THE PARTITIONING AND REMOVAL OF ORGANIC HALIDE ACROSS AN AERATED STABILIZATION BASIN (ASB) TREATING KRAFT MILL WASTEWATER

by

Elizabeth Ann Kostiuk

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
WITH A MAJOR IN CIVIL ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 9 0

STATEMENT BY AUTHOR

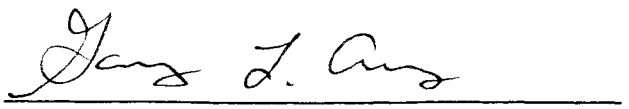
This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: 

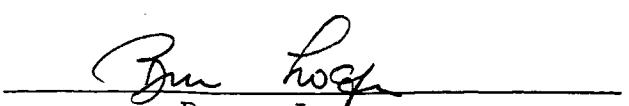
APPROVAL BY THESIS DIRECTORS

This thesis has been approved on the date shown below:



Gary L. Amy
Professor of Civil Engineering

11/30/96
DATE



Bruce Logan
Associate Professor of Civil Engineering

12/11/96
DATE

THIS THESIS IS DEDICATED IN THE
MEMORY OF MY GRANDMOTHER

SOPHIA KOSTIUK

ACKNOWLEDGMENTS

The author would like to thank Dr. Gary Amy for his guidance and patience throughout this project. I am thankful for his willingness to answer all of my questions regardless of their content. Gary has taught me a great deal about water chemistry and has had a positive impact on my academic career. I have also learned to never make a bet with Gary because regardless of the situation he always win.

I would like to thank all of the professors in the environmental engineering department. They have taught me things that I never dreamed I wanted to know. Thank you all.

Special thanks goes to Procter and Gamble Cellulose for their financial support for this project. It has been greatly appreciated. I would like to thank Ed Aprahamian for providing me with so much information, for answering my many questions and for coordinating the sample collection throughout the project.

I am extremely grateful for the endless support and love my family has given to me. To my parents, Jack and Peggy, I give them my love for always being there when I needed a friend. To my sister Vickie and brother Joe, you have always been a great source of inspiration. Thank you grandfather for your love, your pride in me and for always wanting the best for me.

I must thank Bruce Alleman for sharing with me his vast knowledge and inner most secrets on dealing with the TOX machine. I greatly appreciate the humor and all the time he spent helping me conquer that beast.

The great camaraderie shared by all of those in the lab will never be forgotten. Without their help and friendship none of this would have been possible. I will miss you all.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

The research reported herein was conducted to monitor the adsorbable organic halide (AOX) in wastewater from two Kraft mill facilities employing aerated stabilization basins (ASB) to treat the wastewater. Bulk water AOX across the ASB was characterized by apparent molecular weight (AMW) through ultrafiltration. Changes in the AMW fractions were evaluated to identify possible removal pathways for AOX. Seasonal variations such as temperature were explored to identify their influence on the ASBs ability to remove AOX. Benthal solids and interstitial water were utilized to estimate the partitioning of AOX between the water column and the benthic layer. The extent of organic halide partitioning between the overlying water and the benthal zone is indicative of the role biosorption plays in the transport of organic halide from the water column to the benthic layer. An attempt was made to ascertain apparent dehalogenation in the sediment layer of the ASB.

INTRODUCTION

Recent attention has focused on the use of chlorine as a bleaching agent in the pulp and paper industry. A variety of chlorinated organic compounds found in paper mill wastewaters have been identified as having toxic or mutagenic characteristics. With the growing concern over environmental quality and protection, the pulp and paper industry has begun to explore mechanisms for reducing the production and subsequent release of toxic substances into the environment. Possible solutions to this environmental problem include in-mill modifications to reduce the formation of chlorinated organics or improvements to existing wastewater treatment systems to remove toxic compounds prior to discharge into receiving waters.

Before treatment system changes can be implemented, the wastewater must be characterized before, during and after treatment. Wastewaters derived from mills operating under the Kraft or sulfate pulping process contain organic chlorine compounds which range from simple chlorophenols to more chemically complex chlorolignins. Since organic halide composition in the wastewater varies with in-mill operating conditions it has been difficult as well as impossible to identify all of the constituents. As a result, a nonspecific parameter for measuring the totality of chlorinated organic

compounds present in the aqueous phase is being advocated to characterize the wastewater. Adsorbable organic halide (AOX) is the nonspecific parameter employed throughout this research.

The research reported herein involved an AOX monitoring program at two specific Kraft mill facilities. The primary objectives of the research were 1) to develop AOX profiles across an existing treatment system, an aerated stabilization basin (ASB), 2) to define the partitioning of AOX between the water column and the sediment layer in the ASB, 3) to define seasonal variations, 4) to develop a relationship between in-mill production conditions and effluent characteristics, 5) to ascertain apparent dehalogenation in the sediment layer of the ASB and 6) to compare AOX formation and removal under the two separate bleaching processes.

The first mill investigated (Mill #1) is divided into two smaller mills in order to process a paper grade wood stock and a dissolving grade wood stock. Pulp from each of the smaller mills is further processed through a conventional 6-stage pulp bleaching system. This system is composed of a chlorination stage (C), an alkaline extraction stage (E), a hypochlorite stage (H), a chlorine dioxide stage (D), an alkaline extraction stage (E), and finally another chlorine dioxide stage (D).

Spent liquors from the bleaching process are mixed and

treated by an aerated stabilization basin (ASB). A schematic of the ASB is presented in Figure 1. The ASB treatment system consists of an intensely aerated two-cell lagoon followed by a multi-cell facultative lagoon. The overall hydraulic residence time (HRT) of the ASB is 7 to 8 days with the first lagoon having a HRT of 2 days.

Mill #2 is a modern mill which processes paper grade wood stock only. Two sample sets were collected from Mill #2, one prior to modifications of the bleaching system and one after the modifications were complete. The bleaching sequence at Mill #2 deviates from the conventional sequence presented above. Prior to modification, the bleaching sequence consisted of an oxygen stage (O), a chlorine dioxide/chlorine stage (D/C), an alkaline extraction stage (E) and a chlorine dioxide stage (D). Approximately 70 percent chlorine dioxide and 30 percent chlorine was used in the D/C stage. Modification to the bleaching process has eliminated the D/C stage and introduced a D stage using chlorine dioxide.

Wastewater consisting of the spent acid and alkaline liquors from Mill #2 is treated by a two stage aerated lagoon followed by a stabilization basin. Figure 2 is a schematic of the ASB treatment system. The first lagoon is highly aerated (12 aerators) with a HRT of 5 days followed by a less aerated (6 aerators) lagoon with a HRT of 9 days. The stabilization basin has a HRT of 10 days.

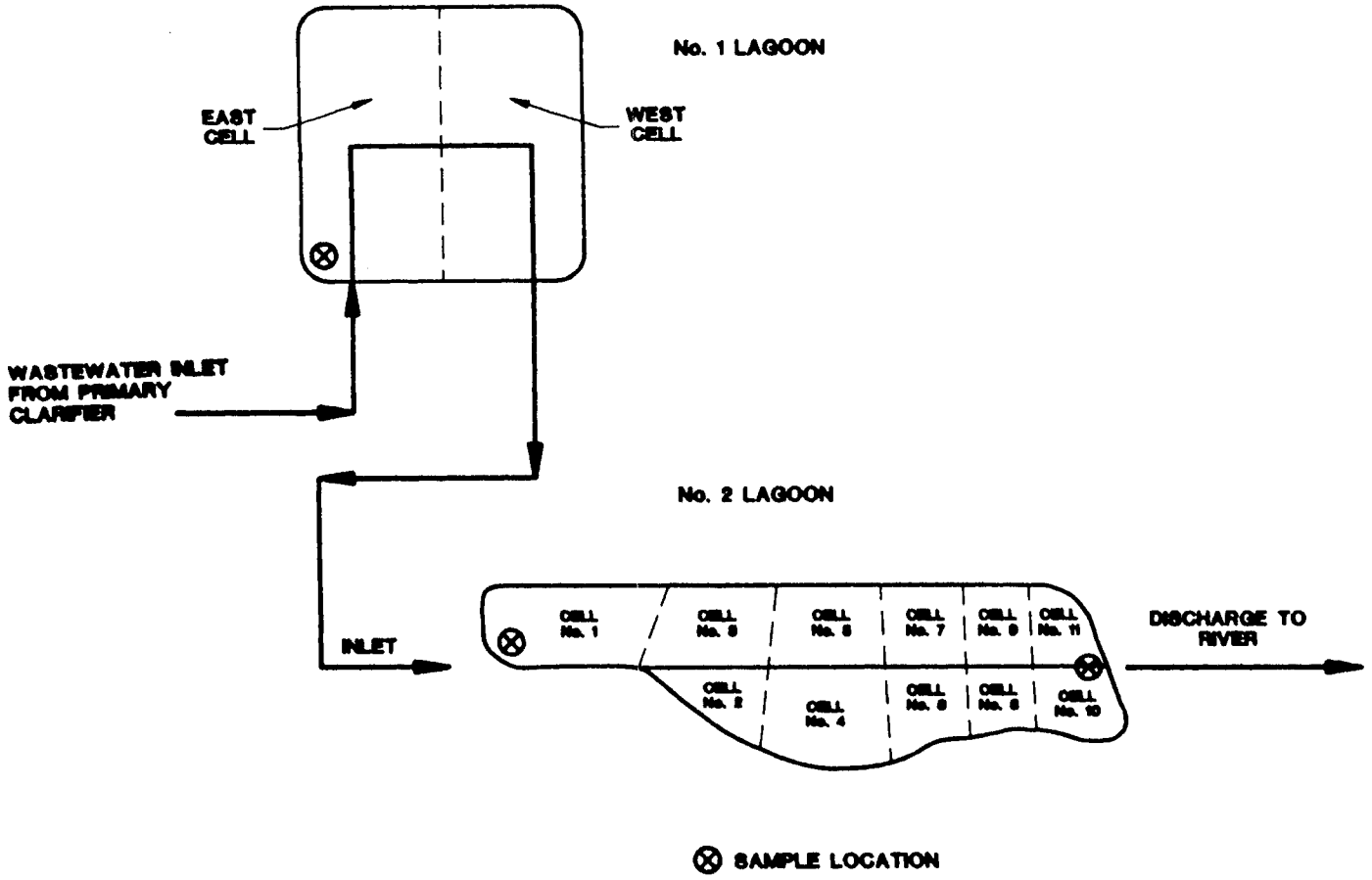


Figure 1. Schematic of Aerated Stabilization Basin at Mill #1

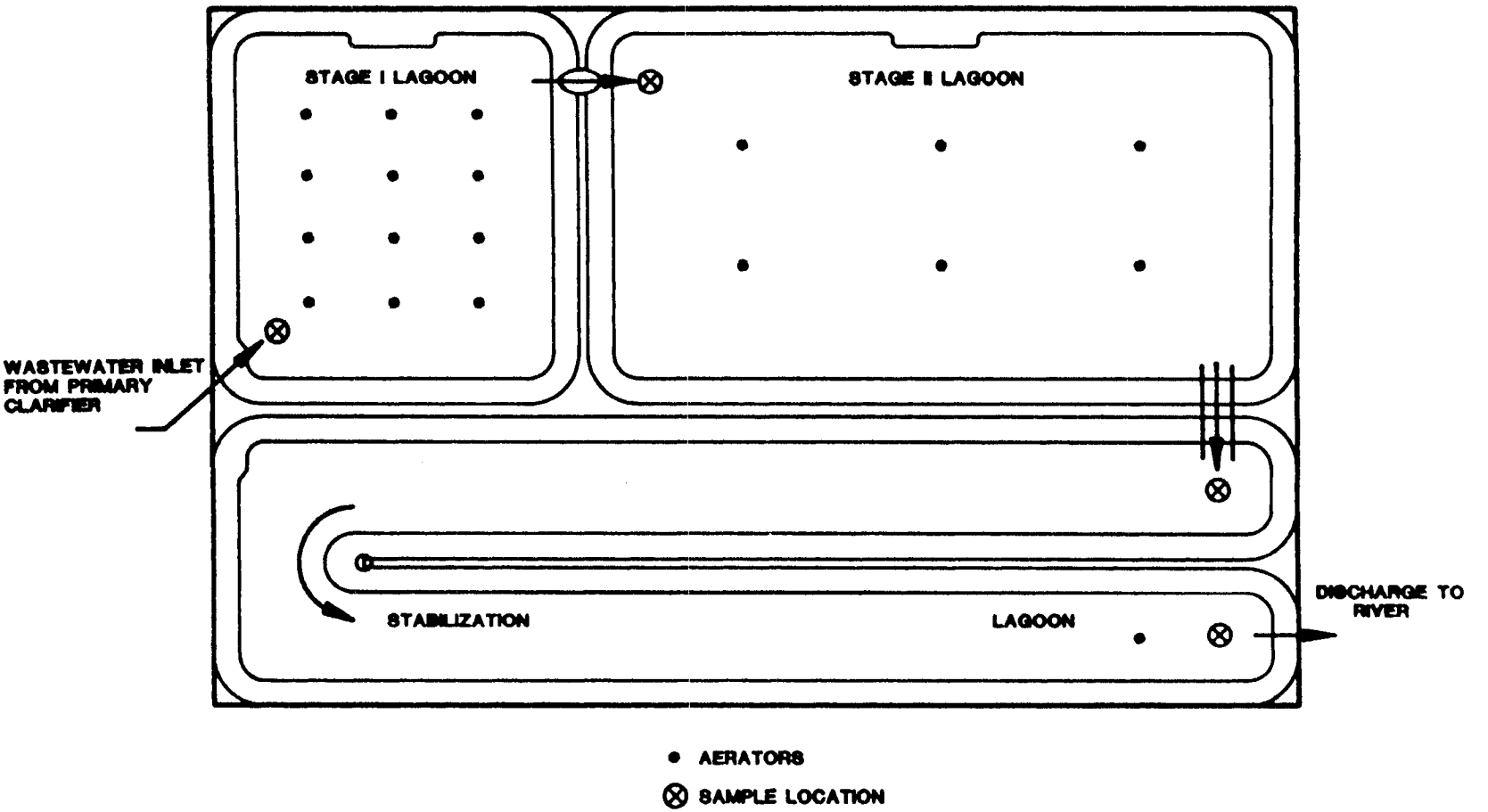


Figure 2. Schematic of Aerated Stabilization Basin at Mill #2

LITERATURE REVIEW

Most pulp and paper manufacturers employ either the Kraft (sulfate) process or the sulfite process to produce chemical pulp. Of the two processes, the Kraft pulping process is most widely used to remove the lignin, an aromatic polymer, from the wood. Removal of the lignin expedites cellulose fiber separation and enhances the papermaking properties of the fibers. Under the Kraft process, wood chips are treated at 160 - 180 °C with a liquor containing sodium hydroxide and sodium sulfite to cleave various ether bonds present in the lignin (1). This process results in greater than 90 percent removal of the lignin (1). In addition, wood polysaccharides and extractives are dissolved by the Kraft liquor.

To further remove the lignin as well as fractions of carbohydrates and extractives requires a multistage bleaching process. The bleaching process involves the application of chlorine in various forms separated by alkali treatment. For softwood Kraft pulps, a typical treatment scheme consists of chlorine (C_1), alkali (E_1), hypochlorite (H), chlorine dioxide (D_1), alkali (E_2), and chlorine dioxide (D_2) (1,2). The C_1 and E_1 stages constitute the prebleaching operation where approximately 70 - 75 percent of the total organic matter found in bleaching spent liquors is derived (1,3). Approximately 70 kg of material per metric ton of pulp will

dissolve from the pulp into the bleaching liquors with an estimated 50 kg of material originating from the residual lignin (1).

During the chlorination stages chlorine reacts primarily with residual lignin by degrading it into water or alkali-soluble chlorinated organic compounds (1,2). Application of alkali creates an environment in which the organically bound chlorine created during chlorination is easily extracted (1,3). It has been estimated that the total amount of organically bound chlorine formed is 4 - 5 kg per metric ton of pulp (1). The composition of the chlorinated organic compounds found in the spent liquors will vary depending on the type of wood used and the degree of treatment obtained (3,4).

An extremely complex organic composition in the spent liquors is a result of the variety of reactions occurring during the multistage bleaching process. Discharge of the combined spent liquors into the environment with little treatment has become an environmental issue for the paper industry. Effluent from bleaching mills have been shown to exhibit toxic or sublethal effects on the aquatic life in the receiving waters (3). For this reason, recent attention has focused on identifying the nature and content of the spent liquors especially the organically bound chlorine compounds.

Although in excess of 80 compounds have been identified, the majority of the compounds present in spent chlorination liquors remains unknown (5,6). Classes of compounds that have been identified include chlorinated acetic acids, keto acids, phenols, guaiacols and catechols (1,2,3,4). A group of ill-defined, high molecular weight compounds designated as chlorolignins are also present in paper mill wastewater (1,7). Many of these compounds have been found to exhibit varying degrees of toxicity, mutagenicity, bioaccumulation potential and environmental persistence (1,3,4,5,6).

Identification of individual compounds is costly and time consuming therefore researchers have concentrated on characterizing effluent streams based on a discrete size distribution. Researchers have used ultrafiltration membranes (Amicon YM series) to fractionate individual waste streams in the bleaching sequence (1,2,3,8,9). Ultrafiltration is the efficient, selective rejection of solutes by convective solvent flow through an anisotropic ("skinned") membrane (9).

Membranes with apparent molecular weight (AMW) cutoffs ranging from 500 to 30,000 have been used to fractionate paper mill wastewater (1,2,8,9). To assure complete passage of the desired fraction diafiltration or washing of the sample was generally carried out. After a specific volume of permeate has been collected reagent-grade water is added to the UF cell and the ultrafiltration process is continued (1,3,10). This

process is repeated several times to maximize the removal of any remaining smaller molecules. Other researchers have turned toward evaluating membrane rejection properties to accurately determine the mass of material in the AMW fraction (10).

Aerated stabilization basins are effective at removing conventional pollutants such as BOD and suspended solids and are moderately useful for reducing organic halide loads. Research has shown that approximately one-third to one-half of the total organic halide is removed by aerated lagoon systems (8). The purgeable organic halide (POX) fraction which includes chloroform is effectively removed from the lagoon via volatilization during aeration (7,11). Removal of the nonpurgeable fraction from the lagoon occurs in several steps which include adsorption of the organic halide onto biomass in the water column; deposition of biomass onto the benthal layer and anaerobic degradation and dehalogenation within the benthal layer (7,11,12).

Adsorption of organic compounds, such as pesticides, onto biomass has been an area of intensive research due to possible hazards associated with pollutant accumulation and possible introduction of the pollutant into the food chain (11,13). Research has also focused on biosorption as a possible cost-effective method for removing biorefractory organic pollutants in aquatic systems (12). Amy et al, have determined the

primary removal mechanism for chlorinated organic compounds in a Kraft mill stabilization basin as the adsorption of the organic halide onto settling biomass (8).

Many researchers have conducted adsorption studies with live and dead organisms to determine if the organic pollutant removal mechanism is due purely to physical adsorption and not to metabolic processes (8,12,14,15). Results from the experiments indicate sorption onto dead cells is equal to or greater than adsorption onto live cells (8,14). Methods of microbial inactivation either by physical or chemical means may alter cell permeability thereby enhancing chemical adsorption (8,14,15). Based on these results, it can be concluded that the observed removal of organic material is due to physical adsorption and not to active uptake or biodegradation.

However, this is not the case for all organic pollutants. Bell and Tsezos studied the adsorption of lindane, diazinon, malathion, pentachlorophenol and 2-chlorobiphenyl onto two inactive microbial communities (Rhizopus arrhizus and activated sludge) (12,15). Their results show adsorption to be the removal mechanism for all of the compounds except malathion. The removal of malathion from solution was assumed to be due to decomposition of the compound by a chemical reaction (12,15).

Researchers have established correlations between chemical parameters and adsorption. An inverse relationship between water solubility and bioaccumulation exists for a range of organic pollutants which include dieldrin, lindane, PCBs and pentachlorophenol (8,12,13). This correlation offers a rough estimate of adsorption by microorganisms whereas the octanol/water partition coefficient (K_{ow}) of the compound offers a positive correlation. Adsorption potential of the compound has been found to be directly proportional to K_{ow}. The octanol/water partition coefficient correctly predicts the order of adsorption for lindane, pentachlorophenol, diazinon and 2-chlorobiphenyl (10,15). Again, malathion deviates from this correlation.

Studies of adsorption kinetics have determined a rapid establishment of equilibrium conditions in the order of minutes to hours (8,14). A study where several bacterial species were exposed to chlordane isomers over a 4 hour period found equilibrium conditions were established within 15 minutes (13). In general, bacterial adsorption equilibrium is reported to occur within 30 minutes (12,13,14,15).

Researchers have established other physical and chemical parameters which influence adsorption of organic compounds onto microorganisms. These parameters include temperature, pH and cell lipid content. It has been shown that temperature has a low impact on adsorption (14). If the driving force for

adsorption is the hydrophobicity of the compound, pH will not play a large role in adsorption. One the other hand, large effects will occur if protonation of the molecule can occur within the test pH range (14).

The lipid content of the cell is an important factor in determining the partitioning of a hydrophobic compound between the aqueous phase and the solid (biomass) phase (8,14). Low molecular weight compounds can penetrate into the cell membrane and those hydrophobic compounds will further partition into the lipid bilayer (6,8). The octanol/water partitioning coefficient, K_{ow}, of a compound provides an indication of solubility in the lipid bilayer (8). Studies have found adsorption increases as the lipid content of the microorganisms increases (6,8,13).

A study found that virgin recycled activated sludge possessed a high adsorptive capacity for the organic halide present in Kraft mill wastewater (8). This study determined partition coefficients of 278 and 450 cm^3 of organic halide per gram of activated sludge for the untreated and treated mill wastewater, respectively. The higher loading of organic halide onto the biomass from the treated wastewater is due to an increase in low molecular weight compounds induced by microbial decomposition across the lagoon. Equilibrium conditions were obtained within 4 hours and lower pH enhanced

the adsorption. Cell viability was found to have little effect on adsorption.

Desorption of the compounds can be an environmental concern if the adsorbed chemicals leach from land-disposed treatment sludge. Lindane, diazinon and 2-chlorobiphenyl were found to completely desorbed from R. arrhizus and activated sludge into distilled/deionized water within 3 days (15). Malathion desorption was found to be temperature dependent. One-hundred percent desorption occurred at 5°C with no desorption occurring at 20°C (15). Desorption experiments with Kraft mill wastewater found approximately 5 to 10 percent of the original absorbed TOX was desorbed within 24 hours at 23°C (8).

Once microorganisms with adsorbed organic compounds have settled onto the benthic layer, degradation and dehalogenation of the compounds can occur. Research has found some organic halide compounds require aerobic conditions for dehalogenation whereas a majority of highly chlorinated compounds require anaerobic conditions (16,17). Dehalogenation of chlorinated benzenes appear to occur only under aerobic conditions whereas chlorinated pesticides and halogenated aliphatics are dehalogenated strictly under anaerobic conditions (18,19,20). Dehalogenation is also known to occur in soil and sewage where facultative conditions exist (20). Since aerobic, anaerobic and possibly facultative conditions exist in the benthic layer

across the stabilization basins dehalogenation of chlorinated organic compounds is likely to occur.

Anaerobic reductive dehalogenation has been identified as the predominant mechanism for degradation and dehalogenation of a majority of chlorinated organic compounds (18,19,20,21). Reductive dehalogenation requires an oxidation-reduction reaction to remove the halogen atom (20). Electrons are transferred from reduced organic substances via microorganisms or abiotic mediators including inorganic ions and biological products such as NAD, flavin and flavoproteins (20).

One study using nitrate, sulfate and carbon dioxide as electron acceptors found that persistence of halogenated aliphatic compounds decreased with an increase in reducing conditions in the environment (19). The study also identified a loss in reactivity of dehalogenation products as sequential halogens were removed (i.e. CCl_4 > $CHCl_3$ > CH_2Cl_2 > CH_3Cl). This loss in reactivity is attributed to increases in bond dissociation energies when the halogen is replaced with a hydrogen atom (19). Research with chlorinated benzoates found persistence to increase with the number of chlorines on the ring structure (21).

The degree of dehalogenation is generally greater in mixed cultures than in pure cultures (16,17). Transformation products from pure culture dehalogenation reactions can accumulate if the organism is not capable of producing the

enzymes required to further reduce the compound or if the product is more toxic to the organism than the original substrate (16). Accumulation of products is less likely to happen if the reactions are occurring in a mixed microbial community since the possibility exists that another organism is capable of producing the required enzyme to further degrade the compound.

Numerous chemical and biological conditions can affect degradation and dehalogenation reactions. Physical/chemical factors include pH, temperature, hydrophobicity, oxidation-reduction potential and presence of capable microorganism (16,22). Biological factors include compound toxicity, adaptation time and competing organisms (16,20). The degree of halogenation, location of the halogen, molecule size, and kind of halogen also affect degradation and dehalogenation (20).

Dehalogenation has been found to occur in the benthic layer of stabilization basins treating Kraft mill wastewater (7). The ratio of total organic halide to total organic carbon (TOX/TOC) indicates the degree of organic chlorination in the aqueous phase. The ratio also provides some insight into treatability of the organic halide via dehalogentation. A study compared TOX/TOC ratios for the water column to that of the interstitial water and found significantly lower ratios in the interstitial water. This comparison suggests

dehalogenation is occurring within the benthic layer. The researchers noted that dehalogenation was found to transpire in the upper 10 cm of the sediment layer with little dehalogenation occurring between 10 cm and 20 cm (7).

Several steps have been taken by the paper industry to reduce the toxicity, mutagenicity, color and organic load of bleachery effluent. These steps include extended delignification, oxygen delignification, modifications to the bleaching process by prebleaching Kraft pulps with oxygen and substitution of chlorine dioxide for chlorine during the first stage of bleaching (1,23). The application of biological treatment to the spent liquors prior to discharge has helped to alleviate the environmental impact on the receiving water (6).

EXPERIMENTAL METHODS

SAMPLE COLLECTION

Mill personnel at both Mill #1 and Mill #2 were responsible for collection of each sample set. A total of five (5) sample sets were collected from Mill #1 to represent seasonal conditions in the ASB with two sample sets depicting winter conditions. Since stock grades for the two different wood types (paper and dissolving) processed at Mill #1 vary, samples were collected approximately 5 to 7 days after the stock grades were changed. This delay allowed for the collection of samples representative of current in-mill processing conditions. With the exception of the second winter sample, stock grade did not vary between the samples.

To provide a profile across the entire ASB system, samples were collected from the ASB influent (Lagoon #1 influent), ASB effluent exiting from Lagoon #2 and an intermediate location (Lagoon #1 effluent/ Lagoon #2 influent). Sample locations are indicated in Figure 1. All bulk water samples were 24 hour composites. The first sample collection (Summer conditions) included bulk water grab samples which represent conditions of the ASB at a snap-shot of time.

Two samples sets were collected from Mill #2, one prior to in-mill bleaching modifications and the other collected

approximately one month following the modifications. Unlike Mill #1, the grade of feed material remains constant at Mill #2. Therefore a time delay before sample collection was not necessary to obtain samples which were representative of current processing conditions. Samples were collected from Stage 1 influent (1, WC), Stage 1 effluent/Stage 2 influent (2, WC), Stage 2 effluent/Stabilization Lagoon influent (3, WC) and the Stabilization Lagoon effluent (4, WC). Sample locations are indicated on Figure 2. Bulk water grab samples were collected at each sampling location and 24 hour composite samples were collected at the ASB influent and effluent.

Bulk water samples were collected in headspace-free, septa-sealed amber glass bottles. Samples for purgeable organic halide analysis were collected in headspace-free, septa-sealed 72 milliliter (ml) vials to minimize loss of any volatile chlorinated organic compounds. Sediment samples collected from the benthic regions of the ASB were placed in polyethylene sampling bags for Mill #1 and in core sampling containers for Mill #2. Immediately after sampling, the samples were stored in commercial blue ice and shipped to the University of Arizona Environmental Engineering laboratory. Upon arrival, the bulk water samples were filtered to isolate Dissolved Organic Matter (DOM). The large amount of time required to filter the bulk water through 0.45 um filters resulted in the selection of Whatman GF/C filters which have

a nominal pore size of 1.2 um. Each filter was pre-washed with 200 ml reagent-grade water and approximately 100 ml of the bulk water was processed through each filter. All samples were stored at 4° C until analysis.

ULTRAFILTRATION PROCEDURE

GF/C filtered bulk water samples were fractionated according to apparent molecular weight (AMW) by ultrafiltration (UF) into the fractions presented in Table 1. To assess analytical procedure the 500-1,000 fraction was replicated. UF was carried out using an Amicon stirred cell (200 ml capacity) and Amicon's YM series of hydrophilic membranes as shown in Table 1. The YM series membranes were selected due to nonspecific protein binding and resistance to common biochemical solvent properties (9).

Before initial use, each membrane was conditioned by soaking the membrane face down in distilled water for one hour, changing the water every fifteen minutes. This conditioning period is required to allow the membrane to become hydrated. Once hydrated, soaking of the membranes is not necessary as long as they remain saturated.

After conditioning, the UF membrane was placed membrane (shiny) side up in the stirred cell and a 70 ml volume of sample was added. The cell was placed on a magnetic stir plate where the stirring was adjusted so that the vortex remained approximately one-third the depth of retentate

Table 1. Apparent Molecular Weight Fractions and Corresponding Ultrafiltration Membranes Used for Separation.

Discrete AMW Fraction	Ultrafiltration Membrane
< 500	YC05
500-1,000	YC05 - YM2 (AMW 500)
1,000-5,000	YM2 - YM5 (AMW 1,000)
5,000-10,000	YM5 - YM10 (AMW 5,000)
10,000-30,000	YM10 - YM30 (AMW 10,000)
> 30,000	YM30 - Bulk* (AMW 30,000)

* Bulk value is determined from samples which are GF/C filtered only (1.2 um).

throughout the filtration process. Nitrogen gas was employed at 55 psig. to drive the filtrate through the membrane. The first 10 ml of filtrate was collected in a graduated cylinder and discarded because it was assumed distilled water trapped in the membrane and in the teflon tubing was removed in this aliquot. Next, approximately 40 ml of the filtrate was collected in acid washed amber bottles until the level of retentate was equal to that of the stirrer. The permeate was stored at 4° C until analysis for AOX and DOC could be accomplished.

After collection of the permeate, the pressure in the stirred cell was released to remove the retentate and to rinse the membrane. Before another sample could be processed, the membrane was flushed by passing approximately 30 ml of reagent grade water through the membrane. Each membrane was reused ten times. Between sample sets, the membranes were stored at 4° C in distilled water.

ULTRAFILTRATION MEMBRANE REJECTION COEFFICIENT DETERMINATION

Ultrafiltration membranes exhibit rejection properties that, if ignored, can result in an underestimation of the low molecular weight material. Factors that influence the transport of organic material through ultrafiltration membranes include pH, temperature, ionic strength, molecule size and shape and membrane pore size distribution (10). A model developed by Logan and Jiang was employed to evaluate

the rejection properties of the YM series membranes used for this study (10). The model, based on a permeation coefficient, is presented below:

$$C_p = p * C_{ro} * F^{p-1}$$

$$F = 1 - (V_f / V_o)$$

Where:

C_p = Instantaneous permeate concentration

p = Permeation coefficient

C_{ro} = Initial concentration of material with an AMW smaller than the nominal membrane molecular weight cut-off

V_f = Final volume of filtrate

V_o = Initial sample volume.

Linearizing the equation results in the following:

$$\ln C_p = \ln (p*C_{ro}) + (p-1) * \ln F$$

To utilize this model, ultrafiltration experiments with the selected YM membranes were performed as discussed above. Depending on the AMW cut-off of the membrane, three to five aliquots (5 ml) of filtrate were collected in individual sample vials. The aliquots were analyzed for either DOC or AOX, yielding values for C_p. A plot of ln (C_p) versus ln (F) yields a slope and y-intercept of (p-1) and ln ($p*C_{ro}$), respectively. These results can be used to calculate the concentration of material that would be obtained if this

analysis was not performed, i.e. if all permeate was collected. The average concentration of the sample after batch ultrafiltration can be determined by applying the following equation:

$$C_f = C_{ro} * ((1-F^p) / (1-F))$$

DISSOLVED ORGANIC CARBON ANALYSIS

Dissolved organic carbon (DOC) analysis was accomplished by using a Dohrmann DC-80 Total Organic Carbon analyzer. The analyzer was calibrated prior to every use with a 400 mg/L standard. Daily calibration of the instrument was necessary to insure accuracy in measurements.

Sample preparation required two steps; 1) pH adjustment below 2 with several drops of concentrated phosphoric acid and 2) nitrogen sparging for five minutes to strip out CO_2. Acidification to pH 2 increases the stripping efficiency of CO_2 and also prevents any significant increase in pH as CO_2 is removed thus allowing complete removal. The mid-level channel which provides accurate analysis of DOC ranging 10 to 800 mg/L was used for all samples. Two hundred microliters (ul) of prepared sample was injected into the analyzer and direct readouts in mg/L were recorded. All samples were analyzed in duplicate to insure accuracy in the measurements. A variance between injections of less than five percent was considered acceptable.

TOTAL ORGANIC HALIDE

Total Organic Halide (TOX) represents a nonspecific parameter for measuring the totality of chlorinated organic compounds present in the aqueous phase. TOX is calculated as the sum of purgeable organic halide (POX) and nonpurgeable organic halide (NPOX). Since the methodology for NPOX determination includes adsorption onto activated carbon the term adsorbable organic halide (AOX) becomes synonymous with NPOX.

Adsorbable Organic Halide (AOX) Analysis - Measurement of AOX was accomplished with a Dohrmann DX-20A analyzer. Sample preparation and evaluation for AOX followed the two step process described by EPA method 506. The first step involves the adsorption of chlorinated organic compounds onto Calgon Filtrasorb-400 granular activated carbon (GAC) 100/200 mesh. Dohrmann has selected this GAC for its halogenated compound adsorption capabilities as well as its initial absence of halogens. The second step for AOX determination involves the pyrolysis of the GAC to determine the content of adsorbed organic halide.

Adsorption of organic halide was accomplished using the adsorption module provide by Dohrmann. The module utilizes high purity carbon dioxide (99.995%) with the sample adsorption channels operated at 20 psi and the nitrate wash channel at 6 psi. The sample channels were washed prior to

sample adsorption with methanol followed by rinsing with distilled water. Flushing of the sample channels is necessary to avoid cross contamination between samples.

Glass mini-columns were packed with the GAC and plugged with cerafelt at both ends. The columns were packed in a consistent manner to insure small deviation in blank values and adsorption times. Prior to sample analysis, four columns were used to obtain a running average blank value that is utilized during the calculation of organic halide present in the sample. Once properly packed, two mini-columns with the appropriate o-rings were attached to a sample channel and then the prepared sample or blank was poured into the channel to begin the adsorption process.

Each sample including the blanks required preparation before adsorption could commence. Since paper mill wastewater is known to contain high concentrations of organic halide the samples were diluted with high purity water prior to processing. Dilution of the samples is necessary to ensure direct readouts ranging from 5.00 to 50.00 ug where the DX-20A is the most accurate. Dilutions for the AMW fractions with sample volumes of 50 ml are presented below:

AMW Fraction	Dilutions
Bulk	1:100
30,000	1:100
10,000	1:50
5,000	1:50
1,000	1:20
500	1:20

A 0.5 ml volume of 0.5 M sodium sulfite and 0.5 ml of concentrated nitric acid was added to the 50 ml diluted sample. The sodium sulfite was used to neutralize chloride ions left in solution and acidification enhances the adsorption. Preparation of the blank involved 50 ml of high purity water and the 5 ml of sodium sulfate and nitric acid. Prepared samples were poured into individual sample channels and then passed through the GAC columns. The columns were removed from the sample channel and placed on the nitrate channel to be washed with 5 ml of 5000 ppm NO_3^- to remove any inorganic chloride. Finally, the GAC columns were ready for pyrolysis in the analyzer module to determine the mass of organic halide adsorbed.

Prior to combustion of the GAC, several steps were taken to ensure the analyzer was stable and operating correctly. First, the titration cell with fresh electrolyte was attached and the analyzer baseline was allowed to stabilize. Then the analyzer was run through a ten minute cycle to remove any halide present on the standard boat and to verify stability. To determine system recovery, a 5 ul volume of a 1 ug/ul as chlorine standard was injected onto a piece of cerafelt in the standard boat and the system was run through a ten minute cycle. The standard was prepared by dissolving 15 milligrams of pentachlorophenol into 50 ml of methanol. Typical recoveries ranged from 95 to 99 percent. Lower recoveries

and/or a high baseline at the end of a ten minute cycle indicated a need for maintenance.

Before any samples were analyzed, individual blank GAC columns (top column followed by bottom column) were combusted in the analyzer on the ten minute cycle. This provided an additional check for proper operation of the analyzer during the pyrolysis of carbon and also provided a blank halide value for the GAC. Direct readout of the blank carbon value was recorded for all four columns. If no problems occurred the machine was ready for normal operation.

Individual sample columns were burned in order from top to bottom and each readout was recorded. Selected fractions were run in duplicate to ensure accuracy of the measurement. Duplicate analysis was considered acceptable if the coefficient of variance was less than 5 percent. AOX mass concentrations were calculated by employing the following equation:

$$AOX(mg/L)=(((T + B) - BL) * DF) / SV$$

Where

AOX = Adsorbable organic halide in milligrams per liter

T = Top column recorded value in micrograms

B = Bottom column recorded value in micrograms

BL = Running average blank value in micrograms

DF = Dilution factor

SV = Sample volume passed through GAC column in milliliters.

An organic halide loading of less than 10 percent on the bottom column is a recommended check for complete capture of AOX. If the AOX loading on the bottom column exceeds 10 percent it is probable that breakthrough occurred and some of the organic halide was not captured. Breakthrough occurred frequently in the 1,000 fraction and occasionally in the 500 fraction. The remaining AMW fractions did not demonstrate breakthrough.

Previous investigation into the problem determined a large percentage of the lower molecular weight compounds were less sorbable and the kinetics of adsorption for these compounds were slower than the contact time provided by the adsorption module (9). For this reason, greater than 10 percent of the organic halide present in the low molecular weight fraction passed through the top column and was adsorbed onto the bottom column. To determine if any AOX passed through the second column a 500 AMW paper mill wastewater fraction was passed through three GAC columns in series. An average of four sample runs indicated an additional 3.5 percent of total AOX was captured on the third column. This study concluded that the breakthrough problem was insignificant and therefore recommended continuation of the two column procedure.

Purgeable Organic Halide (POX) Analysis - POX is that fraction of TOX which is volatile and capable of being removed from the aqueous phase through volatilization pathways such as aeration. Analysis for POX can be accomplished by injecting 10 ml of the sample into the DX-20A sparger unit. However, when a sample of paper mill wastewater was injected foam began to form due to the presence of surfactants in the wastewater. This foaming phenomenon caused the sample to overflow the sparger unit and enter into the pyrolysis section and inlet tube of the analyzer. When this occurred the machine malfunctioned and it became necessary to replace the inlet tube and teflon tubing connecting the sparger unit to the pyrolysis tube. Other studies have also encountered this foaming problem with paper mill wastewater (9).

It is known that chloroform is the major component of the purgeable fraction of organic halide in pulp and paper mill wastewater (9). In an effort to eliminate POX analysis on the DX-20A, chloroform was analyzed on the Hewlett Packard 5790A series Electron Capture Detector (ECD) gas chromatograph (GC). Extraction of chloroform from the aqueous phase followed the EPA method for trihalomethane extraction and analysis.

The method calls for a pentane based liquid-liquid extraction in which 5 ml of pentane is injected into a head-space free 72 ml serum vial via the two syringe technique. The mixture is then shaken for two minutes to allow

partitioning of chloroform into the pentane. After the extraction, 1 ul of the pentane containing chloroform is injected into the GC which is operated on a two stage temperature control program. Results of the chromatograph are recorded on the Hewlett Packard 3390A integrator. Injections were duplicated to ensure accurate analysis of the sample.

The concentration of chloroform present in the sample was determined by using a calibration curve that was generated by analyzing known concentrations of chloroform present in pentane and plotting concentration versus area count. Results from GC analyses on the ASB influent for Mill #1 indicate 1836 ug/L of chloroform was present. This value is only 2.5 percent higher than the 1790 ug/L determined for POX on the DX-20A analyzer. Since error on POX is $\pm$ 5 percent, these results indicate chloroform analysis via the GC method is a good surrogate parameter for the POX fraction. Therefore, it was decided to discontinue use of the DX-20A sparger unit and to use the GC method for determination of POX for the remaining samples.

EXTRACTABLE ORGANIC HALIDE (EOX) PROCEDURE

EOX represents a non-specific parameter for measuring the totality of chlorinated organic compounds present in the solid phase. Partial removal of organic halide from the water column in the stabilization basins is presumed to transpire through adsorption onto settling solids and biomass. Once in

the benthic layer, biological dehalogenation occurs thus adding to the removal of organic halide.

Analysis of the EOX fraction is accomplished via a three step process. First, the benthic samples were centrifuged to separate the solid phase from the interstitial water. The Beckman J2-21 centrifuge when operated at 19,000(g) for 15 minutes provided adequate separation. The interstitial water was decanted, filtered through a GF/C filter and then analyzed for DOC and AOX. A 1000 AMW fraction of the interstitial water was included in the analysis.

Extraction of organic halide from the solid phase is the second step in the procedure. Samples were prepared according to the method outlined in the DX-20A manual except where described below. A 1 gram aliquot of the solid sample, 1 ml of reagent grade water and 5 ml of ethyl acetate were added to a glass vial. Ethyl acetate is the recommended extraction solvent due to its high chloride rejection properties. Octanol was also selected as an extraction solvent due its non-polar characteristic.

Sediment samples taken from Mill #1 during the Summer and Fall were prepared with both ethyl acetate and octanol. Two separate extraction procedures were employed for both solvents. The first procedure required vigorous shaking of the prepared samples for 5 minutes to remove the organic halide adsorbed onto the cell surface thus assuming the

biomass remains "intact". The second procedure was an attempt to disrupt or burst the cells by shaking vigorously the prepared samples for 5 minutes followed by sonication for 15 minutes in a bath sonicator. Bursting the cells is based on the premise that some sorbed organic halide may be intracellular material as opposed to adsorbed onto the cell surface. It was later determined that the sonicator was not powerful enough to burst the cells.

Winter and Spring sediment samples collected from Mill #1 were prepared with ethyl acetate. Again, two extraction procedures were employed. Extraction with the "intact" cells was carried out as described above except the extraction period was extended to 24 hours. To inactivate the cells in manner other than sonication, 0.6 ml of dimethyl sulfoxide (DMSO) was added to the sample and then shaken for 24 hours. A two speed shaker table was utilized for the 24 hour extraction period.

The volume of DMSO was selected by preparing four samples as described above and then adding 0.2, 0.4 and 0.6 ml of DMSO to three of the four samples. After 5 minutes of vigorous shaking, the cells were viewed under an Olympus BH2 microscope to evaluate the impact DMSO had on the cells as compared to those without DMSO. For the 0.2 and 0.4 aliquots there was no noticeable change in the behavior of the cells. However, cells from the 0.6 ml aliquot appeared to be inactivated.

From these results, 0.6 ml of DMSO was considered adequate for inactivating the cells.

Sediment samples collected from Mill #2 were prepared with ethyl acetate and octanol. Extraction with both solvents was carried out with the 24 hour extraction period. Disruption of the cells was not attempted for these samples.

At the end of the extraction period the solvent containing organic halide was decanted into glass vials and stored at 4° C. Analysis of the decanted solution is the final step in the three stage EOX procedure.

EOX analysis was performed on the Dohrmann DX-20A analyzer. Minor hardware modification, as described in the DX-20A manual, were required to switch the analyzer from operating in TOX to EOX mode. The principle of operation for analysis of EOX entails the injection of an aliquot of sample directly into the pyrolysis chamber via a 50 ul syringe with a six inch needle. The recommended injection rate of 0.5 ul/sec was accomplished by using an automatic dispensing adaptor attached to the syringe. Samples were run on the ten minute cycle with direct readout of the mass of chlorine in nanograms.

Before sample analysis could commence, several steps were taken to ensure the analyzer was stable and operating correctly. To determine system recovery, a 5 ul volume of a 1 ug/ul as chlorine standard was injected and analyzed. The

standard was prepared by adding 0.317 grams of chlorobenzene to 100 ml of either ethyl acetate or octanol. System recoveries greater than 95 percent and a low baseline at the end of the run indicated correct operation of the instrument. System blanks for both ethyl acetate and octanol were determined by injecting 42 ul of the chlorine free solvent into the analyzer. Blank values with a direct readout of less than 100 ng were considered acceptable.

A sample volume of 42 ul was injected into the pyrolysis chamber at a rate of 0.5 ul/sec and analyzed on the ten minute cycle. EOX samples extracted with ethyl acetate were run first followed by blank octanol injections and then those samples extracted with octanol. Each sample was run in duplicate to ensure accuracy of the measurement. Variances between duplicate injections of 5 percent were acceptable.

Solid samples used in the extraction contained interstitial water not removed during centrifuging therefore the mass of organic halide detected included that present in the water. EOX concentrations were calculated as follows:

$$\text{Total EOX as } Cl^- \text{ (ng)} = (Q_s / V_i) * V_e * 1000$$

$$\text{Interstitial Water (I.W.) AOX as } Cl^- \text{ (ng)} = V_w * IW * 1000$$

$$\text{Sediment EOX (ug/g)} = (\text{Total EOX} - \text{I.W. TOX}) / M_s$$

Where

Q_s = Direct analyzer readout (ng)

V_i = Sample volume injected (ul)

V_e = Volume of extract (ml)

V_w = Volume of water present in the sediment (ml)

IW = Interstitial water AOX concentration (mg/L)

M_s = Mass of sediment present in the sample (grams).

To determine the actual mass of sediment present in the sample, approximately 5 grams of the sediment was measured into a tin weighing dish and then placed in a 120 °C oven for 24 hours to drive off the water. Difference between the initial and final weight represented the amount of water present and the final weight represented the mass of sediment present. It was assumed that the interstitial water had a density of 1.0 g/ml.

RESULTS AND DISCUSSION

Samples were collected from both mills and analyzed under the standard protocol discussed previously. Results were recorded and interpretated according to the research objectives restated below:

- Develop AOX profiles across the treatment system, an aerated stabilization basin (ASB);
- Define the partitioning of AOX between the water column and the sediment layer in the ASB;
- Define seasonal variations;
- Develop a relationship between in-mill processing conditions and effluent characteristics;
- Ascertain apparent dehalogenation in the sediment layer of the ASB and
- Evaluate AOX formation and removal under two bleaching processes.

Raw data for the samples collected from Mill #1 and Mill #2 are presented in the appendix. Ultrafiltration of the 1K fraction was replicated to confirm the consistency in the ultrafiltration technique. The coefficient of variance (CV) (standard deviation divided by the mean) between the replicate 1K samples were constantly below ten percent based on AOX and DOC analysis. Two samples were collected from each sample location for chloroform analysis to confirm the consistency in

the extraction technique. The CVs were generally lower than ten percent with exception of two samples where the CV exceed 25 percent.

To verify accuracy and consistency in the analytical procedures, selected samples were analyzed in duplicate for AOX, and duplicate injections were run for every DOC and EOX. The coefficient of variance for AOX, DOC and EOX samples were typically lower than ten, five and three percent, respectively. The CVs of duplicate injections for chloroform analysis were consistently lower than three percent. When a CV was greater than norm the analysis was repeated. The low CV values ensure the accuracy of the data by confirming laboratory and analytical procedures.

Bulk water samples collected from Mill #1 for the Summer sample set consisted of 24 hour composite and grab samples. DOC and AOX analysis was conducted on the samples to evaluate the differences between the two sampling techniques. Based on DOC, there appears to be little difference (CV < 10%) between the two sampling techniques. However, CVs of 35 and 27 percent for the L2 Influent and L2 Effluent samples, respectively, indicate a large deviation between the grab and composite samples. This large deviation resulted in the use of 24 hour composite samples across the ASB for the remaining sample sets from Mill #1.

Influent and effluent 24 hour composite and grab samples

were also collected for both samples taken from Mill #2. The coefficient of variance between the composite and grab samples for both sample sets was less than ten percent based on AOX and DOC. The low CV values justified the use of grab samples across the ASB for ultrafiltration and subsequent analyses.

BULK WATER PARAMETERS

Mill #1 - As stated previously, 24 hour composite samples were collected approximately 5 to 7 days after the stock feed material was changed. This allowed conditions in the lagoon system to stabilize prior to sample collection. Table 2 presents the production data for the samples collected from Mill #1. The production data includes in-mill processing conditions as well as ASB conditions.

A summary of bulk water parameters throughout the ASB for Mill #1 appears in Table 3. Overall adsorbable organic halide (AOX) removal ranged from 11 to 50 percent with the greatest removal occurring under Winter conditions. Influent AOX concentrations varied from 24.4 to 39.6 mg/L whereas effluent concentrations fluctuated around 20.0 mg/L. Figure 3 illustrates the AOX profiles across the stabilization basin.

Overall dissolved organic carbon (DOC) removal across the ASB ranged from 21 to 49 percent. As with AOX, the greatest DOC removal occurred under Winter conditions. Under Fall conditions, DOC concentrations throughout the basins are

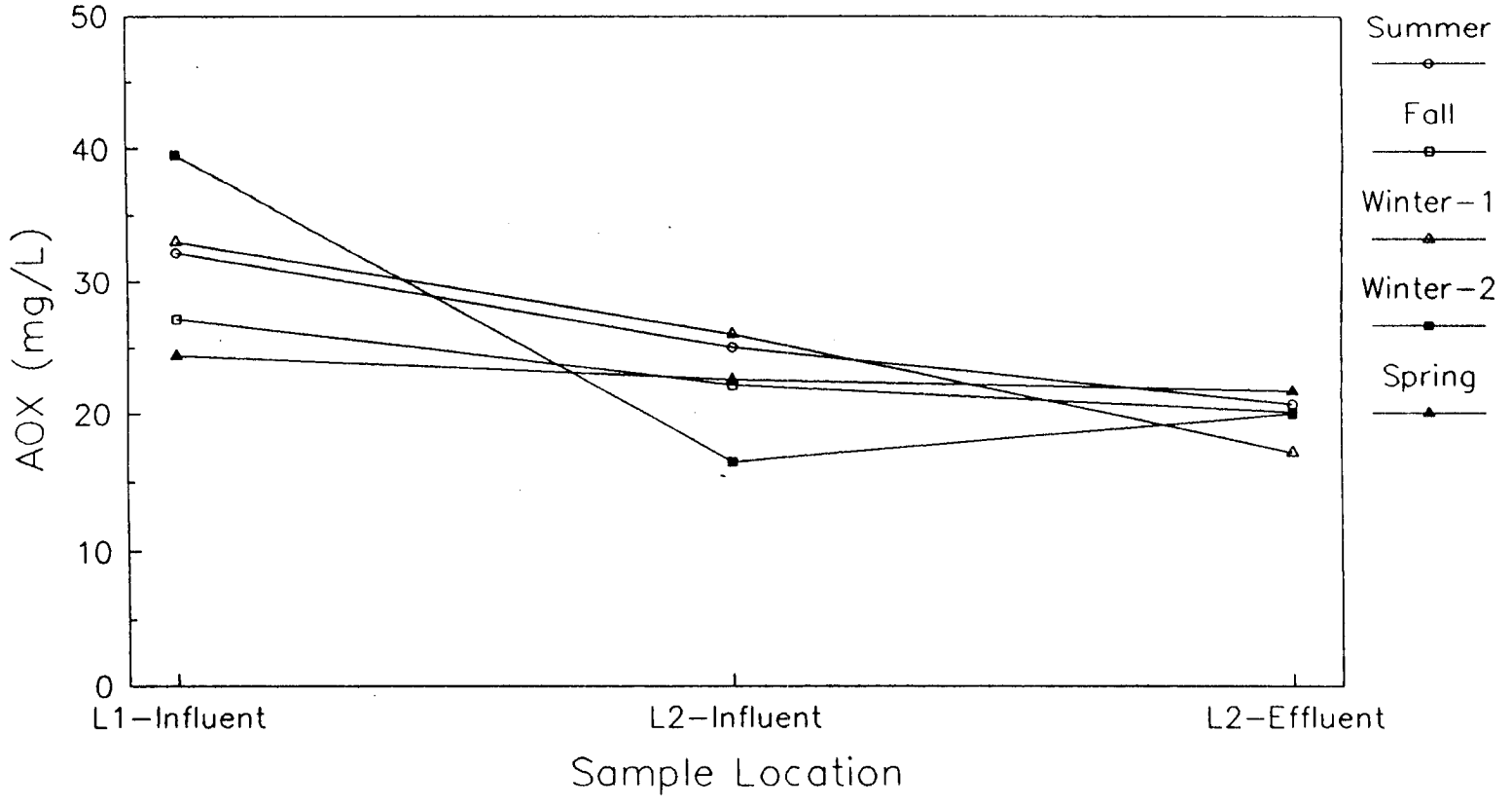


Figure 3. Bulk Water AOX Profile for Mill #1

Table 2. Mill #1 Production Data

PARAMETER	8/21/89	10/27/89	1/16/90	1/30/90	3/22/90
BOD-5 (ppm)					
#1 lagoon	209	247	214	198	193
#2 lagoon	51	84	80	55	47
#2 outlet	32	20	16	24	18
pH					
#1 lagoon	3.6	9.1	6.5	6.0	6.2
#2 lagoon	6.7	7.1	7.0	6.8	6.8
Outfall	7.4	7.1	7.4	7.2	7.0
DO (mg/L)					
#1 East cell inlet	3.9	4.7	3.8	4.2	0.3
#1 East cell outlet	1.0	0.2	0.3	0.2	0.2
#2 Inlet	0.4	0.1	0.4	0.7	0.8
Outfall port	1.3	1.9	2.9	2.7	1.7
Outfall pipe	7.1	8.0	9.1	8.4	7.1
TEMPERATURE (F)					
#1 East cell inlet	106	106	108	106	105
#1 East cell outlet	100	97	95	93	96
#2 Inlet	95	89	86	88	84
Outfall port	90	77	70	73	76
STOCK TYPE					
Mill 1[1]	V-5	V-5	V-5	V-60	V-5
Mill 2[2]	P-1	P-1	P-1	P-1	P-1
STOCK FEED (tons/day)					
Mill 1	499	420	546	309	544
Mill 2	773	763	609	731	765
FLOWRATE (MGD)					
Freshwater	51.9	51.2	49.3	48.4	47.7
Outfall	59.6	48.7	55.3	55.3	52.0

NOTE:
1. Processes dissolving grade feed stock.
2. Processes paper grade feed stock.

Table 3. Mill #1 Bulk Water Parameters

Sample	AOX (mg/L)	DOC (mg/L)	POX (ug/L)	$CHCl_3$ (ug/L)
Summer Sampling				
L1 Influent	32.2	238	1,760	1,840
L2 Influent	25.0	174	60	47
L2 Effluent	20.8	157	58	163
Fall Sampling				
L1 Influent	27.8 (29.4*)	487	n/a	1,750
L2 Influent	22.2	335	n/a	37
L2 Effluent	20.2	330	n/a	26
Winter #1 Sampling				
L1 Influent	33.0 (36.2*)	254 (254*)	n/a	799
L2 Influent	26.0	150	n/a	29
L2 Effluent	17.2	160	n/a	211
Winter #2 Sampling				
L1 Influent	39.6 (37.8*)	275 (309*)	n/a	n/a
L2 Influent	16.5	154	n/a	n/a
L2 Effluent	20.0	140	n/a	n/a
Acid Stream	53.08 (53.64*)	209 (222*)	n/a	n/a
Caustic Stream	27.12 (26.18*)	393 (418*)	n/a	n/a
Spring Sampling				
L1 Influent	24.44	199	n/a	1,596
L2 Influent	22.64	174	n/a	24
L2 Effluent	21.74	157	n/a	20

* Unfiltered Sample

n/a - Not analyzed

approximately twice as high as those representing the other seasons. A review of the production data and discussions with plant personnel did not reveal the cause of the large DOC concentrations. DOC profiles across the basins are illustrated in Figure 4.

Inferences can be made about variations in DOC and AOX between sampling locations while disregarding seasonal influences. DOC and AOX values for all samples were subjected to a statistical analysis by the nonparametric Mann-Whitney rank sum test. Like a t-test, this test provides an indication of whether differences in parameter levels are statistically significant. The analysis was performed on the bulk water AOX and DOC data using a 95 percent confidence level. Results indicate the decrease in AOX from the influent (L1 Influent) to the ASB midpoint (L2 Influent) is not statistically significant. The same is true for decreases in AOX from the midpoint to the ASB effluent (L2 Effluent). Analysis performed on DOC resulted in the same conclusions. The decrease in AOX from the ASB influent to the effluent is statistically significant whereas the decreases in DOC is not statistically significant. These inferences indicate AOX changes across the ASB are significant at the 95 percent confidence interval only when comparisons are made between the influent and effluent but not at the midpoint. Fluctuations in DOC are not significant across the entire ASB at the 95

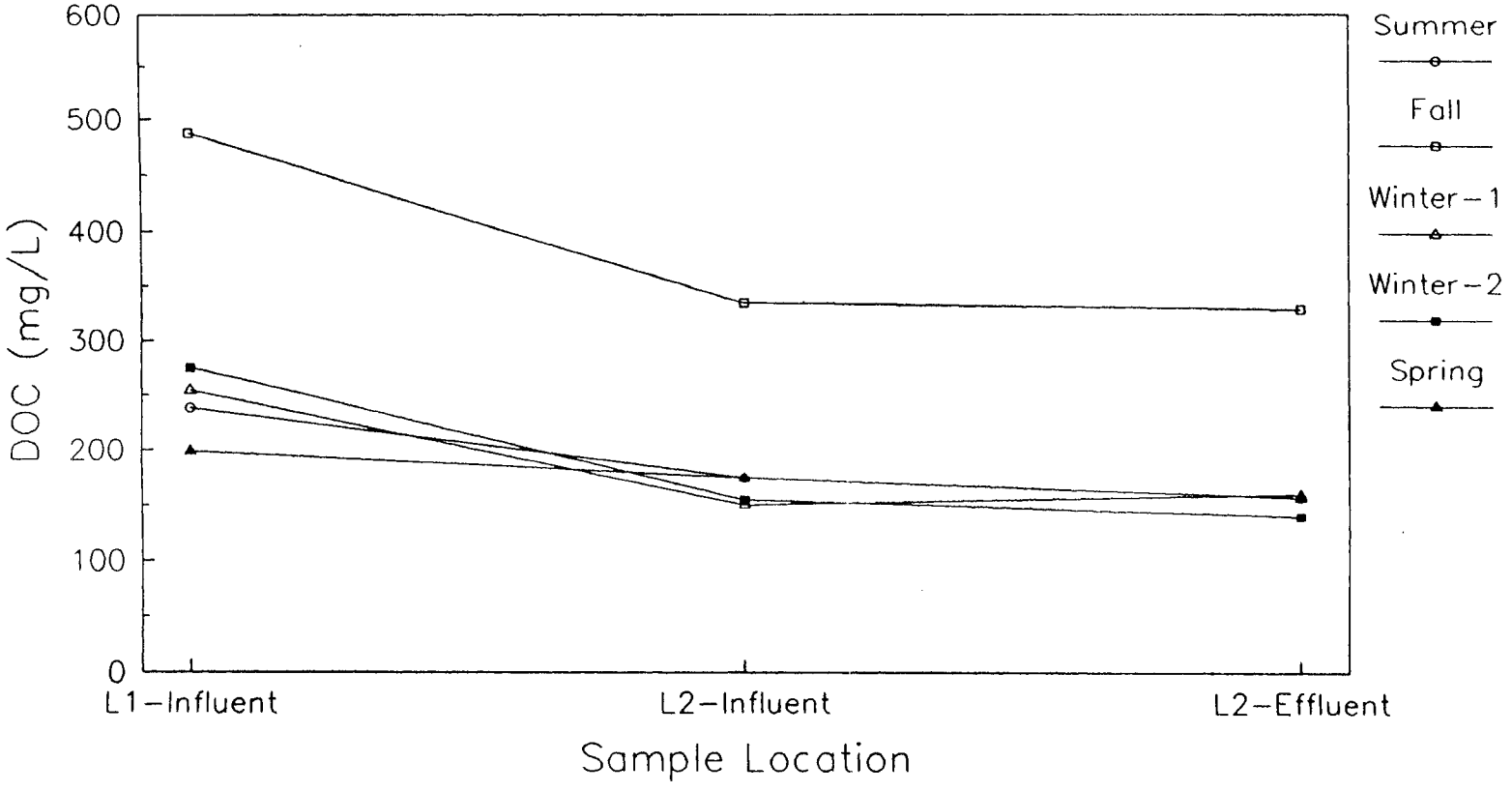


Figure 4. Bulk Water DOC Profile for Mill #1

percent confidence interval.

Samples were collected from the individual acid and caustic spent liquor streams during the Winter period. As shown on Table 3, the acid stream consisted of approximately two times more AOX (53.08 mg/L) than the caustic stream (27.12 mg/L). On the other hand, the spent caustic liquor DOC concentration was twice that of acid stream. Chlorinated organics and unreacted chlorine from the C_1 stage constitute a majority of the AOX found in the spent acid liquor. AOX and DOC present in the spent alkali liquor are a result of the extraction of alkali soluble chlorinated organic compounds formed during the previous acid or chlorination stage.

For softwood Kraft pulps the chlorine charge for the C_1 stage is estimated to be 60 - 70 kg/metric ton of pulp depending upon the residual lignin content (1,23). The chlorine demand of the pulp is determined indirectly via oxidation with potassium permanganate to give a kappa number (23). The lower the kappa number, the lower the chlorine demand of the pulp and hence the chlorine charge.

As stated previously, the purgeable organic halide (POX) fraction can be modelled by chloroform analysis. Results indicate almost all of the chloroform and hence the POX from Mill #1 is removed in the first lagoon by aeration. Influent chloroform concentrations averaged approximately 1,800 ug/L except for the Winter sample where the concentration was 799

ug/L. The Winter chloroform samples were stored for more than one month at 4°C prior to analysis. Consequently, portions of the volatile fraction may have escaped resulting in concentrations lower than expected.

Mill #2 - Two sample sets were collected from Mill #2, a modern mill using a modified bleaching sequence. Sample-1 was collected while the first bleaching stage was operating with 70 percent chlorine dioxide and 30 percent chlorine. Approximately one month after modification of the first bleaching stage to 100 percent chlorine dioxide, the second sample set was collected. The intent of the first stage modifications was to reduce AOX production. Table 4 presents the production data at the time the two samples were collected. The data represents in-mill production conditions as well as ASB conditions.

A summary of bulk water parameters throughout the ASB for Mill #2 appears in Table 5. Overall AOX removals were 18 and 43 percent for Sample-1 and Sample-2, respectively. AOX entering the ASB for Sample-2 was approximately 40 percent lower than the AOX in Sample-1. This gives a preliminary indication that modifications to the first bleaching stage by eliminating chlorine was successful at the reducing AOX charge. However, additional data are required to confirm this conclusion. For both samples, the greatest removal occurred across the Stage 1 lagoon (Figure 2), beyond this stage AOX

Table 4. Mill #2 Production Data

Parameter	Sample-1 6-21-90	Sample-2 9-24-90
BOD_5 (mg/L)		
Influent	311	342
1-2	141	109
2-3	27	83
Effluent	26.3	70.1
pH		
Influent	7.48	7.96
1-2	7.38	7.69
2-3	7.48	7.49
Effluent	7.50	7.58
Temperature (F)		
Influent	-	-
1-2	102	96
2-3	96	86
Effluent	84	82
Color (PCU)		
Influent	1900	1650
Effluent	2100	1750
TSS		
Influent	251	251
Effluent	38.0	33.0
Flowrate (MGD)		
Influent	11.04	9.81
Effluent	5.78	5.62
Stock Type	Paper grade	Paper grade
Stock Feed (tons/day)	850	1000

Table 5. Mill # 2 Bulk Water Parameters

Sample	AOX (mg/L)	DOC (mg/L)	$CHCl_3$ (ug/L)
Sample-1			
1, WC	14.66	251	595
2, WC	11.94	210	-
3, WC	12.07	223	ND
4, WC	11.96	217	ND
Wet Well	16.68	427	-
Acid Sewer	92.25	507	-
Sample-2			
1, WC	8.82	473	76
2, WC	5.85	256	-
3, WC	5.02	283	ND
4, WC	5.64	225	ND

ND - Not Detected

concentrations remained relatively constant.

A 14 and 52 percent reduction in DOC was observed for Sample-1 and Sample-2, respectively. The influent DOC concentration for Sample-2 was approximately twice that of Sample-1. This increase in DOC may be due to in-mill changes that altered the characteristics of the wastewater being discharged into the lagoon system at the time of sampling. Similar effluent DOC concentrations of 218 and 225 mg/L were detected for Sample-1 and Sample-2, respectively. As with AOX, a majority of the DOC removal transpired in the Stage 1 lagoon with little removal occurring beyond this stage. Again, additional data are required to evaluate the impact the modifications had on DOC.

Samples were collected from the acid sewer and the wet well prior to modifications at Mill #2. The acid sewer consists of the spent acid liquors and the wet well consists of several waste streams including the spent alkali liquors. As shown on Table 5, the acid sewer consisted of approximately six times more AOX than the wet well. Chlorinated organic compounds and unreacted chlorine from the first bleaching stage constitute a majority of the AOX found in the acid sewer. Unlike Mill #1, DOC concentrations were similar for both sample locations.

As with Mill #1, the volatile fraction of organic halide was modelled by chloroform analysis. The results indicate all

of the chloroform is removed by aeration in the Stage 1 lagoon. Chloroform levels were not detected beyond Stage 1 for both samples.

The data indicates approximately eight times more chloroform is created when chlorine is employed during the bleaching process. Some general conclusions can be drawn from studies conducted by municipal water treatment facilities employing chlorine as a disinfectant. A direct correlation has been established between the application of chlorine for disinfection and the generation of chloroform (24). Since trihalomethanes (THMs) which include chloroform are regulated under the Safe Drinking Water Act, many water treatment facilities are turning to other disinfectants to reduce the amount of THMs generated. Chlorine dioxide has been found to be an effective disinfectant without producing halogenated by-products such as THMs. The reduction in halogenated by-products is similar to the results found at Mill #2 where the amount of chlorinated organic compounds including chloroform was reduced after stage 1 was modified to 100 percent chlorine dioxide. Again, additional data are required to accurately assess the impact the modifications had on chloroform formation.

MOLECULAR WEIGHT DISTRIBUTIONS

An apparent molecular weight (AMW) characterization of a

wastewater sample provides a "fingerprint" that can be useful in assessing the performance of a treatment process. A fingerprint based on either AOX or DOC can be derived from molecular weight fractionation of water column samples via ultrafiltration. These fingerprints can be used 1) to define the potential applicability of a treatment process to remove AOX and DOC 2) to monitor the efficiency of a process in removing different AMW fractions of AOX and DOC and/or 3) to monitor potential biological treatment performance. Changes in AMW fractions across a lagoon system treating Kraft mill wastewater can be attributed to either microbial activity such as molecule cleavage or physical/chemical sorption (8).

Discussed below are molecular weight fingerprints for the samples collected from Mill #1 followed by Mill #2. These fingerprints were used to evaluate the ASBs ability to remove specific molecular weight fractions or convert material (AOX or DOC) from one molecular weight fraction to another. Also, the overall ability of the ASB to remove AOX and DOC was evaluated. Of particular interest is the AMW fraction less than 1,000. Many compounds identified within this fraction such as chlorophenols are reported to bioaccumulate and contribute to the toxicity and mutagenicity of spent bleaching liquors (1,3,4,8).

As with the bulk water, the fraction with an AMW < 1K from Mill #1 was subjected to the Mann-Whitney rank sum test.

Results from the statistical analysis indicate AOX fluctuations between the influent and the mid-point as well as the influent and the effluent are statistically significant at the 95 percent confidence interval. AOX fluctuations between the mid-point and the effluent were determined to not be statistically significant. This trend holds true for changes in DOC across the ASB at the 95 percent confidence level. Unlike the bulk water, fluctuations in AOX and DOC between the influent and the mid-point are meaningful in evaluating the removal of this fraction.

Summer Sampling Period - A molecular weight fingerprint based on AOX from the Summer samples is illustrated in Figure 5. All of the AMW fractions show a decrease in material through the ASB system except for the fraction greater than 30,000 AMW and the fraction between 5,000 and 10,000 AMW. Bulk water AOX for the Summer samples was reduced from 32.2 to 20.7 mg/L indicating a removal of approximately 36 percent. The greatest reduction of material occurred in the 500 to 1,000 fraction and the fraction less than 500 AMW where approximately 69 and 81 percent, respectively, of AOX was removed.

Of the chlorinated organic compounds entering the ASB approximately 45 percent of the AOX has an AMW less than 1,000. After treatment, the < 1K fraction was reduced to 18 percent of the total AOX. As stated previously, several of

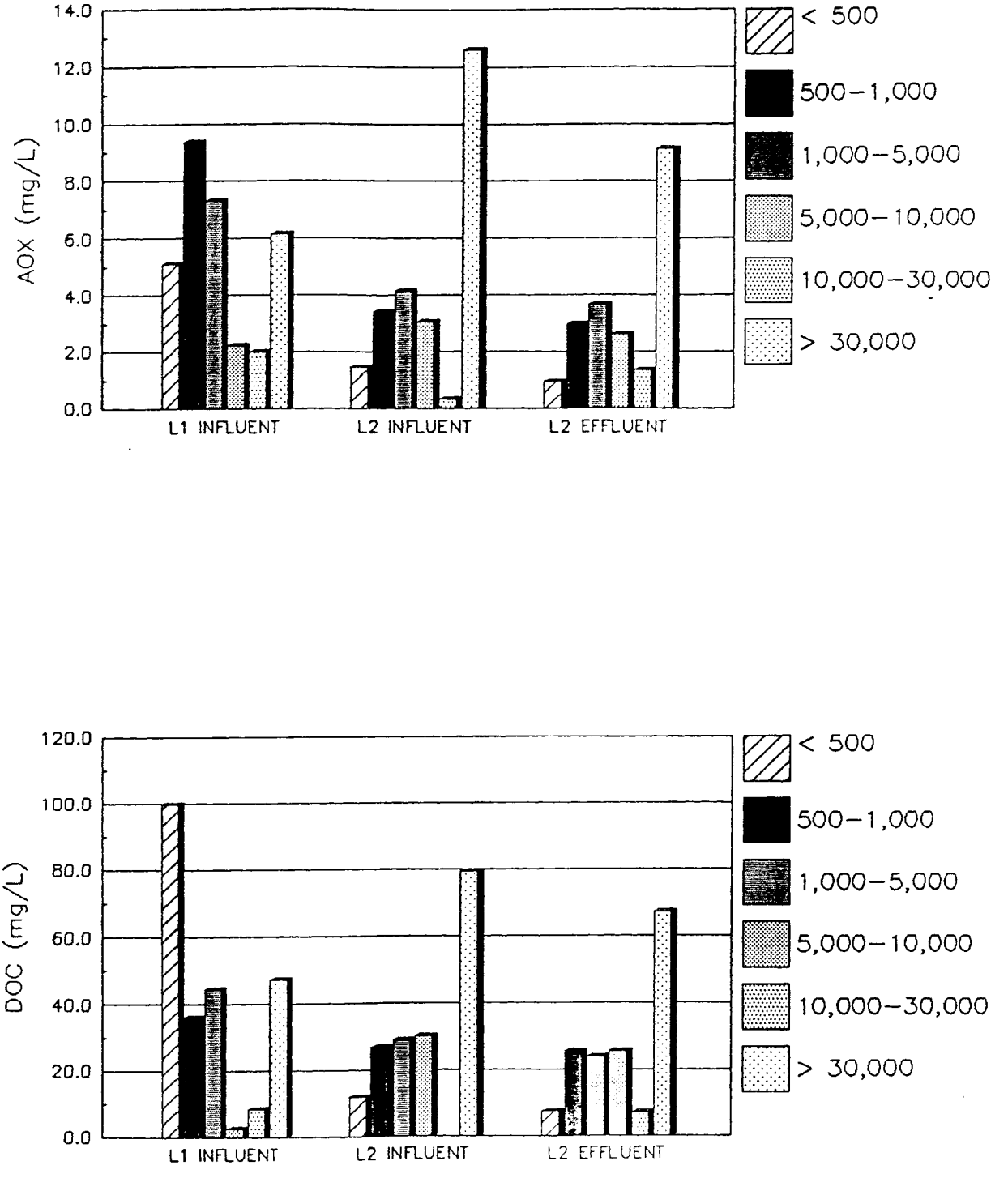


Figure 5. AOX and DOC Molecular Weight Fingerprints for the Mill #1: Summer Sample

the compounds identified in the < 1K fraction are known to contribute to the toxicity and mutagenicity of spent bleaching liquors. Therefore, removal of this fraction in the ASB reduces the risk of discharging spent bleaching liquors into natural water systems. AOX discharged from the ASB is primarily large biorefractory material.

Illustrated in Figure 5 is the molecular weight fingerprint for the Summer samples based on DOC. All fractions exhibit the same trend as the AOX fingerprint. At the time of sampling, the treatment system was removing approximately 34 percent of the total DOC present. Removals ranged from 15 to 92 percent for the AMW fractions with the < 0.5K fraction experiencing the greatest reduction. More than half of the DOC entering the treatment system has an apparent molecular weight less than 1,000. This fraction is reduced to approximately 21 percent of the total DOC after treatment.

Fall Sampling Period - A molecular weight fingerprint based on AOX from the Fall samples is illustrated in Figure 6. All of the AMW fractions show a decrease in material through the ASB system except for the fraction greater than 30,000 AMW. The fraction between 1,000 and 5,000 AMW remained unchanged across the system. A 26 percent reduction in bulk water AOX across the lagoon system was recorded. Individual AOX removal within the molecular weight fractions ranged from

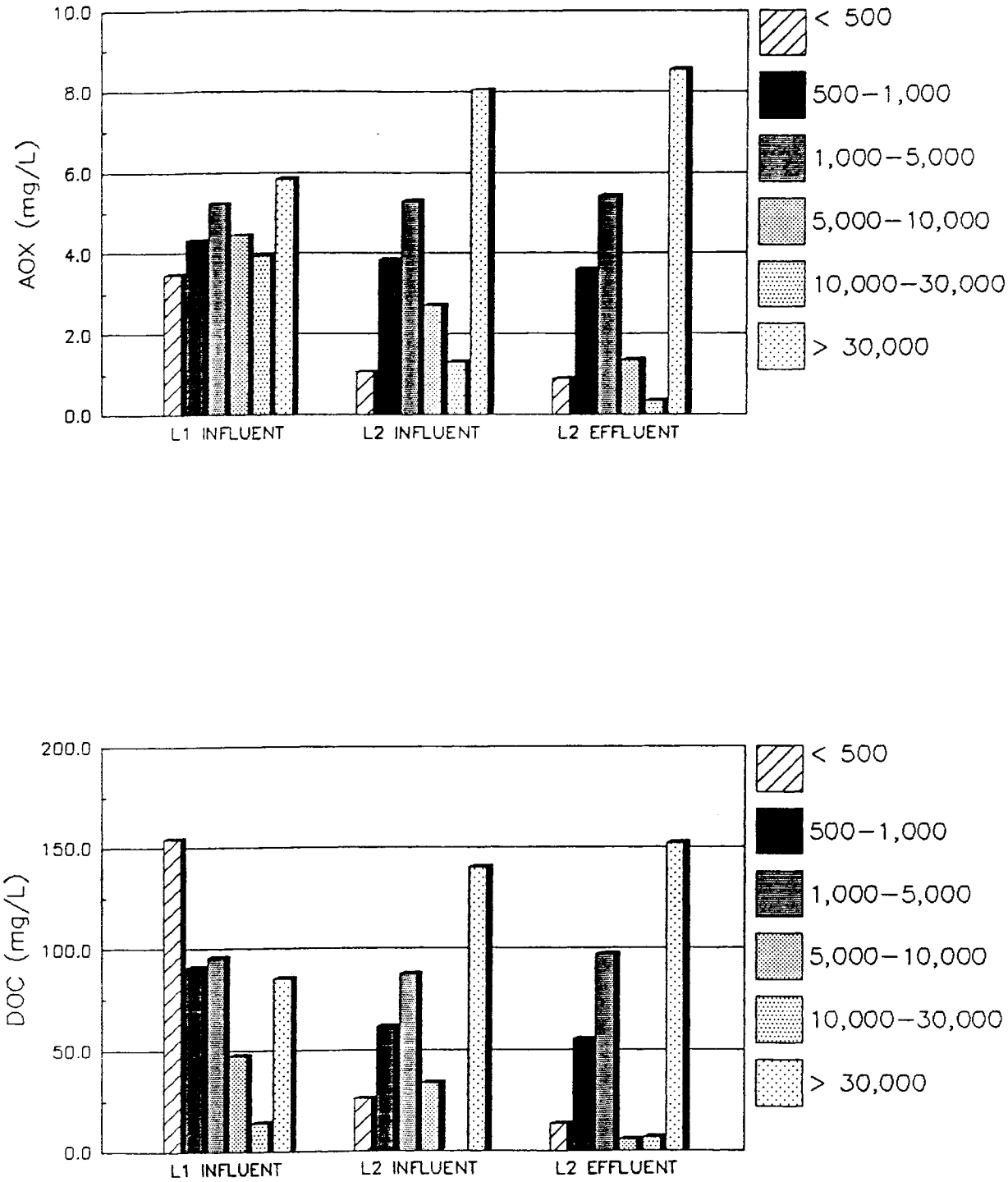


Figure 6. **AOX and DOC Molecular Weight Fingerprints for the Mill #1: Fall Sample**

7 percent for the 1 - 5K fraction to 91 percent for the 10 - 30K fraction.

Figure 6 is a graphical representation of the DOC fingerprint for the Fall samples. The DOC fingerprint mimics the trends discussed above for the AOX fractions. DOC for the 10 - 30K fraction from the L2 Influent sample was negative and therefore set to zero to develop the fingerprint. Overall DOC across the ASB decreased by 32 percent with the greatest decrease occurring in the 5 - 10K and the < 0.5K fractions. As with the Summer DOC concentrations, the < 1K fraction constitutes roughly half of the DOC entering the treatment system and 20 percent of the effluent DOC.

Winter Sampling Period - Two sets of Winter samples were collected roughly two weeks apart. Abbreviated characterization was performed on both sample sets to depict apparent molecular weight fractions of > 30K, 1 - 30K and < 1K. As discussed above, separate acid and caustic waste stream samples were also collected with the second (1-30-90) sample.

Figure 7 illustrates the abbreviated AOX profile for both Winter sampling periods. Overall AOX removal across the ASB is approximately 50 percent for both Winter samples. This reduction in AOX is slightly greater than those recorded for the Summer and Fall samples. All of the molecular weight fingerprints show a decrease in material across the basins

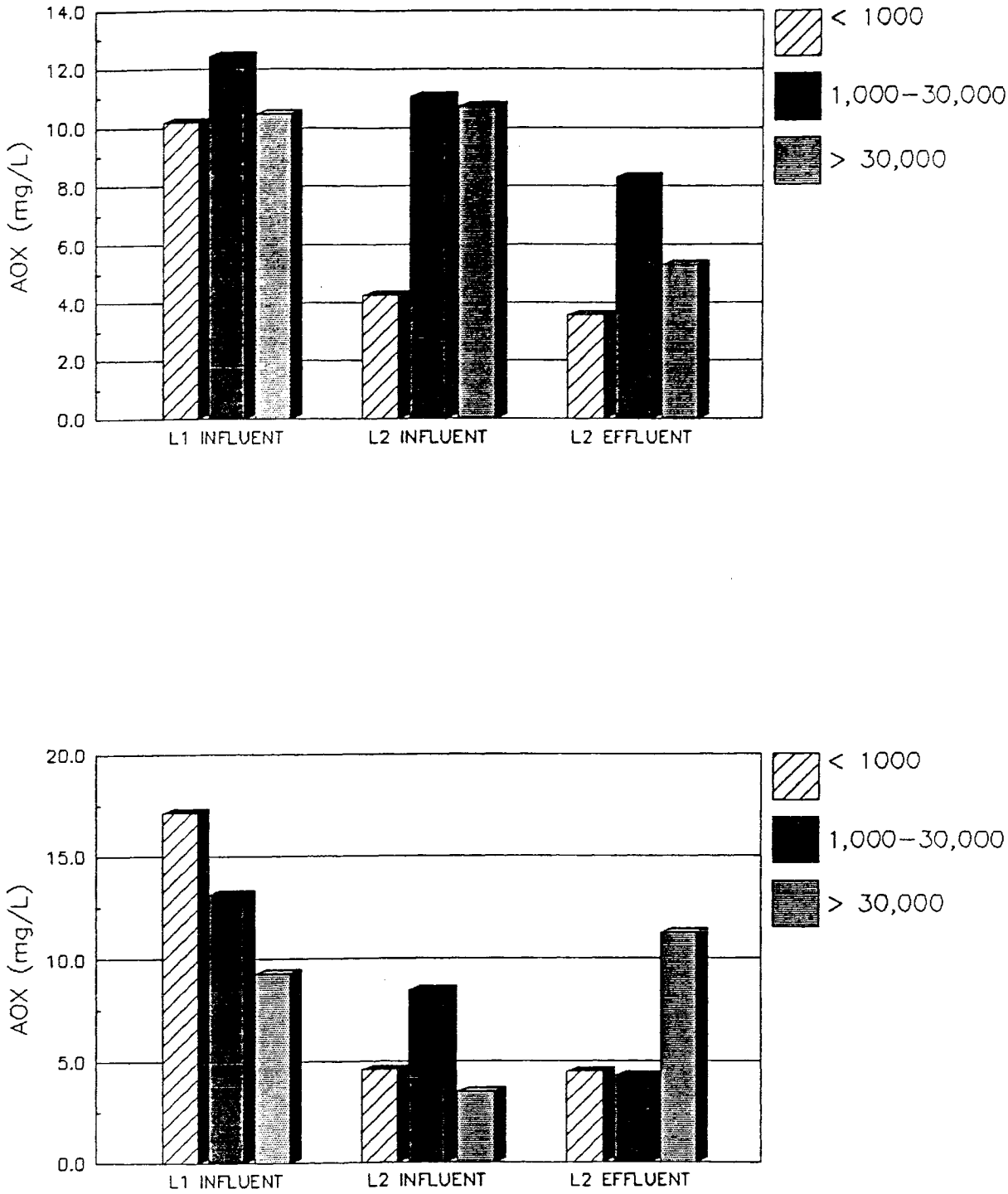
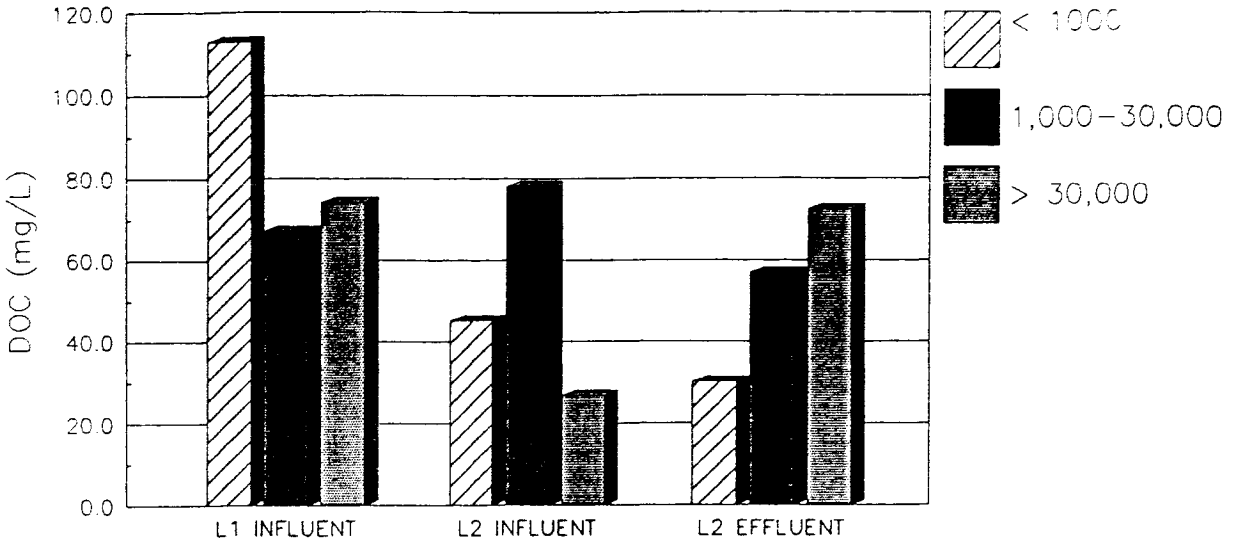


Figure 7. AOX Molecular Weight Fingerprints for Mill #1: Winter-1 and Winter-2 Samples

with the exception of a slight increase in the > 30K fraction of the second sample. In both cases, the < 1K fraction experienced the greatest decrease with 64 percent in the first sample and 74 percent in the second sample. AOX material in the effluent consisted of approximately 20 percent of the < 1K fraction.

The abbreviated DOC profiles for both Winter samples are presented in Figure 8. DOC was reduced across the ASB by 37 and 49 percent in Sample-1 and Sample-2, respectively. All of the fractions indicate a decreasing trend with the exception of the 1 -30K fraction of the second sample which was nearly unchanged. The greatest DOC removal was observed in the < 1K fraction for both samples.

Spring Sampling Period - Molecular weight fingerprints for the Spring samples based on AOX are presented in Figure 9. The overall AOX removal of 11 percent was significantly lower than the removals observed for the other samples. A review of the production data indicates the dissolved oxygen (DO) levels across the ASB were lower than the previous samples. The lower DO levels may have inhibited microbial activity which is known to be the major contributor to AOX and DOC removal. The 10 - 30K, 0.5 - 1K and the < 0.5K fractions show a decrease in material across the treatment system. On the other hand, the remaining fractions indicate an increase in AOX material across the basins.



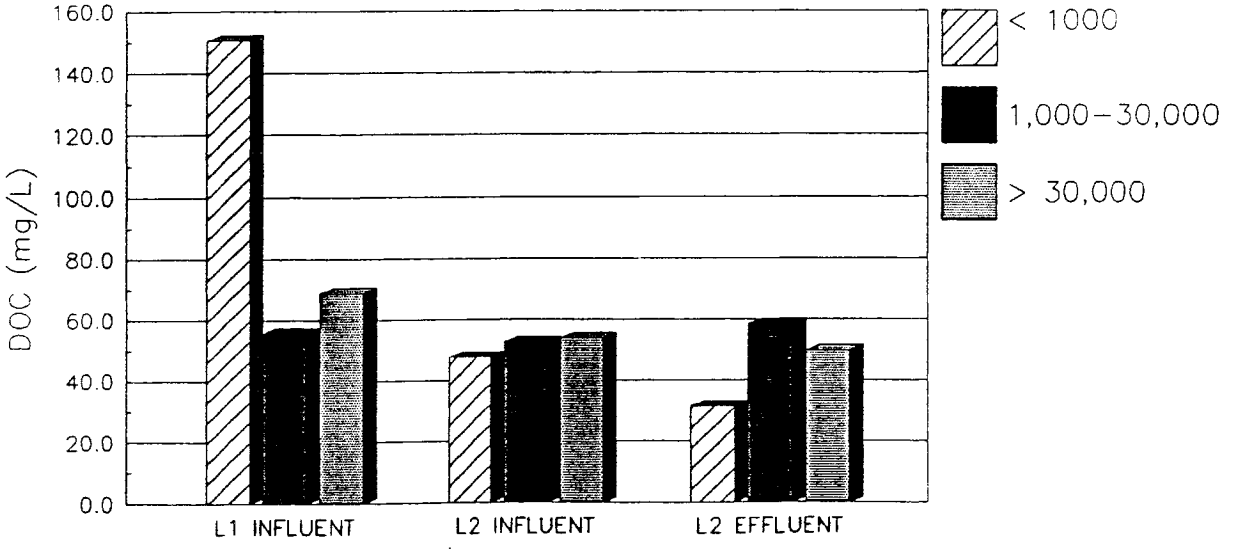


Figure 8. DOC Molecular Weight Fingerprints for Mill #1: Winter-1 and Winter-2 Samples

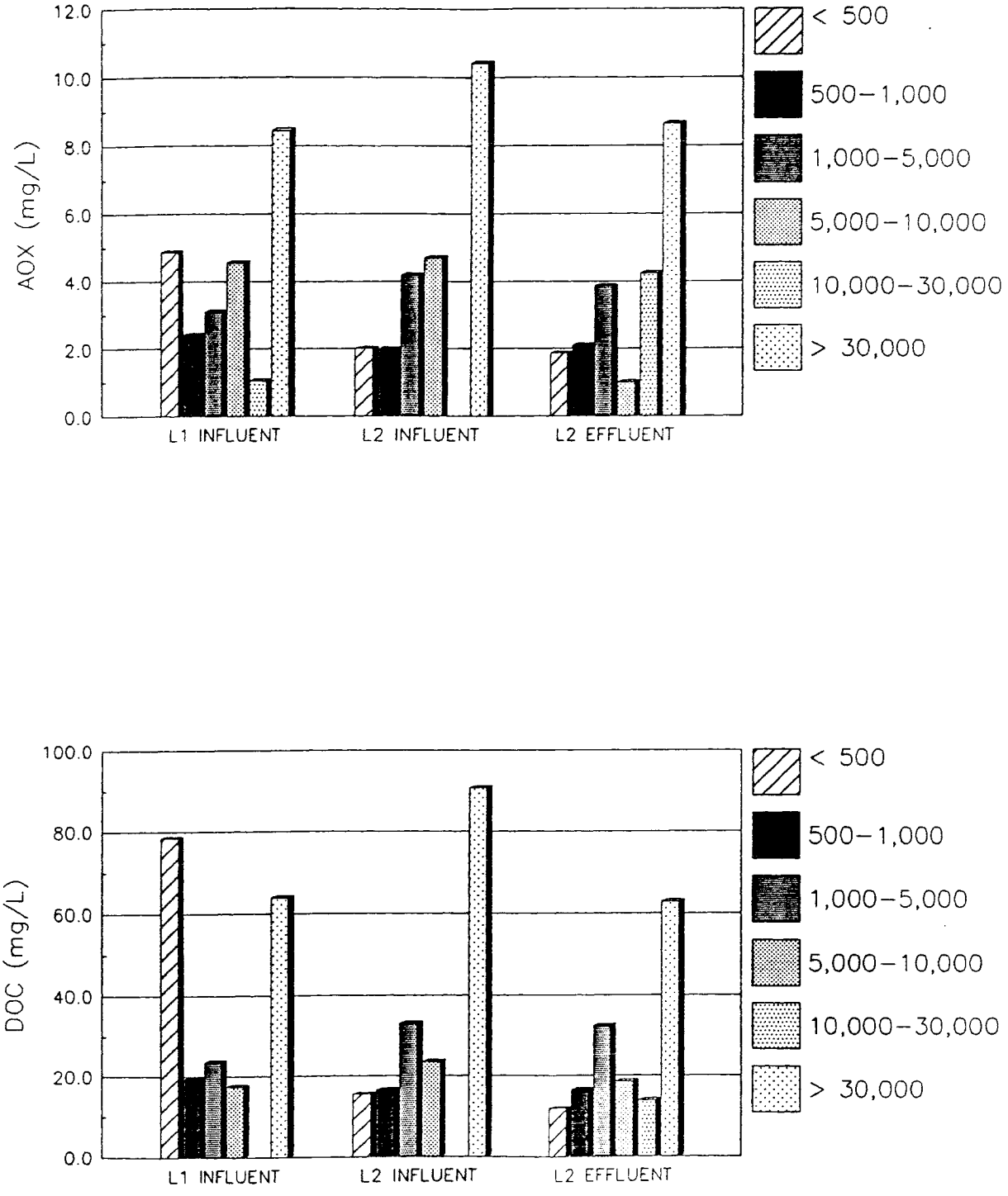
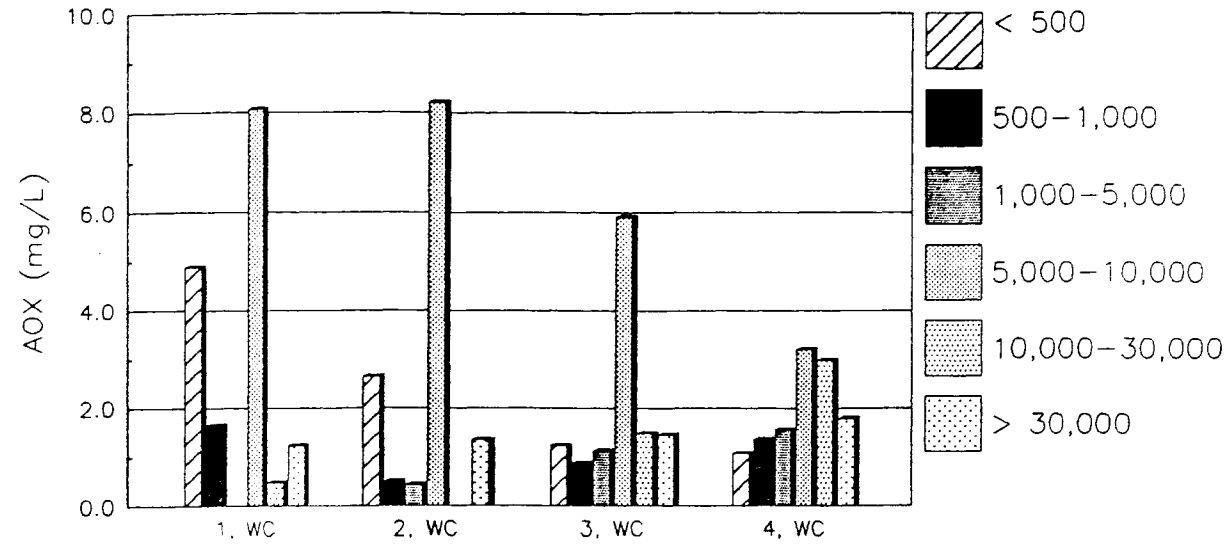


Figure 9. AOX and DOC Molecular Weight Fingerprints for the Mill #1: Spring Sample

Figure 9 illustrates the DOC molecular weight fingerprints for the Spring samples. As with the AOX, overall DOC removal of 21 percent was much lower than the other samples. All of the DOC fractions follow the trend discussed above for AOX. For both AOX and DOC, the 10 -30K fraction for the L2 Influent sample was negative and therefore was set to zero to develop the molecular weight fingerprint.

Mill #2: Sample-1 - Figure 10 graphically represents the molecular weight fingerprints based on AOX for the first samples taken from Mill #2. Unlike samples from Mill #1, the fractions do not illustrate a distinct decreasing trend except for the 5 - 10K and < 0.5K fractions. The 10 -30K fraction was negative and therefore was set to zero to develop the molecular weight fingerprint. The remaining fractions did not change significantly across the ASB. Therefore the bulk water AOX removal discussed previously is a direct result of decreases in the 5 - 10K and < 0.5K fractions.

Characterization of DOC by discrete molecular weight fractions is presented in Figure 10. Again there is no distinct decreasing trend for the DOC fractions across the ASB. A possible explanation for the discrepancy in DOC as well as AOX may lie in the ultrafiltration process, primarily in the membranes. Dehydration of the membrane, use of a membrane more than the recommended ten times and/or disfigurations in the membrane can contribute to improper



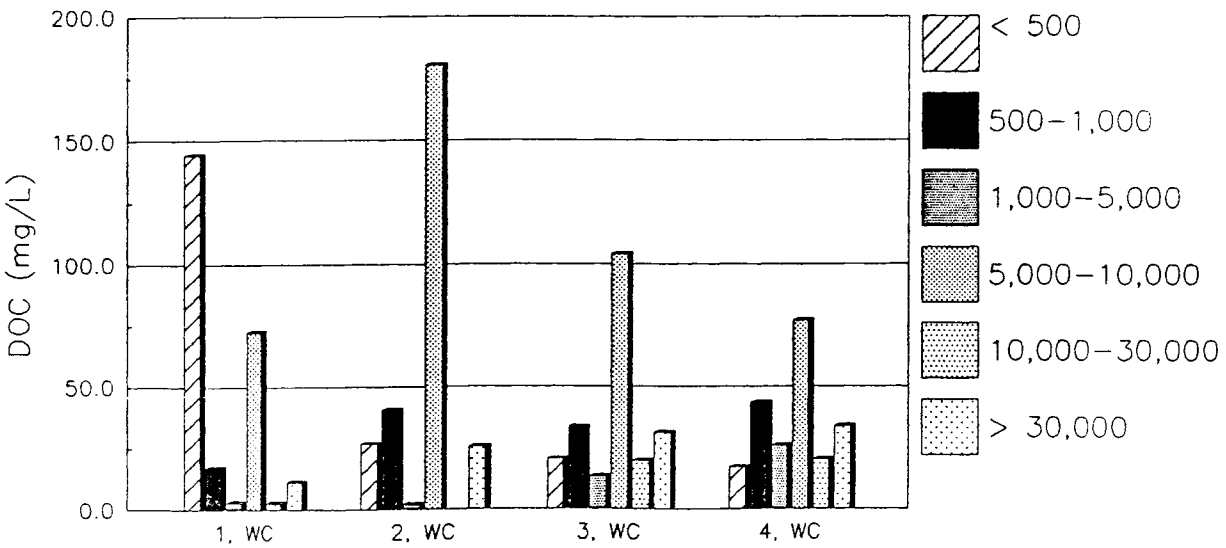


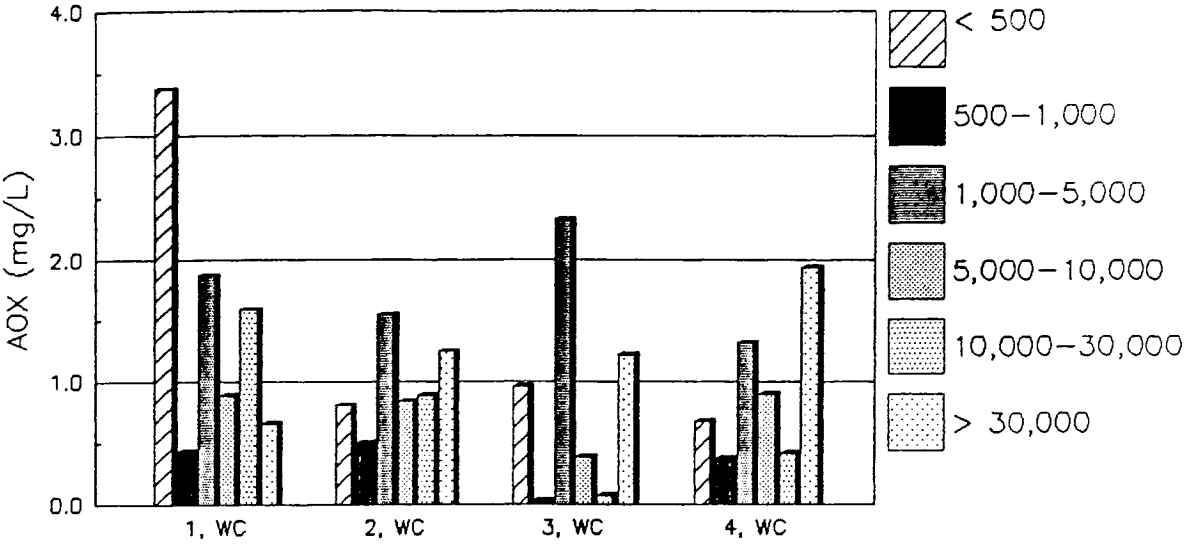
Figure 10. AOX and DOC Molecular Weight Fingerprints for Mill #2: Sample-1

separation of material. Membrane rejection properties can also influence the passage of material through the membrane. An indication of incorrect separation would be the presence of more material in a smaller AMW fraction when compared to that in a larger AMW cutoff. For example, the 10K fraction for Sample-1 contained 250 mg/L of DOC whereas the 30K fraction contained 185 mg/L. Duplicate injections confirmed these results.

Another example of improper separation can be illustrated with the replication of the 1K fraction. The first 1K fraction for Sample-1 contained 162 mg/L of DOC whereas the replicate 1K fraction indicated 198 mg/L of DOC.

Mill #2: Sample-2 - Figure 11 depicts the molecular weight fingerprints based on AOX for Sample-2. All of the AMW fractions show a decreasing trend across the ASB with the exception of the > 30K and the 1 - 5K fractions. This trend was noticed in several samples taken from Mill #1. The greatest AOX reduction occurred in the < 0.5K fraction with approximately 80 percent of the material being removed.

Figure 11 presents the molecular weight fingerprints based on DOC for Sample-2. As shown, a decreasing trend in DOC is evident for most of the molecular weight fractions. The greatest DOC removal occurred in the 10 - 30K and the < 0.5K fractions. This trend was noticed in the Fall sample taken from Mill #1.



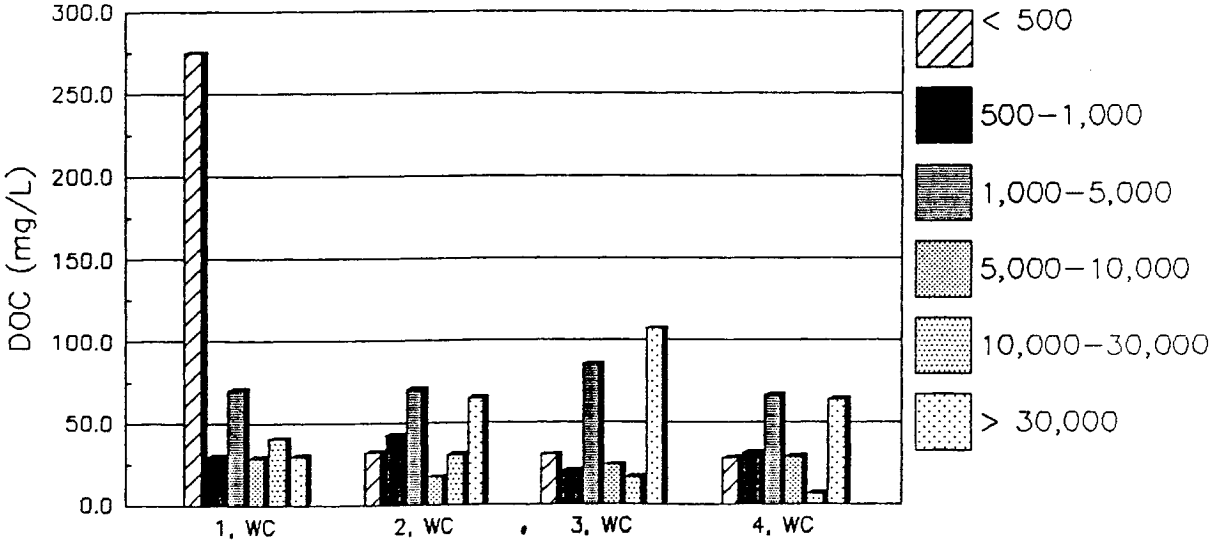


Figure 11. AOX and DOC Molecular Weight Fingerprints for Mill #2: Sample-2

> 30K Fraction Discrepancy - All of the samples except for the first Winter sample from Mill #1 demonstrated an increase in AOX and DOC material for the > 30K fraction. A possible explanation for this discrepancy is the presence of some measurable, nonfilterable, "colloidal" AOX entering the system. As this colloidal material travels through the lagoon system it may possibly breakdown (i.e. hydrolyze) into smaller, yet > 30K material. Since filtration is required for sample preparation, the colloidal material present in the ASB influent samples is filtered out. However, the material that has broken down prior to the influent to lagoon 2 will pass through the filter. As a result this material is not detected in the L1 Influent samples but is measured in the L2 Influent and L2 Effluent samples.

To test this hypothesis, a unfiltered aliquot taken from the basin influent samples was analyzed for AOX. Table 6 depicts the filtered and unfiltered AOX concentrations for the ASB influent and the separate acid and caustic waste streams. Results indicate there is no clear trend between the filtered and unfiltered samples with only the Fall, Winter-1 and acid stream indicating slightly larger AOX in the unfiltered sample. The difference between each sample set is negligible with the greatest standard deviation being 2.23 mg/L. Additional data are required to prove or disprove this "colloidal" hypothesis.

Table 6. Comparison of AOX for Filtered and Unfiltered ASB Influent Samples.

Sample	Filtered AOX (mg/L)	Unfiltered AOX (mg/L)
Mill #1		
Fall	27.18	28.58
Winter-1	33.04	36.20
Winter-2	39.56	37.80
Acid Stream	53.08	53.64
Caustic Stream	27.12	26.18
Mill #2		
Sample-1	15.50	15.18
Sample-2	10.14	9.96

Another possible explanation is the initial filtration method may have contributed to this discrepancy. Whatman GF/C filters with an nominal pore size of 1.2 um was used to filter the wastewater. With this pore size, microorganisms present in the wastewater can pass through the filter. These organisms were removed during the ultrafiltration process for all of the fractions except the bulk water. Samples collected after the aerated portion of the lagoon system contain more microorganisms than the influent samples. The increase in microorganisms may contribute to the increase in DOC for the > 30K fraction. However, this does not explain the increase in AOX for this fraction.

Sporadic increases in other AMW fractions may be due to degradation of larger material into that fraction without subsequent degradation of the fraction. The discrepancy may also be attributed to a non steady operating conditions in the mill. This may be especially true for the Spring samples where many of the AMW fractions experience increases across the ASB.

ULTRAFILTRATION MEMBRANE REJECTION COEFFICIENTS

Rejection coefficients for the YM series membranes were determined by applying the model presented previously. A composite influent sample from Mill #2 Sample-2 was used to determine the coefficients based on DOC. Results from the

ultrafiltration rejection coefficient experiments are presented in Table 7. Rejection properties of the membranes do not affect the material distribution for the 1 - 5K and the 0.5 - 1K fractions. However, rejection properties of the YC05 (500 AMW) membrane result in an underestimation of DOC material in the < 0.5K fraction. On the other hand, an overestimation of DOC in the > 30K and the 5 - 10K fractions are due to rejection properties of the YM30, YM10 and YM5 membranes.

Transport of material through ultrafiltration membranes is influenced by membrane pore size distribution, temperature, pH, cell pressure, solution ionic strength as well as molecule size, shape and affinity for the different membrane materials (10). Therefore, to properly determine the desired characteristics (i.e. DOC or AOX) of discrete molecular weight fractions, rejection properties of the ultrafiltration membranes must be evaluated for each membrane and wastewater processed. For example, a rejection coefficient experiment based on AOX for the Sample-2 composite influent wastewater was performed with a YM2 membrane. The permeation coefficient, p, was determined to be 0.83 which is greater than p=0.76 calculated based on DOC for the same membrane and wastewater. This illustrates the differences in membrane rejection properties between organic halide and organic carbon.

Table 7. Ultrafiltration Rejection Coefficient Data Based on DOC Analysis

	Bulk	30,000	10,000	5,000	1,000	500
P[1]	1	0.94	0.98	0.81	0.76	0.69
C_{ro}[2]	402	399	348	322	252	190
C_f[3]	402	386	344	287	216	154

	> 30K	10-30K	5-10K	1-5K	0.5-1K	< 0.5K
C_{ro}	3	51	26	70	62	190
C_f	16	42	57	71	62	154
% C_{ro}[4]	0.75	12.7	6.5	17.4	15.4	47.3
% C_f[5]	4	10.4	14.2	17.7	15.4	38.3

Note:

1. P is the permeation coefficient for each membrane.
2. C_{ro} represents the initial concentration of material in the sample with an apparent molecular weight smaller than the nominal membrane molecular weight cut-off in mg/L.
3. C_f represents the filtrate concentration in mg/L.
4. Percentage C_{ro} of the bulk water DOC; 402 mg/L.
5. Percentage C_f of the Bulk water DOC; 402 mg/L.

Since time constraints did not permit determination of rejection coefficients for every membrane and wastewater processed, only assumptions can be applied to the discrete molecular weight fraction data presented above. It is assumed that the AMW fractions based on DOC will follow the trend discussed previously. First of all, the amount of material in the 10 - 30K, 1 - 5K and 0.5 - 1K fractions will remain unchanged and have been accurately reported. Second, the < 0.5K fractions have been underestimated indicating the wastewater contains more material in this fraction than reported. Finally, reported DOC values for the > 30K and 5 - 10K fractions are greater than what is actually present in wastewater. Since rejection coefficient data based on AOX are incomplete, no assumptions can be made for the AMW fractions based on AOX.

SEASONAL VARIATIONS

Table 8 presents the overall removal of AOX and DOC for the samples taken from Mill #1. The greatest removal of AOX and DOC occurred in the Winter samples whereas the least removal occurred in the Spring. The primary removal mechanism of AOX is assumed to be by adsorption of organic halide onto settling biomass. Physical factors such as temperature and pH are known to influence adsorption capacity (8,14). Studies have determined adsorption capacity has an inverse

Table 8. Overall Removal of AOX and DOC from Mill #1

Sample	% AOX	% DOC
Summer	36	34
Fall	26	32
Winter-1	48	37
Winter-2	49	49
Spring	11	21

relationship with temperature and a direct relationship with pH (8,14).

One of the objectives of this research was to determine if seasonal variations, specifically temperature, influence the ASBs ability to remove AOX. To reduce the influence in-mill operating conditions have on AOX removal, mill operating conditions were held nearly constant, where possible, between the samples.

A review of the production data presented earlier in Table 2 for Mill #1 indicates the temperature across the ASB during the Winter sampling period was generally lower than the other seasons. The lower temperatures may account for the significantly higher overall removals. If the inverse relationship holds true, the highest ASB temperatures which occurred in the Summer would result in the lowest removal of AOX and DOC. However, the Spring samples produced the lowest removal with ASB temperatures similar to those found in the Fall. This would indicate other ASB parameters such as pH and dissolved oxygen (DO) may influence AOX and DOC adsorption in the treatment system. As stated previously, DO across the ASB were lower for the Spring samples resulting in a reduction in microbial activity.

A statistical analysis would be useful to determine if the overall removals between the season are significantly different. Analyses could be conducted to evaluate the affect

of temperature, dissolved oxygen and pH on the overall removals. However, additional sample sets representing each season are required to accurately perform the statistical analysis.

COMPARISON BETWEEN MILL #1 AND MILL #2

Mill #1 is operated as a conventional bleaching facility whereas Mill #2 is operated under a modified bleaching process. In all cases, influent and effluent AOX concentrations from Mill #1 were greater than those from Mill #2 (Table 3 and Table 5). The modified bleaching process which employed 70 percent chlorine dioxide and 30 percent chlorine in the first bleaching stage produced less AOX than the conventional mill utilizing only chlorine for stage 1 bleaching. Complete elimination of chlorine from stage 1 in Mill #2 further reduced the AOX production by approximately one-half. Studies have shown that the amount of chlorinated material produced via the chlorination and extraction stages is a function of the amount of chlorine applied to the pulp (23). It has been found that the formation of AOX is reduced proportionally as the amount of chlorine applied to the pulp is reduced (23).

Operation of the bleaching process under either the conventional or modified method does not appear to influence the DOC concentration in the wastewater. Both Mill #1 and

Mill #2 generally have influent DOCs at approximately 250 mg/L with the exception of Sample-2 from Mill #2. The ASB at Mill #1 is more efficient in removing DOC to an approximate level of 150 mg/L whereas DOC in the effluent of Mill #2 is roughly 220 mg/L. Additional data from Mill #2 is needed to accurately establish removal efficiencies.

To explain the variations in ASB removal efficiency for DOC, in-mill production data and ASB parameters were reviewed. Mill #1 and Mill #2 production data for the sampling dates were presented in Table 2 and Table 4, respectively. Mill #1 is divided into two smaller mills to produce pulp from two different wood types; a dissolving grade and a paper grade. The pulp from the two smaller mills is processed through the same conventional bleaching process to remove residual lignin. Therefore, the DOC and AOX in the spent bleaching liquors, and hence the wastewater, is a result of the two different stock types. One the other hand, DOC and AOX in the spent bleaching liquors from Mill #2 is derived from a paper grade feed stock. The lower effluent DOC concentrations from Mill #1 may be a result of the DOC characteristics of the dissolving grade material. DOC derived from the dissolving grade feed stock may be easier to degraded than the DOC derived from the paper grade feed stock. Since the spent bleaching liquors at Mill #1 are mixed prior to entering the ASB it is impossible to evaluate the DOC from each feed stock.

ASB parameters for pH and temperature were comparable for both ASBs, however BOD_5 in the effluent of Mill #2 was consistently higher. Since the wastewater from Mill #2 remains in the ASB nearly three times longer than at Mill #1 higher DOC removals should be realized. However, this is not the case. This would indicate in-mill processing conditions such as feed stock and pulping and/or bleaching conditions and not ASB parameters are responsible for the lower DOC removals from Mill #2. As stated above, the type of feed stock may produce DOC which is resistant to biological degradation. Also, the different bleaching schemes may extract biologically resistant material. Further research is needed to determine the impact variations in the Kraft pulping process and stock types have on DOC degradation in the ASB.

PARTITIONING OF AOX

Insight into ASB removal mechanisms can be explained by an evaluation of AOX partitioning onto settling biomass and sediment layer solids. A recent study demonstrated the important role of biosorption on the removal of organic halide in an ASB (8). Determination of the partitioning of organic halide between the water column and the biomass will enable a mass balance to be conducted across the ASB to ascertain apparent dehalogenation.

Extractable organic halide (EOX) measurements were

conducted on sediment samples collected from Mill #1 and Mill #2. As discussed previously, various extraction procedures were employed to maximize the recovery of organic halide. Presented in Table 9 are the Mill #1 EOX and interstitial water AOX values as well as the corresponding sediment/water partition coefficients for the different extraction procedures.

Summer and Fall samples were subjected to a 5 minute extraction period where the Winter and Spring samples were extracted for 24 hours. Extending the extraction procedure resulted in higher overall EOX values. As a result, the 24 hour extraction period was applied to the Mill #2 sediment samples.

The extraction solvents, ethyl acetate and octanol, made a considerable difference in the amount of organic halide extracted from the benthal solids. In all cases, octanol was not effective in extracting the organic halide. Physical properties such as hydrophobicity and polarity of the solvents and the organic halide sorbed onto the benthal solids influences the degree of extraction. Dipole moments for the solvents were reviewed to ascertain their polarity relative to water. The dipole moments for octanol, ethyl acetate and water are reported as 1.60, 1.78 and 1.87 debyes, respectively (25,26). As the dipole moment increases, the polarity of the compound increases; thus ethyl acetate exhibits a higher

Table 9. Sediment EOX and Interstitial Water AOX Values for Mill #1.

Parameter	Sampling Region L1 Influent	L2 Influent	L2 Effluent
Summer Sample[1]			
AOX (mg/L)	4.00	8.52	5.28
EOX (ug/g)[2]	19.7	645	702
	0.76	68	91
K_p (cm^3/g)[3]	4.93	75.7	133
	0.19	7.98	17.2
Fall Sample[1]			
AOX (mg/L)	n/a	5.58	6.18
EOX (ug/g)[2]	n/a	277	383
	n/a	75	76
K_p (cm^3/g)[3]	n/a	49.6	62.0
	n/a	13.4	12.3
Winter-1 Sample[4]			
AOX (mg/L)	n/a	8.4	9.9
EOX (ug/g)[5]	n/a	979	739
	n/a	951	837
K_p (cm^3/g)[6]	n/a	116.5	74.6
	n/a	113.2	84.6
Spring Sample[4]			
AOX (mg/L)	n/a	14.17	9.69
EOX (ug/g)[5]	n/a	1046	728
	n/a	1044	788
K_p (cm^3/g)[6]	n/a	73.8	75.2
	n/a	73.6	81.3

NOTE:
1. Extraction period - 5 minutes
2. First EOX value derived by extraction with ethyl acetate, second EOX value derived by extraction with octanol.
3. First K_p based on ethyl acetate extraction, second K_p based on octanol extraction.
4. Extraction period - 24 hours
5. First EOX value derived by extraction with ethyl acetate, second value extraction with ethyl acetate and DMSO.
6. First K_p based on ethyl acetate extraction, second K_p based on extraction with ethyl acetate and DMSO.

degree of polarity when compared to octanol which is classified as a non-polar compound. Ethyl acetate is also slightly water soluble while octanol is a highly hydrophobic compound.

Considering this, the adsorbed organic halide may have a range of properties with respect to polarity and hydrophobicity. The lower EOX values with octanol suggest the adsorbed organic halide is somewhat polar but not necessarily hydrophilic in nature. Researchers have found an inverse relation between water solubility and biosorption (12,13,15). Based on these two observations it may be inferred that the organic halide sorbed onto the biomass is relatively polar and partially insoluble in water. As a result, the organic halide tends to partition into ethyl acetate which exhibits comparable physical properties of polarity and water solubility. This is demonstrated by the significantly higher ethyl acetate EOX values compared to the octanol EOX values.

Ethyl acetate was selected as an extraction solvent due to its excellent chloride rejection properties whereas octanol was selected due to its non-polar characteristics. Since these two solvents are physically different, as discussed above, extraction with these solvents may not necessarily yield the same compounds. It has been assumed that a majority of the organic halide sorbed onto the benthic solids is relatively polar and partially insoluble in water. However,

there may be some compounds which are highly non-polar and are easily extracted with the octanol. Without further investigation it is unrealistic to assume 100 percent extraction of the organic halide has occurred with the ethyl acetate.

Extraction procedures incorporating sonication or the chemical DMSO were based on the premise that some sorbed organic halide may be intra-cellular material as opposed to adsorbed onto the cell surface. As stated previously, the sonicator was determined to not be powerful enough to actually rupture the cells. Therefore, the reported EOX values represent organic halide sorbed onto the surface of the benthic material.

As shown on Table 9 Winter-1 and Spring EOX values with and without DMSO are comparable (CV < 8%). Three possible conclusions can be drawn from these results; 1) sorption of organic halide is primarily onto the cell surface and not intra-cellular, 2) the amount of intra-cellular material is insignificant when compared the material sorbed onto the cell surface and 3) the concentration of DMSO was ineffective at increasing the permeability of the cell membrane. The concentration of DMSO was based on inactivation of the cells as viewed under the microscope. However, this method did not provide a means for determining if the concentration of DMSO was significant to increase the permeability of the cell

membrane. Without further investigation no conclusions can be drawn regarding the premise of intra-cellular material.

Sediment/water partition coefficients estimated from the ratio of EOX to interstitial water AOX ranged from 4.93 to 133 cm^3/g. A majority of the partition coefficients based on extraction with ethyl acetate fluctuated around 75 cm^3/g. The L1 Influent Summer sediment sample was sandy in character resulting in the lowest K_p of 4.93 cm^3/g. The sediment samples acquired from the other two sampling locations were highly organic in character thus the higher partition coefficients. For this reason, sediment sampling from the inlet to the first lagoon at Mill #1 was discontinued after the Summer sample set.

Table 10 presents the EOX data for samples collected from Mill #2. Extraction of the sediment samples was conducted with ethyl acetate and octanol for 24 hours. Again, lower EOX values were measured for the octanol samples. K_ps based on ethyl acetate for both sample sets range from 155 to 314 cm^3/g. One exception is the Sample-2 effluent sample which had a high interstitial AOX value and a low EOX value resulting in the low 40 cm^3/g partition coefficient. The high interstitial AOX value may be due to benthal feedback as a result of modifications to the bleaching process.

Partitioning of organic halide between the water column and biomass was greater for Sample-1, where chlorine dioxide

Table 10. Mill #2 Sediment EOX and Interstitial Water AOX Values.

	Sampling Region		
Parameter[1]	2, WC	3, WC	4,WC
Sample-1			
AOX (mg/L)	5.08	2.80	3.42
EOX (ug/g)	1041	878	844
K_p (cm^3/g)	204.8	313.6	246.7
Sample-2			
AOX (mg/L)	5.3	5.60	11.85
EOX (ug/g)	822	1013	472
K_p (cm^3/g)	155.1	181	40.0

NOTE:
1. Based on a 24 hour extraction with ethyl acetate.

and chlorine was used in the bleaching process. After the elimination of chlorine, the partitioning was reduced. Again, additional data are required to confirm this observation.

The partition coefficients for Mill #2 are generally higher than those for Mill #1. Conditions in the ASB such as temperature, pH and type of microorganisms can influence the degree of partitioning. In-mill conditions such as feed stock type can influence the characteristics of the organic halide in the wastewater and thus the partitioning of the organic halide.

A study conducted with virgin biomass from recycled activated sludge and Kraft mill wastewater determined average partition coefficients ranging from 322 to 459 cm^3/g (8). The K_ps determined in the study are higher than those determined from Mill #1 and Mill #2. The study also identified decreases in temperature and pH tend to increase organic halide partitioning (8). The temperature effect is evident for the Mill #1 samples. Temperatures across the ASB were generally lower for the Winter-1 samples and the corresponding K_ps were generally higher than the other samples.

Previous work by Amy et al. indicates adsorption of organic halide onto settling biomass is the necessary transport step required for anaerobic dehalogenation and degradation in the benthal layer (8). The limiting step in organic halide removal is probably the amount of biomass

produced in the aerated lagoon. Organic halide removal is a function of the usable organic material entering with the AOX that is available for biomass production.

APPARENT DEHALOGENATION

Anaerobic reductive dehalogenation of chlorinated organic compounds by microorganisms is believed to be the primary mechanism for chlorine removal in the benthic layer of the ASB. Ratios of AOX/DOC can be used to evaluate changes in the degree of halogenation of the dissolved organic matter (DOM). Observing the ratios of AOX/DOC across the ASB can provide insight into any preferential removal of highly chlorinated versus slightly chlorinated compounds.

Table 11 presents Mill #1 AOX/DOC ratios for the bulk water, the < 1K fraction of the bulk water, the interstitial water and the corresponding < 1K fraction. Bulk water DOM was generally found to be more halogenated than the < 1K fraction. The high bulk water DOC concentration in the Fall samples is responsible for the lower degree of halogenation. There appears to be little change in the AOX/DOC ratio for bulk water DOM across the ASB. However, the AOX/DOC ratio of the < 1K fraction tends to increase across the system. This trend may be attributed to the breakdown of the low molecular weight unchlorinated compounds in the water column.

A comparison of bulk water to interstitial water AOX/DOC

Table 11. Mill #1 and Mill #2 AOX/DOC (mg/mg) Ratios For The Bulk Water and The Interstitial Water.

SAMPLE	BULK WATER	< 1K	INTERSTITIAL WATER	< 1K
Summer Sample				
L1 Influent	0.135	0.107	0.118	-
L2 Influent	0.144	0.126	0.104	-
L2 Effluent	0.133	0.119	0.085	-
Fall Sample				
L1 Influent	0.056	0.032	-	-
L2 Influent	0.066	0.056	0.044	-
L2 Effluent	0.061	0.066	0.049	-
Winter-1 Sample				
L1 Influent	0.130	0.090	-	-
L2 Influent	0.174	0.094	0.039	0.080
L2 Effluent	0.108	0.119	0.059	0.055
Winter-2 Sample				
L1 Influent	0.144	0.114	-	-
L2 Influent	0.107	0.096	-	-
L2 Effluent	0.143	0.142	-	-
Acid Stream	0.253	0.218	-	-
Caustic Stream	0.069	0.027	-	-
Spring Sample				
L1 Influent	0.123	0.075	-	-
L2 Influent	0.130	0.123	0.076	0.200
L2 Effluent	0.139	0.133	0.105	0.053
Mill #2				
Sample-1				
1, WC	0.059	0.037	-	-
2, WC	0.057	0.049	0.033	0.028
3, WC	0.054	0.038	0.025	-
4, WC	0.055	0.040	0.019	0.034
Sample-2				
1, WC	0.019	0.013	-	-
2, WC	0.023	0.019	0.024	0.024
3, WC	0.018	0.019	-	0.029
4, WC	0.025	0.018	-	0.029

ratios reveals the degree of halogenation is lower in the benthic layer. This supports the hypothesis of reductive dehalogenation of the chlorinated organic matter in the benthic layer. There is no clear trend in the < 1K fraction of the interstitial water indicating the need for additional data to further evaluate changes in this fraction.

Also presented on Table 11 are the AOX/DOC ratios for Mill #2 samples. The degree of halogenation in the bulk water is lower in Mill #2 than in Mill #1. With the modification to the bleaching system, the degree of halogenation in Mill #2 was further reduced due to the lower AOX charge to the ASB. Both the bulk water and the < 1K fraction AOX/DOC ratios remain fairly constant across the treatment system.

The interstitial water from Sample-1 at Mill #2 indicates a decreasing trend in the AOX/DOC ratio across ASB. However, additional data are required to further evaluate this trend. For both Sample-1 and Sample-2, the < 1K fraction of the interstitial water appears to have the same degree of halogenation as that of the bulk interstitial water.

A comparison between Mill #1 and Mill #2 indicate the AOX/DOC ratio for the bulk water is consistently larger for Mill #1. The lower AOX/DOC ratios for Mill #2 are a result of less AOX entering the ASB system. This trend is evident in the < 1K fraction and in the interstitial water.

The above discussion presents the degree of halogenation

of DOM across the ASB. However, the potential ability of an ASB to dehalogenate AOX compounds is difficult to discern from simple AOX and DOC measurements. It is a complex task to distinguish microbial dehalogenation effects from the chemical sorption effects that occur simultaneously in the ASB.

AOX Mass Balance - In an attempt to derive a conservative estimate of benthal dehalogenation, a two step mass balance was conducted on AOX across the ASB for both mills. The first step involved an AOX balance around the water column to obtain the amount of AOX transported to the benthic layer. A mass balance was then conducted on the benthic layer to arrive at the apparent dehalogenation. The mass balance conducted on Mill #1 was based on the following assumptions:

- an average influent AOX concentration of 31 mg/L,
- an average removal of 1.86 mg/L of AOX by volatilization,
- an average effluent AOX concentration of 20 mg/L,
- a benthal accumulation rate of 2 cm/year,
- a benthal solids content of 30% solids by weight,
- a benthic layer density of 1.02 g/ml,
- an average solid-phase loading (EOX) of 880 ug/g,
- an average interstitial water AOX concentration of 8.36 mg/L,
- flowrate through the ASB of 14,300 m^3/day (54 MGD) and,
- an ASB area of 611,100 m^2.

Assumptions regarding lagoon performance are based on discussions with plant personnel. Organic halide concentrations were taken as the average of the five samples

collected from Mill #1 in order to represent the average yearly rate of dehalogenation in the benthic layer.

Results from the mass balance presented in Table 12 show 93 percent of the AOX transported to the benthic layer is removed by dehalogenation with biosorption accounting for the remaining 7 percent. A similar study conducted on a conventional Kraft mill found 96 to 98 percent removal of AOX in the benthic layer by dehalogenation (7). These results indicate AOX transported to the benthic layer of ASBs will effectively be dehalogenated.

A mass balance conducted for Mill #2 was based on the following assumptions:

- an average influent AOX concentration of 12 mg/L,
- an average removal of 340 ug/L of AOX by volatilization,
- an average effluent AOX concentration of 9 mg/L,
- a benthal accumulation rate of 9 cm/year,
- a benthal solids content of 40% solids by weight,
- a benthic layer density of 1.02 g/ml,
- an average solid-phase loading (EOX) of 850 ug/g,
- an average interstitial water AOX concentration of 5.7 mg/L,
- flowrate through the ASB of 2,906 m^3/day (11 MGD) and,
- an ASB area of 244,440 m^2.

Unlike Mill #1, the mass balance for Mill #2 did demonstrate dehalogenation in the benthic layer. This result leads to questions regarding the validity of the assumptions. Of all the assumptions, the benthal accumulation rate is the

Table 12. Estimated AOX Mass Balance Across the Aerated Stabilization Basins at Mill #1.

COMPONENT	AOX MASS (10^{10} mg/year)
ASB Influent	16.2
ASB Effluent	10.4
Volatilization	0.97
Transport to Benthic Layer	4.77
Interstitial Water AOX	0.0071 (0.15%)
Benthic Solids Loading	0.329 (6.9%)
Apparent Dehalogenation	4.43 (93%)

most questionable. Conversations with plant personnel indicate the accumulation rate is a rough estimate at best. A sensitivity analysis conducted on the accumulation rate indicates approximately 3 cm/year is required for minimum dehalogenation.

In an attempt to complete the mass balance for Mill #2, an accumulation rate was estimated based on a yield coefficient of 0.5 mg of biomass per mg of BOD. An average BOD value of 278 mg/L derived from the difference between the average influent and the average effluent BOD was used to estimate the amount of biomass generated in the lagoon. Average BOD values were taken from the production data found in Table 4. The estimated amount of biomass generated along with the total suspended solids entering the lagoon was used to calculate an accumulation rate of 0.074 cm/year. The mass balance was recalculated based on the above assumptions and the new estimated accumulation rate. Results from the mass balance are presented in Table 13. As shown, 98 percent of the organic halide transported to the benthic layer is dehalogenated. Biosorption accounts for the remainder of the organic halide. These results, similar to those found for Mill #1, indicate the microorganisms will effectively dehalogenate the AOX transported to the benthic layer.

Table 13. Estimated AOX Mass Balance Across the Aerated Stabilization Basins at Mill #2.

COMPONENT	AOX MASS (10^9 mg/ year)
ASB Influent	12.7
ASB Effluent	9.5
Volatilization	0.36
Transported to Benthic Layer	2.84
Interstitial Water AOX	0.0006 (0.02%)
Benthic Solids Loading	0.038 (1.3%)
Apparent Dehalogenation	2.80 (98.6%)

CONCLUSIONS

Samples were collected from two Kraft pulp mills to meet the objectives established for this research. Both 24 hour composite and grab samples of the bulk water were employed for the characterization of the wastewater. Sediment samples were collected to evaluate removal mechanisms which include partitioning of the organic halide between the water column and sediment layer and dehalogenation in the benthic layer. Statistical analysis ensured the accuracy and consistency of the data.

The ASB at Mill #1 is capable of removing up to 50 percent of the AOX and DOC entering the system. ASB parameters such as temperature, pH and dissolved oxygen influenced the ASBs removal ability. In-mill operating conditions such as stock feed type also influence the formation and removal of AOX. In order to optimize removal of AOX, additional studies evaluating the influences of ASB parameters and in-mill operating conditions are recommended.

Prior to modifications, Mill #2 removed less than 20 percent of the parameters investigated. The overall removal of AOX increased to 43 after chlorine was eliminated from the first bleaching stage. The elimination of chlorine appears to have reduced the amount of AOX entering the ASB. However, elimination of chlorine appears to have had little impact on

DOC formation and removal. Additional data are required to further evaluate the impact the elimination of chlorine had on the formation and removal of AOX and DOC.

Apparent molecular weight fingerprints were used to establish AOX and DOC profiles across the treatment system. Mill #1 profiles indicate a decrease in all the molecular fractions except for the > 30K fraction. Changes in the fractions can be attributed to either microbial activity such as molecule cleavage or physical/chemical sorption. There is a pattern of preferential utilization of the material with an AMW less than 1000. The material < 1K AMW constituted approximately 30 to 60 percent of the AOX and DOC entering the system. In all cases, this fraction was reduced to less than 20 percent of the total material after treatment. The < 1K fraction also experienced the greatest decrease across the basin when compared to the other molecular weight fractions. This trend suggests molecule cleavage and biosorption of the organic halide is most effective when the molecule size is less than 1000 AMW. The organic halide being discharged from Mill #1 into natural waters is assumed to be of the large biorefractory type.

AOX and DOC molecular weight fingerprints were established for Mill #2. Fingerprints for Sample-1 did not indicate a distinct decreasing trend whereas Sample-2 did show a decreasing trend. The discrepancy in Sample-1 can be

attributed to inconsistency in the ultrafiltration process. In most cases, the greatest change in the fractions for both samples occurred between the first and second sampling locations. The greatest AOX and DOC removal in Sample-2 occurred in the < 0.5K fraction while the 0.5 - 1K fraction exhibited an increase. Without further samples from the mill, changes between the molecular weight fractions cannot be effectively evaluated. Based on the results from Mill #1 and from other studies it may be assumed the < 1K fraction will experience the greatest removal in the ASB.

The entrance of "colloidal" AOX material into the ASB was hypothesized as a possible explanation to the consistently increasing > 30K fraction. Results based on filtered and unfiltered L1 Influent samples were inconclusive. Additional research is required to accurately determine the origin of this increase.

Investigations into the rejection properties of the YM series membranes indicate an underestimation of DOC material in the < 0.5K fraction and an overestimation of the > 30K and the 5 - 10K fractions. Results also show rejection properties are different for organic halide when compared to organic carbon. Since rejection coefficients were not determined for every sample and membrane, only assumptions can be made regarding the reported DOC values. Assuming the above results hold for every molecular weight distribution based on DOC, the

amount of material would shift from the higher molecular weights (> 30K and 5 - 10K) to the < 0.5K fraction. If this is the case, larger removals in the < 0.5K fraction may be noticed. For this reason, future work pertaining to ultrafiltration of paper mill wastewater should take into consideration membrane rejection properties.

Analysis of the bulk water indicated the ASB at Mill #1 is capable of removing up to 50 percent of the AOX and DOC entering the system. Variations in the removals is believed to be influenced primarily by temperature in the ASB. The data indicate the greatest removal occurred during the Winter when the ASB temperature was the lowest. Biosorption, the primary mechanism for AOX removal, has been shown to increase with decreasing temperature. Additional data taken throughout the seasons is required to statistically prove the importance temperature plays on AOX removal across the ASB.

Bulk water parameters for Mill #1 and Mill #2 were compared to determine the influence of the bleaching process on the formation and removal of organic halide. In all cases, influent and effluent AOX concentrations were greater in Mill #1. Overall removal of AOX was generally greater in Mill #1 when compared to Mill #2 prior to bleaching modifications. However after the elimination of chlorine from the bleaching process, the AOX removal in Mill #2 was greater than the Mill #1 samples with the exception of the two Winter samples. It

can be inferred that the application of chlorine in the first bleaching stage is primarily responsible for the formation of AOX. To reduce the organic halide load in the wastewater, the bleaching process at Mill #1 should be modified to eliminate chlorine in the first bleaching stage.

ASB removal mechanisms were evaluated by measuring AOX partitioning onto settled biomass. The amount of adsorption occurring is indicated by the extractable organic halide (EOX) parameter. Several extraction methods were tested to maximize the desorption of organic halide from the sediment solids. Results suggest maximum organic halide extraction will occur when ethyl acetate is used as the extraction solvent in conjunction with a 24 hour extraction period. Further studies are required to determine if 100 percent of the sorbed organic halide is being removed under these extraction conditions.

The assumption that some sorbed organic halide may be intra-cellular as opposed to adsorbed onto the cell surface was tested by attempting to disrupt the cells. Even though the chemical DMSO effectively inactivated the cells, increased EOX values were not measured. In all cases, the EOX values were similar to those determined without DMSO. It is possible that the concentration of DMSO did not successfully increase the permeability of the cell membrane thus allowing the extraction of any organic halide. Based on these results, the assumption of intra-cellular material can not be confirmed.

Research has shown a positive correlation between adsorption and cell lipid content. For this reason, further research should be conducted to identify the lipid content of the benthic organisms. Also, other methods to disrupt the cells should be investigated. Possible methods include sonication with a sonicator capable of lysing the cells or the application of chemicals such as detergents to disrupt the cells followed by sequential washing of the sediment material.

Sediment/water partition coefficients (K_p) under the optimum extraction conditions averaged 75 cm^3/g for Mill #1 whereas K_ps for Mill #2 ranged from 155 to 314 cm^3/g. Temperature, pH, biomass characteristics and the nature of the AOX can contribute to the variations in partitioning between the two mills. The results confirms the assumption that adsorption plays an integral role in the removal of AOX.

The evaluation of AOX/DOC ratios for the bulk water and interstitial water indicate the DOM in the interstitial water is less halogenated than that of the bulk water at both mills. In all cases, the bulk water AOX/DOC ratio was greater than that of the interstitial water. Apparent dehalogenation by benthal organisms is a possible explanation. Another indication of possible dehalogenation is the consistently higher bulk water AOX concentrations compared to that of the interstitial water. However it is difficult to separate the effects of microbial activity from that of physical/chemical

adsorption by simple evaluation of AOX and DOC data.

The degree of halogenation in the bulk water was found to be lower in Mill #2 when compared to Mill #1. Modifications to the bleaching process at Mill #2 further reduced the degree of halogenation of DOM. Elimination of chlorine has reduced the degree of halogenation by reducing the amount of AOX entering the system.

A mass balance across the ASB was conducted to establish a conservative estimate of dehalogenation in the benthic layer. Results from Mill #1 indicate 93 percent of the organic halide transported to the benthal layer is dehalogenated. Based on an estimated accumulation rate at Mill #2, approximately 98 percent of the organic halide transported to the benthic layer will be dehalogenated. These results are similar to those conducted on an ASB at another Kraft mill facility. It can be concluded that microorganisms can effectively dehalogenate the chlorinated organic material transported to the benthic layer.

In an ASB, adsorption onto settling biomass is the necessary mechanism for transporting the organic halide to the benthic layer where it is effectively dehalogenated and degraded. The key to AOX removal is to optimize the transport mechanism by increasing the production of biomass. The formation of biomass is a function of the usable organic material entering the ASB with the AOX. This study has

demonstrated organic molecules with an AMW less than 1000 are preferentially removed across the ASB. Thus, increasing this fraction of organic material will likely increase the ASBs ability to remove AOX. Finally, optimizing ASB parameters such as temperature will enhance the adsorption process.

APPENDIX

RAW DATA FOR MILL #1 AND MILL #2

MILL #1 - RAW DATA
12-Dec-90

SUMMER SAMPLING
AUGUST-SEPTEMBER

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS	DOC (mg/L)						REPLICATE		
TYPE	SAMPLE ID	BULK	REPLICATE BULK	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	238.2	257.7	191.0	182.8	180.2	135.8	143.1	99.8
COMPOSITE	L2 INFLUENT	174.4	160.2	94.8	97.5	67.3	38.6	41.4	11.7
COMPOSITE	L2 EFFLUENT	156.6	164.1	89.3	82.2	56.8	32.9	35.1	7.5
GRAB	L1 INFLUENT	272.0							
GRAB	L2 INFLUENT	145.2							
GRAB	L2 EFFLUENT	165.1							

ANALYSIS	AOX (mg/L)						REPLICATE		
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	32.21*	32.82	26.04	24.02	21.80	14.49	14.23	5.12
COMPOSITE	L2 INFLUENT	25.04	25.46	12.44	12.10	9.04	4.88	4.64	1.46
COMPOSITE	L2 EFFLUENT	20.76	20.22	11.62	10.25	7.62	3.93	3.62	0.95
GRAB	L1 INFLUENT	31.96							
GRAB	L2 INFLUENT	15.04							
GRAB	L2 EFFLUENT	14.04							

* Average value from three of four data points

ANALYSIS	AOX/DOC						REPLICATE		
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	0.135	0.127	0.136	0.131	0.121	0.107	0.099	0.051
COMPOSITE	L2 INFLUENT	0.144	0.159	0.131	0.124	0.134	0.126	0.112	0.125
COMPOSITE	L2 EFFLUENT	0.133	0.123	0.130	0.125	0.134	0.119	0.103	0.126
GRAB	L1 INFLUENT	0.118							
GRAB	L2 INFLUENT	0.104							
GRAB	L2 EFFLUENT	0.085							

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS	DOC (mg/L)						REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	238.2	47.2	8.3	2.5	44.4	36.0	43.3	99.8
COMPOSITE	L2 INFLUENT	174.4	79.6	-2.7	30.2	28.7	26.9	29.7	11.7
COMPOSITE	L2 EFFLUENT	156.6	67.3	7.0	25.4	23.9	25.4	27.6	7.5

ANALYSIS	AOX (mg/L)						REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	32.21*	6.17	2.02	2.22	7.31	9.37	9.11	5.12
COMPOSITE	L2 INFLUENT	25.04	12.60	0.34	3.06	4.16	3.42	3.18	1.46
COMPOSITE	L2 EFFLUENT	20.76	9.14	1.37	2.63	3.69	2.98	2.67	0.95

* Average value from three of four data points

ANALYSIS	AOX/DOC						REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	0.135	0.131	0.245	0.881	0.165	0.260	0.210	0.051
COMPOSITE	L2 INFLUENT	0.144	0.158	-0.127	0.101	0.145	0.127	0.107	0.125
COMPOSITE	L2 EFFLUENT	0.133	0.136	0.195	0.104	0.154	0.117	0.097	0.126

ANALYSIS	DOC (mg/L)	
TYPE	SAMPLE ID	
I.W.	W. LAGOON	49.9
I.W.	CELL 1	69.8
I.W.	CELL 1 1K	28.6
I.W.	CELL 2	75.0
I.W.	CELL 2 1K	26.0

ANALYSIS	AOX (mg/L)	
TYPE	SAMPLE ID	
I.W.	W. LAGOON	4.00
I.W.	CELL 1	8.52
I.W.	CELL 1 1K	1.88
I.W.	CELL 2	5.28
I.W.	CELL 2 1K	1.55

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE intact	ETHYL ACETATE sonicated	OCTANOL intact	OCTANOL sonicated
SEDIMENT	W. LAGOON	19.70	19.90	0.76	7.85
SEDIMENT	CELL 1	644.65	185.70	68.45	102.80
SEDIMENT	CELL 2	702.10	299.10	90.75	140.65

* 5 minute extraction period

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	L1 INFLUENT	1836.0	-	-
GRAB	L2 INFLUENT	38.3	55.0	25.3 %
GRAB	L2 EFFLUENT	168.0	157.0	4.8 %

ANALYSIS POX (ug/L) **

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	L1 INFLUENT	1790.0	1725.0	2.6 %
GRAB	L2 INFLUENT	97.0	23.0	87 %
GRAB	L2 EFFLUENT	58.0	-	-

** Practical detection limit - 100 ug/L, due to the foaming characteristics of the water.

ANALYSIS Color (CU)

SAMPLE ID	COMPOSITE	GRAB
L1 INFLUENT	1900	2150
L2 INFLUENT	1900	1900
L2 EFFLUENT	1900	2250

MILL #1 - RAW DATA
12-Dec-90

FALL SAMPLING
NOVEMBER-DECEMBER

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	REPLICATE BULK	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	487.2	495.1	401.9	388.0	340.5	245.0	-	154.3
COMPOSITE	L2 INFLUENT	334.8	336.3	194.8	208.0	174.2	87.0	92.5	26.0
COMPOSITE	L2 EFFLUENT	330.0	330.0	177.9	171.1	165.4	68.3	63.1	13.3

ANALYSIS	AOX (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT*	28.58	30.24	-	-	-	-	-	-
COMPOSITE	L1 INFLUENT	27.18	28.40	21.36	17.43	12.99	7.77	-	3.46
COMPOSITE	L2 INFLUENT	22.22	-	14.19	12.88	10.17	4.88	2.93	1.06
COMPOSITE	L2 EFFLUENT	20.16	-	11.62	11.27	9.91	4.49	4.16	0.90

* Sample not filtered

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	0.056	0.057	0.053	0.045	0.038	0.032	-	0.022
COMPOSITE	L2 INFLUENT	0.066	-	0.073	0.062	0.058	0.056	0.032	0.041
COMPOSITE	L2 EFFLUENT	0.061	-	0.065	0.066	0.060	0.066	0.066	0.068

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	487.2	85.3	13.9	47.5	95.6	90.6	-	154.3
COMPOSITE	L2 INFLUENT	334.8	140.0	-13.2	33.8	87.2	61.1	66.5	26.0
COMPOSITE	L2 EFFLUENT	330.0	152.1	6.8	5.7	97.1	54.9	49.8	13.3

ANALYSIS	AOX (mg/L)						REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	27.18	5.82	3.93	4.44	5.22	4.31	-	3.46
COMPOSITE	L2 INFLUENT	22.22	8.03	1.31	2.71	5.29	3.82	1.87	1.06
COMPOSITE	L2 EFFLUENT	20.16	8.54	0.35	1.36	5.42	3.59	3.26	0.90

ANALYSIS	AOX/DOC						REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	0.056	0.068	0.283	0.093	0.055	0.048	-	0.022
COMPOSITE	L2 INFLUENT	0.066	0.057	-0.099	0.080	0.061	0.063	0.028	0.041
COMPOSITE	L2 EFFLUENT	0.061	0.056	0.051	0.239	0.056	0.065	0.065	0.068

ANALYSIS	DOC (mg/L)	
TYPE	SAMPLE ID	
I.W.	L2 INFLUENT	117.5
I.W.	L2 INFLUENT	134.0
I.W.	L2 EFFLUENT	149.3
I.W.	L2 EFFLUENT	204.4

ANALYSIS	AOX (mg/L)	
TYPE	SAMPLE ID	
I.W.	L2 INFLUEN	5.38
I.W.	L2 INFLUEN	5.78
I.W.	L2 EFFLUEN	6.18
I.W.	L2 EFFLUEN	11.02

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE intact	ETHYL ACETATE sonicated	OCTANOL intact	OCTANOL sonicated
SEDIMENT	L2 INFLUENT	257.4	88.2	73.0	56.9
SEDIMENT	L2 INFLUENT	296.2	114.1	76.8	51.2
SEDIMENT	L2 EFFLUENT	416.0	129.2	82.1	70.5
SEDIMENT	L2 EFFLUENT	350.0	116.1	69.0	85.6

* 5 minute extraction period

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	L1 INFLUENT	1752.2	-	-
GRAB	L2 INFLUENT	29.1	45.6	31.2 %
GRAB	L2 EFFLUENT	26.8	24.4	6.6 %

ANALYSIS Color (CU)

SAMPLE ID	COMPOSITE
L1 INFLUENT	2300
L2 INFLUENT	2200
L2 EFFLUENT	2200

MILL #1 - RAW DATA
12-Dec-90

WINTER SAMPLING (1-16-90)
JANUARY-FEBRUARY

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT*	264.5	-	-
COMPOSITE	L1 INFLUENT	254.2	180.0	112.9
COMPOSITE	L2 INFLUENT	150.0	123.2	45.2
COMPOSITE	L2 EFFLUENT	159.6	87.1	30.2

* Sample not filtered

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT*	36.20	-	-
COMPOSITE	L1 INFLUENT	33.04	22.60	10.18
COMPOSITE	L2 INFLUENT	26.04	15.32	4.27
COMPOSITE	L2 EFFLUENT	17.20	11.88	3.59

* Sample not filtered

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT	0.130	0.126	0.090
COMPOSITE	L2 INFLUENT	0.174	0.124	0.094
COMPOSITE	L2 EFFLUENT	0.108	0.136	0.119

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000
COMPOSITE	L1 INFLUENT	254.2	74.2	67.1
COMPOSITE	L2 INFLUENT	150.0	26.8	78.0
COMPOSITE	L2 EFFLUENT	159.6	72.5	56.9

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000
COMPOSITE	L1 INFLUENT	33.04	10.44	12.42
COMPOSITE	L2 INFLUENT	26.04	10.72	11.05
COMPOSITE	L2 EFFLUENT	17.20	5.32	8.29

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000
COMPOSITE	L1 INFLUENT	0.130	0.141	0.185
COMPOSITE	L2 INFLUENT	0.174	0.400	0.142
COMPOSITE	L2 EFFLUENT	0.108	0.073	0.146

ANALYSIS	DOC (mg/L)		ANALYSIS	AOX (mg/L)
TYPE	SAMPLE ID		TYPE	SAMPLE ID
I.W.	L2 INFLUENT	213.9	I.W.	L2 INFLUENT
I.W.	L2 INFL-1K	28.4	I.W.	L2 INFL-1K
I.W.	L2-EFFLUENT	167.8	I.W.	L2-EFFLUENT
I.W.	L2-EFFL-1K	26.5	I.W.	L2-EFFL-1K

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE intact	ETHYL ACETATE (dup)	ETHYL ACETATE lysed **
SEDIMENT	L2 INFLUENT	1001.6	956.4	940.0
SEDIMENT	L2 EFFLUENT	738.5	-	837.1

* 24 hour extraction period
** DSMO present during extraction

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	c.v. *
GRAB	L1 INFLUENT	799.0	3.99
GRAB	L2 INFLUENT	29.1	4.60
GRAB	L2 EFFLUENT	210.6	10.1

* Duplication between injections

MILL #1 - RAW DATA
12-Dec-90

WINTER SAMPLING (1-30-90)
JANUARY-FEBRUARY

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT*	308.7	-	-
COMPOSITE	L1 INFLUENT	275.4	206.4	150.6
COMPOSITE	L2 INFLUENT	154.5	100.6	47.8
COMPOSITE	L2 EFFLUENT	139.9	90.0	31.6
GRAB	ACID*	222.2	-	-
GRAB	ACID	209.5	192.6	141.1
GRAB	CAUSTIC*	418.0	-	-
GRAB	CAUSTIC	393.2	259.7	191.9

* Sample not filtered

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT*	37.80	-	-
COMPOSITE	L1 INFLUENT	39.56	30.28	17.15
COMPOSITE	L2 INFLUENT	16.51	13.02	4.58
COMPOSITE	L2 EFFLUENT	20.01	8.74	4.48
GRAB	ACID*	53.64	-	-
GRAB	ACID	53.08	47.20	30.76
GRAB	CAUSTIC*	26.18	-	-
GRAB	CAUSTIC	27.12	14.94	5.11

* Sample not filtered

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	30,000	1,000
COMPOSITE	L1 INFLUENT	0.144	0.147	0.114
COMPOSITE	L2 INFLUENT	0.107	0.129	0.096
COMPOSITE	L2 EFFLUENT	0.143	0.097	0.142
GRAB	ACID	0.253	0.245	0.218
GRAB	CAUSTIC	0.069	0.058	0.027

DESCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000	< 1,000
COMPOSITE	L1 INFLUENT	275.4	69.0	55.8	150.6
COMPOSITE	L2 INFLUENT	154.5	54.0	52.8	47.8
COMPOSITE	L2 EFFLUENT	139.9	49.9	58.4	31.6
GRAB	ACID	209.5	16.8	51.5	141.1
GRAB	CAUSTIC	393.2	133.5	67.8	191.9

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000	< 1,000
COMPOSITE	L1 INFLUENT	39.56	9.28	13.13	17.15
COMPOSITE	L2 INFLUENT	16.51	3.49	8.44	4.58
COMPOSITE	L2 EFFLUENT	20.01	11.27	4.26	4.48
GRAB	ACID	53.08	5.88	16.44	30.76
GRAB	CAUSTIC	27.12	12.18	9.83	5.11

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	> 30,000	1,000-30,000	< 1,000
COMPOSITE	L1 INFLUENT	0.144	0.135	0.235	0.114
COMPOSITE	L2 INFLUENT	0.107	0.065	0.160	0.096
COMPOSITE	L2 EFFLUENT	0.143	0.226	0.073	0.142
GRAB	ACID	0.253	0.349	0.319	0.218
GRAB	CAUSTIC	0.069	0.091	0.145	0.027

MILL #1 - RAW DATA
12-Dec-90

SPRING SAMPLING
APRIL-MAY

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	REPLICATE BULK	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	198.8	199.2	135.0	138.9	121.4	97.9	61.0	78.4
COMPOSITE	L2 INFLUENT	174.4	173.8	83.7	88.7	65.1	32.1	30.7	15.5
COMPOSITE	L2 EFFLUENT	156.5	157.1	93.6	79.6	61.0	28.6	25.9	12.0

ANALYSIS	AOX (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	24.44	24.20	16.00	14.95	10.39	7.30	6.80	4.88
COMPOSITE	L2 INFLUENT	22.64	21.80	12.22	12.89	8.18	3.99	3.76	2.00
COMPOSITE	L2 EFFLUENT	21.74	21.98	13.10	8.85	7.84	3.97	3.30	1.87

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
COMPOSITE	L1 INFLUENT	0.123	0.121	0.119	0.108	0.086	0.075	0.111	0.062
COMPOSITE	L2 INFLUENT	0.130	0.125	0.146	0.145	0.126	0.124	0.122	0.129
COMPOSITE	L2 EFFLUENT	0.139	0.140	0.140	0.111	0.129	0.139	0.127	0.156

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	198.8	63.9	-4.0	17.5	23.5	19.5	-17.3	78.4
COMPOSITE	L2 INFLUENT	174.4	90.7	-5.0	23.5	33.1	16.6	15.2	15.5
COMPOSITE	L2 EFFLUENT	156.5	62.9	14.0	18.6	32.5	16.6	14.0	12.0

ANALYSIS AOX (mg/L) REPLICATE

TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	24.44	8.44	1.05	4.56	3.09	2.42	1.92	4.88
COMPOSITE	L2 INFLUENT	22.64	10.42	-0.67	4.71	4.19	1.99	1.76	2.00
COMPOSITE	L2 EFFLUENT	21.74	8.64	4.25	1.01	3.87	2.10	1.43	1.87

ANALYSIS AOX/DOC REPLICATE

TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,000	1-5,000	500-1,000	500-1,000	500
COMPOSITE	L1 INFLUENT	0.123	0.132	-0.266	0.261	0.131	0.124	-0.111	0.062
COMPOSITE	L2 INFLUENT	0.130	0.115	0.135	0.200	0.127	0.120	0.115	0.129
COMPOSITE	L2 EFFLUENT	0.139	0.137	0.304	0.054	0.119	0.126	0.102	0.156

ANALYSIS DOC (ug/L)

TYPE	SAMPLE ID	
I.W.	L2 INFLUENT	186.4
I.W.	L2 INFL-1K	23.2
I.W.	L2 EFFLUENT	92.5
I.W.	L2 EFFL-1K	17.5

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	
I.W.	L2 INFLUEN	14.17
I.W.	L2 INFL-1K	4.63
I.W.	L2 EFFLUEN	9.69
I.W.	L2 EFFL-1K	0.93

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE intact	ETHYL ACETATE (dup)	ETHYL ACETATE lysed	ETHYL ACETATE (dup)
SEDIMENT	L2 INFLUENT	1045.5	-	1043.6	-
SEDIMENT	L2 EFFLUENT	725.7	730.9	778.1	796.8

* 24 hour extraction period

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	L1 INFLUENT	1802.0	1390	18.25 %
GRAB	L2 INFLUENT	24.5	24.0	1.46 %
GRAB	L2 EFFLUENT	19.3	19.5	0.73 %

MILL #2
RAW DATA - Sample-1
PRIOR TO BLEACHING MODIFICATIONS
12-Dec-90

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	REPLICATE BULK	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	250.9	-	239.6	236.8	164.4	161.5	197.6	144.2
GRAB	2, WC	210.0	-	184.5	250.0	69.6	67.5	62.9	26.9
GRAB	3, WC	223.0	-	191.7	171.8	67.6	54.2	62.9	20.6
GRAB	4, WC	217.7	-	183.8	163.5	86.6	60.6	70.2	17.2
COMPOSITE	INFLUENT	283.1	240.1						
COMPOSITE	EFFLUENT	197.0	179.7						
GRAB	WET WELL	427.1					194.7		
GRAB	ACID SEWER	507.1					369.3		

ANALYSIS	AOX (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	14.66		13.43	12.96	4.89	6.53	6.84	4.88
GRAB	2, WC	11.94		10.60	11.78	3.57	3.14	3.26	2.64
GRAB	3, WC	12.07		10.62	9.15	3.24	2.11	2.28	1.23
GRAB	4, WC	11.96		10.18	7.20	3.99	2.43	2.79	1.07
COMPOSITE	INFLUENT *	15.18							
COMPOSITE	INFLUENT	15.50							
COMPOSITE	EFFLUENT *	12.62							
COMPOSITE	EFFLUENT	10.30							
GRAB	WET WELL	16.68					5.19		
GRAB	ACID SEWER	92.25					41.25		

* Sample not filtered

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	0.058	-	0.056	0.055	0.030	0.040	0.035	0.034
GRAB	2, WC	0.057	-	0.057	0.047	0.051	0.047	0.052	0.098
GRAB	3, WC	0.054	-	0.055	0.053	0.048	0.039	0.036	0.060
GRAB	4, WC	0.055	-	0.055	0.044	0.046	0.040	0.040	0.062
COMPOSITE	INFLUENT	0.054	-						
COMPOSITE	EFFLUENT	0.064	-						
GRAB	WET WELL	0.039	-				0.027		
GRAB	ACID SEWER	0.182	-				0.112		

* Sample not filtered

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	250.9	11.3	2.8	72.4	2.9	17.3	53.4	144.2
GRAB	2, WC	210.0	25.5	-65.5	180.4	2.1	40.6	36.0	26.9
GRAB	3, WC	223.0	31.3	19.9	104.2	13.4	33.6	42.3	20.6
GRAB	4, WC	217.7	33.9	20.3	76.9	26.0	43.4	53.0	17.2

ANALYSIS	AOX (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	14.66	1.23	0.47	8.07	-1.64	1.65	1.96	4.88
GRAB	2, WC	11.94	1.34	-1.18	8.21	0.43	0.50	0.62	2.64
GRAB	3, WC	12.07	1.45	1.47	5.91	1.13	0.88	1.05	1.23
GRAB	4, WC	11.96	1.78	2.98	3.21	1.56	1.36	1.72	1.07

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	0.058	0.109	0.168	0.111	-0.566	0.095	0.037	0.034
GRAB	2, WC	0.057	0.053	0.018	0.046	0.205	0.012	0.017	0.098
GRAB	3, WC	0.054	0.046	0.074	0.057	0.085	0.026	0.025	0.060
GRAB	4, WC	0.055	0.053	0.147	0.042	0.060	0.031	0.032	0.062

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	152.5	43.5
I.W.	3T 15'	112.1	-
I.W.	4T 16'	176.3	24.8

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	5.08	1.22
I.W.	3T 15'	2.80	-
I.W.	4T 16'	3.42	0.85

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	0.033	0.028
I.W.	3T 15'	0.025	-
I.W.	4T 16'	0.019	0.034

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE	Replicate	OCTONAL	Replicate
SEDIMENT	2T 13'	1040.5	-	353.1	-
SEDIMENT	3T 15'	878.0	-	536.8	-
SEDIMENT	4T 16'	846.8	840.7	272.6	342.5

* 24 hour extraction period

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	1, WC	578.0	612.0	4.04 %
GRAB	3, WC	ND	ND	-
GRAB	4, WC	ND	ND	-

ANALYSIS Color (CU)

TYPE	SAMPLE ID	BULK
GRAB	1, WC SURFACE	1500
GRAB	2, WC	1250
GRAB	3, WC	1250
GRAB	4, WC	1100
COMPOSITE	INFLUENT	1100
COMPOSITE	INFLUENT	1600

MILL #2
RAW DATA - Sample-2
AFTER BLEACHING MODIFICATIONS
12-Dec-90

AVERAGE MOLECULAR WEIGHT PROFILE

ANALYSIS	DOC (mg/L)							REPLICATE	
			REPLICATE						
TYPE	SAMPLE ID	BULK	BULK	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	473.2		443.7	403.5	374.8	304.5	290.0	275.1
GRAB	2, WC	255.6		190.8	160.5	143.9	73.9	65.5	31.9
GRAB	3, WC	282.7		175.5	159.4	135.5	50.2	53.5	30.1
GRAB	4, WC	224.7		160.9	154.6	125.6	59.4	55.5	28.1
COMPOSITE	INFLUENT *	385.4							
COMPOSITE	INFLUENT	401.9					216.0		
COMPOSITE	EFFLUENT *	254.0							
COMPOSITE	EFFLUENT	271.5					54.0		

* Sampled not filtered

ANALYSIS	AOX (mg/L)							REPLICATE	
			BULK						
TYPE	SAMPLE ID	BULK	REPLICATE	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	8.82		8.16	6.57	5.68	3.81	3.40	3.37
GRAB	2, WC	5.85		4.60	3.71	2.87	1.32	1.30	0.81
GRAB	3, WC	5.02		3.80	3.72	3.33	1.00	0.96	0.96
GRAB	4, WC	5.64		3.70	3.28	2.38	1.06	0.96	0.68
COMPOSITE	INFLUENT *	9.96							
COMPOSITE	INFLUENT	10.14							
COMPOSITE	EFFLUENT *	5.44							
COMPOSITE	EFFLUENT	5.24							
							0.98		

* Sample not filtered

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	BULK REPLICATE	30,000	10,000	5,000	1,000	1,000	500
GRAB	1, WC SURFACE	0.019	-	0.018	0.016	0.015	0.013	0.012	0.012
GRAB	2, WC	0.023	-	0.024	0.023	0.020	0.018	0.020	0.025
GRAB	3, WC	0.018	-	0.022	0.023	0.025	0.020	0.018	0.032
GRAB	4, WC	0.025	-	0.023	0.021	0.019	0.018	0.017	0.024
COMPOSITE	INFLUENT *	0.026	-						
COMPOSITE	INFLUENT	0.025	-						
COMPOSITE	EFFLUENT *	0.021	-						
COMPOSITE	EFFLUENT	0.019	-						

* Sample not filtered

DISCRETE MOLECULAR WEIGHT FRACTIONS

ANALYSIS	DOC (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	473.2	29.5	40.2	28.7	70.3	29.4	14.9	275.1
GRAB	2, WC	255.6	64.8	30.3	16.6	70.0	42.0	33.7	31.9
GRAB	3, WC	282.7	107.2	16.1	23.9	85.3	20.2	23.4	30.1
GRAB	4, WC	224.7	63.8	6.3	29.0	66.2	31.2	27.4	28.1

ANALYSIS	AOX (mg/L)							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	8.82	0.66	1.59	0.89	1.87	0.44	0.03	3.37
GRAB	2, WC	5.85	1.25	0.89	0.84	1.55	0.51	0.49	0.81
GRAB	3, WC	5.02	1.22	0.08	0.39	2.33	0.04	0.00	0.96
GRAB	4, WC	5.64	1.94	0.42	0.90	1.32	0.38	0.28	0.68

ANALYSIS	AOX/DOC							REPLICATE	
TYPE	SAMPLE ID	BULK	> 30,00	10-30,000	5-10,00	1-5,000	500-1,000	500-1,000	500
GRAB	1, WC SURFACE	0.019	0.022	0.040	0.031	0.027	0.015	0.002	0.012
GRAB	2, WC	0.023	0.019	0.029	0.051	0.022	0.012	0.015	0.025
GRAB	3, WC	0.018	0.011	0.005	0.016	0.027	0.002	0.000	0.032
GRAB	4, WC	0.025	0.030	0.067	0.031	0.020	0.012	0.010	0.024

ANALYSIS DOC (mg/L)

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	218.8	51.3
I.W.	3T 15'	NA	36.9
I.W.	4T 16'	NA	38.1

ANALYSIS AOX (mg/L)

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	5.30	1.22
I.W.	3T 15'	5.60	1.07
I.W.	4T 16'	11.85	1.10

NA - Not analyzed due to formation of precipitate

ANALYSIS AOX/DOC

TYPE	SAMPLE ID	BULK	1,000
I.W.	2T 13'	0.024	0.024
I.W.	3T 15'	-	0.029
I.W.	4T 16'	-	0.029

ANALYSIS EOX (ug/g) *

TYPE	SAMPLE ID	ETHYL ACETATE	Replicate	OCTANOL	Replicate
SEDIMENT	2T 13'	828.1	816.3	463.4	374.3
SEDIMENT	3T 15'	1013.3		650.2	
SEDIMENT	4T 16'	471.7		397.5	

* 24 hour extraction period

ANALYSIS Chloroform (ug/L)

TYPE	SAMPLE ID	BULK	REPLICATE BULK	c.v.
GRAB	1, WC	78.0	73.0	4.68 %
GRAB	3, WC	ND	ND	-
GRAB	4, WC	ND	ND	-

ND - None detected

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. 134-138.

3. Bjorseth, A., Carlberg, G., and Moller, M., "Determination of Halogenated Organic Compounds and Mutagenicity Testing of Spent Bleach Liquors." The Science of the Total Environment 11, 1979 pp. 197-211.

4. Walden, C. C., and Howard, T. E., "Toxicity of Pulp and Paper Mill Effluents." TAPPI Journal Vol. 60, No. 1, January 1977 pp.122-125.

5. Carlberg, G. E., Drangsholt, H., and Gjos, N., "Identification of Chlorinated Compounds in the Spent Chlorination Liquor From Differently Treated Sulphite Pulps With Special Emphasis on Mutagenic Compounds." The Science of the Total Environment 48, 1986 pp. 157-167.

6. Leuenberger, C., Giber, W., Coney, R., Graydon, J. W., and Monlar-Kubica, E., "Persistent Chemicals in Pulp Mill Effluents: Occurrence and Behaviour in an activated Sludge Treatment Plant." Water Resources Vol. 19, No. 7 1985 pp. 885-894.

7. Bryant, C., Amy, G., Neill, R., and Ahmand, S., "Partitioning of Organic Chlorine Between Bulk Water and Benthal Interstitial Water Through A Kraft Mill Aerated Lagoon." Water Science and Technology Vol. 20, No. 1, 1988 pp. 73-79.

8. 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.

9. Alleman, B. C., "Molecular Weight Distributions of Total Organic Halide in Aerated Stabilization Basin Treating Paper and Pulp Wastewater." MS. Thesis, University of Arizona, 1986.

10. Logan, B. E., and Jiang, Q., "Molecular Size Distributions of Dissolved Organic Matter." Journal of Environmental Engineering, Vol. 116, No. 6, 1990.

11. Bryant, C., Amy, G., and Alleman, B., "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.

12. 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.

13. Grimes, D. J., and Morrison, S. M., "Bacterial Bioconcentration of Chlorinated Hydrocarbon Insecticides from Aqueous Systems." Microbial Ecology Vol. 2 1975 pp. 43-59.

14. 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.

15. Bell, J., 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.

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

17. 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.

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

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

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

21. Suflita, J., Horowitz, A., Shelton, D., and Tiedje, J., "Dehalogenation: A Novel Pathway for the Anaerobic Biodegradation of Haloaromatic Compounds." Science Vol. 218, December 10, 1982 pp. 1115-1117.

22. Pitter, P., "Determination of Biological Degradability of Organic Substances." Water Resources Vol. 10 1976 pp. 231-235.

23. Heimburger, S., Blevins, D., Bostwick, J., and Donnini, G., "Kraft Mill Bleach Plant Effluents: Recent Developments Aimed at Decreasing Their Environmental Impact, Part 1." TAPPI Journal October 1988, pp. 51-59.

24. Personal communication with Dr. Gary Amy, The University of Arizona, 1990.

25. McClellan, A. L., "Tables of Experimental Dipole Moments Volume 2." Chevron Research Company, Rahara Enterprises.

26. "CRC Handbook of Chemistry and Physics", 62nd Edition, CRC press, Inc. 1981-1982.