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ANAEROBIC TREATMENT OF KRAFT MILL BLEACH PLANT WASTEWATERS:

PROGRESS REPORT

WTC-BIO-05-1988

REVIEW NOTICE

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A Report By

Environment Canada Conservation and Protection Wastewater Technology Centre

September 1988

Report WTC-BIO-05-1988

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PROGRESS REPORT

Environment Canada Wastewater Technology Centre Burlington, Ontario, Canada

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BACKGROUND

1

Between 1969 and 1980, expenditures by the Canadian pulp and paper industry for pollution abatement amounted to about C\$ 661 million (1). As a result of these measures, in 1980, 72% of Canadian production was in compliance with federal regulations governing the discharge of BOD (biochemical oxygen demand) in liquid effluents. However, at the same time, only 25% of Canadian mills were in compliance with the federal toxicity requirement. There has been considerable change in the Canadian pulp and paper industry over the last one or two decades to improve the compliance status of Canadian mills. These changes have involved the installation of ex-plant wastewater treatment facilities as well as the improvement of manufacturing practices to reduce the quantity and frequency of discharges from pulping operations (2)

In the kraft pulping sector, the recovery of cooking chemical from black liquor greatly reduces the potential loading of organic material from pulping operations. However, the condensates produced in kraft thermal recovery plants can represent a significant residual source of pollution. Pulp washing also generates a high BOD effluent that is usually sewered. Perhaps the most problematic wastewaters originating in kraft mills are the effluents from bleaching operations. These streams are often of relatively high organic concentration, and are known to contain high levels of colour and toxicity (2,3). Recently, several new approaches to pulp bleaching have been developed to reduce the BOD and toxicity loading associated with conventional chlorine bleaching (2).

As a whole, the Canadian pulp and paper industry has invested considerable resources to make in-plant changes and to construct ex-plant treatment facilities to meet the federal pulp and paper effluent regulations. In spite of this investment, the current levels of compliance are still not acceptable. In the kraft industry, many of the remaining BOD and toxicity problems are associated with high strength effluents from pulp washing, liquor recovery and bleaching. In order to improve upon current compliance levels in the Canadian pulp and paper industry, programs for the development and demonstration of treatment processes for high strength, toxic waste streams are required.

1.1 Anaerobic Treatment of Pulp and Paper Wastewaters

The requirement for cost-effective treatment of concentrated organic wastewaters leads logically to the consideration of anaerobic biological technology as a primary treatment option. Several advantages of anaerobic treatment over conventional aerobic treatment are summarized in Table 1. These advantages have already been recognized in many other countries where active anaerobic research and development programs for pulp and paper applications have been underway for some time (4). In a small number of cases, this development activity has resulted in the construction and start-up of full scale facilities which

incorporate anaerobic treatment technology. These advantages have also been recognized in Canada, where several pilot scale and full scale development projects are currently in progress (Table 2).

Table 1. Advantages of Anaerobic Treatment Technology

. Reduced Capital Cost for High Rate Anaerobic Treatment

- . No Power Requirement for Aeration
- . Reduced Biosludge Production
- . Reduced Nutrient Requirements for Biological Treatment
- . Fuel Grade Biogas Produced as Bioproduct
- . Reductive Dehalogenation of Organochlorines

Table 2. Canadian Pilot and Full Scale Scale Studies, August, 1988.

STURGEON FALLS, ONTARIO (NSSC & Hardboard)

 Negotiations for full scale plant in progress

 BATHURST, NEW BRUNSWICK (CTMP & NSSC)

 Full Scale UASB system under construction

 ST. GEORGE, N.B. (NSSC)

 Full Scale UASB system under construction

 MISSISSAUGA, ONTARIO

 UASB pilot study

 KAPUSKASING, ONTARIO (TMP & Magnefite)

 Hybrid reactor pilot study
 QUESNEL RIVER, B.C. (CTMP & TMP)

 Full scale UASB under construction

 PORT ALICE, B.C. (Bleached Sulfite)

 Hybrid reactor pilot study under development

1.2 Status of Research

Research and demonstration work carried out in Canada and other countries has confirmed the potential for anaerobic treatment of pulp and paper wastewaters. However, considerable additional information is required to insure that further Canadian development activities will result in cost-effective treatment technology that can significantly increase the effluent compliance status of pulp and paper mills. Some of the major points to be considered are indicated below.

1. Data from laboratory screening studies confirms the potential of anaerobic treatment technology for a variety

of pulp and paper wastewaters, including many of those currently exceeding Canadian compliance levels.

- 2. Available data also indicate that anaerobic treatment may be associated with problematic phenomena such as inhibition of anaerobic microorganisms, sulfide production, precipitation or adsorption of organics under anaerobic conditions, and the presence of residual COD and toxic material.
- 3. Although a number of anaerobic pilot scale studies are in the planning or operational stages, the majority of the data available at the present time deal with wastewaters from semichemical and CTMP pulping. Studies of many of the other high strength and toxic effluents in the pulp and paper industry have not been undertaken.
- 4. Data on the chemical constituents, sources of toxicity, and treatability of high yield pulping effluents is very limited.
- 5. Almost no information is available on toxicity reduction or generation during anaerobic treatment. Limited experience from Scandinavia suggests an advantage for anaerobic detoxification of chlorination effluents.
- 6. The anaerobic treatability characteristics of nonconventional pulp bleaching effluents have not been determined. Innovative bleaching sequences may produce less toxic, more easily biodegradable wastewaters.
- 7. Although it is generally assumed that aerobic posttreatment will be required to produce non-toxic effluents, design data for integrated anaerobic-aerobic systems do not exist.
- 8. Information is not available to confirm that anaerobic + aerobic treatment is more cost-effective for high strength, toxic pulp and paper effluents than aerobic treatment alone.

2 OBJECTIVES

The overall goal of Environment Canada's anaerobic program is to develop and demonstrate technically-effective, least-cost treatment systems for the high strength wastewaters produced by existing and emerging pulp and paper manufacturing processes. To be considered technically satisfactory, these treatment approaches must result in compliance with federal and provincial effluent regulations for the pulp and paper industry. For wastewaters produced in kraft mill bleach plants the program objectives are:

1. To produce chemical characterization data on the

conventional and toxic constituents of wastewaters from kraft mills using different bleaching sequences, and to determine the toxicity of the wastewaters using a variety of bioassay procedures.

- 2. To compare the effluent characteristics and loadings from bleach plants utilizing conventional bleaching, to those from bleach plants which incorporate oxygen delignification, or substantial chlorine dioxide substitution.
- 3. Determine the ability of an anaerobic system to tolerate or adapt to the inhibitory characteristics of the selected wastewaters.
- 4. Determine the comparative anaerobic treatability characteristics of effluents from non-conventional bleaching sequences.
- 5. Determine the fate of toxic wastewater components during anaerobic treatment.
- 6. Determine the levels and types of toxicity produced during anaerobic treatment, ie sulfide, ammonia, biosolids, etc.
- 7. Determine criteria for selecting and blending specific waste streams from kraft mills to facilitate anaerobic treatment and detoxification of the final effluent.
- 8. Determine co-treatment and post-treatment design requirements to ensure compliance with BOD, SS and toxicity regulations.

The following material summarizes the interim results from experimental work carried out under objectives 1 and 2 above.

3 MATERIALS AND METHODS

3

3.1 Sample Collection, Preservation and Storage

Water and pulp samples were collected over single, 6-8 hour shifts during periods of normal operation of the bleach plants on softwood pulp. At one mill, samples were also collected from a parallel plant that was bleaching hardwood pulp. Each sample was obtained by compositing 3 equal manually collected grap samples taken over the 6-8 hour period. The composite samples were then split and preserved as required for specific chemical analyses or toxicity testing as noted below.

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Samples that were collected for the more routine or common wastewater analyses were preserved using standard Wastewater Technology Centre (WTC) procedures (5). For resin and fatty acid measurements, split samples were transported and stored unpreserved, in 1 litre glass bottles. Water samples for adsorbable organic halogen (AOX) were collected in 250 ml glass bottles. For most AOX samples, 1.0 ml of 0.1 N Na₂SO₃ was added to each bottle before the sample was taken. The amount of Na₂SO₂ added was determined from measurements of the residual chlorine The contents were acidified to pH 2 levels in the samples. with nitric acid after sample collection was completed. For chlorination stage filtrates, 4.0 ml of the Na₂SO₃ solution was added. Volatile chlorinated organics were determined in samples that were collected in headspace-free 40 ml septum bottles. Toxicity testing was done on 1 litre unpreserved samples transported in glass bottles. Samples of brownstock and bleached pulp were collected and shipped in 5 litre glass bottles. A11 samples were transported to the WTC in Burlington, Ontario, or, to the toxicity testing laboratory in Brampton, Ontario, within 24 hours of collection. Upon arrival at the laboratory, samples were stored for 1 or 2 days at 4°C while they were prepared for analysis. Samples requiring longer term storage prior to testing or analysis, were frozen and stored at -10⁰C.

3.2 Routine Analytical Procedures

Unless otherwise noted below, all chemical analyses were conducted using standard WTC procedures (5). Total sulfur , concentrations were measured with a combustion/titration procedure using a Leco Furnace. Inorganic sulfur compounds were determined using ion chromatography with a conductivity detector. Carbohydrates were measured by a colorimetric method employing phenol and sulfuric acid/hydrazine sulfate. The resulting complex was read at 4900 A. For lignin, TAPPI Standard T13 method was used without the solvent extraction step. Hydrolysis with 73% H_2SO_4 was followed by gravimetric quantification. Chloride concentrations were determined by single column ion chromatography with a conductivity detector using a 5 mM p-Chlorate was measured in a similar hydroxybenzoic acid eluant. fashion but with a 0.5 mM KOH eluant. Extractives were estimated by extraction of an acidified sample with Freon (1,1,2,trichloro-1,2,2-trifluoroethane) followed by gravimetric

quantification (6).

Resin and fatty acid concentrations were measured by a modification of the method described by Voss and Rapsomatiotis (7). Samples, at pH 9, were partitioned with methyl t-butyl ether, dried, and derivatized with diazomethane. Derivatized compounds were then analyzed by gas chromatography with a flame ionization detector. The resin and fatty acids reported were: linoleic, oleic, pimaric, sandaracopimaric, o-methylpodocarpic, isopimaric, palustric, dehydroabietic, abietic, neoabietic, 12chlorodehydroabietic and 14-chlorodehydroabietic, and 12,14,dichlorodehydroabietic. This method is currently under investigation by the Ontario Ministry of the Environment for monitoring of resin and fatty acids levels in pulp and paper wastewaters.

Chloroform and carbon tetrachloride were analyzed by purging the samples with helium and adsorbing the volatile components onto a tenax trap. The volatiles were thermally desorbed and injected onto a GC column in a Varian 3700 gas chromatagraph with an electron capture detector.

3.3 Measurement of Organic Halogen

Halogenated organic compounds were measured by two techniques. The first method is capable of measuring combined organic halides (chlorine, bromine and iodine) in waters and wastewaters. Fluorine-containing species are not determined by For analysis, up to 50 ml of an acidified sample this method. was passed under pressure through a granular activated carbon column at a prescribed flowrate of 3-4 mL per minute. The column was then washed with nitrate solution (5 g NO_3^{-}/L) to remove trapped inorganic halides. The activated carbon containing the adsorbed organic halides was then combusted and the resulting HX gas generated was trapped in acetic acid and titrated The estimated organic halogen is referred microcoulometrically. to as "adsorbable organic halogen", AOX. The adsorption and combustion/titration (DX-20) equipment were manufactured by Dohrmann.

Neutron activation analysis (NAA) was used as an alternative for the specific measurement of organic chlorine. An appropriate aliquot of a well mixed, properly preserved sample, of up to 30 ml in volume, was poured into a pyrex culture tube containing 80 mg granular activated carbon. The tube was capped and placed on a shaker for one hour. The contents were then filtered, washed with nitrate solution, and placed in a scintillation vial. The content of organic chlorine was then determined with neutron activation analysis. Since chlorine was expected to be the dominant halogen appearing in pulp and paper samples, the adsorbable organic chlorine, AOCl, determined by neutron activation, should be very similar to the AOX determined by combustion/titration.

The organochlorine content of pulp samples was analyzed by a combination of the two techniques. An aliquot of wet pulp was filtered and washed with nitrate solution. The AOX content of the liquid filtrate and the nitrate washings was then determined using the combustion/titration method. The washed

pulp was placed in a scintillation vial, and the AOCl content of the pulp solids was measured by neutron activation analysis.

Detailed descriptions of the two methods for halogenated organics are presented in Appendix A. Both methods are currently under investigation by Environment Canada for application to pulp and paper wastewaters.

3.4 Toxicity and Mutagenicity Testing

Wastewater aquatic toxicity was determined by Beak Consultants Ltd. with a standardized acute lethality toxicity testing protocol (8) using <u>Daphnia magna</u>. Several microbial toxicity and mutagenicity tests were conducted by the National Water Research Institute (NWRI) in Burlington. Brief descriptions of the NWRI protocols used are contained in Appendix A.

4 RESULTS AND DISCUSSION

4.1 Comparison of AOX Methods

During the preliminary stages of this study, two different methods were used for the measurement of the organochlorine content of wastewater samples. Figure 1 summarizes the results obtained with both methods for approximately 25 different samples collected from kraft bleach plant streams and from combined kraft mill effluent sewers. Each sample was analyzed by both combustion/titration and by neutron A data point shown in Figure 1 represents the activation. resulting AOX concentration obtained by each method for a specific wastewater sample. Replicate analyses completed on all of the samples are also included in the data presented in Figure 1.

When both analytical techniques produced identical measurements of the AOX concentrations, the resulting point was located on the diagonal of Figure 1. Any systematic deviation from the diagonal represents consistent over- or under-prediction by one of the techniques. In both the high and low concentration ranges, the AOX concentrations determined by both methods showed excellent agreement. The random distribution of the data about the diagonals indicates that this agreement was consistent over a range of sample types and concentrations between 0.8 and 279 mg AOX/L.

Table 3 further compares the two methods by presenting the relative deviations, or coefficients of variation, at high and low AOX concentrations. In this case the same sample was analyzed 20 times with one of the methods and the reproducibility was reported as a coefficient of variation. The variability of the neutron activation technique appeared to be slightly greater than that of the combustion/titration method. However, both methods were considered to be satisfactory since, in all cases, the coefficients of variation were less than 8%.

| Measurement Technique | N | AOX Mean (mg/L) | Concentration Coefficient of Variation (%) |
|-----------------------|----|-----------------------|--|
| Combustion/Titration | 20 | 11.0 | 2.85 |
| Combustion/Titration | 20 | 209.3 | 3.22 |
| Neutron Activation | 20 | 15.4 | 4.32 |
| Neutron Activation | 20 | 178.5 | 7.40 |
| | | | |

Table 3. Reproducibility of AOX Measurement Techniques

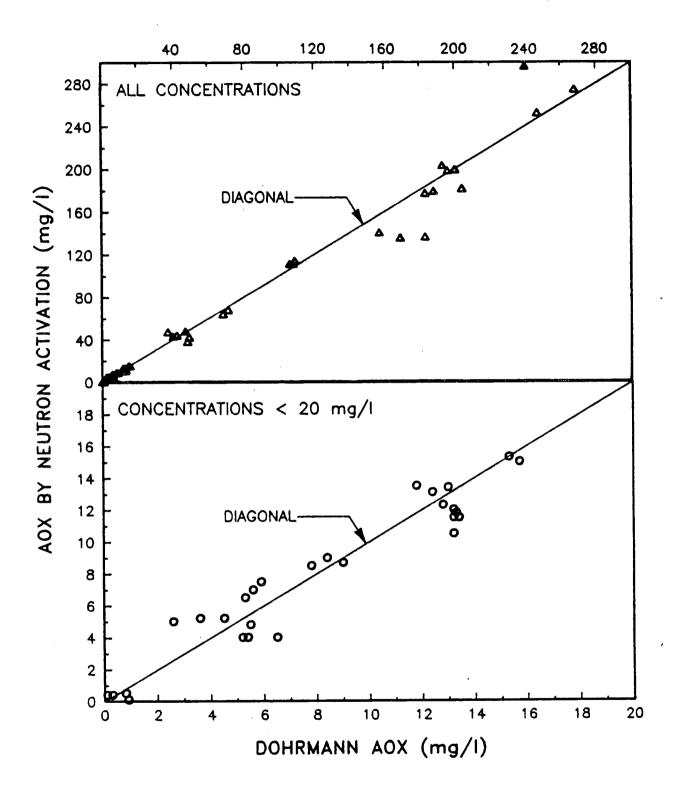


Figure 1. Comparison of Adsorbable Organic Halogen (AOX) determined by combustion/titration (Dohrmann) and neutron activation.

4.2 Bleach Plant Descriptions

Wastewater samples were collected from several process streams within four kraft mill bleach plants (Table 4). With the exception of plant "D", all mills were pulping softwood at the time of sampling, and in the opinion of mill personnel, were operating under normal conditions (Table 5).

Table 4. Characteristics of Bleach Plants

Plant "A": C/D Eo H E2 D , Spruce and Jack Pine Plant "B": D/C Eo D1 E2 D2 , Jack Pine (80%), Spruce (20%) Plant "C": O, C/D Eo H D , Mixed Softwood Plant "D": O, C/D Eo H D , Hardwood

Table 5. Selected Bleach Plant Operating Parameters

| Parameter* | Α | Bleac B | D | |
|--|-------------|------------|-------------|-------------|
| Incoming K Number Chlorine Charge | 23.5 | 19 32,3 | 11.1 | 8.4 |
| Chlorine Dioxide Charge Hypochlorite Charge | 20.2 3.7 | 44.8 | 15.7 2.9 | 13.8 4.1 |

* Chemical charges expressed as equivalent chlorine (kg/adt).

The specific bleach plants sampled were selected to generate wastewater characterization and anaerobic treatability data for a range of available bleaching technologies. Bleach plant "A" most closely resembled a conventional chemical bleach plant, with 7% ClO₂ substitution in the chlorination stage. Bleach plant "B" utilized 50% ClO₂ substitution. Plants "C" and "D" used oxygen delignification followed by bleaching lines with 10% and 20% ClO₂ substitution respectively. The latter two plants also provided an opportunity to compare data for the bleaching of hardwood and softwood pulps under similar process conditions.

4.3 Wastewater Chemical Characteristics

Within any one bleach plant, samples were taken from several interstage process streams, from incoming make-up water

sources, from all sewered wastewater streams, and at the request of one mill, from the influent and effluent of the biological Samples of brownstock and bleached stock were treatment plant. Although the objective of the program was to also collected. obtain data for the sewered bleach plant wastewaters only, the additional samples were taken to determine whether the wastewater contaminants of interest originated inside or outside of the bleach plant. Bleached pulp samples were collected to assess the quantity of chlorinated organics that exit the bleach plant with the bleached stock, and that could ultimately be sewered elsewhere in the mill. Samples were also collected from at least one condensate at each mill. The condensate characteristics were of interest in the event that future treatability studies indicate that anaerobic treatment of the bleach plant wastewaters requires a supplementary source of relatively high strength With the exception of the biological biodegradable material. treatment plant effluent referred to above, none of the sampled streams are discharged directly to the environment. These streams undergo downstream blending and/or dilution, and in some cases, treatment, prior to final discharge.

The complete set of chemical characterization data obtained for all streams sampled is presented in Appendix B. Since none of the make-up water sources contained significant quantities of contaminants, the discussion below concentrates primarily on selected characteristics of the sewered wastewater streams in the four bleach plants. The characteristics highlighted are those considered to be the most relevant to the ongoing investigation of anaerobic treatability.

Wastewaters From Softwood Bleaching. There were a total 4.3.1 of 8 sewered streams from the 3 plants that were bleaching softwood at the time of sampling (Table 6). In plant "A", bleed flows from the Eo- and H-stage seal tanks are discharged to a combined alkaline sewer. At each of the softwood bleach plants, most of the sewered streams contain sufficient Chemical Oxygen Demand (COD > 1000 mg/L) to consider anaerobic treatment technology. However, as indicated by the relatively low BOD/COD ratios (BOD is Biochemical Oxygen Demand), most of this COD is poorly biodegradable. At the present time, the intent of the current study is to focus on the application of anaerobic technology for dechlorination of the wastewater organochlorine , compounds. In other locations, this has been accomplished to varying extents without the production of methane (9). It may therefore be erroneous to assume that the usual criterion of high COD concentration is a requirement for an application of anaerobic biotechnology in which dechlorination, rather than methanation, is the primary goal.

With two exceptions, all of the streams were toxic as determined by static bioassays with <u>Daphnia magna</u>. Although a pattern in aquatic toxicity is difficult to discern, chlorination filtrates appeared to be more toxic than the alkaline filtrates. The two non-toxic streams were both alkaline filtrates from the bleach plant that was preceded by oxygen delignification.

The wastewater organochlorine concentrations (Adsorbable Organic Halogen, AOX) did not differ significantly between mills.

AOX concentrations were highest in the acid filtrates (180 to 218 mg/L), and slightly lower in the alkaline extraction filtrates (139 to 176 mg/L). For the two mills with hypochlorite bleaching, the alkaline hypochlorite filtrates contained much lower levels of AOX (22 to 42 mg/L).

Table 6. Selected Characteristics of Softwood Bleaching Wastewaters.

| DESCRIPTION | AOX (mg/L) | TOXICITY (LC 50) | COD (mg/L) | BOD (mg/L) | BOD/COD (%) |
|---------------------|---------------------------------------|---------------------|---------------|---------------|----------------|
| Plant A, Softwood | · · · · · · · · · · · · · · · · · · · | | | | |
| C-STAGE SEAL TANK | 218 | 6.3 | 1120 | 330 | 29.5 |
| COMBINED ALK. FILT. | 109 | 20.1 | 1320 | 360 | 27.3 |
| EO-STAGE SEAL TANK | 166 | 17.9 | 2200 | 540 | 24.5 |
| H-STAGE SEAL TANK | 22 | 3.85 | 80 | 3 | 4 |
| Plant B, Softwood | | | | | |
| D/C SEAL TANK | 180 | 17.6 | 2800 | 450 | 16.1 |
| EO SEAL TANK | 139 | 16.6 | 8000 | 975 | 12.2 |
| Plant C, Softwood | | | | | |
| C-STAGE SEAL TANK | 198 | 8.7 | 1450 | 330 | 22.8 |
| E-STAGE SEAL TANK | 176 | 100 | 2330 | 330 | 14.2 |
| H-STAGE SEAL TANK | 42 | N.L. | 605 | 90 | 14.9 |

ND = Not Determined; N.L. = Non-Lethal.

Comparison of Wastewater Characteristics from Softwood 4.3.2 and Hardwood Pulp Bleaching. Selected analytical characteristics for samples from the parallel softwood and hardwood bleach plants with oxygen delignification are presented in Table 7. The softwood data are the same as those shown in Table 6 above. As expected, the AOX, COD and BOD concentrations were all lower for hardwood bleaching than for softwood bleaching. Using the conventional COD concentration criterion, the strengths of the hardwood wastewasters are only marginally suitable for anaerobic treatment. As indicated by the BOD/COD ratios, there was some variablility in biodegradability within each bleach plant, but on average, there was no major difference in the apparent wastewater biodegradability between the two plants. AOX levels in hardwood wastewaters were significantly lower than those of The measured AOX concentrations for the softwood effluents. 27% 548 of the corresponding ranged from to hardwood concentrations measured for softwood bleaching. In contrast to the data from all of the softwood bleach plants, the LC_{50} results from hardwood bleaching indicated that the chlorination filtrates were significantly less toxic (43.6%) than the alkaline extraction filtrates (21.2%). For both softwood and hardwood bleaching, the hypochlorite filtrates were the least toxic

streams. The LC₅₀ for hardwood hypo filtrate was 54.7%. Surprisingly, the softwood hypochlorite filtrate was the only sewered stream from any of the bleach plants that was not acutely lethal to <u>Daphnia magna</u>.

| Table 7. | Comparison of | Selected | Wastewater | Characteristics | From |
|----------|----------------|----------|------------|-----------------|------|
| | Softwood and H | | | | |

| AOX (mg/L) | TOXICITY (LC 50) | COD (mg/L) | BOD (mg/L) | BOD/COD (%) |
|---------------|---|--|--|---|
| | | | | |
| 198 | 8.7 | 1450 | 330 | 22.8 |
| 176 | 100 | 2330 | 330 | 14.2 |
| 42 | N.L. | 605 | 90 | 14.8 |
| | | | | |
| 108 | 43.6 | 740 | 84 | 11.4 |
| 48 | 21.2 | 1160 | 236 | 20.3 |
| 16 | 54.7 | 302 | 6 | 2 |
| | (mg/L) 198 176 42 108 48 | (mg/L) (LC 50) 198 8.7 176 100 42 N.L. 108 43.6 48 21.2 | (mg/L) (LC 50) (mg/L) 198 8.7 1450 176 100 2330 42 N.L. 605 108 43.6 740 48 21.2 1160 | International International International International International 198 8.7 1450 330 176 100 2330 330 42 N.L. 605 90 108 43.6 740 84 48 21.2 1160 236 |

ND = Not Determined; N.L. = Non-Lethal.

4.4 Toxicity Correlations

4.4.1 Acute Toxicity vs Chemical Parameters. One of the objectives of this study was to assess the correlation between chemical composition and aquatic toxicity of bleach plant wastewaters, and between aquatic toxicity determined with Daphnia magna and a series of microbial toxicity and mutagenicity tests. For all of the seal tank samples collected in this study, a preliminary examination of the relationship between chemical composition and aquatic toxicity was carried out. Figures 2, 3 and 4 indicate that there was essentially no correlation between Daphnia magna LC_{50} and wastewater strength as measured by BOD, COD or TOC (Total Organic Carbon).

The relationship between total resin and fatty acids (RFA) and aquatic toxicity is shown in Figure 5. Although the statistical correlation between the two parameters is not strong $(r^2 = -0.33)$, in general, there is a trend to lower toxicity with lower RFA concentrations. This trend did not hold for the five data points located close to the origin. The acute toxicities of these bleach plant process streams were very high, even though they contained low concentrations of resin and fatty acids. The RFA method used in this study included only three chlorinated resin acids in the target list of compounds. In many of the samples summarized in Figure 5, there may have been additional chlorinated RFAs present that were not quantified, but which might have contributed to sample toxicity.

The use of a more general measure of chlorinated organic compounds might be expected to produce a better correlation to

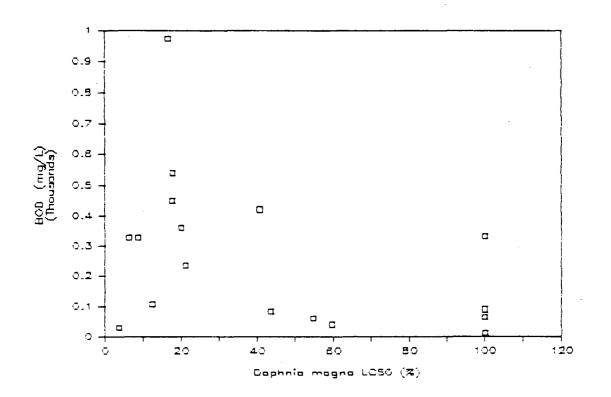


Figure 2. Relationship between BOD and toxicity in bleach plant seal tank samples.

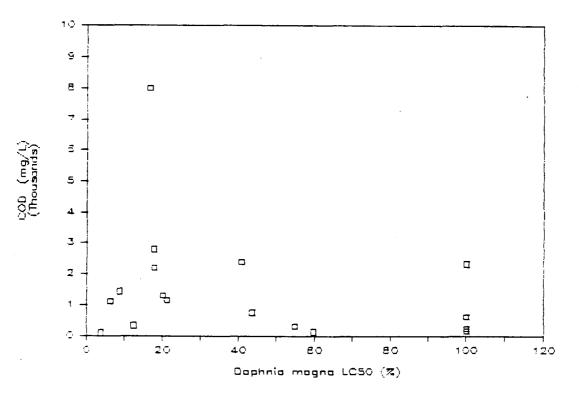


Figure 3. Relationship between COD and toxicity in bleach plant seal tank samples.

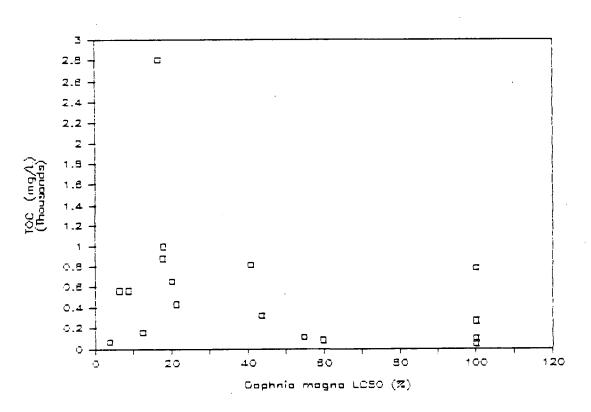


Figure 4. Relationship between TOC and toxicity in bleach plant seal tank samples.

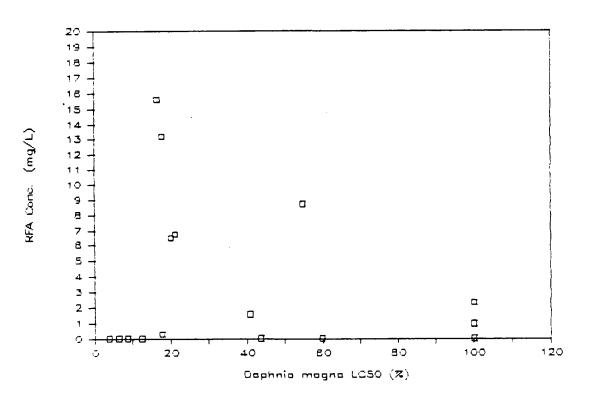


Figure 5. Relationship between RFA concentration and toxicity in bleach plant seal tank samples.

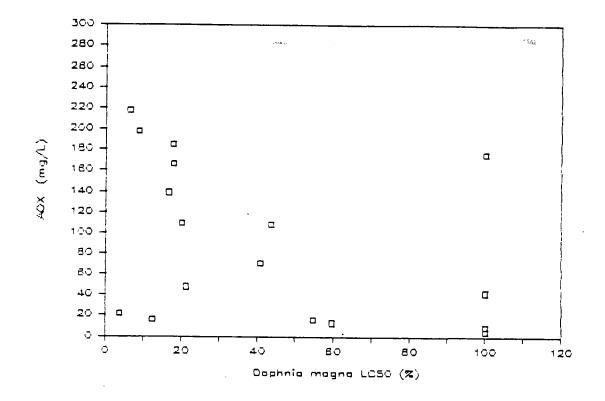


Figure 6. Relationship between AOX and toxicity in bleach plant seal tank samples.

wastewater toxicity. Figure 6 shows the correlation between measured AOX concentrations and <u>Daphnia magna</u> toxicity. With the exception of the data point farthest from the origin, there appears to be an indication of a weak negative correlation between AOX and LC_{50} ($r^2 = -0.57$). Even though the evidence for a statistically significant relationship is not convincing, the correlation of toxicity to AOX was higher than that to any of the other chemical parameter examined. Additional data will be required to assess this issue further.

4.4.2 Microbial Toxicity and Genotoxicity. As described in more detail in Appendix A, several microbial toxicity assays, and one microbial genotoxicity test, were applied to all of the wastewaters collected during the kraft bleach plant sampling programs (Appendix B). These tests were of interest to determine whether the <u>Daphnia magna</u> acute toxicity bioassay could be replaced by one or more microbial tests that require smaller sample volumes for toxicity determination. This would allow toxicity measurements to be made after the completion of many of the small volume anaerobic treatability tests that are planned for later stages of the study. The microbial tests used were:

- . Microtox,
- . Algal ATP,
- . Bacterial ATP-TOX,
- . <u>Spirillum volutans</u>, and,
- . SOS Chromotest.

Figure 7 shows scatterplot diagrams of the results of all pairs of tests, including those using <u>Daphnia magna</u>. This type of plot makes it fairly easy to track a trend in the data from plot to plot, and to compare all the test procedures against one another. It is important to note that each of the tests defines significant toxicity in different terms. For instance, an induction factor of 0.2 is considered to be non-mutagenic in the SOS Chromatest, while a similar LC_{50} value in a <u>Daphnia</u> bioassay, or an EC_{50} for Microtox, would indicate very high toxicity. In the case of the <u>Spirillum</u> test, results are either positive [0], indicating toxicity, or negative [1].

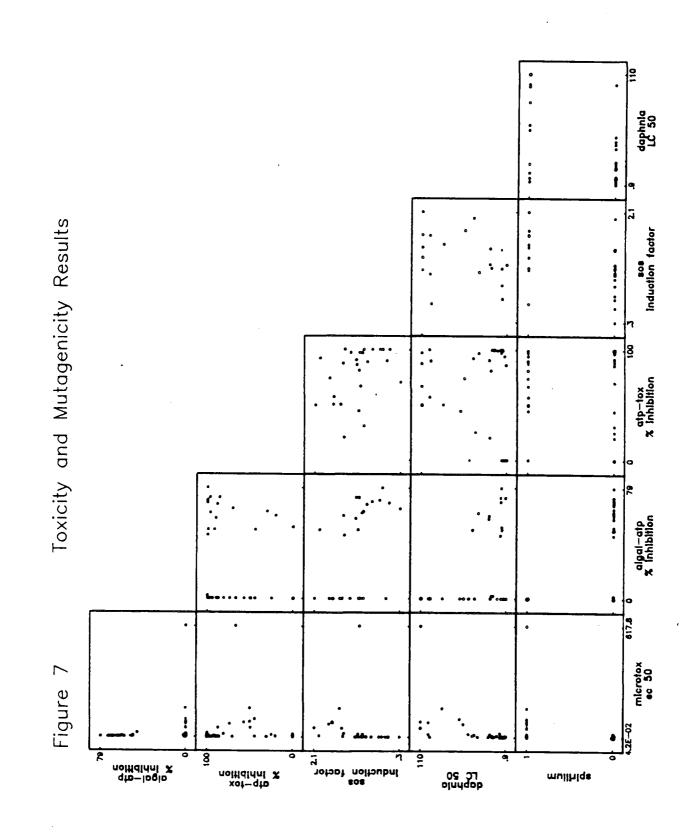
A thorough analysis of the toxicity characteristics measured by these tests has not yet been completed. However, Figure 7 indicates that Spirillum produced both toxic and nontoxic responses for wastewaters that covered a wide range of toxicities as determined by the other tests. However, it is difficult to assess a correlation between positive/negative data from the Spirillum test and the scaled results of the other The Microtox test appeared to be the most sensitive tests. That is, there were predominantly low indicator of toxicity. EC50 results for almost every data value produced by the other These low Microtox values may be partially attributable tešts. to difficulties encountered in correcting for the high background colour in many of the bleach plant samples.

It is apparent from the plots of Figure 7, that none of the tests produced results that correlated strongly to those of any other procedure, including <u>Daphnia</u>. Work will be continued to determine whether more significant correlations can be drawn to selected chemical measurements that were made for these wastewaters.

4.5 Organochlorine Discharges.

The major objective of current study is to examine the potential for applying anaerobic biological treatment technology for the removal of BOD, toxicity and organochlorine compounds from kraft mill bleach plant wastewaters. To avoid the requirement for making expensive and time-consuming measurements of specific chlorinated organic compounds to assess the performance of an anaerobic system, it was decided that a lumpedparameter estimate of organochlorine content would be utilized. For water samples, Adsorbable Organic Halogen (AOX) using either combustion/titration, or neutron activation, was chosen as the most applicable method. Samples containing few suspended solids were analyzed by either AOX approach. For higher particulate concentrations, and for pulp samples, the neutron activation technique was routinely used. Both techniques measured the nonvolatile organochlorine components of pulp mill wastewaters.

At the time of sample collection, it was also of interest to determine the concentrations and types of volatile chlorinated organics in bleach plant process streams. Therefore, grab samples were collected in headspace-free septum bottles for analysis by a purge and trap, gas chromatographic technique. As shown in Table 8 for the sewered streams, only chloroform and carbon tetrachloride were identified routinely in



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significant quantities. In several samples, additional peaks were obtained on the chromatograph, but at such low concentrations as to be negligible. The sum of the measured concentrations of chloroform and carbon tetrachloride, expressed in terms of chlorine, were assumed to be approximately equal to the Purgeable Organic Halogen (POX).

Figures 8 through 11 illustrate the POX and AOX concentrations of the samples collected from several washer seal tanks. These sources included both sewered and recycled streams. The highest POX concentration measured was 10 mg/L in the chlorination stage filtrate from Plant "A", however, a number of other samples from plants "A", "C" and "D" contained similar levels of POX. Three of the four hardwood bleach plant (Plant "D") filtrates exhibited POX levels of 6 to 8 mg/L. The fourth hardwood filtrate, from the chlorine dioxide stage, was much lower in volatile organochlorines (< 1 mg/L). The bleach plant with the highest degree of chlorine dioxide substitution produced filtrates that were consistently low in POX (< 1.3 mg/L).

| | PURGI | | |
|----------------------------|-------|----------------------------|-----|
| DESCRIPTION | | CCl ₄ (mg/L) | |
| Plant A, Softwood | | ····· | |
| C-STAGE SEAL TANK | 10 | 0.0018 | 218 |
| COMBINED ALKALINE FILTRATE | 1.6 | 0.01 | 109 |
| EO-STAGE SEAL TANK | 0.78 | 0.0058 | 166 |
| H-STAGE SEAL TANK | 7.8 | 0.008 | 22 |
| Plant B, Softwood | | | |
| D/C SEAL TANK | 1.2 | 0.0004 | 180 |
| EO SEAL TANK | 0.18 | 0.0004 | 139 |
| Plant C, Softwood | | | |
| C-STAGE SEAL TANK | 7.8 | ND | 198 |
| E-STAGE SEAL TANK | 1.4 | 0.008 | 176 |
| H-STAGE SEAL TANK | 0.5 | 0.24 | 42 |
| Plant D, Hardwood | | | |
| C-STAGE SEAL TANK | 6.8 | 0.23 | 108 |
| E-STAGE SEAL TANK | 8 | 0.038 | 48 |
| H-STAGE SEAL TANK | 6.6 | 0.01 | 16 |

| Table 8. | Volatile | Organo-Chlorine | Compounds | and | AOX | in | Bleach |
|----------|-----------|-----------------|-----------|-----|-----|----|--------|
| | Plant Was | stewaters | | | | | |

ND = Not Determined; N.L. = Non-Lethal.

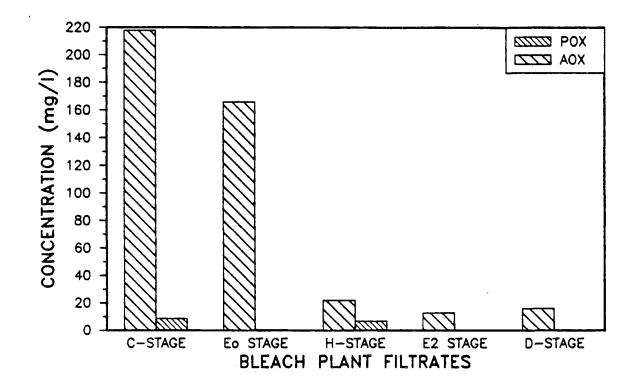


Figure 8. AOX and POX content of filtrates from softwood bleach plant "A".

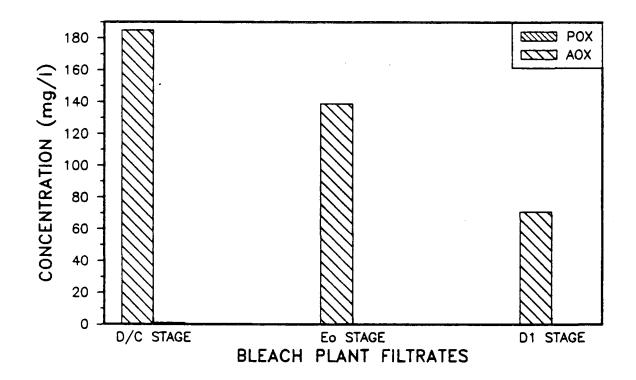


Figure 9. AOX and POX content of filtrates from softwood bleach plant "B".

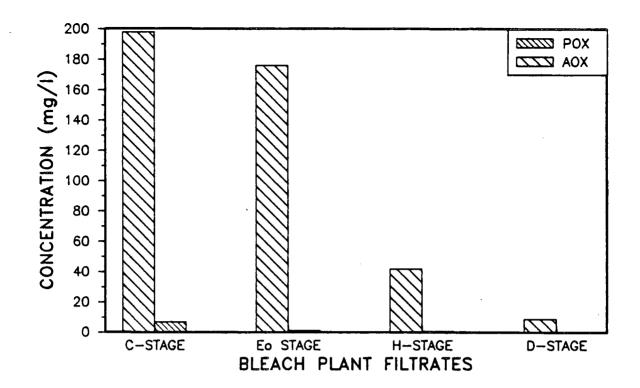


Figure 10. AOX & POX content of filtrates from softwood bleach plant "C".

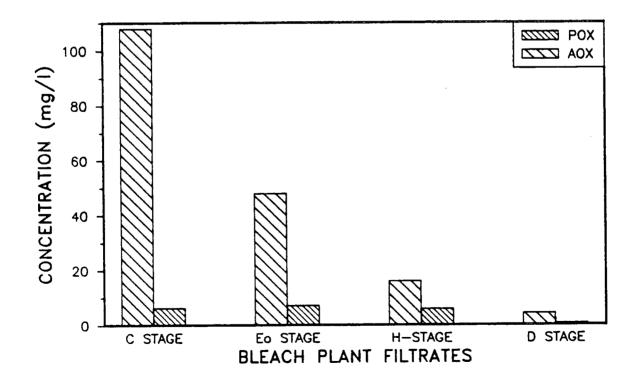


Figure 11. AOX & POX content of filtrates from hardwood bleach plant "D".

The contributions of volatile compounds to the total concentrations of organic halogen measured in the individual filtrates were highly variable. In most cases, the POX comprised less than 5% of the total organic halogen. The notable exceptions were the filtrates from the hardwood bleach plant, in which the percentage of POX ranged from 5.3% in the C-stage filtrate, to 26% in the hypochlorite stage. The hypochlorite stage from the softwood bleach plant "A" also contained about 24% The higher contributions observed for the two hypochlorite POX. filtrates are due primarily to the low concentrations of AOX present in these samples, rather than to high concentrations of POX.

It has recently been recommended that the discharge rates of organically bound chlorine be used as a regulatory parameter for Ontario kraft mills (Bonsor et al., 10). The total discharge rates of of POX to the contributions organochlorine compounds from the four bleach plants are shown in Figure 12. For the three softwood bleach plants, the POX constituted less than 3% of the total mass of organochlorine discharged. At these levels the contribution of POX was considered to be negligible. In the hardwood bleach plant, volatile compounds were far more significant, comprising 12.4% of the total organochlorines discharged in the sewered filtrates.

Figure 13 summarizes the measured and predicted AOX + POX discharge rates for the four bleach plants surveyed. The measured rates were determined from measurements of the sewered streams in each bleach plant, as well as the water associated with the bleached stock. At one mill, the discharge rate measured in the bleach plant was compared to a measurement over the same period in the untreated combined mill effluent. The combined mill effluent value was within 10% of that measured in the bleach plant. The predicted values were calculated from the Germgard equation as proposed by Bonsor <u>et al.</u> (10).

Organic Chlorine = k x (C + H/2 + D/5) kg/adt

where k is a constant assumed to be 0.12 kg/adt,

- C is the total chlorine charge, kg/adt,
- H is the hypochlorite charge as equivalent chlorine, kg/adt, and,
- D is the chlorine dioxide charge as equivalent chlorine, , kg/adt.

The measured organochlorine discharge rates ranged from a high of 8.0 kg/adt for softwood bleach plant "A" with 7% Clo_2 substitution, to a low of 1.1 kg/adt for oxygen delignification and 20% Clo_2 -substituted hardwood bleaching at Plant "D". Plants "B" and "C" discharged intermediate quantities, of AOX + POX, 2.0 and 3.5 kg/adt respectively. Among the softwood bleach plants, the high degree of Clo_2 substitution at Plant "B" appears to be more effective in reducing organochlorine discharges than the use of oxygen delignification with a lower Clo_2 substitution (Plant "C"). Samples from the two parallel bleach plants ("C" and "D") indicated that the organochlorine discharged from hardwood bleaching was less than one-third of

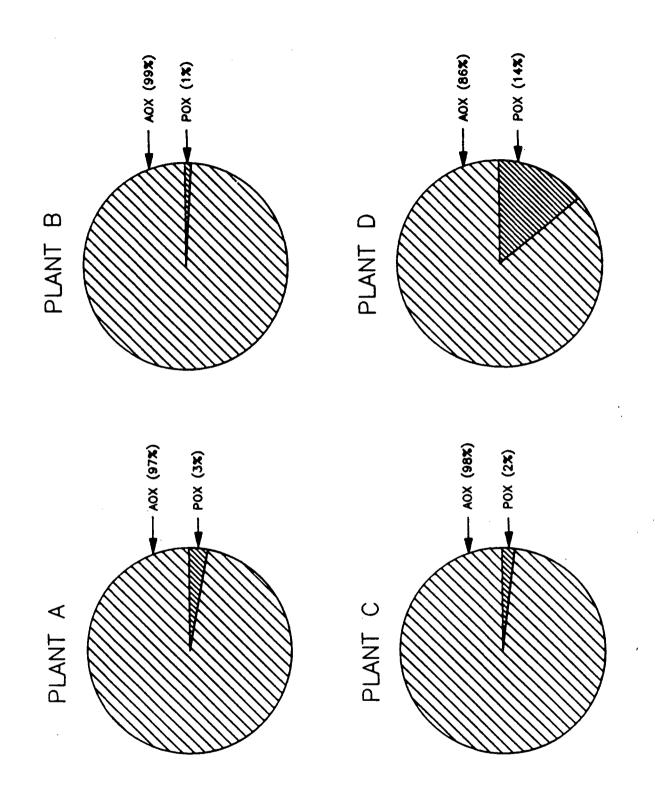


Figure 12. Percent contributions of AOX and POX to total organochlorine discharges.

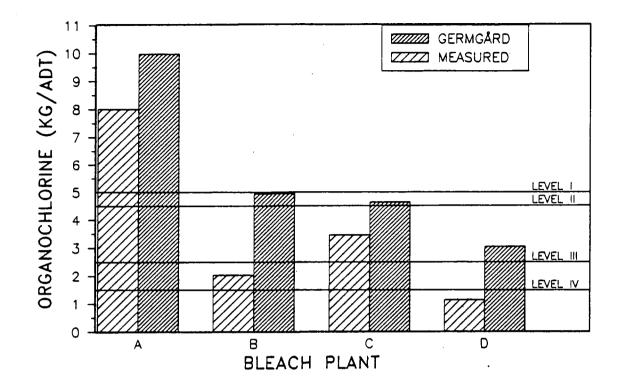


Figure 13. Measured and predicted unit organochlorine (AOX + POX) discharge rates.

that generated with softwood.

Figure 13 also demonstrates that the Germgard equation consistently overpredicted the measured organochlorine discharges. For softwood bleaching the predicted values exceeded the measured values by 25%, 144% and 34% for plants "A", "B" and "C" respectively. Better agreement can be obtained for "A" and "C" by adjustment of the value of the constant in the Germgard equation as discussed by Bonsor et al. (10). However, for bleach plant "B" an unrealistic extent of adjustment would be necessary to produce reasonable agreement between the measured and predicted results. It has been suggested that the Germgard relationship has only a limited capability for predicting the benefits of high degrees of ClO, substitution on the AOX discharge rate. The Germgard equation is inherently simplistic. As more empirical data is reported it may be shown to be an inadequate predictor of organochlorine production (McCubbin, N., Personal Communication).

The extent of overprediction by the Germgard equation appeared to be most significant for the hardwood bleach plant. In this case the Germgard value was 166% of the measured organochlorine discharge rate. The reason for this large discrepancy is not known at present.

Individual sources of organochlorine are detailed in Table 9. Figure 14 summarizes the relative contributions of each stream leaving the bleach plant to the total organochlorine discharged. In every case, the chlorination and extraction filtrates accounted for at least 86% of the total. In the softwood bleach plants, the chlorination filtrates appeared to be the largest single source. The alkaline extraction seal tank was the dominant source in the hardwood plant. For plants "C" and "D", in which hypochlorite filtrates are sewered separately, these relatively dilute streams contributed 13% and 8% of the respective totals.

Table 9. Summary of Organochlorine Discharges by Source.

| DESCRIPTION | DISCHARGI AOX | E RATES POX | |
|----------------------------|------------------|----------------|------|
| Plant A, Softwood | | | |
| C-STAGE SEAL TANK | 4.19 | 0.17 | 4.36 |
| COMBINED ALKALINE FILTRATE | 3.54 | 0.05 | 3.59 |
| BLEACHED STOCK WATER | 0.06 | | 0.06 |
| Totals | 7.79 | 0.22 | 8.01 |
| Plant B, Softwood | | | |
| D/C SEAL TANK | 1.34 | 0.008 | 1.35 |
| EO SEAL TANK | 0.68 | 0.001 | 0.68 |
| BLEACHED STOCK WATER | 0.01 | | 0.01 |
| Totals | 2.03 | 0.009 | 2.04 |
| Plant C, Softwood | | | |
| C-STAGE SEAL TANK | 1.39 | 0.05 | 1.42 |
| E-STAGE SEAL TANK | 1.51 | 0.011 | 1.52 |
| H-STAGE SEAL TANK | 0.45 | 0.007 | 0.46 |
| BLEACHED STOCK WATER | 0.03 | | 0.03 |
| Totals | 3.38 | 0.068 | 3.43 |
| Plant D, Hardwood | | | |
| C-STAGE SEAL TANK | 0.39 | 0.026 | 0.42 |
| E-STAGE SEAL TANK | 0.54 | 0.09 | 0.63 |
| H-STAGE SEAL TANK | 0.06 | 0.025 | 0.08 |
| BLEACHED STOCK WATER | 0.01 | | 0.01 |
| Totals | 1.0 | 0.14 | 1.14 |

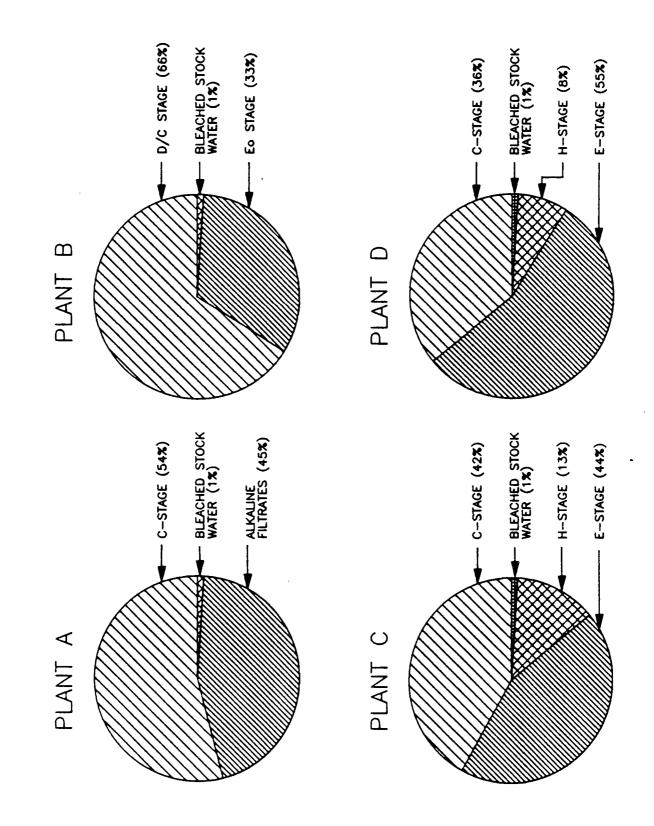


Figure 14. Contributions by source to total organochlorine discharge.

5 WORK IN PROGRESS

5.1 Anaerobic Biomass Acclimation.

Laboratory scale chemostats are being used to develop cultures of anaerobic bacteria acclimated to the presence of kraft mill bleach plant wastewaters. Two, 4-liter chemostats are operating at retention times between 30 and 50 days with a feed consisting of a neutralized mixture of chlorination and alkaline extraction filtrates from bleach plants "A", "B" and "C". The mixture is also being supplemented with acetic acid, which serves as a readily biodegradable substrate for methane-forming bacteria. To date, the quantity of methane produced in each chemostat has been approximately equal to that expected from the amount of acetate added in the feed. Data on AOX removal has not yet been obtained.

5.2 Batch Treatability Testing of Bleach Plant Filtrates.

Batch anaerobic treatability tests of each of the sampled filtrates are currently in progress. The significance of biomass acclimation for fermentation of the filtrates is being examined by comparing the treatability characteristics with unacclimated biomass, to those obtained with the acclimated biomass produced in the chemostats described above.

5.3 Activated Carbon Adsorption Studies.

It was initially hypothesized that activated carbon might be the best choice of support medium for the development of a fixed film high rate anaerobic process. This assumption was based on the fact that in previous studies with toxic wastewaters, the activated carbon served both as a biomass support medium, and as a sink for toxic compounds. By removing some of the toxics through adsorption, the wastewater toxicity was reduced enough to permit the growth of anaerobic bacteria. Preliminary experiments have been completed to determine the extent of adsorption obtained with bleach plant wastewaters, and to assess whether this adsorption increases the activity of Data from these experiments are under , anaerobic bacteria. Negotiations are also underway with researchers at Bayer review. AG in West Germany, to obtain samples of a chemically-modified polyurethane carrier material developed for anaerobic treatment of industrial wastewaters. The German researchers have had considerable success in applying this material to bleached sulfite mill effluents.

5.4 Continuous Flow Treatability Studies.

Laboratory scale reactors for continuous flow anaerobic treatability studies are under design and construction. The continuous flow studies will be started after a source of bleach plant wastewater has been finalized from the batch experiments described above. The bleach plant demonstrating the highest

degree of wastewater treatability in the batch tests will be chosen for more extensive study in the continuous flow experiments.

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APPENDIX A

. DETERMINATION OF AOX

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. MICROBIAL TOXICITY AND MUTAGENICITY TESTS

1 -

ADSORBABLE ORGANIC HALOGEN - COMBUSTION METHOD

Scope and Application

This method is capable of measuring organic halides (chlorine, bromine and iodine) in waters and wastewaters. Fluorine-containing species are not determined under these conditions.

Summary of Method

Up to 50 mL of an acidified sample (pH2 with HNO_3) is passed under pressure through a granular activated carbon column at a prescribed flow rate. The column is then washed with nitrate solution to remove any trapped inorganic halides. The carbon containing the adsorbed organic halides is combusted and the resulting Hx gas generated is trapped in acetic acid and titrated microcoulometrically.

Interferences

Contamination is the main source of interference upon this method, consequently reagents, glassware and other sample processing hardware must be of highest purity and cleanliness. Activated carbon must have minimal exposure time to the laboratory atmosphere and under no circumstances should it be used in, or adjacent to, laboratories that employ halogenated organic solvents.

Particles will cause the carbon column to choke, therfore samples with particulates must either be diluted or filtered prior to adsorption.

Filtering and mixing will cause losses of volatile organic halogens and should therefore be executed with this in mind.

Apparatus and Materials

- Adsorption Module Dohrmann or equivalent pressurized unit
- Granular Activated Carbon Xertex 100/200 mesh or equivalent with background Cl⁻ value of <1 ng/mg and satisfactory adsorption efficiencies of molecular weight species of <500 through >10 000.
- Cerafelt (Available from Johns-Manville or Dohrmann), or equivalent.
- Combustion/microcoulometric-titration unit Dohrmann or equivalent system.
- Data acquisition system.

Reagents

- Distilled/deionized water.
- Sodium Sulfite (0.1 m) dissolve 12.6 g reagent grade Na₂SO₃
 in 1 litre of water.
- Potassium Nitrate $(5 \times 10^3 \text{ mg NO}_3^-/\text{L})$ dissolve 8.2 g reagent grade KNO₃ in 1 litre of water.
- Nitric Acid concentrated reagent grade.
- Acetic Acid 70% aq.
- Trichlorophenol standard dissolve 0.1855 g reagent grade $Cl_3C_6H_2OH$ in 50 mL glass distilled methanol and dilute up to 100 mL with water. 1 mL = 1 x $10^3 \mu g Cl^-$
- Carbon dioxide 99.9% pure gas.
- Oxygen 99.9% pure gas.
- Nitrogen pre-purified.

Sample Collection and Preservation:

A minimum of 100 mL of sample should be collected as this will allow at least duplicate analyses to be performed on a sample. After collection in an amber bottle fitted with teflon lined caps, 0.5 mL of 0.1 m $Na_2 SO_3$ is added to neutralize any residual chlorine; <u>NB</u>: greater doses of $Na_2 S_2 O_3$ may be required depending on the stream being sampled. Add HNO₃ to reduce the pH to 2.0. Cap headspace free and refrigerate at 4°C or lower until analyses. No statistically significant changes have been observed in AOX concentration over a six-week period under these conditions.

Procedure

Place two cerafelt plugged, pyrex, carbon packed columns in the respective column holders. Attach the two plastic holders together in series and thread them onto the bottom of the sample reservoir on the adsorption unit, taking care to include the rubber 'O' rings at the top and bottom of each column.

Transfer up to 80 mL of sample to the reservoir, cap tightly and pressurize the system. Regulate the pressure so as to give a flow of 3-4 mL per minute. When the sample flow terminates, rinse the reservoir with 10-20 mL H₂O followed by a second rinse of 10-20 mL KNO₃ solution (5 x 10^3 ppm NO₃⁻). Transfer the columns and holders to the nitrate rinse reservoir. Rinse with 4-5 mL of KNO₃ wash solution. The contents of the columns are then ejected into a guartz "solids combustion boat" and immediately transferred to the combustion/microcoulometric AOX analyser. Once a stable baseline is established, the instrument is started and the contents of the boat are pyrolyzed.

Calculations

 $\frac{C_{s} - C_{b}}{V} = \mu g/L \text{ adsorbable organic halide}$ Where $C_{s} = \mu g Cl^{-} \text{ found in sample}$ $C_{b} = \mu g Cl^{-} \text{ found in blank}$ V = volume of sample analysed.

Quality Control

Blanks should be run every five samples while standards should be run every ten samples in order to verify calibration.

Samples should be run in duplicate with one spike for every five samples.

Method Performance

Working with the maximum volume of sample (i.e. 80 mL), the detection limit of this method is 8 μ g/L. Analyses (20) run on an industrial wastewater with a mean value of 11.05 μ g/mL produced a std. deviation = 0.32, variance = 0.099 and coefficient of variation = 2.85%. Spike recovries on several different matrices generated in the pulp and paper industry have rendered values of 85-100%.

J. Fraser 1988

ADSORBABLE ORGANIC CHLORINE, BROMINE, IODINE BY NEUTRON ACTIVATION

Scope and Application

This method may be used for the analysis of specific organic halogens with the exception of fluorine. This method is recommended for dealing with samples which contain suspended solids.

Summary of Method

An appropriate aliquot of a well mixed, properly preserved sample (up to 30 mL) is poured into a pyrex culture tube containing 80 mg granular activated carbon. The tube is capped and placed on a shaker for one hour after which the contents are filtered, washed, and placed in a scintillation vial for analysis.

Interferences

Contamination is the main source of interference upon this method, consequently reagents, glassware and other sample processing hardware must be of highest purity and cleanliness. Activated carbon must have minimal exposure time to the laboratory atmosphere and under no circumstances should it be used in, or adjacent to, laboratories that employ halogenated organic solvents.

Filtering and mixing will cause losses of volatile organic halogens and should therefore be executed with this in mind.

Apparatus and Materials

- 50 mL culture tubes with screw caps.
- Wrist arm shaker.
- Filter apparatus including 0.45 µm membrane filters, vacuum pump, vacuum flask and membrane filter holder.
- Scintillation vials polyethylene snap cap containers.
- Granular activated carbon Xertex 100/200 or equivalent.
- Access to a slow poke reactor.
- Gamma ray detector and data handling system.
- Potassium nitrate solution (5 x 10^3 ppm NO₃⁻).

- Distilled/Deionized water.
- Sodium Sulphite (0.1 m) 12.6 g of reagent grade Na_2SO_3 in 1 litre of H_2O_2 .
- Reagent grade HNO3.
- Trichlorophenol (1000 ppm) dissolve 0.1856 g of reagent grade fresh trichlorophenol in 50 ml of glass distilled methanol and dilute to 100 mL with water.

Sample Collection and Preservation:

A minimum of 100 mL of sample should be collected as this will allow at least duplicate analyses to be performed on a sample. After collection in an amber bottle fitted with teflon lined caps, 0.5 mL of 0.1 m Na₂SO₃ is added to neutralize any residual chlorine; NB: greater doses of Na₂S₂O₃ may be required depending on the stream being sampled. Add HNO₃ to reduce the pH to 2.0. Cap headspace free and refrigerate at 4°C or lower until analyses. No statistically significant changes have been observed in AOX concentration over a six-week period under these conditions.

Procedure:

Transfer up to 30 mL of preserved sample to a 50 mL culture tube containing 80 mg GAC. Cap tightly and place the tubes on a Burell wrist arm shaker. Start the shaker and make sure that complete mixing is in effect; allow the contents to shake for one hour. Vacuum filter the mixture through a 0.45 μ m membrane filter and wash the solute with 10-20 mL of 5 x 10³ ppm NO₃⁻ solution. Carefully fold the membrane filter and place it in a scintillation vial, cap tightly, code it and submit it for neutron activation analysis. The method used for this is irradiation using the rabbit method with a slowpoke reactor having a neutron flux of 5 x 10¹² neutrons/cm²/sec. Chlorine is then analysed using the 1642-KeV gamma ray produced by 37.1-min ³⁸Cl; Bromine uses the 616-KeV gamma ray from 17.7-min Br; Iodine is analysed using the 442-KeV gamma ray from 25-min¹²⁸I.

Quality Control:

Blanks should be run every five samples while standards should be run every ten samples in order to verify calibration.

Samples should be run in duplicate with one spike for every five samples.

Method Performance:

Working with the maximum volume of sample (30 mL), the detection limit of this method is 1 μ g/mL. With larger culture tubes and mixing apparatii, this detection limit may be reduced accordingly. Analyses (20)

run on an industrial wastewater with a mean value of $359 \ \mu g/mL$ produced a std. deviation = 26.6 with a coefficient of variation of 7.40%, while analyses (20) run on a wastewater with a mean of 77 $\mu g/mL$ produced a std. deviation = 3.33 and a coefficient of variation of 4.31%. Spike recoveries on several different matrices generated in the pulp and paper industry have shown values of 80-100%.

J. Fraser 1988

DATA REPORT

Microbiological Toxicity and Mutagenicity Testing of Pulp and Paper Mill Wastewaters

Materials and Methods

Wastewater Collection and Preparation

Six to eight-hour composite wastewater samples were collected from various process streams from three kraft and one neutral sulphite semi-chemical mill (Table 1). They were transported to the Wastewater Technology Centre (WTC) in Burlington, Ontario within 24 hours of collection. The pH was adjusted to between 6.5 and 7.0 on all the wastewaters, except for one set of Sturgeon Falls wastewaters which were submitted for Daphnia bioassays at Beak Consultants. Both pH-adjusted and non-adjusted results are reported for those samples. The insoluble component of all the wastewaters was removed by centrifugation at 15,000 rpm for about 20 minutes. In a duplicate set of Sturgeon Falls wastewaters, glass fibre filtration was used for solids removal.

Analytical Methods

Toxicological type analyses included <u>Daphnia magna</u>, microtox, algal assays, the ATP-TOX system toxicity test, and Spirillum toxicity test. Daphnia bioassay results are reported as LC50 values which correspond to the concentration of the wastewater that is lethal to fifty percent of the Daphnia magna over a 96 hour incubation period.

The microtox toxicity analyzer developed by Beckman employs a bioluminescent strain of marine bacteria (Photobacterium phosphoreum). The principal of the microtox test is that the bioluminescence diminishes in response to exposure to toxicants. This reduction in light emittance is reported in terms of an effective concentration (EC_{50}). The EC_{50} denotes the concentration of toxicant required to inhibit 50% of the luminescence in P. phosphoreum.

In the algal-ATP assay, the ATP production in <u>Selenastrum</u> capricornutum is compared both in the presence and absence of possible toxicants. ATP-content is measured indirectly using light emission from the ATP-dependent luciferin-luciferease reaction. Results are given as percent inhibition of the algae in the presence of 100% wastewater concentration.

ATP-TOX system also uses the measurement of ATP as an indication of growth inhibition. It, however uses bacterial cells, not algae.

A toxic response in the <u>Spirillum volutans</u> test is indicated by a disruption in the co-ordinated movement of the flagellated bacterium, <u>Spirillum volutans</u> after 2 hours exposure to a toxicant. Results are given as a positive, which indicates a toxic effect, or a negative, if 90% of the bacteria are still mobile after the 2 hours exposure time. These were changed from a negative to a 1 and from a positive to a 0 for the purposes of graphical analysis.

The S.O.S. chromotest is used to detect a genotoxic response. An unrelated enzyme gene, B-galactosidase was introduced to the gene responsible for induction of the S.O.S. repair mechanism in the micro-organism provided in the S.O.S. kit. S.O.S. repair is induced by the bacteria in an attempt to repair DNA that is damaged by exposure to genotoxic agents. Since the B-galactosidase enzyme gene is incorporated into the S.O.S. repair operon, the B-galactosidase activity can be used as an indicator of S.O.S. repair hence exposure to a genotoxic agent. B-galactosidase activity is indicated by a color change. Results are provided in terms of an induction factor. Values greater than one indicate genotoxicity in the test sample relative to a control.

APPENDIX B

DETAILED LISTINGS OF CHEMICAL ANALYTICAL DATA

LEGEND

| BOD (UF) (F) | 5-day biochemical oxygen demand unfiltered sample filtered sample |
|-------------------------------|---|
| COD(UF & F) | chemical oxygen demand |
| TKN(UF & F) | total Kjeldahl nitrogen |
| TP(UF & F) | total phosphorus |
| NH ₄ -N | ammonia as nitrogen |
| NO2 | nitrite |
| NO ₃ | nitrate |
| TOC | total organic carbon |
| H ₂ S-S | hydrogen sulphide as sulphur |
| 50 ₃ | sulphite |
| SO4 | sulphate |
| s ₂ 0 ₃ | thiosulphate |
| AOX | adsorbable organic halide or total organic chlorine |
| C10 ₃ | chlorate |

Metals

| Ai | aluminum |
|----|-----------|
| Са | calcium |
| Cđ | cadmium , |
| Cr | chromium |
| Cu | copper |
| Fe | iron |
| Mn | manganese |
| Ni | nickel |
| Рb | lead |
| Zn | zinc |
| | |

ł

| Na | sodium |
|----|-----------|
| Со | cobalt |
| Mg | magnesium |

Resin Fatty Acids (RFA)

| DHA | dehydroabietic acid | | | | | |
|--------|--------------------------------------|--|--|--|--|--|
| C-23:0 | percent recovery of fatty acid spike | | | | | |
| T.S.S. | total suspended solids | | | | | |
| V.S.S. | volatile suspended solids | | | | | |

Purgeable Organic Halides

| CCI4 | carbontetrachloride | | | |
|-------|---------------------|--|--|--|
| CHC13 | chloroform | | | |

Other Abbreviations

| NA | not | available |
|------|-----|------------|
| N.L. | non | lethal |
| ND | non | detectable |

| | BLEACH PLAN | 17 (41)14 | Company of the second | | ess otherwi: | an indiant | a sa N | |
|--|-------------|--------------|-----------------------|------------|---------------|----------------------|----------|-------------|
| | FUD (UF) | BUDGED | CODCUE) | EKNOF) | TP(UE) | Se indicad COD(F) | TKN(F) | TP(F) |
| | | 1.1.5 | | 1.4.7% | | | | |
| | NA | NĤ | NH 1100 | NA | NA | NA | NA | NA |
| U STRUE SEAL THNK | 450 | 3.30 | 1120 | 2.8 | 2.2 | 960 | | 2.6 |
| CUMB. ALCHLINE FILTRATE | 405 | 360 | 1320 | 1.1 | Ū.4 | 1280 | 1.1 | 0.4 |
| EG STHEE SEAL TANK | 585 | 540 | 2200 | 2 | 0.7 | 2280 | 2.1 | 0.7 |
| H STAGE SEAL TANK | 30 | 30 | 80 | 0.3 | ् <u>ण.</u> 1 | <1 | 0.2 | <0.1 |
| EC-STRUE GEAL TANK | 40 | 40 | 120 | 0.8 | 0.2 | 03 | 0.9 | <0.1 |
| DESTAGE SCAL LANK | 109 | 107 | 320 | 0.8 | <0.1 | 180 | 0.8 | 0.2 |
| #1 EVHPORATOR CONDENSATE | | 115 | 440 | 1.4 | <0.1 | 220 | 1.4 | <0.1 |
| #2 EVAPORATOR CONDENSATE | | 142 | 460 | 1.2 | <0.1 | 240 | 1.3 | <0.1 |
| COMBINED FOUL WATER | 660 | 650 | 1220 | 15.1 | 0.2 | 1060 | 15.1 | <0.1 |
| BLERCHED PULP | NĤ | NĤ | NA | NA | NA | NA | NA | NA |
| field blank | NA | NĤ | NA | NA | NA | NA | NA | NA |
| | V(1), | ATHE ORG | ANIC ACIDS- | | | | | |
| | ACETIC | PROP. | BUTYRIC | ISO-BUTYR | pН | FIL. | CR | CD |
| C-STAGE SEAL TANK | 23 | 0 | Û | 0 | 2.0 | 1.25 | 98 | <.010 |
| COMB. ALKALINE FILTRATE | 27 | Û | 0 | 0 | 10.0 | 0.275 | 13.8 | <.010 |
| EG STAGE SEAL TANK | 17 | 0 | 0 | 0 | 10.0 | 0.56 | 15.4 | <.010 |
| H-STAGE SEAL TANK | 0 | 0 | 0 | 0 | 8.9 | 0.137 | 7.9 | <.010 |
| EC-STAGE SEAL TANK | 0 | 0 | 0 | 0 | 10.8 | 0.52 | 22.5 | <.010 |
| D-STAGE SEAL TANK | 0 | 0 | 0 | 2 | 2.8 | 0.42 | 31 | <.010 |
| #1 EVAPORATOR CONDENSATE | 0 | 0 | 0 | 0 | 9.1 | 0.21 | 1 | <.010 |
| #2 EVAPORATOR CONDENSATE | | 0 | 0 | 0 | 8.7 | 0.2 | 0.4 | <.010 |
| COMBINED FOUL WATER | Ũ | Û | 2 | 0 | 8.0 | 0.21 | 0.65 | <.010 |
| | DESTN CE | ATTY ACIDS | | | | | | |
| | linoleic | oleic | | condoror i | sopimaric | oplustric | DHA | abietic |
| | THOIGIC | OVETC | hima in | copimaric | sopraa to | paruso ic | LANT | CDICLIC |
| C STAGE SEAL THNK | ND | ND | ND | ND | ND | ND | ND | ND |
| COMB. ALKALINE FILTRATE | NO | ND | NO | ND | ND | 5.68 | ND | ND |
| EO STAGE SEAL TANK | ND | NE | ND | ND | ND | 11.2 | ND | ND |
| H-STAGE SEAL THAK | ND | | | ND | | ND | ND | |
| E2-STAGE SEAL TANK | ND | ND ND | ND ND | ND | ND ND | ND ND | ND | ND ND |
| D-STAGE SEAL TANK | ND | ND ND | ND | ND | ND | ND | ND | ND |
| #1 EVAPORATOR CONDENSATE | | | 0.527 | ND ND | 1.12 | MD ND | ND | ND 0.524 |
| #1 EVHPORATOR CONDENSATE #2 EVHPORATOR CONDENSATE | | 9.96 12.9 | 0.527 | | | | | |
| | | 12.9 | | ND MD | 1.63 | 1.63 | NO MO | 0.956 |
| COMBINED FOUL WATER | ND | 0.568 | NÐ | ND | 0.292 | 1.09 | ND | 0.454 |

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| | NH4+ | N02 | NU3- | 100 | H25 | 503 | 504 | 5203 |
|---------------------------|---------|---------|-----------|--------|---------|----------------|--------|------|
| BEUNNETUCE | NĤ | NA | NĤ | NĤ | NA | NĤ | NA | NA |
| C STRUE SERL FRINK | 0.3 | <0.1 | 0.3 | 560 | 0.1 | NA | 42 | <10 |
| COMB. HERHEINE FELTPATE | 1.4 | 0.2 | <0.1 | 652 | 3 | NĤ | 34 | 186 |
| EG STHGE GEAL TANK | 2.2 | 0.3 | <0.1 | 992 | 0.4 | NA | 60 | 105 |
| H-STAGE SEAL LANK | <0.1 | < 0.1 | 0.3 | 64 | 0.1 | NA | <10 | <10 |
| EUS STRIGE SEAL TANK | 0.2 | <0.1 | 0.3 | 83 | NĤ | NA | <10 | <10 |
| D-STAGE SEAL TANK | 0.3 | < 0.1 | 0.4 | 156 | 0.3 | NA | 30 | 198 |
| # 1 EVHPORHTOR CONDENSETE | 0.8 | < 0.1 | <0.1 | 89 | 5.9 | NĤ | 18 | 117 |
| #2 EVAPORITOR CONDENSITE | 0.7 | 0.1 | <0.1 | 112 | 8.4 | NA | 16 | 126 |
| COMBINED FOUL WATER | 10.5 | •0.1 | < 0.1 | 350 | 24.7 | NA | <10 | NA |
| BLEACHED PHUP | NA | NFI | NA | NA | NA | NA | NA | NH |
| field blank | NA | NĤ | NB | NA | NB | NA | NA | NB |
| the says and | | | | ····· | ETALS | | | |
| | CR | CU | FE | MN | NI | PB | ZN | NA |
| CHSTAGE SEHL TANK | 0.091 | 0.028 | 101 | 3.99 | 0.052 | <.020 | 0.474 | 224 |
| COMB. ALKHI INE FILTER F. | 0.027 | 0.029 | 0.407 | 0.235 | 0.042 | <.020 | 0.069 | 780 |
| EO STAGE SEAL TANK | 0.057 | <.010 | 0.507 | 0.3 | 0.041 | < .0 20 | 0.073 | 978 |
| H-STAGE SEAL TANK | 0.037 | <.010 | 0.3 | 0.035 | 0.043 | <.020 | 0.047 | 160 |
| E2-STAGE SEAL TANK | 0.025 | <.010 | 0.223 | 0.037 | 0.019 | 0.268 | 0.051 | 429 |
| D-STAGE SEAL TANK | 0.047 | 0.02 | 0.525 | 0.216 | 0.016 | <.020 | 0.136 | 170 |
| #1 EVAPORATOR CONDENSHTE | 0.049 | <.010 | 0.267 | 0.014 | <.010 | < .0 20 | 0.05 | 12.8 |
| #2 EVHPORATOR CONDENSATE | 0.018 | 0.012 | 0.14 | 0.013 | <.010 | <.020 | 0.053 | 18.5 |
| COMBINED FOUL WATER | 0.018 | 0.043 | 0.176 | 0.016 | <.010 | <.020 | 0.053 | 14.5 |
| | | | | | | | | |
| | neom | chlorom | dichloro- | TOTAL. | C-23:0 | T.S.S. | V.S.S. | |
| | abietic | DHA | DHA | REA | (% rec) | | | |
| C-STAGE SEAL TANK | ND | NO | ND | ND | 94.4 | 23 | 25 | |
| COMB. ALKALINE FILTRATE | 041 | 0.546 | 0.27 | 6.496 | 97.1 | 58 | 48 | |
| Ed STAGE SEAL TANK | 0.521 | 1.01 | 0.46 | 13.191 | 109 | 53 | 45 | |
| H-STAGE SEAL TANK | ND | ND | NB | ND | 79.8 | 57 | 57 | |
| E2~STAGE SEAL TANK | ND | ND | ND | ND | 93.6 | 23 | 27 | |
| BESTAGE SEAL TANK | MD | NO | NO | ND | 97.7 | 7 | 13 | |
| #1 EVAPORATOR CONDENSATE | NO | ND | ND | 12.131 | 96.1 | 23 | 18 | |
| #2 EVAPORATOR CONDENSATE | NÐ | 1.1 | ND | 18.918 | 94.9 | 13 | 23 | |
| COMBINED FOUL WATER | t4D | ND | ND | 2.404 | 89.4 | 10 | 17 | |

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| | TOTAL SULPHUR | HOX | NUOD SUGAR | METHANOL | ACID SOL. LIGNIN | ACID INS. LIGNIN | CL. | CL03 |
|--------------------------|------------------|-----------|---------------|-----------|---------------------|---------------------|------|------|
| BRUNNLTOCH | NA | 24.3 ug/g | NB | NA | NB | NA | NĤ | NA |
| CENTRON SELLE CLINE | 102 | 209 | 305 | 305 | 1400 | 916 | 2886 | 157 |
| COMB, ALENIAN FALLPHIE | 108 | 117 | 213 | 213 | 440 | 392 | 616 | 10 |
| EG STAGE SENE FROM | 114 | 145 | 312 | 312 | 920 | 660 | 846 | 4 |
| HENTINGE SEAL LEADE | 138 | 22.4 | 25 | <10 | 840 | 312 | 231 | -1 |
| ELL STAGE OF ALL FENT | 168 | 12 | 59 | $< \! 10$ | 320 | 288 | 168 | <1 |
| ELSTAGE SEAL ANNE | 156 | 12.3 | 155 | <10 | 1040 | 352 | 350 | 287 |
| #1 EVEPOPERUR CONTRACTOR | 140 | 0.3 | 10 | 52 | 44() | 252 | <10 | NH |
| #2 EVAPORHTOP LUNDENSHIE | 132 | 0.2 | 14 | 55 | 280 | 112 | <10 | NĤ |
| COMBINED FOUR ARTER | 200 | 0.2 | 14 | 587 | 440 | 152 | <10 | ŃA |
| BUERCHED FOLD | NB | 76.9 ug∕g | NA | NĤ | NĤ | NA | NA | NĤ |
| field blank | NĤ | 3. i | NĤ | NĤ | NA | NĤ | NA | NĤ |

| | 00 | MG |
|--------------------------|-------|------|
| CHISTRUE SEAL LENK | <.010 | 16 |
| COMB. ALKALINE FULLPATE | <.010 | 3.6 |
| EG STAGE SEAL TANK | <.010 | 3.38 |
| H-STAGE SERIE FOND | <.010 | 2.96 |
| E2-STAGE SEAL THAT | <.010 | 5.53 |
| D-STAGE SEAL FANK | <.010 | 7.7 |
| #1 EVEPORETOR CONDENSETE | <.010 | 0.24 |
| #2 EVAPORATOR CONDENSATE | <.010 | 0.24 |
| COMBINED FOUL WRITEP | <.010 | 0.28 |

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| C STAGE SEAL THNE |
|--------------------------|
| COMB. ALKALINE FILLADATE |
| EG STAGE SEAL TANK |
| H-STREE SEAL TONK |
| E2-STAGE SEAL (AND) |
| O-STAGE SEAL TANK |
| #1 EVAPORATOR CONDENSITE |
| #2 EVAPORHTOR CONULNSHIE |
| COMPINED FOUL WHITEP |

| | CHC | EX3 RECT. | PHENOL. | DOXICITY LC50 |
|--------------------------|----------|-----------|---------|---------------|
| | | | | (% volzvol) |
| ERPORTE TOTAL | MA | MEL | MB | NA |
| C STAGE SEAL TANK | ≤ 1 | 7.4 | Û. 1 I | 634 |
| COMB. ALCHING FILTPAIL | - 1 - | 7.8 | 0.19 | 20.09 |
| EG STAGE SEAL TANK | < 1 | 9.2 | 0.27 | 17.86 |
| H STAGE SEAL THNK | <1 | 1.8 | 0.04 | 3.,75 |
| ECHSTAGE SEAL TANK | < 1 | 1.5 | 0.02 | 59., 78 |
| DESTREE SEAL THNK | < 1 | 1.4 | <0.1 | 12.4 |
| #1 EVHPORITOR CONDENSHTE | <1 | 50.2 | 14.2 | 0.,88 |
| #2 EVHPORATOR CONDENSATE | <1 | 33.5 | 17.6 | 402 |
| COMBINED FOUL NATEP | <1 | 35.5 | 8.56 | 6.,76 |
| BLEACHED PULP | NH | MH | NA | NA |
| field blank | NA | NA | NA | NA |

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C-STAGE SEAL TANK COMB. ALKALINE FILTRATE ED STAGE SEAL TANK H-STAGE SEAL TANK E2-STAGE SEAL TANK D-STAGE SEAL TANK #1 EVAPORATOR CONDENSATE #2 EVAPORATOR CONDENSATE COMBINED FOUL WATER

C-STAGE SEAL TANK COMB. ALKALINE FILIWATE E0 STAGE SEAL TANK H-STAGE SEAL TANK E2-STAGE SEAL TANK D-STAGE SEAL TANK #1 EVAPORATOR CONDENSATE #2 EVAPORATOR CONDENSATE COMBINED FOUL WATER

| 0014 | CHC1-3 | | | | | |
|--------|--------|---|--|--|--|--|
| 0.0018 | 10 | | | | | |
| Ü. 01 | 1.6 | | | | | |
| 0.0058 | 0.78 | | | | | |
| 00088 | 7.8 | | | | | |
| 0.0009 | 0.23 | | | | | |
| ND | 0.024 | | | | | |
| NA | NB | • | | | | |
| NĤ | NA | | | | | |
| NĤ | NĤ | | | | | |

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| | BEERCH PLH | | | | و المراجع الم | | | | |
|------------------|-------------------------|------------|---------------------|-----------------------|-------------------|----------|--------|---------|-----------------|
| | (a)) a esult BUD(UE) | | сади опъ СОФСЛЕЭ | TENCUES | TP(UF) | 00D(F) | TKN(F) | TP(F) | NH4~N |
| BROWN FOOD MOTER | NĤ | NĐ | NIA | NA | NĤ | NE | NB | NÐ | NĤ |
| 910 HOL WITEP | 302 | 267 | 1050 | 3.3 | ·Ū.1 | 780 | 3.1 | <0.1 | 2.6 |
| 020 SLHE HINK | 450 | 420 | 3800 | 0.9 | 3.9 | 5500 | 0.8 | 4.2 | 0.3 |
| EG SEDE FRIE | 975 | 9.40 | 8000 | 5.5 | 3.3 | 7200 | 5.1 | 3.8 | 4.2 |
| EEE SEEN, TENNE | 420 | .391 | 2400 | 1.5 | 1 | 2020 | 1.6 | 11 | 0.5 |
| "B" ARTE ARTER | 111 | 78 | 1350 | 1.4 | 0.3 | 1100 | 0.5 | 0.2 | 0.6 |
| FILLO FILMM | NĤ | NA | NĤ | NB | NH | NE | NA | NĤ | NB |
| BLERCHED PULP | NG | MEL | NA | NA | NR | NA | NA | NE | NĤ |
| | | - VOLATILE | ORGANIC A | CI05 | | | | | |
| | ACTEIC F | ROPIONIC | BUTYPIC | ISOBUTYRIC | РH | A1 | Ca | Cd | £r |
| "H" HOT WHIER | Ð | Û | 0 | 0 | 6.5 | 0.24 | 7.33 | <.010 | <.010 |
| oza: Serie Trink | 0 | Û | 0 | 0 | 1.9 | Э | 162 | <.010 | 0.472 |
| Eo SEAL TANK | 18 | 0 | 0 | 0 | 10.2 | 0.5 | 23.5 | <.010 | 0.67 |
| DT SEAL TANK | 0 | Û | 0 | 0 | 2.9 | 2.1 | 70 | <.010 | 1.22 |
| "H" NHITE WATER | Û | 0 | 0 | 0 | 4.1 | 0.5 | 8.4 | <.010 | 0.04 |
| | | RESIN FAT | TY ACIDS | | | | | | |
| | I INOLEIC | OLETC | FIMHPIC (| SANDARA- COPIMARIC | ISO- P PIMARIC | ALUSTRIC | LIHA | ABIETIC | NEO~ ABIETIC |
| "Н" НОТ ИНТЕР | ND | 0.384 | 0.315 | ND | 0.7 | ND | ND | ND | ND |
| DVC SEAL THNK | ND | ND | ND | ND | ND | ND | ND | NO | ND |
| EG SERL FRINK | ND | ND | ND | ND | ND | 2.02 | 1.38 | ND | 0.408 |
| DA SERL TRNK | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| "8" NHITE WATER | ND | NEI | ND | ND | ND | ND | ND | NŰ | ND |
| | 01013-0 | 0014 | | | | | | | |
| | CHC13 | CC14 | | | | | | | |
| | (mg/L) | (ng/mL) | | | | | | | |

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| | s and a mail of | stronge now y | |
|-----------------|-----------------|---------------|--|
| "A" HOT MATER | NA | - MĤ | |
| 170 SEHL THNK | 1.2 | 0.41 | |
| Eo SEAL TANK | 0.18 | 0.42 | |
| DI SEAL TANK | 0.1 | 0.04 | |
| "U" NHITE WATER | NĤ | NĤ | |
| | | | |

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| | NO.2 | NUB | 100 | H.25 S | C1- | 604 | 5203 | TOTAL SULPHUR | FIDX |
|------------------|-----------------|-------|------------|--------|-------|-------|-----------|------------------|-----------------------|
| BEGINGTOCK MATTE | NHÀ | ME | NA | NĤ | NF | NĤ | NA | NA | 5.7 uq/q |
| "A" HET NHTER | <0.1 | <0.1 | 161 | 4.8 | 8 | 13 | 43 | 78 | ō.3 |
| 0.40 SEAL LEINE | .0 . 1 | 0.3 | 876 | 0.4 | 2711 | 88 | ≤ 10 | 84 | 184.5 |
| EG SEHL THNK | 0.7 | 0.4 | .3802 | AU. 1 | 2446 | 113 | NA | 270 | 139 |
| DI SEH THEK | «Tt.1 | 0.5 | 816 | 0.4 | 1918 | 189 | 45 | 190 | 70.8 |
| "D" NHELE MALER | < 0.1 | 0.2 | 125 | 0.4 | 52 | 46 | <10 | 79 | 7 |
| FIELD BLANE | NA | NFI - | NA | 0.2 | NEL | NA | NA | NR | NA |
| REFECTED PULP | NB | NĤ | MA | NB | NĤ | NA | NĤ | NB | 51.9 ug/g |
| - | | | | METALS | | | | | and the second second |
| | Сы | Fe | Mn | Mi | Pb | Zn | Na | Co | Mg |
| "H" HUT WHTER | 0. ŭ 4 5 | 0.163 | 0.016 | <.010 | <.020 | 0.041 | 22 | <.010 | 2 |
| 070 SEAU TANK | 0.051 | 1.43 | 5.49 | 0.025 | <.820 | 0.792 | 685 | <.010 | 30 |
| EG SEUL TRNK | Ú., 086 | 2.1 | ∃.4 | 0.01 | <.820 | 0.336 | 2655 | <.010 | 10.5 |
| OL SEAL TANK | 0.066 | 2.11 | 2.94 | 0.053 | <.820 | 0.442 | 1327 | <.010 | 19.2 |
| "B" WHITE WATER | 0.04 | 0.324 | 0.053 | <.010 | <.820 | 0.096 | 95.5 | <.010 | 4.75 |

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| | CHEORO~ D | ICHLORO- | TOTAL | 0-23 :0 |
|-----------------|-----------|----------|--------|----------------|
| | DHÀ | DHA | REH | (X REC) |
| "A" HUT WATER | ND | NEC | 1.399 | 95.9 |
| 0/C SEHL THINK | 0.283 | MCE | 0.283 | 111 |
| EU SEAL TANK | 11.3 | 0.443 | 15.551 | 113 |
| BI SEAL TANK | 1.56 | ND | 1.56 | 115 |
| "B" WHITE WATER | 2.45 | NÜ | 2.15 | 112 |

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"A" HOT WATER DZC SEAL TANK EG SEAL TANK DI SEAL TANK "B" WHITE WATER

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| | NODE | METHANOL | HOID SOL. | ACTO INS. | C103 | C102 | EXTRACT. | TOXICITY |
|-------------------------|-------|----------|-----------|-----------|------|------|----------|----------|
| | SUGAR | | LÍGNIN | LÍGNIN | | | | 1.050 |
| BROWNSTOCK, WHILE P | NĤ | 网络 | NR | NA | NA | NA | NÐ | NA |
| "ल" मर्वेद्य जाना दृष्ट | 8 | 252 | 1520 | 92 | NA | NFI | NA | 7.49 |
| 0.40 SEAL THNK | 201 | 374 | 1080 | 88 | 251 | <1 | 9.1 | 17.63 |
| Eo SEAL TANK | 621 | 365 | 880 | 1596 | 501 | <1 | 32.5 | 16.59 |
| DI SEAL TANK | 158 | 73 | 1960 | 100 | 837 | <1 | 18.3 | 40.84 |
| "8" WHITE WATER | 22 | <10 | 840 | 192 | NA | NA | 151.4 | 48.34 |
| FIELD BLÄNK | NA | NĤ | NA | NA | NĤ | NA | NE | NA |
| BLENCHED PULP | NA | NA | NĤ | NA | NA | NA | NA | NA |

"A" HOT WATER D/C SEAL TANK EG SEAL TANK DI SEAL TANK "B" WHITE WATER

"A" HOT WHTER D/C SEAL TANK Eo SEAL TANK D1 SEAL TANK "B" WHITE WATER

"A" HOT WATER D/C SEAL TANK Eo SEAL TANK OJ SEAL TANK "8" WHITE WATER

| | LEHCH PLAND | | | | | | |
|----------------------------|--------------------------|---------|---------------------------|---------------------|---------|--------|--------|
| I | ersolts in my BOD(UE) | | OTPER PROFILE COLOURIN | ndicated TKN(UF) | TP (UE) | 000(F) | TKN(F) |
| STRA, HROMASTOCK | ME | 1461 | NF 1 | NB | NĤ | NA | NA |
| SURT, CHSTRUE SEAC TANK | 1 10 | .2-101 | 1450 | 2.3 | 3.1 | 1410 | 2.1 |
| SULT, E-STRUE SHOW P WATER | 3 | d. | 1.1 | 1.6 | 0.2 | <10 | 0.3 |
| SOFT, E STADE SEAR TANK | 31.30 | .2011 | 2330 | 1.4 | 0.8 | 2180 | 1.6 |
| STIFT, HESTHER SEAL TANK | ាព | L.H.1 | 60% | 1 | 0.4 | 560 | 0.6 |
| SUFT, D-STHUE SHOWER WATER | 30 | 17 | 250 | 2.2 | <0.1 | 120 | 0.3 |
| SUEL, LESTAGE SEAL TANE | են | ીદ | 214 | 1.5 | < 0.1 | 210 | 0.5 |
| BEERCHED PULP | NB | NĒ | NA | NA | NĤ | NFI | NH |
| HERD, BROWNSTOCK | NB | 14F1 | NH. | NĤ | NA | NE | NĤ |
| HHPD, C-SINGE SEAL TANK | 84 | 63 | 740 | 1.5 | 6.9 | 630 | 0.7 |
| HEPD, E-STAGE SEAL TANK | | (21.11) | 1160 | 3 | 3.4 | 1040 | 1.1 |
| HHRD, H-STHGE SEAL TANK | ь0 | -4Ú | 30.2 | B.1 | 2.0 | 260 | 0.4 |
| HAPD, D-STAGE SHOWER MANK | 45 | 30 | 312 | 3.1 | 0.9 | 270 | <0.1 |
| HERD, D-STAGE SEAL TANK | 9 | 4 | 138 | 1.7 | 2.8 | 20 | <0.1 |
| BLEACHED PULP | MA | NE | NA | NB | NA | NĤ | NA |
| SIFPIPPER FEED | 1560 | 1080 | 6140 | 777 | 0.5 | 4110 | 80.5 |
| INFLUENT, BIOPLANI | 162 | 293 | 1450 | 9.2 | 1.6 | 1280 | 3.9 |
| EFFLUENT, BIOPLANT | ΝĤ | 3.1 | 415 | 11.7 | 2.1 | 370 | 1.5 |
| fieldblank | NA | MA | 18 | 1.6 | <0.1 | NĤ | NA |
| - | | | LE ORGANIC | : ACI85 | | | |
| | REFIC | PPOP. | BUTYRIC | ISO-BUTYR | TOTAL. | AL. | CA |
| SOLT, CHSIMGE SEAL TANK | 0 | Ű | 0 | 0 | <2 | 1 | 121 |
| SOFT, E-STHGE SHOWEP WHIER | 0 | Û | 0 | 0 | <2 | 0.074 | 9.12 |
| SOFT, E-STAGE SEAU TANK | 0 | 0 | 0 | Û | <2 | 0.585 | 62 |
| SUFT, H-SINGE SEAL TANK | D | Û | 0 | 0 | <2 | 0.2 | 22.3 |
| SUFT, D-STRGE SHOWER WATER | 0 | 0 | 0 | Û | <5 | 0.144 | 9.02 |
| SUFT, DESTAGE SEAL TANK | 0 | θ | 0 | 0 | -2 | 0.45 | 28.2 |
| HARD, CHSTAGE SEAL TANK | 0 | Û | 0 | 0 | <2 | 1.29 | 295 |
| HHRD, E-STAGE SEAL TANK | 0 | 8 | 0 | 0 | <2 | 0.417 | 57 |
| HARD, H-STAGE SEAL TANK | 0 | 0 | 0 | Û | <2 | 0.175 | 106 |
| HARD, D-STAGE SHOWER THNK | Ũ | 0 | 0 | Û | 12 | 0.164 | 27.5 |
| HERD, DESTREE SEAL LANK | 0 | 0 | 0 | Û | <2 | 0.175 | 149 |
| STRIPPER FLED | 32 | Ũ | 0 | 21 | 53 | 0.15 | 4.22 |
| INFLUENT, BIOPLANT | 23 | Û | 0 | 0 | 23 | 1.38 | 92 |
| EFFLUENT, BIOPLANT | Ū | Û | 0 | 0 | <2 | 0.99 | 84.5 |
| Fire) dt cliante | MA | MA | NĤ | NB | NB | 0.457 | 0.935 |

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| | TP(F) | NI44+ | NO2 | N03 | THC | HQS | 503 |
|----------------------------|-------|--------|-------|--------------|------------------------|-------|-------|
| SOFT, BROWNSTOCK | NĤ | NĤ | NB | NB | NB | NA | NĤ |
| SOFT, CHSTREE SEAL TANK | 1.8 | 0.4 | <Ü.1 | 0.1 | 559 | 0.2 | NA |
| SOFT, E-STREE SHOWER WATER | 0.1 | 0.2 | <0.1 | 0.1 | 7.6 | < 0.1 | NFI |
| SONT, E-STAGE SEAL TANK | 0.5 | 1.2 | < 0.1 | <0 .1 | 776 | 0.4 | NĤ |
| SOFT, H-STAGE SEAL TANK | 0.4 | 0.3 | <0.1 | 0.1 | 271 | 0.4 | NA |
| SOFT, D-STAGE SHOWER WATER | 0.3 | 0.3 | <0.1 | <0.1 | 54 | 0.3 | NA |
| SOF1, D-STAGE SEAL TANK | 0.1 | 0.4 | <0.1 | 0.2 | 104 | 0.2 | NA |
| BLEACHED PULP | NA | NĤ | NA | NA | NFI | NĤ | NA |
| HARD, BROWNSTOCK | NĤ | NĒ | NĤ | NA | MA | NĤ | NA |
| HARD, CHSTAGE SEAL TANK | 3.8 | 0.2 | < 0.1 | 0.2 | 323 | 0.4 | NĤ |
| HARD, E-STAGE SEAL TANK | · 1 | 0.4 | <0.1 | 0.1 | 435 | 0.3 | NB |
| HARD, H-STAGE SEAL TANK | 0.9 | 0.2 | < 0.1 | 0.1 | 113 | 0.3 | NĤ |
| HARD, D-STAGE SHOWER TANK | 0.5 | 0.2 | < 0.1 | <0.1 | 38 | 0.4 | NA |
| HARD, D-STAGE'SEAL TANK | 1.2 | 0.2 | <0.1 | <0.1 | 42 | 0.8 | NA |
| BLEACHED PULP | NĤ | NA | NĤ | NA | NA | - NA | NA |
| STRIPPER FEED | 0.1 | 58.2 | <0.1 | <0.1 | 1021 | 199 | NA |
| INFLUENT, BIOPLANT | 0.6 | 1 | <0.1 | <0.1 | 452 | 1.8 | NA |
| EFFLUENT, BIOPLANT | 0.2 | 2.42 | <0.1 | <0.1 | 128 | 1.2 | NA |
| fieldblank | NA | Ξ MA , | NA | NB | NA | NB | NA |
| | | | | | METALS | | |
| | CÐ | CR | CU | FE | MN | NI | PB |
| SOFT, CHSTAGE SEAL TANK | <.020 | 0.074 | 0,054 | 1.96 | 4.62 | 0.164 | 0.1 |
| SOFT, E-STAGE SHOWER WATER | <.020 | <.020 | <.020 | 0.225 | 0.032 | <.020 | <.020 |
| SOFT, E-STAGE SEAL TANK | <.020 | 0.025 | 0.032 | 0.842 | 3.17 | 0.05 | <.020 |
| SOFT, H-STAGE SEAL TANK | <.020 | 0.025 | 0.032 | 0.717 | 0.85 | 0.087 | <.020 |
| SOFT, D-STAGE SHOWER WATER | <.020 | <.020 | <.020 | 0.3 | 0.015 | <.020 | <.020 |
| SOFT, D-STRGE SEAL TANK | <.020 | 0.22 | 0.035 | 1.22 | 1.05 | 0.125 | 0.5 |
| HARD, C-STAGE SEAL TANK | <.020 | 0.06 | 0.05 | 3.62 | 3.97 | 0.167 | 0.15 |
| HARD, E-STAGE SEAL TANK | <.020 | <.020 | 0.022 | 0.73 | 1.36 | 0.03 | <.020 |
| HARD, H-STAGE SEAL TANK | <.020 | <.020 | 0.055 | 0.605 | 1 | 0.052 | <.020 |
| HARD, D-STAGE SHOWER TANK | <.020 | <.020 | 0.025 | 0.525 | 0.178 | 0.032 | <.020 |
| HARD, O-STAGE SEAL TANK | <.020 | 0.03 | 0.025 | 0.75 | t.32 | 0.065 | <.020 |
| STRIPPER FEED | <.020 | < 020 | <.020 | 0.182 | 0.027 | 0.02 | <.020 |
| INFLUENT, BIOPLANT | <.020 | 0.02 | 0.025 | 1.42 | 1.82 | 0.045 | <.020 |
| EFFLUENT, BIOPLANT | <.020 | <.020 | 0.025 | 0.825 | 2.65 | 0.04 | <.020 |
| fieldblank | <.020 | <.020 | 0.022 | 0.85 | <.020 | <.020 | <.020 |
| | | | | | | | |

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| | 114 | 5200 | TUTAL | AOX | NOOD | METHANOL | ACID SOL. |
|----------------------------|-------|------|---------|-------|-------|----------|-----------|
| | | | SULPHUR | | SUGAR | | LICNIN |
| STORI, BPOWNSIOUN | NB | NA | NĤ | 4.8 | NA | NA | NA |
| SUET, CHSTHGE SEAL TANK | 428 | <10 | NA | 198 | 235 | 185 | 2080 |
| SURT, E-STHGE SHOWEP WATER | 37 | <10 | 116 | 10.5 | < 1 | 30 | 2120 |
| SUBT, E-STAGE SEAL TANK | 164 | <10 | 53 | 176 | 166 | 89 | 1680 |
| SOFT, H-STHGE SEAL TANK | 54 | <10 | 95 | 42 | 64 | 21 | 2040 |
| SOFT, DESTAGE SHOWLP WATER | 112 | <10 | 63 | 5.6 | 34 | <10 | 5440 |
| SUET, DESTAGE SEAL TANK | 238 | <10 | 137 | 8.9 | 80 | 115 | 3560 |
| BLERCHED PULP | NA | NA | NA | 57.6 | NA | NA | NH |
| HHRD, BROWNSTOCK | NĤ | MA | NA | 1.9 | NA | NB | NH |
| HHRD, CHSTHGE SEAL TANK | 82 | <10 | 74 | 108 | 281 | 72 | 1520 |
| HAPO, E-STAGE SEAL TANK | 132 . | <10 | 63 | 48 | 83 | 62 | 2120 |
| NARD, HESTAGE SEAL TANK | 247 | <10 | 158 | 16 | 43 | <10 | 440 |
| HHRD, D-STRIGE SHOWER TANK | 141 | <10 | 116 | 5.6 | 20 | <10 | 1240 |
| HHRD, DHSTAGE SEAL TANK | 309 | <10 | 200 | 4.3 | 19 | <10 | 520 |
| BLEACHED PULP | NB | NA | NA | 112.9 | NĤ | NA | , NA |
| STRIPPER FEED | 13 | 1110 | 179 | 1 | <1 | NA | 800 |
| INFLUENT, BIOPLANT | 164 | 87 | 105 | 24 | 66 | 85 | 1200 |
| EFFLUENT, BIOPLANT | 156 | <10 | 169 | 14 | 20 | <10 | 1400 |
| fieldblank: | NĤ | NA | NA | NĤ | <1 | NB | 680 |

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| | Z'N | NĤ | CO |
|----------------------------|-------|-------|-------|
| SOFT, C-STAGE SERU TRNK | 0.875 | 325 | <.020 |
| SUFT, E-STREE SHOWER WATER | 0.042 | 4.75 | <.020 |
| SOFT, E-STAGE SEAL TANK | 0.325 | 1550 | <.020 |
| SOFT, HESTAGE SEAL TANK | 0.125 | 465 | <.020 |
| SOFT, D-SINGE SHOWER WATER | 0.05 | 134 | <.020 |
| SUFT, D-STAGE SEAL TANK | 0.151 | 168 | <.020 |
| HARD, C-STAGE SEAL TANK | 1.6 | 158 | <.020 |
| HARD, E-STAGE SEAL TANK | 0.592 | 1290 | <.020 |
| HIND, H-STHEE SEAL TANK | 0.25 | 258 | <.020 |
| HARD, D-STAGE SHOWER TANK | 0.094 | 101 | <.020 |
| HARD, DHSTAGE SEAL TANK | 0.637 | 60.2 | <.020 |
| STRIPPER FEED | 0.05 | 15.8 | <.020 |
| INFLUENT, BIOPLANT | 0.372 | 409 | <.020 |
| EFFLUENT, BIOPLANT | 0.188 | 285 | <.020 |
| f relablant: | 0.042 | 0.472 | . 828 |
| | | | |

| | 8010 INS. | CL ~ | CL03 | CL02 | EXTRACT. | PHENOL. | TOXICITY LC 50 |
|------------------------------|-----------|------|----------|------|----------|---------|----------------|
| | LIGNIN | | | | | | (% VOLZVOL) |
| SOFT, BROWNSTOCK | NĤ | NA | NĤ | NĤ | NA | NĤ | NE |
| SOFT, CHSTHGE SEAL TANK | 268 | 2505 | 97 | <1 | 18.89 | 0.09 | 8.73 |
| SUPT, E-STRIGE SHOWLR WRITER | 240 | 5 | <1 | <1 | 2.35 | 0.02 | <100 |
| SUFT, E-STAGE SEAL TANK | 204 | 1621 | 95 | <1 | 7.03 | 0.30 | 99.99 |
| SOFT, H-STAGE SEAL TANK | 308 | 648 | 29 | <1 | 5.10 | 0.12 | N.L. |
| SOFT, D-STAGE SHOWER WATER | 116 | 124 | 63 | <1 | 7.47 | 0.01 | 82.13 |
| SOFT, D-STAGE SEAL TANK | 208 | 289 | 163 | <1 | 1.62 | <0.01 | N.L. |
| BLEACHED PULP | NĤ | NA | NĤ | NA | NA | NA | NE |
| HARD, BROWNSTOCK | NB | NA | NĤ | MĤ | NA | NA | NĤ |
| HARD, C-STAGE SEAL TANK | 148 | 1468 | 125 | <1 | 4.39 | 0.05 | 43.61 |
| HARD, E-STAGE SEAL TANK | 252 | 1373 | 120 | <1 | 13.74 | 0.10 | 21.21 |
| HARD, H-STAGE SEAL TANK | 176 | 420 | 87 | <1 | 6.90 | 0.06 | 54.77 |
| HARD, D-STAGE SHOWER TANK | 152 | 72 | - 70 | <1 | 23.42 | 0.11 | 100 |
| HARD, D-STAGE SEAL TANK | 128 | 184 | 162 | < 1 | 7.13 | 0.02 | N.L. |
| BLEACHED PULP | NA | NĤ | NA | NA | NFI | NA | NB |
| STRIPPER FEED | 104 | <1 | 85 | <1 | 233.00 | 41.67 | 1.67 |
| INFLUENT, BIOPLANT | 216 | 510 | 55 | <1 | 15.47 | 0.95 | 97.93 |
| EFFLUENT, BIOPLANT | 248 | 509 | 12 | <1 | 3.59 | 0.06 | N.L. |
| fieldblank | 72 | <1 | ≤ 1 | <1 | 1.20 | <0.01 | NA |

SOFT, C-STAGE SEAL TANK SOFT, E-STAGE SHOWER WATER SOFT, E-STAGE SEAL TANK SOFT, H-STAGE SEAL TANK SOFT, D-STAGE SHOWER WATER SOFT, D-STAGE SHOWER WATER SOFT, D-STAGE SEAL TANK HARD, C-STAGE SEAL TANK HARD, E-STAGE SEAL TANK HARD, D-STAGE SEAL TANK HARD, D-STAGE SHOWER TANK HARD, D-STAGE SEAL TANK STRIPPER FEED INFLUENT, BIOPLANT EFFLUENT, BIOPLANT fieldblack

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DEENCH PEANIN "(" (soffwood) 8 "D" (bandwood) results in mg/L unless otherwise indicated

| | рH | lindero | olein | pinaric | sandara- | isopunaric |
|----------------------------|------|---------|-------|---------|-----------|------------|
| | | | | | copimaric | |
| SOFT, CHSTAGE SEAL TANK | 2.2 | ND | NO | ND | ND | NEI |
| SUPT, E-STAGE SHOWER WHIER | 7.6 | ND | ND | ND | ND | ND |
| SHET, E STRGE SEAL TANK | 11.0 | ND | ND | ND | ND | 0,922 |
| SOFT, HESTAGE SEAL TANK | 9.5 | NO | ND | ND | ND | 0.305 |
| SOFT, D-SINGE SHOWER WATER | 6.0 | ND | NÜ | ND | ND | NÐ |
| SURT, DHSTAGE SEAL TANK | 2.6 | ND | ND | ND | ND | ND |
| HHFD, C-STAGE SEAL TANK | 2.6 | ND | ND | ND | ND | NE |
| HOPD, E-STHGE SEAL TANK | 11.6 | ND | ND | ND | ND | 1.23 |
| HUPD, H-STAGE SEAL TANK | 6.9 | MÜ | NEU | ND | ND | 3.47 |
| HHRD, AFSTAGE SHOWER TANK | 2.1 | ND | ND | ND | ND | ND |
| HHRD, D-SCHGE SEAL TANK | 3.1 | ND | ND | ND | ND | ND |
| STRIPPER FEED | 8.9 | 0.943 | 0.48 | 0.114 | 0.,28 | 0.357 |
| INFLUENT, BIOPLAND | 8.6 | 13.9 | 0.964 | ND | ND | 0.409 |
| EFFLUENT, BIOPLANT | 7.9 | ND | ND | ND | ND | ND |
| Fieldh) ani | NA | ND | ND | ND | ND | ND |

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| | palustric | DHA | abietic | neo- abietic | chloro- DHA | dichloro- OHA | TOTAL REA |
|----------------------------|-----------|-------|---------|-----------------|----------------|------------------|--------------|
| SOFT. CHSTAGE SEAL TANK | ND | ND | ND | NÐ | ND | ND | ND |
| SOFT, E-STAGE SHOWER WATER | 2 ND | NED | NO | ND | ND | ND | ND |
| SOFT, E-STAGE SEAL TANK | ND | NÐ | ND | 0.202 | 0.458 | 0.706 | 2.288 |
| SOFT, H-STAGE SEAL TANK | ND | NÐ | ND | ND | 0.378 | 0.278 | 0.961 |
| SULT, D-STREE SHOWER WATER | R ND | ND | ND | ND | ND | NO | ND |
| SOFT, D-STAGE SERV. TANK | ND | ND | ND | ND | ND | NO | ND |
| HARD, C-STAGE SEAL TANK | ND | ND | ND | ND | ND | NO | ND |
| HARD, E-STAGE SEAL TANK | ND | ND | 1.63 | 3.37 | 0.296 | 0.195 | 6.721 |
| HARD, H-STAGE SEAL TANK | ND | 3.03 | ND | ND | 2.23 | ND | 8.73 |
| HARD, D-STAGE SHOWER TANK | , ND | ND | NO | ND | ND | ND | ND |
| HARD, D-STAGE SEAL TANK | ND | NÜ | ND | ND | NE | NO | NE |
| STRIPPER FEED | 104 | ND | 0.583 | 0.341 | ND | ND | 4.138 |
| INFLUENT, BIOPLANT | 2.14 | 0.736 | 1.13 | ND | ND | NO | 18.673 |
| EFFLUENT, BIOPLANT | ND | ND | ND | ND | ND | ND | NO |
| fieldblank | ND | ND | ND | · ND | 140 | ND | NO |

| | | 1.5.5. | V.S.S. |
|-----------------------------|-------------------|--------|--------|
| | 0-23:0 | | |
| , | $(2, m_{\rm MO})$ | | |
| SOMI, COSTAGE SEAL IAND | 114 | 505 | 490 |
| SOFT, E-STHGE SHOWER WATER | 108 | 111 | 45 |
| SULT, FESTAGE SEAL TANK | 1.30 | 0 | 0 |
| SUFT, HESTIGE SEAL TANK | 108 | 65 | 135 |
| SOFT, DESTROE SHOWER WRITER | 83.2 | 90 | 245 |
| SULT, DISTAGE SEAL TANK | 81.1 | 0 | 0 |
| HHRD, COSTHGE SEAL TANK | 116 | 455 | 475 |
| HARD, E-STAGE SEAL TANK | NĤ | 115 | 45 |
| HARD, H-STHGE SEAL TANK | 96.5 | 50 | 80 |
| HARD, D-STAGE SHOWER TANK | 111 | 180 | 160 |
| HERD, DHSTERGE SEAL TANK | 111 | 0 | 0 |
| STRIPPER FEED | 107 | 0 | 0 |
| INFLUENT, BIOPLANT | NA | 65 | 65 |
| EFFLUENT, BIOPLANT | 100 | 65 | 30 |
| fieldblank | 109 | NA | NĤ |

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