.64	0.00	0.00	0.00	0.00	0.01	0.02	0.02
95% CI	0.00	0.08	0.01	0.41	0.01	0.33	0.00	0.01	0.00	0.00	0.01	0.02	0.04
min	0.00	0.02	0.00	0.39	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	-0.01
max	0.02	0.30	0.07	2.84	0.09	1.68	0.00	0.04	0.00	0.00	0.06	0.17	0.28
g ADT-1 bleached pulp													
mean	0.0	2.0	0.1	3.9	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.1	0.1
95% CI	0.1	1.5	0.0	1.3	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
min	0.0	0.2	0.0	1.7	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	0.3	6.4	0.2	9.4	0.2	4.6	0.0	0.2	0.0	0.0	0.3	0.5	0.9

Pentachlorophenol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	2	0	2	1	2	0	1	1	0	0	0	0
95% CI	0	1	0	3	1	1	0	0	0	0	0	0	0
min	0	1	0	0	0	0	0	0	0	0	0	0	0
max	0	5	1	14	3	4	2	2	2	2	1	1	1

kg d-1													
mean	0.00	0.01	0.00	0.01	0.09	0.02	0.01	0.10	0.11	0.07	0.12	0.00	0.00
95% CI	0.00	0.00	0.00	0.01	0.06	0.01	0.01	0.06	0.05	0.04	0.07	0.00	0.00
min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.03	0.02	0.05	0.36	0.05	0.08	0.28	0.26	0.25	0.36	0.01	0.00

g ADT-1 bleached pulp													
mean	0.0	0.2	0.0	0.0	0.3	0.1	0.0	0.3	0.3	0.2	0.3	0.0	0.0
95% CI	0.0	0.1	0.0	0.0	0.2	0.0	0.0	0.2	0.2	0.1	0.2	0.0	0.0
min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	0.0	0.5	0.1	0.2	0.9	0.1	0.2	0.8	0.8	0.8	1.0	0.0	0.0

Total Chlorophenols

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	6	61	17	480	4	120	8	6	6	6	7	30	30
95% CI	4	22	8	112	4	33	5	2	2	2	3	8	8
min	0	21	5	256	0	31	0	0	0	1	0	15	15
max	18	108	56	910	18	219	27	11	13	12	13	70	70

kg d-1													
mean	0.06	0.37	0.22	1.53	0.51	1.27	0.35	1.02	0.94	1.00	2.02	0.23	0.10
95% CI	0.04	0.13	0.10	0.45	0.42	0.36	0.21	0.40	0.41	0.37	0.81	0.07	0.10
min	0.00	0.13	0.05	0.70	0.00	0.23	0.00	0.00	0.00	0.11	0.00	0.00	-0.19
max	0.18	0.65	0.64	3.29	1.97	2.34	1.20	1.77	2.09	1.87	3.86	0.44	0.57

g ADT-1 bleached pulp													
mean	0.7	5.0	0.8	5.8	1.5	3.8	1.0	3.1	3.1	3.0	6.2	0.7	0.3
95% CI	0.4	2.9	0.4	1.3	1.3	1.3	0.6	1.3	1.5	1.2	2.5	0.2	0.3
min	0.0	1.1	0.2	3.1	0.0	0.6	0.0	0.0	0.0	0.3	0.0	0.0	-0.5
max	1.7	14.1	2.7	10.9	7.2	9.1	3.5	5.5	8.0	6.3	12.5	1.4	1.8

4,5-Dichloroguaiacol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	16	82	81	409	0	126	13	1	3	8	3	7	7
95% CI	7	24	22	152	1	25	8	1	2	4	2	4	4
min	6	30	15	153	0	59	0	0	0	2	0	0	0
max	40	151	160	884	3	226	38	4	8	22	12	22	22

kg d-1													
mean	0.16	0.49	1.03	1.32	0.03	1.39	0.58	0.11	0.43	1.40	0.78	0.06	0.02
95% CI	0.07	0.14	0.34	0.58	0.06	0.34	0.35	0.14	0.28	0.67	0.59	0.03	0.03
min	0.06	0.18	0.15	0.45	0.00	0.40	0.00	0.00	0.00	0.23	0.00	0.00	-0.06
max	0.40	0.91	2.27	3.19	0.38	2.40	1.66	0.79	1.20	3.94	3.72	0.17	0.17

g ADT-1 bleached pulp													
mean	2.0	6.3	3.9	4.9	0.1	4.2	1.8	0.3	1.4	4.6	2.3	0.2	0.1
95% CI	0.9	2.7	1.1	1.8	0.2	1.1	1.1	0.4	1.0	2.8	1.6	0.1	0.1
min	0.6	1.6	0.7	1.8	0.0	1.2	0.0	0.0	0.0	0.6	0.0	0.0	-0.2
max	4.4	13.5	7.7	10.6	1.1	8.9	5.0	2.3	4.9	16.4	9.6	0.4	0.5

3,4,5-Trichloroguaiacol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	3	196	10	830	0	283	3	1	1	2	1	51	51
95% CI	1	44	2	134	0	52	1	0	1	1	0	10	10
min	0	79	5	393	0	100	2	0	0	0	0	12	12
max	7	278	20	1205	3	392	5	3	3	4	3	76	76
kg d-1													
mean	0.03	1.18	0.12	2.57	0.05	3.06	0.13	0.13	0.18	0.27	0.39	0.40	0.17
95% CI	0.01	0.26	0.04	0.52	0.05	0.68	0.03	0.07	0.08	0.14	0.14	0.09	0.14
min	0.00	0.47	0.05	1.19	0.00	0.74	0.06	0.00	0.00	0.00	0.00	0.00	-0.22
max	0.07	1.67	0.28	4.23	0.27	5.10	0.24	0.43	0.46	0.80	0.87	0.76	0.60
g ADT-1 bleached pulp													
mean	0.4	14.3	0.5	10.0	0.1	9.3	0.4	0.4	0.5	0.8	1.1	1.2	0.5
95% CI	0.2	4.4	0.1	1.6	0.1	2.7	0.1	0.2	0.2	0.5	0.4	0.3	0.4
min	0.0	4.5	0.2	4.7	0.0	1.8	0.2	0.0	0.0	0.0	0.0	0.0	-0.6
max	1.0	26.9	1.0	14.5	0.7	21.2	0.6	1.3	1.1	3.3	2.5	1.9	1.9

4,5,6-Trichloroguaiacol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	3	34	13	160	1	44	4	1	2	2	1	6	6
95% CI	2	5	3	31	1	11	1	0	1	1	1	2	2
min	0	20	5	59	0	0	1	0	0	0	0	1	1
max	7	41	20	262	4	68	7	3	6	6	4	12	12
kg d-1													
mean	0.03	0.20	0.16	0.50	0.13	0.48	0.17	0.16	0.27	0.38	0.41	0.05	0.02
95% CI	0.02	0.03	0.04	0.11	0.08	0.13	0.04	0.07	0.13	0.18	0.22	0.02	0.02
min	0.00	0.12	0.04	0.18	0.00	0.00	0.05	0.00	0.00	0.00	0.12	0.00	-0.03
max	0.07	0.25	0.26	0.76	0.40	0.82	0.26	0.47	0.92	0.87	1.60	0.12	0.10
g ADT-1 bleached pulp													
mean	0.4	2.5	0.6	1.9	0.4	1.4	0.5	0.5	0.8	1.1	1.2	0.2	0.1
95% CI	0.4	0.8	0.1	0.4	0.2	0.5	0.1	0.2	0.4	0.5	0.6	0.1	0.1
min	0.0	1.1	0.2	0.7	0.0	0.0	0.2	0.0	0.0	0.0	0.3	0.0	-0.1
max	1.6	5.3	0.9	3.1	1.0	3.4	1.0	1.5	2.8	3.0	4.6	0.3	0.3

Tetrachloroguaiacol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	1	66	1	270	3	130	1	0	0	0	0	22	22
95% CI	0	17	0	94	1	73	0	0	0	0	0	4	4
min	0	27	0	52	0	23	0	0	0	0	0	12	12
max	2	101	2	619	7	553	2	1	0	3	2	40	40
kg d-1													
mean	0.01	0.40	0.02	0.81	0.34	1.47	0.04	0.05	0.05	0.07	0.13	0.17	0.08
95% CI	0.00	0.10	0.01	0.28	0.15	0.99	0.01	0.02	0.01	0.07	0.06	0.04	0.07
min	0.00	0.16	0.00	0.16	0.00	0.17	0.02	0.02	0.03	0.00	0.03	0.00	-0.08
max	0.02	0.61	0.03	1.85	0.73	7.30	0.07	0.10	0.06	0.40	0.44	0.29	0.32
g ADT-1 bleached pulp													
mean	0.1	4.5	0.1	3.2	1.0	4.6	0.1	0.1	0.1	0.2	0.4	0.5	0.2
95% CI	0.0	0.9	0.0	1.1	0.4	3.2	0.0	0.1	0.0	0.2	0.1	0.1	0.2
min	0.0	1.6	0.0	0.6	0.0	0.4	0.1	0.0	0.1	0.0	0.1	0.0	-0.2
max	0.2	6.3	0.1	7.4	2.4	22.6	0.3	0.4	0.2	1.0	1.1	0.7	1.0

Total Chloroguaiacols

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	23	378	105	1668	5	583	21	3	6	13	6	87	87
95% CI	7	76	25	266	2	102	9	1	2	4	2	17	17
min	8	164	26	753	0	219	7	0	2	5	2	25	25
max	45	496	200	2468	12	904	44	6	12	29	18	135	135
kg d-1													
mean	0.23	2.27	1.34	5.21	0.52	6.41	0.92	0.45	0.93	2.13	1.72	0.68	0.29
95% CI	0.07	0.45	0.40	1.10	0.26	1.54	0.35	0.17	0.31	0.76	0.78	0.16	0.25
min	0.08	0.98	0.25	2.28	0.02	1.62	0.28	0.05	0.34	0.79	0.60	0.00	-0.39
max	0.45	2.98	2.85	8.91	1.38	11.94	1.96	1.01	1.98	5.47	5.36	1.28	1.06
g ADT-1 bleached pulp													
mean	2.9	27.7	5.1	20.0	1.5	19.4	2.8	1.3	2.8	6.8	5.0	2.0	0.8
95% CI	1.2	8.3	1.2	3.2	0.8	5.7	1.2	0.5	1.0	3.2	2.1	0.5	0.7
min	1.3	9.3	1.3	9.0	0.1	4.1	0.9	0.1	1.0	2.5	1.8	0.0	-1.1
max	6.7	52.0	9.6	29.6	4.0	40.2	6.7	2.9	6.0	22.7	13.9	3.1	3.3

4,5-Dichlorocatechol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	24	8	188	134	17	47	43	6	5	5	4	42	42
95% CI	13	4	64	36	7	29	15	2	2	2	2	10	10
min	1	0	69	27	2	15	9	2	2	0	0	19	19
max	59	18	434	261	41	178	96	12	14	12	10	80	80
kg d-1													
mean	0.24	0.05	2.38	0.43	1.96	0.46	1.92	1.00	0.74	0.74	1.34	0.32	0.14
95% CI	0.13	0.03	0.98	0.14	0.84	0.23	0.67	0.32	0.28	0.36	0.50	0.09	0.14
min	0.01	0.00	0.82	0.08	0.16	0.10	0.39	0.28	0.29	0.02	0.04	0.00	-0.29
max	0.59	0.11	6.28	0.94	5.05	1.32	4.79	2.23	2.15	1.88	3.05	0.70	0.66
g ADT-1 bleached pulp													
mean	3.7	0.7	9.0	1.6	6.2	1.4	5.6	3.0	2.2	2.1	4.0	0.9	0.4
95% CI	3.2	0.5	3.1	0.4	2.9	0.7	1.9	1.0	0.8	1.0	1.8	0.3	0.4
min	0.1	0.0	3.3	0.3	0.4	0.3	1.2	0.7	0.7	0.0	0.1	0.0	-0.8
max	14.4	2.3	20.8	3.1	16.3	3.6	11.8	6.4	5.4	5.5	12.7	2.0	2.0

3,4,5-Trichlorocatechol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	81	11	391	156	2	28	78	10	6	5	3	35	35
95% CI	42	6	98	36	1	9	27	3	1	2	1	5	5
min	10	0	153	63	0	0	27	1	2	1	1	18	18
max	172	25	730	300	8	57	172	16	12	11	5	47	47
kg d-1													
mean	0.81	0.07	4.89	0.48	0.26	0.30	3.51	1.54	0.98	0.74	0.87	0.27	0.10
95% CI	0.42	0.03	1.55	0.12	0.15	0.11	1.19	0.47	0.22	0.27	0.17	0.07	0.08
min	0.10	0.00	2.18	0.19	0.00	0.00	1.19	0.09	0.23	0.16	0.44	0.00	-0.19
max	1.72	0.15	10.54	0.90	0.77	0.74	8.59	2.75	1.92	1.60	1.49	0.45	0.39
g ADT-1 bleached pulp													
mean	11.8	0.8	18.8	1.9	0.7	0.9	10.4	4.7	2.9	2.2	2.6	0.8	0.3
95% CI	9.3	0.6	4.7	0.4	0.4	0.4	3.7	1.7	0.7	0.7	0.5	0.2	0.2
min	1.0	0.0	7.4	0.8	0.0	0.0	3.4	0.2	0.6	0.4	1.1	0.0	-0.5
max	41.9	3.3	35.0	3.6	2.4	3.1	25.0	11.4	5.3	4.4	3.6	1.6	1.2

Tetrachlorocatechol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	19	7	60	16	2	9	11	1	1	1	1	9	9
95% CI	9	2	20	12	1	6	3	0	0	0	0	2	2
min	3	2	21	0	0	1	2	0	0	0	0	3	3
max	37	14	147	64	10	31	21	2	1	2	1	13	13
kg d-1													
mean	0.19	0.04	0.71	0.05	0.23	0.09	0.50	0.18	0.11	0.11	0.17	0.07	0.03
95% CI	0.09	0.01	0.22	0.03	0.16	0.06	0.15	0.05	0.03	0.04	0.05	0.02	0.02
min	0.03	0.01	0.26	0.00	0.00	0.01	0.11	0.02	0.02	0.02	0.03	0.00	-0.05
max	0.37	0.09	1.69	0.15	1.11	0.32	0.85	0.31	0.21	0.29	0.35	0.12	0.11
g ADT-1 bleached pulp													
mean	2.5	0.5	2.9	0.2	0.7	0.3	1.5	0.6	0.3	0.3	0.5	0.2	0.1
95% CI	1.5	0.2	1.0	0.1	0.5	0.2	0.5	0.2	0.1	0.1	0.1	0.1	0.1
min	0.2	0.1	1.0	0.0	0.0	0.0	0.3	0.0	0.0	0.1	0.1	0.0	-0.1
max	6.9	0.8	7.1	0.8	3.2	1.3	3.2	1.2	0.6	0.8	0.9	0.5	0.3

Total Chlorocatechols

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	124	26	638	306	21	84	132	17	11	10	8	86	86
95% CI	63	10	161	64	7	29	43	4	2	3	2	14	14
min	17	2	265	92	4	42	61	3	7	4	2	50	50
max	259	49	1216	499	41	197	282	28	21	22	13	141	141
kg d-1													
mean	1.24	0.16	7.97	0.95	2.44	0.85	5.93	2.72	1.83	1.59	2.38	0.65	0.27
95% CI	0.63	0.06	2.54	0.23	0.82	0.23	1.91	0.71	0.35	0.48	0.57	0.17	0.24
min	0.17	0.01	3.77	0.28	0.39	0.41	2.69	0.39	1.05	0.56	0.55	0.00	-0.54
max	2.59	0.29	17.58	1.66	5.11	1.74	14.09	4.44	3.31	3.50	3.98	1.26	1.15
g ADT-1 bleached pulp													
mean	18.0	2.0	30.6	3.7	7.6	2.6	17.4	8.2	5.4	4.6	7.1	2.0	0.8
95% CI	13.9	1.1	7.7	0.8	2.8	0.9	5.8	2.5	1.2	1.3	2.1	0.6	0.7
min	1.6	0.1	12.7	1.1	1.0	1.2	7.7	1.0	2.9	1.4	1.6	0.0	-1.5
max	63.1	6.4	58.4	6.0	16.5	5.6	40.0	17.8	9.8	8.6	16.5	3.8	3.6

5-Chlorovanillin

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	2	4	24	57	0	16	6	0	1	0	0	0	0
95% CI	2	2	8	18	1	3	3	0	1	0	0	1	1
min	0	0	0	18	0	6	0	0	0	0	0	0	0
max	9	11	49	138	5	28	19	3	3	2	0	3	3
kg d-1													
mean	0.02	0.03	0.31	0.18	0.05	0.16	0.27	0.08	0.12	0.02	0.00	0.00	0.00
95% CI	0.02	0.01	0.13	0.07	0.08	0.04	0.15	0.08	0.10	0.05	0.00	0.00	0.00
min	0.00	0.00	0.00	0.05	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.09	0.07	0.72	0.49	0.52	0.34	0.85	0.49	0.53	0.33	0.00	0.01	0.02
g ADT-1 bleached pulp													
mean	0.3	0.3	1.1	0.7	0.1	0.5	0.8	0.2	0.3	0.1	0.0	0.0	0.0
95% CI	0.3	0.1	0.4	0.2	0.2	0.2	0.4	0.2	0.3	0.2	0.0	0.0	0.0
min	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
max	1.1	0.6	2.4	1.7	1.5	1.4	2.4	1.4	1.4	1.1	0.0	0.0	0.1

6-Chlorovanillin

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
Mean	0.0	207.4	122.1	672.8	0.1	267.8	43.5	0.5	0.1	0.2	0.0	39.2	39.2
95% CI	0.1	29.6	59.3	131.4	0.2	59.0	5.9	0.6	0.2	0.5	0.1	17.0	17.0
Min	0.0	139.9	45.8	328.2	0.0	84.7	38.3	0.0	0.0	0.0	0.0	8.5	8.5
Max	0.5	268.4	298.3	954.7	1.5	340.6	53.8	3.0	1.0	3.0	0.5	98.6	98.6
kg d-1													
Mean	0.00	1.24	1.63	2.06	0.02	3.05	1.92	0.08	0.01	0.03	0.01	0.30	0.15
95% CI	0.00	0.18	0.91	0.48	0.04	0.9	0.3	0.11	0.02	0.07	0.02	0.10	0.16
Min	0.00	0.84	0.44	0.99	0.00	0.63	1.69	0.00	0.00	0.00	0.00	0.00	-0.12
Max	0.00	1.61	4.31	2.93	0.23	4.48	2.37	0.57	0.15	0.45	0.15	0.72	0.77
g ADT-1 bleached pulp													
Mean	0.0	15.0	5.9	8.1	0.1	8.8	5.0	0.3	0.0	0.1	0.0	0.9	0.4
95% CI	0.0	3.7	2.8	1.6	0.1	3.2	0.5	0.4	0.1	0.3	0.1	0.3	0.5
Min	0.0	8.6	2.2	3.9	0.0	1.6	4.4	0.0	0.0	0.0	0.0	0.0	-0.3
Max	0.1	24.6	14.3	11.5	1.0	18.6	5.8	2.4	0.6	1.8	0.5	1.8	2.4

5,6-Dichlorovanillin

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	29	2	156	8	56	6	1	1	1	0	5	5
95% CI	1	8	1	35	5	12	3	0	0	1	0	2	2
min	0	8	0	90	0	0	0	0	0	0	0	1	1
max	4	57	5	285	26	78	15	3	3	6	1	13	13
kg d-1													
mean	0.00	0.18	0.02	0.49	0.91	0.59	0.25	0.22	0.20	0.21	0.14	0.03	0.02
95% CI	0.01	0.05	0.01	0.14	0.52	0.14	0.12	0.06	0.06	0.13	0.08	0.02	0.02
min	0.00	0.05	0.00	0.22	0.00	0.00	0.00	0.05	0.06	0.06	0.00	0.00	-0.02
max	0.04	0.34	0.06	1.03	2.37	0.89	0.66	0.41	0.50	0.79	0.51	0.12	0.10
g ADT-1 bleached pulp													
mean	0.1	2.2	0.1	1.9	2.5	1.7	0.7	0.7	0.6	0.6	0.4	0.1	0.1
95% CI	0.2	0.8	0.0	0.4	1.4	0.5	0.3	0.2	0.2	0.3	0.2	0.0	0.1
min	0.0	0.4	0.0	1.1	0.0	0.0	0.0	0.1	0.2	0.2	0.0	0.0	0.0
max	0.9	4.6	0.2	3.4	6.6	3.7	1.6	1.5	1.5	1.9	1.5	0.3	0.3
95% CI	13.0	17.5	11.0	6.0	3.2	10.7	8.7	3.6	3.1	4.1	3.4	1.3	2.0
Min	0.0	0.0	0.0	18.4	2.1	10.8	0.5	5.5	4.8	7.0	10.2	0.0	-3.6
Max	72.2	101.5	81.7	57.4	20.2	77.7	49.9	27.9	22.9	30.1	32.9	8.6	9.0

Total Chlorovanillins

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
Mean	2.8	241.1	150.4	880.1	8.9	342.9	68.9	2.3	2.0	1.7	0.5	43.7	43.7
95% CI	2.3	33.7	66.5	173.1	5.2	62.8	9.6	0.7	0.8	0.9	0.3	18.5	18.5
Min	0.0	172.6	54.3	436.7	0.0	148.0	57.9	0.3	0.4	0.3	0.0	12.6	12.6
Max	9.4	299.2	349.2	1209.9	25.6	434.0	85.4	4.9	5.1	5.6	1.4	106.1	106.1
kg d-1													
Mean	0.03	1.45	2.01	2.72	0.98	3.87	3.04	0.38	0.33	0.27	0.15	0.33	0.16
95% CI	0.02	0.20	1.03	0.67	0.55	1.0	0.4	0.14	0.12	0.14	0.09	0.12	0.18
Min	0.00	1.04	0.64	1.31	0.00	1.10	2.56	0.05	0.06	0.06	0.00	0.00	-0.13
Max	0.09	1.80	5.05	4.15	2.81	5.71	3.76	0.94	0.82	0.79	0.51	0.83	0.83
g ADT-1 bleached pulp													
Mean	0.4	17.5	7.2	10.6	2.8	11.2	7.9	1.2	1.0	0.8	0.4	1.0	0.5
95% CI	0.4	4.5	3.2	2.1	1.4	3.8	0.7	0.5	0.4	0.4	0.3	0.3	0.5
Min	0.0	9.6	2.6	5.2	0.0	2.7	7.3	0.1	0.2	0.2	0.0	0.0	-0.4
Max	2.0	29.0	16.8	14.5	8.1	23.7	9.2	3.9	2.5	2.1	1.5	2.0	2.5

Total Chlorophenolic Compounds

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
Mean	123	555	826	3196	39	1030	170	28	25	31	21	244	244
95% CI	64	194	228	504	10	175	67	5	4	6	3	42	42
Min	0	0	0	1537	8	586	3	14	12	17	12	132	132
Max	296	884	1702	4780	68	1424	328	43	37	49	30	381	381
kg d-1													
Mean	1.23	3.33	10.44	9.99	4.48	11.24	7.60	4.56	4.03	4.99	6.27	1.87	0.81
95% CI	0.64	1.16	3.51	2.11	0.98	2.80	2.91	0.86	0.75	0.91	0.86	0.43	0.70
Min	0.00	0.00	0.00	4.65	0.85	4.34	0.17	2.21	1.91	2.70	3.72	0.00	-1.25
Max	2.96	5.30	24.60	17.27	6.37	18.73	15.57	6.88	6.03	7.41	9.11	3.22	2.97
g ADT-1 bleached pulp													
Mean	17.4	41.0	39.7	38.3	13.5	33.7	22.3	13.9	12.3	15.2	18.7	5.6	2.4
95% CI	13.0	17.5	11.0	6.0	3.2	10.7	8.7	3.6	3.1	4.1	3.4	1.3	2.0
Min	0.0	0.0	0.0	18.4	2.1	10.8	0.5	5.5	4.8	7.0	10.2	0.0	-3.6
Max	72.2	101.5	81.7	57.4	20.2	77.7	49.9	27.9	22.9	30.1	32.9	8.6	9.0

3,4-Dichloro-5-(dichloromethyl)-5-hydroxy-2-furanone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	44	0	138	5	3	18	48	2	1	1	0	1	1
95% CI	16	0	33	2	2	13	10	1	0	0	0	1	1
min	4	0	34	1	0	0	21	0	0	0	0	0	0
max	83	1	236	10	12	86	77	9	3	2	2	7	7
kg d-1													
mean	0.44	0.00	1.69	0.02	0.38	0.17	2.15	0.25	0.11	0.17	0.11	0.01	0.01
95% CI	0.16	0.00	0.47	0.01	0.23	0.10	0.43	0.21	0.08	0.06	0.07	0.01	0.01
min	0.04	0.00	0.49	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00	0.00	-0.01
max	0.83	0.00	3.41	0.04	1.26	0.58	3.41	1.41	0.46	0.38	0.44	0.04	0.06
g ADT-1 bleached pulp													
mean	5.4	0.0	6.6	0.1	1.1	0.5	6.3	0.7	0.3	0.5	0.3	0.0	0.0
95% CI	2.3	0.0	1.6	0.0	0.6	0.4	1.2	0.6	0.2	0.2	0.3	0.0	0.0
min	0.4	0.0	1.6	0.0	0.0	0.0	2.9	0.0	0.0	0.0	0.0	0.0	0.0
max	11.9	0.1	11.3	0.1	3.2	2.0	9.1	4.1	1.3	1.2	1.8	0.1	0.2

Unchlorinated Monoterpenes and 2-Cyclopentenones

a-Pinene

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	27	1091	20	1	0	0	0	14	14
95% CI	0	0	0	0	16	1085	11	2	0	0	0	7	7
min	0	0	0	0	0	364	0	0	0	0	0	0	0
max	0	0	0	0	107	7558	66	10	0	0	0	34	34
kg d-1													
mean	0.00	0.00	0.00	0.00	3.12	11.92	0.91	0.16	0.00	0.00	0.00	0.10	0.06
95% CI	0.00	0.00	0.00	0.00	1.89	12.70	0.45	0.31	0.00	0.00	0.00	0.05	0.05
min	0.00	0.00	0.00	0.00	0.00	3.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	12.37	84.80	3.08	1.63	0.00	0.00	0.00	0.34	0.23

B-Pinene

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	59	1968	27	5	5	1	1	3	3
95% CI	0	0	0	0	29	1949	16	5	7	1	1	2	2
min	0	0	0	0	11	784	0	0	0	0	0	0	0
max	0	0	0	0	199	13598	92	25	34	4	5	7	7
kg d-1													
mean	0.00	0.00	0.00	0.00	6.82	21.50	1.22	0.80	0.81	0.16	0.30	0.02	0.01
95% CI	0.00	0.00	0.00	0.00	3.43	22.81	0.66	0.77	1.14	0.17	0.31	0.02	0.02
min	0.00	0.00	0.00	0.00	1.27	7.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	23.00	152.57	4.30	4.08	5.43	0.77	1.59	0.07	0.05

Fenchol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	21	1438	9	12	2	3	1	19	19
95% CI	0	0	0	0	7	1331	4	6	1	3	1	8	8
min	0	0	0	0	3	6	0	0	0	0	0	0	0
max	0	0	0	0	43	9302	20	34	5	15	2	40	40
kg d-1													
mean	0.00	0.00	0.00	0.00	2.43	15.71	0.41	1.92	0.32	0.48	0.30	0.14	0.08
95% CI	0.00	0.00	0.00	0.00	0.83	15.58	0.16	0.93	0.16	0.51	0.31	0.06	0.06
min	0.00	0.00	0.00	0.00	0.35	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	4.97	104.37	0.93	5.55	0.80	2.87	0.64	0.40	0.28

Camphor

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	12	406	5	21	4	0	2	635	635
95% CI	0	0	0	0	3	360	2	7	5	0	2	98	98
min	0	0	0	0	5	100	0	8	0	0	0	482	482
max	0	0	0	0	26	2503	9	47	23	0	10	938	938
kg d-1													
mean	0.00	0.00	0.00	0.00	1.39	4.44	0.23	3.37	0.65	0.00	0.61	4.74	2.74
95% CI	0.00	0.00	0.00	0.00	0.35	4.21	0.08	1.08	0.81	0.00	0.61	0.75	0.77
min	0.00	0.00	0.00	0.00	0.58	0.93	0.00	1.33	0.00	0.00	0.00	3.86	-3.20
max	0.00	0.00	0.00	0.00	3.01	28.08	0.42	7.67	3.68	0.00	3.18	9.38	6.48

Isoborneol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	27	2817	19	15	2	0	4	38	38
95% CI	0	0	0	0	11	2440	4	11	1	0	1	18	18
min	0	0	0	0	4	930	8	0	0	0	0	0	0
max	0	0	0	0	61	17298	29	50	6	0	6	74	74
kg d-1													
mean	0.00	0.00	0.00	0.00	3.12	30.78	0.86	2.41	0.32	0.00	1.21	0.28	0.16
95% CI	0.00	0.00	0.00	0.00	1.30	28.56	0.16	1.70	0.16	0.00	0.31	0.14	0.14
min	0.00	0.00	0.00	0.00	0.46	8.69	0.40	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	7.05	194.08	1.35	8.16	0.96	0.00	1.91	0.74	0.51

Terpinen-4-ol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	40	1846	13	18	1	0	2	301	301
95% CI	0	0	0	0	5	1831	11	8	1	0	2	121	121
min	0	0	0	0	27	514	0	0	0	0	0	0	0
max	0	0	0	0	50	12734	48	43	3	0	9	507	507
kg d-1													
mean	0.00	0.00	0.00	0.00	4.63	20.17	0.59	2.89	0.16	0.00	0.61	2.25	1.30
95% CI	0.00	0.00	0.00	0.00	0.59	21.43	0.45	1.24	0.16	0.00	0.61	0.93	0.95
min	0.00	0.00	0.00	0.00	3.11	4.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	5.78	142.88	2.24	7.02	0.48	0.00	2.86	5.07	3.50

a-Terpineol

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	434	9920	38	149	5	3	8	4062	4062
95% CI	0	0	0	0	63	1830	28	51	4	2	6	329	329
min	0	0	0	0	263	5806	0	75	0	0	0	3402	3402
max	0	0	0	0	657	14894	118	342	20	7	31	4861	4861
kg d-1													
mean	0.00	0.00	0.00	0.00	50.20	108.39	1.72	23.90	0.81	0.48	2.43	30.31	17.54
95% CI	0.00	0.00	0.00	0.00	7.44	21.42	1.15	7.89	0.65	0.34	1.83	2.52	2.58
min	0.00	0.00	0.00	0.00	30.32	54.28	0.00	12.44	0.00	0.00	0.00	27.22	-22.62
max	0.00	0.00	0.00	0.00	75.95	167.11	5.51	55.81	3.20	1.34	9.86	48.61	33.56

Dimethyl-2-cyclopentenone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	22	572	21	11	5	2	2	202	202
95% CI	0	0	0	0	7	501	18	5	3	2	2	14	14
min	0	0	0	0	2	157	0	2	0	0	0	154	154
max	0	0	0	0	48	3526	85	24	13	11	10	232	232
kg d-1													
mean	0.00	0.00	0.00	0.00	2.54	6.25	0.95	1.76	0.81	0.32	0.61	1.51	0.87
95% CI	0.00	0.00	0.00	0.00	0.83	5.86	0.74	0.77	0.49	0.34	0.61	0.11	0.11
min	0.00	0.00	0.00	0.00	0.23	1.47	0.00	0.33	0.00	0.00	0.00	1.23	-1.02
max	0.00	0.00	0.00	0.00	5.55	39.56	3.97	3.92	2.08	2.10	3.18	2.32	1.60

Trimethyl-2-cyclopentenone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	16	736	1	8	11	7	3	216	216
95% CI	0	0	0	0	3	681	1	3	3	2	2	18	18
min	0	0	0	0	4	248	0	0	6	3	0	170	170
max	0	0	0	0	23	4777	3	14	22	11	9	250	250
kg d-1													
mean	0.00	0.00	0.00	0.00	1.85	8.04	0.05	1.28	1.78	1.13	0.91	1.61	0.93
95% CI	0.00	0.00	0.00	0.00	0.35	7.97	0.04	0.46	0.49	0.34	0.61	0.14	0.14
min	0.00	0.00	0.00	0.00	0.46	2.32	0.00	0.00	0.98	0.49	0.00	1.36	-1.13
max	0.00	0.00	0.00	0.00	2.66	53.60	0.14	2.28	3.52	2.10	2.86	2.50	1.73

Tetramethyl-2-cyclopentenone

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	0	0	0	5	223	1	0	1	1	1	51	51
95% CI	0	0	0	0	4	298	1	0	1	1	1	34	34
min	0	0	0	0	0	34	0	0	0	0	0	0	0
max	0	0	0	0	17	2003	3	0	4	4	4	172	172
kg d-1													
mean	0.00	0.00	0.00	0.00	0.58	2.44	0.05	0.00	0.16	0.16	0.30	0.38	0.22
95% CI	0.00	0.00	0.00	0.00	0.47	3.49	0.04	0.00	0.16	0.17	0.31	0.26	0.27
min	0.00	0.00	0.00	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	0.00	0.00	0.00	0.00	1.97	22.47	0.14	0.00	0.64	0.77	1.27	1.72	1.19

Chlorinated Monoterpene Hydrocarbons and Alcohols

Monoterpene 1

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	1	0	30	38	0	51	9	13	11	6	4	122	122
95% CI	2	0	5	14	0	32	3	6	2	3	3	59	59
min	0	0	18	9	0	0	0	0	3	0	0	8	8
max	11	0	49	80	0	137	17	37	16	15	15	337	337
kg d-1													
mean	0.01	0.00	0.37	0.12	0.00	0.56	0.42	2.08	1.74	0.99	1.07	1.02	0.24
95% CI	0.02	0.00	0.09	0.04	0.00	0.36	0.14	0.93	0.34	0.55	0.96	0.54	0.31
min	0.00	0.00	0.20	0.03	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	-0.79
max	0.11	0.00	0.70	0.23	0.00	1.75	0.76	6.11	2.64	2.95	4.49	2.87	1.18
g ADT-1 bleached pulp													
mean	0.1	0.0	1.4	0.5	0.0	1.6	1.3	6.0	5.1	3.0	3.6	3.0	0.7
95% CI	0.2	0.0	0.2	0.2	0.0	1.0	0.4	2.5	1.2	1.9	3.4	1.5	0.9
min	0.0	0.0	0.9	0.1	0.0	0.0	0.0	0.0	1.9	0.0	0.0	0.0	-2.3
max	1.1	0.0	2.3	1.0	0.0	4.3	2.1	15.4	8.6	12.3	18.0	7.0	3.7

Monoterpene 2

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	6	6	95	28	0	30	26	7	11	9	4	31	31
95% CI	7	5	20	16	0	20	10	3	6	4	3	14	14
min	0	0	27	0	0	0	0	0	0	0	0	6	6
max	35	19	147	115	0	120	59	17	39	23	12	77	77
kg d-1													
mean	0.06	0.04	1.19	0.09	0.00	0.32	1.19	1.16	1.71	1.44	1.09	0.27	0.06
95% CI	0.07	0.03	0.32	0.06	0.00	0.21	0.47	0.47	1.01	0.66	0.83	0.14	0.13
min	0.00	0.00	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.38
max	0.35	0.12	2.13	0.41	0.00	1.28	2.63	2.54	6.13	3.41	3.54	0.90	0.63
g ADT-1 bleached pulp													
mean	0.7	0.4	4.6	0.3	0.0	0.9	3.5	3.4	5.2	4.5	3.3	0.8	0.2
95% CI	0.7	0.3	1.0	0.2	0.0	0.6	1.3	1.3	3.2	2.4	2.4	0.4	0.4
min	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.1
max	3.3	1.2	7.1	1.4	0.0	3.1	6.8	6.7	19.8	13.8	9.2	2.6	1.9

Monoterpene 3

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	0	6	111	43	0	68	33	21	14	12	8	63	58
95% CI	0	8	31	31	0	25	13	11	9	11	10	20	21
min	0	0	11	5	0	17	8	0	0	0	0	19	0
max	2	31	179	178	0	127	83	62	57	71	59	123	123
kg d-1													
mean	0.00	0.04	1.40	0.14	0.00	0.71	1.48	3.34	2.29	1.89	2.45	0.51	0.16
95% CI	0	0.05	0.47	0.11	0.00	0.28	0.59	1.89	1.67	1.69	2.81	0.20	0.20
min	0.00	0.00	0.16	0.01	0.00	0.15	0.34	0.00	0.00	0.00	0.00	0.00	-0.47
max	0.02	0.18	2.51	0.62	0.00	1.50	3.64	11.48	10.59	10.68	17.07	1.10	1.01
g ADT-1 bleached pulp													
mean	0.0	0.6	5.3	0.5	0.0	2.1	4.2	9.6	6.9	6.7	7.7	1.6	0.5
95% CI	0	0.8	1.5	0.4	0.0	0.7	1.5	5.2	4.8	6.8	8.2	0.7	0.6
min	0.0	0.0	0.5	0.1	0.0	0.5	1.1	0.0	0.0	0.0	0.0	0.0	-1.3
max	0.2	4.0	8.6	2.1	0.0	3.8	8.9	33.0	30.4	43.4	49.1	3.4	3.1

Monoterpene 4

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	13	4	126	53	0	23	27	15	10	13	8	91	91
95% CI	11	4	58	21	0	16	11	9	3	6	8	46	46
min	0	0	16	0	0	0	0	0	0	0	0	0	0
max	50	14	437	111	0	100	56	59	23	32	49	208	208
kg d-1													
mean	0.13	0.02	1.63	0.17	0.00	0.26	1.23	2.31	1.59	2.12	2.33	0.83	0.12
95% CI	0.11	0.02	0.88	0.08	0.00	0.21	0.51	1.36	0.47	0.91	2.40	0.45	0.23
min	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.75
max	0.50	0.08	6.32	0.40	0.00	1.31	2.48	8.33	3.60	4.86	14.20	1.78	0.83
g ADT-1 bleached pulp													
mean	1.2	0.2	6.1	0.6	0.0	0.9	3.6	6.2	4.7	6.5	6.8	2.5	0.4
95% CI	1.1	0.2	2.8	0.3	0.0	0.8	1.3	3.2	1.4	3.3	6.8	1.4	0.7
min	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-2.2
max	4.7	0.7	21.0	1.3	0.0	5.5	6.6	20.4	9.3	19.8	40.8	6.8	2.6

Monoterpene 5 (2-endo-6-endo-dichlorobornane)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	28	30	374	93	0	58	115	26	15	28	28	50	66
95% CI	15	12	172	27	0	28	51	9	7	7	12	20	40
min	0	0	83	31	0	15	0	3	5	9	2	17	17
max	85	54	1009	164	0	182	315	53	42	47	72	142	262
kg d-1													
mean	0.28	0.18	4.81	0.29	0.00	0.59	5.09	4.24	2.41	4.59	8.41	0.43	0.24
95% CI	0.15	0.07	2.51	0.10	0.00	0.26	2.15	1.44	1.00	1.13	3.58	0.20	0.36
min	0.00	0.00	0.80	0.08	0.00	0.17	0.00	0.48	0.77	1.42	0.69	0.00	-0.33
max	0.85	0.32	14.51	0.58	0.00	1.55	13.88	7.58	6.71	7.74	20.98	1.14	2.15
g ADT-1 bleached pulp													
mean	3.0	2.1	17.9	1.1	0.0	1.9	15.0	12.3	6.9	13.3	24.2	1.4	0.7
95% CI	1.4	1.2	8.3	0.3	0.0	1.0	6.2	4.1	2.7	3.2	9.9	0.8	1.1
min	0.0	0.0	4.0	0.4	0.0	0.4	0.0	1.3	2.4	3.7	1.8	0.0	-0.9
max	8.0	6.4	48.5	2.0	0.0	6.4	35.7	22.7	17.4	23.3	60.3	4.6	6.6

Monoterpene 6

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	5	1	216	160	0	18	31	6	6	4	2	18	38
95% CI	4	1	65	89	0	12	18	4	4	2	2	8	44
min	0	0	81	0	0	0	0	0	0	0	0	0	0
max	20	4	412	486	0	68	99	18	27	13	14	46	280
kg d-1													
mean	0.05	0.01	2.76	0.52	0.00	0.18	1.39	0.87	0.99	0.60	0.64	0.15	0.21
95% CI	0.04	0.01	0.96	0.32	0.00	0.12	0.78	0.57	0.70	0.38	0.75	0.08	0.38
min	0.00	0.00	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.10
max	0.20	0.02	5.77	1.73	0.00	0.72	4.35	2.69	4.25	1.95	4.16	0.37	2.30
g ADT-1 bleached pulp													
mean	0.4	0.0	10.3	1.9	0.0	0.5	4.1	2.6	2.8	1.9	2.0	0.5	0.7
95% CI	0.4	0.1	3.1	1.1	0.0	0.3	2.1	1.8	1.9	1.3	2.2	0.3	1.2
min	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.3
max	1.9	0.2	19.8	5.8	0.0	1.8	10.6	10.1	11.0	7.9	10.8	1.5	7.1

Monoterpene 7

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	14	15	473	500	0	121	69	21	20	10	9	27	27
95% CI	22	9	119	146	0	67	27	7	3	2	7	15	15
min	0	0	168	107	0	10	0	0	15	0	0	0	0
max	110	45	798	982	0	304	152	41	36	18	44	67	67
kg d-1													
mean	0.14	0.09	6.04	1.61	0.00	1.27	3.14	3.44	3.26	1.65	2.77	0.22	0.04
95% CI	0.22	0.05	1.84	0.56	0.00	0.71	1.22	1.13	0.53	0.43	2.26	0.16	0.10
min	0.00	0.00	1.61	0.26	0.00	0.09	0.00	0.00	2.19	0.00	0.00	0.00	-0.33
max	1.10	0.27	11.19	3.50	0.00	3.36	6.71	6.65	5.82	2.79	13.89	0.79	0.32
g ADT-1 bleached pulp													
mean	1.3	1.1	22.7	6.0	0.0	3.7	9.1	10.0	9.6	5.0	8.1	0.7	0.1
95% CI	2.0	1.1	5.7	1.8	0.0	2.0	3.2	3.3	1.5	1.6	6.9	0.5	0.3
min	0.0	0.0	8.1	1.3	0.0	0.3	0.0	0.0	5.4	0.0	0.0	0.0	-1.0
max	10.4	5.8	38.3	11.8	0.0	8.7	19.3	17.0	15.1	10.4	43.0	2.3	1.0

Total Chlorinated Monoterpene Hydrocarbons

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	43	62	1424	995	0	312	333	109	87	82	59	401	401
95% CI	16	23	408	309	0	32	133	35	23	19	32	125	125
min	0	0	597	340	0	228	49	18	52	19	22	151	151
max	76	124	2757	1956	0	393	746	234	202	168	214	675	675
kg d-1													
mean	0.43	0.37	18.22	3.26	0.00	3.29	14.78	17.45	13.99	13.28	17.65	3.55	0.58
95% CI	0	0.14	6.32	1.17	0.00	1	5.77	5.28	3.58	3.03	9.27	1.53	1.00
min	0.00	0.00	5.73	1.03	0.00	2.05	2.47	2.90	8.50	3.19	7.91	0.00	-3.16
max	0.76	0.75	39.83	6.85	0.00	5.10	32.85	33.24	32.22	25.49	62.34	7.46	2.19
g ADT-1 bleached pulp													
mean	4.5	4.5	68.3	11.9	0.0	9.7	43.8	50.1	41.3	40.9	52.1	10.7	1.8
95% CI	1	2.8	19.6	3.7	0.0	2	15.0	13.8	10.1	13.8	26.6	4.8	3.0
min	0.0	0.0	28.7	4.1	0.0	5.1	6.2	8.4	21.3	9.2	22.8	0.0	-9.1
max	7.0	16.2	132.3	23.5	0.0	13.5	80.3	82.7	83.5	103.6	179.1	21.4	6.9

Monoterpene 8 (dichloro-2-endo-hydroxybornane)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	12	24	68	97	0	33	96	34	39	24	13	47	47
95% CI	19	10	35	35	0	15	53	16	27	17	14	20	20
min	0	3	6	15	0	0	17	0	0	0	0	13	13
max	91	50	212	189	0	86	242	93	191	92	69	127	127
kg d-1													
mean	0.12	0.15	0.87	0.31	0.00	0.34	4.26	5.51	6.24	4.01	4.08	0.38	0.11
95% CI	0.19	0.06	0.51	0.12	0.00	0.15	2.34	2.55	4.26	3.02	4.47	0.17	0.08
min	0.00	0.02	0.06	0.04	0.00	0.00	0.80	0.00	0.00	0.00	0.00	0.00	-0.20
max	0.91	0.30	3.06	0.66	0.00	0.82	10.67	14.92	30.44	16.89	21.90	1.02	0.30
g ADT-1 bleached pulp													
mean	1.1	1.6	3.3	1.2	0.0	1.0	12.5	15.8	17.9	13.0	14.7	1.2	0.3
95% CI	1.7	0.7	1.7	0.4	0.0	0.5	6.4	6.8	11.2	10.0	18.0	0.6	0.3
min	0.0	0.5	0.3	0.2	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	-0.6
max	8.4	4.1	10.2	2.3	0.0	2.5	26.1	38.6	78.9	48.5	90.9	3.3	1.0

Monoterpene 10 (2a,6B-dichloro-p-menthane-1a,8-diol)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	102	183	1261	747	0	390	508	102	48	30	9	129	129
95% CI	67	41	312	222	0	137	153	30	22	18	7	22	22
min	14	83	492	20	0	174	98	44	7	0	0	76	76
max	357	258	2134	1365	0	1122	927	209	112	97	30	181	181
kg d-1													
mean	1.02	1.10	15.45	2.33	0.00	4.14	22.84	16.57	7.81	4.76	2.83	0.99	0.39
95% CI	1	0.24	4.65	0.76	0.00	1.55	6.85	5.14	3.48	2.77	2.22	0.29	0.37
min	0.14	0.50	6.85	0.05	0.00	2.20	4.48	7.05	1.09	0.00	0.00	0.00	-0.47
max	3.57	1.55	29.92	4.87	0.00	11.94	40.83	34.15	17.00	15.16	9.50	1.55	1.41
g ADT-1 bleached pulp													
mean	12.9	13.5	60.6	9.0	0.0	12.1	66.5	47.0	25.2	14.5	9.0	3.1	1.1
95% CI	8	4.3	15.0	2.7	0.0	4.2	16.6	12.9	13.2	8.2	7.6	1.1	1.0
min	1.3	4.7	23.6	0.2	0.0	6.2	13.9	22.3	2.7	0.0	0.0	0.0	-1.3
max	33.7	24.8	102.5	16.4	0.0	29.2	116.4	85.8	69.1	39.0	39.4	5.6	3.6

Monoterpene 11 (2a,7-dichloro-p-menthane-1B,8-diol)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	8	16	1495	133	0	27	490	47	6	2	0	39	39
95% CI	6	6	391	56	0	18	175	24	5	1	1	20	20
min	0	0	98	21	0	0	23	0	0	0	0	0	0
max	23	30	2969	352	0	76	981	129	29	5	5	90	90
kg d-1													
mean	0.08	0.10	18.82	0.43	0.00	0.27	22.17	7.72	0.98	0.28	0.13	0.31	0.12
95% CI	0	0.04	6.13	0.21	0.00	0.17	8.04	3.90	0.73	0.23	0.29	0.21	0.10
min	0.00	0.00	1.41	0.05	0.00	0.00	1.07	0.00	0.00	0.00	0.00	0.00	-0.10
max	0.23	0.18	42.33	1.23	0.00	0.60	43.31	21.06	4.58	0.93	1.59	0.90	0.34
g ADT-1 bleached pulp													
mean	0.7	1.3	71.8	1.6	0.0	0.8	64.0	21.6	3.2	0.8	0.4	1.0	0.4
95% CI	1	0.8	18.8	0.7	0.0	0.5	20.3	10.4	2.5	0.6	0.9	0.7	0.3
min	0.0	0.0	4.7	0.3	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0	-0.3
max	2.1	3.8	142.5	4.2	0.0	2.1	124.5	52.9	14.8	2.7	5.1	2.9	1.1

Monoterpene 12 (2B,7-dichloro-p-menthane-1,8-diol)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	14	17	575	141	0	55	138	33	19	10	2	28	28
95% CI	14	9	140	42	0	36	57	12	10	9	3	13	13
min	0	0	123	0	0	0	0	0	0	0	0	0	0
max	57	39	935	322	0	208	353	68	55	41	12	55	55
kg d-1													
mean	0.14	0.10	7.29	0.45	0.00	0.60	6.23	5.22	3.16	1.56	0.77	0.20	0.09
95% CI	0	0.05	2.25	0.16	0.00	0.43	2.58	1.93	1.55	1.46	0.83	0.12	0.11
min	0.00	0.00	1.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.12
max	0.57	0.23	13.52	1.15	0.00	2.44	15.55	10.88	8.38	6.51	3.70	0.47	0.43
g ADT-1 bleached pulp													
mean	1.5	1.2	27.6	1.7	0.0	1.7	17.9	14.7	10.1	4.6	2.6	0.6	0.2
95% CI	1	0.7	6.7	0.5	0.0	1.2	6.4	5.1	5.6	4.2	3.1	0.3	0.3
min	0.0	0.0	5.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.3
max	4.7	3.6	44.9	3.9	0.0	7.6	38.0	28.2	34.1	17.7	15.4	1.5	1.4

Monoterpene 13 (2a,7-dichloro-p-menthane-1a,8-diol)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	1	10	1663	68	0	26	542	48	40	40	8	56	56
95% CI	1	8	442	34	0	17	192	28	29	25	7	60	60
min	0	0	47	11	0	0	42	0	0	0	0	0	0
max	5	30	2940	181	0	73	1031	148	150	125	32	349	349
kg d-1													
mean	0.01	0.06	20.77	0.22	0.00	0.26	24.41	7.69	6.58	6.48	2.31	0.46	0.08
95% CI	0	0.05	6.75	0.13	0.00	0.17	8.67	4.33	4.68	3.98	2.09	0.48	0.08
min	0.00	0.00	0.68	0.03	0.00	0.00	1.91	0.00	0.00	0.00	0.00	0.00	-0.09
max	0.05	0.18	41.93	0.65	0.00	0.80	45.37	23.65	22.62	19.93	10.22	2.79	0.32
g ADT-1 bleached pulp													
mean	0.1	0.6	79.9	0.8	0.0	0.8	70.5	22.4	21.8	19.8	7.6	1.5	0.3
95% CI	0	0.4	21.2	0.4	0.0	0.5	21.2	12.3	16.9	12.1	7.7	1.6	0.3
min	0.0	0.0	2.3	0.1	0.0	0.0	5.9	0.0	0.0	0.0	0.0	0.0	-0.3
max	0.5	1.7	141.2	2.2	0.0	2.3	128.8	61.3	92.0	51.6	42.4	9.0	1.0

Monoterpene 14 (2a,6B,7-trichloro-p-menthane-1,8-diol)

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	13	3	943	43	0	25	298	31	31	30	23	27	27
95% CI	11	3	292	27	0	31	119	25	22	16	15	22	22
min	0	0	24	0	0	0	28	0	0	0	0	0	0
max	56	10	1754	190	0	155	619	127	110	94	76	103	103
kg d-1													
mean	0.13	0.02	11.83	0.14	0.00	0.22	13.49	4.95	5.09	4.88	6.7[illegible]	0.20	0.09
95% CI	0	0	4.31	0.10	0.00	0.22	5.41	3.89	3.63	2.66	4.37	0.19	0.07
min	0.00	0.00	0.34	0.00	0.00	0.00	1.26	0.00	0.00	0.00	0.00	0.00	0.00
max	0.56	0.06	25.01	0.68	0.00	1.05	27.25	20.35	17.38	14.96	21.40	0.88	0.32
g ADT-1 bleached pulp													
mean	1.7	0.2	45.3	0.5	0.0	0.7	38.5	14.4	17.1	15.1	20.3	0.6	0.3
95% CI	1	0	14.0	0.3	0.0	0.7	13.3	11.1	13.2	8.4	13.0	0.6	0.2
min	0.0	0.0	1.1	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0
max	5.2	0.6	84.2	2.3	0.0	3.0	71.8	63.0	67.8	38.8	59.8	2.3	0.8

Total Chlorinated Monoterpene Alcohols

ug L-1	No.1 BP C Stage	No.1 BP E Stage	No.2 BP CD Stage	No.2 BP Eo Stage	No.1 Sewer	No.2 Sewer	No.3 Sewer	Pond 19 Inlet	Pond 19 Outlet	Pond 23 Outlet	Outfall	J Pond Outlet	J Pond Fill
mean	121	261	6033	1310	0	441	2176	327	191	106	45	277	277
95% CI	53	64	1550	370	0	118	775	86	102	62	39	58	58
min	18	102	802	258	0	209	276	146	10	0	0	89	89
max	238	386	10429	2471	0	848	4086	613	536	271	188	398	398
kg d-1													
mean	1.21	1.57	74.73	4.09	0.00	4.56	97.29	52.69	31.20	17.33	13.89	2.16	0.83
95% CI	1	0	24.25	1.38	0.00	0.97	35.27	13.79	16.32	10.12	12	1	1
min	0.18	0.61	11.51	0.93	0.00	2.67	12.62	22.13	1.59	0.00	0.00	0.00	-0.96
max	2.38	2.31	148.71	8.81	0.00	6.80	179.86	97.96	85.67	41.34	59.73	3.98	2.50
g ADT-1 bleached pulp													
mean	15.8	19.4	289.6	15.7	0.0	14.1	281.2	150.2	99.8	55.1	47.8	6.4	2.3
95% CI	8	6	74.4	4.4	0.0	4.0	84.2	35.3	57.2	35.7	49	3	2
min	2.0	5.8	38.5	3.1	0.0	7.3	39.1	83.3	5.2	0.0	0.0	0.0	-2.7
max	37.0	36.2	500.7	29.7	0.0	28.2	491.6	253.8	290.5	166.5	247.9	13.2	7.9

Total Chlorinated Monoterpenes

ug L-1

mean	162	320	7486	2430	0	717	2562	451	281	189	105	653	653
95% CI	62	66	1925	708	0	82	947	107	119	79	59	132	132
min	52	183	1409	911	0	475	344	220	61	19	30	416	416
max	307	444	12278	4367	0	823	4832	739	738	439	288	1004	1004

kg d-1

mean	1.62	1.92	93.19	7.89	0.00	7.52	113.35	72.51	45.61	30.64	31.86	5.53	1.31
95% CI	1	0	30.44	3	0.00	1	43	16.87	19.00	12.85	18	2	2
min	0.52	1.10	20.22	3.04	0.00	5.60	15.75	34.58	10.19	3.19	10.39	0.00	-4.12
max	3.07	2.66	175.09	15.56	0.00	10.69	212.72	118.13	117.89	66.45	83.75	9.72	4.69

g ADT-1 bleached pulp

mean	20.1	23.8	359.4	29.2	0.0	22.3	333.4	207.0	142.6	96.5	102.3	16.1	3.6
95% CI	8	8	92.4	8	0.0	4	102	41.4	64.8	50.2	64	6	5
min	5.8	10.4	67.6	10.9	0.0	14.1	48.8	111.6	33.0	9.2	28.5	0.0	-11.8
max	41.6	52.4	589.5	52.4	0.0	30.7	563.9	306.0	348.2	270.1	314.3	29.3	14.9