National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UNIVERSITY OF ALBERTA

Impact of TMP/CTMP Mill Effluents on Chlorination Byproduct Formation in Drinking Water Treatment Plants

BY

Daniel Conrad

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science

IN

ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

Edmonton, Alberta

Spring, 1994

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

ISBN 0-612-11180-6

UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR: Daniel Conrad

TITLE OF THESIS: Impact of TMP/CTMP Mill Effluents on Chlorination Byproduct Formation in Drinking Water Treatment Plants

DEGREE: Master of Science in Environmental Science

YEAR THIS DEGREE GRANTED: 1994

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves all other publication and other rights in association with the copyright in the thesis, and except as hereinbefore provided neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission.

Daniel Conrad

5909 - 53 Street
Vegreville, Alberta
T9C 1J3

April 12/94

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled, Impact of TMP/CTMP Mill Effluents on Chlorination Byproduct Formation in Drinking Water Treatment Plants, submitted by Daniel Conrad in partial fulfilment of the requirements for the degree of Master of Science in Environmental Science.

Dr. P.M. Huck

Daniel W Smith
Dr. D.W. Smith

Dr. S.E. Hrudey

Coutts
Dr. R.T. Coutts

April 12, 1994

ABSTRACT

Chlorination by-products likely to be formed in drinking water treatment plants downstream from thermomechanical pulp (TMP) and chemithermomechanical pulp (CTMP) mills were identified and specific compounds which are, or are proposed to be regulated were quantified. The high temperatures, chemicals and relatively low volumes of water used in these processes generate high strength wastes which contain a large proportion of organic compounds refractory to biological treatment, as indicated by the high chemical oxygen demand (COD).

Ferulic acid (4-hydroxy-3-methoxycinnamic acid) was used as a lignin model compound to examine the effects of chlorination conditions upon the detected chlorination by-products. Experimental factors, which included ferulic acid concentration measured as total organic carbon (TOC), (2 mg TOC/L, 5 mg TOC/L) and chlorine dose expressed as a molar ratio of Cl_2 to ferulic acid (2:1, 6:1), include levels which are typical of drinking water treatment. Sample pH (6, 9) was set using a carbonate buffer. Reaction times were typical of a drinking water treatment plant (1.6 hours) and distribution system residence times (160 hours.) Reaction products were identified and quantified by gas chromatography with quadrupole mass spectroscopy detection.

Chlorine doses, approximating typical drinking water treatment levels produced a large variety of chlorine substituted phenolics including guaiacols, vanillins, catechols and triols. Higher chlorine doses were associated with less chlorine incorporated, but higher levels of chloroform, and chloroacids. The strong bacterial mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (compound MX) was also detected.

Biologically treated effluents from a TMP mill and CTMP mill diluted in natural waters were filtered and chlorinated under conditions similar to normal drinking water treatment conditions. Experimental factors studied included, effluent type (TMP, CTMP), effluent concentration (0.5%, 3.0%) and receiving water quality (glacial, humic). Effluents in general, significantly increased chlorine demand ($p \leq 0.05$) at the concentration levels studied. Unlike the model compound solutions, only a single chlorophenolic was detected, 2,4,6-trichlorophenol which has potent taste and odour properties. The production of chloroform, chloroacids, and compound MX was found to be associated with effluent type and receiving water quality.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Peter Huck, for his guidance, advice and encouragement in the course of my studies and thesis research program.

The support of the Alberta Environmental Centre is respectfully noted and appreciated, in particular, Dr. R.D. Smillie, Dr. C.I. Johnson, and the Trace Analysis Program staff for providing analytical support, and Mrs. Charlene Petryshyn for her care and patience in the preparation of this manuscript.

The author wishes to thank the following individuals and their companies for their cooperation, assistance and advice during this project; Mr. B. Steinbach of Alberta Newsprint Company Ltd., Ms. W. Lyka of Millar Western Pulp Ltd., and Mr. T. Andrews of Weldwood of Canada Ltd.

I could not have completed my research program without the support and assistance of my wife, Connie, and children, Sara and Thomas.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

4-CC	4-chlorocatechol
4-CG	4-chloroguaiacol
46-DCG	4,6-dichloroguaiacol
adt	air dried tonne
AEC	Alberta Environmental Centre
AMU	atomic mass units
APHA	American Public Health Association
AWWA	American Water Works Association
BCTMP	bleached chemithermomechanical pulp
BKME	bleached kraft mill effluents
BOD	biochemical oxygen demand
C1	chlorine, first stage
ClHyG	chloro-4-hydroxyguaiacol
Cltriol	chloro-1,2,4-benzenetriol
ClV	chlorovanillin
ClVG	chloro-4-vinylguaiacol
COD	chemical oxygen demand
CTMP	chemithermomechanical pulp
D1	chlorine dioxide, first stage
D2	chlorine dioxide, second stage
DClVC	dichloro-4-vinylcatechol
DClVG	dichloro-4-vinylguaiacol
Dihybenz	3,4-dihydroxybenzaldehyde
DOC	dissolved organic carbon
E1	alkali extraction, first stage
E2	alkali extraction, second stage
GC/MS	gas chromatography/mass spectroscopy
H	hypochlorite, stage
HAA5	five haloacetic acids
HyG	4-hydroxyguaiacol
IC	missing single confirmation ion

M	molecular ion
MAC	maximum acceptable concentration
MCL	maximum contaminant levels
MLE	maximum likelihood estimate
MSD	mass selective detector
MX	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
m/z	mass/charge ratio
NAQUADAT	National Water Quality Data Base
NCSS	Number Cruncher Statistical System
ND	not detected
NR	not run
PHENAN	phenanthrene
SIM	selected ion monitoring
TClVG	3,5,6-trichloro-4-vinylguaiacol
THMFP	trihalomethane formation potential
TMP	thermomechanical pulp
TOC	total organic carbon
TOX	total organic halogen
TTHM	total trihalomethanes
WPCF	Water Pollution Control Federation

1.0 INTRODUCTION

The pulp and paper industry uses a large volume of water in the production of fiber products. After utilization in the pulp and paper making process, water containing various solutes from wood and process chemicals is treated and eventually discharged to a receiving surface water.

Concerns have been expressed over the perceived risk to human health by pulp and paper discharges into drinking water sources. This was especially apparent during the review hearings for the proposed Alberta-Pacific kraft mill at Athabasca, Alberta (Alberta Environment, 1990) and subsequent studies which dealt extensively upon the role of chlorinated organic compounds. In Alberta, Canada, the Athabasca River is the drinking water source for several communities including the city of Fort McMurray. The Athabasca River Basin is the site of several large pulp mills consisting of three types: bleached kraft pulp, thermomechanical pulp (TMP) and bleached chemithermomechanical pulp (BCTMP). The nature of the effluents from these various processes will be different and thus their behaviour during drinking water treatment will likely be different as well.

The main review of the Scientific Review Panel for the Alberta-Pacific mill (Jaakko Pöyry Oy, 1990) concluded that none of the permissible maximum concentrations of compounds specific to pulp mill effluents and regulated under the Canadian Drinking Water Guidelines would be exceeded at Fort McMurray, the first major community downstream on the Athabasca River. The review panel did not address the role of drinking water treatment, which includes disinfection with chlorine, upon a raw water containing pulp mill effluent. Chlorine is the most commonly used disinfectant in conventional water treatment plants and is likely to remain so for the foreseeable future.

Previous studies on the effects of pulp mill effluents have dealt to a large extent with bleached kraft mills, in particular with the identification of contaminants, the evaluation of environmental and health effects of effluents and individual compounds, the effect of mill operating conditions and to a lesser extent the effects of mill effluents on drinking water quality. The drinking water studies have dealt with taste and odour and mutagenic measures of the effects of pulp mills. Much of the literature has dealt with the chlorinated by-products formed under pulp bleaching conditions (high chlorine doses applied at acidic pH and elevated temperatures) which are more rigorous than and not directly applicable to drinking water treatment conditions.

The studies which exist on the TMP and chemithermomechanical pulping (CTMP) processes and their effects on receiving waters have dealt with water quality issues such as effluent treatment and effluent toxicity. The impacts downstream of these newer pulping technologies on drinking water treatment plants have not been examined.

Of the various components of pulp mill effluents, lignin compounds are the most resistant to the biological treatment normally provided. Therefore, research examining impacts of effluents on downstream drinking water treatment should focus on the lignin component.

2.0 OBJECTIVES

The objectives of the present study are to:

1) demonstrate the potential for disinfection by-product formation and evaluate the effects of drinking water chlorination conditions upon by-product formation using a lignin model compound and
2) characterize and quantify the chlorination by-products resulting from the chlorination of TMP and CTMP mill effluents diluted in natural waters.

3.0 LITERATURE REVIEW

3.1 Pulp Mill Effluents

3.1.1 Summary of Pulping Processes

The kraft pulping process removes 90% or more of the lignin present in wood chips in a 160 to 180°C liquor containing sodium hydroxide and sodium sulphide. This is achieved by cleavage of the ether bonds in lignin and dissolution of the subsequent products (Kringstad and Lindström, 1984). Spent liquor is treated for chemical recovery, followed by evaporation and combustion.

Residual lignin is removed by oxidative bleaching. A typical bleaching sequence may consist of successive treatments (termed stages) of chlorine (C1), alkali (E1), chlorine dioxide (D1), alkali (E2), chlorine dioxide (D2) and often a hypochlorite stage (H) between the initial alkali and chlorine dioxide stages. Substantial depolymerization of lignin as well as the substitution of chlorine renders the lignin degradation products more polar and hence more soluble.

TMP and CTMP processes, in contrast with the kraft process, are high pulp yield processes, typically 90% or more (Kurdin, 1980), based on the amount of fibre produced per unit of wood. Less lignin is dissolved in these processes, and thus, pulp yields are higher. The TMP process steams raw wood chips at relatively low pressure for a short period to soften lignin before mechanical refining. TMP is often used for the production of newsprint paper. The CTMP process softens the wood chips by impregnating the chips with chemicals (often sodium sulfite) after pH adjustment to 9 or 10 with sodium hydroxide. This is followed by steaming and refining. CTMP allows the utilization of hardwoods and produces higher strength pulps.

If brighter pulps are required, the pulps from TMP and CTMP processes may be bleached by reductive or oxidative bleaching. Sodium dithionate is often used for reductive bleaching while peroxide (with sodium silicate) is the most common oxidative bleaching agent. The mechanism of bleaching is generally thought to be the reduction or oxidation of chromophores present in the various pulp constituents including lignin.

3.1.2 Kraft Mill Effluents

3.1.2.1 Identification of Contaminants in Kraft Pulp Bleaching Liquors

The liquors from kraft pulp bleaching have been extensively studied. A few of the most comprehensive papers will be reviewed as they suggest likely chlorination by-products arising from lignin containing effluents.

Kringstad and Lindström (1984) provided one of the first comprehensive reviews of the chemical composition of spent pulp bleaching liquors. It was estimated that 30% of the organically bound chlorine from the spent C1 liquor and 5% of the organically bound chlorine from the spent E1 liquor consists of low molecular weight material <1000 atomic mass units (AMU). The majority of material was relatively high molecular weight compounds, which have been found to have a low aromatic nuclei content and consist to a large extent of cross-linked unsaturated aliphatic compounds. It was felt by the authors that these compounds are relatively benign biologically.

The low molecular weight compounds were divided into three main groups: acidic, phenolic and neutral compounds. The acidic group was divided into five further categories: fatty, hydroxy, dibasic, aromatic and resin acids. The phenolic group consisted of chlorinated phenols, guaiacols, vanillins and catechols found in softwood kraft pulps and chlorinated syringols and syringaldehydes found in birch kraft pulps. The neutral fraction was dominated quantitatively by methanol and hemicelluloses and to a lesser extent by chlorinated acetones, chloroform, dichloromethane and 1,1-dichloromethylsulfone.

Strongly mutagenic compounds were identified in bleach kraft effluents which have also been found in chlorinated drinking waters and thus will be mentioned here including: 1,3-dichloroacetone, 2-chloropropenal and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (compound MX). Spent C1 liquors were found to contain suspected human carcinogens such as carbon tetrachloride, chloroform, chlorinated benzenes and phenols.

Suntio, Shiu and MacKay (1988), compiled a list of 250 compounds found in pulp mill bleaching effluents and categorized these in terms of relevant physical properties, production and bioaccumulation potential. The highest concentrations of contaminants in the C1 and E1 stages were found for the low molecular weight acids (as a group), particularly, formic, acetic and glyceric acid (100-1000 g/tonne each). In the neutral fraction, methanol (5000 g/tonne) and chloroform (10-200 g/tonne) predominate. Concentrations of chlorinated compounds were highest for chloroform (10-200 g/tonne), chlorinated phenols, guaiacols, vanillins, syringols and syringaldehydes (typically 0.1-20 g/tonne) dichloroacetic acid (12 g/tonne) and trichloroacetic acid (88 g/tonne).

McKague, Jarl, and Kringstad (1990) completed an inventory of 313 compounds found in bleachery effluents or whole mill effluents as of 1989. The increased number of compounds identified, as compared with Kringstad and Lindström (1984), consist quantitatively of chlorinated aliphatic, saturated and unsaturated acids.

The reviews discussed demonstrate that a large number of compounds are produced from chlorine bleached kraft pulps. A number of these compounds have implications for treated drinking water quality in terms of disinfection by-products expected when effluents containing lignin are chlorinated. Specifically these are chloroform, chloroacetones, chloropropenal, di- and trichloroacetic acids, a variety of substituted chorophenolics, and compound MX, a chlorofuranone.

3.1.2.2 Effect of Kraft Mill Effluents on Drinking Water Quality

The effects of pulp mill effluents on drinking water quality have dealt largely with chemical pulping processes such as bleached kraft.

Wigilius et al. (1986) studied the contribution of biologically treated bleached kraft mill effluent to chlorinated organic and mutagenic substances in drinking water produced downstream from the mill. The study showed that the bleached kraft mill effluents (BKME) were capable of long range transport and caused a substantial increase in organic chlorine in drinking water produced downstream from the mill. Minimal increases in mutagenicity for acidic extracts were the only significant differences between treated water upstream and downstream from the mill and the diluted pulp mill effluent. Seasonal differences were noted in that winter samples of pulp mill effluent displayed more gas chromatograph peaks than summer samples. Chlorination of aquatic humic substances during disinfection was shown to have a more significant contribution to Ames mutagenicity than BKME at this particular site.

Kovacs and Voss (1986) performed a taste and odour study on the effect of BKME on drinking water quality. Taste and odour quality were impaired at BKME concentrations (in glacial river water) of 0.1 to 0.4%. Effluent biotreatment and potable water treatment (coagulation/flocculation/sedimentation, sand filtration, disinfection, and adsorption with granular activated carbon) reduced but did not eliminate BKME associated taste and odour.

Kringstad et al. (1985) described the behaviour of high molecular weight chlorolignins (molecular weight >2000 AMU), and aquatic humic acid for the formation of Ames test mutagens and chlorophenolic compounds when chlorinated under conditions similar to those used in water disinfection. The production of chlorophenolics was less for chlorolignins than humic acid. Humic acid appeared more prone to forming Ames mutagens than chlorolignins.

The biological uptake of mutagens from drinking water and pulp mill effluents was studied by Monarca et al. (1984). The authors found that a smaller portion of the organic halogen from a C1 stage effluent was found in the urine of rats as compared to a drinking water sample. Only the drinking water group displayed any trace of mutagenic activity in their urine. This low recovery was felt to be due to detoxification by liver enzymes and the fact that a large portion of the lower molecular weight compounds in pulp mill effluent are potentially bioaccumulated.

Vartiainen and Liimatainen (1986) tested the effect of drinking water treatment on a surface water source with a high humic content and receiving some unbleached pulp mill effluent. Raw water displayed only weak mutagenicity. After treatment which includes prechlorination, coagulation, flotation, filtration, lime treatment and post-chlorination the water displayed a marked increase in mutagenicity.

Studies dealing with the effect of kraft mill effluents on drinking water quality have concentrated on mutagenic measures as well as taste and odour. Specific compounds have, in general, not been studied. It appears likely that the chlorination of humic materials may yield more mutagenic compounds than bleached kraft effluents. The interaction of chlorine with organics originating from different pulping processes remains to be addressed.

3.1.3 TMP/CTMP Mill Effluents

3.1.3.1 Characterization and Treatment of TMP/CTMP Mill Effluents

The higher pulping yields from TMP and CTMP mills results in lower pollution levels than chemical pulp mills (Kurdin, 1980), however the effluents from these processes are warm and concentrated (Rintala and Vuoriranta, 1988). Soluble materials are dissolved due to the higher pressures and temperatures during steaming and the dissolution of materials during chemical pretreatment (Kosiková et al., 1984) and bleaching (Lorås, 1980). Studies of aerobic treatment of TMP and CTMP effluents discussed later have shown that decreases in biochemical oxygen demand (BOD) are greater than decreases in chemical oxygen demand (COD) and result in typical effluent concentrations for BOD of less than 100 mg/L and for COD of 1000 mg/L or more. The COD:BOD ratio demonstrates that CTMP effluents consist to a large extent of organics which are not easily biodegradable but may have considerable potential for further chemical oxidation.

The organic contaminants found in effluents include carbohydrates, lignin compounds and wood extractives (Rintala and Vuoriranta, 1988, Pichon et al., 1986). Of these compounds the lignin compounds are the most resistant to biological treatment (Sierra-Alvarez and Lettinga, 1991). During treatment of TMP and CTMP effluents, carbohydrates are easily degraded while lignins are poorly degraded (Björklund Jansson, 1980, Lo et al., 1991). Lignin from ground wood and phenolic compounds have been shown to form mutagenic compounds on chlorination (Rapson et al., 1980). The effluents from TMP and CTMP mills may thus have the potential for the formation of chlorination by-products during conventional disinfection.

Treatment of TMP/CTMP effluents has been an active area of study. Kovacs and Voss (1992) surveyed the effluents of 9 mills operating with primary clarification and no biological treatment for biological toxicity and chemical characteristics. The five TMP mills in this survey utilized spruce and fir for their wood furnish and hydrosulphite bleaching. The final effluents were high strength and coloured containing 360-900 mg BOD/L, 806-2904 mg COD/L and 252-868 units of colour.

Björklund Jansson (1980) characterized a fibre board TMP effluent before and after biological treatment by trickling filter and aerated lagoon. The untreated effluent in this study consisted of 15-22% lignin, 15.7-17.3% carbohydrates, 1.3-2.2 % extractives, and 7.4-8.6% uronic acid residues. Removal efficiencies of 38% for lignin, 94% for carbohydrates, 10% for extractives and 28% for uronic acid residues were achieved by the trickling filter. Removal efficiencies of 65% for lignin, 73% for carbohydrates, 89% for extractives and 6% for uronic acid residues were achieved by the aerated lagoon. The residual lignin was modified by biological treatment, reducing the methoxy content and producing a higher proportion of acid soluble lignin.

Kosíková et al. (1984) studied CTMP processing of spruce wood pulp with sodium sulphite. The dissolved organic matter consisted of 30% lignin and 35% saccharides. The introduction of sulpho groups caused partial dissolution of lignin. From model compound experiments it was estimated that 5% of lignin-saccharidic bonds of the benzyl ether type were cleaved by sodium sulphite under CTMP conditions. As a consequence of hydrolytic and sulphonation reactions CTMP effluents contain sulfonated lignins, lignin hemi-cellulose complexes and xylan polyuronides.

Lo et al. (1991) studied the sources of pollutants in a CTMP mill. The highest loadings in terms of BOD were from CTMP washing, filtrates and dilution water. High levels of pollutant removal from the CTMP washing effluent were achieved by aerobic treatment using lab-scale chemostats. BOD removals of 94%, COD removals of 80% resin fatty acid removals of 98% and lignosulphonate removals of 50% were reported.

Urbantas and MacEwan (1985) compared effluent BOD and COD for the TMP and CTMP processes. TMP effluent had a higher BOD per gram of dissolved material (due to low molecular weight carbohydrates) than CTMP and thus would be easier to biodegrade. Pulping aids and higher temperatures decreased yield for CTMP effluents. Reduced yield was reflected in higher BOD but especially higher COD levels. The reduction in yield was accounted for by lignin losses. This work was confirmed by Malinen et al. (1985) who found that CTMP effluent had higher BOD and COD concentrations than TMP effluent. Yield losses were correlated with both BOD and COD. COD was most sensitive to yield losses. Increased temperature, sodium sulphite and hydrogen peroxide (bleach) charge was reflected by increased BOD and especially COD. The authors noted that whole effluent from peroxide bleached CTMP effluents would have a total BOD loading of 50-65 kg/air dried tonne (adt) and a COD loading of 95-120 kg/adt which is several times higher than effluent from bleached kraft pulp mills.

The biodegradation of TMP and CTMP effluents has been studied by a variety of aerobic processes and typical results are summarized in Table 1.

Table 1. TMP/CTMP Aerobic Treatment Efficiencies

Process	Removal (%)	
	BOD	COD
Aerated Lagoon[a] Trickling Filter[a] (TMP, pilot scale)	82 70	58 57
Activated Sludge[b] (CTMP, lab scale)	75	50
Activated Sludge[c] without added nutrients with added nutrients (TMP, lab scale)	40-60 90-95	35-50 80-85
Oxidation Ditch[d] (CTMP, pilot scale)	95-99	63-73
Biological Filter[e] (TMP, pilot scale)	85-99	71-85

Notes:
[a] Björklund Jansson (1980)
[b] Malinen et al. (1985)
[c] Vuoriranta et al. (1987)
[d] Bennet et al. (1990)
[e] Kantardjieff et al. (1990)

Anaerobic treatment of TMP and CTMP effluents has several advantages over aerobic treatment namely, energy savings by obviating the need for supplied air and recovering methane which supplies an alternative energy source. However, several components of the waste stream are toxic to anaerobic microbes, specifically wood extractives, hydrogen peroxide and chelating agents (Gunnarsson et al. 1989) as well as sulphate (Pichon et al., 1989) and low molecular weight lignins (Sierra-Alvarez and Lettinga, 1991).

The different biodegradability of TMP and CTMP effluents has been noted above. Pichon et al. (1986) noted that 30-40% of the COD load of a CTMP effluent may be due to lignin as compared to 35-40% for organic acids and 10-15% for polysaccharides. The efficiency of anaerobic treatment will therefore be limited due to the lignin content. Removals by anaerobic treatment (pilot scale upflow packed bed anaerobic filters with CTMP effluent) of 80% BOD and 60% COD were noted by Pichon et al. (1986). Removals of 90% BOD and 44% COD for a full scale treatment plant handling BCTMP effluents were noted by Gunnarsson et al. (1989). During mechanical pulping, only 15-30% of the dissolved solids is due to lignin (Sierra Alvarez et al., 1991). Sierra Alvarez et al. (1991) noted up to 87% conversion of the total COD to methane and volatile fatty acids for a TMP effluent indicating a high anaerobic biodegradability.

Resin acids are only partially degraded under anaerobic conditions (MacLean et al. 1990), and so to meet toxicity regulations for effluent an aerobic treatment is also required. Vuoriranta et al. (1987) treated a clarified whitewater from a TMP mill with lab scale upflow sludge blanket reactors followed by an activated sludge reactor. This treatment removed 90-95% of the BOD and 80-85% of the COD from the influent TMP whitewater. Less sludge with better handling properties was produced from this arrangement than an activated sludge reactor which required added nutrients to meet the same treatment levels. MacLean et al. (1990) treated a combined TMP/BCTMP effluent with a pilot scale upflow anaerobic sludge blanket reactor followed by a two day hydraulic residence time aerated stabilization basin. Overall treatment efficiency of this system was 90% BOD and 60% COD removal.

Lignin in TMP/CTMP waste waters appears to be a significant source of organic matter which is resistant to biological treatment. In a review of microbial degradation of lignin, Kirk and Farrell (1987) note that the microbial resistance of lignin is due to its high molecular weight, and variety of interphenylpropane linkages. These structural features of lignin dictate that biodegradative systems must be extracellular, nonspecific and nonhydrolytic. Complete decomposition of lignin appears to be limited to white rot fungi. Fungi probably do not play an important role in biological treatment systems so lignin biodegradation is likely limited to modification and removal, perhaps by adsorption mechanisms. Kirk and Farrell (1987) suggest further that anaerobic degradation appears limited to low-molecular weight fragments freed by other organisms. Aerobic bacteria can degrade certain lignocellulosic materials as well as lignin fragments produced abiotically. (Slow abiotic degradation, of ether linkages involving the alpha C in the interphenyl propane unit, which is favoured by high-temperature, acidic or alkaline environments releases small lignin fragments.)

3.2 Chlorination By-Products: Identification and Formation Mechanisms

3.2.1 Chlorination of Lignin and Lignin Model Compounds

Much of the literature dealing with lignin chlorination involves pulp bleaching conditions as mentioned above.

Rapson et al. (1980) demonstrated that chlorination of lignin separated from ground wood formed mutagenic compounds. Thus lignin rather than carbohydrates or extractives was determined to be the main source of mutagenicity of chlorinated ground wood pulp. Acetovanillone almost duplicated the mutagenicity of softwood pulp when chlorinated under similar conditions. Lignin model compounds and phenols were chlorinated in aqueous solution with up to 32 equivalents of chlorine per mole of compound. Plots of mutagenicity versus equivalents of chlorine per mole of substrate show evidence of mutagen formation and destruction (or possible toxicity formation). Different mutagen formation mechanisms were thus suggested for phenols involving aromatic compounds at low chlorine ratios and aliphatic compounds from ring fracture at higher chlorine ratios.

Pierce (1978) in a review of aqueous chlorination of organic compounds defined the probable modes of reaction between chlorine and the phenyl propane unit of lignin. These include addition, oxidation and electrophilic displacement of the side chain, electrophilic substitution in the aromatic nucleus, oxidative ring cleavage and demethylation of the methoxy function. The chlorinated derivatives of these reactions would likely include chloroguaiacols, chlorocatechols, cholorobenzoquinones, chloromuconic acids and a variety of chlorinated aliphatics such as chloroform, ketones and aliphatic acids.

Lignin model compounds which contain specific moieties present in the lignin macromolecule have been used in an attempt to clarify mutagen formation (Rapson et al.,

1980) and chlorination mechanism. Model compounds used in mechanistic studies have included guaiacol, vanillin, and syringyl alcohol as summarized by Pierce (1978), and acetovanillone (Johnson, 1991).

Johnson (1991) characterized the by-products formed upon the chlorination of acetovanillone at Cl_2:compound (mole) ratios from 1:1 to 6:1. Initial reaction products (1:1 dose) identified were chloro- aceto-vanillones, catechols, guaiacols and o-benzoquinones. At higher chlorine doses (3:1) the initial products displayed further reaction producing different compounds. The 6-membered ring remained intact but hydrolysis of chlorine from these products resulted in mono-chlorinated derivatives. At the highest doses ($\geq$ 4:1) ring fracture compounds predominate and were responsible for the increased mutagenicity of these solutions. The ring fracture compounds include chloroacetones in the neutral fraction and chloroketoacids in the polar acid fraction. The polar ketoacids appeared to be the major source of mutagenicity.

Norwood et al. (1980) studied the chlorination of various model compounds including the lignin model 4-hydroxy-3-methoxycinnamic acid (ferulic acid). At a Cl_2:C ratio of 1.71 (17.1 Cl_2:ferulic acid) 0.109 moles of chloroform were produced per mole of ferulic acid. At a ratio of 5:1 Cl_2:ferulic acid, mono and dichlorovinyl guaiacols, mono and dichloroferulic acid were identified reaction products. At a ratio of 20:1 Cl_2:ferulic acid, chloroform, dichloroacetic and trichloroacetic acid were identified.

Model compounds have also been used to study the formation of relatively minor constituents which have quite potent mutagenic properties such as compound MX. Holmbom et al. (1987) chlorinated various lignin model compounds including ferulic acid at pH 7 and a Cl_2: total organic carbon (TOC) dose of 1mg:1mg. Under these conditions 4 μg MX/g of ferulic acid were produced.

3.2.2 Chlorination of Humic Substances

Humic substances consist of high molecular weight, amorphous, acidic, organic compounds which occur ubiquitously in natural waters, as products of biological activity. Humic substances are divided into fulvic acids, humic acids and humins depending upon their solubility to acid and base. Fulvic acids predominate in natural surface waters with smaller amounts of humic acid also present (AWWA Committee Report, 1979). Fulvic acids are generally of lower molecular weight, contain more oxygen and carboxyl functional groups, but less carbon and nitrogen than humic substances (AWWA Committee Report, 1979).

Aquatic humic substances have been implicated as the precursors of chlorinated disinfection by-products such as trihalomethanes (Rook, 1977), chloroacids (Christman et al. 1983) and chloroketones (Coleman, 1984). As such precursors, their presence in waters receiving CTMP mill effluent will have a major influence in addressing the significance of a CTMP mill's potential impact upon drinking water quality. The brief review which follows will concentrate upon the relative abundance of the chlorinated by-products formed from humic substances at various reaction conditions, proposed mechanisms and the role of humic substance characteristics in chlorinated by-product formation.

Bruchet et al. (1990) demonstrated that the concentration of polyhydroxy aromatics was higher in humic fractions from terrestrial sources which explained their higher trihalomethane formation potential (THMFP). Changes in THMFP could thus be explained for seasonal differences and storm events which are associated with runoff.

Christman et al. (1983) found that chloroform, dichloroacetic acid, trichloroacetic acid and dichlorosuccinic acid were the major reaction products from the chlorination of an aquatic fulvic acid accounting for 53% of the total organic halogen (TOX) found. Reaction conditions were quite severe in terms of chlorine dose (4 moles HOCl/mole C) approximately ten times normal drinking water levels. It has been shown above that high chlorine doses favour the formation of ring fracture and highly chlorinated products.

Reckhow and Singer (1985) proposed a model for the formation of chloroform, trichloroacetic acid and dichloroacetic acid from fulvic acid. The model proposes that diketone moieties, which are formed from oxidation mechanisms, rapidly substitute with chlorine. Hydrolysis of these chloroketones forms dichloroacetic acid. Trichloromethyl species (ex. trichloroacetone) yield some chloroform and dichloroacetic acid. Trichloroacetic acid is formed when an oxidizable functional group is adjacent to the ketone function. Phosphate buffer was implicated in promoting trichloroacetone degradation.

Rechow et al. (1990) studied ten humic and fulvic acids for characterization and reaction with chlorine in terms of chlorine consumption and incorporation as well as by-product yield. Chlorine doses were higher than drinking water doses (≈ 4 mg Cl_2/mg C). Humic acids were found to be higher in nitrogen, aromatic carbon, and phenolic content. Fulvic acids were found to be richer in oxygen, aliphatic carbon, and carboxyl content. Humic acids produced more chloroform, TOX, trichloroacetic acid, dichloroacetic acid and dichloroacetonitrile. Yields as a percentage of TOX were more similar, however, trichloroacetic acid formation was favoured in humic solutions. Chlorine consumption was correlated with phenolic structures and aromatic amines which are termed activated aromatic centres. On average, 7.9 molecules of Cl_2 react with each activated aromatic centre. Chlorine incorporation was found to be a function of nitrogen content/chlorine consumption. Trichloroacetic acid formation was found to be related to highly conjugated precursors (perhaps trichloroacetyl derivatives which have reduced rates of hydrolysis). Chlorine incorporation was reduced at pH 12 relative to pH 7 perhaps due to the shift in protonation of the reactive species but more likely from base catalyzed hydrolysis of carbon-chlorine bonds. Chloroform was found in much greater quantity than trichloroacetic acid at pH 12, although total R-CCl_3 content remained constant. On the basis of the haloform reaction increased pH accelerates TOX and R-CCl_3 formation by increasing the stability of carbanions.

Norwood et al. (1987) characterized humic material and studied the relationship of phenolic content to chlorination mechanism. Aliphatic and substituted aromatic carbon constituted the majority of carbon in the particular fulvic acid studied. The major products of aqueous chlorination at pH 11 and a HOCl:C molar ratio of 2:1 were chloroform, dichloroacetic acid, trichloroacetic acid and other phenolic ring rupture compounds. Chemical degradation of an isolated fulvic acid yielded phenolic products with vanillyl and syringyl structures related to lignin. 3,5-dihydroxybenzoic acid was another phenolic compound produced in large amounts. This structure has been shown to undergo halogenation by a ring rupture mechanism to produce chloroform and other aliphatic chlorinated acids. Vanillyl phenol structures were least affected by reaction with chlorine at a HOCl:C molar ratio of 0.3:1 at pH 5-7. However, 3,5-dihydroxybenzoic acid and p-hydroxybenzaldehyde structures were much reduced by chlorination at these conditions. Although phenolic structures were implicated in organohalide generation, phenolic structures constitute a small portion of the total carbon.

Hanna et al. (1991) characterized five aquatic humic substances before and after chlorination. Carboxyl groups were prominent for unreacted and chlorinated humic substances. Chlorination caused a reduction in phenols, methoxyl carbon, aryl carbon and ketones and a relative increase in carbohydrate and alkyl carbon. Ketone and methoxyl functional groups were more reactive than oxygenated carbon which in turn is more reactive than other forms of aromatic carbon. Alkyl and carboxyl carbon have approximately equal reactivity with chlorine while carbohydrate carbon has the least reactivity. Methoxy substituted aromatics, phenols and aryl ketones were thus felt to be suitable model compounds for chlorination studies.

3.3 Summary

Effluents from bleached kraft mills have been well studied, and a large portion of the low molecular weight organochlorine compounds have been identified. In terms of their effects on drinking water, studies have dealt with aesthetic properties and mutagenicity rather than specific contaminants.

Effluents from TMP and CTMP mills have been studied in terms of effluent characterization for sum parameters such as BOD and COD as well as effluent treatment for receiving water quality parameters. Lignin solubilized by the pulping process is poorly treated in biological treatment.

The effects of TMP and CTMP mill effluents on drinking water quality because of their reaction with chlorine disinfectants have not been addressed.

A considerable potential number of chemical reactions between lignin and chlorine exist. Lignin and lignin model compound studies demonstrate this although most studies use kraft mill chlorine bleaching conditions (low pH and high chlorine dose) and are not directly applicable to drinking water treatment.

The high strength wastes from TMP and CTMP mills which contain a considerable amount of refractory organics such as lignin may thus have considerable potential for the formation of chlorination by-products when chlorinated under drinking water treatment plant conditions.

Humic substances have demonstrated a potential for producing numerous chlorination by-products and several reaction pathways suggested for their formation. The ubiquitous nature of humic substances in natural waters suggest that their contribution to chlorination by-products must be considered when assessing the effects of TMP and CTMP mills on drinking water treatment plants.

4.0 EXPERIMENTAL DESIGN

4.1 Selection of Model Compound and Analytes

Lignin is a complex biopolymer which is formed in plants by the enzyme-mediated polymerization of three substituted cinnamyl alcohols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol in ratios which are species dependant (Crawford, 1981). In the present study, ferulic acid (4-hydroxy-3-methoxy cinnamic acid, Figure 1), which contains the guaiacol moiety prominent in both hardwood and softwood lignins as well as a propyl substituent similar to that found in various linkages between lignin constituents, is used as a lignin model compound. The use of a model compound for a chlorination study simplifies analysis by promoting the formation of low molecular weight compounds which are more likely to be biologically active while excluding the likely inactive high molecular weight compounds which complicate analysis. The use of a model compound with more limited reaction pathways also indicates possible effects of drinking water treatment conditions on chlorination by-product formation.

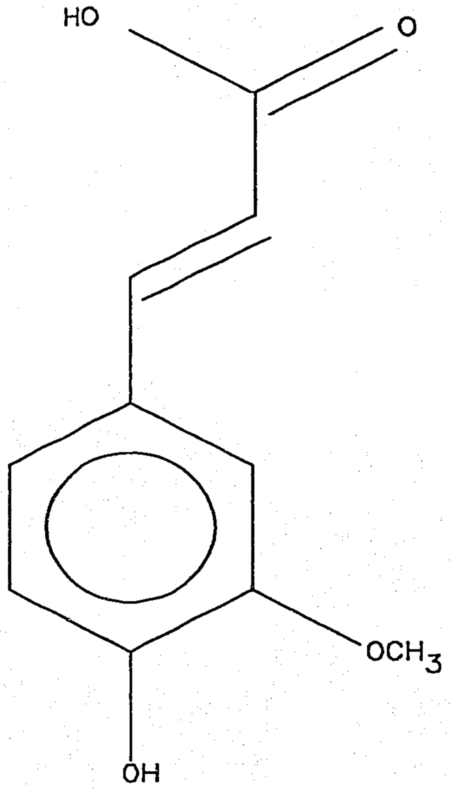


Figure 1. Ferulic Acid (4-hydroxy-3-methoxycinnamic acid)

The target analytes examined were restricted to those chlorination by-products identified in drinking waters, with measured aesthetic, mutagenic or carcinogenic properties, which are also likely to be formed from lignin precursors. These compounds have also been identified in kraft pulp mill effluents (Suntio et al., 1988, Kringstad and Lindstrom, 1984). The target analytes for this study and the rationale for their inclusion are summarized in Table 2.

Table 2. Target Analytes

Compound	Range of Drinking Water Concentrations (ug/L)	Toxicology/ Regulations
Chloroform	0.7 to 540[a]	MLE[b] 104 ug/L MCL TTHM[c] 80 ug/L
Dichloroacetic Acid	12 to 79[a]	MLE[b] 257 ug/L MCL HAA5[d] 60 ug/L
Trichloroacetic Acid	4 to 103[a]	MLE[b] 0.69 ug/L
Haloketones	--	bacterial mutagens
Chlorophenols	1 to 2[a]	aesthetic, weakly mutagenic, tumor promotors MAC[e] 5 ug/L
3-Chloro-4-(Dichloromethyl)-5-Hydroxy-2(5H)-Furanone (MX)	0.015 to 0.067[f] 0.02 to 0.061[g]	strong bacterial mutagen

Notes:

[a] from Bull and Kopfler, 1991.

[b] Maximum Likelihood Estimate at 10^{-6} level of cancer risk based on animal studies from Bull and Kopfler, 1991.

[c] Maximum Contaminant Levels for Total Trihalomethanes proposed under the Disinfection/Disinfection By-Product Rule from McGuire, 1993.

[d] Maximum Contaminant Levels for mono-, di-, and tri-chloroacetic acids and mono- and di-bromoacetic acids proposed under the Disinfection/Disinfection By-Product Rule from McGuire, 1993.

[e] Maximum Acceptable Concentration for 2,4,6-trichlorophenol from Guidelines for Canadian Drinking Water Quality, 1993.

[f] Kronberg et al., 1988.

[g] Hemming et al., 1986.

Regulations for carcinogens drinking water are based largely on carcinogenicity studies of laboratory animals. Chloroform has been shown to cause kidney tumors in rats when administered in drinking water at 400 mg/L (40 mg/kg per day time weighted average dose) (Jorgenson et al., 1985). Dichloroacetic acid and trichloroacetic acid have been shown to cause liver tumors in mice at 300 mg/L (60 mg/kg per day time weighted average dose) (Bull and Kopfler, 1991). 2,4,6-trichlorophenol has been shown to be an animal carcinogen but in addition, causes embryotoxic effects as do 2-chlorophenol and 2,4-dichlorophenol at drinking water concentrations of 3 mg/L (Exon and Koller, 1985). 2,4-chlorophenol has been demonstrated to depress the immune response at doses of 30 mg/L. Chlorophenols also have potent taste and odour properties. The aesthetic objective for 2,4,6-trichlorophenol is 2 µg/L (Health and Welfare Canada, 1993).

Various haloketones have been shown to be mutagenic and thus contribute to the mutagenicity of drinking waters (Bull and Kopfler, 1991). Compound MX is a powerful bacterial mutagen as well as a potent clastogen in mammalian cells (Meier et al., 1987) and is responsible for a large fraction of the mutagenicity in drinking water (Hemming et al., 1986).

4.2 Model Compound Study

A lignin model compound, ferulic acid was used to assess the role disinfection conditions will have upon disinfection by-product formation. In addition potential by-products from CTMP mills which may contain lignin and from waters containing lignin derived humics may be identified. Factors that were studied were suggested from a literature review and were: ferulic acid concentration, chlorine dose, pH and reaction time.

A two level factorial experiment (Box et al., 1978) was designed to assess the significance of these factors. Factorial designs require relatively few runs per experimental factor studied allowing the evaluation of a large number of factors. This experimental design allows the independent estimate of linear coefficients and their interactions in a regression equation indicating major trends and directions for future study. The coefficients in the regression represent the effect of changing the particular factor by one-half of the range studied. When the experimental levels are coded -1 and +1, they are equivalent to the change in predicted concentration from the intercept or '0' level in the regression equation. Coded experimental levels allow the direct comparison of experimental factors independent of the units of each factor. This design allows the development of a central composite design (Box et al., 1978) if it is deemed necessary to estimate higher order coefficients. In fact, midpoints at the 0 level (3.5 mg TOC, 4:1 Cl_2:ferulic acid ratio, pH 7.5, 16 hours) were replicated, but were used only to estimate experimental variance and intercepts. Experimental levels are summarized in Table 3.

Table 3. Model Compound Experimental Levels

Factor	Level	
	low (-)	high (+)
Ferulic acid (mg TOC/L)	2	5
Chlorine dose moles Cl_2/mole ferulic acid	2:1	6:1
pH	6	9
Log [time (hours)] Actual time	0.204 (1.6)	2.204 (160)

Ferulic acid concentration was selected to yield dissolved carbon concentrations of 2 and 5 mg/L which are typical of humic drinking waters. After measuring the chlorine demand of the ferulic acid, initial chlorine dose was varied on a molar ratio basis of Cl_2:ferulic acid from 2:1 to 6:1. The lower level is equivalent to 1.2 mg Cl_2/mg C which again approximates drinking water treatment levels. The upper level was chosen to examine the variation in reaction mechanism which would likely occur at higher chlorine doses. pH was varied between 6 and 9 which is the range of pH likely to be encountered in drinking waters. Finally, reaction time was varied between 1.6 and 160 hours representing a minimal residence time within the treatment plant and a residence time of nearly seven days likely to be encountered within a relatively large distribution system.

The experimental design chosen, results in 16 trials (2^4 design) if all of the first order effects and their interactions are calculated. The experiments were run in two experimental blocks (due to reagent stability and volume considerations) using the fourth order interaction as the blocking variable. The coded experimental levels, blocking, and run order for each trial are summarized in Table 4.

Reagent blanks in laboratory water were run in triplicate.

Table 4. Model Compound Experimental Design

Trial No.	Run No.	Ferulic Acid	Cl_2 Dose	pH	Time
BLOCK NO. 1					
1	10	-	-	-	-
2	3	+	+	-	-
3	8	+	-	+	-
4	12	-	+	+	-
5	2	+	-	-	+
6	1	-	+	-	+
7	4	-	-	+	+
8	6	+	+	+	+
9	5	0	0	0	0
10	11	0	0	0	0
11	9	0	0	0	0
12	7	0	0	0	0
BLOCK NO. 2					
13	16	+	-	-	-
14	24	-	+	-	-
15	19	-	-	+	-
16	22	+	+	+	-
17	14	-	-	-	+
18	18	+	+	-	+
19	20	+	-	+	+
20	13	-	+	+	+
21	15	0	0	0	0
22	17	0	0	0	0
23	23	0	0	0	0
24	21	0	0	0	0

4.3 TMP/CTMP Effluents Study

In this study, actual TMP and CTMP mill effluents diluted in natural waters were chlorinated at levels which ensured the maintenance of a small concentration of free residual chlorine (≤0.5 mg/L) after 20 hours. This study was designed to identify and characterize specific disinfection by-products with measured health effects and so assess the potential impact of TMP/CTMP mills on drinking water treatment when diluted in various qualities of river water. Experimental factors examined were mill process, effluent concentration and river water source. Experimental levels are summarized in Table 5.

Table 5. TMP/CTMP Mill Effluent Experimental Levels

Factor	Level	
	low (-)	high (+)
Mill process	TMP	CTMP
Effluent concentration (volume %)	0.5	3.0
Receiving water quality	glacial, upstream	humic, tributary

The different mill processes were chosen upon the basis of pulping processes which dissolve different amounts of organic materials from wood. Effluent concentrations were chosen that might represent likely concentrations based on varying receiving water flow and not necessarily upon actual conditions within the river basin receiving these effluents. However, the 0.5 volume % concentration of mill effluent is not atypical for drinking water treatment plants in other localities receiving pulp mill effluents and is lower than other laboratory studies. (See for example Wigilius et al., 1988.) Receiving water quality was varied by obtaining glacial river water upstream of any pulp mill discharges and water from a humic-laden tributary of this river unaffected by pulp mill discharges.

The effluent experiments were run in two blocks as above. The coded experimental levels, blocking, and run order for each trial are summarized in Table 6.

The two river water samples, without effluent, were also tested.

Table 6. TMP/CTMP Mill Effluent Experimental Design

Trial No.	Run No.	Block No.	Mill Process	Effluent Concentration	Receiving Water Quality
1	3	1	-	-	-
2	6	2	+	-	-
3	8	2	-	+	-
4	4	1	+	+	-
5	7	2	-	-	+
6	5	1	+	-	+
7	2	1	-	+	+
8	9	2	+	+	+
9	1	1	0	0	0
10	10	2	0	0	0
11	11	2	0	0	0

5.0 MATERIALS AND METHODS

5.1 Model Compound Experiments

5.1.1 Materials

The following materials were used in the model compound chlorination experiments:

1) Laboratory Water (reverse osmosis, deionized, distilled, circulated through a Barnstead NanoPure II system with dual organic removal cartridges and a single high purity deionizing cartridge and final filtration to 0.2 microns).

2) 4-Hydroxy-3-methoxycinnamic acid (99% purity, Aldrich Chemical) recrystallized from hot laboratory water and dried in a vacuum dessicator over silica gel prior to use.

3) Sodium bicarbonate (Fisher Scientific, Certified ACS Grade).
4) Sodium carbonate decahydrate (BDH Chemicals Ltd., Analar Grade).
5) Sulphuric acid (BDH Chemicals Ltd., Analar Grade).
6) Sodium hypochlorite (BDH Chemicals Ltd., 5% available chlorine).
7) One liter (nominal capacity) amber bottles (Eagle Picher Environmental Services, cleaned and residue analyzed at factory to meet United States Environmental Protection Agency pesticide, and base/neutral/acid specifications for low concentration water for organics analysis (Document Number OLCO1.0)).

Actual bottle volumes were measured to contain 1.055 litres and stock solutions were accordingly adjusted to facilitate dispensing. Stock solutions of ferulic acid were prepared containing 0.3414g of ferulic acid in one liter of laboratory water and adjusted to pH 5 with 0.1 N sodium hydroxide (BDH Chemicals Ltd.). Stock solutions of sodium hypochlorite were prepared to contain 5.275 mg Cl_2/mL and 1.055 mg Cl_2/mL by diluting the reagent solution and standardizing according to Standard Method 5710 B. (APHA-AWWA-WPCF, 1989). The 1.055 mg Cl_2/mL NaOCl solution was pH adjusted to 9.5 with 0.1 N sulphuric acid and prepared fresh weekly. Stock solutions of sodium bicarbonate and sodium carbonate were prepared fresh for each block of experiments and contained 84.4 mmoles/L and 2.11 mmoles/L respectively. Carbonate buffers are most common in natural waters and were used to set pH conditions for these experiments to avoid any bias in by-product formation as has been noted in previous studies with phosphate buffers. The appropriate mixture of salt and acid producing the appropriate pH for each experimental level may be calculated from the formula:

$$pH = pKa + \log[salt]/[acid] \quad (1)$$

or

$$[H^+]/Ka = [salt]/[acid] \quad (2)$$

where pKa is the log of the dissociation constant for the acid and $[H^+]$, [acid] and [salt] refer to the hydrogen ion, acid and conjugate base of the acid concentrations respectively in moles/litre.

5.1.2 Chlorination Methods

The chlorine demand of a ferulic acid solution containing 5 mg of TOC was determined according to Standard Method 5710 B. (APHA-AWWA-WPCF, 1989) with the following modifications. Sample volumes were one litre, chlorine dose was 30 mg/L and reaction times were varied between 0.5 and 2.5 hours.

The chlorination experiments were carried out according to the following procedure. Each experimental trial was prepared in three one litre amber bottles for subsequent acidic, phenolic and base neutral extractions. To 800 mL of laboratory water, were added 4 mmoles of sodium bicarbonate with gentle stirring (from a 50 mm teflon coated magnetic stir bar), followed by sufficient 0.02 N sulphuric acid or sodium carbonate solution to adjust the pH to the required experimental condition. Ferulic acid was then dispensed and allowed to mix briefly before adding the required amount of 1.055 mg Cl_2/mL NaOCl solution, again with stirring. The bottle was immediately filled with laboratory water and sealed with a teflon cap ensuring that no head space was present. Samples were mixed for 15 minutes further before placing in a darkened environmental chamber (Tabai Espec Corporation Model PLI6) at 20.0°C for the designed reaction time.

5.1.3 Sample Extraction and Analysis

Upon completion of reaction, 40 mL samples were taken immediately from each trial and submitted for analysis of volatile non-polar organics utilizing purge and trap extraction and capillary gas chromatography/mass spectroscopy (GC/MS) according to Alberta Environmental Centre (AEC) Method No. A102.1 (Alberta Environmental Centre, 1992). Quantification of target compounds was achieved using selected characteristic fragment ions (termed selected ion monitoring SIM). Total ion chromatograms were also recorded (in scan mode) which permitted the detection and tentative identification of unknown compounds. Instrumental analysis and quantification of chloroform was performed by technical staff at the Alberta Environmental Centre.

Acid extractions were performed within the amber bottle using a stir bar method based on AEC Standard Operating Procedure SA06.0 (Alberta Environmental Centre, 1992). Sample portions of 800 mL were spiked with 10 μg each, of mucochloric acid and mucobromic acid, acidified to pH <2, using 10 mL of 25% sulphuric acid, and immediately extracted for one hour with 100 mL of ethyl acetate (Fisher Scientific optima grade). The organic phase was separated and the aqueous phase re-extracted as above. A third extraction was then made using 50 mL of ethyl acetate. Ethyl acetate solutions were combined and dried by passing through a filtering funnel containing ethyl acetate rinsed anhydrous granular sodium sulphate (Fisher Scientific ACS grade). The dried ethyl acetate was sealed in a glass stoppered flask with teflon tape and stored at 4°C until ready for further treatment. Ethyl acetate was removed using a vacuum rotary evaporator (Sybron Brinkman) operating at 40°C and 220 mbars of pressure leaving ≈ 1 mL of liquid. The ethyl acetate solution was transferred to a 4 mL reactivial before evaporating to near dryness under a gentle stream of ultra high purity nitrogen (Air Gas Canada). The residue was derivatized with 1 mL of nitrogen purged methanol (Fisher Scientific pesticide grade) containing 2 volume % of sulphuric acid at 70°C for one hour in a teflon sealed reactivial (Altech). Upon completion, the mixture was quenched with 2 mL of 2 wt.% sodium bicarbonate in laboratory water. The solution was extracted four times with 1.5 mL portions of hexane (Fisher Scientific pesticide grade) which were dried by passing through a pasteur pipette containing ≈ 1 g of anhydrous sodium sulphate. The hexane fraction was concentrated under a gentle stream of nitrogen to 1.00 mL in graduated centrifuge tube. 95μL were withdrawn and transferred to autosampler vial with glass insert along with 5μL of internal standard (containing 500 ng of 2,4,6-tribromophenol) and sealed with a crimp cap. This sample was stored at -18°C until submitted for chloroacid analysis. The remaining 905 μL was further concentrated to 95 μL in a conical autosampler vial under a gentle stream of nitrogen and internal standard added as above before sealing with a crimp cap. This sample was stored at -18°C until submitted for chlorofuranone analysis.

Submitted acid and chlorofuranone samples were analyzed in SIM mode using a Hewlett Packard 5970 mass selective detector (MSD) coupled to a Hewlett Packard 5890 GC. The GC column was a 30 meter J&W DB1 (0.20 mm id, 25 μm film thickness) fused silica capillary column coupled directly to the mass spectrometer. GC-MSD conditions were: carrier gas, helium (inlet pressure 103 kPa); splitless injection with th injector at 285°C; GC oven at 50°C initially and after 5 min. heated to 100°C at a rat of 12.5°C/min., followed by heating to 150°C at a rate of 2.5°C/min., and finally heate to 285°C at a rate of 7.5°C/min. Total run time was 47 min. The GC interphas temperature was 285°C.

Acids and chlorofuranones were identified by retention time and 3 characteristi fragment ions. Quantitation and confirmation ions are given in Table 7.

Table 7. Characteristic Ions for Acids and Chlorofuranones

Compound[a]	Quantification Ion	Confirmation Ions	
Dichloroacetic Acid	59	82.95	84.95
Trichloroacetic Acid	116.90	118.90	81.95
Mucochloric Acid	150.90	152.90	146.95
Mucobromic Acid	240.80	190.90	192.90
MX	146.90	200.90	202.90
2,4,6-tribromophenol	329.80	331.80	

[a] acids and MX as methyl esters, 2,4,6-tribromophenol was acetylated.

Analytes were quantified using the internal standard employing a log/log relativ response curve. Acid standards were prepared over several orders of concentration froi 50 to 50,000 ng/mL from sodium dichloroacetic acid (Aldrich 98%) and sodiui trichloroacetic acid (Aldrich 97%) which were derivatized according to the methylatic procedure described above and submitted with the samples for analysis. Chloroaci standards also contained derivatized mucochloric and mucobromic surrogates, representin 40% to 100% recovery of the 10 μg portions originally spiked, and equivalent portioi of the internal standard. Chloroacids and compound MX concentrations were correcte accounting for the recovery of these surrogates.

A sample of derivatized compound MX (60% purity) was obtained from Ms. Susan Andrews, Department of Civil Engineering, University of Alberta and standards prepared in the range of 275 to 1350 ng/mL.

Instrumental analyses of chloroacids and chlorofuranones were performed by technical staff at the Alberta Environmental Centre which permitted the quantification of the target compounds and surrogate recovery using supplied standards.

Chlorophenolics were acetylated in situ according to AEC Method No. AE130.0 (Alberta Environmental Centre, 1992) and extracted with methyl t-butyl ether (BDH Canada Ltd.) according to AEC Standard Operating Procedure SA06.0. This method was designed to identify and quantify bleached kraft mill target analytes including chlorinated phenols, guaiacols, catechols and veratroles. Following concentration and solvent exchange the samples were submitted for analysis by technical staff of the Alberta Environmental Centre using capillary GC/MSD with the MSD operating in the SIM mode.

Separate portions of the acid and phenolic extracts were analyzed using technical staff at the Alberta Environmental Centre using a Hewlett Packard 5987 GC/MS operating in the scan mode permitting the identification of additional acidic and phenolic chlorination products. Instrument conditions for this analysis are given in AEC Method No. A105.1 (Alberta Environmental Centre, 1992).

Base/neutral extractions were performed within the amber bottle using a stir bar method based on AEC Standard Operating Procedure SA06.0 (Alberta Environmental Centre, 1992). Sample portions of 800 mL were spiked with base neutral surrogates of AEC Method No. A105.1 (Alberta Environmental Centre, 1992), the pH adjusted to pH $\geq$ 11 with 10 mL of 75% sodium carbonate solution, and immediately extracted for one hour with 100 mL of hexane (Fisher Scientific pesticide grade). The organic phase was separated and the aqueous phase re-extracted twice, as above. The dried hexane solution was sealed in a glass stoppered flask sealed with teflon tape and stored at 4°C until further treatment. Hexane was removed using a vacuum rotary evaporator operating at 40°C and 340 mbars of pressure leaving $\approx$ 3 mL of liquid. The hexane solution was transferred to a graduated centrifuge tube and further concentrated to 1 mL under a gentle stream of ultra high purity nitrogen. The hexane extracts were then analyzed according to AEC Method No. A105.1 (Alberta Environmental Centre, 1992) by technical staff of the Alberta Environmental Centre recording only the GC/MS data in scan mode.

5.2 Pulp Mill Effluent Studies

5.2.1 Sources of Effluents and River Water

The biologically treated effluents from two pulp mills located within and near the town of Whitecourt were included in this study.

The Alberta Newsprint Company mill is currently operated as a TMP mill using spruce and lodgepole pine supplied largely from wood chips produced by area sawmills. Hydrosulphite "brightening" (reductive bleaching) of the pulp which is used for newsprint is practised. Recycled paper has also made up a portion of the fibre supply. Raw water for the mill is obtained from the Athabasca River and is treated by alum for clarification purposes during summer and lime softening during winter months. The effluent treatment system consists of coarse screening, primary clarification, a dump pond to handle hydraulic surges to the clarifier, an aerated equalization basin, activated sludge basin, secondary clarification and an aerated polishing pond. Nutrient addition (ammonia in the activated sludge basin and phosphoric acid in the equalization basin), pH adjustment of the screened effluent with lime, and cooling or heating as required in the equalization pond are other features of this treatment system.

The Millar Western Pulp Ltd. mill is operated as a two line alkaline peroxide process (patent pending) CTMP mill processing whole logs as well as wood chips for the production of pulp used in a variety of products. One line uses softwood to produce pulp for tissue and paper towel production while the other uses aspen to produce pulp for writing sheets and coated paper. Raw water for the mill is obtained from the McLeod River and treated by alum coagulation in summer and lime softening in winter. Mill effluent is treated by screening, primary clarification, extended aeration activated sludge, and secondary clarification. Nutrient addition, effluent cooling as required and pH adjustment are additional features of this treatment system as well.

Samples of final treated effluent were obtained from the two mills on the same day on two occasions, May 27, and June 14, 1993 when the waste treatment systems had indicated stable operation for several weeks. Samples were collected from the final effluent sampling line after purging for two minutes. The sample bottles used for collection were 4 L amber solvent bottles that had contained pesticide grade methyl t-butyl ether and had been air dried until no solvent odour remained. Sample bottles were rinsed three times with effluent, filling ≈ 25% of the bottle volume for each rinse. pH and temperature of the effluent were recorded at this time. Three 4 L bottles were collected for study at AEC in Vegreville. Additional samples were collected and preserved according to AEC protocols (Alberta Environmental Centre, 1987) for characterization analysis at a commercial laboratory. Samples were stored on freezer packs in coolers and transported within 3 hours to the commercial laboratory and within four hours to refrigerated storage at AEC.

Two river waters were examined in this study, the Athabasca River, which is glacial in origin, sampled at Hinton Alberta, upstream of any pulp mill discharges, and the Sakwatamau River, a humic tributary of the Athabasca, unaffected by industrial discharge, sampled east of the bridge crossing on Highway 32 North.

Raw water from the Athabasca River which feeds the bleached kraft mill operated by Weldwood of Canada Ltd. was collected from the raw water sampling line. Samples were collected as above, although several weeks later on June 22, and July 29, 1993 due to local storm events and a laboratory accident which compromised the earlier sample. Six 4 L bottles of river water were collected for study at AEC as well as samples for characterization. Samples were transported within four hours to the commercial laboratory and five hours to storage at AEC.

The Sakwatamau River was sampled on the same days as the two pulp mills. Samples were taken in midstream, at a depth of 10 cm. Six 4 L bottles of river water were collected for study at AEC as well as samples for characterization.

Effluent and water characterization analyses were performed by Chemex Labs Alberta Inc. located in Edmonton, Alberta. Analytical methods are listed and cross referenced with the National Water Quality Data Base (NAQUADAT Code) in Appendix 1 along with precision and surrogate recovery measures.

Effluents and river waters were pressure filtered through laboratory water and sample rinsed glass fiber filters with 0.7 micron pore size using ultra high purity nitrogen. All glassware and stainless steel filtration devices were rinsed with pesticide grade methanol, dried, and rinsed with laboratory water and sample before use. Filtered samples were composited and stored in methanol rinsed and dried amber bottles without head space at 4°C.

Chlorine demand studies on effluents and river waters were performed on 100 mL samples in amber bottles without phosphate buffer. Chlorine doses were ≡ 50 mg/L and residual (total) chlorine was determined by an iodometric method, Standard Method 4500-Cl B. (APHA-AWWA-WPCF, 1989).

Additional chlorine determinations differentiating free and combined chlorine, were performed to determine suitable chlorine doses for chlorination by-product studies. These determinations were made using N,N-diethyl-p-phenylenediamine indicator and ferrous ammonium sulphate titrant (diluted to 1.00 mL ≡ 10 µg Cl as Cl_2) according to Standard Method 4500-Cl F. APHA-AWWA-WPCF, 1989).

5.2.2 Chlorination Methods

The chlorination experiments of effluents diluted in river waters were carried out according to the following procedure. Each experimental trial was prepared in two one litre amber bottles for subsequent acidic, phenolic and base neutral extractions. To 800 mL of river water, were added the appropriate volume of effluent with gentle stirring, followed by the addition of the required amount of 1.055 mg Cl_2/mL NaOCl solution, again with gentle stirring. The bottle was immediately filled with river water and sealed with a teflon cap ensuring that no head space was present. Samples were mixed for 15 minutes further before placing in a darkened environmental chamber (Tabai Espec Corporation Model PLI6) at 20.0°C for 20 hours.

5.2.3 Sample Extraction and Analysis

Upon completion of reaction, samples were immediately sampled for volatile non-polar organics. Residual free and combined chlorine were determined using Standard Method 4500-Cl F. (APHA-AWWA-WPCF, 1989) as described above. pH was also determined at this time using a Corning 135 pH meter calibrated at pH 7 and 10.

Acid extractions were run on 800 mL samples as above but with only mucochloric acid used as an extraction analysis surrogate. Ethyl acetate extracts were spiked with mucobromic acid which was used as an analytical surrogate. Ethyl acetate extracts were taken to dryness only within the reactivial rather than in a concentration vessel as done previously. This eliminated the necessity of redissolving the dried residue into methanol and transferring to the reactivial.

Chlorophenolic extracts were prepared as above but with reduced sample size (500 mL).

Base/neutral extracts were prepared as above but with 400 mL sample sizes and methyl t-butyl ether used as the extractant in an attempt to examine for the presence of polar compounds. Extracts were concentrated in a Kuderna Danish apparatus at 70°C and solvent exchanged with isooctane as per AEC Method 130.0 (Alberta Environmental Centre, 1992).

5.2.4 Total Organic Halogen Analysis

TOX was determined for the glacial river water, trial 3 and trial 4 in the following manner. Non-purgeable adsorbable organic halide (NPAOX) was determined according to AEC Method No. AE128.1 (Alberta Environmental Centre, 1992) on samples purged with nitrogen. An aliquot of the original unpurged sample was submitted for the analysis of volatile non-polar organics according to AEC Method No. 102.1 (Alberta Environmental Centre, 1992). TOX was determined as the sum of NPAOX and volatile organic halides.

5.3 Statistical Analyses

Regression analyses and response surfaces were produced using methods contained in the regression and graphics subroutines of Number Cruncher Statistical System (NCSS) version 5.03 software (NCSS, 1992).

6.0 RESULTS AND DISCUSSION

6.1 Model Compound

6.1.1 Chlorine Demand of Ferulic Acid

Results from the experiment studying chlorine consumption as a function of time are shown in Figure 2. Chlorine consumption is expressed as moles of Cl_2 consumed per mole of ferulic acid. Chlorine determinations were performed in duplicate and the averages plotted. The experimental trial at 2.5 hours was replicated and used to estimate precision. The standard deviation at 2.5 hours was estimated to be 0.07 moles Cl_2 per mole of ferulic acid. Experimental data was analyzed by non-linear regression using a simple empirical model (forced through the origin) of the form $y = a+bX/(1+cX)$ where y is chlorine consumption as moles of Cl_2 per mole of ferulic acid, X is time in hours and a, b, and c are empirical constants. The model was not chosen to imply a mechanism, but only predict an "ultimate" chlorine demand. At long reaction times (large X), the model approaches a limiting value of b/c which is equivalent to the ultimate chlorine demand. This model is highly significant, $p<0.001$ and $R^2=0.999$). Chlorine demand appears to approach a limiting value of ≈8.1 moles of Cl_2 per mole of ferulic acid. After 2.5 hours, 7.93 moles of Cl_2 per mole of ferulic acid were consumed. This result compares favourably with the work of Rechow et al. (1990) who found that on average 7.9 molecules of Cl_2 react with each activated aromatic centre; in this case an aromatic phenolic group. After 30 minutes, in the experiments reported here, 7.21 moles of Cl_2 per mole of ferulic acid had reacted. This result confirms the earlier work of Norwood et al. (1980) who found that ferulic acid reaction with chlorine was rapid and that after 40 minutes, 7.63 moles of Cl_2 react with each mole of ferulic acid. The data indicates that the reaction between ferulic acid and chlorine is rapid under the experimental conditions of 25°C in the presence of phosphate buffer. The chlorine demand exerted within 0.5 hours is 91% of that exerted by 2.5 hours.

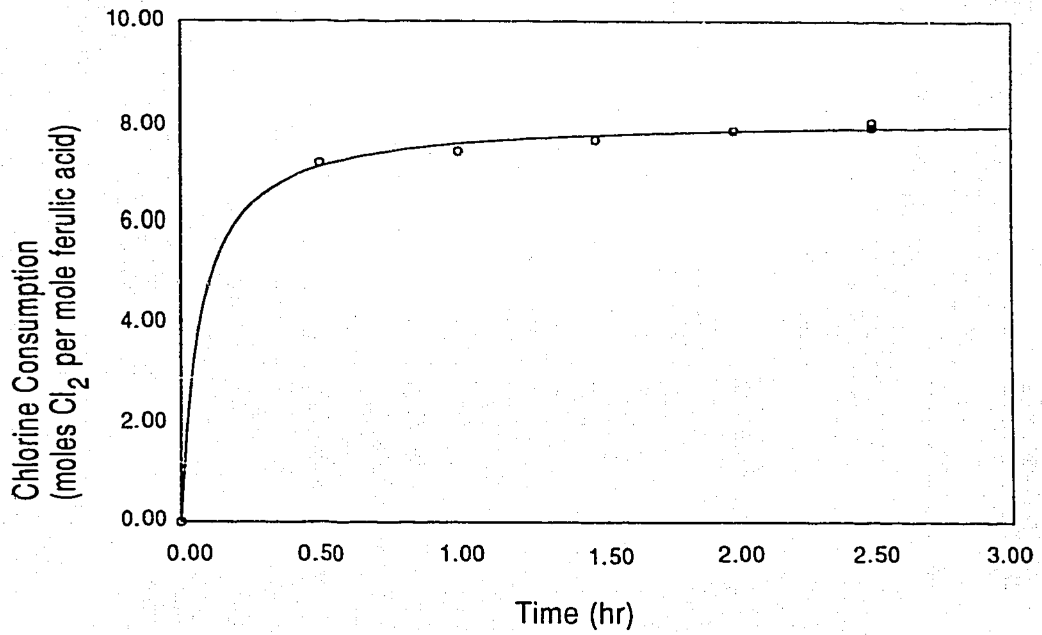


Figure 2. Chlorine consumption (moles Cl_2 per mole ferulic acid) vs. time.

6.1.2 Chlorination By-Products

In the model compound experiments, chlorine doses were varied between 2 and 6 moles of Cl_2 per mole of ferulic acid. The chlorine demand experiments indicate that minimal if any chlorine residual should be present under these conditions and in fact no chlorine residual was detected using the iodometric test. The destruction of chemical mutagens by dechlorinating agents is well known (Fielding and Horth, 1987) and so no chlorine quenching agents were added prior to acid and base/neutral extractions which may have introduced some bias in by-products detected. The volatile non-polar organics sample bottles had sodium thiosulphate which is routinely added to quench free chlorine. The chlorophenolic extraction involves the addition of ascorbic acid as an anti-oxidant, which introduces potential changes, in that quinones are detected as corresponding dihydroxy compounds.

Chloroform was the only by-product formed which was detected in the volatile non-polar organic analysis. Dichloroacetic acid, trichloroacetic acid, and compound MX were detected in the acid extracts. The analyses of chloroform, dichloroacetic acid, trichloroacetic acid, and compound MX are shown in Appendix 2, Table A2.1. The '0' level replicates of the target compounds indicate that the reproducibility of results measured as standard deviation varied from ± 4.8 µg/L for chloroform to ± 34.4 µg/L for dichloroacetic acid.

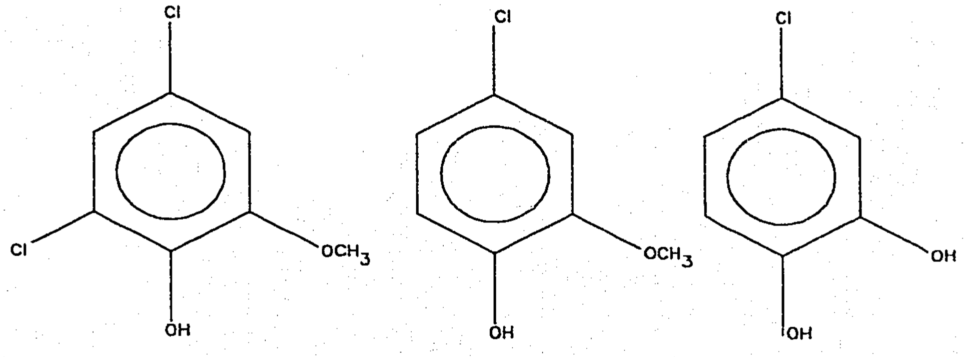
The standard deviation for trichloroacetic acid and compound MX was smaller ± 1.5 µg/L and 11 ng/L respectively.

Expressed as relative standard deviation, the reproducibility varies from 18% for chloroform to 56% for trichloroacetic acid.

This degree of variation is likely due to a number of experimental factors including mixing and analytical factors which propagate errors. Thus, the chloroacids and compound MX which require intensive sample preparation including extraction, concentration, derivatization, reextraction and additional concentration show poorer reproducibility than chloroform. The '0' level replicates are used in the estimates of error in subsequent regression analyses and are provided here only to provide a context for comparison of individual results.

With the exception of chlorovinylguaiacols, which were still extractable at pH 11, no compounds of significance were detected in the base/neutral extracts. This may have been due to inappropriate solvent polarity in that the products of chlorination are likely to be polar. Another reason could be due to analyte losses during concentration. This may explain why dichloroacetone, a polar volatile compound, was not detected in any of the extracts. Methyl t-butyl ether, a more polar solvent was used in subsequent effluent experiments.

In contrast the chlorophenolic extracts produced many chlorinated and oxidized by-products. Analytical results of clorophenolics associated with effluents from bleached kraft pulp mills are summarized in Appendix 2, Table A2.2. Only 4,6-dichloroguaiacol, 4-chloroguaiacol, and 4-chlorocatechol were produced in measurable amounts. Structures for these compounds in their underivatized form are shown in Figure 3.



4,6–Dichloroguaiacol
(46 DCG)

4–Chloroguaiacol
(4 CG)

4–Chlorocatechol
(4 CC)

Figure 3. Detected chlorophenolics associated with pulp and paper effluents.

The chlorophenolic extracts were also examined for major chlorination by-products by GC-MS operating in the scan mode. The substantial production of phenolic compounds is illustrated by a representative total ion chromatogram shown in Figure 4 and Table A2.3 in Appendix 2.

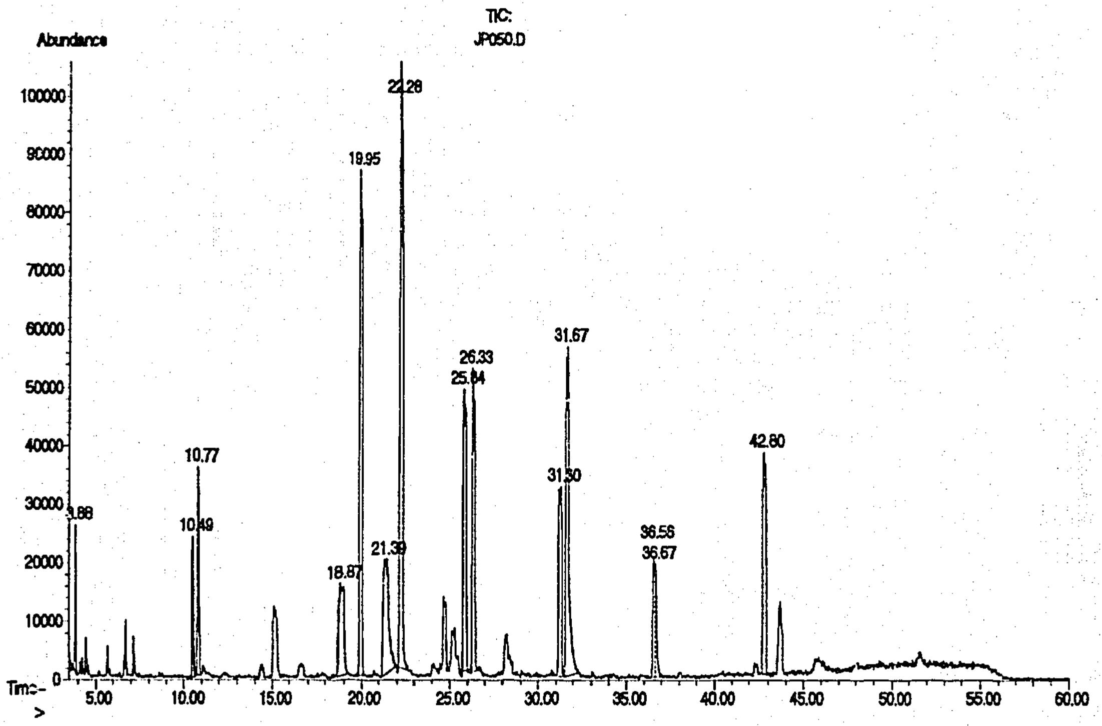
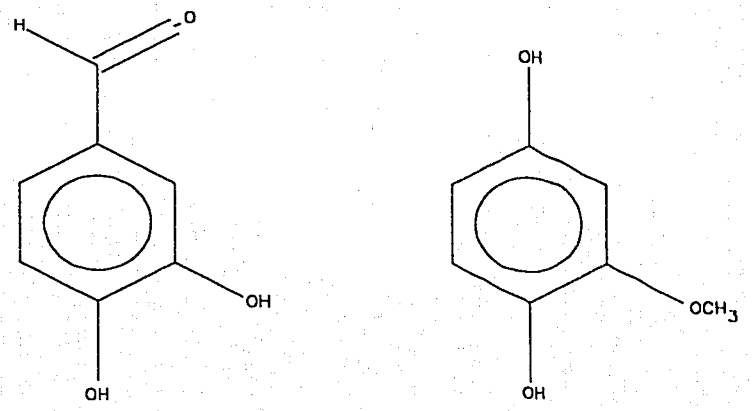


Figure 4. Total ion chromatogram of the acetylated phenolic extract from trial 16 illustrating the number of phenolic compounds produced from the chlorination of ferulic acid.

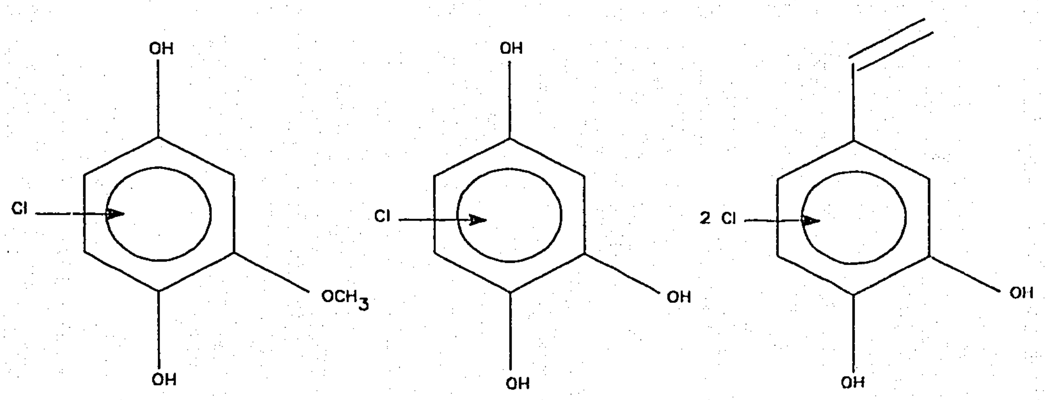
Total ion counts for 14 additional acetylated phenolic compounds are given in Appendix 2, Table A2.3. The total ion responses for acetylated 4,6-dichloroguaiacol, which was quantified with external standards, and phenanthrene which was used as an analytical internal standard for these extracts are included. Tentative structures for these compounds in their underivatized form are shown in Figures 5-8. Mass spectra and fragmentation pathways of the acetylated compounds which are congruous with the proposed structures are given in Appendix 3.



3,4-Dihydroxybenzaldehyde
(DiHybenz)

4-Hydroxyguaiacol
(HyG)

Figure 5. Proposed structures of dihydroxy and trihydroxy compounds.

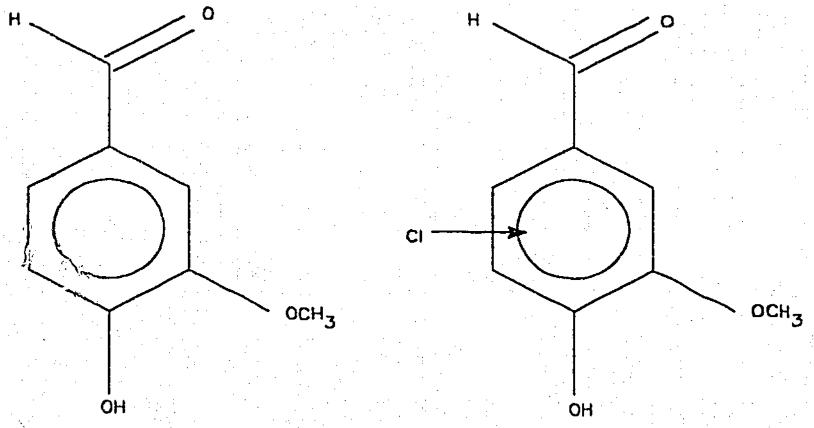


Chloro-4-hydroxyguaiacol
(ClHyG)

Chloro-1,2,4-benzenetriol
(Cltriol)

Dichloro-4-vinylcatechol
(DClVC)

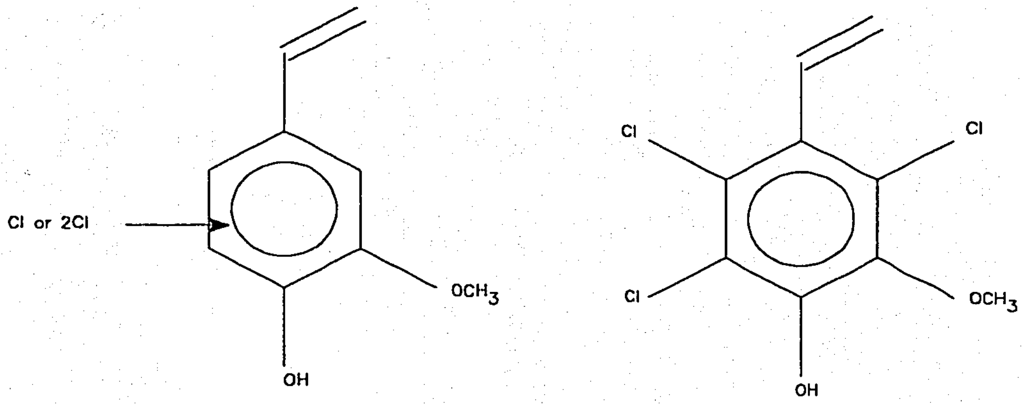
Figure 6. Proposed structures of chlorinated dihydroxy and trihydroxy compounds.



Vanillin

Chlorovanillin
(ClV)

Figure 7. Proposed structures of vanillin and chlorovanillin.



Chloro and Dichloro-4-vinylguaiacol
(ClVG and DClVG)

3,5,6-Trichloro-4-vinylguaiacol
(TClVG)

Figure 8. Proposed structures of chloro, dichloro, and trichloro-4-vinylguaiacol.

The proposed structures suggest that a variety of chemical reactions between ferulic acid and aqueous chlorine are possible. The carboxylic acid functional group and double bond of the side chain are potentially reactive with chlorine, as are the aromatic ring and methoxy functional group. Oxidative decarboxylation appears to be a common reaction mechanism among the phenolic compounds detected and that electrophilic substitution in the aromatic nucleus is also favoured.

The production of adehydes suggests that a form of retro-aldol reaction of the hydrolyzed double bond or perhaps a form of oxidative cleavage of the double bond present on the side chain occurs.

Possible reactions between ferulic acid and aqueous chlorine are summarized in Figure 9.

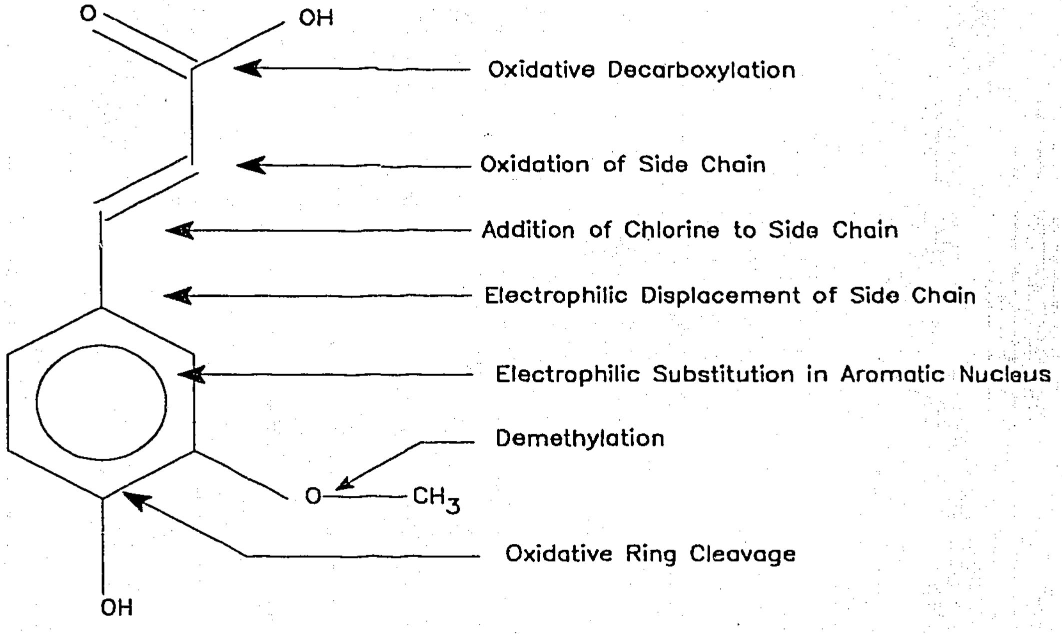


Figure 9. Summary of reactions possible between ferulic acid and aqueous chlorine.

The tentatively identified compounds include dihydroxy and trihydroxy compounds (3,4-dihydroxybenzaldehyde and 4-hydroxyguaiacol) as well as chlorinated dihydroxy and trihydroxy compounds (chloro-4-hydroxyguaiacol, chloro-1,2,4-benzenetriol and dichloro-4-vinylcatechol). These compounds may be residues of benzoquinones, produced as artifacts by ascorbic acid which is used in the chlorophenolic extraction to prevent oxidation of catechols. 3,4-Dihydroxybenzaldehyde was only detected in trial 14 (6:1 Cl_2 dose, pH 6 and 1.6 hours reaction time). 4-Hydroxyguaiacol was found only at 1.6 hours reaction time and pH 6. These compounds may exist only for a short time before further reaction.

Vanillin and two chlorovanillin isomers were also inferred to be present. The spectra of vanillin matched that of an external standard (Aldrich Chemical 99%). Chlorovanillin matched the literature spectra of 5-chlorovanillin produced by Hyötyläinen and Knuutinen (1993). Vanillin and chlorovanillins were produced under a larger variety of experimental conditions than the dihydroxy and trihydroxy compounds.

The compound 4,6-dichloroguaiacol was prominent in the chlorophenolic extracts, especially under the conditions of high chlorine dose and alkaline pH. The average production of 4,6-dichloroguaiacol in response to the various experimental factors is shown in Figure 10.

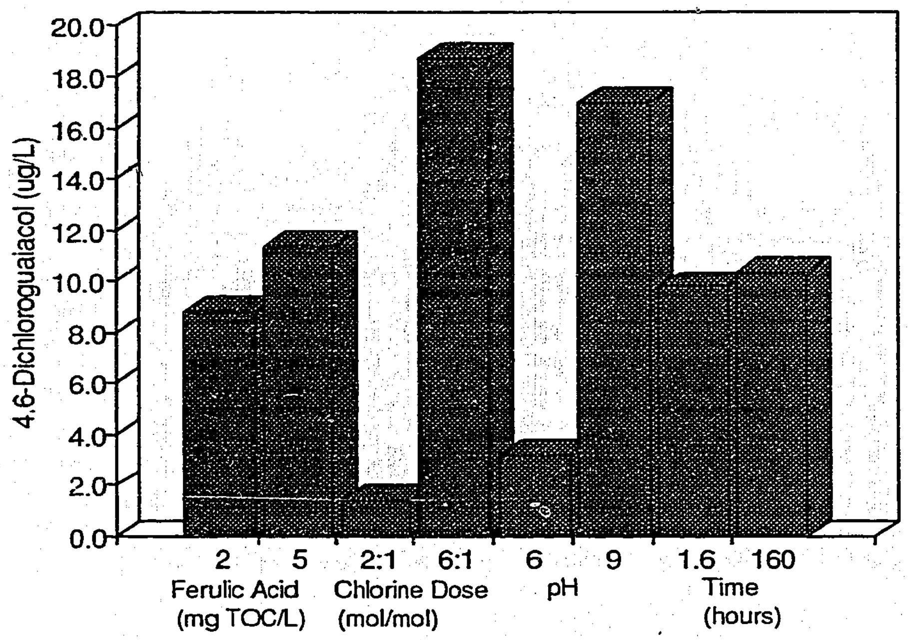


Figure 10. Average production of 4,6-dichloroguaiacol from ferulic acid at the experimental levels studied.

The results plotted for each of the levels of a given parameter (ex. 2:1 and 6:1 chlorine dose) include equal numbers of measurements made at both upper and lower levels of the other parameters (ferulic acid concentration, pH and time). Comparing the relative production of 4,6-dichloroguaiacol between levels of a common factor, represents the mean effect of that factor. For example, increasing chlorine dose from a 2:1 molar ratio (-1 level) to a 6:1 molar ratio (+1 level) increases the average production of 4,6-dichloroguaiacol from approximately 1.5 µg/L to 18.5 µg/L. Increasing pH has a similar large effect upon 4,6-dichloroguaiacol production while ferulic acid concentration and time have much smaller effects. The statistical significance of the apparent effects for the experimental factors studied will be discussed later. As mentioned previously, the value of the effect calculated by regression analysis represents the effect of increasing that factor from the '0' level to the +1 level as opposed to the effect of increasing the factor from the -1 to +1 level discussed above.

The presence of 4,6-dichloroguaiacol was confirmed with external standards in the pulp and paper chlorophenolics analysis. The 4,6-dichloroguaiacol may be produced by electrophilic aromatic substitution in the '6' position and electrophilic aromatic displacement of the side chain as proposed by Knuutinen (1984).

Two isomers each of mono and dichloro-4-vinylguaiacol were detected in large amounts relative to the production of other by-products. A compound identified as 3,5,6-trichloro-4-vinylguaiacol was also detected. The mass fragmentation spectra of these chloro-4-vinylguaiacols are analogous to the mass fragmentation of 4-vinylguaiacol (2-methoxy-4-vinylphenol) produced by Shibata et al. (1978). A common fragmentation pathway is suggested for all of these 4-vinylguaiacols shifted by 34 mass units for each chorine that substitutes for hydrogen. These compounds may be produced by oxidative decarboxylation and subsequent electrophilic aromatic substitution.

The chlorophenolic extracts were dominated by the presence of two compounds and their isomers tentatively identified as chloro-4-vinylguaiacol 1 and 2, and dichloro-4-vinylguaiacol 1 and 2. Although the exact position of chlorine substitution cannot be deduced from the mass spectra available, the hydroxyl substituent is ortho and para directing for electrophilic aromatic substitution. Thus the '6' (ortho) position which is unoccupied would be a likely position for substitution. The directing nature of the hydroxyl substituent may then also explain the observed ratio of the two isomers of monochloro-4-vinylguaiacol. The methoxyl group is also ortho and para directing which would activate the '3' and '5' position. Kinetic and steric considerations may in fact have a significant role to play in the relative amounts formed of the various isomers as well.

Suitable standards for the exact quantification of these compounds were not available commercially. If similar responses for total ion counts for similar acetylated compounds are assumed, than 4,6-dichloroguaiacol can be used to produce an approximate calibration for estimating the concentrations of other by-products. A linear regression of ln (46-DCG/phenan) vs. ln [46-DCG μg/L] for concentrations greater than 1 μg/L is highly significant ($p<0.001$, $R^2=0.794$). The estimated concentrations for the chloro-4-vinylguaiacols, dichloro-4-vinylguaiacols, and chlorovanillin 2 are shown in Appendix 2, Table A2.4. The production of the compounds produced in largest amounts, chloro-4-vinylguaiacol 2 and dichloro-4-vinylguaiacol 2, in response to the experimental factors studied, are summarized in Figures 11 and 12.

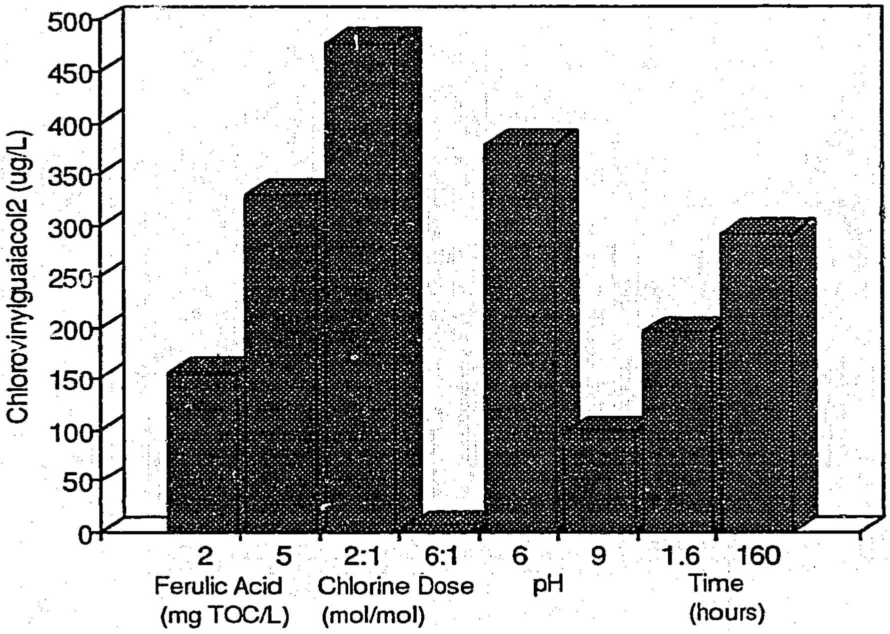


Figure 11. Average production of chloro-4-vinylguaiacol 2 from ferulic acid at the experimental levels studied.

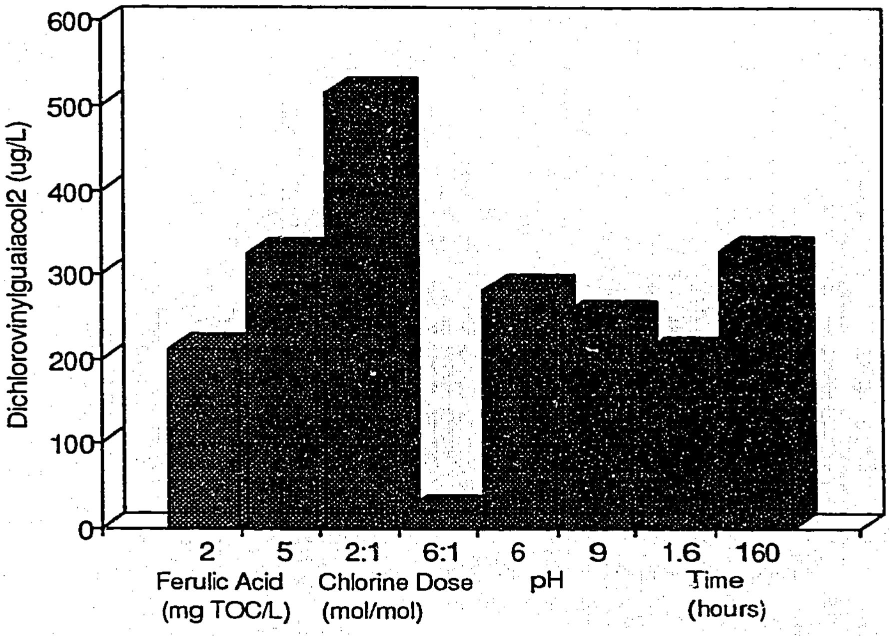


Figure 12. Average production of dichloro-4-vinylguaiacol 2 from ferulic acid at the experimental levels studied.

It is apparent that the chloro-4-vinylguaiacols are produced under low chlorine dose conditions which are much less than the chlorine demand. The formation of chloro-4-vinylguaiacol 2 also appears to be favoured at pH 6 while pH seems to have a much smaller effect on dichlorovinylguaiacol 2 formation. The response of chloro-4-vinylguaiacol to the experimental factors will be examined later in more detail by regression analysis. The five major chlorophenolic products account for up to 28 wt% of the TOC from ferulic acid originally added, as in trial 5 as shown in Table A2.4. The experimental conditions of trial 5 were ferulic acid 5 mg as TOC/L (equivalent to 41.7 µmoles/L), Cl_2 molar ratio of 2:1, (equivalent to 83.3 µmoles of Cl_2/L), pH 6 and time 160 hours. Figure 13 demonstrates that the highest production of chlorophenolics occurs at low chlorine doses. Regression analysis of chlorophenol production versus the experimental factors (described in detail below) indicates that the effect of chlorine dose is significant ($p<0.001$).

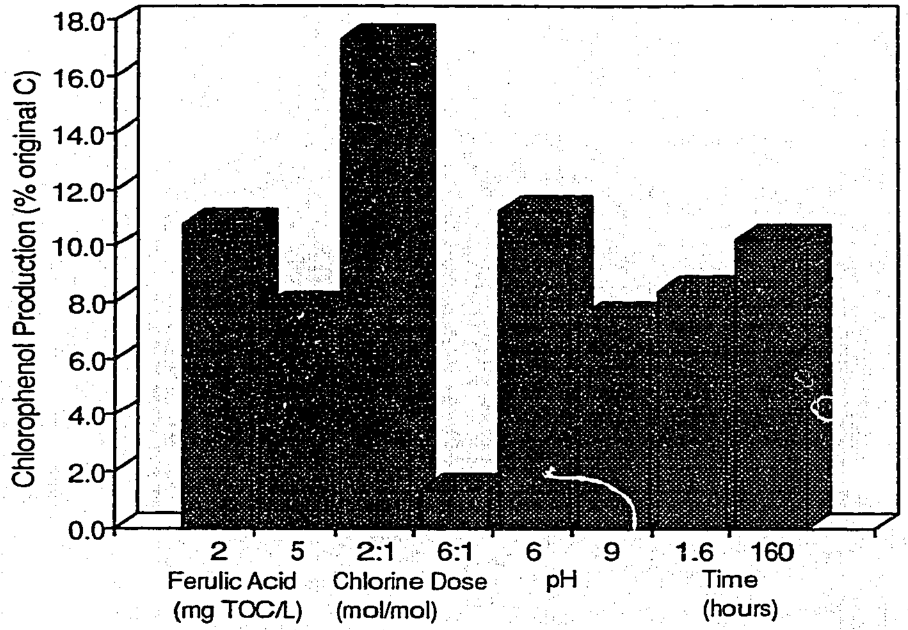


Figure 13. Average production of five major chlorophenolics expressed as a percentage of TOC from ferulic acid at the experimental levels studied.

Converting the products to µmoles (as the acetylated derivative) allows the estimation of per cent chlorine incorporated in these by-products. Table 8 summarizes these calculations for trials 1 and 5 which had the highest yield of the five major by-products based on ferulic acid. Approximately 20% of the chlorine added was incorporated into the five major by-products under the most favourable conditions.

Table 8. By-Product Chlorine Incorporation

Trial No.	Cl_2 Added (µmoles)	ClVG1 (µmoles)	ClVG2 (µmoles)	DClVG1 (µmoles)	DClVG2 (µmoles)	ClV2 (µmoles)	Cl Incorporated (µmoles)	Cl Incorporated %
1	33.3	0.16	2.24	0.22	1.61	0.04	6.10	18.3
5	83.3	0.77	6.45	0.56	3.61	0.13	15.69	18.8

Regression analyses examined the effects on concentration for chloro-4-vinylguaiacols, dichloro-4-vinylguaiacols and 4,6-dichloroguaiacol in μg/L (y), of the experimental factors of ferulic acid concentration (X1), Cl_2 ratio (X2), pH (X3) and (log) time (X4), including first order (bi) effects, second order (bij) and third order (bijk) interactions. A representative multiple regression analyses and analyses of variance report as generated by NCSS is included in Appendix 4. The results of fitting the polynomial model: $y=b_0+b_1X1+b_2X2+b_3X3+b_4X4+b_{12}X1X2+b_{13}X1X3+b_{14}X1X4+$
$b_{23}X2X3+b_{24}X2X4b_{34}X3X4+b_{123}X1X2X3+b_{124}X1X2X4+b_{234}X2X3X4$
are summarized in Appendix 5, Table A5.1.

A summary of the main effects only are shown in Table 9.

Table 9. Main Effects from Chlorophenolic Regression Analyses

Y	b_0	b_1	b_2	b_3	b_4
46-DCG	11.14	(1.06)	8.42	7.17	(0.060)
ClVG1	26.26	12.46	-27.35	-13.00	8.75
ClVG2	183.45	87.24	-236.08	-144.51	(48.05)
DClVG1	42.64	10.78	-24.45	(-2.93)	(8.14)
DClVG2	238.87	56.62	-247.64	(-15.27)	59.61

( ) Figures in brackets do not differ from 0 at $\alpha \leq 0.05$.

4,6-Dichloroguaiacol responds in a significant ($\alpha \leq 0.05$) and positive manner to both chlorine dose and pH. High chlorine dose and pH are experimental factors which favour oxidation. The speciation of chlorine at pH 9 is largely as the OCl^-, while the HOCl form predominates at pH 6. The OCl^- species has been implicated with reactions which are oxidative rather than substitutive. In addition the phenol substituent may be in the phenolate form at high pH which may activate the ring for electrophilic substitution. The interaction terms between ferulic acid and pH and chlorine dose and pH are also significant and positive in effect which would be expected if the conjectured changes in reaction mechanism are correct. A graphical representation of the regression response surface illustrating the effect of chlorine dose and pH at a ferulic acid concentration of 2 mg TOC/L and a reaction time of 160 hours is shown in Figure 14. The positive effects of chlorine dose and pH are apparent as are their interactive terms. The interaction term suggests that a high chlorine dose at pH 6 or conversely low chlorine dose at pH 9 would result in only minimal increases of 4,6-dichloroguaiacol.

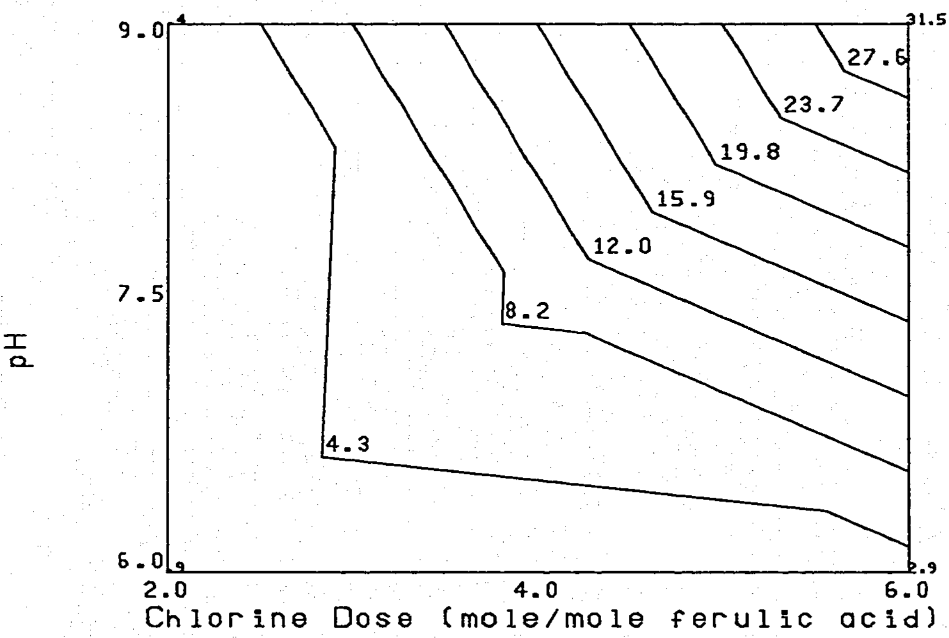


Figure 14. Response surface showing approximate contours of 4,6-dichloroguaiacol (μg/L) projected onto the pH chlorine dose plane at a ferulic acid concentration of 2 mg/L and time of 160 hours.

The behaviour of 4,6-dichloroguaiacol contrasts with the behaviour of chloro-4-vinylguaiacol 1 and chloro-4-vinylguaiacol 2 which respond in a significant and negative manner to chlorine dose and pH. Thus, low chlorine doses and pH 6 favours the production of chloro-4-vinylguaiacols. In Figure 15 is illustrated the effects of chlorine dose and pH as well as their interaction for chloro-4-vinylguaiacol 2. The interaction terms between ferulic acid and pH are negative as would be expected if the form of substrate was important in determining the nature of by-products. This is illustrated in Figure 16.

However, the chlorine dose and pH interaction terms are significant and positive in effect which is not expected if the form of the reactant governs the reaction mechanism. It may be that the form of the substrate may be more important than that of the reactant species.

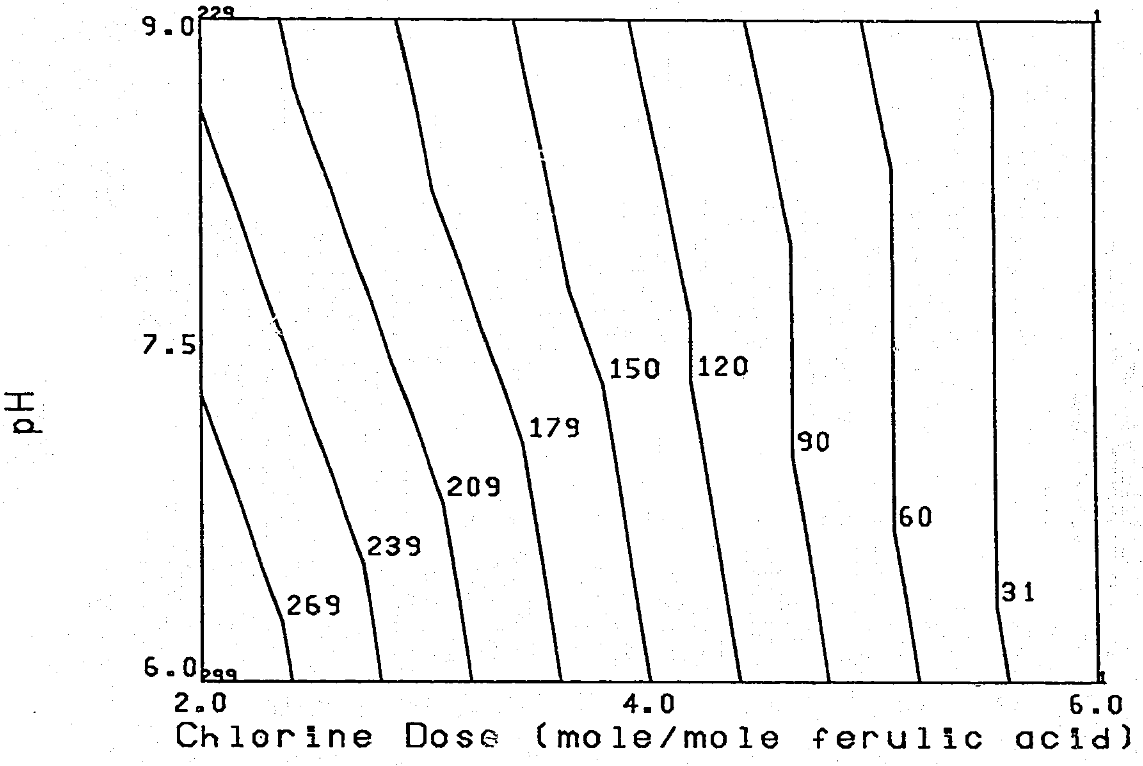


Figure 15. Response surface showing approximate contours of chloro-4-vinylguaiacol 2 (µg/L) projected onto the pH-chlorine dose plane at a ferulic acid concentration of 2 mg/L and time of 160 hours.

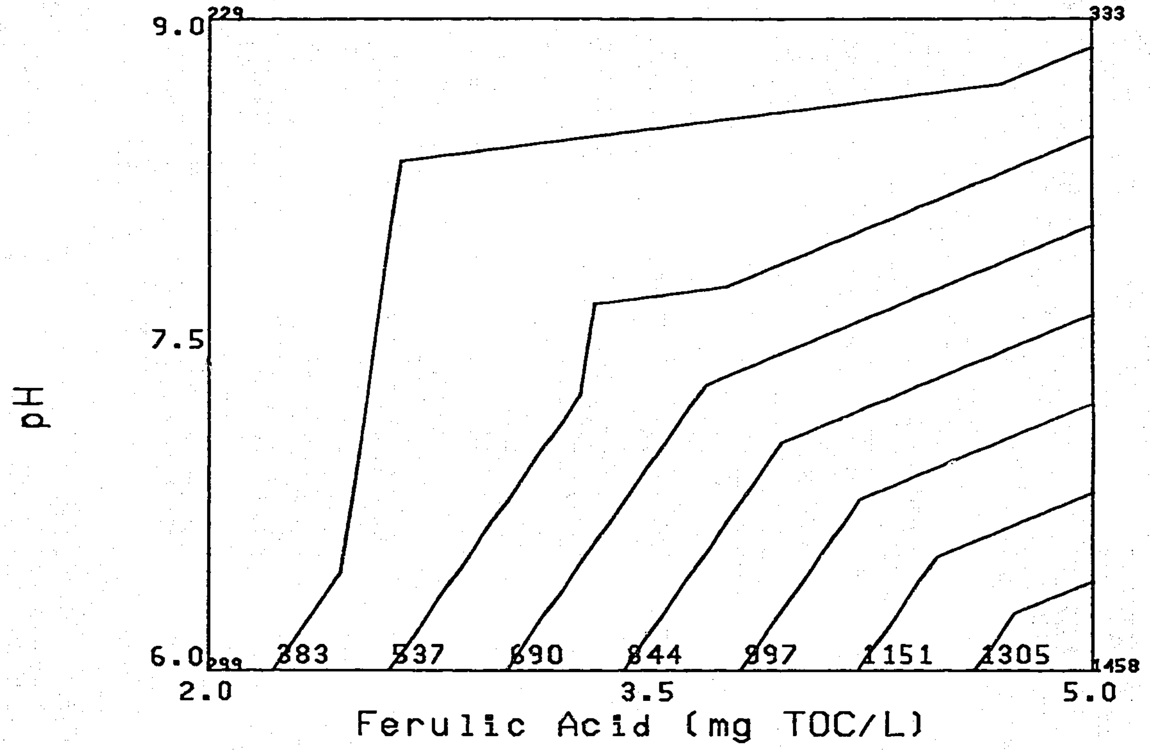


Figure 16. Response surface showing approximate contours of chloro-4-vinylguaiacol 2 (μg/L) projected onto the pH-ferulic acid plane at a chlorine dose of 2:1 and time of 160 hours.

The dichloro-4-vinylguaiacols respond in a manner similar to the chloro-4-vinylguaiacols in terms of ferulic acid concentration and chlorine dose, as shown in Table 9. The effects of chlorine dose and ferulic acid concentration are shown in Figure 17. As expected, increased ferulic acid concentration enhances dichloro-4-vinylguaiacol production while increasing chlorine dose reduces dichloro-4-vinylguaiacol concentrations. The effect of pH is not significant for the dichloro-4-vinylguaiacols.

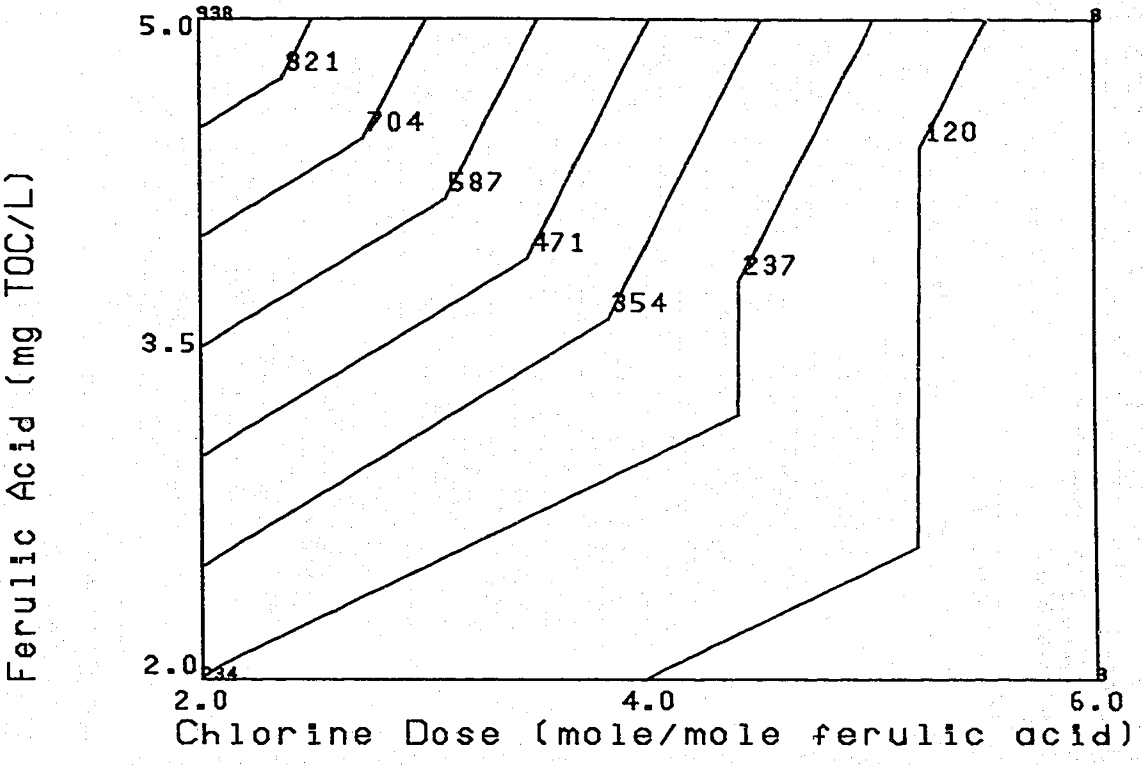


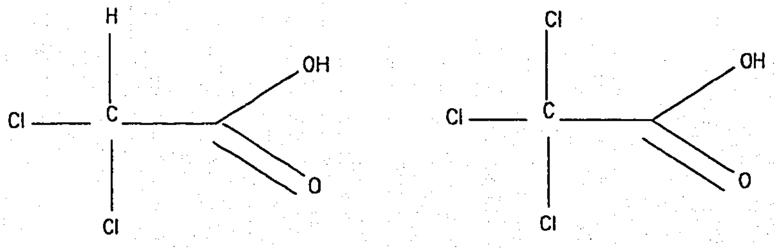
Figure 17. Response surface showing approximate contours of dichloro-4-vinylguaiacol 2 μg/L projected onto the chlorine dose-ferulic acid plane at a pH of 6 and time of 160 hours.

To summarize the effects of the experimental factors studied, it appears that the chloro and dichloro-4-vinylguaiacol production is increased by increased substrate concentration and decreased chlorine dose. pH has significant effects for chloro-4-vinylguaiacols. The effect of time is significant for some isomers but in general does not have the largest effect. The interaction terms of time and ferulic acid are positive and significant for chloro-4-vinylguaiacol 1, dichloro-4-vinylguaiacol 1 and dichloro-4-vinylguaiacol 2 which indicates that the reaction of ferulic acid and chlorine occurs to a significant extent after 1.6 hours. The interaction of time and chlorine dose are significant and negative in effect, perhaps indicating the occurrence of such reactions as alkaline hydrolysis, which would reduce the measured concentrations.

Different reaction mechanisms were suggested by the effects of chlorine dose and to a certain extent by pH. The substitution reactions appear to be favoured by low chlorine dose. Implications for drinking water treatment are suggested by the production of chlorophenolics at chlorine doses less than the chlorine demand. Utilities attempting to minimize chlorine doses or which practice prechlorination before organic removal may enhance the production of chlorophenolics which have potent taste and odour properties (Bull and Kopfler, 1991).

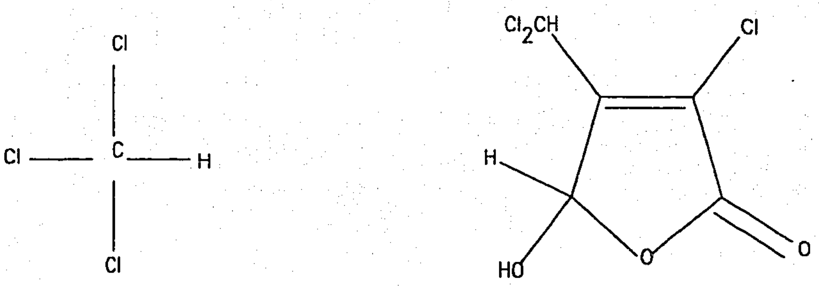
6.1.3 Target Analytes

The detected target compounds consisted of chloroform from the non-polar volatile organic analyses, and dichloroacetic acid, trichloroacetic acid and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone from the acid extracts. These compounds are illustrated in Figure 18.



Dichloroacetic Acid

Trichloroacetic Acid



Chloroform

3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone

Figure 18. Target compound structures.

Analytical results of the target compounds are summarized in Appendix 2, Table A2.1. Compound MX, dichloroacetic acid and trichloroacetic acid were corrected for recovery using the mucochloric acid surrogate. The concentrations of chloroform, trichloroacetic acid and compound MX are all within the ranges noted for treated drinking waters in Table 1. Dichloroacetic acid was occasionally produced in amounts lower and higher than those found in drinking waters.

The average production of chloroform and dichloroacetic acid in response to the experimental factors is shown in Figures 19 and 20 respectively.

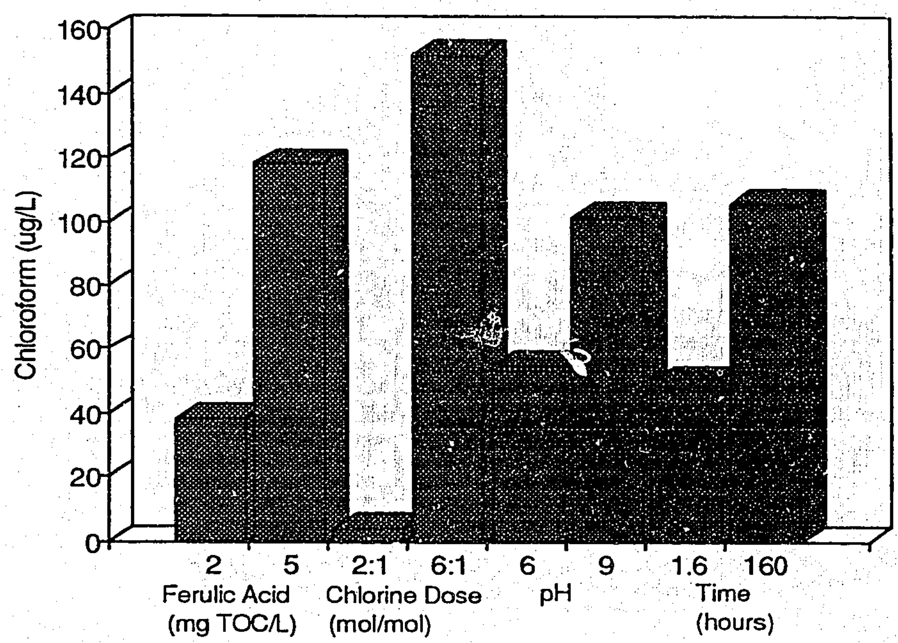


Figure 19. Average production of chloroform from ferulic acid at the experimental levels studied.

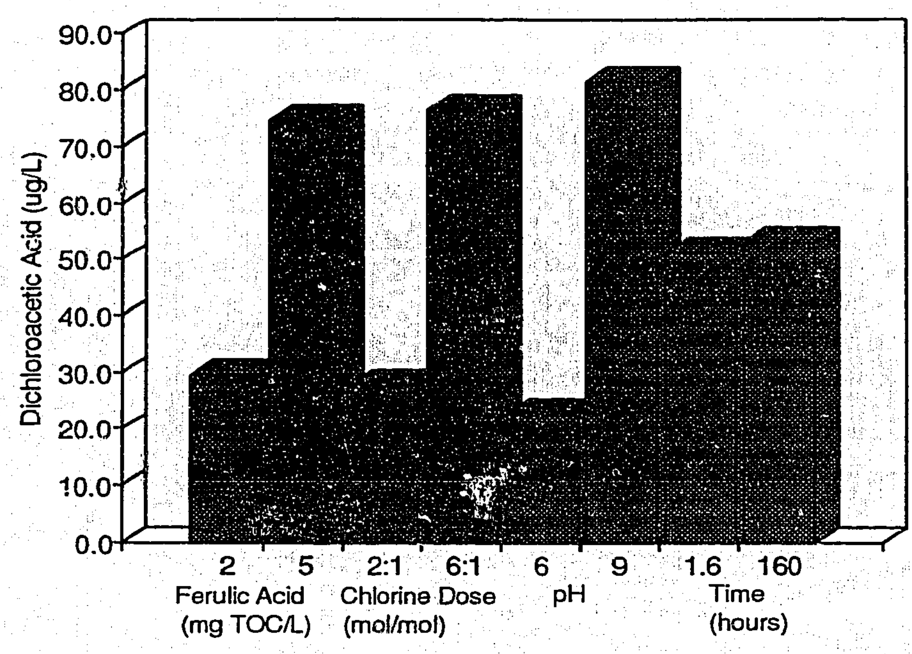


Figure 20. Average production of dichloroacetic acid from ferulic acid at the experimental levels studied.

The production of chloroform expressed as an average value at each experimental level shows that the largest increases are caused by chlorine dose and ferulic acid concentration. pH and time have smaller effects. For dichloroacetic acid pH appears to have the largest effect although only marginally greater than the effects of ferulic acid concentration and chlorine dose. The effect of time appears to be insignificant for dichloroacetic acid.

Chloroform and dichloroacetic acid were occasionally produced in quite high amounts. Trial 8, yielded the highest concentrations of chloroform and dichloroacetic acid which together accounted for 4.7% of the initial chlorine. The conditions of trial 8 were: ferulic acid, 5 mg as TOC/L (41.7 µmoles/L), chlorine dose 6:1 (molar ratio Cl_2:ferulic acid), pH 9, and time 160 hours.

Trial 8 was also associated with a rather low production of chlorophenolics. (See Table 10.) Including the contributions of the dichloro-4-vinylguaiacols and chlorovanillin from trial 8, accounts for only an additional 0.60 μmoles of chlorine, raising the estimate of incorporated chlorine to only 5% of that initially added. This estimate is substantially less than the percent chlorine incorporated in trials 1 and 5, 18.3% and 18.8% respectively. (See Table 8). The chlorine dose, at both trials 1 and 5, was 2:1 (molar ratio) which suggests that chlorine incorporation is highest at low chlorine dose. This has important implications for drinking water treatment. As mentioned previously for phenolic compounds, this would result in the production of chlorophenolics which have been associated with strong taste and odour properties (Bull and Kopfler, 1991). Higher chlorine doses, on the other hand, may result in the production of such important disinfection by-products as chloroform and dichloroacetic acid.

Trichloroacetic acid concentrations were approximately one-tenth those of chloroform and dichloroacetic acid.

Compound MX concentrations were exceedingly low (non-detectable to 50 ng/L) but are significant in drinking water terms due to the potent mutagenicity of compound MX. The production of compound MX relative to initial ferulic acid concentration was calculated. The highest MX production was observed for trial 6 (ferulic acid concentration 3.23 mg/L, chlorine dose 6:1 molar ratio Cl_2:ferulic acid, pH 6, and time 160 hours) equivalent to 12.7 μg MX/g of ferulic acid. The lowest measurable rate was observed for trial 8 (ferulic acid concentration 8.08 mg/L, chlorine dose 6:1 molar ratio Cl_2:ferulic acid, pH 9, and time 160 hours) equivalent to 1.47 μg MX/g of ferulic acid. The average production rate at the "0" level (5.66 mg ferulic acid/L, chlorine dose 4:1 molar ratio Cl_2:ferulic acid, pH 7.5 and time 16 hours) was 5.65 μg MX/g of ferulic acid. These production rates are comparable with those measured by Holbom et al. (1990), who noted a production rate of 4 μg MX/g of ferulic acid when chlorinated under conditions equivalent to 1.85 moles Cl_2 per mole of ferulic acid, pH 7, time of 16 to 20 hours and a ferulic acid concentration of 30 mg/L. Holbom et al. (1990) also noted that phenol, catechol and p-hydroxybenzoic acid produced compound MX at approximately double the rate of ferulic acid.

Analytical results for chloroform, dichloroacetic acid, trichloroacetic acid and compound MX were analyzed by regression according to a polynomial model in a manner similar to the chlorophenolics. Results of the full regression analyses are shown in Appendix 5, Table A5.2. The main effects only are summarized in Table 10.

Table 10. Main Effects from Target Compound Regression Analysis

Y	b_0	b_1	b_2	b_3	b_4
Chloroform	60.78	40.06	74.08	(23.26)	27.63
Dichloroacetic Acid	58.20	(22.57)	24.45	29.53	(0.87)
Trichloroacetic Acid	3.59	2.46	3.35	(-0.50)	(-0.74)
Compound MX	22.24	(1.87)	(6.12)	(-3.36)	(-2.17)

The main effects of ferulic acid concentration, chlorine dose and time as well, as the interactions of ferulic acid with chlorine dose and chlorine dose with time were all significant and positive in their effect on chloroform production. The effect of pH was positive and significant at $\alpha=0.06$, as was the interaction of chlorine dose and pH. Higher chloroform production was thus associated with higher model compound concentrations, higher chlorine doses and alkaline pH. These results confirm earlier work which indicated that trihalomethane formation increases with increased chlorine dose and alkaline pH (Peters et al., 1980; Kavanaugh et al., 1976).

The effects of chlorine dose and ferulic acid concentration as well as their interaction is shown in Figure 21.

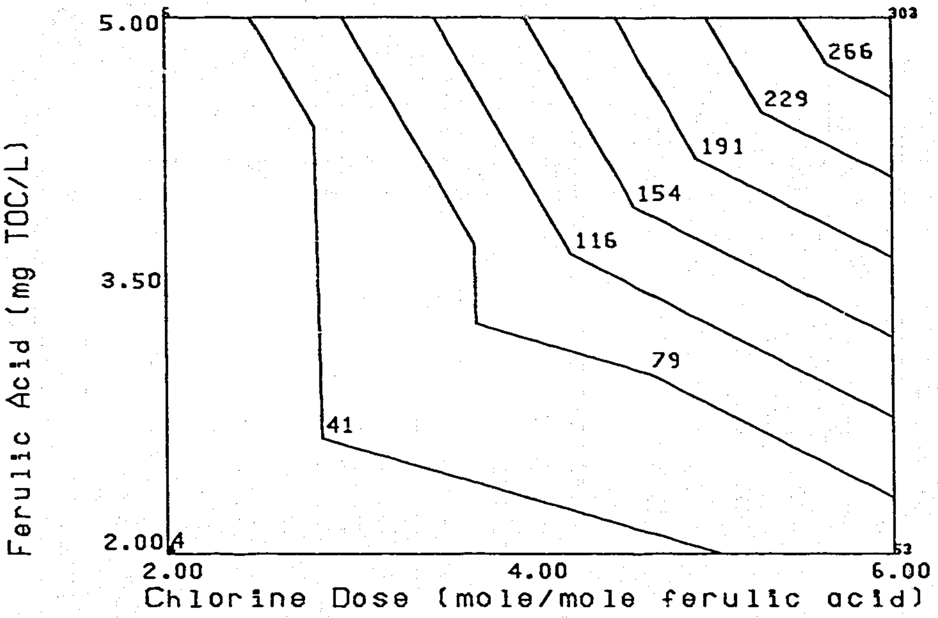


Figure 21. Response surface showing the approximate contours of chloroform (μg/L) projected onto the ferulic acid concentration and chlorine dose plane at a pH of 6 and time of 160 hours.

The main effects of chlorine dose and pH were significant and positive in their effect for dichloroacetic acid. The effects of chlorine dose and pH are apparent in Figure 22. Ferulic acid concentration was positive in effect as well, but at α=0.06. The polynomial model is not significant for dichloroacetic acid (α=0.16). Other models which include higher order (ex. quadratic terms are probably more appropriate for describing the behaviour of dichloroacetic acid.

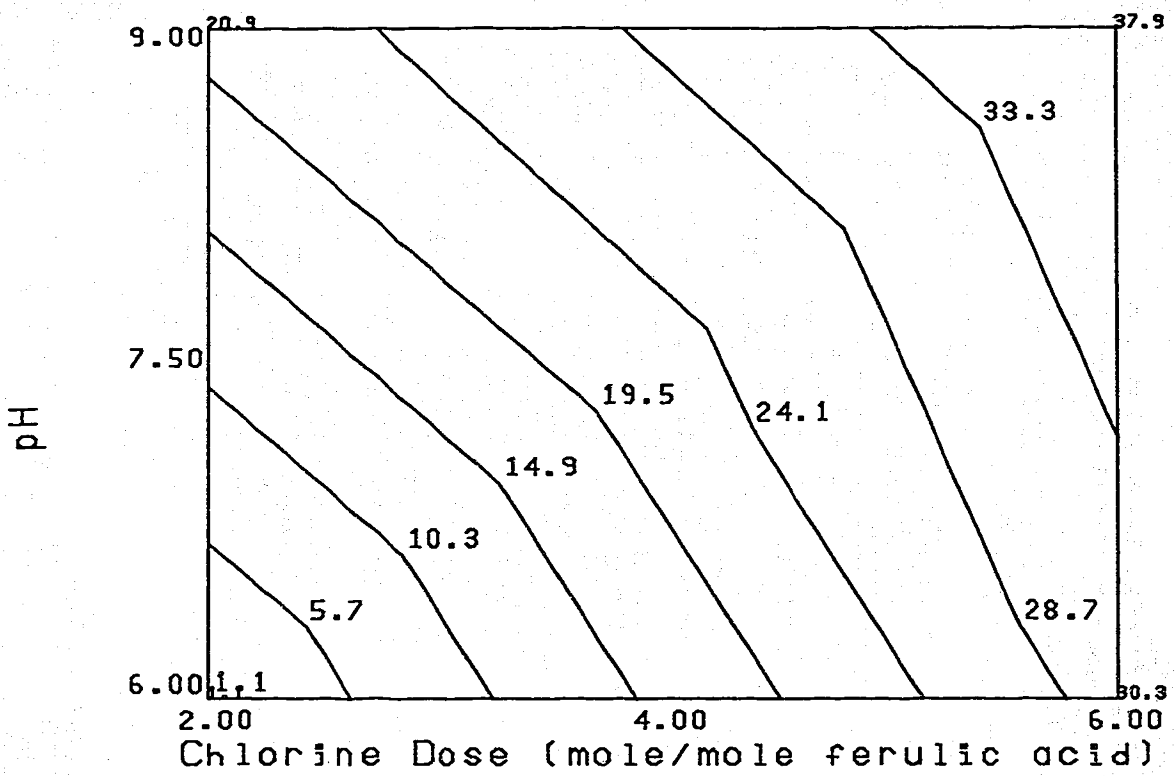


Figure 22. Response surface showing the approximate contours of dichloroacetic acid (μg/L) projected onto the pH and chlorine dose plane at a ferulic acid concentration of 2 mg as TOC/L and time of 160 hours.

The main effects of ferulic acid concentration and chlorine dose as well as their interaction were significant and positive in their effect on trichloroacetic acid. The effects of chlorine dose and their interaction are apparent in Figure 23.

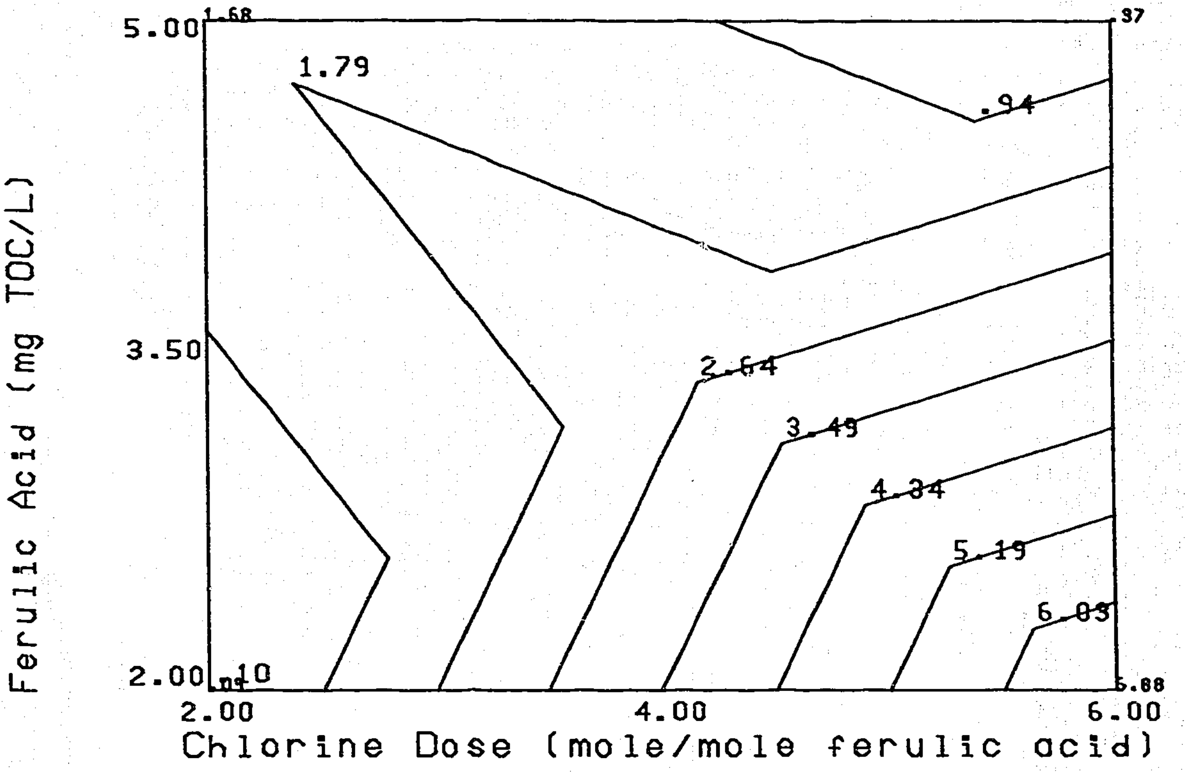


Figure 23. Response surface showing the approximate contours of trichloroacetic acid (µg/L) projected onto the ferulic acid concentration and chlorine dose plane at a pH of 6 and time of 160 hours.

Compound MX was detected in only one trial in the second block of experiments excluding the "0" level replicates. This may have been due to low analyte recoveries. The recovery of mucochloric acid and mucobromic acid which have structural similarities to compound MX (see Figure 22) were quite low. The recovery of the methyl esters of mucochloric acid and mucobromic acid were 34±13% and 36±17% respectively. Systematic losses of this extent would result in a poorer detection limit as surrogate corrections can only be applied to detectable quantities. (In this series of experiments the ethyl acetate solvent was removed and samples taken to dryness in graduated centrifuge tubes followed by extraction with the acidified methanol reagent and transfer to the reactivial. This step was improved in effluent experiments and an increase in surrogate recovery was noted. (See Section 7.2.4).

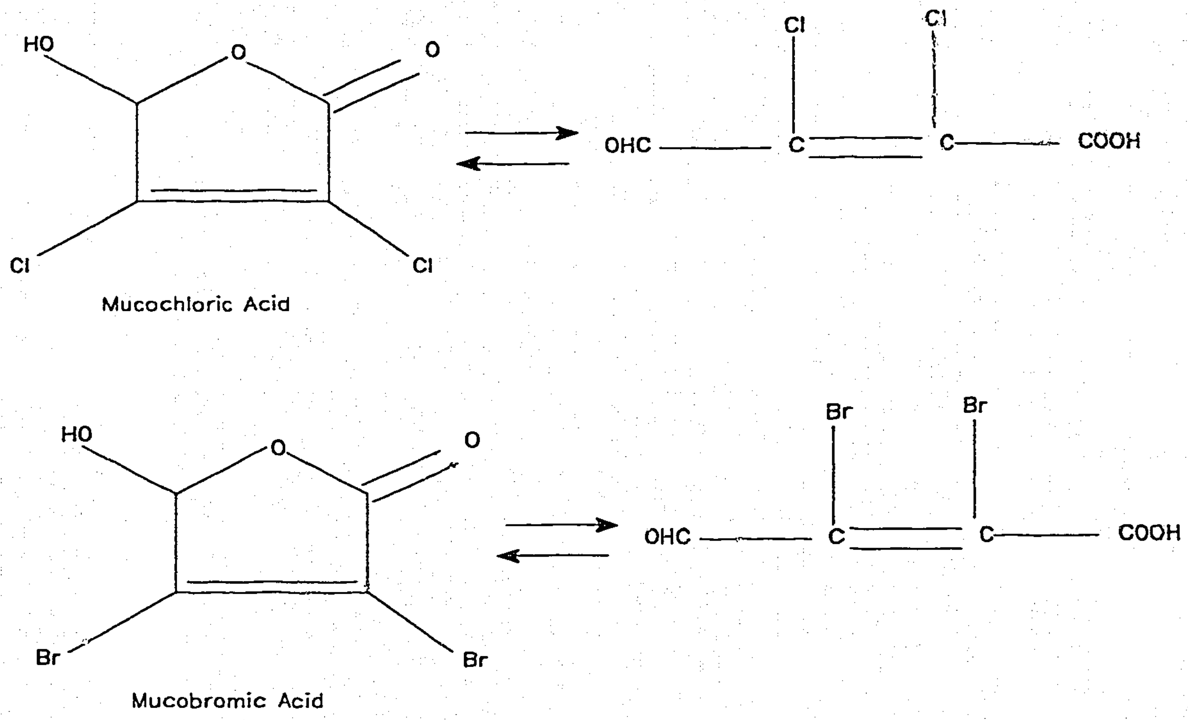


Figure 24. Structures of mucoacid surrogates.

The presence of non-detectables precludes any statistical analysis of the results without some knowledge of the data distribution. The use of "0" or one-half of the minimum detectable concentration would tend to overestimate the statistical significance of effects. However, using the minimum detectable concentration for the purpose for evaluating the effects of experimental factors is a conservative approach since the actual concentration is likely some fraction of the minimum detectable concentration. Eliminating higher order interactions which are not significant (i.e. a large probability of type I error) allows the estimation of significant effects. The minimum detectable concentrations were calculated using the minimum reportable response of the instrument (27 pg/injection) which was equivalent to 27 ng/mL of final concentrated sample volume and the accounting for the fraction of surrogate recovered and extracted according to equation 3.

$$\mathrm{MX(ng/L)} = \frac{\mathrm{ng/mL \bullet (mL\ extract) \bullet (1000mL/L)}}{\mathrm{mL\ extracted \bullet (recovery)}} \quad (3)$$

Only the main effects were calculated for compound MX. None of the factors was significant at $\alpha \leq 0.05$. Chlorine dose was significant at $\alpha \leq 0.08$. Compound MX appears to be preferentially formed at higher chlorine doses as are the other target compounds. This suggests that the precursors of compounds MX are associated with highly oxidized, chlorinated by-products.

6.2 Effluent Experiments

6.2.1 Effluent and River Water Analysis

Samples of effluents and river waters were analyzed by a commercial laboratory and results are summarized in Table 11. All characterization samples were analyzed without filtration, except where specified, while all chlorination samples were filtered prior to analysis (see 6.2.1).

The treated effluent from the CTMP mill was found to have higher dissolved organic carbon (DOC), COD, colour and tannin and lignin than the TMP mill. This is due to process differences which result in differing wood yields and have been discussed in 3.1.1. The alkalinity of the CTMP mill is also higher than the TMP mill. The BOD for both mills was quite low compared to the COD reflecting the high efficiency of secondary effluent treatment in removing BOD. Refractory organics measured as COD are treated to a lesser extent.

As expected, the humic tributary had higher levels of DOC, COD, colour and alkalinity than the glacial river.

6.2.2 Chlorine Demand of Filtered Effluents in Filtered River Water

The chlorine demand of the filtered effluents in filtered river waters was measured in triplicate at four concentrations (0, 0.5, 1.75, and 3.0 volume%) after 0.5 hours and 20 hours reaction time. The initial chlorine dose was equivalent to 50 mg Cl_2/L. Total residual chlorine was measured and chlorine demand calculated from the initial dose, corrected for "blank" chlorine consumption.

Table 11. Characterization Analyses of Treated Effluents and River Waters

Analyte	Units	TMP Mill (6/14/93)	CTMP Mill (6/14/93)	Glacial River (7/29/93)	Humic Tributary (6/14/93)
Ca	mg/L	86.0	28.8	32.0	39.2
Mg	mg/L	10.4	18.6	8.60	8.00
Na	mg/L	115.	1370.	1.14	19.5
Sulphate	mg/L	270.	532.	28.1	15.0
PP Alkalinity	mg/L	< 0.1	1.0	< 0.1	< 0.1
Total Alkalinity	mg/L	196.	2476.	80.4	169.
pH	Units	7.67	8.30	7.86	8.18
Carbonate	mg/L	< 0.5	1.2	< 0.5	< 0.5
Bicarbonate	mg/L	239.	3016.	98.0	206.
Hydroxide	mg/L	< 0.5	< 0.5	< 0.5	< 0.5
Tannin and Lignin	mg/L	1.5	48.6	0.1	0.7
Turbidity	NTU	4.5	7.9	19.0	1.4
Colour (True)	PtCo Units	135.	450.	< 5	10.
BOD	mg/L	2.9	12.0	< 0.1	< 0.1
COD	mg/L	80.	670.	< 5	25.
Sulphide	mg/L	0.02	0.12	< 0.01	0.07
Total Inorganic C	mg/L	41.8	520.	13.5	36.0
Dissolved Inorganic C	mg/L	41.8	520.	13.5	36.0
TOC	mg/L	33.6	257.	0.7	11.0
Dissolved Organic C	mg/L	31.5	249.	0.7	10.3
Total C	mg/L	75.4	777.	14.2	47.0
Total Ammonia N	mg/L	0.14	0.22	< 0.01	0.02
Total Kjeldahl N	mg/L	1.52	15.2	0.20	0.56
Organic N	mg/L	1.38	15.0	0.20	0.54
Total Phosphorus as P	mg/L	4.35	0.230	0.008	0.008
Total Filterable Residue	mg/L	853.	4180	153.	253.
Total Residue	mg/L	860.	4367.	NA	313.

NA - Not Analyted

Results are summarized in Figures 25 to 28.

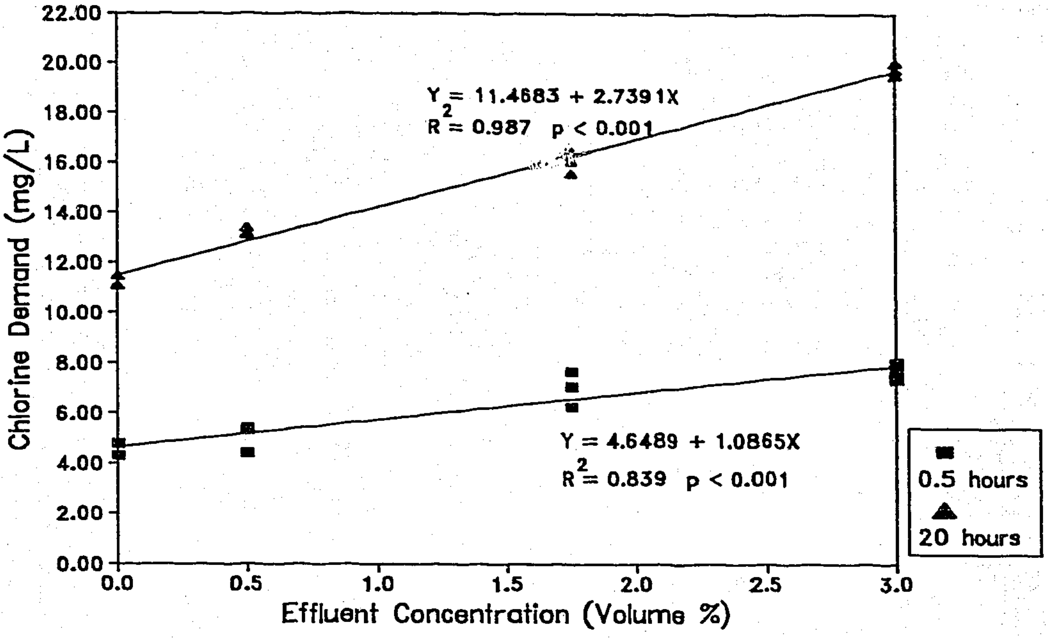


Figure 25. Chlorine demand of filtered CTMP mill effluent in filtered humic tributary water.

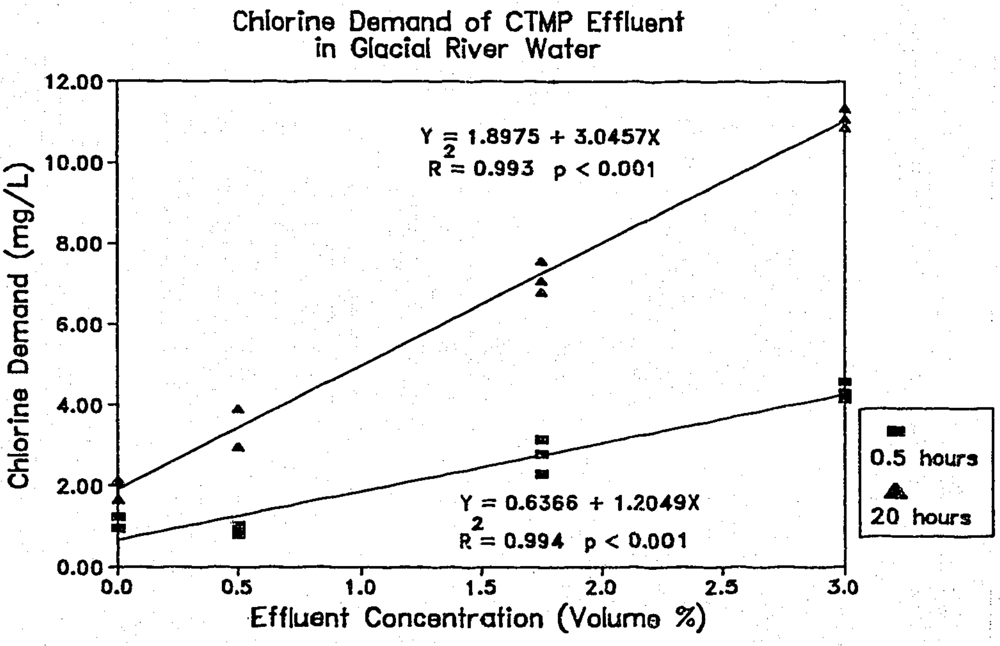


Figure 26. Chlorine demand of filtered CTMP mill effluent in filtered glacial river water.

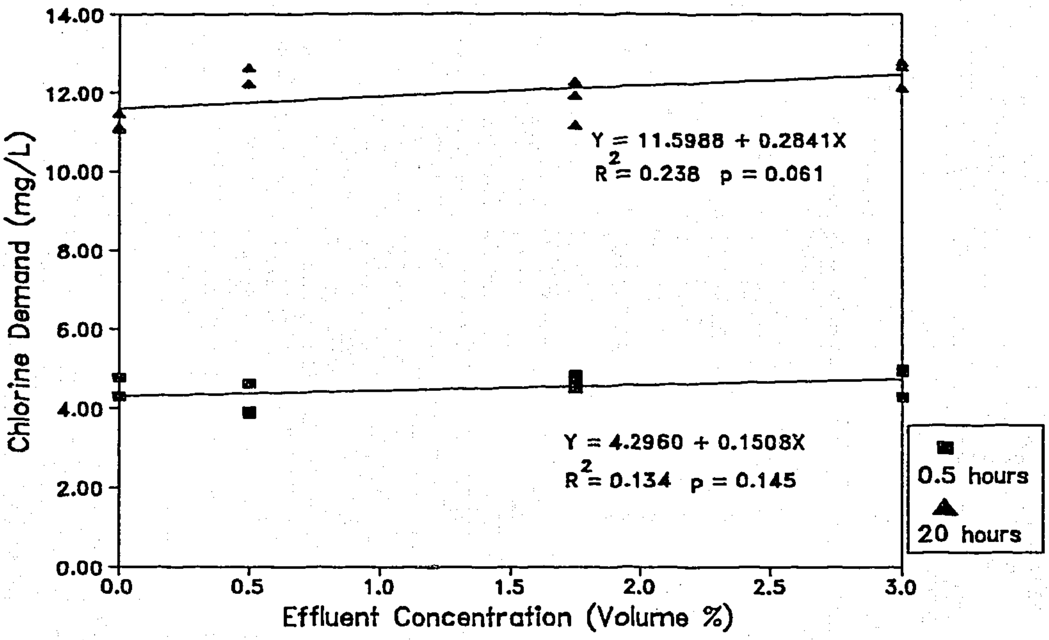


Figure 27. Chlorine demand of filtered TMP mill effluent in filtered humic tributary water.

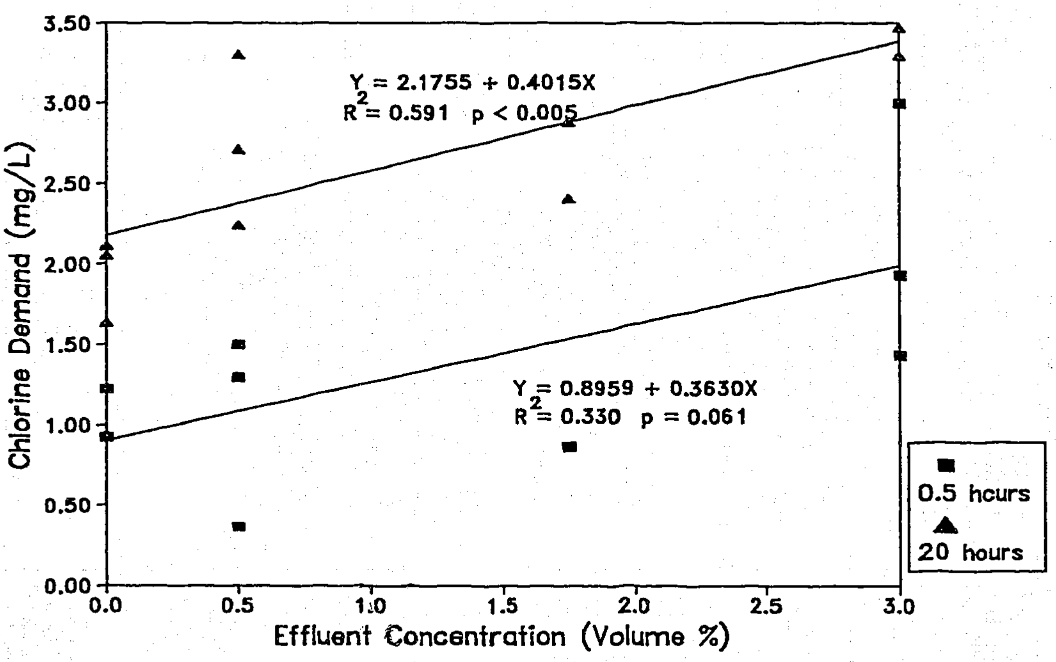


Figure 28. Chlorine demand of filtered TMP mill effluent in filtered glacial river water.

In Figure 25 it is demonstrated that the CTMP mill effluent exerts a significant ($p<0.001$) increase in chlorine demand when diluted in a humic tributary river water at both 0.5 and 20 hours. (Note that in a single coefficient model, the level of significance that may be attached to the model from an F-test and to the slope term from a t-test (i.e. is $b=0$) are equal. The effect of effluent concentration is more pronounced at 20 hours, causing an increase in chlorine demand of 2.7 mg/L for each one per cent increase in effluent concentration. The increase in chlorine demand and the effect of effluent concentration between 0.5 hours and 20 hours is substantial and indicates that significant reaction occurs between chlorine and organic material over a long time period. This has implications for drinking water in that free chlorine residual would be lost in the distribution system where residence times of several days in large systems is not uncommon.

It is shown in Figures 25 and 26 that the effect of CTMP mill effluent on chlorine demand is independent of dilution water. Chlorine demand is increased by the same amount in each natural water.

TMP mill effluent, even after 20 hours reaction time, has a much less significant effect ($p=0.061$) when diluted in the humic tributary water (see Figure 27).

The effect of TMP mill effluent is somewhat more pronounced when diluted in glacial river water (see Figure 28). A one per cent increase of TMP mill effluent results in a significant ($p<0.005$) increase of 0.4 mg/L of chlorine demand. The increase in the effect of effluent concentration with time is less apparent for TMP mill effluent than was apparent for the CTMP mill.

Comparing the slopes (mg/L Cl_2 demand per volume percent increase of effluent) of TMP and CTMP mill effluents at 20 hours reaction time demonstrates that the effect of CTMP mill effluent is 7.6 times that of the TMP mill when diluted in glacial river water and 9.6 times that of the TMP mill when diluted in humic tributary water. The increase in sample DOC as a function of effluent concentration in each water source is summarized in Figure 29. Data points were calculated from DOC results in Table 11. The points are connected to demonstrate the different increases in DOC for each sample type. A comparison of the slope indicates that the relative increase of DOC (mg DOC/L per volume percent increase of effluent) for the CTMP mill effluent samples is 8.1 times that of the TMP mill effluent samples when diluted in glacial river water. When diluted in humic water, the relative increase in DOC for the CTMP mill is 11.3 times that of the TMP mill. The similarity in relative slopes for chlorine demand and DOC (per unit of effluent) between the CTMP and TMP mill effluents suggests that the DOC for each mill has similar reactivity and that differences in chlorine demand are simply a function of sample DOC.

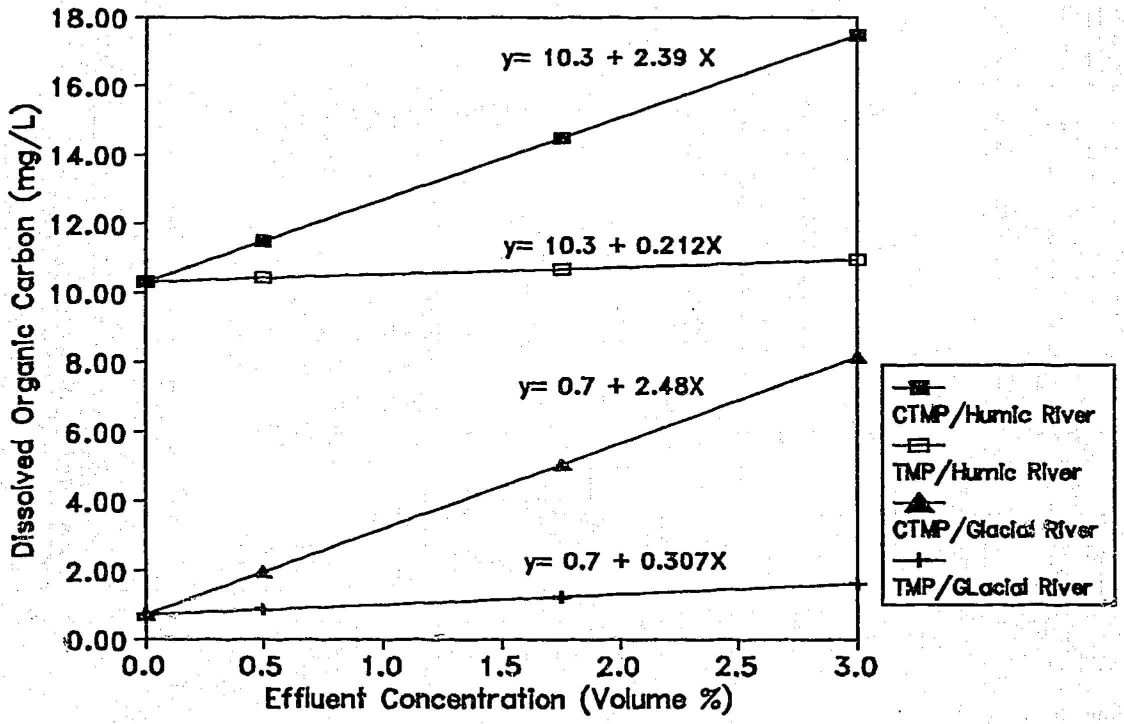


Figure 29. DOC concentrations for the chlorine demand samples.

6.2.3 Experimental Conditions

Chlorine doses for the chlorination by-product study of effluents were determined in the following manner. Chlorine dose was reduced from the 50 mg/L used above, to doses which ensured a detectable residual of free chlorine after 20 hours reaction time. Several scoping experiments, in which free and combined residual chlorine were determined, were run at each experimental trial to set the actual dose used in the chlorination by-product studies. Free and combined chlorine as well as pH was measured on the actual experimental trials prior to commencing extractions.

Chlorine doses and actual residual chlorine and pH analysis are summarized in Table 12. The DOC concentrations varied over a significant range in the trials evaluated from 0.85 to 17.5 mg/L.

The chlorine doses were chosen to reflect drinking water treatment conditions which aim to maintain a residual of disinfectant rather than maintaining a constant chlorine:organic carbon ratio. The target for free chlorine residual was 0.5 mg Cl_2/L. The measured free chlorine residuals actually varied from 0.01 to 0.68 mg Cl_2/L. Chlorine:DOC weight ratio varied between 1.57 (glacial river blank) to 0.57 (trial 5). The experimental samples also contained significant residual combined chlorine from the organic nitrogen originally present, especially, in the humic river water. The final pH of the experimental trials varied only slightly from 8.09 to 8.34. An error in dispensing chlorine for trial 9 was noted and results from trial 9 were not included in statistical analysis.

Table 12. Effluent Chlorination By-Products: Experimental Conditions

Trial No.	Effluent	Concentration (Volume %)	River Water Source	DOC[a] mg/L	Chlorine Dose mg Cl_2/L	Residual Chlorine		pH
						Free	Combined	
1	TMP (-)	0.5 (-)	Glacial (-)	0.85	1.10	0.568	0.043	8.15
2	CTMP (+)	0.5 (-)	Glacial (-)	1.94	1.70	0.490	0.087	8.25
3	TMP (-)	3.0 (+)	Glacial (-)	1.62	1.75	0.490	0.089	8.15
4	CTMP (+)	3.0 (+)	Glacial (-)	8.15	7.30	0.561	0.102	8.09
5	TMP (-)	0.5 (-)	Humic (+)	10.4	5.90	0.143	0.261	8.32
6	CTMP (+)	0.5 (-)	Humic (+)	11.5	6.70	0.036	0.251	8.12
7	TMP (-)	3.0 (+)	Humic (+)	10.9	6.50	0.010	0.242	8.16
8	CTMP (+)	3.0 (+)	Humic (+)	17.5	12.20	0.102	0.395	8.32
9	TMP/CTMP (0)	1.75 (0)	Glacial/Humic (0)	7.86	5.10[b]	0.139	0.221	8.23
10	TMP/CTMP (0)	1.75 (0)	Glacial/Humic (0)	7.86	5.70	0.524	0.118	8.27
11	TMP/CTMP (0)	1.75 (0)	Glacial/Humic (0)	7.86	5.70	0.553	0.245	8.29
12	-	-	Humic Blank	10.3	6.20	0.312	0.320	8.34
13	-	-	Glacial Blank	0.7	1.10	0.680	0.126	8.24

[a] Calculated from Table 15.

[b] Incorrect chlorine addition - results not included in subsequent analyses.

( ) figures in brackets show coded experimental levels.

6.2.4 Chlorination By-Products

No chloroketone compounds were detected in the base/neutral extracts when analyzed by GC-MSD operating in scan mode. This was in spite of the fact that a more polar solvent, methyl-t-butyl ether, was used for extraction. The compound 4,6-dichloroguaiacol was detectable in the chlorophenolics fraction at a concentration of approximately 3 µg/L when analyzed by GC-MSD operating in scan mode (see Tables 9 and 8 for trials 2 and 6). Accounting for the smaller volumes extracted for the base/neutrals suggests a detection limit of approximately 6 µg/L when utilizing the GC-MSD in the scan mode. Chloroketones do not appear to be a major chlorination by-product of natural waters and CTMP mill effluents considering that the solutions contained up to 17.5 mg DOC/L.

GC-MSD scans of the chlorophenolic fractions did not reveal the presence of any chlorinated by-products. GC-MSD scans of the acid fractions were not run due to the paucity of chlorinated products detected in the model compound acid extracts.

Chlorophenolic extracts analyzed by GC-MSD in SIM mode for pulp and paper related chlorophenolics found only a single product, 2,4,6-trichlorophenol.

Analytical results for 2,4,6-trichlorophenol are summarized in Appendix 2, Table A2.5. A small amount of 2,4,6-trichlorophenol was detected in the humic river water blank as compared with the experimental trials. Trial 4 would exceed the MAC for 2,4,6-trichlorophenol, 5 µg/L (Health and Welfare Canada, 1993). Trials 4 and 8 would exceed the aesthetic objective for 2,4,6-trichlorophenol, 2 µg/L (Health and Welfare Canada, 1993).

Regression analysis was used to examine the effects on concentration in µg/L of 2,4,6-trichlorophenol (Y), of the following experimental factors: effluent type (X1), effluent concentration (X2) and receiving water quality (X3) including main effects (bi), and their interactions (bij). The results of fitting the experimental results to the polynomial model:

$$Y=b_0+b_1X1+b_2X2+b_3X3+b_{12}X1X2+b_{13}X1X3+b_{23}X23$$

are summarized in Table A5.3.

Only effluent type had a significant effect at $\alpha \leq .05$ on the production of 2,4,6-trichlorophenol. The effect of effluent concentration was significant at $\alpha \leq 0.10$. The effect of receiving water quality was significant at only $\alpha \leq 0.30$. (This finding is confirmed by the very low concentration of 2,4,6-trichlorophenol (0.073 µg/L) which was detected in the humic river.) This demonstrates that the effluents from CTMP mills have the potential to produce chlorination by-products with potent taste and odour properties.

Concentrations of 2,4,6-trichlorophenol approaching aesthetic objectives of 2 µg/L are only likely to be achieved at relatively high concentrations of mill effluent. However, 2,4,6-trichlorophenol has been implicated as a precursor of 2,4,6-trichloroanisole via biological methylation of the hydroxyl group. 2,4,6-Trichloroanisole is a much more potent taste and odour compound than 2,4,6-trichlorophenol with an odour threshold concentration of 2 ng/L (Brownlee et al., 1993). 2,4,6-Trichloroanisole may be formed in a treated water distribution system by the activity of fungi and actinomycetes which are capable of biologically methylating 2,4,6-trichlorophenol (Nyström et al., 1992). The study of Nyström et al. (1992) indicated that certain actinomycetes isolated from a Swedish tap water were capable of producing 4 ng of 2,4,6-trichloroanisole from 10 ng of added 2,4,6-trichlorophenol. The production of 2,4,6-trichlorophenol in chlorinated natural waters containing TMP and CTMP mill effluents suggests that significant taste and odour compounds may be produced in drinking water distribution systems affected by these effluents.

Analyses of chloroform, dichloroacetic acid, trichloroacetic acid and compound MX are summarized in Table A2.6. Mucochloric acid and mucobromic acid were used as extraction and analytical surrogates respectively. For this block of experiments, mucochloric acid and mucobromic acid surrogate recovery was improved due to the improvements in sample concentration and handling discussed previously. Mucochloric acid (10 µg) which was spiked into the aqueous sample was recovered at a level equivalent to 78 ± 13%. Mucobromic acid which was spiked into the ethyl acetate extracts was recovered at a level equivalent to 88 ± 14%. This indicates a recovery of approximately 88% across both the extraction portion and the concentration, derivatization and extraction portions of the chloroacid compounds sample preparation. Dichloroacetic acid, trichloroacetic acid and compound MX concentrations were corrected for the recovery of mucochloric acid.

Reproducibility calculated as the standard deviation from the '0' level replicates was ±2.6 µg/L for chloroform, ±7.32 µg/L for dichloroacetic acid, ±2.97 µg/L for trichloroacetic acid and ±2.81 ng/L for compound MX.

Summary graphs for the analytical results obtained in the glacial and humic rivers are shown in Figures 30 and 31 respectively.

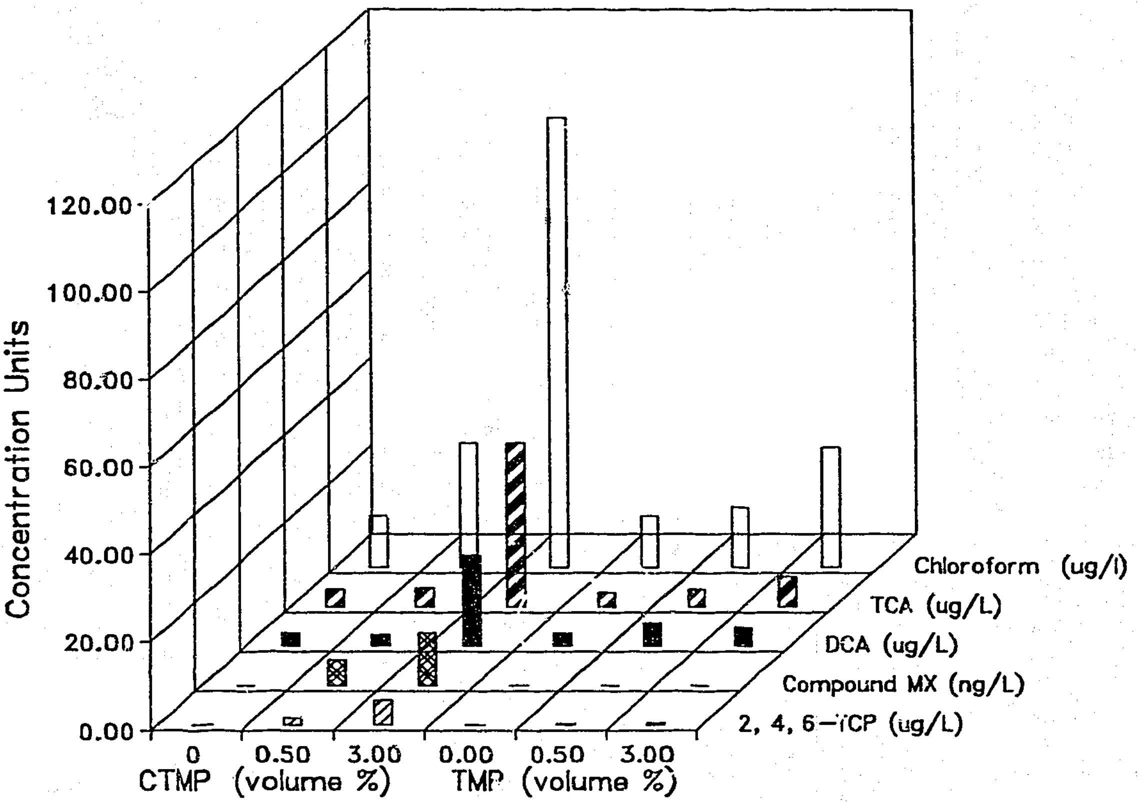


Figure 30. Summary of analytical data obtained from glacial river water samples. (0.0 volume % corresponds to the river water without effluent.)

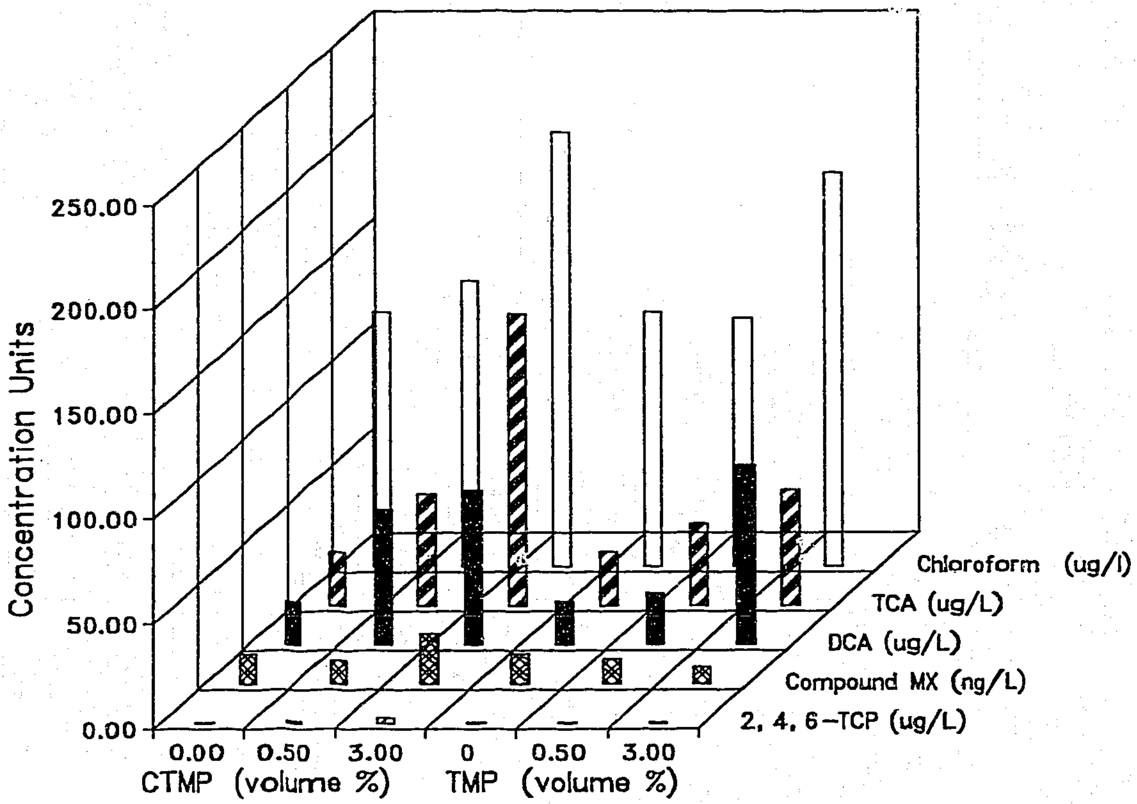


Figure 31. Summary of analytical data obtained from the humic river water samples (0.0 volume % corresponds to the river water without effluent.)

In glacial river water, the increase in analyte concentration appears larger for the CTMP mill effluent samples as compared to the TMP mill effluent samples for the compounds tested. Large increases in both chloroform and trichloroacetic acid concentrations are apparent as effluent concentrations increase.

Similar trends are noted in the humic river water samples, although analyte concentrations are, in general, higher in the humic river samples. The incremental effect of the effluents thus have a less apparent relative effect due to the high background analyte production from the humic river.

The concentrations of dichloroacetic acid and trichloroacetic acid are similar for samples of effluents diluted in natural waters. This contrasts with the model compound results in which dichloroacetic acid was produced in much higher amounts than trichloroacetic acid (see Table A2.1). The fact that chlorine in excess of the chlorine demand is present likely increases the degree of chlorine substitution.

Chloroform concentrations in the effluent samples are similar to the model compound results but display less variation due to the similar reaction conditions for each trial.

The production of chloroform was normalized to DOC concentrations and the results are shown in Table 13.

Table 13. Normalized Chloroform Production

Trial No.	Chloroform Production (μg/mg DOC)
1	16.2
2	14.8
3	16.8
4	12.6
5	11.3
6	11.8
7	17.2
8	11.9
10	12.3
11	12.8
12	11.8
13	16.8

Normalizing the production of chloroform to the DOC concentration reduces the variation observed in experimental results. The production of chloroform in the glacial river varies from 12.6 to 16.2 μg/mg while in the humic river, chloroform production is approximately 11.6 μg/mg with the exception of trial 7 which was anomalously high. Analytical constraints precluded the reanalysis of this trial. It is probably not appropriate to compare the production rates between river water sources and mill effluents since chlorine doses were set to maintain an effective residual rather than maintain a constant chlorine to DOC ratio. Chlorine dose was shown to have the largest effect on chloroform production in the model compound experiments.

The chloroform production rates per unit of organic carbon were lower than the highest recorded for ferulic acid (1.7% for effluent vs. 7.6% by weight for ferulic acid) but once again are much more consistent due to less variation in reaction conditions.

Chloroform, dichloroacetic acid and trichloroacetic acid also accounted for a small portion of the original chlorine dose. The highest chlorine incorporation was found for the humic river samples and particularly (excluding trial 7, an apparent anomaly) for trial 6. The amount of chlorine accounted for by the three target compounds accounted for only 5.7% of the original chlorine dose in trial 6. The chlorine:carbon ratio (mg/mg) in this trial was 0.58:1, nearly the lowest ratio encountered. This is analogous with the findings for ferulic acid where the highest incorporation rates were found at the lowest chlorine doses. However, a much larger portion of the ferulic acid was accounted for by chlorophenolic compounds which were not produced by the chlorination of natural waters and mill effluents. Insufficient chlorine was added in the model compound experiments to satisfy the chlorine demand as opposed to the effluent experiments where surplus chlorine is present. It may be that aromatic compounds such as chlorophenolics which are produced at low chlorine to substrate ratios are oxidized to other forms when surplus chlorine is present leaving only the highly substituted and oxidized chlorination by-products. Adin et al. (1991) suggested that two competitive pathways exist for the formation of trihalomethanes from humic materials, a direct one and another via organochlorine intermediates. The conversion of organochlorine intermediates to trihalomethanes is of a higher order with respect to chlorine, and thus organochlorine intermediates accumulate while trihalomethanes decrease at low levels of chlorine and excess humics.

The chlorine demand experiments provide additional evidence of the role of chlorine to substrate ratio in determining the nature of chlorination by-products. The chlorine demand experiments in which a large surplus of chlorine is added, demonstrate a higher chlorine demand than the chlorination doses used in the by-product experiments which provide a measurable residual after 20 hours. This can be explained as the high chlorine doses produce more highly oxidized by-products (thus the higher chlorine demand) than found with low chlorine doses.

The question remains as to whether other undetected compounds account for a measurable portion of incorporated chlorine. To answer this, additional samples corresponding to the glacial river water blank and 3 percent effluent in glacial river water (trials 13, 3 and 4) were prepared as before, according to the conditions of Table 12. These solutions were prepared several weeks after the completion of experimental trials using stored samples from the original study. Only glacial river water was available for this series of experiments. TOX was determined as the sum of NPAOX and volatile organic halides. Chloroform was the only volatile organic halide detected. Results and TOX calculations are summarized in Appendix 2, Table A2.7.

Chlorine incorporation and the fraction of TOX accounted for by the target compounds plus 2,4,6-trichlorophenol are summarized in Table 14. Chlorine incorporation on a molar basis varied from 19 to 30 percent. The percentage of TOX accounted for by the target compounds varied from 21.2% to 27.0%.

These findings are comparable to those of Reckhow and Singer (1990) who found, on average, 27.6% and 24.6% chlorine incorporation for five fulvic and five humic substances respectively. For those authors, a higher percentage of TOX was accounted for by chloroform, chloro acids, trichloroacetone and dichloroacetonitrile (44.8% to 50.3%). This may be due to the higher chlorine dose used (2 mg Cl_2/mg TOC vs 1 mg Cl_2/mg TOC on average for this study).

The portion of TOX unaccounted for in this study may be due to undetected compounds (e.g. dichloroacetone and trichloroacetonitrile or other higher molecular weight compounds such as chlorolignins or chlorohumins).

Table 14. Chlorine Incorporation

Trial No.	Cl_2 Consumption (mg Cl_2/L)	TOX (mg Cl/L)	% Chlorine Incorporation		Target Compounds[a] (% TOX)
			Wt.	Molar	
3	1.04	0.156	15	30	26.1
4	6.98	0.666	9.5	19	21.2
13	0.41	0.040	9.8	19.6	27.0

[a] Chloroform, dichloroacetic acid, trichloroacetic acid, and 2,4,6-trichlorophenol as equivalent weight of Cl.

Concentrations of compound MX were similar to those obtained with ferulic acid but at a reduced production rate (< 3 µg MX/g TOC) and demonstrate less variation likely due to more similar reaction conditions.

Compound MX was not detectable in trials 1 and 3 even with improved surrogate recovery. The presence of non detectables precludes any statistical analysis of the results without some understanding of the data distribution as discussed previously. The use of "0" or one-half of the minimum detectable concentration would tend to overestimate the effect of the humic river water source and the CTMP mill. The minimum detectable concentration was used for the purpose of evaluating the effects of experimental factors, and higher order interactions which were not significant (i.e. a large probability of type I error) were ignored.

Results from the chemical analysis of target compounds were analyzed by regression for main effects and interactions between the experimental factors. Table A5.3 summarizes the results of the regression analysis. Significant main effects are shown in Figure 32.

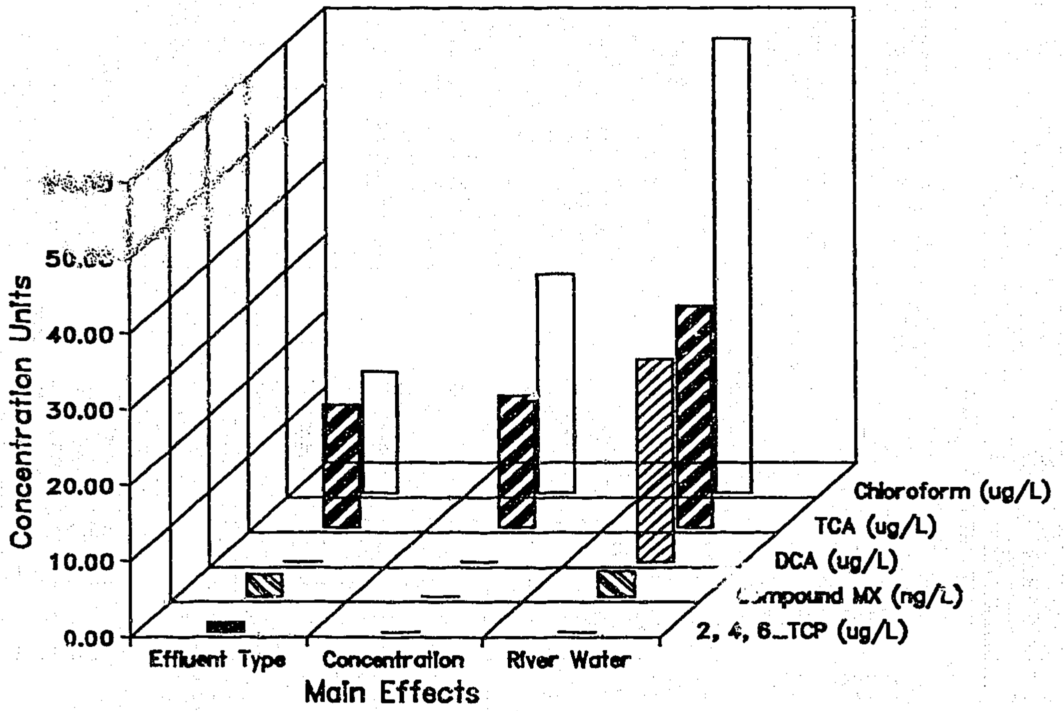


Figure 32. Significant main effects for the target compounds and 2,4,6-trichlorophenol.

The main effects of effluent type, effluent concentration and receiving water quality are all significant (α≤0.05) and positive in their effect upon chloroform concentration. Receiving water quality had the largest effect. Changing river water sources from glacial to humic resulted in an increase in chloroform concentration of nearly 60 µg/L. Increasing the concentration of effluent from 0.5 to 3.0% resulted in an increase of chloroform of 29 µg/L which was nearly double the effect of different effluent types.

The effects of receiving water quality and effluent concentration for the TMP mill effluent and CTMP mill effluent are illustrated in Figures 33 and 34 respectively. Note that the plots assume a continuum of experimental factors.

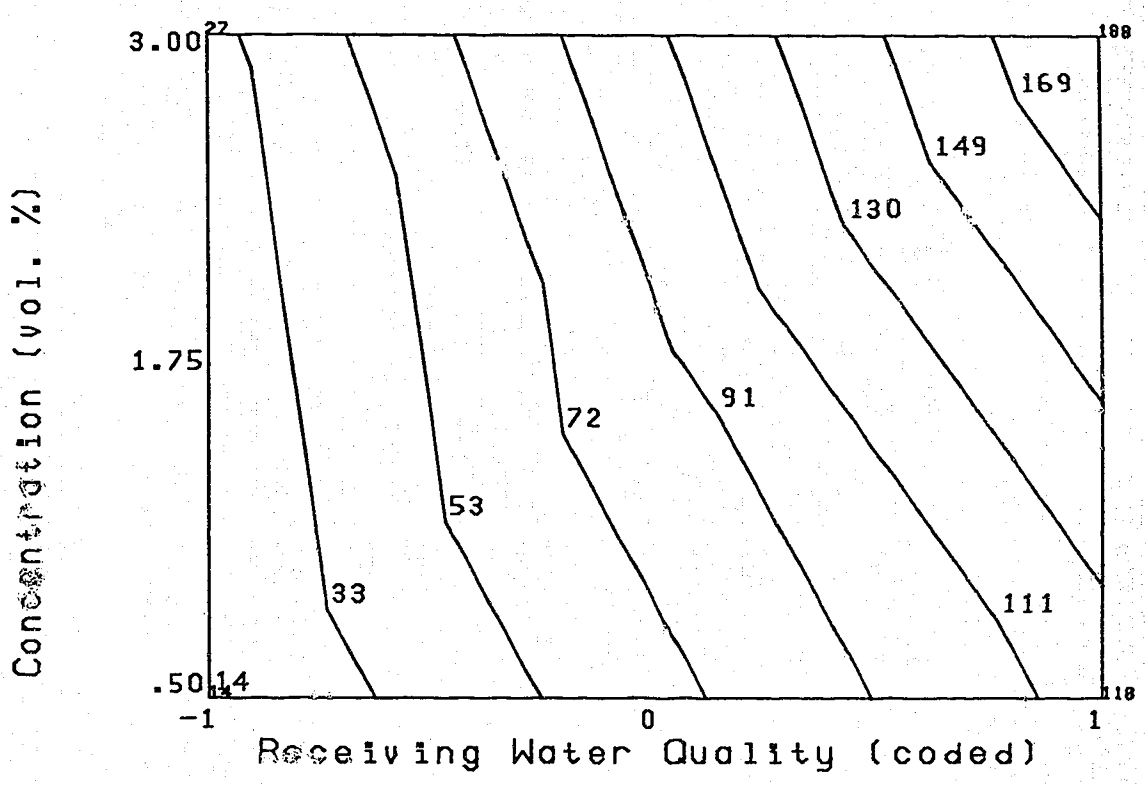


Figure 33. Response surface showing the approximate contours of chloroform (µg/L) projected onto the receiving water quality effluent concentration plane for the TMP mill. (Coded levels of Receiving Water Quality, -1 and +1, refer to glacial and humic respectively.)

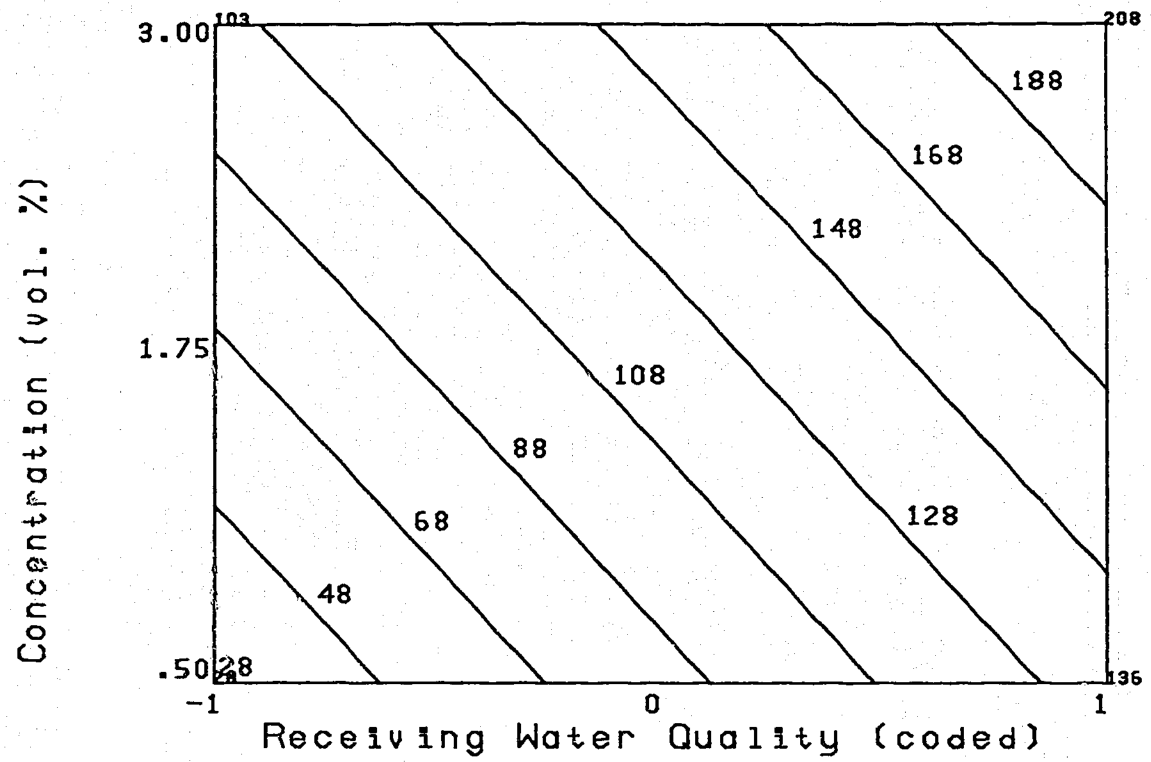


Figure 34. Response surface showing the approximate contours of chloroform (µg/L) projected onto the receiving water quality effluent concentration plane for the CTMP mill. (Coded levels of Receiving Water Quality, -1 and +1, refer to glacial and humic respectively.)

Only receiving water quality was significant ($\alpha \leq 0.05$) in its effect on dichloroacetic acid. Higher dichloroacetic acid concentrations are produced from samples diluted in the humic river.

Trichloroacetic acid concentration, in contrast to dichloroacetic acid, was found to be sensitive to receiving water quality, effluent type and effluent concentration as well as the interaction of effluent type and effluent concentration ($\alpha \leq 0.05$). The effects were all positive in nature with receiving water quality having the largest effect and effluent type and effluent concentration having approximately equal effects. The effects of receiving water quality and effluent concentration for the TMP mill effluent and CTMP mill effluent are illustrated in Figures 35 and 36 respectively.

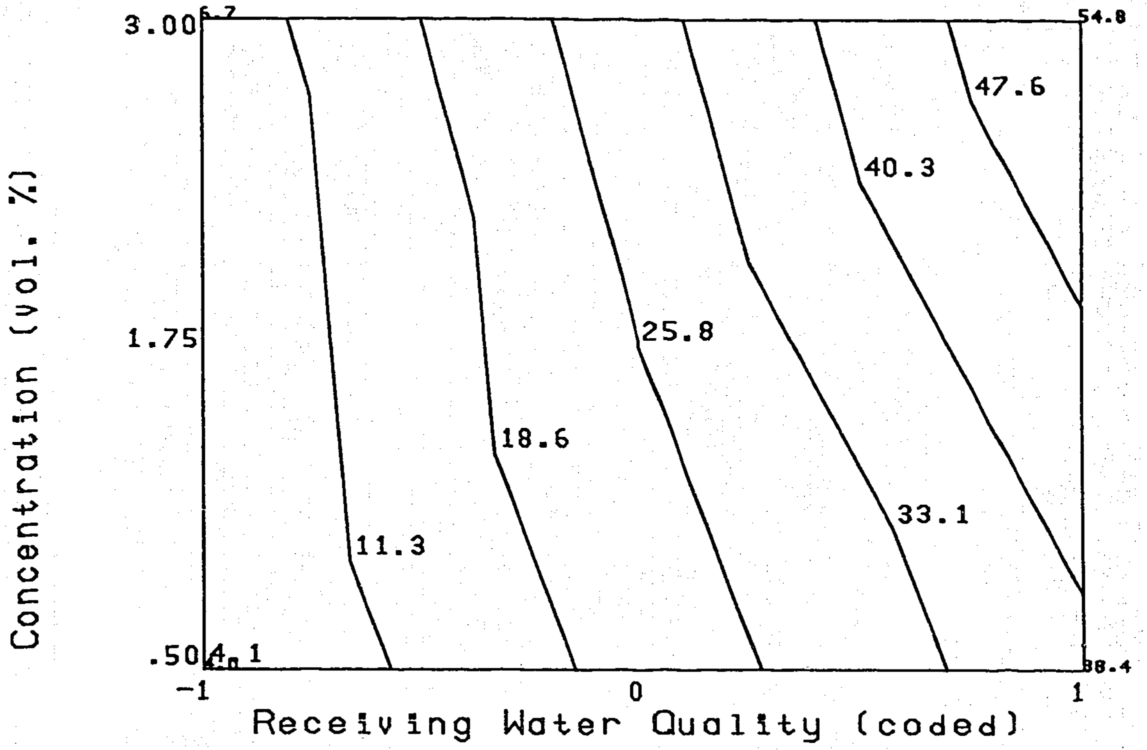


Figure 35. Response surface showing the approximate contours of trichloroacetic acid (μg/L) projected onto the receiving water quality, effluent concentration plane for the TMP mill. (Coded levels of Receiving Water Quality, -1 and 1, refer to glacial and humic respectively.)

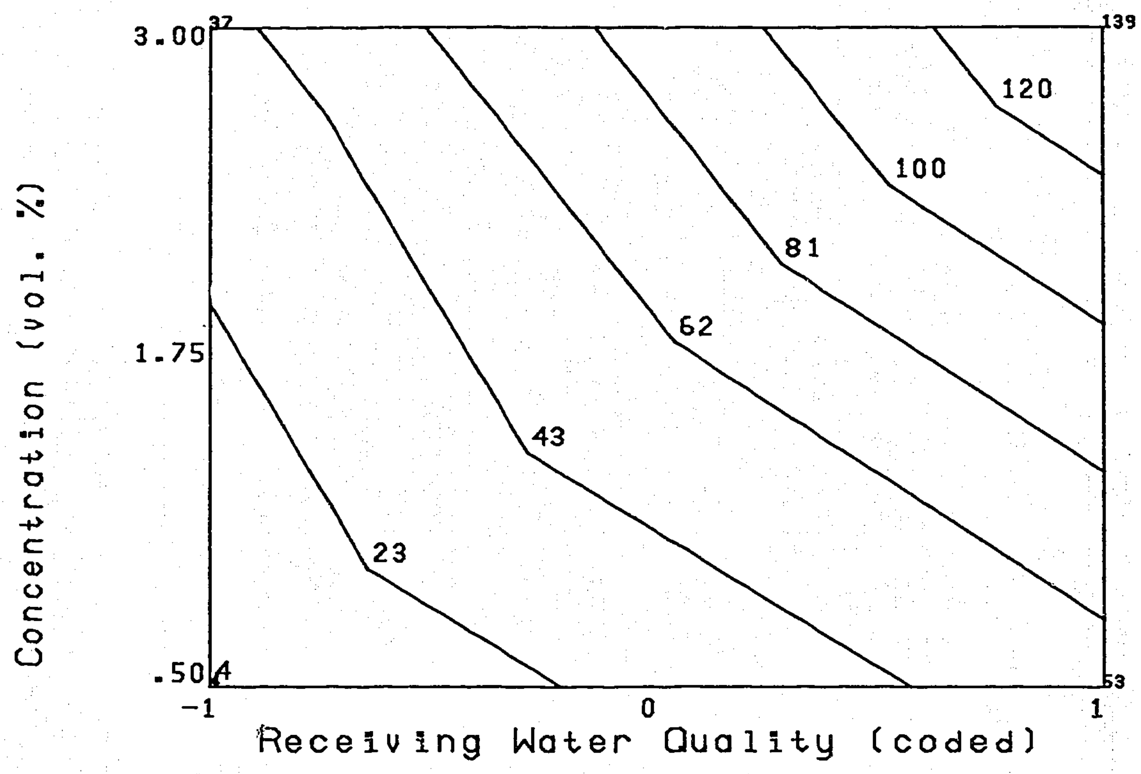


Figure 36. Response surface showing the approximate contours of trichloroacetic acid (μg/L) projected onto the receiving water quality, effluent concentration plane for the CTMP mill. (Coded levels of Receiving Water Quality, -1 and +1, refer to glacial and humic respectively.)

Two regressions are shown for compound MX. Both regressions were run with the minimum detectable concentrations substituted for trials 1 and 3 which is a conservative approach as discussed above. The higher order interactions which were not significant with a large Type I error were eliminated from the second regression analysis so that the main effects of effluent type, effluent concentration, and receiving water quality may be evaluated. The second regression demonstrates that both receiving water quality and effluent type have significant ($\alpha \leq 0.05$) effects upon compound MX of approximately equal magnitude. The effects of receiving water quality and effluent type are illustrated in Figure 37.

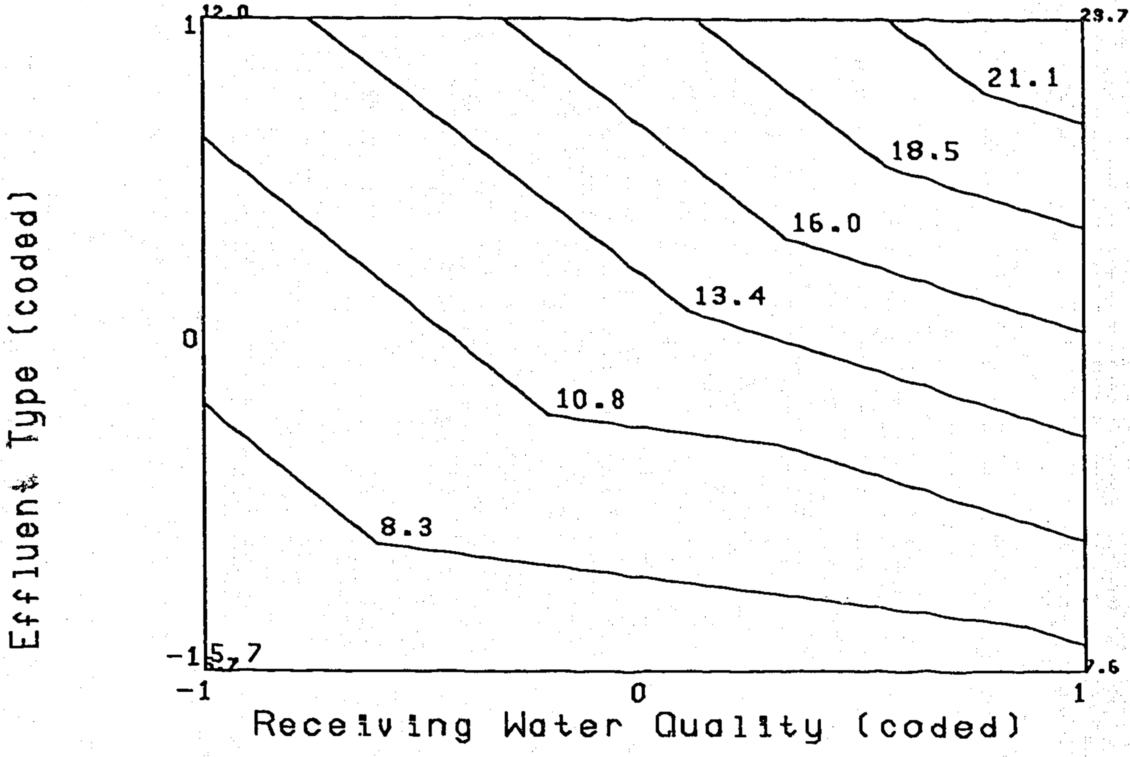


Figure 37. Response surface showing the approximate contours of compound MX (ng/L) projected onto the receiving water quality, effluent type plane for an effluent concentration of 3.0 volume %. (Coded levels of Receiving Water Quality, -1 and +1, refer to glacial and humic respectively, coded levels of Effluent Type, -1 and +1, refer to TMP and CTMP respectively.)

In summary, as expected, TMP and CTMP mills diluted in natural waters are capable of reacting with chlorine producing chlorine substituted by-products. The detected by-products included chloroform, dichloroacetic acid, trichloroacetic acid, 2,4,6-trichlorophenol and trace amounts of compound MX. A small portion of original chlorine is incorporated under the conditions of drinking water treatment in which a measurable chlorine residual is maintained. The contributions to total by-product production appear to be larger from humic waters rather than effluents at the effluent concentrations likely to be encountered. However, mill effluents contribute a significant amount to the production of chloroform and trichloroacetic acid. The production of chloroform is more similar when weighted for DOC for the effluent receiving water combinations studied.

Mill effluents have the potential to cause the production of 2,4,6-trichlorophenol a potent taste and odour compound and potential precursor of other more potent taste and odour compounds.

The production of compound MX from solutions of mill effluents and natural waters was demonstrated and a conservative analysis of effects indicates that both CTMP effluent and humic waters contain its precursors.

Chlorination by-product formation for the effluent/natural water combinations appears to be more comparable to the higher chlorine dose trials of the model compound experiments. No significant amounts (in terms of major by-product formation) of substituted phenolic compounds were detected in the effluent experiments. However, the more highly oxidized target compounds with significant health effects were produced. Although the chlorine doses for the effluent experiment were lower on a weight basis, they did provide excess chlorine measured as free residual. The difference in effective dose is due to the higher chlorine demand of the model compound. This suggests that for model compound studies, chlorine doses which ensure a measurable residual are of more value in predicting the chlorinated by-products formed in natural waters than lowe chlorine doses.

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The model compound experiments demonstrate the following:

1. The chlorination by-products formed indicate that a number of oxidation and substitution reactions occur between ferulic acid and aqueous chlorine involving both the propyl side chain and 3-methoxy-4-hydroxy substituted aromatic ring which are also found in natural lignin.
2. Chlorine incorporation is favoured by conditions of low chlorine dose (2:1 molar ratio) and high ferulic acid concentration and to a lesser extent by lower pH and longer reaction time, conditions which favour the formation of chlorinated phenolics.

3. The target analytes chloroform, dichloroacetic acid, trichloroacetic acid, and compound MX are preferentially formed at high chlorine doses (6:1 molar ratio).
4. Ferulic acid is a useful lignin and humic substance model compound at chlorine doses which satisfy the chlorine demand producing target analytes at concentrations typical of those found when natural waters are chlorinated.

The effluent experiments demonstrate that:

5. TMP and CTMP mill effluents contribute significantly to chlorine demand at the concentrations studied, and the increase is independent of river water quality. Thus, the relative contribution of mill effluents to total chlorine demand will be higher in natural waters with low levels of DOC.
6. The organic material in TMP and CTMP effluents, refractory to biological treatment, is capable of reaction with chlorine producing compounds which are or may be regulated in the future. 2,4,6-Trichlorophenol, chloroform, dichloroacetic acid, and trichloroacetic acid as well as the strong bacterial mutagen, compound MX were formed.
7. The production of target analytes is related to the total DOC of the effluent and receiving water, and thus, receiving water quality in actual practice may have the largest effect on the nature and amounts of chlorination by-products formed, as was found for chloroform, dichloroacetic acid, and trichloroacetic acid with the experiments described here. The magnitude of effect for a mill's effluent will depend on the flow conditions and amount of natural organic matter present in the receiving water.
8. The CTMP process contains more DOC in its effluent, and thus, has a greater potential for by-product formation than a similarly sized TMP mill.
9. The concentration of the potent taste and odour compound 2,4,6-trichlorophenol was most strongly correlated with effluent type and was produced at much lower amounts in the chlorinated river waters which did not contain TMP or CTMP effluents. Additional taste and odour compounds may be produced within distribution systems.

7.2 Recommendations

The contributions to DOC from TMP and CTMP mill effluents are additive to that present in the receiving water and will be reflected in increased chlorine demand. The results of the above study have implications for drinking water treatment and suggest the following recommendations.

1. Raw water sources receiving effluents from TMP and CTMP mills may require the optimization of organic removal processes such as coagulation/flocculation.
2. The point of chlorination should be as far along in the treatment train as possible minimizing the DOC available for reaction with chlorine.
3. Disinfectant residuals and disinfectant by-products should be checked throughout the distribution system due to the long term chlorine demand and reactivity demonstrated by the effluents and natural waters.

The work reported here which shows that TMP and CTMP mill effluents have significant effects on drinking water quality, especially in waters with low levels of DOC, has implications for mill siting and licensing.

1. Site-specific mixing and dilution conditions and receiving water quality (in terms of DOC) should be considered in determining the impact of locating CTMP and TMP mills upstream of drinking water treatment plants.
2. The unit processes available and disinfectant chemistry of down stream drinking water treatment plants should be considered when assessing the effects of TMP and CTMP mill effluents on drinking water quality.

Finally, several areas for additional research which were beyond the scope of this study are suggested.

1. Improve analytical methods to minimize sample handling and expand the range of analytes available.
2. Examine the effects of drinking water treatment processes in removing chlorination by-product precursors.
3. Examine additional pulp mill effluents for their potential reaction with aqueous chlorine.

4. Study the fate of chlorination by-products within an actual drinking water distribution system.

8.0 REFERENCES

Adin, A., Katzhendler, J., Alkaslassy, D. and Rav-Acha, C. 1991. Trihalomethane Formation in Chlorinated Drinking Water: A Kinetic Model. Water Research. 25(7):797-805.

Alberta Environmental Centre. 1987. Methods Manual for Chemical Analysis of Water and Wastes. ed. F.P. Dieken. Alberta Environmental Centre AECV87-M1. 1987.

Alberta Environmental Centre. 1992. Methods Manual for Chemical Analysis of Trace Organics and Pesticides in Environmental Samples. ed. R.D. Smillie. Alberta Environmental Centre AECV92-M2. 1992.

Alberta Environment. 1990. The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board. March, 1990. 93 p.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollution Control Federation (WPCF). 1989. Standard Methods for the Examination of Water and Waste Water. 17th edition, American Public Health Association. Washington, D.C. 1989.

American Water Works Association (AWWA) Committee Report. 1979. Organics Removal by Coagulation: A Review and Research Needs. Committee Report. Journal of the American Water Works Association. 71(10):588-683.

Bennet, D.H., Falter, C.M., Campbell, A.G., Reeser, D.M. Johnson, W.H. and Gibson, L. 1990. Efficiency of a Pilot-Scale Waste Treatment System to Reduce Toxicity of CTMP Effluents. TAPPI 1990 Environmental Conference Proceedings. Seattle, WA. April 9-11, 1990. pp. 321-331.

Björklund Jansson, M. 1980. Chemistry of Fiber Building Board Mill Effluent Mill Effluent Before and After Biological Treatment. Tappi Journal. 63(7):78-80.

Box, G.E.P., Hunter, W.G. and Hunter, J.S. Statistics for Experimenters. An Introduction to Design, Data Analysis and Model Building. John Wiley and Sons, Inc. New York, 1978. 653 p.

Brownlee, B.G., MacInnis, G.A. and Noton, L.R. 1993. Chlorinated Anisoles and Veratroles in a Canadian River Receiving Bleached Kraft Mill Effluent. Identification, Distribution and Olfactory Evaluation. Environmental Science and Technology. 27(12):2450-2455.

Bruchet, A., Rousseau, C. and Mallevialle, J. 1990. Pyrolysis-GC-MS for Investigating High-Molecular-Weight THM Precursors and Other Refractory Organics. Journal of the American Water Works Association. 82(9):66-74.

Bull, R.J. and Kopfler, F.C. 1991. Health Effects of Disinfectants and Disinfection By-Products. AWWA Research Foundation and American Water Works Association. Denver, CO. 1991. 192 p.

Christman, R.F., Norwood, D.L., Millington, D.S., Johnson, J.D. and Stevens, A.A. 1983. Identity and Yields of Major Halogenated Products of Aquatic Fulvic Acid Chlorination. Environmental Science and Technology. 17(10):625-628.

Coleman, W.E., Munch, J.W. Kaylor, W.H., Streicher, R.P., Ringhand, H.P. and Meier, J.R. 1983. Gas Chromatography/Mass Spectroscopy Analysis of Mutagenic Extracts of Aqueous Chlorinated Humic Acid. A Comparison of the Byproducts to Drinking Water Contaminants. Environmental Science and Technology. 18(9):674-681.

Crawford, R.L. 1981. Lignin Biodegradation and Transformation. John Wiley and Sons. New York. 154 p.

Environment Canada. 1991. National Water Quality Data Base.

Exon, J.H. and Koller, L.D. 1985. Toxicity of 2-Chlorophenol, 2,4-Dichlorophenol, and 2,4,6-Trichlorophenol. In: Water Chlorination: Chemistry, Environmental Impact and Health Effects. Vol. 5. Lewis Publishers, Chelsea, MI. 1985. pp. 307-330.

Fielding, M. and Horth, H. 1987. The Formation and Removal of Chemical Mutagens During Drinking Water Treatment. In: Organic Micropollutants in the Environment. Proceedings of the Fifth European Symposium. Angletti, G. and Bjφrseth, A. eds. Rome Italy. October 20-22, 1987. pp. 284-298.

Gunnarson, L., Andersson, P.-E. and Olsson, L.-E. 1989. Anaerobic Treatment of CTMP Effluent from Peroxide Bleached Softwood. TAPPI 1989 Environmental Conference Proceedings. Orlando, FA. April 17-19, 1989. pp. 535-542.

Hanna, J.V.. Johnson, W.D., Quezeda, R.A., Wilson, M.A. and Xiao-Qiao. 1991. Characterization of Aqueous Humic Substances Before and After Chlorination. Environmental Science and Technology. 25(6):1160-1164.

Health and Welfare Canada. 1993. Guidelines for Canadian Drinking Water Quality. 5th ed. 24p.

Hemming, J., Holmbom, B., Reunanen, M. and Kronberg, L. 1986. Determination of the Strong Mutagen 3-Chloro-4-(Dichloromethyl)-5-Hydroxy-2(5H)-Furanone in Chlorinated Drinking and Humic Waters. Chemosphere, 15(5):549-556.

Holmbom, B., Kronberg, L., Backlund, P., Långvik, V-A., Hemming,J., Reunanen, M., Smeds, A. and Tikkanen, L. 1987. Formation and Properties of 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, A Potent Mutagen in Chlorinated Waters. In: Water Chlorination: Chemistry, Environmental Impact and Health Effects. Vol. 6. Lewis Publishers, Chelsea, MI. 1990. pp. 125-135.

Jaako Pöyry Oy. 1990. Complementary Scientific Review of the Proposed Alberta-Pacific Pulp Mill Project Environmental Impact Assessment. June, 1990. 138 p.

Johnson, C.I. 1991. Mutagenicity in Pulp Chlorination Filtrate. University of Toronto, 1991. 161 p. PhD Dissertation.

Jorgenson, T.A., Meierhenry, E.F., Rushbrook, C.J., Bull, R.J. and Robinson, M. 1985. Carcinogenicity of Chloroform in Drinking Water to Male Osborne-Mendel Rats and Female B6C3F1 Mice. Fundamental and Applied Toxicology. 5(4): 760-769.

Kantardjieff, A., Jones, J.P., Zaloum, R. and Arneda, L. 1990. Degradation of Toxic Compounds in TMP Mill Effluents by Biological Aerated Filter. TAPPI 1990 Environmental Conference Proceedings. Seattle, WA. April 9-11, 1990. pp. 251-259.

Kirk, T.K. and Farrell, R. 1987. Enzymatic "Combustion": The Microbial Degradation of Lignin. Annual Reviews of Microbiology. 41:465-505.

Knuutinen, J. 1984. Synthesis, Structure Verification and Gas Chromatographic Determination of Chlorinated Catechols and Guaiacols Occurring in Spent Bleach Liquors of Kraft Pulp Mills. PhD Thesis. University of Jyväskyla. 1984.

Kosíková, B., Joniak, D. and Polcin, J. 1984. Behaviour of Lignin-Sacchardic Spruce Wood Complex in Thermal Mechanical Pulping. II. CTMP Process. Cellulose Chemistry and Technology. 18:73-78.

Kovacs, T.G. and Voss, R.H. 1992. Biological and Chemical Characterization of Newsprint/ Speciality Mill Effluents. Water Research. 26(6):771-780.

Kringstad, K.P. and Lindstrom, K. 1984. Spent Liquors from Pulp Bleaching. Environmental Science and Technology. 18(8):236A-248A.

Kringstad, K.P., de Sousa, F. and Strömburg, L.M. 1985. Studies on the Chlorination of Chlorolignins and Humic Acid. Environmental Science and Technology. 19(5):427-431.

Kronberg, L., Holmbom, B., Reunanen, M. and Tikkanen, L. 1988. Identification of the Ames Mutagenic Compound 3-Chloro-4-(Dichloromethyl)-5-Hydroxy-2(5H)-Furanone in Chlorine-Treated Humic Water and Drinking Water Extracts. Environmental Science and Technology. 22(9):1097-1103.

Kurdin, J.A. 1980. Refiner Mechanical and Thermomechanical Pulping. In: Pulp and Paper Chemistry and Chemical Technology. Third Edition, Volume 1. Casey, J.P., ed. New York, pp. 197-252.

Lo, S-N., Liu, H.W., Rosseau, S. and Lavallee, H.C. 1991. Characterization of Pollutants at Source and Biological Treatment of a CTMP Effluent. Appita, 44(2): 133-138.

Lorås, V. 1980. Bleaching. In: Pulp and Paper Chemistry and Chemical Technology. Third Edition, Volume 1. Casey, J.P., ed. New York, pp. 633-764.

Maclean, B., de Vegt, A. and van Driel, E. 1990. Full-Scale Anaerobic/Aerobic Treatment of TMP/BCTMP at Quesnel River Pulp. TAPPI 1990 Environmental Conference Proceedings. Seattle, WA. April 9-11, 1990. pp. 647-661.

Malinen, R., Virkola, N.-E. and Turunen, E. 1985. Effluent Characterization and Treatment of Chemithermomechanical Pulping. SPCI Mechanical Pulping Conference Proceedings. Stockholm May 6-10, 1985. pp. 267-273.

McGuire, M.J. 1993. Content of the D/DBP and Related Rules. In: Disinfectants and Disinfection By-Products: Understanding the Proposed D/DBP Rule. American Water Works Association. Denver, CO. 1993. pp. 33-52.

McKague, A.B., Jarl, M. and Kringstad, K.P. 1990. An Up-To-Date List of Compounds Identified in Bleachery Effluents as of January 1989. SSVL Miljo '90: Subject "Bleaching"

Meier, J.R., Blazak, W.F. and Knohl, R.B. 1987. Mutagenic and Clastogenic Properties of 3-Chloro-4-(Dichloromethyl)-5-Hydroxy-Furanone: A Potent Bacterial Mutagen in Drinking Water. Environmental and Molecular Mutagenesis. 10:411-424.

Monarca, S., Hongslo, J.K., Kringstad, A. and Carlberg, G.E. 1984. Mutagenicity and Organic Halogen Determination in Body Fluids and Tissues of Rats Treated with Drinking Water and Pulp Bleachery Effluents. Chemosphere. 13(12):1271-1281.

NCSS, 1992. Number Cruncher Statistical System. Version 5.03. Kaysville, Utah.

Norwood, D.L., Johnson, J.D., Christman, R.F., Hass, J.R. and Bobenreith, M.J. 1980. Reactions of Chlorine with Selected Aromatic Models of Humic Material. Environmental Science and Technology. 14(2):187-190.

Norwood, D.L., Christman, R.F. and Hatcher, P.G. 1987. Structural Relationship of Aquatic Humic Material. 2. Phenolic Content and Its Relationship to Chlorination Mechanism in an Isolated Aquatic Fulvic Acid. Environmental Science and Technology. 21(6):791-798.

Nyström, A., Grimvall, A., Krantz-Rülcker, C., Sävenhed, R. and Åkerstrand, K. 1992. Drinking Water Off-Flavour caused by 2,4,6-Trichloroanisole. Water Science and Technology. 25(2):241-249.

Pichon, M., Meyer, F. and Francois, E. 1986. Anaerobic Treatment of CTMP Wastewater. Proceedings EUCEPA Symposium. Helsinki, May 19-22, 1986. pp.131-139.

Pichon, M., Rouger, J. and Junet, E. 1989. Effects of Sulphate Reduction on Anaerobic Treatment of CTMP WasteWaters. TAPPI Proceedings of the Wood and Pulping Chemistry Conference. Raleigh, N.C. May 22-25, 1989. pp. 735-738.

Pierce, R.C. 1978. The Aqueous Chlorination of Organic Compounds: Chemical Reactivity and Effects on Environmental Quality. National Research Council Canada Publication No. 16450. Ottawa, Canada. 135 p.

Rapson, W.H. Nazar, M.A. and Butsky, V.V. 1980. Mutagenicity Produced by Aqueous Chlorination of Organic Compounds. Bulletin of Environmental Contamination and Toxicology. 24:590:596.

Reckhow, D.A. and Singer, P.C. 1985. Mechanisms of Organic Halide Formation during Fulvic Acid Chlorination and Implications with Respect to Preozonation. In: Water Chlorination: Chemistry, Environmental Impact and Health Effects. Vol. 5. Lewis Publishers, Chelsea, MI. 1985. pp. 1229-1257.

Reckhow, D.A., Singer, P.C. and Malcolm, R.L. 1990. Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations. Environmental Science and Technology. 24(11):1655-1664.

Rintala, J. and Vuoriranta, P. 1988. Anaerobic-Aerobic Treatment of Thermomechanical Pulping Effluents. Tappi Journal. 71(9):201-207.

Rook, J.J. 1977. Chlorination Reactions of Fulvic Acids in Natural Waters. Environmental Science and Technology. 11(5):478-472.

Shibata, S., Katsuyama, A. and Noguchi, M. 1978. On the Constituents of an Essential Oil of Kudzu. Agricultural and Biological Chemistry. 42(1):195-197.

Sierra-Alverez, R. and Lettinga, G. 1991. The Methanogenic Toxicity of Wastewater Lignins and Lignin Related Compounds. Journal of Chemical Technology and Biotechnology. 50(4):443-455.

Sierra-Alverez, R., Kortekaas, S., van Eekert, M. and Lettinga, G. 1991. The Anaerobic Biodegradability and Methanogenic Toxicity of Pulping Wastewaters. Water Science and Technology. 24(3/4):113-125.

Suntio, L.R., Shiu, W.Y. and Mackay, D. 1988. A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents. Chemosphere. 17(7):1239:1290.

Urbantas, R.G. and MacEwan, H.D 1985. Characterization of Effluents from Chemimechanical, Chemithermomechanical and Thermomechanical Pulping of Black Spruce. Preprints of the Canadian Pulp and Paper Association 71st Annual Meeting. Montreal Jan. 29-30, 1989. pp. A213-A219.

Vartiainen, T. and Liimatainen, A. 1986. High Levels of Mutagenic Activity in Chlorinated Drinking Water in Finland. Mutation Research. 169(1/2):29-34.

Vuoriranta, P., Rintala, J. and Morange, H. 1987. Anaerobic-Aerobic versus Aerobic Treatment of Concentrated Pulp and Paper Mill Effluent. Water Science and Technology. 19(7):1219-1221.

Wigilius, B., Boren, H., Grimvall, A., Carlberg, G.E., Hagen, I. and Brögger, A. 1988. Impact of Bleached Kraft Mill Effluents on Drinking Water Quality. The Science of the Total Environment. 74:75-76.

APPENDIX, 1

ANALYTICAL METHODS, DETECTION LIMITS AND TYPICAL QUALITY CONTROL DATA

Table A1. Analytical Methods, Detection Limits and Typical Quality Control Data

Parameter Description	Naquadat Code	Detection Limit	Units	Date Analyzed	QA/QC Batch Number	Duplicates Rr	% Recovery	Check Warning Limit		% Recovery	Check Warning Limit	
								Lower	Upper		Lower	Upper
Ca-(AA) Dissolved	20103L	0.01	mg/L	10-08-93	1	0.4	101.8	96.7	104.0	98.4	97.1	103.9
Mg-(AA) Dissolved	12102L	0.01	mg/L	10-08-93	1	2.2	98.8	96.0	103.4	99.2	96.4	102.5
Na-(Flame Photometer)	11103L	0.2	mg/L	08-08-93	1	3.0	98.4	92.4	106.8	102.0	97.6	104.5
Sulphate - Dissolved	16306L	0.5	mg/L	06-08-93	2	0.5	99.6	91.5	108.3	98.6	91.1	107.8
PP Alkalinity	10151L	0.1	mg/L	Not Applicable								
Total Alkalinity	10111L	0.1	mg/L	09-08-93	3	0.1	Not Applicable					
pH	10301L	0.01	Units	09-08-19	3	0.1	Not Applicable					
Carbonate	06301L	0.5	mg/L	Not Applicable								
Bicarbonate	06201L	0.5	mg/L	Not Applicable								
Total Hardness	10602L	0.5	mg/L	Not Applicable								
Hydroxide	08501L	0.5	mg/L	Not Applicable								
Tannin and Lignin	06551L	0.1	mg/L	11-08-93	1	3.0	89.7	88.1	110.0	93.0	89.5	105.8
Turbidity	02074L	0.1	NTU	Not Applicable								
Colour (True)	02021L	5.	PtCo Units	Not Applicable								
BOD	08202L	0.1	mg/L	Not Applicable						95.7	77.4	122.0
COD	08301L	5.	mg/L	19-08-93	1	2.5	Not Applicable					
Sulphide	16101L	0.01	mg/L	27-08-93	1	0.0	115.0	75.3	114.6	107.5	72.7	113.4
Total Inorganic C	06052L	0.5	mg/L	16-08-93	1	0.2	98.4	92.4	109.8	93.3	80.4	121.1

Table A.1 (Continued)

Parameter Description	Naquadat Code	Detection Limit	Units	Date Analyzed	QA/QC Batch Number	Duplicates Rr	% Recovery	Check Warning Limit		% Recovery	Check Warning Limit	
								Lower	Upper		Lower	Upper
Dissolved Inorganic C	06152L	0.5	mg/L	16-08-93	1	0.2	98.4	92.4	109.8	93.3	80.4	121.1
TOC	06005L	0.2	mg/L	10-08-93	2	0.0	102.6	95.0	106.1	104.8	95.0	111.2
Dissolved Organic C	06104L	0.2	mg/L	10-08-93	2	0.0	102.6	95.0	106.1	104.8	95.0	111.2
Total C	Calc	0.5	mg/L	Not Applicable								
Total Ammonia N	07505L	0.01	mg/L	12-08-93	10	0.7	90.0	86.8	108.2	106.5	90.2	105.8
Total Kjeldahl N	07015L	0.02	mg/L	10-08-93	11	2.0	100.6	88.7	112.9	92.0	90.2	114.5
Organic N	07403L	0.02	mg/L	Not Applicable								
Total Phosphorus as P	15406L	0.003	mg/L	20-08-93	1	1.0	98.9	89.6	112.5	94.0	90.0	113.2
Total Filterable Residue	10451L	1.	mg/L	12-08-93	1	1.5	Not Applicable					

Rr	Range Ratio
QA/QC	Quality Assurance/Quality Control
(AA)	Atomic Absorption Spectroscopy
PP	Phenolphthalein

APPENDIX 2

RAW DATA

Table A2.1. Model Compound: Results of Target Compound Analyses

Trial No.	Chloroform (μg/L)	Dichloroacetic Acid (μg/L)	Trichloroacetic Acid (μg/L)	Compound MX (ng/L)
1	1.43	2.11	0.18	(<10.8)
2	55.8	95.1	23.7	49.7
3	2.11	57.0	0.42	(<22.7)
4	82.2	90.1	1.81	22.6
5	6.15	21.0	1.68	(<20.1)
6	52.7	30.3	6.88	41.0
7	1.46	20.9	0.31	(<10.4)
8	325	238	15.0	11.9
9	24.5	78.3	2.74	36.3
10	19.9	20.8	2.94	49.7
11	26.3	131	5.67	12.3
12	20.8	91.8	1.11	35.6
13	4.86	10.6	1.36	(<7.5)
14	9.71	19.1	1.64	(<15.8)
15	5.64	34.2	0.35	(<6.45)
16	241	101	8.36	25.5
17	3.69	1.08	0.09	(<10.6)
18	303	0.62	0.37	(<15.1)
19	5.96	73.6	0.72	(<5.30)
20	147	37.9	0.99	11.0
21	29.5	73.4	2.89	32.6
22	27.4	58.1	2.07	29.9
23	34.7	NR	NR	NR
24	27.7	52.8	1.36	28.1

( ) - figures in brackets are the estimated minimum detectable concentrations based on minimum reportable concentrations, volume extracted and surrogate recovery.
NR - not run
ND - not detected

Table A2.2. Model Compound: Pulp and Paper Chlorophenolics Analyses (µg/L)

Trial No.	4-chloroguaiacol	4,6-dichloroguaiacol	4-chlorocatechol
1	0.166	1.19	ND
2	0.392	2.41	0.133
3	0.633	0.575	ND
4	ND	22.3	0.025
5	0.262	3.53	0.014
6	0.080	2.93	0.064
7	0.33	0.385	ND
8	ND	42.6	0.043
9	0.435	12.5	0.040
10	0.251	11.3	ND
11	0.528	16.2	0.039
12	0.463	11.1	ND
13	0.164	3.39	0.009
14	0.21,IC	10.3	0.041
15	0.299	0.438	ND
16	ND	37.3	0.074
17	ND	0.930	ND
18	0.075,IC	0.392	0.277
19	0.497	0.642	ND
20	ND	31.5	0.149
21	0.25	14.4	0.051
22	0.309	12.6	0.050
23	0.300	13.0	0.031
24	0.266	11.3	0.038

IC = missing confirmation ion
ND = not detected

Table A2.3. Model Compound: Chlorophenolic Analyses (Reported as Detectable Total Ion Counts)

Trial No.	DiHyBenz	Cltriol	Vanillin	46-DCG	HyG	ClV1	ClV2	ClVG1
1			22740		282389		123469	515633
2			328293	51377	1075175		58136	15498
3			48321				311730	137170
4		97331		399705		147661	734448	
5		12283					370816	2410600
6		216583		49001			30283	
7			219168			27417	194974	605644
8		146511		797954		343189	1781610	
9		38383	60000	137401		137860	1039060	220400
10		28585	68144	123107		129664	956890	253952
11			64194	159219		65186	1154892	222883
12		26275	77932	123769		122755	1169752	361655
13			14606		537940		485990	2091790
14	73209	47740		172602	297418	32004	237244	462493
15			60719				57965	282597
16		280331		891652		451583	1311764	
17			25453			17396	201378	422413
18		1216210		80401			32360	
19			395340				452650	1506840
20		69100		376781		281158	850947	
21		162862	76657	192246		181857	1088353	188094
22		109372	82218	205493		238156	1262674	233666
23		41638	70845	186661		168892	1321998	92804
24		31431	66132	166468		154075	1063189	193357

DiHyBenz = dihydroxybenzaldehyde
Cltriol = chlorobenzenetriol
46-DCG = 4,6-dichloroguaiacol
HyG = 4-hydroxyguaiacol
ClV1 = chlorovanillin1
ClV2 = chlorovanillin2
ClVG1 = chloro-4-vinylguaiacol1

Table A2.3. (Continued)

Trial No.	ClVG2	ClHyG	PHENAN	DClVG1	DClVG2	DClVC1	DClVC2	TClVG
1	8297526	82164	103221	814019	6783815		68384	
2	72173	97756	85417	52765		38487		
3	985926		142435	170929	1987259		59807	
4			98334	405505	712129			47752
5	23092799		93553	2011100	14454029			
6			113247	43427		40593	199015	105112
7	3223183		92965	635759	7782017			
8			136052	473956	441580			62448
9	1154200		146208	789770	3011590	68064	38337	
10	996432		110585	979093	2873145		237052	
11	875309		110048	916831	2608916		197941	
12	1582057		81671	476397	3757130		193996	
13	20251710	118249	158234	1753730	15958430	41300	210584	16781
14	707663	146227	139088	156256	539451			
15	3544178		142693	578988	9145238			
16			159240	530750	528234			104045
17	6182953		134855	581439	4781470	519[illegible]		
18	40750		137639		138279	136496		
19	7571100		146849	2174800	20932430			
20			156951	238521	260208			
21	658364		145805	989077	2629766	77244		
22	862791		123345	1059211	2907573		405887	
23	758069		63065	518516	2587465	96101		
24	732094		130999	453912	2406882	66455	200600	

ClVG2 = chloro-4-vinylguaiacol2
ClHyG = chloro-4-hydroxyguaiacol
Phenan = phenanthrene (internal standard)
DClVG1 = dichloro-4-vinylguaiacol1
DClVG2 = dichloro-4-vinylguaiacol2
DClVC1 = dichloro-4-vinylcatechol1
DClVC2 = dichloro-4-vinylcatechol2
TClVG = 3,5,6-trichloro-4-vinylguaiacol

Table A2.4. Model Compound: Estimated Chloro-4-vinylguaiacol and Chlorovanillin Concentrations

Trial No.	ClVG1 (ug/L)	ClVG2 (ug/L)	DClVG1 (ug/L)	DClVG2 (ug/L)	ClV2 (ug/L)	Sum of TOC (ug/L)	Production (as wt % of added TOC)
1	37.0	507	56.8	419	9.62	523	26.1
2	1.63	6.93	5.16	<3.00	5.65	12.2	0.24
3	7.84	50.3	9.64	97.3	17.0	89.6	1.79
4	<1.00	<1.00	30.9	52.5	54.0	66.0	3.30
5	173	1460	146	938	29.7	1410	28.2
6	<1.00	<1.00	3.29	<3.00	2.34	5.27	0.26
7	47.5	229	49.7	526	16.3	427	21.4
8	<1.00	<1.00	26.3	24.6	91.7	68.6	1.37
9	12.0	56.9	39.8	140	51.5	146	4.18
10	17.8	64.4	63.4	175	62.0	186	5.30
11	15.8	57.3	59.9	160	74.4	178	5.09
12	33.0	132	42.8	299	99.7	298	8.50
13	92.5	785	78.3	627	23.4	818	16.4
14	25.2	37.6	9.06	29.1	13.4	58.5	2.92
15	15.5	168	30.4	409	3.48	306	15.3
16	<1.00	<1.00	25.2	25.1	59.2	52.7	1.05
17	23.8	298	32.2	234	11.8	306	15.3
18	<1.00	2.58	<3.00	8.16	2.08	10.3	0.21
19	72.8	333	103	869	23.5	685	13.7
20	<1.00	<1.00	12.0	13.1	39.9	31.7	1.58
21	10.3	33.6	49.3	124	54.0	130	3.73
22	14.8	50.8	61.6	160	72.7	174	4.96
23	11.7	84.6	89.1	269	143	274	7.82
24	11.7	41.1	26.2	126	58.4	128	3.65

Results reported as < are calculated from minimum detectable response.

Table A2.5 Effluent Samples: Results of 2,4,6-Trichlorophenol Analysis

Trial No.	246-TCP (µg/L)
1	0.187 (IC)
2	1.30 (IC)
3	0.280 (IC)
4	5.48 (IC)
5	0.216 (IC)
6	0.608 (IC)
7	0.446 (IC)
8	2.56 (IC)
10	2.90 (IC)
11	1.72 (IC)
12	0.073 (IC)
13	ND

246-TCP - 2,4,6-trichlorophenol
ND - Not Detected
IC - Missing single confirmation ion.

Table A2.6 Effluent Samples: Results of Target Compound Analyses

Trial No.	Chloroform (µg/L)	Dichloroacetic acid (µg/L)	Trichloroacetic acid (µg/L)	Compound MX (ng/L)
1	13.8	5.14	4.04	ND (<4.33)
2	28.2	2.34	4.11	5.76
3	27.3	4.28	6.66	ND (<5.68)
4	103	20.5	37.3	12.0
5	118	24.0	38.4	11.4
6	136	64.2	53.2	11.1
7	188	85.0	54.8	7.61
8	208	73.5	139	23.7
10	96.9	15.6	30.0	8.65
11	101	26.0	34.2	4.68
12	121	20.7	25.5	14.3
13	11.8	2.98	3.29	ND (<3.30)

ND Not Detected

( ) Figures in brackets estimated minimum detectable concentration for that particular trial calculated from minimum detectable amount, surrogate recovery and the concentration factor.

Table A2.7 TOX Analyses

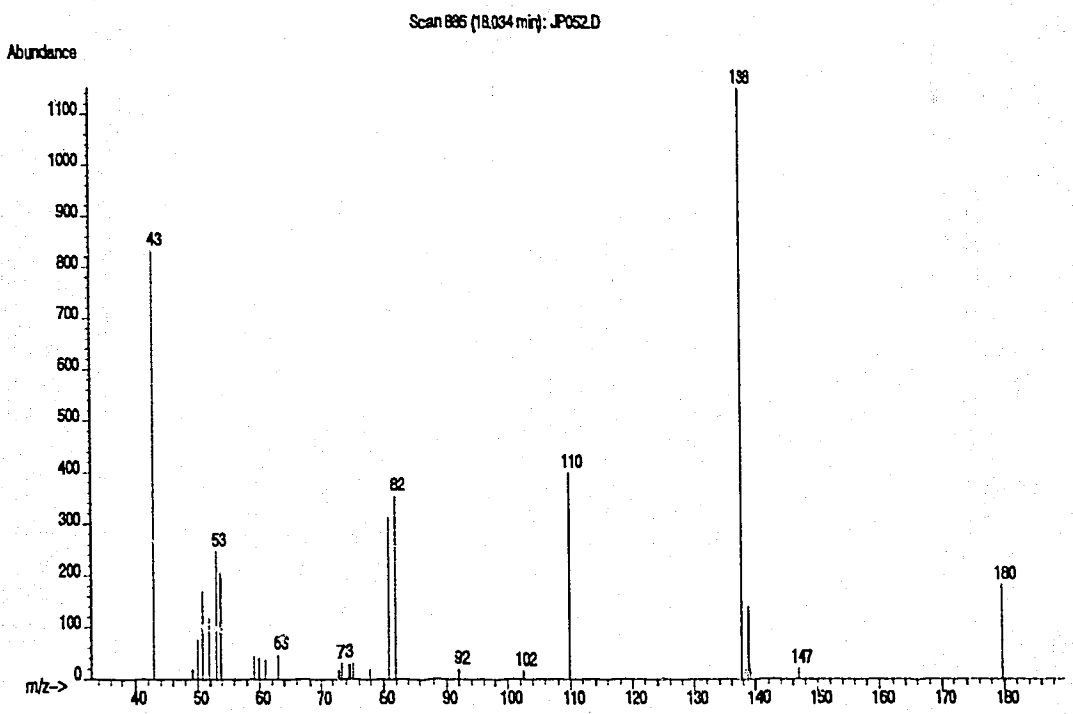
Trial No.	Cl_2 Dose (mg Cl_2/L)	Total Cl_2[a] Residual (mg Cl_2/L)	Cl_2 Consumed (mg Cl_2/L)	NPAOX (mg Cl/L)	$CHCl_3$ (mg/L)	TOX[b] (mg Cl/L)
3	1.75	0.71	1.04	0.122	0.038	0.156
4	7.30	0.32	6.98	0.563	0.115	0.666
13	1.10	0.69	0.41	0.033	0.008	0.040

[a] Sum of free plus combined chlorine.

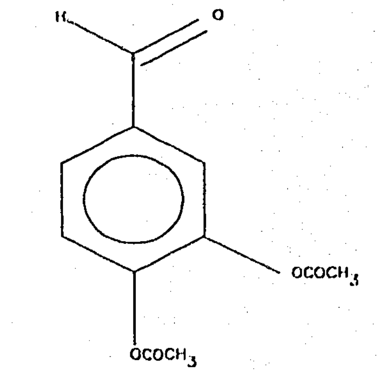
[b] TOX=NPAOX + mg $CHCl_3$ x 0.892 (3 x 35.45/119.35)

APPENDIX 3

TENTATIVE IDENTIFICATION OF ACETYLATED CHLOROPHENOLIC BY-PRODUCTS



m/z	Formation
180	$[M\text{-}CH_2CO]^{+\cdot}$
138	$[M\text{-}2CH_2CO]^{+\cdot}$
110	$[138\text{-}CO]^{+\cdot}$
82	$[138\text{-}2CO]^{+\cdot}$
81	$[138\text{-}2CO,\text{-}{\cdot}H]^{+}$ $[138\text{-}CO,\text{-}H{\cdot}CO]^{+}$
54	$[138\text{-}3CO]^{+\cdot}$
53	$[138\text{-}3CO,\text{-}H{\cdot}]^{+}$ $[138\text{-}2CO,\text{-}HCO{\cdot}]^{+}$

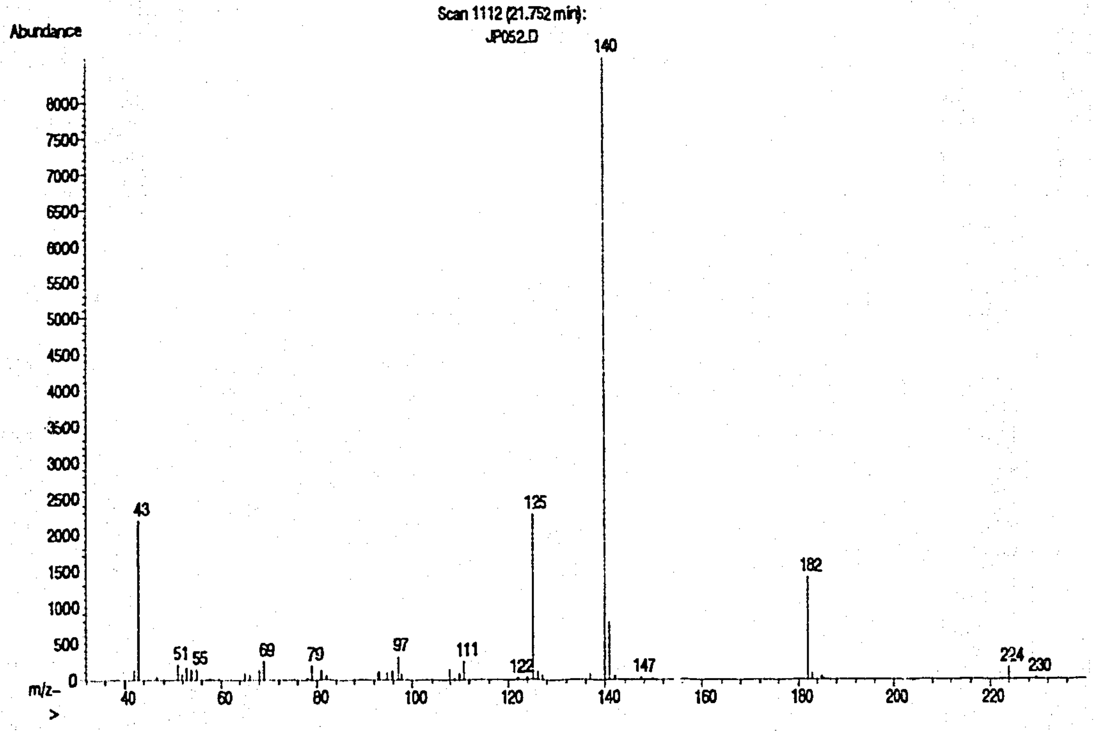


Acetylated 3,4-Dihydroxybenzaldehyde

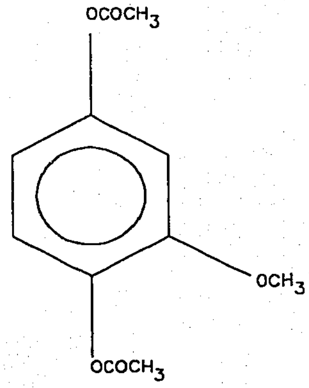
(DiHybenz)

m/z = mass/charge ratio
M = molecular ion

Figure A3.1. a) Mass spectrum (Trial 14). b) Proposed fragmentation pathway. c) Tentative structure of acetylated 3,4-dihydroxybenzaldehyde.

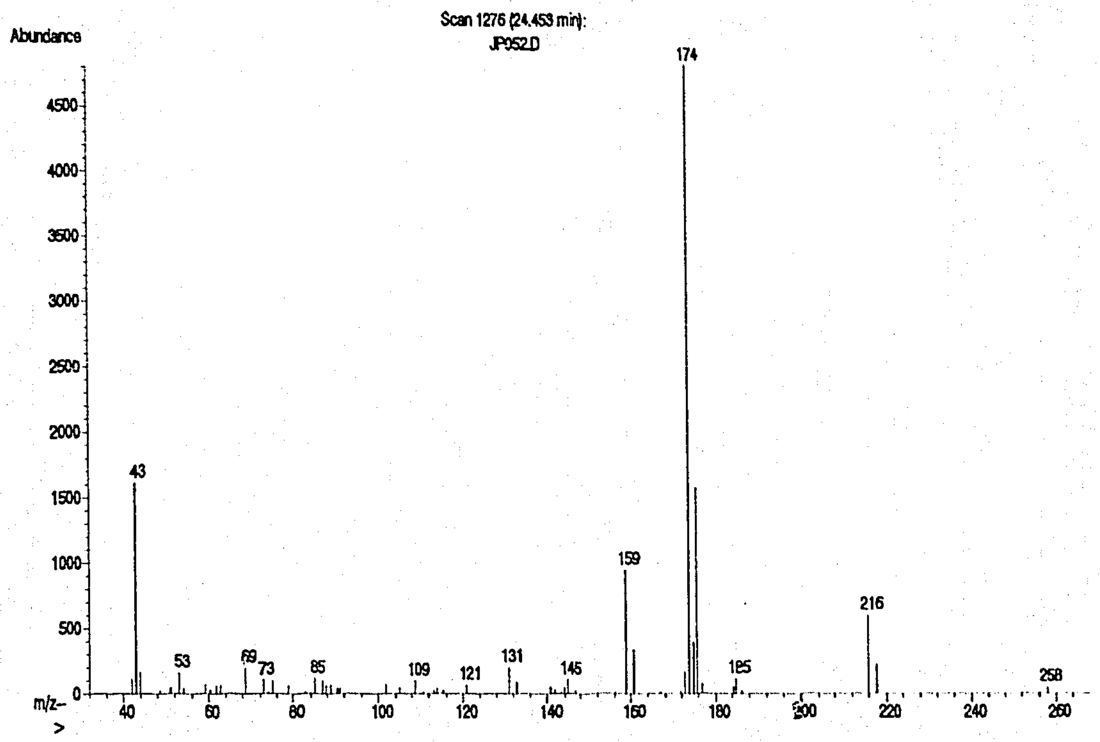


m/z	Formation
224	$[M]^{+\cdot}$
182	$[M-CH_2CO]^{+\cdot}$
140	$[M-2CH_2CO]^{+\cdot}$
125	$[140-{}^{\cdot}CH_3]^{+}$
111	$[140-H^{\cdot}CO]^{+}$
97	$[140-{}^{\cdot}CH_3-CO]^{+}$
69	$[140-{}^{\cdot}CH_3-2CO]^{+}$

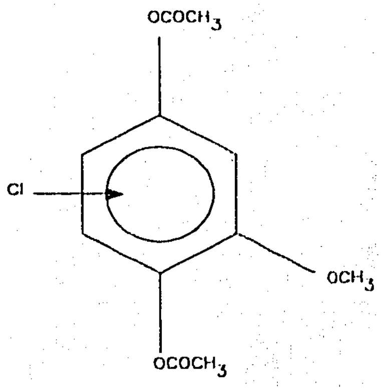


Acetylated 4—Hydroxyguaiacol (HyG)

Figure A3.2 a) Mass spectra (Trial 14). b) Proposed fragmentation pathway. c) Tentative structure of acetylated 4-hydroxyguaiacol.



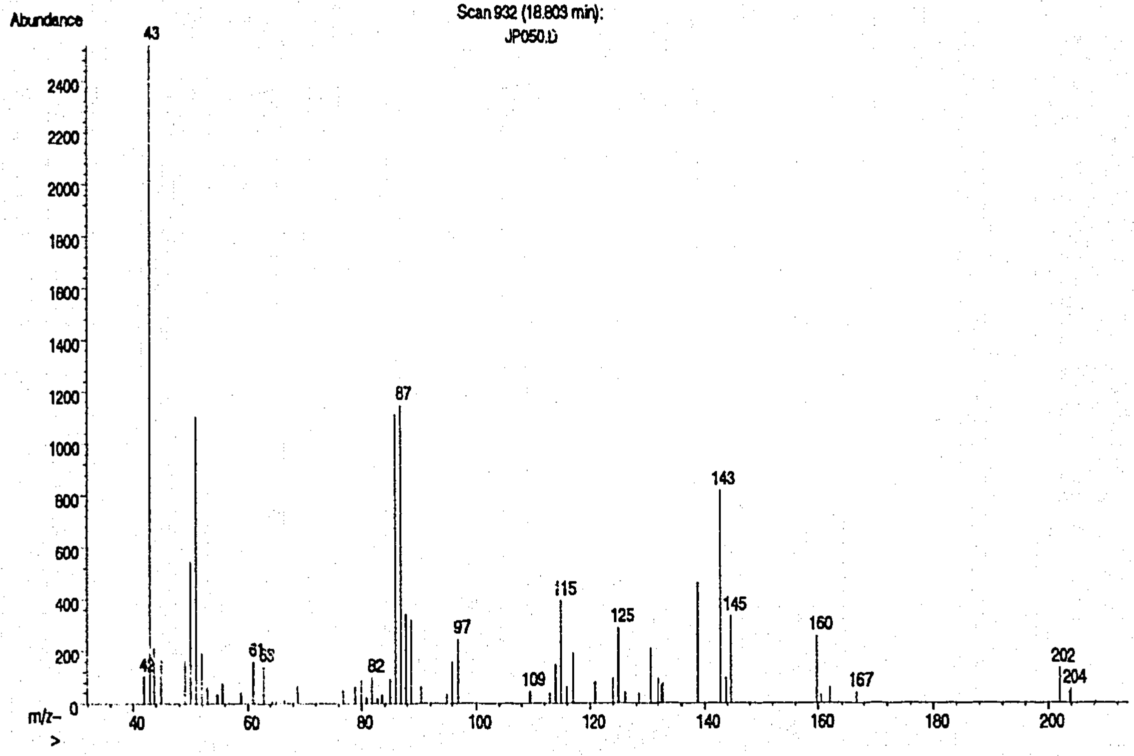
m/z	Formation
258	$[M]^{+\cdot}$
216	$[M\text{-}CH_2CO]^{+\cdot}$
174/176	$[M\text{-}2CH_2CO]^{+\cdot}$
159/161	$[174/176\text{-}CH_3]^{+}$
131	$[159\text{-}CO]^{+}$
69	$[131\text{-}C_2H_2]^{+}$



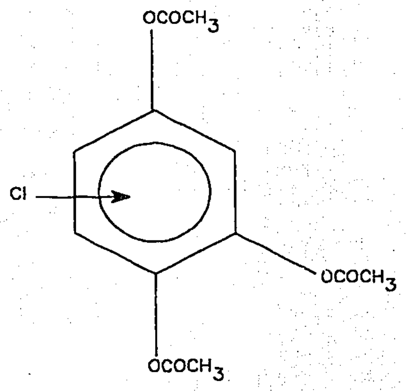
Acetylated Chloro-4-hydroxyguaiacol

(ClHyG)

Figure A3.3 a) Mass spectra (Trial 14). b) Proposed fragmentation pathway. c) Tentative structure of acetylated Chloro-4-hydroxyguaiacol.

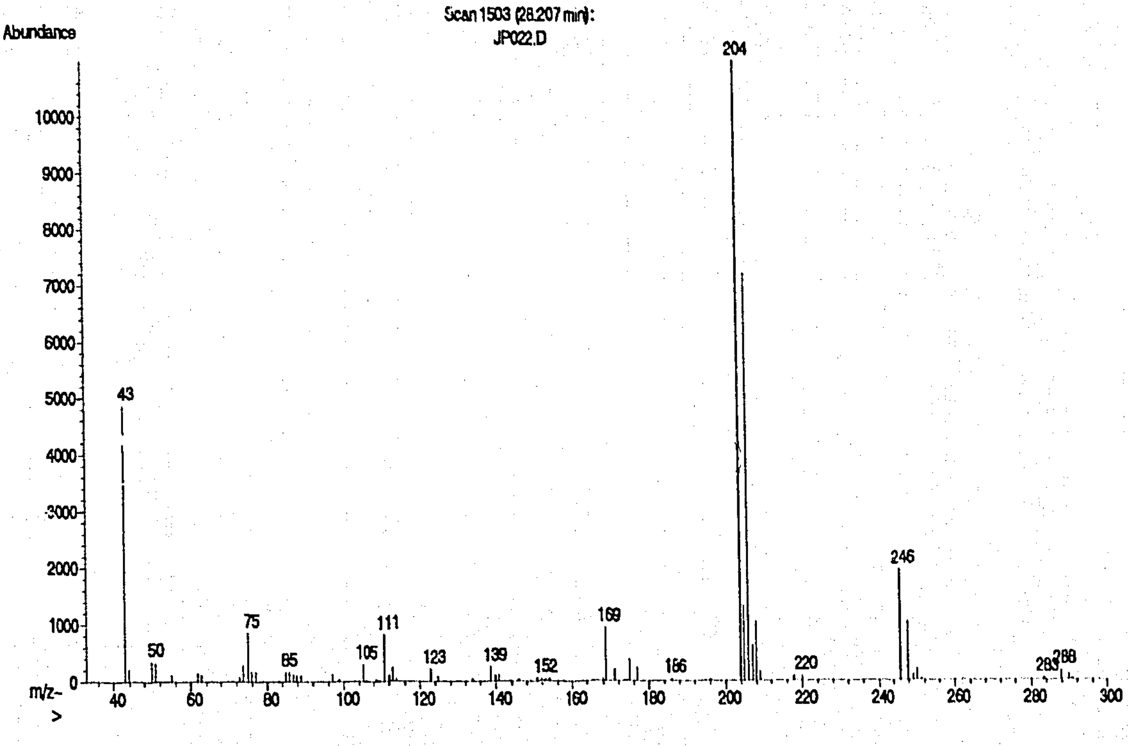


m/z	Formation
202/204	$[M\text{-}CH_2CO]^{+\cdot}$
160/162	$[M\text{-}2CH_2CO]^{+\cdot}$
143/145	$[160/162\text{-}\cdot OH]^{+}$
115/117	$[143/145\text{-}CO]^{+}$
87/89	$[115/117\text{-}CO]^{+}$
86/88	$[87/89\text{-}\cdot H]^{+\cdot}$
51	$[87\text{-}HCl]^{+}$
50	$[86\text{-}HCl]^{+\cdot}$

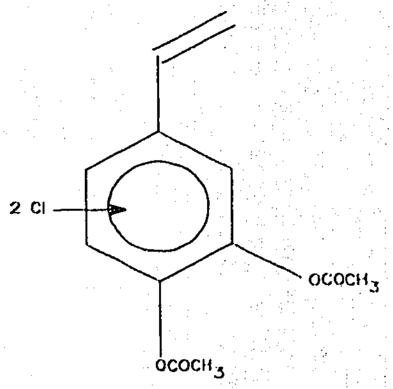


Acetylated Chloro—1,2,4—benzenetriol
(Cltriol)

Figure A3.4 a) Mass spectra (Trial 16). b) Proposed fragmentation pathway. c) Tentative structure for acetylated Chloro-1,2,4-benzenetriol.

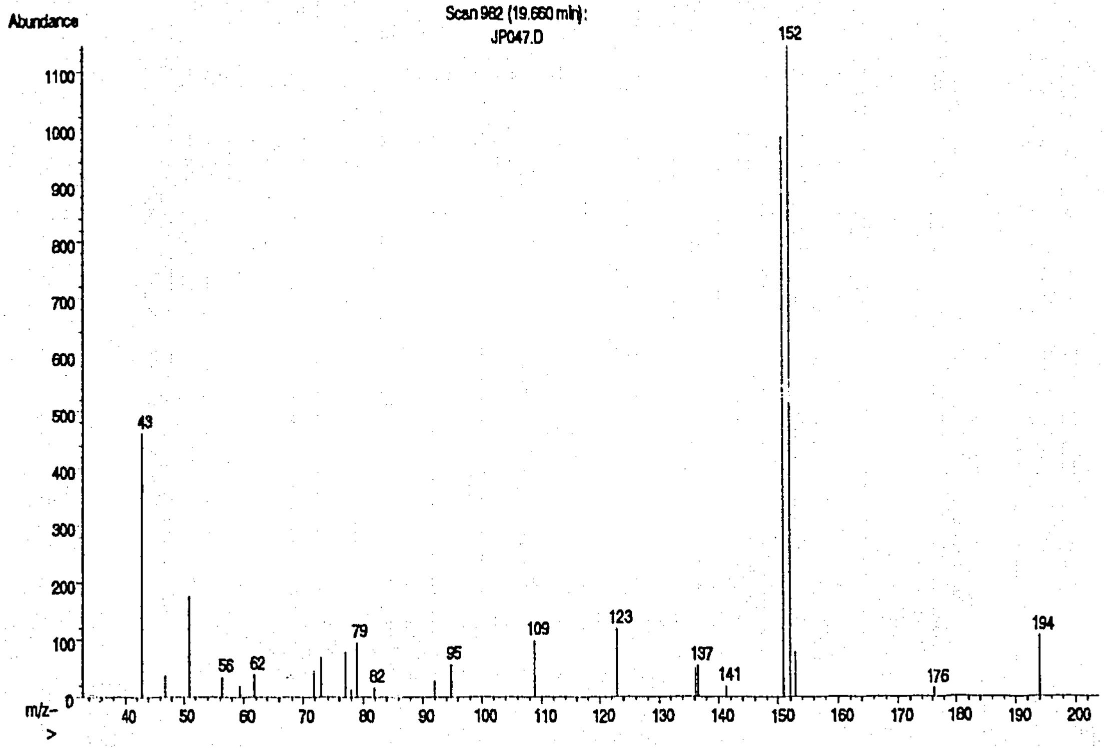


m/z	Formation
288	$[M]^{+\cdot}$
246	$[M-CH_2CO]^{+\cdot}$
204/206/208	$[M-2CH_2CO]^{+\cdot}$
169	$[204-35]^{+}$

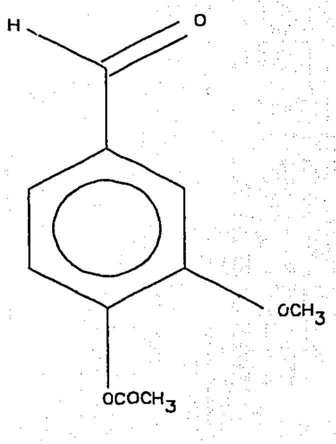


Acetylated Dichloro-4-vinylcatechol
(DCIVC)

Figure A3.5 a) Mass spectra (Trial 5). b) Proposed fragmentation pathway. c) Tentative structure of acetylated Dichloro-4-vinylcatechol.

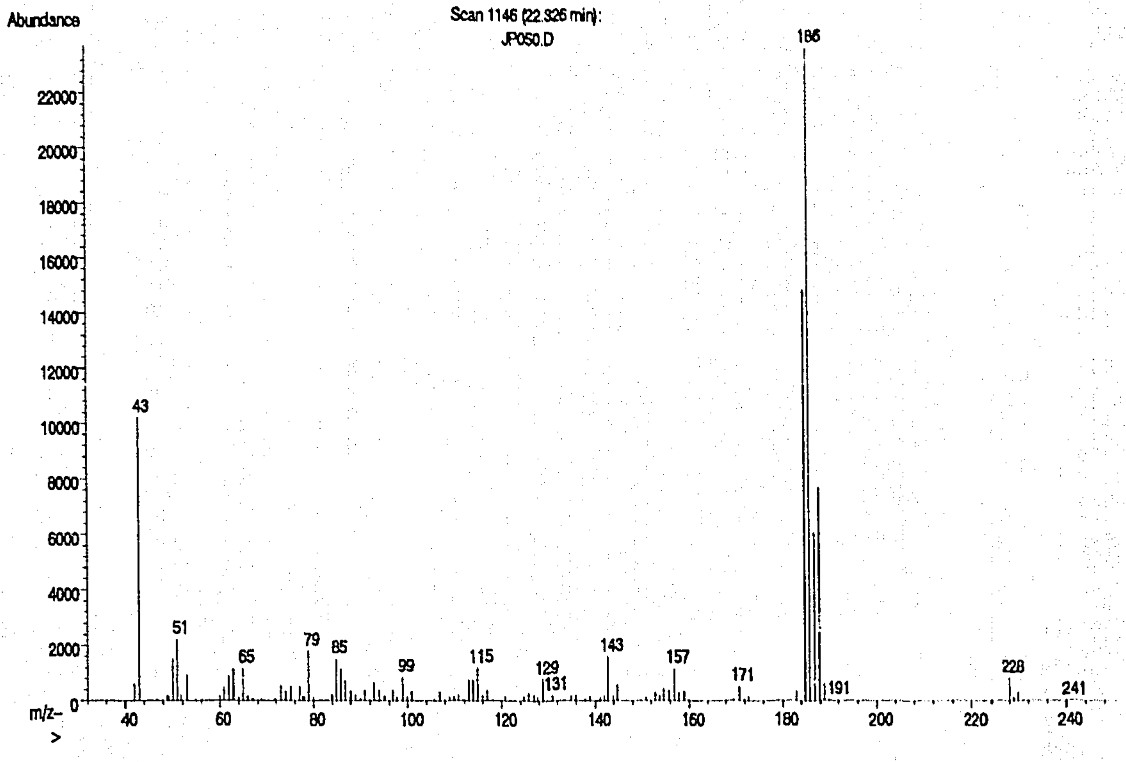


m/z	Formation
194	$[M]^{+\cdot}$
152	$[M\text{-}CH_2CO]^{+\cdot}$
151	$[152\text{-}\cdot H]^{+}$
137	$[152\text{-}\cdot CH_3]^{+}$
136	$[152\text{-}\cdot H,\text{-}\cdot CH_3]^{+\cdot}$
123	$[152\text{-}H\cdot CO]^{+}$
109	$[137\text{-}CO]^{+}$
95	$[123\text{-}CO]^{+}$

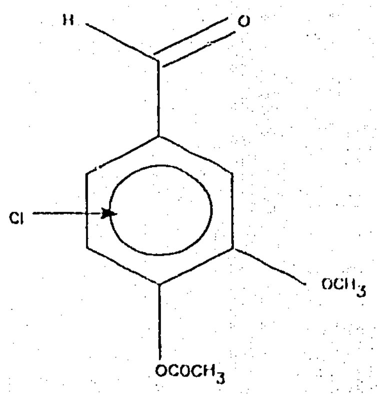


Acetylated Vanillin

Figure A3.6 a) Mass spectra (Trial 15). b) Proposed fragmentation pathway. c) Structure of acetylated Vanillin.

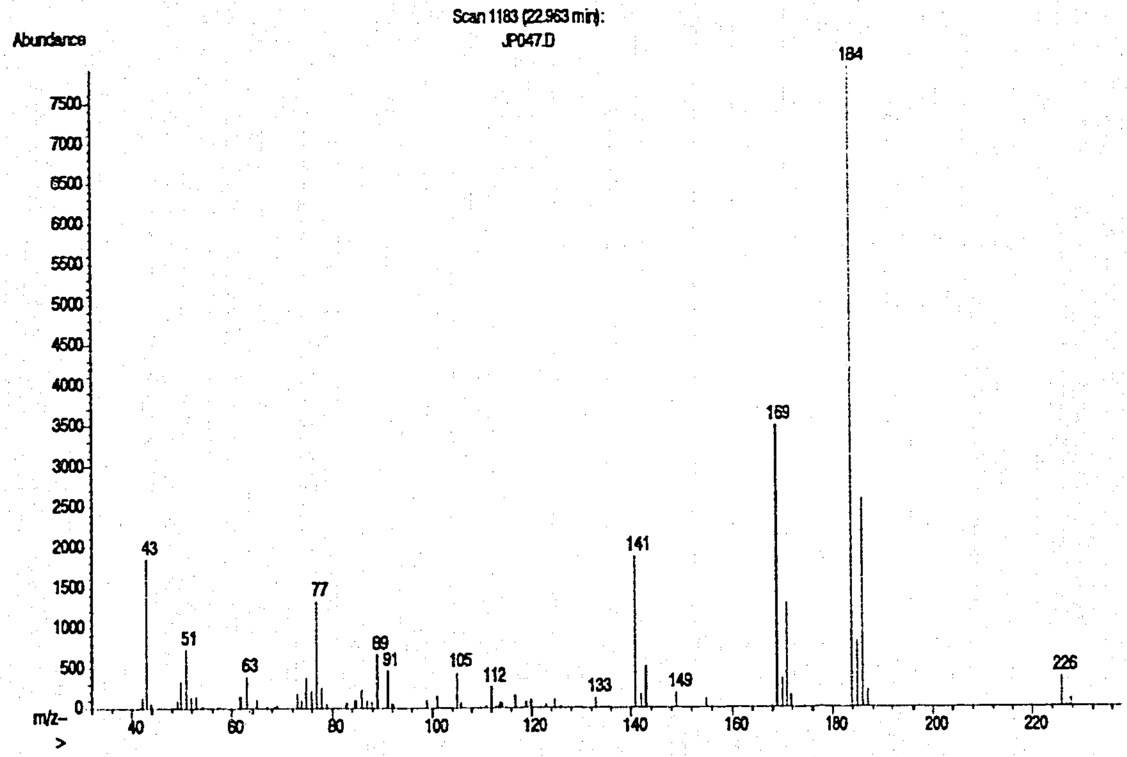


m/z	Formation
228	$[M]^{+\cdot}$
186/188	$[M-CH_2CO]^{+\cdot}$
185/187	$[M-{}^{\cdot}H]^{+}$
171	$[186-{}^{\cdot}CH_3]^{+}$
157	$[185-CO]^{+}$
143	$[171-CO]^{+}$
115	$[143-CO]^{+}$
79	$[115-HCl]^{+}$
51	[79-CO]

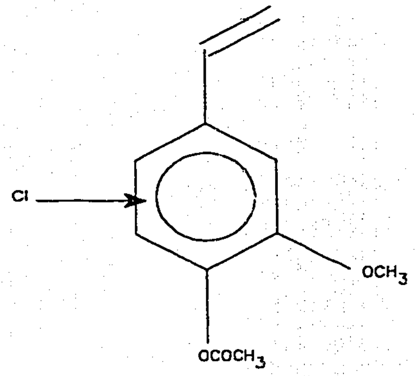


Acetylated Chlorovanillin
(CIV)

Figure A3.7 a) Mass spectra (Trial 16). b) Proposed fragmentation pathway. c) Tentative structure of acetylated Chlorovanillin.

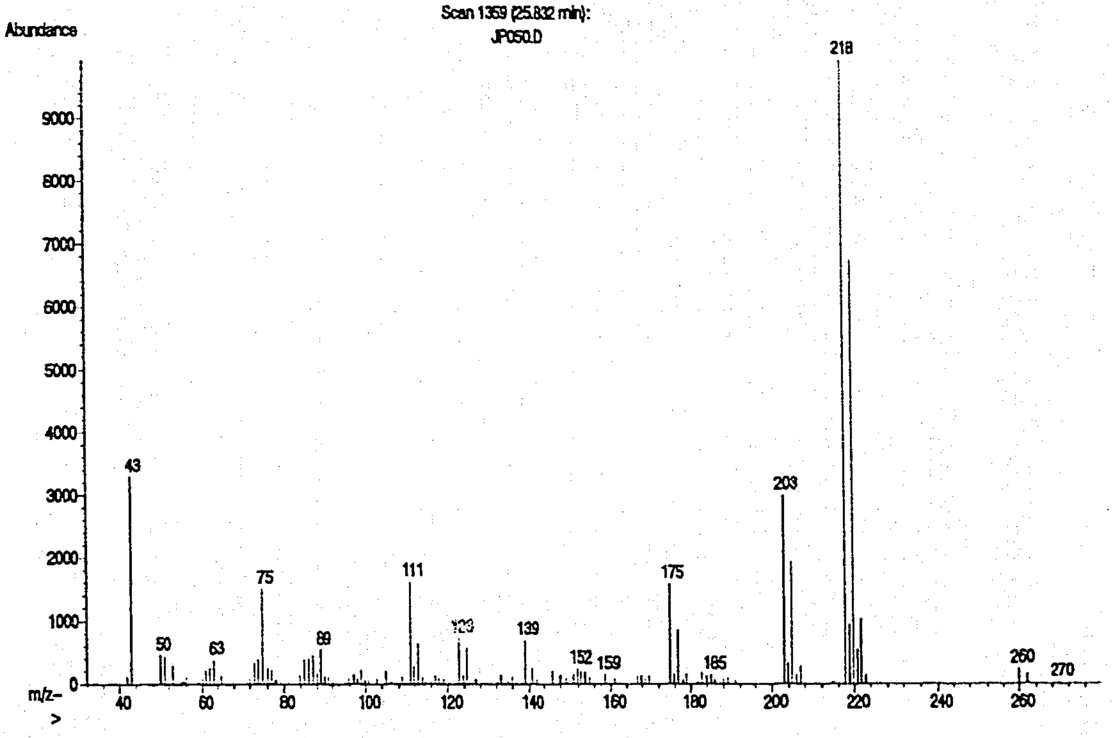


m/z	Formation
226/228	$[M]^{+\cdot}$
184/186	$[M\text{-}CH_2CO]^{+\cdot}$
169/171	$[184/186\text{-}{\cdot}CH_3]^+$
141/143	$[169/173\text{-}CO]^+$
105	$[141\text{-}HCl]^+$
77	$[105\text{-}CO]^+$
51	$[77\text{-}C_2H_2]^+$

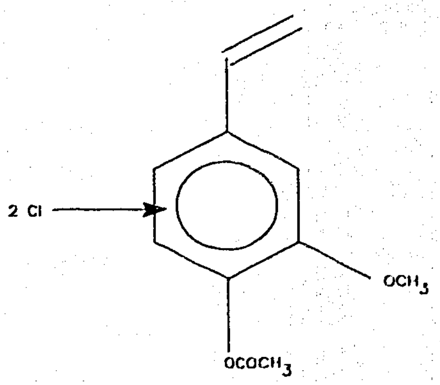


Acetylated Chloro-4-vinylguaiacol
(ClVG)

Figure A3.8 a) Mass spectra (Trial 15). b) Proposed fragmentation pathway. c) Tentative structure of acetylated Chloro-4-vinylguaiacol.

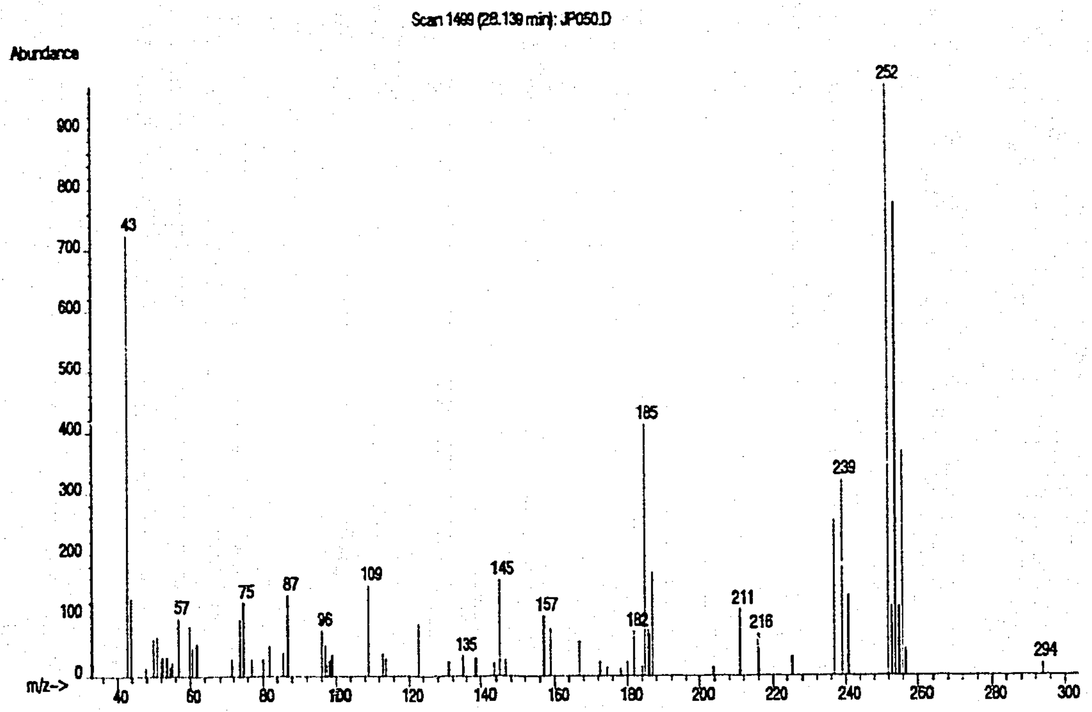


m/z	Formation
260	$[M]^{+\cdot}$
218/220/222	$[M\text{-}CH_3CO]^{+\cdot}$
203/205	$[218/220\text{-}{}^{\cdot}CH_3]^+$
175/177	$[218/220\text{-}CO]^+$
139/141	$[175/177\text{-}HCl]^+$
111/113	$[139/141\text{-}CO]^+$
75	[111-HCl]

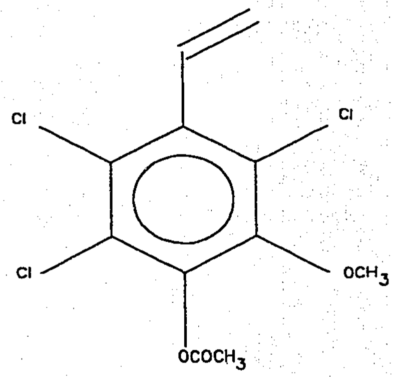


Acetylated Dichloro-4-vinylguaiacol
(DCVG)

Figure A3.9 a) Mass spectra (Trial 16). b) Proposed fragmentation pathway. c) Tentative structure of acetylated Dichloro-4-vinylguaiacol.



m/z	Formation
294	$[M]^{+\cdot}$
252/254/256	$[M\text{-}CH_2CO]^{+\cdot}$
237/239	$[252/254\text{-}CH_3]^{+}$
145	$[237\text{-}2CO\text{-}HCl]^{+}$
109	$[145\text{-}HCl]^{+}$



Acetylated 3,5,6–Trichloro–4–vinylguaiacol
(TCIVG)

Figure A3.10 a) Mass spectra Trial 16). b) Proposed fragmentation pathway. c) Tentative structure of acetylated 3,5,6-Trichloro-4-vinylguaiacol.

APPENDIX 4

SAMPLE MULTIPLE REGRESSION AND ANALYSIS OF VARIANCE REPORT

```
----------------------------Multiple Regression----------------------------
Date/Time          01-05-1994  14:38:05
Data Base Name     C:\ncss\thesis\new
Description        Merge of MODLCMPD and TEST created 08-18-1993


                   Multiple Regression Report

Dependent Variable: 4,6_DCG
Independent   Parameter   Stndized   Standard     t-value  Prob.   Seq.    Simple
Variable      Estimate    Estimate   Error        (b=0)    Level   R-Sqr   R-Sqr
Intercept     11.14392    0.0000     .5518119     20.20    0.0000
X1            1.058125    0.0745     .6758288     1.57     0.1519  0.0056  0.0056
X2            8.4195      0.5931     .6758288     12.46    0.0000  0.3574  0.3518
X3            7.170875    0.5052     .6758288     10.61    0.0000  0.6126  0.2552
X4            .058875     0.0041     .6758288     0.09     0.9325  0.6126  0.0000
X1X2          .908875     0.0640     .6758288     1.34     0.2116  0.6167  0.0041
X1X3          1.76025     0.1240     .6758288     2.60     0.0285  0.6321  0.0154
X1X4          .381        0.0268     .6758288     0.56     0.5867  0.6328  0.0007
X2X3          7.546625    0.5316     .6758288     11.17    0.0000  0.9154  0.2826
X2X4          .573125     0.0404     .6758288     0.85     0.4184  0.9171  0.0016
X3X4          1.248       0.0879     .6758288     1.85     0.0979  0.9248  0.0077
X1X2X3        2.811       0.1980     .6758288     4.16     0.0024  0.9640  0.0392
X1X2X4        -.18375     -0.0129    .6758288     -0.27    0.7918  0.9642  0.0002
X1X3X4        -.336375    -0.0237    .6758288     -0.50    0.6306  0.9647  0.0006
X2X3X4        1.73025     0.1219     .6758288     2.56     0.0307  0.9796  0.0149


                   Analysis of Variance Report

Dependent Variable: 4,6_DCG

Source     df    Sums of Squares   Mean Square   F-Ratio      Prob. Level
                 (Sequential)
Constant   1     2980.485          2980.485
Model      14    3158.114          225.5796      30.87        0.000
Error      9     65.77123          7.307914
Total      23    3223.886          140.1689

Root Mean Square Error      2.703315
Mean of Dependent Variable  11.14392
Coefficient of Variation    .2425821

R Squared                   0.9796
Adjusted R Squared          0.9479
```

APPENDIX 5

REGRESSION ANALYSES

Table A5.1. Model Compound: Summary of Chlorophenolic Regression Analyses (Coded Data)

Y	b_0	b_1	b_2	b_3	b_4	b_{12}	b_{13}	b_{14}	b_{23}
46-DCG[a]	11.14	(1.06)	8.42	7.17	(0.060)	(0.91)	1.76	(0.38)	7.55
ClVG1	26.26	12.46	-27.35	-13.00	8.75	-15.40	-10.24	9.42	9.89
ClVG2	183.45	87.24	-236.08	-144.51	(48.05)	-90.88	-88.90	(70.91)	139.00
DClVG1	42.64	10.78	-24.45	(-2.93)	(8.14)	-10.22	(-5.64)	11.88	12.18
DClVG2	238.87	56.62	-247.64	(-15.27)	59.61	61.21	-54.73	76.26	(24.27)

Y	b_{24}	b_{34}	b_{123}	b_{124}	b_{134}	b_{234}	r^2	Pr>F
46-DCG[a]	(0.57)	(1.25)	2.81	(-0.18)	(-0.34)	1.73	0.948	0.001
ClVG1	-11.85	(3.38)	13.19	(-6.47)	(-5.29)	(-0.28)	0.871	0.001
ClVG2	(-53.17)	(-4.92)	92.54	(-66.88)	(-43.25)	(10.04)	0.798	0.005
DClVG1	-11.34	(3.72)	(7.24)	-8.94	-0.14	(-4.95)	0.806	0.005
DClVG2	-67.21	(46.53)	55.38	-67.49	(10.45)	(-48.90)	0.889	0.001

[a] From GCMSD operating in SIMS mode.

r^2 Variation explained by the model including all terms.

Pr>F Level at which Type I error (∝) maybe set.

( ) Figures in brackets - coefficient does not differ from 0 at ∝ ≤0.05.

Table A5.2. Model Compound: Summary of Target Compound Regression Analyse
(Coded Data)

Y	b_0	b_1	b_2	b_3	b_4	b_{12}	b_{13}	b_{14}	b_{23}
Chloroform	60.78	40.06	74.08	(23.26)	27.63	39.21	(2.21)	(14.45)	(23.38)
Dichloroacetic Acid	58.20	(22.57)	24.45	29.53	(0.87)	(9.57)	(13.22)	(7.77)	(10.67)
Trichloroacetic Acid	3.59	2.46	3.35	(-0.50)	(-0.74)	2.05	(0.17)	(-1.27)	(-0.31)
Compound MX[a]	22.24	(1.87)	(6.12)	(-3.36)	(-2.17)	-	-	-	-

Y	b_{24}	b_{34}	b_{123}	b_{124}	b_{134}	b_{234}	r^2	Pr>F
Chloroform	27.23	(-9.14)	(2.83)	(13.57)	(-11.01)	(-8.66)	0.794	0.005
Dichloroacetic Acid	(-0.71)	(10.10)	(7.34)	(2.63)	(19.56)	(10.86)	0.40	0.16
Trichloroacetic Acid	(-0.80)	(1.49)	(0.46)	(-1.37)	2.24	(1.49)	0.58	0.05
Compound MX[a]	-	-	-	-	-	-	0.28	0.19

[a] Main effects only using minimum detectable concentrations.

- Not run due to confounding of effects.

r^2 Variation explained by the model including all terms.

Pr>F Level at which Type I error ($\propto$) maybe set.

( ) Figures in brackets - coefficient does not differ from 0 at $\propto \leq 0.05$.

Table A5.3. Effluent Samples: Summary of 2,4,6-Trichlorophenol and Target Compound Regression Analyses (Coded Data)

Y	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	r^2	Pr>F
246-TCP	1.571	1.102	(0.808)	(-0.427)	(0.727)	(-0.476)	(-0.263)	0.674	0.14
Chloroform (µg/L)	101.95	15.93	28.74	59.74	(7.86)	(-6.52)	(6.73)	0.964	0.01
Dichloroacetic acid (µg/L)	32.05	(5.26)	(10.94)	26.80	(-4.10)	(1.91)	(6.624)	0.646	0.16
Trichloroacetic acid (µg/L)	40.16	16.17	17.24	29.14	12.48	(8.50)	(8.28)	0.924	0.02
Compound MX (ng/L)	9.49	(2.93)	(2.04)	(3.26)	(2.66)	(1.00)	(0.14)	0.550	0.22
Compound MX (ng/L)	9.49	2.93	(2.04)	3.26	(2.66)	-	-	0.680	0.05

246-TCP 2,4,6-trichlorophenol.
r^2 Variation explained by the model including all terms.
Pr>F Level at which Type I error (∝) maybe set.
( ) Figures in brackets - coefficient does not differ from 0 at ∝ ≤0.05.
\- Coefficient not included.