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**Benthal feedback of chlorinated organics from an aerated lagoon**

**Bulusu, Somayaji Venkateshwara, M.S.**

**The University of Arizona, 1992**

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Ann Arbor, MI 48106



**BENTHAL FEED BACK OF  
CHLORINATED ORGANICS FROM AN AERATED LAGOON**

by

Somayaji Bulusu

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A Thesis Submitted to the Faculty of the  
**DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS**

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For the Degree of

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WITH A MAJOR IN CIVIL ENGINEERING**

In the Graduate College

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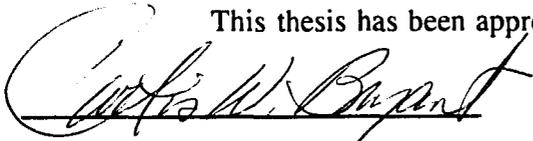
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**APPROVAL BY THESIS DIRECTOR**

This thesis has been approved on the date shown below :



**Dr. Curtis W. Bryant**  
Associate Professor in Civil Engineering  
and Engineering Mechanics

4/7/92

Date

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Dedicated  
to my  
Parents

*Lakshmi and Kameshwara Rao*

## TABLE OF CONTENTS

1. LIST OF TABLES.....	7
2. INTRODUCTION.....	10
3. LITERATURE REVIEW.....	13
4. MATERIALS & METHODS.....	22
Sample Collecton.....	22
Experimental Apparatus.....	22
Adsorbable Organic Halide (AOX) Analysis.....	25
Inorganic Halide (IX) Analysis.....	28
Sludge Analysis.....	28
Total suspended solids (TSS) Measurement.....	29
5. RESULTS & DISCUSSION.....	31
Liquid Halide Measurements.....	31
Sludge Halide Measurements.....	39
Overall Organic Halide Reduction.....	46
Comparison with Other Modes of Treatment.....	46
Chlorine Mass Balance.....	49

**TABLE OF CONTENTS ( Continued)**

6. CONCLUSIONS.....	53
7. APPENDIX A.....	55
8. APPENDIX B.....	88
9. REFERENCES.....	104

**LIST OF TABLES**

1.	Characteristics of Kraft Wastewater and Benthall Sludge.....	56
2.	Liquid AOX Data:	
	Set No. 1.....	57
	Set No. 2.....	58
	Average values of AOX.....	59
3.	AOX Mass Balance on the Benthall Reactor with Full-Strength Wastewater.....	61
4.	AOX Mass Balance on the Benthall Reactor with Distilled Water.....	62
5.	AOX Mass Balance on the Benthall Reactor with Partially-Diluted Kraft Wastewater.....	63
6.	AOX Mass Balance on the Benthall Reactor Nutrient Amended, Partially-Diluted Kraft Wastewater Reactor.....	64
7.	Liquid Inorganic Halide Data.....	65
8.	Liquid IX Component of the Mass Balance on the Benthall Reactor with Full-Strength Kraft Wastewater.....	67
9.	Liquid IX Component of the Mass Balance on the Benthall Reactor with Distilled Water.....	68
10.	Liquid IX Component of the Mass Balance on the Benthall Reactor with Partially-Diluted Kraft Wastewater.....	69
11.	Liquid IX Component of the Mass Balance on the Benthall Reactor with Nutrient-Amended, Partially-Diluted Kraft Wastewater.....	70
12.	Solid Halide Data:	
	Set No. 1.....	72
	Set No. 2.....	73

**LIST OF TABLES (Continued)**

	Average values of Solid Halide Data.....	74
13.	Average values of Solid Halide Measurements of the Benthall Reactor with Full-Strength Kraft Wastewater.....	75
14.	Halide Distributions for Benthall Deposits with Different Overlying Water Conditions over 84-Day Experiment.....	76
15.	Overall Organic Halide Reduction Measurement.....	77
16.	Summary of Total Halide Distribution across Benthall Reactors.....	78
17.	Solid Total Halide (mg/gm) Measurement in Static, Resuspended and Completely Mixed Reactors.....	79
18.	Solid Total Organic Halide (mg/gm) Measurement in Static, Resuspended and Completely Mixed Reactors.....	80
19.	Total suspended solids Measurement of Overlying Waters.....	81
20.	Total suspended solids Measurement: Sludge.....	82
21.	Moisture Content of Sludge in Reactors at the end of 84-Day Experiment.....	83
22.	Gas-Phase AOX Analysis on the Benthall Reactor with Full-Strength Kraft Wastewater over 28-Day Experiment.....	84
23.	Gas-Phase AOX Analysis on the Benthall Reactor with Full-Strength Kraft Wastewater over 28-Day Experiment.....	85
	Typical Calculation of Gas-Phase Analysis on the Benthall Reactor with Full-Strength Kraft Wastewater over 28-Day Experiment.....	86

## ABSTRACT

This research studied the destruction of organic halides initially attached to sludge solids resulting from the secondary treatment of Kraft wastewater. The sludge solids were evaluated for Adsorbable organic halide (AOX) in static benthal deposits as a function of overlying water and the reduction in organic loading on static benthal sludges was compared with the resuspended and completely mixed deposits. Organic chlorine on the sludge was most effectively reduced under full strength Kraft wastewater. There were no significant increases in inorganic chloride content in the overall system in spite of decrease in total organic chlorine. The sum of sludge, water and gas-phase halides was not constant across the sludge/water system but decreased by at least 50% in each of the reactors.

## 1. INTRODUCTION

There is a growing concern about the potential environmental and public health problems due to the release of chlorinated organic chemicals from paper industry wastewaters. A number of regulatory agencies in many countries are considering regulation on the discharge of adsorbable organic halide (AOX) from bleached pulp mill effluents. Chlorine used in the bleaching process produces a variety of chlorinated organic compounds. These compounds vary from simple compounds such as chlorophenols (MW < 300) to complex compounds such as chlorolignins (MW > > 1000). Many of these compounds exhibit not only higher toxicity and mutagenicity, but also resistance to biological and chemical degradation (1,6,12). It is the low molecular compounds that are of most concern, but the high molecular weight fraction (MW > 1000) is the major part of the organochlorine compounds present in bleaching effluents. Higher molecular weight halo-organics have been found to be less bioactive due to poorer adsorbance. Chlorination stage wastewaters contain predominantly low molecular weight chlorinated organics and the extraction stage wastewaters contain most of the high molecular weight (> 25000) AOX (Kringstad et.al., 1984).

An important objective of paper and pulp facilities is to lower the organic halide to an acceptable range with minimal cost. Two ways of achieving this goal include: (i) modification of in-mill operations to reduce the formation of chlorinated organics and; (ii) improvements to the existing wastewater treatment systems to enhance the removal

efficiencies of these compounds.

Most paper and pulp mills employ aerated stabilization basins (ASBs) for the removal of biochemical oxygen demand (BOD), suspended solids (SS), and nitrogenous compounds. Activated sludge systems are also frequently employed to treat paper and pulp wastewaters. Approximately one-third to one-half of the adsorbable organic halide (AOX) is removed from pulp and paper wastewaters using either treatment system (LaFond and Ferguson, 1991; Gergov et al., 1988; Bryant et al., 1987). In both of the systems, the low molecular weight fraction is reduced more effectively than the high molecular weight fraction (Bryant and Barkely, 1990), but activated sludge is somewhat superior in the removal of high molecular weight fraction of adsorbable organic halide (AOX).

AOX removal from the bulk water to the benthic layer is achievable either by adsorption of chlorinated organics onto the biomass or chemical precipitation of the compounds, followed by sedimentation to the benthic zone (16,19). The anticipated removal path consists of aerobic cleaving of the ring structure of aromatic compounds, conversion of high molecular weight chlorinated compounds to low molecular weight chlorinated compounds, and subsequent dehalogenation in near the aerobic/anaerobic benthic interface. Organic halide can also be adsorbed onto cellulose fiber material present in the Kraft wastewater. Warren and Gehr (1987), reported that cellulose fibers exhibit a significant adsorption capacity for specific organic polyelectrolytes added for

waste treatment. Loadings of chlorinated organics adsorbed on the ASB solids have been measured (Barkely and Bryant, 1988). Leuenberger et al.,(1985) measured the loading of chlorinated organics on activated sludge solids. The eventual fate of the adsorbed chlorinated organic matter is yet to be clearly defined.

Different operating conditions lead to aerobic, anaerobic or mixed aerobic/anaerobic conditions of the sludges. In aerated stabilization basins, the sludges may deposit in the anaerobic benthic environment. In activated sludge systems, the sludges may be recycled where aerobic conditions prevail. Sludges may be digested in mixed aerobic or anaerobic reactors, although sludge digestion is not widely used at present.

This research studied the destruction of organic halides initially attached to sludge solids resulting from the secondary treatment of Kraft wastewater. There were four elements to the study. First, solids were evaluated for AOX in static benthic deposits as a function of overlying water quality. Secondly, since some aerated stabilization basins in the industry include nutrient addition, the effects of nutrient addition on TOX removal were examined and compared with a nutrient limited system. Third, an attempt was made to measure the chlorine distribution across gas, liquid and solid phases to define a complete chlorine mass balance. Finally, the TOX reduction in the static benthic deposits was compared with the resuspended and completely mixed deposits.

## 2. LITERATURE SURVEY

### Background

There are number of processes available for treating pulp, but paper and pulp manufacturers use two major processes. One is the Kraft (sulfate) process and the other is the sulfite process (1), with the former most widely used. In the pulping process, lignin (an aromatic polymer) is removed to facilitate the separation of fiber and improve papermaking properties of the wood (1). During the Kraft process the wood is treated with alkaline liquor containing sodium hydroxide and sodium sulfide at a temperature of about 160°C - 180°C. At this temperature the alkaline liquor initiates the breaking of ether bonds in the lignin causing lignin to hydrolyze. About 90% - 95% of lignin can be eliminated during this process. Apart from the removal of lignin, various other cellulose and wood extractives are also dissolved by the alkaline liquor. The amount of residual lignin in pulp after alkaline delignification determines the yield loss in bleaching and also the amount of bleaching agents required to achieve complete lignin removal. There are several measures to reduce the residual lignin content of the pulp prior to bleaching. Internal process modifications like extended delignification or oxygen delignification reduce the quantity of lignin entering the chlorination stage and can significantly reduce the production of AOX. Some lignin modified by alkaline condensation reactions remains in the pulp and is removed by a subsequent bleaching treatment using chlorine-based chemicals.

Under the bleaching process, chlorine is introduced in various forms in acidic solutions separated by alkali treatment (1). For the softwood pulp, a typical treatment includes the application of chlorine (C1), alkali (E1), hypochlorite (H), chlorine dioxide (D1), alkali (E2) and chlorine dioxide (D2) [2]. Approximately 60 to 70 kg of organic matter is dissolved in the bleaching process per metric ton of pulp (1,3). Researchers have reported various alternative chemicals to chlorine compounds to use in the pulp bleaching sequences. The substitution of chlorine dioxide for chlorine in the first bleaching stage will significantly lower the production of chlorinated organic compounds. The work by Gullichen (1991) suggest that a 90% substitution of  $\text{ClO}_2$  alone would reduce AOX levels equal to that achieved with extended delignification, oxygen delignification and effluent treatment in combination. Similar results were observed in a study by McFarlane et. al.,(1991). The measures to extend delignification prior to bleaching would reduce the load of organic substance, while modifications of bleaching process reduce the formation of chlorinated organic compounds.

When chlorine is used as a pulp bleaching agent, the bleaching process results in the formation of a wide range of organochlorine compounds. The broad range of compounds varies from simple organo-chlorine compounds to a more ill-defined group of compounds. Chlorine reacts primarily with the residual lignin by degrading it into water or chlorinated organic chlorophenolic compounds (1,2). The lower the residual lignin level, the less likely a high organic halide value becomes. The amount of organochlorine liberated during bleaching process depends upon the type of wood used,

specific treatment sequence, and the degree of treatment (1,4).

#### Chlorine in Wastewater Effluents: Methods

Several methods are in practice to determine the amount of total organic chlorine present in the paper and pulp wastewater. These include gas chromatography/mass spectrometry, spectroscopy with a plasma emission source, neutron activation analysis, gas chromatography with halogen specific detectors, and pyrolysis/microcoulometry (2,3,4,5,7).

Adsorbable organic halide (AOX) is a non-specific measure of halogenated organic chemicals. When chlorine-containing chemicals react with pulps, some of the chlorine forms chlorinated organic compounds measurable as adsorbable organic halide. Total organic chlorine (TOCl) is a non-specific parameter used to measure the amount of organically-bound chlorine. Both the methods are used to separate organically-bound chlorine from inorganic chloride ions. Activated carbon is used for adsorbing the organic matter in the AOX method whereas in TOCl method, a resin is employed to perform the adsorption step.

The Xertex-Dhormann model 20 total organic halide (TOX) analyzer measures organically-bound chlorine by pyrolysis/microcoulometry method (9). Bethge (10) has reported that the ratio of AOX to TOCl in pulp mill effluents is in the range of 1.1 to

1.3 while others have suggested a conversion factor as large as 1.4. This ratio will vary between mills as well as between waste streams at a single mill.

All the methods described above measure only that organic chloride that is adsorbable, so all of the methods can precisely be described as AOX methods. AOX is one of the parameters to characterize papermill wastewater effluents. Temperature and pH play an important role in assessing the TOX values of the wastewater samples. Total organic chlorine values may decrease about 10% when stored at 5° C in a 2-day period, and more at higher temperature (4). In case of C-stage liquors, the TOX will decrease considerably if the pH is increased (4).

Majority of paper mill wastewaters contain very low fraction of non adsorbable organic halides (NAOX) and, therefore, the total organic halide of wastewater essentially comprises of adsorbable organic halide (AOX) fraction alone. Hence some researchers, in the past, have used both AOX and TOX to refer the total organic halide of wastewaters.

#### Adsorbable Organic Chlorine in Bleaching Wastewaters

Most of the AOX contained in bleached pulp mill wastewater consists of high molecular weight material ( $MW > 1000$ ). In untreated bleach wastewaters, 80% of the organo-chlorine is in the form of high molecular weight fraction (15). Bryant et al. (16)

documented that the high molecular fraction of the AOX in combined untreated bleached Kraft mill wastewater ranged from 60 to 85% of the total AOX whereas the high molecular fraction of the AOX in the ASB (Aeration Stabilization Basin) effluent ranged from 70 to 85% of the total AOX. The low molecular weight fraction of AOX is more biologically active than high molecular weight fraction. Of this low molecular weight fraction, approximately 3 to 12% are volatile compounds (16,17). The low molecular weight fraction of AOX is composed of over 200 identified chemicals comprising 10% to 50% of the low molecular weight AOX.

The values of total organic halide (TOX) in a Kraft mill wastewater varied from 26,000 to 60,000 ug/L (18). Aeration stabilization basins are effective in removing biochemical oxygen demand (BOD), suspended solids (SS), and nitrogenous compounds. The BOD removal efficiency in these lagoons can be as high as 90%. Removals of approximately one-third to one-half of both the total TOX as well as lower molecular weight (MW < 1000) TOX have been reported based on seven day hydraulic residence time (18).

#### Mechanisms of Removal of Chlorinated Organics

Important candidate mechanisms for the removal of chlorinated organics from the bleaching wastes include adsorption, biological degradation and anaerobic dehalogenation. The purgeable fraction of the TOX, mainly chloroform, is actively removed from the

lagoon via volatilization during aeration (16,19). Removal of the nonpurgeable fraction from the lagoon include biosorption of organic halide comprised of both adsorption onto biomass with subsequent deposition within the benthal zone as well as desorption from settled biomass (16,19,20). One important pathway for removal of chlorinated organic compounds in a Kraft mill aeration basin was the adsorption of the organic halide onto the settling biomass (21). However, biosorption alone does not completely account for AOX removal from wastewaters (42,43). Several adsorption studies were conducted with the live and dead biomass to investigate whether the organic pollutant removal mechanism was due to by physical adsorption or by metabolic process (20,21,22,33). Adsorption onto the dead biomass is the same or greater than adsorption onto live biomass, which suggests that adsorption is not a metabolic process. There are various factors that effect the extent of adsorption mechanism and are discussed later.

Degradation and dehalogenation can occur within the benthal layer of aerated stabilization basins (19). Most of the organic compounds can be degraded anaerobically and some organic compounds require an aerobic environment for degradation (24,25). Anaerobic degradation of chlorinated compounds was noticed for chlorinated pesticides (28,29,30,31) and chlorophenols (26,27), whereas chlorinated benzenes degraded under aerobic conditions (32). Reduction of chlorinated organics was also achieved by sequential anaerobic/aerobic treatment of Kraft wastewaters (11,44). Anaerobic reductive dehalogenation has been recognized as an important mechanism for degradation and dehalogenation of most of the chlorinated organic compounds found in paper mill

wastewater (30,31,32). In reductive dehalogenation, transfer of electrons from the reduced organic substance takes place via microorganisms where the halogen atom is replaced by a hydrogen atom (32).

The degree of dehalogenation is greater in mixed cultures than in pure cultures (24,25). When the organism in the pure culture is not capable of producing the required enzymes to further degrade the compound, accumulation of transformation products from the dehalogenation reactions can occur. It is also possible that the product could be more toxic to the culture than the original substrate (24). In mixed culture, there is an opportunity for another organism which is capable of producing the required enzyme to further degrade the compound of interest, thus avoiding the accumulation of products.

There are various physical, chemical and biological factors that can restrain the degradation and dehalogenation reactions. Physical and chemical factors include pH, temperature, oxidation-reduction potential and presence of suitable microorganisms is a vital biological factor (24,36).

#### Factors Affecting Adsorption

The octanol/water partition coefficient of the compound establishes a reasonable relationship with the absorbability. The adsorption potential of the compound onto the

biomass has been found to be directly proportional to octanol/water partition coefficient. Temperature, pH and cell lipid content have also been found to influence the adsorption potential of the organic compounds in the papermill wastewater. Increase in temperature has not shown any substantial effect on the adsorbability of paper mill wastewater activated sludge (21). The absorption capacity for the high molecular weight (> 1000) organic compounds tends to increase at a lower temperature and pH. At low pH, the Kraft mill wastewater showed a better adsorption onto activated sludge (21). Researchers have reported that adsorption increases with the increase in lipid content of the microorganisms (21,34,35) and decreases with increase in water solubility of compounds (21,35,41).

Bell et al. (22) have observed that certain compounds like lindane, diazion and 2-chlorobiphenyl desorb from *Rhizopus arrhizus* and activated sludge into distilled water in three days. Intensive research has also been carried out on the interaction of microbial activity with various organic pollutants present in the paper mill wastewater. Malathion was adsorbed and then chemically decomposed by the microbial biomass into water soluble products. This chemical decomposition has not only been exhibited by the living cells but also by the dead cells and isolated microbial cell walls (23). Malathion desorption was also observed to be a function of temperature. At 5° C, all the malathion was completely desorbed, but at 25° C there was no desorption (22).

### Environmental Effects of Paper Industry Wastewaters

Bleaching effluents contain many hydrophobic compounds with a potential to bioaccumulate. These compounds can have direct effects on human health through fishery resources as human food intake. Fish, lymnaea and mussels from waters receiving bleachery effluents have been found to accumulate organochlorine compounds such as chlorinated alkanes, phenols, cymenes and veratroles (37,38,39). Fish have been found to contain up to 2000 ppm organic chlorine in the fat (40). Several studies have been conducted with bleached pulp mill wastes in the Gulf of Bothnia to study the impact of aquatic effects of the AOX. Elevated levels of enzyme ethoxy-resorufin-o-deethylase (EROD) were reported in fish collected near the bleached mill (41). The increase in levels of the enzyme EROD in fish is believed to be caused by the presence of some chlorinated organic chemicals such as chlorinated dioxins and PCBs (41). The chlorinated resin and fatty acids were also reported to be potential chemicals that can bioaccumulate in fish flesh. The efforts to lower the chlorine usage in the bleaching process should reduce the formation of more highly chlorinated and potentially more bioaccumulative chemicals.

### 3. MATERIALS & METHODS

Six static benthal batch reactors with different overlying waters were run for 84-day periods in the first phase of the experiment. The liquids were evaluated for various intermediate time intervals and solids were evaluated at the beginning and end of the experiment. A pair of reactors were operated containing both undiluted Kraft and distilled overlying waters. No attempt was made to completely seal the reactors allowing effluent gases to escape into the atmosphere. In the second phase of the experiment, liquids, solids and gas-phase halides were evaluated with granular activated carbon (GAC) traps attached to the four Kraft overlying virtis reactors in an effort to make a complete chlorine mass balance. All attempts were made to completely seal the reactors allowing effluent gases to escape only through the carbon traps.

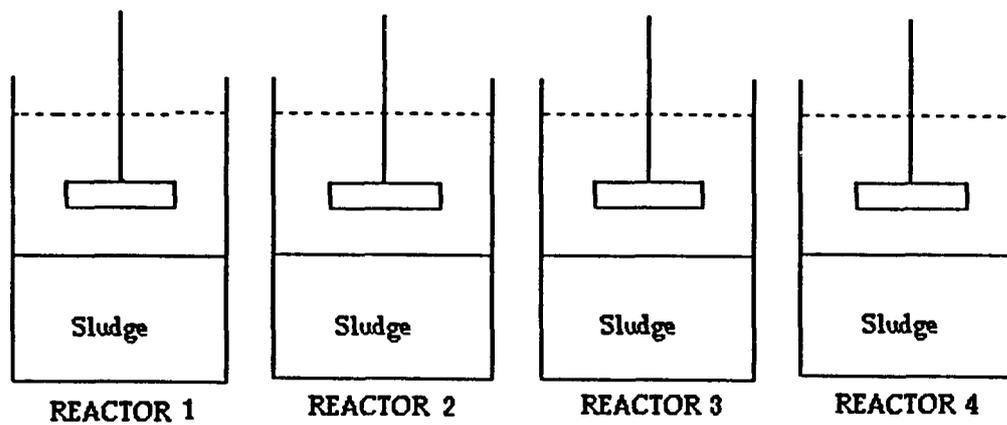
#### SAMPLE COLLECTION

Combined Kraft wastewater was collected following the primary settling basin and prior to the secondary treatment. Sludge was collected from a benthal deposit in an aerated stabilization basin. The collected samples were shipped to the University of Arizona Environmental Engineering laboratory for analysis. The samples of wastewater and sludge were stored at 4°C.

#### EXPERIMENTAL APPARATUS

Samples of Kraft ASB benthal sludge were placed in six identical batch reactors. A sludge volume of approximately 0.46 liters was placed in the bottom of each reactor and overlaid by 0.795 liters of either: (i) undiluted Kraft wastewater; (ii) distilled water; (iii) a 1:1 mixture of Kraft wastewater and distilled water; (iv) an identical 1:1 mixture amended with nutrient nitrogen and phosphorous. Duplicate deposits were run for undiluted Kraft wastewater and distilled water. Figure 1 is a schematic of the experimental setup. The overlying liquids were mechanically aerated at a rate of approximately 1.0 L/min. Aeration was controlled so that the benthal solids retained their static configuration. Liquid adsorbable organic halide (AOX) and inorganic halide (IX) were measured at intermediate times during the experiment but, specific chlorinated compound identification was not attempted. In the first phase of the experiment, solid total halide (TX) and total organic halide (TOX) were measured at the beginning and end of the 84-day experiment.

In the second phase of the experiment, four static benthal reactors with Kraft overlying water were operated at 2,7,14 and 28 day time periods and solid TX and TOX were measured. Gas traps were set up to four to catch and quantify volatile halides. The gas trap attached at the gas exit of each reactor consisted of two glass columns filled with approximately 20 mg of granular activated carbon. Witco 377 carbon was used in the gas traps because of its ability to entrap the gas phase halide. Activated carbon samples were analyzed at intermediate times to estimate the volatilization rate from each of the reactors.



Reactor	Overlying Water
1	Undiluted Kraft
2	Distilled water
3	1:1 mix of Kraft water and Distilled water
4	1:1 mixture amended with nutrients

Figure 1. Schematic of the Experimental Set up.

A sequential benthic resuspension reactor was operated on a 1 hour, 3 hours, 21 hours, 4 days, and 14 days cycle sequence. In a virtis omniculture two-liter reactor, one liter of ASB sludge was placed in the bottom of the reactor with one liter Kraft wastewater above the sludge. The contents of the reactor were mechanically mixed by bubbling air at a rate of about 1.0 L/min and then allowed to settle for the remainder of the defined treatment cycle. A 500 mL volume of wastewater was exchanged at the end of each treatment cycle and samples were analyzed for sludge TOX and TX.

In completely mixed benthic process, one liter of Kraft wastewater and one liter of ASB benthic sludge were mechanically mixed in a virtis omniculture two-liter vessel. The liquid layer was aerated at a rate of about 1.0 L/min and the samples were taken at 1 hour, 3 hours, 21 hours, 4 days and 14 days time intervals and were analyzed for sludge TX.

#### Total Organic Halide

Total organic halide (TOX) represents the amount of dissolved and suspended chlorinated organic compounds present in the aqueous phase. The concentration of organic compounds was measured with a Xertex-Dhormann DX-20 total organic halide (TOX) analyzer. This analyzer reads the concentration of TOX in micrograms ( $\mu\text{g}$ ) of halogen present.

The analysis consists of two steps. The first step involves adsorption of organo-chlorine compounds onto granular (100/200 mesh) activated carbon (GAC). Glass mini-columns were packed with the GAC and plugged with cerafelt at both ends. Proper care was taken in packing the columns to minimize deviations in blank readings.

Adsorption of organic halide was done using the adsorption module. A pair of mini-columns packed with 40 mg of granular activated carbon (GAC) were mounted in series, and the sample was passed through the columns with a high grade nitrogen operated at 20 psi. Two columns are recommended for greater accuracy and to guard against breakthrough of the AOX. Virgin carbon was run through the combustion chamber of the analyzer to determine if there was any halogen fraction present. Prior to the sample analysis, an average blank value was obtained and was applied in the calculation of organic halide present in the sample. The organic halide was removed from the water by adsorption onto the activated carbon. After adsorption, the carbon was washed with 5 mls of potassium nitrate (5 g/L) solution. Inorganic halide species trapped in the interstitial areas of the carbon were removed by flushing with nitrate solution.

In the second step, the carbon was transferred to a pyrolysis chamber in which the organic halide was combusted in a two-step process that converts first the volatile compounds and then the non volatile compounds to the HCl for subsequent line titration. Prior to running any sample in the combustion chamber, measurements were taken to ensure that the analyzer was stable and within operating conditions. The titration cell

was filled with fresh electrolyte (70% dilution of acetic acid) and the analyzer baseline was allowed to stabilize. Before any sample was analyzed, the quartz boat was run through a combustion chamber without any activated carbon to remove any residual chlorine in the boat. As a final measure, a blank GAC column was run through the combustion chamber. The blank GAC column was washed with 5 ml of distilled water followed by 3 mls of nitrate wash and was run with each set of samples to determine the contributions of AOX from the dilution water and the activated carbon. The readout of the blank carbon value was recorded and applied in the calculation of total organic halide.

Once the machine stabilized and the blanks were run, the individual sample columns were analyzed. All the samples were run in duplicate to check the repeatability of the analytical measurement. Standards for IX were run using NaCl solution to check the accuracy of the instrument.

AOX mass concentrations were calculated using the equation:

$$\text{AOX(mg/L)} = [(T+B)-\text{Blank}]/\text{Volume}$$

where T = mass readout for the top column

B = mass readout for the bottom column

Blank = average mass readout for the blanks

(sum of top and bottom columns)

Volume = volume of sample adsorbed in liters.

### Inorganic Halide Measurement

Inorganic halide (IX) measurement was analyzed by injecting 2 microliters of sample directly into the titration cell of the Dohrman analyzer and measured as milligrams of inorganic halide per liter of wastewater.

The total halide (TX) was calculated as the sum of the adsorbable organic halide and inorganic halide present in the sample.

### SLUDGE ANALYSIS

The total halide (TX) was measured directly by pyrolysis using a Dohrmann DX-20A analyzer. Two methods were employed to measure the total halide content of the sludge. Both methods gave repeatable results. In the first method, approximately 0.1 gms of wet sludge was weighed and directly pyrolyzed. The measured halide reading was adjusted to a loading per dry weight of sludge. In the second method, the sludge was oven dried at 105°C for about an hour before being subjected to pyrolysis. The dry sludge loading was measured based on percentage of water originally present in the sludge. The initial water content of the sludge was measured, prior to the measurement of the total halide

in the sludge. Approximately one gram of sludge was dried at 105°C for about an hour. The difference between the original weight of the sample and the oven dried sample was used to calculate the percentage of water in the sludge.

The sludge inorganic halide was measured by washing approximately 1 gram of wet sludge sample in 4-5 mls of  $\text{KNO}_3$  (5 g/L). The sludge sample was thoroughly mixed and was allowed to settle overnight. The supernatant was carefully withdrawn and was analyzed for IX content. The measured halide was adjusted to a loading per dry weight of sludge. The sludge total organic halide (TOX) was calculated as the difference of sludge total halide (TX) and sludge inorganic halide (IX) present in the sample.

#### Total Suspended Solids (TSS) measurement

All sludge samples were diluted and vacuum filtered using a Whatman GF/C filter. Prior to vacuum filtering, all the filters were placed in a aluminum pan and dried in an oven at 550°C for 5 mins. The filters were allowed to cool in a desiccator for 5 mins and weighted (W1). All the filters were rinsed with distilled water before the samples were vacuum filtered. When the filtered samples were relatively free of water, then the filters were transferred to aluminum pans and dried in an oven at 105°C. After 15 mins, the filters were taken out of the oven, allowed to cool in a desiccator. The weight of the filter with aluminum pan was noted (W2). The total suspended solids (TSS) was determined by:

$$\text{TSS} = (W2 - W1)/V$$

where,

**TSS** = Total Suspended Solids (mg/L)

**W2** = Combined weight of filter and aluminum pan (mg)

**W1** = Initial dry weight of filter and aluminum pan (mg)

**V** = Volume of sludge sample.

#### 4. RESULTS AND DISCUSSION

The purpose of this set of benthic experiments was to study the reduction in chlorine loading on sludges treated under various overlying water conditions. A series of experiments were conducted to measure the chlorine distribution in various organic compounds across gas, liquid, and solid phases in an attempt to establish a complete chlorine mass balance. In benthic studies, six static benthic reactors were operated with different overlying water conditions at a constant aeration of about 1.0 L/min for 84-day period. Reported herein are the liquid, solid, and overall organic halide reduction measurements and an attempted chlorine mass balance. A comparison of the static benthic results was also made with resuspended and completely mixed sludge treatment conditions studied by other researchers.

##### Liquid Halide Measurements:

The halide distribution was measured in overlying water as well as in the sludge at various intervals during the 84-day period. To verify accuracy and consistency in the analytical procedures, duplicate samples were run for all the overlying waters. The individual and average values were reported in appendix Table 2.2. Figure 2 illustrates the average AOX profiles in the overlying waters in four benthic static reactors. Using full strength wastewater (reactor 1), there was a reduction in AOX of about 5.4 mg/L in two days. The liquid AOX concentration approached a steady state after 14 days.

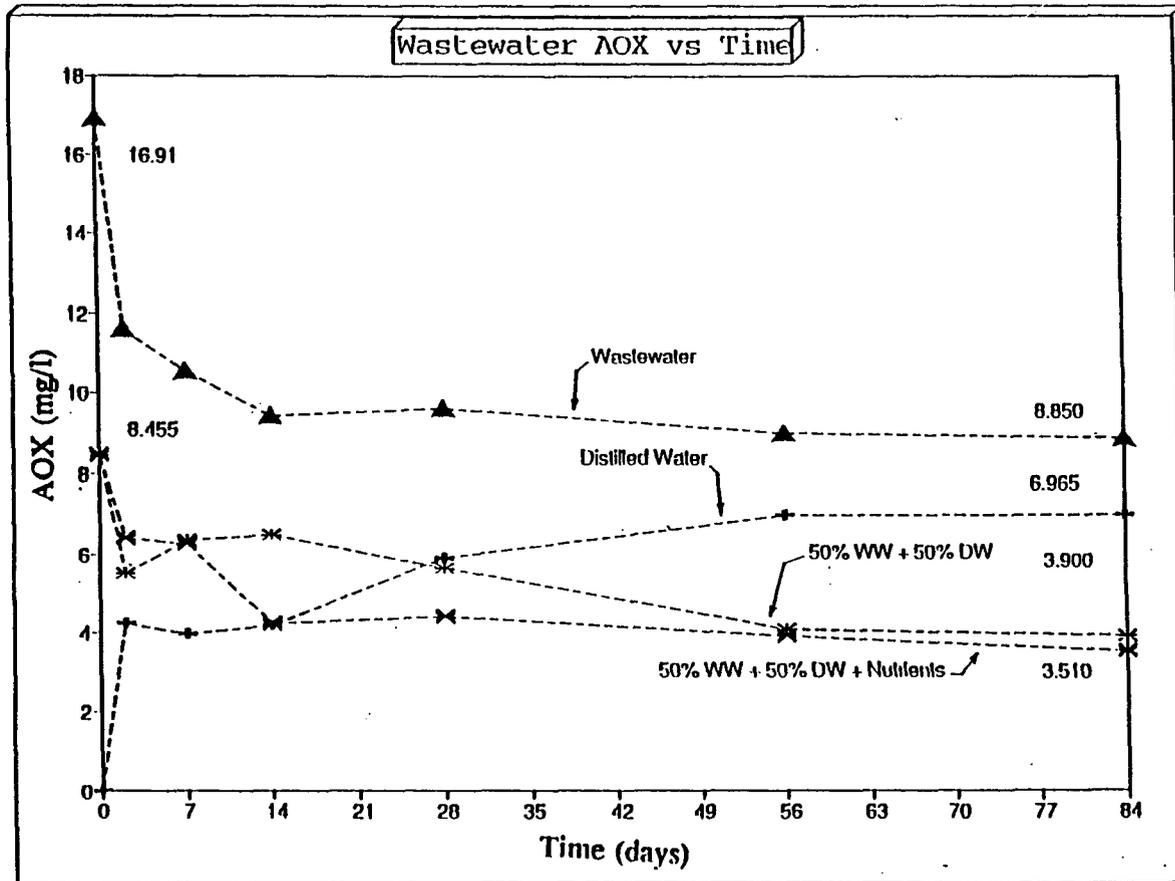


Figure 2. Changes in Halide Concentrations in Overwaters

High molecular weight chlorolignin compounds are more hydrophobic and would possibly be adsorbed onto the surface of the microbial cell. The biomass in wastewater was already in equilibrium before the start of the experiment and would have little adsorption capacity for any further biosorption. One possible reason for initial decrease in AOX would be the settling of biomass with adsorbed halogenated compounds, partial degradation to volatile low molecular AOX and subsequent loss from the system. The formation of biomass would be a function of usable organic matter with adsorbable organic halide in the reactor. The new biomass production in the aerobic zone along with some feedback from the benthic layer would associate with adsorption and degradation of organic compounds to some extent. It is reasonable to expect low molecular weight AOX fraction to be more effective in partitioning into microbial cell than the high molecular weight fraction because of size. However, considering the time frame of two days, the reduction in AOX from the wastewater does not correlate with biomass production and, an explanation of the rapid decrease is not clearly indicated.

In an anaerobic study, Ferguson et.al.,(1991) have observed a 7% AOX reduction due to initial sorption after one hour and 48% at the end of day 28. It was shown that most of the removal was due to biodegradation of soluble AOX. The sludge TOX increased by 2.9 mg/L, which accounted for 7% removal of wastewater AOX. The wastewater AOX removal trend in the present study matches with Ferguson work, but in the present study there was no sludge TOX increase observed, as discussed later in this report.

An increase in the AOX concentration was measured between the 14th and 28th day, probably due to feedback from the benthal deposit as a result of changes in the concentration gradient. From day 28 to the end of experiment, there was little change in the AOX concentration. The resulting steady state condition could be due to the presence of very slowly biodegradable AOX and the lack of suitable substrate for co-metabolism.

The Kraft wastewater reactor performance was characterized by nearly 45% AOX removal in the first two weeks of the experiment followed by a steady removal of about 47% of AOX at the end of day 84. Hypothesized mechanisms for the AOX removal from the wastewater include sorption of organic halide by microbial biomass, precipitation of Kraft lignin onto biomass, volatilization and aerobic biodegradation of organic compounds. The mechanism responsible for the removal of organic compounds involves adsorption into various components of the microbial cell, which results in their removal from the wastewater.

Researchers have reported that adsorption decreases with the increase in water solubility of compounds (41, 42, 43). The Kraft wastewater contains a wide range of low and high molecular organic compounds with different water solubility properties and hence 100% AOX removal could not be achieved by adsorption mechanism alone. Amy et al.(21) observed that lower temperatures favor better adsorption of high molecular weight compounds, but in the present research all the experiments were run at near

constant room temperature.

The Kraft effluents usually contain Kraft lignin in solution along with some cellulosic derivatives such as hydroxyacids and lactones which would contribute to the BOD of the effluent. Ganczarczyk et al., (1972, 1974) have reported that, in an activated sludge process, Kraft lignin in solution forms condensates and adsorbs onto biomass during the wastewater aeration. This would supplement the removal of lignin and hence reduction of organic halide from the liquid. This supports the proposed precipitation mechanism.

Volatilization of some organic compounds during wastewater aeration could be a source of AOX removal. Since approximately 5% of the AOX in pulp and paper mill effluents occur in the form of purgeable organic halide (POX), volatilization is considered to be less significant process in AOX removal. In the present study, volatilization did not appear to be a significant mechanism, measured by the GAC column experiments. The results of GAC column experiments are shown in appendix Table 20 and Table 21.

In the reactor, a portion of the organic matter was used by aerobic microorganisms to obtain energy for the synthesis of cellular material, and some of the compounds were biodegraded to intermediate products. Internalization of AOX would lead to the reduction of AOX as seen in the experiment. However, since the IX did not

increase significantly the actual internalization/adsorption likely did not involve complete reductive dehalogenation, but rather the probable production of volatile organic halides. The net AOX removal was certainly a result of a combination of the above-cited mechanisms. The relative contribution of each of the mechanisms in the net reduction of AOX, however, was not measured.

Lafond et al.(1991) have reported that activated sludge units with sequencing batch operation achieved AOX removals in the range of 14%-25% at a hydraulic residence time (HRT) of 1.1 days and that methanotrophic activity in aerobic reactors resulted in a slight improvement over conventional aerobic treatment. In full-scale aerated stabilization basins, 30%-50% of organically bound chlorine compounds are removed from pulp and paper wastewaters. The removal percent of chlorine compounds in the present study is in close agreement with the continuous flow activated sludge units and full-scale ASBs. A study by Bryant et al., (1987) indicated that a continuous-flow aerobic process produced much lower AOX removal than the anaerobic and benthic upflow processes. The reason for poor performance in the case of the aerobic unit could be due to the short hydraulic residence time of the process and the lack of nutrients. Both anaerobic and upflow processes were equally effective in AOX removal from the wastewater.

In order to understand the importance of benthic feedback of soluble oxygen-demanding materials and desorption of organic halide from the settled biomass into the

overlying water, a static benthal reactor with distilled overlying water was operated for 84-day period. As expected, the reactor with overlying distilled water showed a significant increase in the water halide content in the first two days of the run. Feedback of soluble organic matter from the benthal zone to the liquid column can explain this increase. The feedback phenomenon was not constant throughout the 84-day experiment, but there was a increase in the overlying AOX concentration until the 56th day.

The AOX trend in Figure 2 showed a declining rate of AOX buildup with near steady-state reached after day 28. A possible, but minor, explanation for increase in the AOX is due to the initial absence of microbial community in the overlying water and subsequent repopulation of the aerobic zone with aerobic organisms and suspension of benthal organisms into the overlying water, both of which would contain internalized/adsorbed halogenated compounds. Since little or no biodegradation would occur in the aerobic zone, steady-state would occur once the population of organisms in the aerobic zone had reached steady state and the internalized/adsorbed AOX in this population had also reached steady state.

The soluble concentration gradient between the liquid and benthal zone was postulated to be the major driving force responsible for the increase in AOX content in the overlying water. Former laboratory studies conducted on the oxygen demand exerted by cellulosic benthal deposits showed that the BOD transfer rate in the case of shallow deposits was essentially zero after 100 days exposure (J.J.McKeown et al., 1968). The current 84-day benthal study reasonably agrees with McKeown's work.

Desorption of lindane, diazinon and 2-chlorobiphenyl from *Rhizopus arrhizus* and activated sludge back into water column was measured in three days (Bell et al., 1987). The increase in the AOX in the overlying water of reactor 2 is consistent with the timing of the desorption mechanism. Also, desorption of organics from the benthal layer is a function of temperature and the compound adsorbed onto the biomass (22,35), but in this study specific compound identification was not attempted.

In the partial dilution (50%-50% mix; reactor 3), initial AOX was lower than in the full-strength wastewater reactor due to dilution. AOX removal trends in this 50%-50% mix reactor, however, were similar to those in the full-strength wastewater reactor. Both the concentration curves for reactor 1 and 3 followed almost identical trends in AOX reduction. There was an initial drop in AOX concentration of about 3 mg/L after two days of treatment. The AOX concentration in the overlying water decreased until day 56 and then stabilized. There was about 53% AOX reduction in the overwater by the end of 84 day experiment.

In reactor 4, nitrogen (5 mg/L) and phosphorous (10 mg/L) were introduced as a source of nutrients along with the partial dilution. High nutrient concentration would support the growth of aerobic biomass. Total suspended solids (TSS) measurement of the overlying waters (Table 19 in appendix A) suggested that added nutrients helped slightly higher aerobic biomass growth in reactor 4 versus reactor 3 at the end of the 84-day experiment, and the results are shown in Table 5. The effect of the enhanced

should contribute to higher AOX removal from reactor 4 as compared to reactor 3. With the nutrient addition 5% more AOX reduction was measured versus the partial dilution reactor and 8% more than the full strength Kraft wastewater reactor. The nutrient availability in the overlying water apparently helped enhance the bacterial growth and hence the ability to degrade more organic matter in the aerobic zone. The presence of nutrients produced small changes in reduction in liquid halide concentration, but produced a significant change in the organic chlorine loading of the sludge, to be discussed later herein.

In all the four reactors, the reduction of AOX over time was a function of type of the overlying water. A sludge-overwater AOX equilibrium was reached in a 7-28 day period in all four of the reactors. The reduction in organic chlorine in the sludges did not produce any corresponding increase in inorganic chloride in the liquid phase.

#### Sludge Halide Measurements:

Solid TX and TOX were measured at the beginning and end of the 84-day study in all the four reactors. The results are reported in appendix Table 14 and shown graphically in Fig 3 - Fig 6. There was at least 78% reduction in the solid-phase TOX in all the four reactors. The removal was assumed to be due to degradation of organic halides in the benthic zone and some possible subsequent volatilization. The static benthic reactor configuration subjects the majority of the sludge organic halides to an

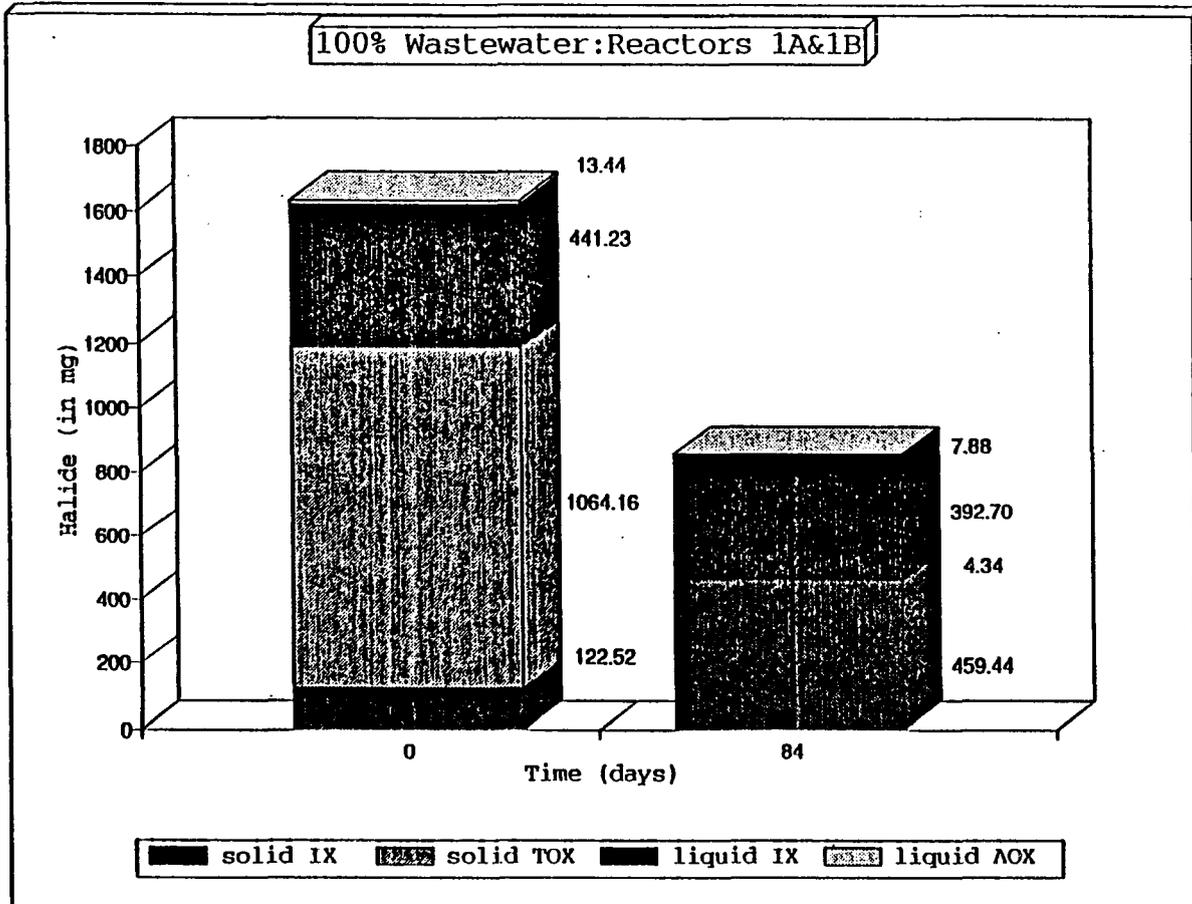


Figure 3. Halide Distributions for Benthic Deposit with Full-Strength Wastewater

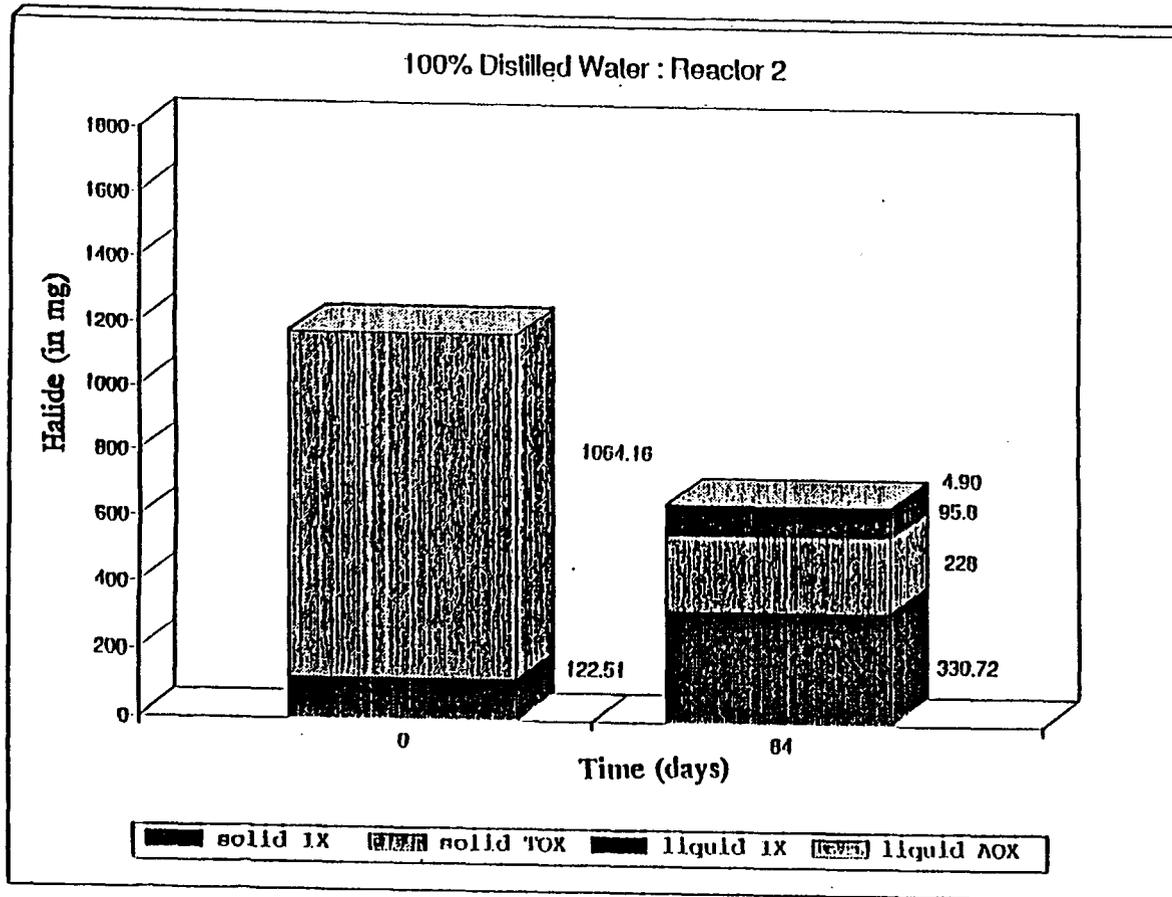
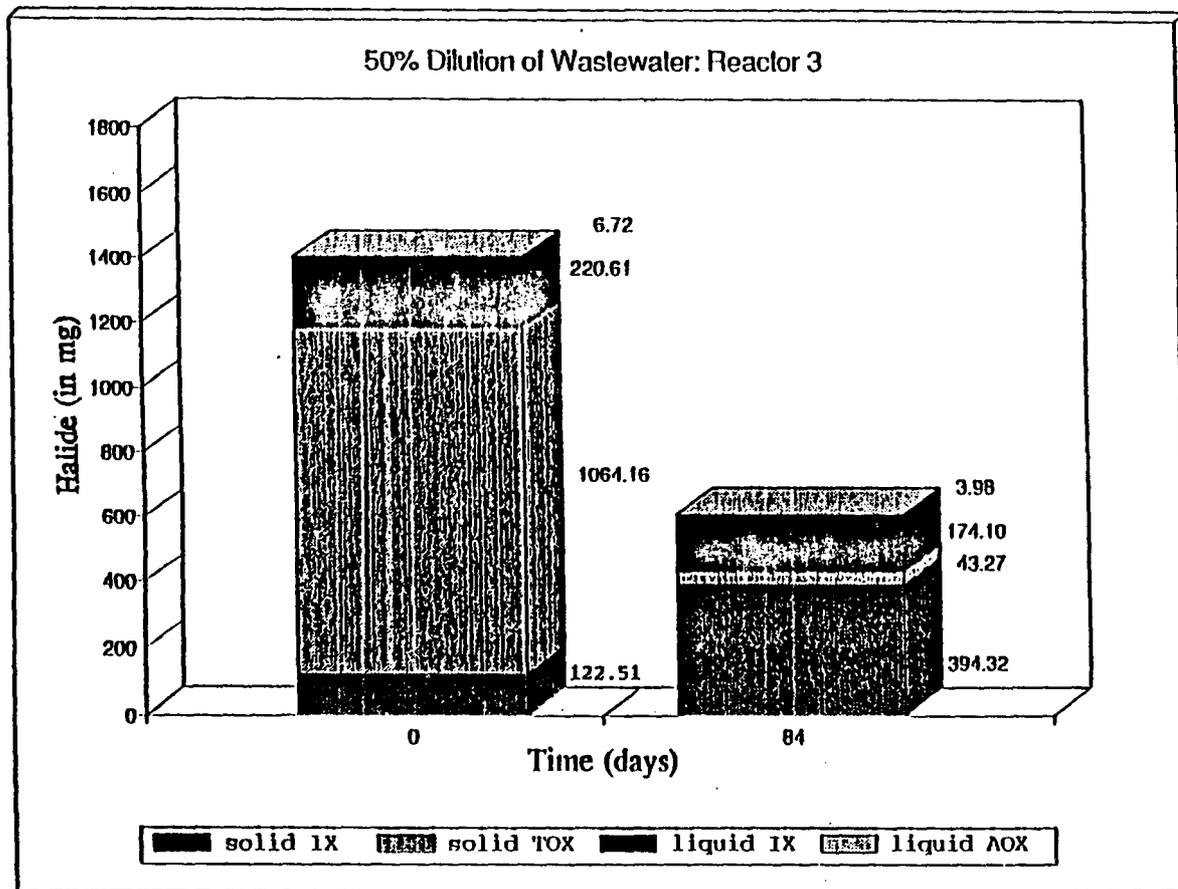
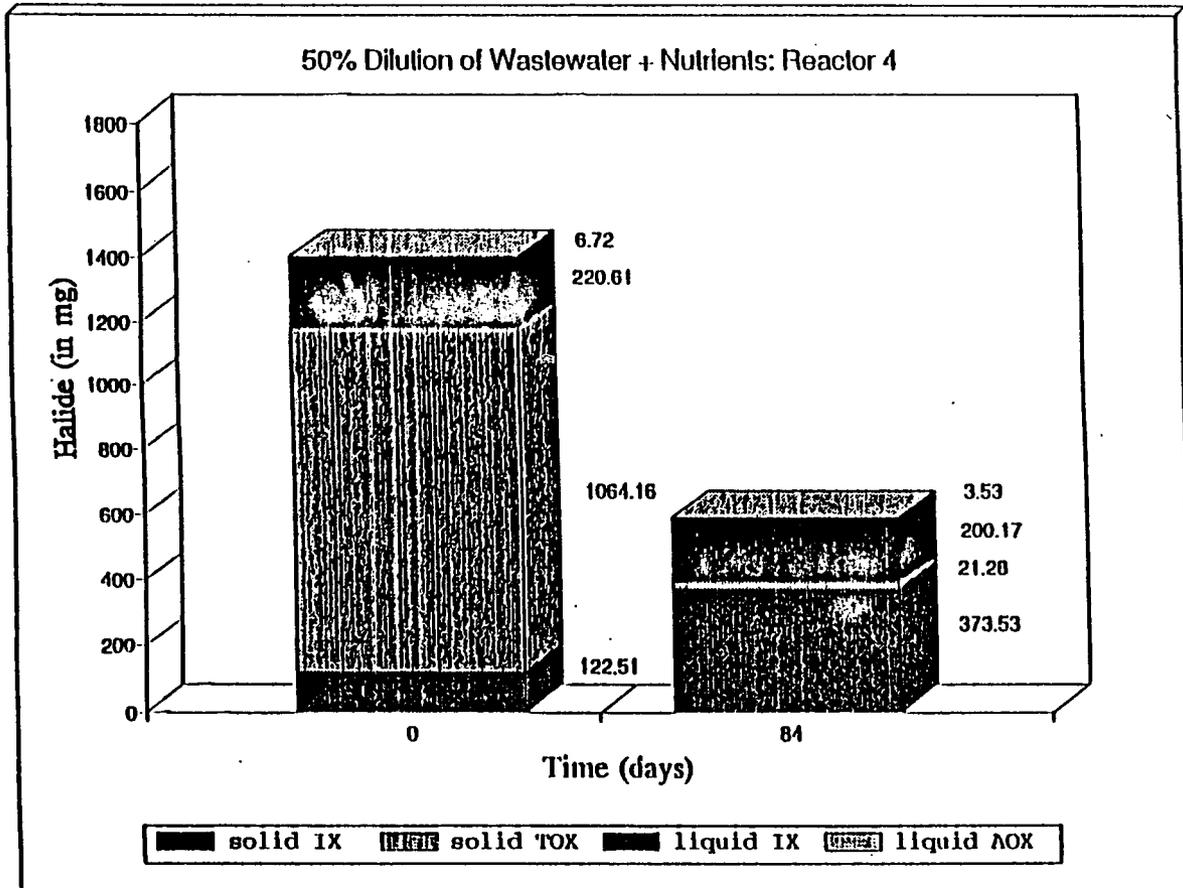


Figure 4. Halide Distributions for Benthic Deposit with Distilled Water



**Figure 5. Halide Distributions for Benthic Deposit with Partially-Diluted Kraft Wastewater**



**Figure 6. Halide Distributions for Benthic Deposit with Nutrient-Amended, Partially-Diluted Kraft Wastewater**

anaerobic environment. This would facilitate extended residence time for the breakdown of high molecular weight organic halides to intermediate by-products. The actual field conditions may not be the same with respect to the aerobic/anaerobic residence times of sludge solids. In full-scale aerated stabilization basins, solids are sequentially deposited and would be exposed to the aerobic benthic layer for some time before their accumulation to anaerobic benthic zone.

In the benthic static reactor with full strength wastewater, there was no significant change in the sludge total halide loading during the first two days of treatment. But, at the end of 84 days, the total halide (TX) reduction was about 60%. The sludge total organic chlorine (TOX) content showed little reduction during the first two days of treatment and almost 100% removal was achieved at the end of the 84 days.

Reduction in chlorine loadings was observed to be a function of sludge treatment condition. Organically-bound chlorine on the sludges was most effectively reduced under full strength Kraft wastewater. Duplicate measurements under this condition gave repeatable results, and the average values are reported in appendix Table 13. The full strength wastewater might contain trace nutrients which would stimulate anaerobic microbial growth in benthic layer. This would result in an increased rate of benthic organic halide reduction.

In the distilled water benthic reactor, the total halide (TX) reduction was about

53% and the total organic chlorine (TOX) was reduced by about 78%. The partially diluted wastewater reactor achieved 63% reduction in total halide and approximately 96% removal of total organic chlorine from the benthal deposit. The reactors with full strength wastewater and partially diluted overwater accomplished similar degradation of total halide and total organic chlorine content.

The addition of nutrients improved the total halide removal fraction (66%) from the benthal deposit relative to the reactor having no nutrients. The removal fraction was marginally higher than the full strength Kraft wastewater reactor, and 98% of total organic chlorine was removed at the end of the 84-day experiment.

The rate of organic halide reduction might have been affected by the availability of anaerobic organisms that are capable of breaking down the various high molecular weight compounds into by-products. Bryant et al., (1991) observed in experimental data that there was a measurable increase in inorganic chloride in dechlorinating of chlorophenolic wastewaters. But in spite of significant TOX reductions in the sludge in this set of experiments, no corresponding increase of inorganic halide was observed in the liquid zone.

TOX degradation in the sludge may have resulted in formation of volatile organic halides rather than halide ions. Attempts to trap these volatile compounds using GAC columns, however, showed only minimal recovery. The fate of the degraded sludge

TOX, therefore, was not completely determined. The missing chlorine in the experimental system might have bound to some compounds, preventing measurement as inorganic halide.

#### Overall Organic Halide Reduction:

Loadings of organically bound chlorine on the sludge/water system were most effectively reduced under full strength wastewater. The smaller reduction was measured in distilled water reactor. Partial dilution achieved 95% reduction of the overall organic halide and the nutrient amended partial dilution had a slightly better percent removal over reactor three. Removal fractions in each of the reactors were tabulated in appendix A Table 15. The 28-day biomass loading was calculated and reported in appendix B.

#### Comparison with other modes of treatment:

Different modes of treatment were compared as a function of reduction in sludge loadings. Sludge was evaluated in sequentially resuspended deposits, completely mixed conditions (K.Fan,1991 and J.W.Detteimer, 1991) and static benthal deposits of this study. The halide distribution was measured across gas, liquid and solid phases in an attempt to define a complete mass balance. Measurements were taken over time periods from one hour to three weeks (Table 17 and Table 18) and were graphically represented in Fig 7 - Fig 8. The increase in inorganic halide on the sequentially resuspended sludge was much smaller than the corresponding reduction in organic halide. Similar trend was

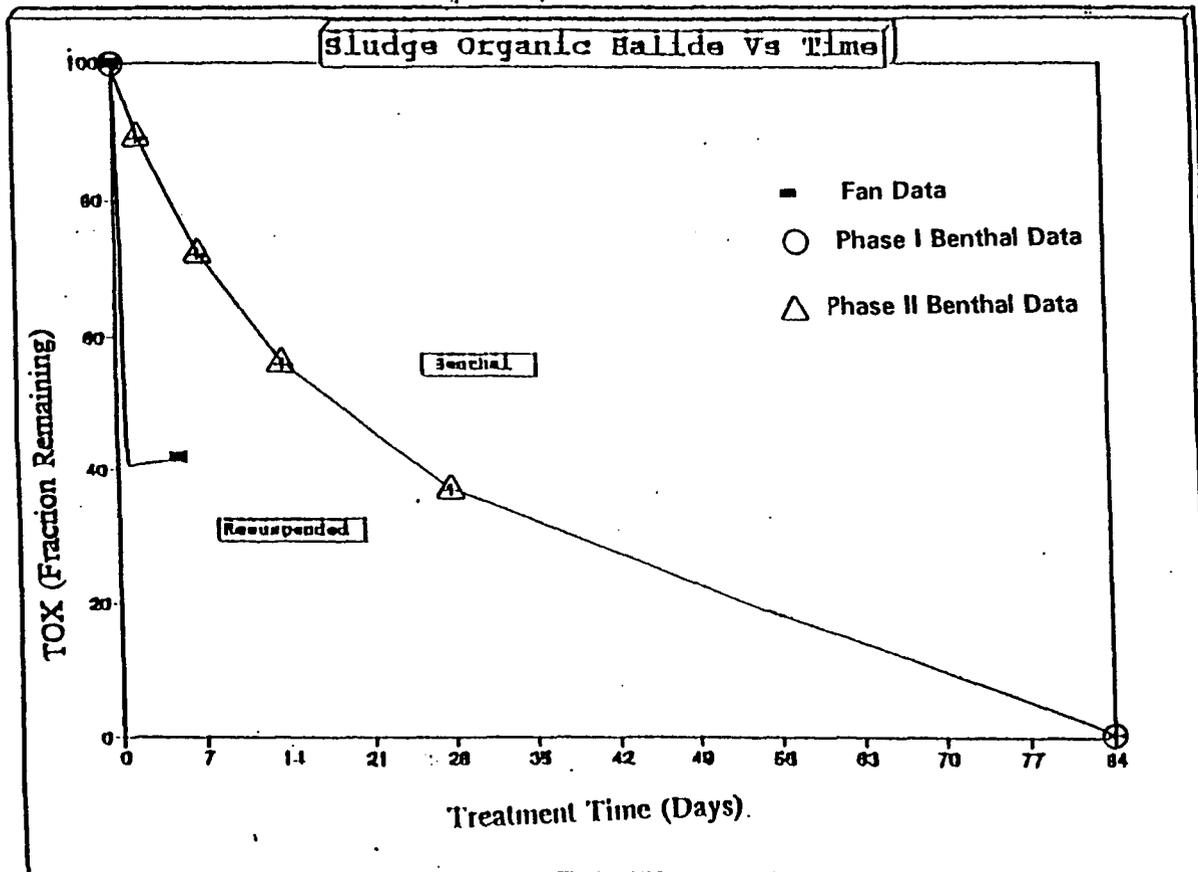


Figure 8. Long-Term Changes in Organic Halide(TOX) on Sludge

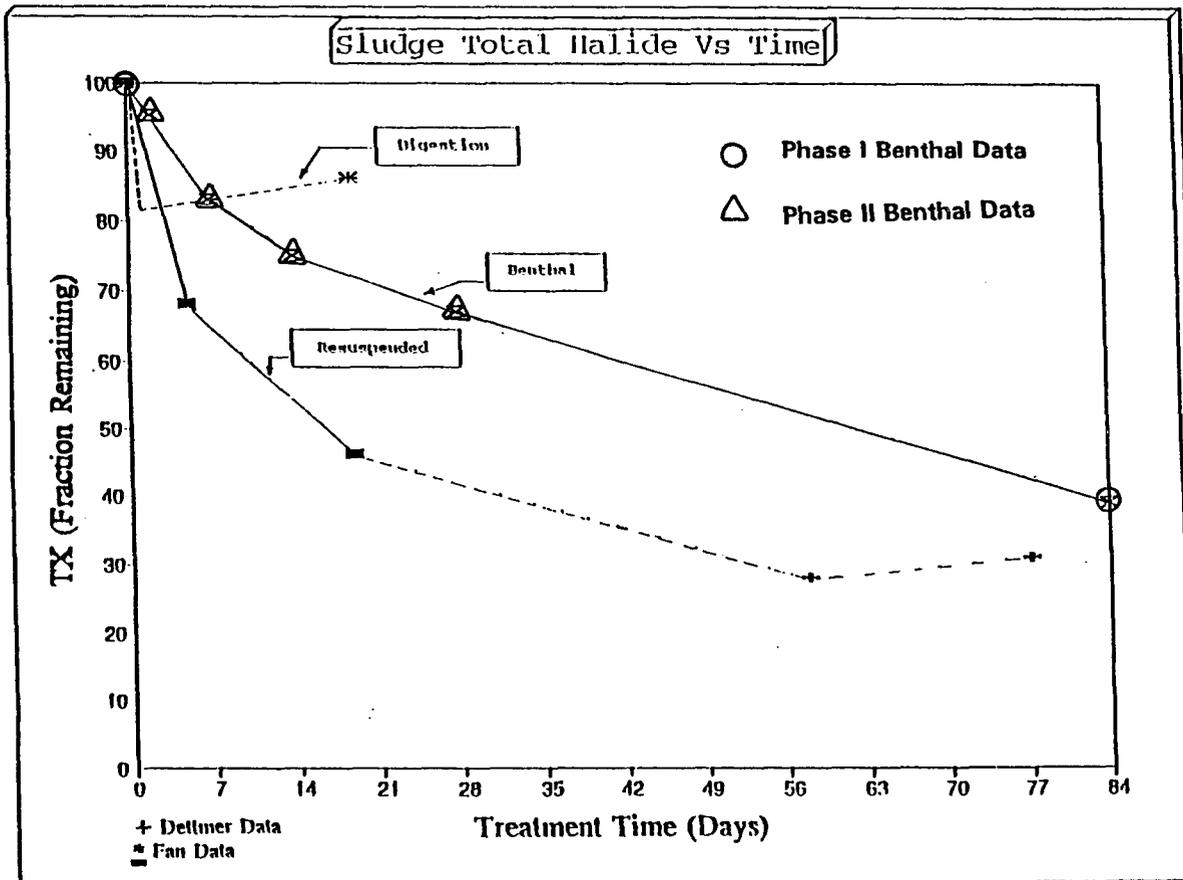


Figure 7. Long-Term Changes in Total Halide(TX) on Sludge

observed in the case of benthal deposits. The gas-phase halide from the sequentially resuspended sludge and wastewater to the air was insignificant when compared with the decrease in total chlorine, as was observed in static benthal deposit.

The sequentially resuspended benthal reactor and the mixed aerobic digester both achieved nearly 20% reduction of total chlorine loading in the first hour and resuspended benthal process reduced the total chlorine content of the sludge by 54% by the end of 5-day period. In the benthal reactor the organic chlorine content of the sludge was reduced nearly to zero at the end of the 84-day experiment. The sludge treatment condition affects the degree of reduction in chlorine loading on sludges. In a sequential anaerobic/aerobic process, aerobic conditions produced an additional 6%-10% liquid organic halide when compared to straight anaerobic units (La fond et al., 1991). This becomes more significant for sludges with longer residence time.

#### Chlorine Mass Balance:

In all experiments, the sum of sludge and water halides was not constant across the reactors. The sludge halides were reduced by at least 50% in each of the reactors. Most of the chloroform should be removed from the system by aeration. Not much research has been done in the area of chlorine distribution across the solid, liquid and gas system. In an effort to measure a complete mass balance across the system herein, activated carbon traps were attached to the four Kraft wastewater reactors and were

analyzed at intermediate times. Only a small amount of chlorine was detected escaping from sludge and wastewater to the gas phase via volatilization. The measured gas-phase chlorine data are listed in appendix Table 22 and Table 23.

The following factors have been hypothesized for the discrepancy in the total chlorine mass balance. First, the reactor system experienced various gas losses which might have contributed to the discrepancy in the AOX mass balance. Desorption of gas-phase halide from the carbon columns might explain the failure to detect the loss. The decrease in reactor AOX concentration as a function of time may have caused AOX desorption. The gas-phase chlorine that was held by the carbon could have been desorbed to the atmosphere when the carbon traps were saturated. Secondly, adsorption to the interior of the reactor could include: (i) plastic fittings inside the reactor; (ii) minimal adsorption to the reactor glass surface; (iii) porous air diffuser. Third, since the reactors were not completely airtight, small amounts of leakage may have become significant over the 28 day duration of the experiment. The experiment did not measure the magnitude of any the above mentioned losses into account in making the chlorine mass balance.

Liebson(1991) in an effort to resolve the discrepancies in the AOX mass balance, conducted a laboratory experiment using the same static benthal reactor. The reactor's potential AOX recovery efficiency was tested by placing a known amount of liquid chloroform in solution ( approximately 0.5 grams) in a reactor with the same carbon

traps that were used in the earlier batch experiment. The reactor was monitored until the liquid phase chloroform was no longer visible. Samples were taken from the carbon traps and were analyzed for AOX content. Results of the experiment showed that the reactor system measured one part in five (20% recovery) of the chloroform that was released in the gas phase. Various losses in the overall system would include adsorption, leakage and carbon trap efficiency. In order to characterize the leakage potential of the system, the reactor was pressurized to 2 psi above atmosphere as measured by a mercury manometer. The reactor was then timed to see how long it would take before the pressure inside the reactor reached atmosphere. In approximately 5 seconds, the reactor reached equilibrium with the atmospheric pressure. The results of this test suggest that the leakage may have played a significant role in the chloroform loss from the reactor system. Nevertheless, Liebson's test showed a recovery significantly greater than that of the static benthal batch tests. Some possible reasons for the variances may include different AOX concentrations and the duration of the experiments. Adsorption effects were not measured in either of the tests and may be responsible for a significant portion of the remaining AOX mass balance. Based on the actual recovery, gas-phase halide amounts were calculated. The 28-day activated carbon loading was measured and reported in appendix B.

A detailed calculation of chlorine mass balance is presented in the Appendix. Further research detailing the adsorption of chlorine to the interior of the reactor system is needed to make a conservative estimate of chlorine mass balance. Extraction of

adsorbed chlorine from the glass surface may be done using ethyl acetate as an extraction solvent. If the inorganic halides are being produced and complexed in a way that prevents inorganic halide measurement, then the total chlorine mass balance across solid, liquid and gas phase would still not close.

## CONCLUSIONS

1. In all the sludge deposits organic chlorine was reduced atleast 78%.
2. Organic chlorine on the sludge was most effectively reduced under full strength wastewater(98%).
3. AOX concentration in the overwater reached steady state in a 7-28 day period in all four conditions studied.
4. There were no significant increases in inorganic chloride content in the overall system in spite of the decrease in total organic chlorine and such trend was not expected.
5. Nutrient addition to the partially diluted Kraft wastewater improved AOX reduction compared to partially diluted reactor without nutrient addition(58% vs 53%).
6. In the all the experiments, the sum of sludge, water and gas phase halides was not constant across the reactors, but decreased by at least 50% in each of the reactors.

The present reactor system that was used to study the chlorine distribution across solid, liquid and gas phases experienced various gas losses and there is need for a suitable packing-material and a more air-tight reactor system to analyze the three-phase environmental processes.

Continuous deposition of solids, as seen in full scale operation of an ASB, would facilitate an opportunity for the aerobic biodegradation as these solids settle down to the benthic zone through aerobic zone. The laboratory scale biotreatment system used in this study did not represent exact conditions that may occur in full scale treatment process, and hence the results observed in this study should be pilot tested before they can be implemented.

**APPENDIX: A**

**TABLES OF AOX, IX, TOX, TSS DATA**

Table 1. Characteristics of Kraft Wastewater and Benthic Sludge.

Parameter	Wastewater	Sludge
AOX(mg/L)	16.91	
IX(mg/L)	555	
IX(ug/gm of dry sludge)		555.55
TOX(mg/L)		4825.45
TX(mg/L)		5381.00
TSS(mg/L)	17.5	1405
Percentage of Water		52

Table 2. Liquid AOX (mg/L) Data: Set No. 1  
Date of test: 02.08.1991

Time (days)	Reactor 1	Reactor 2	Reactor 3	Reactor 4
0	16.91	0.00	8.455	8.455
2	11.74	4.48	5.480	6.340
7	10.67	4.08	6.130	6.460
14	9.61	4.27	6.610	4.240
28	9.56	5.87	5.640	4.360
56	9.07	7.10	4.210	3.930
84	9.00	7.15	3.970	3.880

Table 2.1. Liquid AOX (mg/L) Data: Set No. 2  
Date of test: 04.08.1991

Time (days)	Reactor 1	Reactor 2	Reactor 3	Reactor 4
0	16.91	0.00	8.455	8.455
2	11.48	4.00	5.520	6.400
7	10.44	3.84	6.550	6.040
14	9.26	4.05	6.330	4.170
28	9.61	5.96	5.610	4.380
56	8.85	6.86	3.930	3.880
84	8.70	6.78	3.830	3.140

Table 2.2. Average values of AOX (mg/L) Data:

Time (days)	Reactor 1	Reactor 2	Reactor 3	Reactor 4
0	16.910	0.000	8.455	8.455
2	11.610	4.240	5.500	6.370
7	10.550	3.960	6.340	6.250
14	9.435	4.160	6.470	4.205
28	9.585	5.915	5.625	4.370
56	8.960	6.980	4.070	3.905
84	8.850	6.965	3.900	3.510

AOX Mass Balance on the Benthall Reactor Full-Strength Kraft Wastewater

Sample Calculation:

1. Initially, there was 16.91 mg/L AOX present in the Kraft Wastewater.

2. The reactor 1 contains 0.795 L of Wastewater and, therefore, the amount of AOX (in mg) present in the liquid:

$$16.91 \text{ mg/L} * 0.795 \text{ L} = \underline{13.44 \text{ mg}}$$

3. A sample of 20 ml was put in the reactor, each time 20 ml sample was taken out for analysis.

$$\text{Amount of AOX present in 20 ml sample} = 20 \text{ ml} * \text{L}/1000 \text{ ml} * 16.91 \text{ mg/L} = \underline{0.3382 \text{ mg}}.$$

4. "AOX Out" was calculated based on the AOX present in the reactor at various intermediate times.

5. Delta AOX was the difference between "AOX In" and "AOX Out".

6. Net AOX was calculated as the difference between the initial AOX and the summation of Delta AOX:  $13.440 - 0.8494 = \underline{7.8844 \text{ mg}}$

Table 3. AOX Mass Balance on the Benthall Reactor with Full-Strength Kraft Wastewater.

Type	Time	AOX in mg/L	AOX in Reactor (mg)	AOX IN	AOX OUT	Delta AOX (mg)	Sum of Delta AOX (mg)	Net AOX (mg)
Reactor 1	0	16.910	13.440	0.3382	0.3382	0.0000		13.440
	2	11.610	9.229	0.3382	0.2232	0.1060		
	7	10.550	8.387	0.3382	0.2110	0.1272		
	14	9.435	7.500	0.3382	0.1887	0.1495		
	28	9.585	7.800	0.3382	0.1917	0.1465		
	56	8.960	7.123	0.3382	0.1792	0.1590		
	84	8.850	7.035	0.3382	0.1770	0.1612	0.8494	7.8844

Table 4. AOX Mass Balance on the Benthic Reactor with Distilled Water.

Type	Time	AOX in mg/L	AOX in Reactor (mg)	AOX IN	AOX OUT	Delta AOX (mg)	Sum of Delta AOX (mg)	Net AOX (mg)
Reactor 2	0	0.000	0.000	0.0000	0.0000	0.0000		
	2	4.240	3.370	0.0000	0.0848	-0.0848		
	7	3.960	3.148	0.0000	0.0792	-0.0792		
	14	4.160	3.307	0.0000	0.0661	-0.0661		
	28	5.915	4.702	0.0000	0.1183	-0.1183		
	56	6.980	5.549	0.0000	0.1396	-0.1396		
	84	6.965	5.537	0.0000	0.1393	-0.1393	-0.6293	4.9077

Table 5. AOX Mass Balance on the Benthall Reactor with Partially-Diluted Kraft Wastewater.

Type	Time	AOX in mg/L	AOX in Reactor (mg)	AOX IN	AOX OUT	Delta AOX (mg)	Sum of Delta AOX (mg)	Net AOX (mg)
Reactor 3	0	8.455	6.721	0.1689	0.1689	0.0000		
	2	5.500	4.372	0.1689	0.1100	0.0589		
	7	6.340	5.040	0.1689	0.1268	0.0421		
	14	6.470	5.143	0.1689	0.1294	0.0395		
	28	5.625	4.471	0.1689	0.1125	0.0564		
	56	4.070	3.235	0.1689	0.0814	0.0875		
	84	3.900	3.100	0.1689	0.0780	0.0909	0.8829	3.9829

Table 6. AOX Mass Balance on the Benthai Reactor with Nutrient-Amended, Partially-Diluted Kraft Wastewater.

Type	Time	AOX in mg/L	AOX in Reactor (mg)	AOX IN	AOX OUT	Delta AOX (mg)	Sum of Delta AOX (mg)	Net AOX (mg)
Reactor 4	0	8.455	6.721	0.1691	0.1691	0.0000		
	2	6.370	5.064	0.1691	0.1274	0.0417		
	7	6.250	4.968	0.1691	0.1250	0.0441		
	14	4.205	3.342	0.1691	0.0841	0.0850		
	28	4.370	3.474	0.1691	0.0874	0.0817		
	56	3.905	3.104	0.1691	0.0781	0.0910		
	84	3.510	2.790	0.1691	0.0702	0.0989	0.7413	3.5313

Table 7. Liquid Inorganic Halide (mg/L) Data:

Time (days)	Reactor 1	Reactor 2	Reactor 3	Reactor 4
0	555	0	277.5	277.5
2	555	80	190.0	240.0
7	400	90	215.0	210.0
14	495	170	230.0	220.0
28	365	145	235.0	235.0
56	480	150	225.0	245.0
84	480	140	210.0	245.0

Liquid IX Component of the Mass Balance on the Benthall Reactor with Full-Strength Kraft Wastewater

Sample Calculation:

1. Initial IX present in the Kraft Wastewater = 555 mg/L
2. IX present in reactor 1 =  $555 \text{ mg/L} * 0.795 \text{ L} = \underline{441.23 \text{ mg}}$
3. A 20 ml sample contains  $20 \text{ ml} * \text{L}/1000 \text{ mL} * 555 \text{ mg/L} = \underline{11.10 \text{ mg}}$  of IX
4. "IX Out" was calculated based on the IX present in the reactor at various intermediate times.
5. Delta IX was the difference between "IX In" and "IX Out" i.e.,  $11.10 - 11.10 = \underline{0.00 \text{ mg}}$
6. Net IX was calculated as the difference between the initial IX and the summation of Delta IX

$$441.23 - 11.10 = \underline{392.70 \text{ mg}}$$

Table 8. Liquid IX component of the Mass Balance on the Benthall Reactor with Full-Strength Kraft Wastewater.

Type	Time	IX in mg/L	IX in Reactor (mg)	IX IN	IX OUT	Delta IX (mg)	Sum of Delta IX (mg)	Net IX (mg)
Reactor 1	0	555	441.23	11.10	11.10	0.00		
	2	555	441.23	11.10	11.10	0.00		
	7	400	318.00	11.10	8.00	3.10		
	14	495	393.50	11.10	9.90	1.20		
	28	365	290.17	11.10	7.30	3.80		
	56	480	381.60	11.10	9.60	1.50		
	84	480	381.60	11.10	9.60	1.50	11.10	392.70

Table 9. Liquid IX component of the Mass Balance on the Benthel Reactor with Distilled Water.

Type	Time	IX in mg/L	IX in Reactor (mg)	IX IN	IX OUT	Delta IX (mg)	Sum of Delta IX (mg)	Net IX (mg)
Reactor 2	0	0	00.00	0.0	0.0	0.0		
	2	80	63.60	0.0	1.6	-1.6		
	7	90	71.55	0.0	1.8	-1.8		
	14	170	135.15	0.0	3.4	-3.4		
	28	145	115.27	0.0	2.9	-2.9		
	56	150	119.25	0.0	3.0	-3.0		
	84	140	111.30	0.0	2.8	-2.8	-15.5	95.80

Table 10. Liquid IX component of the Mass Balance on the Benthal Reactor with Partially-Diluted Kraft Wastewater.

Type	Time	IX in mg/L	IX in Reactor (mg)	IX IN	IX OUT	Delta IX (mg)	Sum of Delta IX (mg)	Net IX (mg)
Reactor 3	0	277.5	220.61	5.55	5.55	0.00		
	2	190.0	151.05	5.55	3.80	1.75		
	7	215.0	222.60	5.55	4.30	1.25		
	14	230.0	254.40	5.55	4.60	0.95		
	28	235.0	220.60	5.55	4.70	0.85		
	56	225.0	178.87	5.55	4.50	1.05		
	84	210.0	166.95	5.55	4.20	1.35	7.20	174.10

Table 11. Liquid IX component of the Mass Balance on the Benthall Reactor with Nutrient-Amended Partially-Diluted Kraft Wastewater.

Type	Time	IX in mg/L	IX in Reactor (mg)	IX IN	IX OUT	Delta IX (mg)	Sum of Delta IX (mg)	Net IX (mg)
Reactor 4	0	277.5	220.61	5.55	5.55	0.00		
	2	240.0	190.80	5.55	4.80	0.75		
	7	210.0	166.95	5.55	4.20	1.35		
	14	220.0	174.90	5.55	4.40	1.15		
	28	235.0	186.82	5.55	4.70	0.85		
	56	245.0	194.77	5.55	4.90	0.65		
	84	245.0	194.77	5.55	4.90	0.65	5.40	200.17

Solid Halide Measurements

Sample Calculation for Reactor 1 :

$$\begin{aligned} \text{TX} &= 101.28 \text{ ug}/0.1 \text{ gms of wet sludge} \\ &= 1012.8 \text{ ug/gm of wet sludge} \\ &= [(1012.8 \text{ ug/gm of wet sludge}) / (\text{fraction of solids} = 1 - \text{fraction of liquids})] \\ &= 1012.8/(1-0.52) \text{ ug/ gm of dry sludge} \\ &= \underline{2110 \text{ ug/ gm of dry sludge.}} \end{aligned}$$
  
$$\begin{aligned} \text{IX} &= 0.40 \text{ ug/ 2 ul of sample} \\ &= (0.40 \text{ ug/ 2 ul}) * (5 \text{ ml of NO}_3) * (1000 \text{ ul/ 1 ml}) \\ &= 1000 \text{ ug/ gm of wet sludge} \\ &= 1000/ (1-0.52) \text{ ug/ gm of dry sludge} \\ &= \underline{2083.33 \text{ ug/ gm of dry sludge}} \end{aligned}$$
  
$$\text{TOX} = \text{TX} - \text{IX} = (2110 - 2083.33) \text{ ug/ gm of dry sludge} = 26.67 \text{ ug/ gm of dry sludge.}$$

Table 12. Solid Halide (ug/gm of dry sludge) Data: Set No. 1  
Date of test: 01.24.1991

Time (days)	Reactor Type	TX	IX	TOX
0		5380.80	555.55	4825.25
84	Reactor 1	2110.00	2083.33	26.67
	Reactor 2	2753.00	1553.52	1199.48
	Reactor 3	2268.00	1912.55	355.45
	Reactor 4	1917.00	1804.70	112.30

Table 12.1. Solid Halide (ug/gm of dry sludge) Data: Set No. 2  
Date of Set: 01.28.1991

Time (days)	Reactor Type	TX	IX	TOX
0		5380.80	555.55	4825.25
84	Reactor 1	2096.00	2083.33	12.67
	Reactor 2	2534.20	1576.08	958.12
	Reactor 3	2061.28	1988.63	72.65
	Reactor 4	2017.86	1976.74	41.12

Table 12.2. Average values of Solid Halide (ug/gm of dry sludge) Data.

Time (days)	Reactor Type	TX	IX	TOX
0		5380.80	555.55	4825.25
84	Reactor 1	2103.00	2083.33	19.67
	Reactor 2	2643.60	1564.80	1078.80
	Reactor 3	2164.64	1950.59	214.04
	Reactor 4	1998.43	1890.72	107.71

Table 13. Average Values of Solid Halide Measurements (ug/g dry sludge) of the Benthal Reactor with Full-Strength Kraft Wastewater.

Time (Days)	TX	IX	TOX
0	5381	555.55	4825.45
2	5099	803.57	4295.43
7	4487	1011.90	3475.10
14	4058	1339.28	2718.72
28	3652	1864.88	1787.12
84	2103	2083.33	19.6

Table 14. Halide Distributions (in mg as Cl) for Benthic Deposit with Different Overlying Water Conditions over 84 day Experiment.

Type	Time (days)	Solids		Liquids	
		IX	TOX	IX	AOX
Reactor 1	0	122.52	1064.12	441.23	13.44
	84	459.44	4.34	392.70	7.88
Reactor 2	0	122.52	1064.12	0.00	0.00
	84	330.72	228.0	95.80	4.90
Reactor 3	0	122.52	1064.12	220.61	6.72
	84	394.32	43.27	174.10	3.98
Reactor 4	0	122.52	1064.12	220.61	6.72
	84	373.53	21.28	200.17	3.53

Table 15. Overall Organic Halide Reduction Measurement

Time (Days)	Type	TOX (mg)	AOX (mg)	TOX+AOX (mg)	Reduction	Percent reduction
0	R1	1064.12	16.91	1081.03		
	R2	1064.12	00.00	1064.12		
	R3	1064.12	8.455	1072.57		
	R4	1064.12	8.455	1072.57		
84	R1	4.34	8.850	13.19	1067.84	98
84	R2	228.0	6.965	234.96	829.16	78
84	R3	43.27	3.900	47.17	1025.40	95
84	R4	21.28	3.510	24.79	1047.78	97

Table 16. Summary of Total Halide Distribution Across Benthic Reactors

Type	Time in days	Solids (in mg as Cl)		Liquids (in mg as Cl)					
		IX	TOX	IX	Delta IX	Net IX	AOX	Delta AOX	Net AOX
Reactor 1	0	122.72	1064.12	441.23	0.00	441.23	13.440	0.0000	13.4400
	84	459.44	4.34	381.60	11.10	392.70	7.035	0.8494	7.8844
	Reactor 2	0	122.52	1064.12	0.00	0.00	0.00	0.000	0.0000
	84	330.72	228.00	111.30	-15.50	95.80	5.537	-0.6293	4.9077
Reactor 3	0	122.52	1064.12	220.61	0.00	220.61	6.720	0.0000	6.7200
	84	394.32	43.27	4166.95	7.15	174.10	3.100	0.8829	3.9829
Reactor 4	0	122.72	1064.12	220.61	0.00	220.61	6.720	0.0000	6.7200
	84	373.53	21.28	194.77	5.40	200.17	2.790	0.7413	3.5312

Table 17. Solid Total Halide (mg/gm) measurement in Static, Resuspended and Completely Mixed Reactors.

Time (days)	Static Benthic Reactor	Resuspended Reactor	Completely Mixed Reactor
Initial	5.38	17.02	17.02
0.0416		14.02	14.50
0.1666		12.40	
1		12.31	14.01
2	5.099		
5		11.50	
7	4.487		
14	4.058		
19		7.79	14.68
28	3.652		

Table 18. Solid Total Organic Halide (mg/gm) measurement in Static, Resuspended and Completely Mixed Reactors.

Time (days)	Static Benthic Reactor	Resuspended Reactor
Initial	4.83	11.73
0.0416		7.80
0.1666		8.76
1		4.34
2	4.30	
5		4.93
7	3.48	
14	2.72	
28	1.79	
84	0.19	

Table 19. Total Suspended Solids (TSS) Measurement of Overlying Waters.

Type	Time (Days)	Vol. of Sample (ml)	Wt. of Pan + Filter (gms) (A)	Wt. of Pan + Filter (gms) dried at 105°C (B)	TSS = (B-A)/Vol. of sample (mg/L)	TSS in the reactor (mg)
Wastewater	Initial	30	1.0873	1.0876	10	7.95
Reactor1	84	10	1.0879	1.0897	180	143.1
Reactor	84	10	1.0912	1.0917	50	39.75
Reactor 3	84	10	1.0924	1.0946	220	174.9
Reactor 4	84	10	1.0915	1.0939	240	190.8

Table 20. Total Suspended Solids Measurement (mg/L): Sludge

Sludge Type	Time in Days	Vol. of Sample (ml)	A* (gms)	B* (gms)	C* (gms)	TSS	Avg TSS	VSS	Avg VSS	NVSS	Avg NVSS
Initial	0	10	1.1084	1.2226	1.1173	1420		530		890	
			1.1081	1.2220	1.1162	1390	1405	580	555	810	850
R 1	84	10	1.1126	1.1254	1.1214	1280		400		880	
			1.1124	1.1243	1.1223	1190	1235	200	300	990	935
R 2	84	10	1.1106	1.1229	1.1185	1230		440		790	
			1.1100	1.1209	1.1156	1090	1160	530	485	560	775
R 3	84	10	1.1102	1.2220	1.1166	1200		560		640	
			1.1108	1.1213	1.1152	1150	1175	710	635	440	540
R 4	84	10	1.1105	1.1214	1.1188	1090		260		830	
			1.1104	1.1218	1.1179	1140	1115	390	325	750	790

\* A = Wt. of Pan + Filter; B = Wt. of Pan + Filter after drying at 105°C; C = Wt. of Pan + Filter after drying at 550°C.

Table 21. Moisture Content of Sludge in Reactors  
at the end of 84-day Experiment.

Type	Wt. of Pan (in gms)	Wt. of Pan + Sludge (in gms)	Dry Wt. of Pan + Sludge (in gms)	Moisture Content
Reactor 1	0.9896	2.1248	1.1048	52%
Reactor 2	0.9877	2.3420	1.2826	54%
Reactor 3	0.9879	2.2648	1.2876	56%
Reactor 4	0.9876	2.2697	1.3134	57%

Table 22. Gas-Phase AOX Analysis on the Benthel Reactor with Full-Strength Kraft Wastewater over 28-Day Experiment.

Time in days	Set No.	Position of Carbon Column	Wt. of Carbon Sample (gms)	AOX measured (ug/sample of Carbon)	Wt. of Carbon in the Column (gms)	AOX in the Carbon Column (ug)	Total AOX in the Carbon Column (ug)	Average value of AOX (mg)
2	I	Lower	0.0126	8.14	0.4852	313.45		
		Upper	0.0068	2.38	0.4809	168.32	481.77	
	II	Lower	0.0119	7.88	0.4852	321.29		
		Upper	0.0052	2.26	0.4809	209.00	530.29	0.50603
7	I	Lower	0.0117	6.11	0.4718	246.38		
		Upper	0.0137	2.98	0.4659	101.34	347.72	
	II	Lower	0.0098	5.91	0.4718	284.52		
		Upper	0.0112	2.65	0.4659	110.23	394.75	0.37123

Table 23. Gas-Phase AOX Analysis on the Benthall Reactor with Full-Strength Kraft Wastewater over 28-Day Experiment.

Time in days	Set No.	Position of Carbon Column	Wt. of Carbon Sample (gms)	AOX measured (ug/sample of Carbon)	Wt. of Carbon in the Column (gms)	AOX in the Carbon Column (ug)	Total AOX in the Carbon Column (ug)	Average value of AOX (mg)
14	I	Lower	0.0142	7.16	0.4807	242.38		
		Upper	0.0132	3.50	0.4763	126.29	368.67	
	II	Lower	0.0128	7.01	0.4807	263.26		
		Upper	0.0143	3.62	0.4763	120.57	383.83	0.37625
28	I	Lower	0.0161	17.90	0.4852	539.44		
		Upper	0.0153	2.36	0.4809	74.18	613.62	
	II	Lower	0.0097	9.86	0.4852	493.20		
		Upper	0.0092	2.41	0.4809	125.97	619.17	0.61639

**Typical Calculation of Chlorine Mass Balance on the Benthall Reactor with Full-Strength Kraft Wastewater at the end of Day 28**

Total gas-phase halide removal from the reactor at the end of 28-day experiment was 0.6164 mg. Assuming 20% filter efficiency, the amount of gas-phase halide released at the end of 28-day experiment was 3.082 mg.

The change in sludge halide in Kraft wastewater over 28-day time period of time was calculated as below:

$$\text{Delta TX} = [(\text{ug TX/gm of dry sludge})_{\text{Initial}} - (\text{ug TX/gm of dry sludge})_{\text{Day 28}}] * \text{Amount of sludge present in the reactor.}$$

$$\text{Delta TX} = [(5381) - (3652)] \text{ ug} * 197.58 \text{ gms} * (1-0.52)$$

$$\text{Delta TX} = \underline{163.97 \text{ mg.}}$$

The change in liquid halide in Kraft wastewater over 28-day time period of time was calculated as below:

$$(i) \quad \text{Delta AOX} = [(\text{mg AOX present in the reactor})_{\text{Initial}} - (\text{mg AOX present in the reactor})_{\text{Day 28}}]$$

$$\text{Delta AOX} = [13.440 - 8.3292] \text{ mg}$$

$$\text{Delta AOX} = \underline{5.1108 \text{ mg.}}$$

$$(ii) \quad \text{Delta IX} = [(\text{mg IX present in the reactor})_{\text{Initial}} - (\text{mg IX}$$

$$\begin{aligned} & \text{present in the reactor)}_{\text{Day 28}}] \\ \text{Delta IX} &= [441.23 - 298.27] \text{ mg} \\ \text{Delta IX} &= \underline{142.96 \text{ mg}}. \end{aligned}$$

The overall change in the liquid, solid and gas-phase halides at the beginning and 28-day was 312.04 mg. The fraction of gas-phase halide was not significant as compared to the total halide reduction of 312.04 mg in the reactor. The adsorption and leakage fractions appear to be much more significant than the volatilization of halides in the reactor system.

**APPENDIX: B**

**Carbon loading on GAC & Biomass loading on sludge**

### Carbon Loading Calculation

#### Step 1. Change in Total organic halide (TOX) in the sludge

$$\begin{aligned}
 \text{Initial sludge TOX} &= 4,825.45 \text{ ug/gm of dry sludge} \\
 \text{28-day sludge TOX} &= 1,787.12 \text{ ug/gm of dry sludge} \\
 \text{Delta TOX} &= \underline{3,038.33 \text{ ug/gm of dry sludge}} \\
 &= 3,038.33 \text{ ug/gm of dry sludge} * \text{Amount of sludge in the} \\
 &\quad \text{reactor} * \text{percent of solids} \\
 &= 3,038.33 \text{ ug/gm of dry sludge} * \\
 &\quad [454.44 \text{ gms of wet sludge} * (1-0.52)] \\
 &= 662,754.56 \text{ ug as Cl} \\
 \text{Delta TOX} &= \underline{662.75 \text{ mg as Cl}}
 \end{aligned}$$

#### Step 2. Mass of Chloroform

It is unlikely that all the organic halide reduction results in the formation of a single volatile compound. Probable by-products of the organic halide reduction are chloroform, dichloromethane, chloromethane and other low molecular weight halogenated compounds. In order to simplify the modeling of the reaction system, it was assumed that all organic halide reduction resulted in the formation of chloroform.

The amount of chloroform ( $M_c$ ) would be

$$M_c = 0.66275 \text{ gm as Cl} * [(119.5 \text{ gm of } \text{CHCl}_3/\text{mole}) / (106.5 \text{ gm of Cl/mole})]$$

$$M_c = \underline{743.64 \text{ mg}}$$

### Setp 3. Volume of Air

Air flow through the reactor was 1.0 L/min. Total volume of air ( $V_a$ ) in the reactor over 28-day period

$$V_a = 1.0 \text{ L/1 min} * (60 \text{ min/1 hr}) * (24 \text{ hrs/1 day}) * 28 \text{ days}$$

$$V_a = \underline{40,320 \text{ liters}}$$

### Step 4. Gas-phase chloroform concentration ( $C_G$ )

The chloroform formation may not be uniform through a 28-day period. In order to estimate the average concentration of chloroform, it was assumed that chloroform formation was constant. The average gaseous chloroform concentration ( $C_G = M_c/V_a$ ), in 28-day period would be

$$C_G = 743.64 \text{ mg/40320 liters}$$

$$C_G = 0.0184 \text{ mg/L}$$

$$C_G = \underline{18.44 \text{ ug/L}}$$

### Setp 5. Liquid-phase chloroform concentration ( $C_L$ )

A layer of water, which is a result of humidified air from the reactor, forms on the surface of the granular activated carbon reactor gas trap. The gaseous chloroform dissolves in the layer of water while passing through the carbon bed. Henry's law governs the equilibrium concentrations between the gaseous chloroform and the water layer on the activated carbon. The liquid-phase chloroform concentration ( $C_L$ ) on GAC can be calculated using Henry's law of constant (H). Henry's law of constant for chloroform is  $1.4 * 10^{-1} \text{ [(mg/m}^3\text{)/(mg/m}^3\text{)]}$  (Ref. "Chemodynamics" by Thibodeaux, L.J. 1979).

Liquid-phase chloroform concentration,  $C_L = \text{Gas-phase chloroform conc.}(C_G)^*$

Henry's law of constant (H) for chloroform.

$$C_L = 18.44 \text{ ug/L} * 1.4 * 10^{-1} \text{ [(mg/m}^3\text{)/(mg/m}^3\text{)]}$$

$$C_L = \underline{2.5820 \text{ ug/L}}$$

## Step 6. Carbon loading

### a. Theoretical

In phase II experiment, Witco 377 granular activated carbon was used in the gas traps because of its ability to adsorb gas-phase halide. There was no standard chloroform-carbon isotherm available for Witco 377 activated carbon. Three known standard chloroform-carbon isotherms (Cecarbon GAC 30, Carborundum GAC 30 and an unspecified coal-based carbon) were used to estimate the theoretical carbon loading,  $(X/M)_T$ , (ug of chloroform adsorbed onto the carbon/gm of carbon) and compared with the observed carbon loading using Witco 377 activated carbon. The total surface area for all the activated carbons, from the manufacturer's data, was found to be 900-1050  $\text{m}^2/\text{gm}$ .

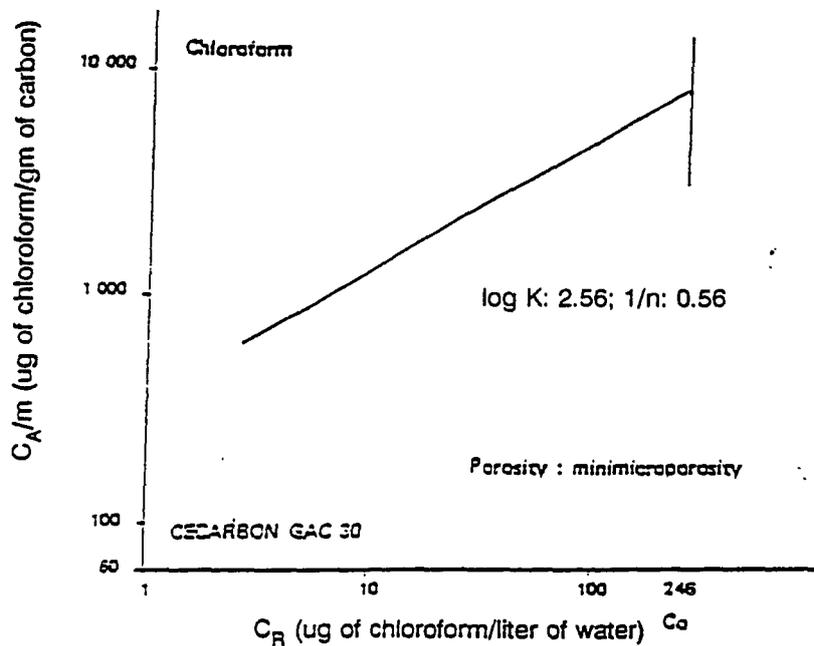
i) From the Cecarbon GAC 30 liquid-phase chloroform-carbon isotherm, theoretical carbon loading,  $(X/M)_T$ , at a chloroform concentration of 2.5820 ug/L

$$(X/M)_T = 617 \text{ ug of chloroform/gm of carbon}$$

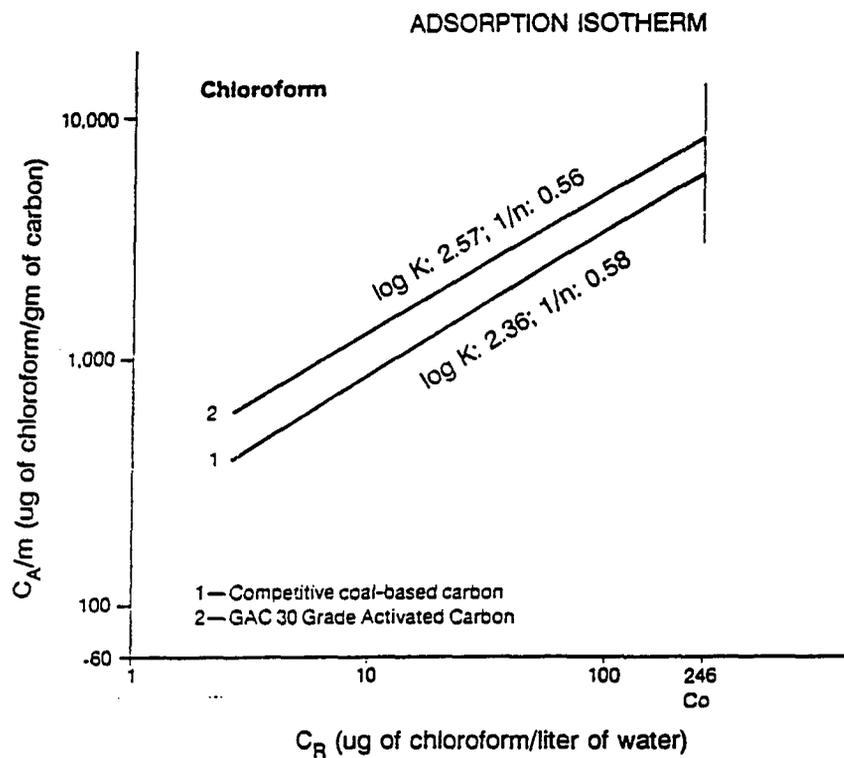
$$(X/M)_T = 617 \text{ ug of CHCl}_3 * \text{[(106.5 gm of Cl/mole)/(119.5 gm of CHCl}_3\text{/mole)]}$$

$$(X/M)_T = \underline{550 \text{ ug of Cl/gm of carbon}}$$

ADSORPTION ISOTHERM ON  
ACTIVATED CARBON FROM COMPACTED COAL



Source: Autochem Inc., Ceca Division



Source: Kennecott Corp., Activated Carbon Division

ii) From the Carborundum GAC liquid-phase chloroform-carbon isotherm, theoretical carbon loading,  $(X/M)_T$ , at a chloroform concentration of 2.5820 ug/L

$$(X/M)_T = 631 \text{ ug of chloroform/gm of carbon}$$

$$(X/M)_T = 631 \text{ ug of CHCl}_3 * [(106.5 \text{ gm of Cl/mole})/(119.5 \text{ gm of CHCl}_3/\text{mole})]$$

$$(X/M)_T = \underline{562 \text{ ug of Cl/gm of carbon}}$$

iii) From the coal-based carbon liquid-phase chloroform-carbon isotherm, theoretical carbon loading,  $(X/M)_T$ , at a chloroform concentration of 2.5820 ug/L

$$(X/M)_T = 397 \text{ ug of chloroform/gm of carbon}$$

$$(X/M)_T = 397 \text{ ug of CHCl}_3 * [(106.5 \text{ gm of Cl/mole})/(119.5 \text{ gm of CHCl}_3/\text{mole})]$$

$$(X/M)_T = \underline{353 \text{ ug of Cl/gm of carbon}}$$

#### b. Measured

The measured carbon loading  $(X/M)_M$ , using Witco 377 grade activated carbon in the experiment was

$$(X/M)_M = 20.26 \text{ ug as Cl/0.0314 gm of carbon}$$

An average carbon blank value was applied in the calculation of measured loading.

$$(X/M)_M = (20.26 - 2 * 0.12) \text{ ug as Cl/0.0314 gm of carbon}$$

$$(X/M)_M = \underline{637 \text{ ug as Cl/gm of carbon}}$$

The theoretical amount of carbon loading using Cecarbon GAC 30 grade activated carbon ranges between the theoretical activated carbon loadings using Carborundum GAC 30 grade activated carbon and the coal-based activated carbon. The measured carbon loading using Witco 377 GAC in the experiment matches closely the theoretical activated carbon loading using Cecarbon GAC 30 grade activated carbon.

Interpretation:

The theoretical and measured X/M values were in close agreement. Based on this simple observation only, the activated carbon used as a reactor trap probably was exhausted. The results of this comparison are consistent with the proposed hypothesis that the organic halide reduction resulted in volatile organics such as chloroform. However, there are still several reasons to question the hypothesis.

First, the theoretical activated carbon loadings were based on the adsorption isotherms representing equilibrium conditions, while the measured activated carbon loading was probably based on non-equilibrium conditions. During the time frame of this study, it was not clear that an equilibrium was reached at either gas-liquid or liquid-GAC interfaces. Any variations in the chloroform concentration of the gas flow would upset an equilibrium condition.

Secondly, three activated carbons were used to estimate the theoretical loadings. None were the same as the Witco 377 used in the experiment. No isotherm for that

activated carbon was available.

Finally, chloroform formation may not have been constant throughout the 28-day experiment, and hence the driving force for the adsorption onto the GAC would have been variable. Desorption of chloroform from the activated carbon could have occurred if the levels of influent chloroform concentrations varied over 28-day period. In order to estimate the change in activated carbon loading due to a possible desorption, it was assumed that 50% of the gas-phase chloroform was desorbed from the activated carbon by the end of 28-day period. Based on three activated carbon isotherms, the change in the carbon loading was calculated to be in the range of 32%. If desorption had occurred, the measured loading on the GAC would have been 32% less than what was measured. However, since the measured loading is within 14% of the ultimate loadings for two GAC packings, it was likely that desorption did not occur.

### **Biomass Loading on sludge**

#### **Step 1. Liquid-phase sludge concentration ( $S_L$ )**

The liquid-phase concentration ( $S_L$ ) in the sludge was calculated on the basis of an observation made by Bryant et al.(1988). In their study, it was observed that TOX levels in overlying water were approximately seven times higher than corresponding levels in core water.

In static benthal deposit, liquid-phase concentration in sludge at the end of 28-day

$$S_L = 1/7 * (\text{liquid-phase concentration in overwater})$$

$$S_L = 1/7 * (9585 \text{ ug/L})$$

$$S_L = \underline{1369.28 \text{ ug/L}}$$

#### **Step 2. Biomass loading**

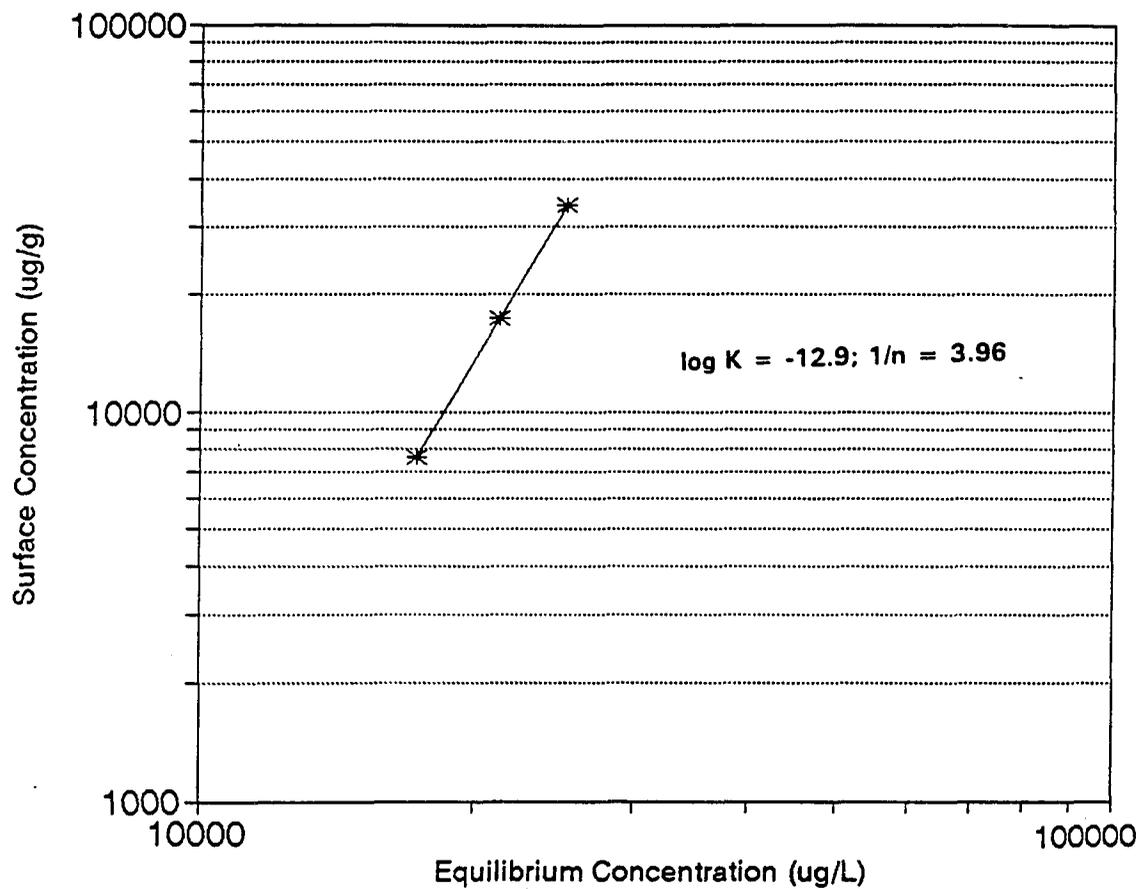
##### **Theoretical: a.1**

The biomass loading (ug of TOX/gm of VSS) was calculated using a Freundlich adsorption isotherm for total TOX on biomass developed by Amy et al. (1988). The highest biomass loadings were observed using biomass associated with a 10-day MCRT (mean cell residence time). Freundlich adsorption isotherm with a 10-day MCRT was used to estimate the biomass loading for 10-day period static benthal sludge.

From the Freundlich adsorption isotherm, corresponding theoretical biomass loading  $(X/M)_T$  for the liquid-phase sludge concentration,  $S_L$ , of 1369.28 ug/L was

$$(X/M)_T = \underline{0.33 \text{ ug TOX/gm VSS}}$$

Adsorption Isotherm for total TOX based  
on 10-Day MCRT



Source: Reference 21

The theoretical biomass loading at 10-day MCRT was found to be low. A possible reason for the lower biomass loading can be explained. Kraft mill wastewaters contain a wide range of compounds varying from chlorophenols (<300 MW) to extremely high molecular weight compounds such as chlorolignins. The high molecular weight compounds are less readily internalized because of their size. However, high molecular compounds may be broken down biologically to low molecular weight compounds. At shorter MCRT, high molecular weight compounds may not be completely broken down to low molecular weight compounds and hence not effectively partition into the organism. This may lead to a lower biomass loading at shorter sludge age.

a.2 Assuming that the liquid-phase sludge concentration would be the same as the overlying water, the corresponding theoretical biomass loading  $(X/M)_T$  for the liquid-phase sludge concentration,  $S_L$ , of 9585 ug/L was

$$(X/M)_T = \underline{736.38 \text{ ug TOX/gm VSS}}$$

b. Measured

The amount of TOX present in the sludge at the end of 28-day period was 857.81 ug/gm of wet sludge. The 28-day VSS was estimated by linear interpretation of the initial and final measurements of VSS. The actual amount of biomass loading observed  $(X/M)_M$ , in the experiment was calculated as below:

$$(X/M)_M = [(857.81 \text{ ug TOX/gm of sludge}) * (197.58 \text{ gms of sludge present in the reactor})] / [(475 \text{ gms of VSS/L of sludge}) * (0.20 \text{ L of sludge in the reactor})]$$

$$(X/M)_M = \underline{1784.06 \text{ ug TOX/ gm VSS}}$$

Thus, regardless of the assumed pore water concentration, the measured biomass TOX loading was much higher than the theoretical loadings. There are two reasons for this observation. First, in the set of calculations, static benthic loading for a 10-day MCRT was estimated using the 10-day MCRT adsorption since it was the longest MCRT available (Amy et al. 1988). From the adsorption isotherm, the trend in the K and  $1/n$  values progressively increase with MCRT and hence the higher surface concentration (ug of TOX/gm of VSS) would result at longer MCRT.

Secondly, at short MCRT's, a non-equilibrium state is possible between the pore water concentration and the TOX adsorbed onto the biomass. As sludge age increases, more organic material would be adsorbed onto the biomass and then biodegraded. The transformation of TOX material in the biomass would result in a decrease in the pore water concentration. Thus, a non-equilibrium state would exist due to the concentration gradient between the pore water and the TOX present in the biomass.

Finally, the time-dependent changes in biomass TOX load over the entire 84-day experiment cannot be described by a simple isotherm, since adsorption was only one of the processes that are occurring in the biomass. From the Figure 9, it was observed that at shorter intervals of time biomass loading gradually decreased with the bulk AOX concentration. At longer intervals of time, the biomass loading was more time-

dependent, and there was an increase in the reduction of sludge organic loading per unit AOX concentration. This increase in sludge reduction was a result of biological degradation rather than adsorption.

In earlier biosorption studies, no appreciable non-adsorbable fraction was measured for similar Kraft wastewater. Thus, a simple isotherm cannot be used to describe the long-term biosorption/biodegradation measured in this benthal system.

**Table B.1. Variation of Biomass Loading with AOX concentration over 84-Day Experiment**

<b>Time (days)</b>	<b>X/M (ug of TOX/gm of dry sludge)</b>	<b>AOX concentration (mg/L)</b>
0	4825.45	16.91
2	4295.43	11.61
7	3475.10	10.55
14	2718.72	9.435
28	1787.12	9.585
84	19.60	8.850

## Variation of Biomass loading with Bulk AOX concentration

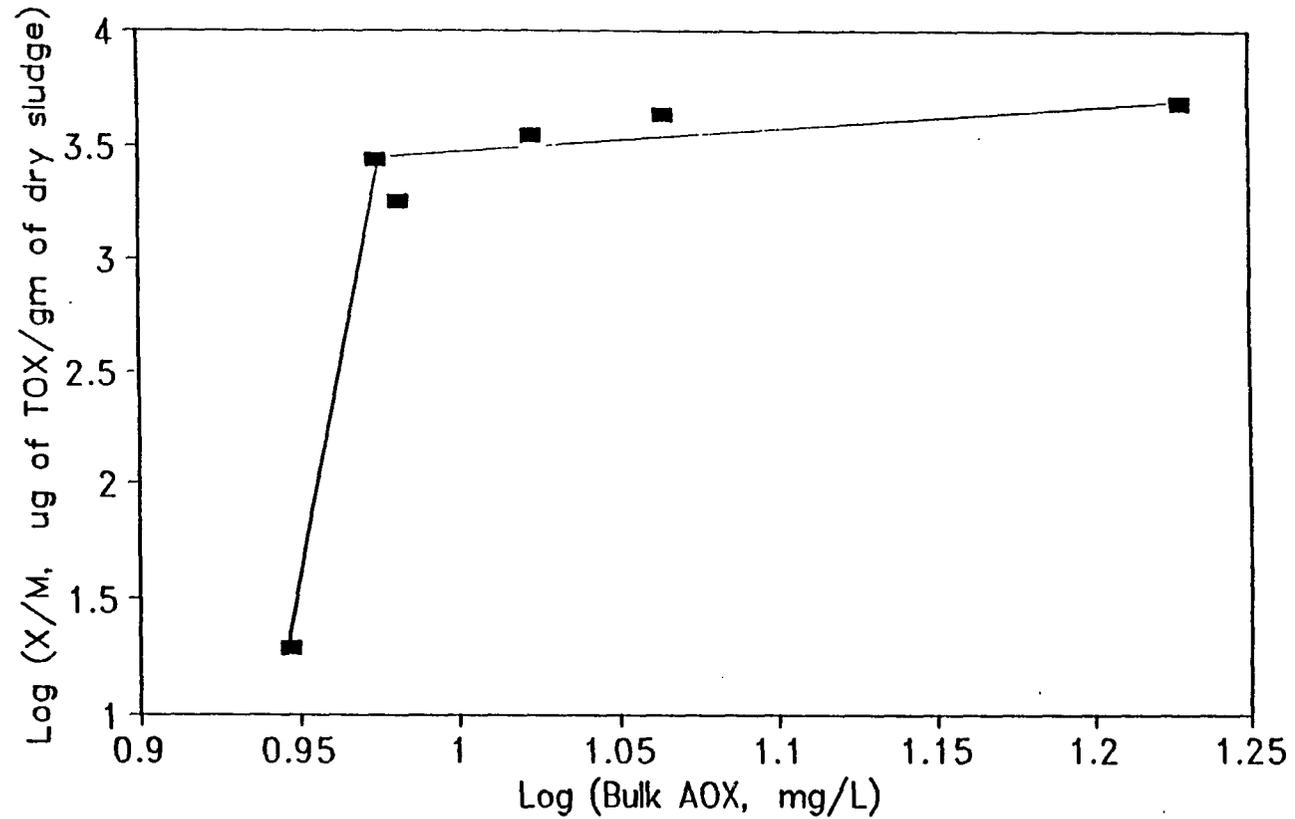


Figure 9. Changes in Biomass Loading with Overlying Full-Strength Kraft Wastewater AOX Concentration

## REFERENCES

1. Kringstad, K.P., and Lindstrom, K. " Spent Liquors From Pulp Bleaching". Environmental Science and Technology, Vol. 18, No. 8, 1984, pp. 236A-248A.
2. Lindstrom, K., and Osterberg, F. " Chlorinated Carboxylic acids in softwood Kraft Pulp Spent Bleach Liquors", Environmental Science and Technology, Vol 20, No. 2, 1986 pp. 133-138.
3. Hardell, H.L., and F. de Sousa. " Characterization of Spent Bleach Liquors": part 1. Spent Liquors From Prebleaching of Pine Kraft Pulp. Svensk Papperstidning, Vol. 4, 1977, pp. 110-120.
4. Sjostrom, L., Radestrom, R and Lindstrom, K. " Determination of Total Organic Chlorine in Spent Bleach Liquors". Svensk Papperstidning, Vol 3, 1982, pp. R7-R13.
5. Bjorseth, A., Carlberg, G., and Moller, M. " Determination of Halogenated Organic Compounds and Mutagenicity Testing of Spent Liquors". The Science of the Total Environment, Vol 11, 1979, pp. 197-211.
6. Carlberg, G.E., Drangsholt, H., and Gjos, N. "Identification of Chlorinated Compounds in the Spent Chlorination Liquor From Differently Treated Sulfite Pulps with Special Emphasis on Mutagenic Compounds". The Science of the Total Environment, Vol 48, 1986, pp. 157- 167.
7. Hardell H.L., and F. de Sousa. " Characterization of Spent Bleach Liquors: part 2. Different Sequences From Prebleaching of Pine and Kraft Pulp". Svensk Papperstidning, Vol 7, 1977, pp. 201-209.
8. Carlberg, G.E., et al., " Chemical Characterization and Mutagenicity Testing of Chlorinated Trihydroxybenzenes Identified in Spent Bleach Liquors From a Sulphite Plant", The Science of the Total Environment, Vol 15, No. 1, 1980.
9. EPA Method 506 Organic Halide (Total): Adsorption-Pyrolysis-Titrimetric method (Tentative). Standard Methods for the Examination of Waste and Wastewater, 1985, pp. 516-525.
10. Bethge, P.O. " Determination of Chlorinated Organics in Pulp and Paper Mill Effluents", Colloquium on Measurement of Generic Organic Chlorine Compounds, University of Toronto, February 16-17, 1989; as cited by Bonsor, N., McCubbin, N., and Spragne, J. B., " Kraft Mill Effluents in Ontario", Report Prepared for the Pulp and Paper Sector of MISA, Ontario 25, Ministry of the Environment, April, 1988.

11. LaFond, R.A., and Ferguson, J.F. " Anaerobic and Aerobic Biological Treatment for Removal of Chlorinated Organics from Kraft Bleaching Wastes", 1991 TAPPI (part 2) proceedings.
12. Martinsen, K., Kringstad, A., and Carlberg, G. " Methods For Determination of Sum Parameters and Characterization of Organochlorine Compounds in Spent Bleach Liquors From Pulp Mills and Water, Sediment and Biological Samples From Receiving Waters", Water Science Technology, Vol 20, No. 2, 1988, pp. 13-24.
13. Reckhow, D.A., and Singer, P.C., " Chlorination By-Products in Drinking Waters: From Formation Potentials to Finished Water Concentrations", American Water Works Association Journal, April, 1990, pp. 173-180.
14. Glaze, W.H., and Henderson IV, J.E., " Formation of Organochlorine Compounds From the Chlorination of a Municipal Secondary Effluent", Journal of the Water Pollution Control Federation, Vol 47, No. 10, October 1975, pp. 2511-2515.
15. SSVL, " Environmental Impacts of Bleach Plant Effluent- Project Report for 1982-1985, SSVL-85 Report No.44, December, 1985.
16. Bryant, C.W., Amy, G.L., and Alleman, B.C., " Organic Halide and Organic Carbon Distribution and Removal in a Pulp and Paper Wastewater Lagoon", Journal of the Water Pollution Control Federation, Vol. 59, No. 10, October, 1987, pp. 890-896.
17. Hall, E.R., Fraser, J., Garden, S., and Cornacchio, L.A., " Organo-chlorine Discharges in Wastewaters from Kraft Mill Bleach Plants", Pulp and Paper Canada, 90(11), November, 1989, pp. T421-T425.
18. Bryant, C.W., and Amy, G.L., " Seasonal and In-Mill Aspects of Organic Halide Removal by an Aerated Stabilization Basin Treating a Kraft Mill Wastewater", Water Science Technology, Vol 21, 1989, pp. 231-239.
19. Bryant, C.W., Amy, G.L., Neil, R., and Ahmed, S., " Partitioning of Organic Chlorine Between Bulk Water and Benthic Interstitial Water Through a Kraft Mill Aerated Lagoon", Water Science Technology, Vol. 20, No. 1, 1988, pp. 73-79.
20. Bell, J.P., and Tsezos, M., " Removal of Hazardous Organic Pollutants by Adsorption on Microbial Biomass", Water Science and Technology, Vol 19, 1987, pp. 409-416.
21. Amy, G., Bryant, C., Alleman, B., and Barkley, W., " Biosorption of Organic Halide in a Kraft Mill Generated Lagoon", Journal of the Water Pollution Control

Federation, Vol. 60, No. 8, August 1988, pp. 1445-1453.

22. Bell, J.P., and Tsezos, M., " Removal of Hazardous Organic Pollutants by Biomass Adsorption", Journal of the Water Pollution Control Federation, Vol. 59, No. 4, April 1987, pp. 191-198.

23. Bell, J.P., and Tsezos, M., " A Mechanistic Study on the Fate of Malathion Following Interaction with Microbial Biomass", Water Science Technology, Vol. 25, No. 9, 1991, pp. 1039-1046.

24. Egli, C., Scholtz, R., Cook, A., and Leisinger, T., " Anaerobic Dechlorination of Tetrachloromethane and 1,2-dichloroethane to Degradable Products by Pure Cultures of *Desulfobacterium* sp. and *Methanobacterium* sp". Federation of European Microbiological Societies Microbiology Letters 43 1987 pp. 257-261.

25. Grady, C.P., " Biodegradation: Its Measurement and Microbiological Basis", Biotechnology and Bioengineering, Vol. 27, May 1985, pp. 660-674.

26. Boyd, S., and Shelton, D., " Anaerobic Biodegradation of Chlorinated Phenols in Fresh and Acclimated Sludge", Applied Environmental Microbiology, Vol. 47, 198.

27. Hakulinen, R., and Salkinoja-Salonen, M., " Treatment of Kraft Bleaching Effluents", International Pulp Bleaching Conference, 1982.

28. Murthy, V.B.K., Kaufman, D.D., and Fries, G.F., " Degradation of Pentachlorophenol (PCP) in Aerobic and Anaerobic Soil", Journal of Environmental Science and Health, B(14), No. 1, pp. 1-14.

29. Mikesell, M.D., and Boyd, S.A., " Reductive Dechlorination of the Pesticides 2,4-D, 2,4,5-T, and Pentachlorophenol in Anaerobic Sludges", Journal of Environmental Quality, Vol. 14, 1985, pp. 337-340.

30. Vogel, T., Criddle, C., and McCarty, P., " Transformations of Halogenated Aliphatic Compounds", Environmental Science and Technology, Vol. 21, No. 8, 1987, pp. 722-736.

31. Bouwer, E., and Wright, J., " Transformations of Trace Halogenated Aliphatics in Subsurface Microcosms with Anoxic Biofilms", Journal of Contaminant Hydrology, February, 1987.

32. Kobayashi, H., and Rittmann, B., " Microbial Removal of Hazardous Organic Compounds", Environmental Science and Technology, Vol. 16, No. 3, 1982, pp. 170A-183A.

33. Baughman, G., and Paris, D., " Microbial Bioconcentration of Organic Pollutants From Aquatic Systems - A Critical Review", CRC Critical Reviews in Microbiology, January, 1981, pp. 205-225.
34. Leuenberger, C., Giber, W., Coney, R., Graydon, J.W., and Monlar-Kubica, E., " Persistent Chemicals in Pulp Mill Effluents: Occurrence and Behavior in an Activated Sludge Treatment Plant", Water Resources, Vol. 19, No. 7, 1985, pp. 885-894.
35. Grimes, D.J., and Morrison, S.M., " Bacterial Bioconcentration of Chlorinated Hydrocarbon Insecticides from Aqueous Systems", Microbial Ecology, Vol. 2, 1975, pp. 43-59.
36. Pitter, P., " Determination of Biological Degradability of Organic Substances", Water Resources, Vol. 10, 1976, pp. 231-235.
37. Lander, L., Lindstrom, K., Karlsson, M., Nordin, J., and Sorensen, L., " Bioaccumulation in Fish of Chlorinated Phenols From Kraft Pulp Mill Bleachery Effluents", Bull. Environ. Contam. Toxicol., Vol. 18, 1977, pp. 663-673.
38. Carlberg, G.E., Drangsholt, H., Gjos, N., and Tveten, G., " Analysis of Organochlorine Compounds in Water, sediment and Fish From Iddefjorden. In: Proceedings from the Seventeenth Nordic Symposium on Water Research, Porsgrunn, Nordforsk Publication 1, 1981, pp. 131-140.
39. Neilson et.al., "Tri-and Tetrachloroveratrole, Metabolites Produced by Bacterial o-methylation of tri-and Tetrachloroguaiacol: an Assessment of their Bioconcentration Potential and their effects on fish reproduction. Can.J.Fish.Aquatic Science, Vol 41, 1984, pp. 1502-1512.
40. Carlberg et.al., "Environmental Impact of Organochlorine Compounds Discharged from the pulp and Paper Industry", 1989.
41. Owens, J.W., "A review of the Scandanavian Research on the Aquatic impacts of Bleached Pulp Mill Effluents", NCASI Special Report, 1990.
42. Hall, E.R., and Randle, W.G., " AOX Removals From Bleached Kraft Mill Wastewater: A Comparison of Three Biological Treatment Processes" Water Science and Technology, Vol 26, 1992, No. 1-2, pp. 387-396.
43. Bryant, C.W and Barkley, W.A., "The capabilities of Conventional Treatment Systems for Removal of Chlorinated Organic Compounds from Pulp and Paper Wastewaters, 1990. Invited paper. Pacific Paper EXPO Technical Conference, Vancouver, B.C.

44. Hakulinen, R and Salkinoja-Salonen, M.S., "Treatment of Pulp and Paper Industry Wastewaters in an Anaerobic Fluidized Bed Reactor", Process Biochem., 1982, Vol. 2, pp. 18-22.