

United States
Environmental Protection
Agency

Office of Water
Office of Water Regulations
and Standards (WH-552)
Washington, DC 20460

EPA-440/1-88-025 ✓
March 1988



U.S. EPA/Paper Industry Cooperative Dioxin Screening Study



U. S. ENVIRONMENTAL PROTECTION AGENCY/PAPER INDUSTRY
COOPERATIVE DIOXIN SCREENING STUDY

MARCH 1988

U. S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER
OFFICE OF WATER REGULATIONS AND STANDARDS
WASHINGTON, D.C. 20460

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ACKNOWLEDGMENTS

Alexander C. McBride was USEPA's project director for this study and Gary A. Amendola was USEPA's project manager. Russell O. Blosser, NCASI, was the project manager for the paper industry. The principal authors of this report were Gary A. Amendola, USEPA, and Raymond C. Whittemore, Ph.D., NCASI. Francis Thomas, USEPA, and Lawrence E. LaFleur, NCASI, served as quality assurance officers. Analysis of samples for 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran were conducted at the Brehm Laboratory, Wright State University, Dayton, Ohio, under the direction of Thomas O. Tiernan, Ph.D. Analysis of samples for selected chlorinated phenolics were conducted at the NCASI West Coast Regional Center, Corvallis, Oregon, under the direction of Lawrence E. LaFleur.

The authors acknowledge the contributions of the following people who participated in the conduct of the field studies: David R. Barna, Jonathan L. Barney, Danforth G. Bodien, Daniel S. Granz, David A. Parrish, and Raymond E. Thompson, USEPA; Andre L. Caron, James J. McKeown, and Steven Norton, NCASI; and the many other people from participating paper companies, state pollution control agencies, and USEPA, whose assistance was essential for the successful completion of this project. The authors also acknowledge the assistance of the Michigan Division of Dow Chemical U.S.A. in conducting analyses of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans for selected samples. Ms. Carol Kopcak, USEPA, typed this report.

Finally, the authors acknowledge the efforts and contributions of Russell O. Blosser, senior vice president, NCASI, who provided guidance and direction throughout the conduct of this study.

DISCLAIMER

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EXECUTIVE SUMMARY

As a result of the National Dioxin Study findings of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) in native fish collected downstream from a number of pulp and paper mills and subsequent findings of 2378-TCDD in bleached kraft pulp and paper mill wastewater sludges, the United States Environmental Protection Agency (USEPA) planned a detailed process evaluation study at one mill. Through subsequent discussions with the paper industry, USEPA and the industry agreed in June 1986 to conduct a cooperative screening study of five bleached kraft pulp and paper mills on a shared resource basis. Three mills were selected on the basis of known 2378-TCDD levels in sludges and two mills were volunteered by their parent companies to attain the geographical diversity desired for the study. The selection of the five mills, which represent about 6 percent of the bleached kraft mills in the United States, was not intended to characterize the entire industry. The principal objectives of the study were:

1. Determine, if present, the source or sources of 2378-TCDD and other polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at five bleached kraft pulp and paper mills; and
2. Quantify the untreated wastewater discharge loadings, final effluent discharge loadings, sludge concentrations, and wastewater treatment system efficiency for 2378-TCDD and other PCDDs and PCDFs.

Field work for the five-mill study was conducted during the period June 1986-January 1987 through the combined efforts of four USEPA regional offices, five state environmental control agencies, the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), and the participating paper companies. The analytical methods development program and analyses of samples for selected PCDDs and PCDFs were conducted at the Brehm Laboratory, Wright State University. Selected samples were analyzed for certain chlorinated phenolics by NCASI.

This report is limited to presentation of the complete data and the scientific and technical findings resulting from the cooperative study. Consideration of public and occupational health, environmental, consumer product, and regulatory issues that may be associated with study findings is beyond the scope of this report. Additional research is being planned and implemented by both government and industry to deal with such issues.

To accomplish the first study objective, it was necessary to design a general comprehensive study plan of all major and minor mill inputs, intermediates, and mill exports. The general plan was modified as necessary to conform to the specific circumstances of each mill. Because chlorine and chlorine derivatives are first introduced in substantial quantities in the bleaching process, emphasis was placed on detailed process sampling in bleacheries.

The principal mill exports sampled were bleached pulps, treated process wastewater effluents, and wastewater sludges dewatered for disposal. Although bleached pulps are converted into paper products at each mill, bleached pulps were considered mill exports for purposes of this study. This eliminated the need to sample and quantify mass outputs of numerous paper machines which were not always related to bleachery operations during field sampling.

The second objective was addressed by sampling combined untreated wastewaters, intermediate and final wastewater sludges, and treated process wastewater effluents. Evaluation of noncontact cooling waters and possible atmospheric emissions were not included in the study design.

Initially, the analytical program required, where possible, for each sample, isomer-specific analyses of tetrachloro dibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs) and, where possible, for selected samples, isomer-specific analyses of 2378-substituted penta- through hepta- CDDs and CDFs, and OCDD and OCDF. However, based upon analyses of a limited number of preliminary samples and a limited number of USEPA analyses of samples from other mills, the scope of the analytical program was reduced. The preliminary analyses indicate that 2378-TCDD and 2378-TCDF are the principal PCDDs and PCDFs found in the pulp and paper mill matrices, particularly when considered in light of USEPA's 2378-TCDD toxicity equivalents approach. Accordingly, all samples were analyzed for 2378-TCDD and 2378-TCDF, since the extensive analytical methods development work required for isomer-specific analyses of the other compounds did not appear warranted.

Specific findings and observations from this study are summarized in the sections that follow. They are grouped in a manner similar to the organization of the report.

Data Quality and Data Limitations

1. The analytical protocol for 2378-TCDD and 2378-TCDF developed for this study was found to be satisfactory for isomer-specific determinations of 2378-TCDD and 2378-TCDF in selected pulp and paper mill sample matrices. Intra-laboratory method validation experiments for pulp, sludge, and wastewater effluent samples

indicate the performance of the analytical method with respect to precision and spike recovery is demonstrably uniform. The method performance does not appear to be sensitive to any specific matrix or chemical effects which might be associated with the manufacturing processes at a given mill. Limited inter-laboratory comparisons incorporating different sample preparation, analytical methods, and calibration standards confirmed the presence of 2378-TCDD and 2378-TCDF in selected samples. However, a consistent bias was observed for quantitation of both 2378-TCDD and 2378-TCDF.

2. With few exceptions, the data quality assurance objectives established for this study for 2378-TCDD and 2378-TCDF were achieved.

- (a) Laboratory precision expressed as relative percent difference between duplicate analyses for thirty-five 2378-TCDD determinations was 15 percent mean (range 1-138 percent); and for thirty-three 2378-TCDF determinations, 16 percent mean (range 0-62 percent).
- (b) Field precision for eight 2378-TCDD determinations was 14 percent mean (range 4-19 percent); and for nine 2378-TCDF determinations, 22 percent mean (range 0-99 percent).
- (c) For thirty-five 2378-TCDD determinations, accuracy expressed as percent spike recovery was 103 percent mean (range 66-168 percent); and for thirty-five 2378-TCDF determinations, 102 percent mean (range 58-153 percent).
- (d) Including results from intra-laboratory method validation experiments, 97 percent of the analyses met the quality assurance objectives for laboratory precision and accuracy. Ninety-five percent of 133 determinations for 2378-TCDD and for 2378-TCDF resulted in analytical data suitable for project objectives.
- (e) Target analytical detection levels of 1 ppt for solid samples were achieved for all but one sample for 2378-TCDD and all but one sample for 2378-TCDF (different samples). Target analytical detection levels of 0.01 ppt for liquid samples were achieved for all but three samples for 2378-TCDD and all but two samples for 2378-TCDF (different samples).

3. Mass flow calculations for 2378-TCDD and 2378-TCDF combine analytical results with mass flow rates of solid materials (pulp, sludges) and liquids (waters, wastewaters). The mass flow rates for pulp and final treated wastewater effluents are considered to be accurate within less than ± 10 percent while mass flow rates for sludges, within less than ± 10 percent to 15 percent. Mass flow rates for internal plant wastewaters were generally based upon best engineering estimates and are considered accurate to

less than ± 20 percent to 25 percent. The reliability of reported bleach plant chemical application rates varied considerably from mill to mill, and in two cases were best engineering estimates. Non-detect analyses were treated as zero for mass balance calculations. The calculations and analyses presented in this report should be viewed accordingly.

PCDDs and PCDFs Found in Pulp and Paper Mill Matrices

1. Analyses of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from samples obtained at a number of bleached kraft pulp and paper mills processing primarily virgin fiber uniformly show that 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF) are the principal PCDDs and PCDFs found. This is particularly evident when the data are considered in light of USEPA's 2378-TCDD toxic equivalents approach for dealing with mixtures of PCDDs and PCDFs.

2. Data for the five mills included in this study show there is a characteristic 2378-TCDF/2378-TCDD ratio associated with individual bleach lines and individual mills, ranging from about 2 to about 18. This observation suggests that once 2378-TCDD and 2378-TCDF are formed, they are not altered in further processing or in wastewater treatment. Factors accounting for the differences in 2378-TCDF/2378-TCDD ratios across bleach lines and across mills have not been determined, nor has the possible process significance been formulated.

Sources of 2378-TCDD and 2378-TCDF

1. 2378-TCDD and 2378-TCDF are formed during the bleaching of kraft hardwood and softwood pulps with chlorine and chlorine derivatives at mills included in this study.

2. 2378-TCDD was not detected in seven unbleached kraft pulps collected at the five mills at detection levels ranging from 0.3 ppt to 1.0 ppt. 2378-TCDF was not detected in four of seven unbleached pulps at detection levels less than 0.3 ppt, but was found in three pulps collected at two mills at levels ranging from 1.1 to 2.3 ppt. The positive 2378-TCDF findings in unbleached pulps may be attributed to reuse of contaminated paper machine white waters for brownstock pulp washing or dilution.

3. 2378-TCDD was found in seven of nine bleached pulps collected at the five mills at concentrations ranging from 3 to 51 ppt and 2378-TCDF was found in eight of nine bleached pulps at levels ranging from 8 to 330 ppt. The median and mean concentrations are presented below:

	<u>2378-TCDD</u>	<u>2378-TCDF</u>
Median	5 ppt	50 ppt
Mean	13 ppt	93 ppt

4. 2378-TCDD and 2378-TCDF were found in most untreated bleach line filtrates sampled from the five mills. Wastewaters from caustic extraction stages (E and E₀) generally contained the highest concentrations and mass discharges from the bleach lines sampled.

5. The distributions of 2378-TCDD and 2378-TCDF in bleach line exports (bleached pulp and bleach plant wastewaters) were found to be highly variable from bleach line to bleach line. However, 2378-TCDD and 2378-TCDF were partitioned similarly to bleached pulps and bleach plant wastewaters within each bleach line.

6. 2378-TCDD was found in paper machine wastewaters from three of five mills and 2378-TCDF was found in paper machine wastewaters from each mill. The levels of 2378-TCDD and 2378-TCDF found in paper machine wastewaters were significantly less than found in the respective bleach plant wastewaters at four of five mills.

7. 2378-TCDD was found in one of five sludge landfill leachate or runoff samples at 0.025 ppt, while 2378-TCDF was found in four of five samples at levels ranging from 0.01 to 0.11 ppt. 2378-TCDD and 2378-TCDF were not detected in coal-fired power boiler ash samples from two mills at detection levels less than 1.0 ppt.

8. 2378-TCDD and other TCDDs were found in a sample of blue dye collected during preliminary sampling at one mill at levels of 3.4 and 53 ppt, respectively.

Formation of 2378-TCDD and 2378-TCDF

1. The rates of formation of 2378-TCDD and 2378-TCDF normalized to lbs/ton (kg/kkg) of air dried brownstock pulp are summarized below:

	10 ⁻⁸ lbs/ton (kg/kkg) of Brownstock Pulp	
	<u>Bleach Line Exports</u> <u>(eight bleach lines)</u>	<u>Total Mill Exports</u> <u>(five mills)</u>
<u>2378-TCDD</u>		
Range	ND-20(10)	0.14(0.07)-11(5.5)
Median	4.1(2.0)	3.0(1.5)
Mean	8.0(4.0)	4.4(2.2)
<u>2378-TCDF</u>		
Range	2.6(1.3)-360(180)	1.5(0.75)-130(65)
Median	12.5(6.3)	19(9.5)
Mean	68 (34)	41(21)

The range computed from bleach line exports exceeds that computed from total mill exports because of the integration of results from mills with multiple bleach lines in the mill export calculations. The extent to which these data are representative of long-term operations at the five mills, or are representative of the bleached kraft industry as a whole is not known.

2. Although the data from this study are limited, the results suggest casual relationships between the formation of 2378-TCDD and 2378-TCDF and (1) the degree of bleaching across bleach lines as estimated by the chlorine and chlorine equivalents applied to the unbleached pulp, and (2) the amount of lignin removed in the pulp across chlorination and caustic extraction stages as estimated by the difference in permanganate number (K) and CEK (permanganate number after caustic extraction). Attempts were made to develop statistical correlations with the limited data. However, the results were generally poor.

3. Bleach lines processing exclusively softwood pulps had higher rates of formation of 2378-TCDD and 2378-TCDF than bleach lines processing exclusively hardwood pulps. However, bleaching conditions on the softwood and hardwood bleach lines were different, and thus, it is not possible to conclude that the general wood species bleached is the determinant variable in formation of 2378-TCDD and 2378-TCDF.

Wastewater Treatment System Findings

1. 2378-TCDD was found in treated wastewater effluents from three of five mills at levels ranging from 0.015 to 0.12 ppt and 2378-TCDF was found in four of five effluents at levels from 0.011 to 2.2 ppt.

2. 2378-TCDD was found in wastewater treatment sludges collected from each of the five mills at levels from 17 to 24 ppt (primary sludges), 11 to 710 ppt (secondary sludges) and 3.3 to 180 ppt (combined sludges). 2378-TCDF was found at 32 to 380 ppt (primary sludges), 75 to 10900 ppt (secondary sludges) and 34 to 760 ppt (combined sludges).

3. Mass balance calculations around the wastewater treatment systems for three mills showed that about 50 percent to 80 percent of the 2378-TCDD and 40 percent to 60 percent of the 2378-TCDF found in treatment system exports (treated effluent, wastewater sludge) can be accounted for by treatment system inputs. For two mills the treatment system input loadings exceeded the export loadings by more than 200 percent. The poor mass balances are attributed to uncertainties in sludge, influent, and effluent flow rates, the sequencing of sampling at certain mills, and, to some extent, analytical variability associated with trace level analyses near method detection limits.

4. There is no evidence to suggest that 2378-TCDD and 2378-TCDF are destroyed in wastewater treatment systems. Rather, they may be transferred, to varying degrees, to wastewater treatment sludges. At two mills, about 10 percent to 15 percent of the 2378-TCDD and 2378-TCDF contained in untreated wastewater streams was transferred to the sludges in the wastewater treatment systems, while at the remaining three mills more than 80 percent transfer to sludges is indicated. The precise distribution of these compounds in the effluent between suspended solids and the liquid phase was not determined in this study.

5. The distributions of 2378-TCDD and 2378-TCDF between wastewater treatment exports (treated effluents and wastewater sludges) were highly variable from mill to mill. However, the partitioning of 2378-TCDD and 2378-TCDF between treated effluents and wastewater sludges was consistent within each mill. Mills with higher total suspended solids in effluents had higher levels of 2378-TCDD and 2378-TCDF partitioned to the effluent rather than to the sludge.

Pulp and Paper Mill Exports

1. The distributions of 2378-TCDD and 2378-TCDF among pulp and paper mill exports (bleached pulp, treated effluents, wastewater sludges) were highly variable from mill to mill, but the partitioning of 2378-TCDD and 2378-TCDF to the exports was consistent within each mill.

2. Mass balance calculations indicate that bleach plant sources accounted for about 90 percent to 140 percent of 2378-TCDD measured in mill exports at three mills, and more than 300 percent at another mill. 2378-TCDD was not detected in bleached pulp or bleach plant wastewaters at one mill. For 2378-TCDF, bleach plant sources were found to account for 70 to 130 percent of the amount measured in mill exports at four mills, and more more than 300 percent in the last mill. The poor mass balance results at some mills are attributed to uncertainties in mass flow rates of wastewater, sludge, and pulp, and, to some extent, analytical variability associated with trace level analyses near method detection limits.

Chlorinated Phenolics

1. For this study, chlorinated phenolics include selected chlorinated phenols, chlorinated guaiacols, and chlorinated vanillins. Chlorinated phenolics were formed in the bleaching process at each of the five mills. These compounds were not detected in treated intake process waters but were found in bleach plant filtrates and wastewater treatment system influents and effluents. Chlorinated phenolics were distributed differently at each mill.

2. Wastewaters from caustic extraction stage (E and E₀) washers accounted for most of the chlorinated phenolics. This finding is similar to findings for 2378-TCDD and 2378-TCDF in bleach line filtrates.

3. The amounts of chlorinated phenolics found in C-stage and E-stage filtrates were normalized to lbs/ton (kg/kkg) of air-dried brownstock pulp and are summarized below:

10⁻³ lbs/ton (kg/kkg) of Air-Dried Brownstock Pulp

<u>Sum of Chlorinated Phenolics</u>	<u>Sum of C-Stage and E-Stage Filtrates (eight bleach lines)</u>
Range	9.3-54 (4.2-24)
Mean	35 (17)
Median	34 (17)

4. With the limited data available, correlations between the presence of chlorinated phenolics and 2378-TCDD or 2378-TCDF in wastewater treatment system influents or effluents were not attempted. Because chlorinated phenolics were analyzed only for the water matrix, an evaluation of total chlorinated phenolics exports from bleach plants (i.e., pulp and wastewaters) could not be made. With the limited and incomplete wastewater data available, mass balance calculations between internal bleach plant filtrates and wastewater treatment system influents were not attempted.

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY

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LIST OF ATTACHMENTS

- A. USEPA/Paper Industry Cooperative Dioxin Screening Study;
June 1986, Amendment July 16, 1986.
- B. USEPA/Paper Industry Cooperative Dioxin Screening Study;
Sampling Procedures, Sample Preservation, and Sample Handling.
- C. Analytical Protocol for the Determination of 2,3,7,8-Tetra-
chlorodibenzo-P-Dioxin and 2,3,7,8-Tetrachlorodibenzofuran in
Paper Mill Process Samples (Woodchips and Paper Pulp) and
Paper Mill Effluents (Sludge, Ash, Mud, Treated and Untreated
Wastewater): Dioxin I Analyses; Wright State University,
Dayton, Ohio, June 1987.
- D. NCASI Methods for the Analysis of Chlorinated Phenolics in Pulp
Industry Wastewaters; Technical Bulletin No. 498; July 1986;
Revised May 1987.
- E. Analytical Results for 2378-TCDD and 2378-TCDF
(Master Sample Lists).
- F. Mass Flow Rates of 2378-TCDD and 2378-TCDF.
- G. Analytical Results for Chlorinated Phenolics, Total Suspended
Solids, and Biochemical Oxygen Demand.

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY

I. INTRODUCTION

As a result of National Dioxin Study¹ findings of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) in native fish collected downstream from a number of pulp and paper mills (levels from <5 to 85 parts per trillion (ppt)), and subsequent findings of 2378-TCDD in bleached kraft pulp and paper mill wastewater sludges (levels from <10 to 410 ppt), the United States Environmental Protection Agency (USEPA) planned a detailed process evaluation study at one mill. Through subsequent discussions with the paper industry, USEPA and the industry agreed in June 1986 to conduct a cooperative screening study of five bleached kraft pulp and paper mills on a shared resource basis (Attachment A). Three mills were selected on the basis of known 2378-TCDD levels in sludges and two mills were volunteered by their parent companies to attain the geographical diversity desired for the study. The selection of the five mills, which represent about 6 percent of the bleached kraft mills in the United States, was not intended to characterize the entire industry. The principal objectives of the study were:

1. Determine, if present, the source or sources of 2378-TCDD and other polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at five bleached kraft pulp and paper mills; and
2. Quantify the untreated wastewater discharge loadings, final effluent discharge loadings, sludge concentrations, and wastewater treatment system efficiency for 2378-TCDD and other PCDDs and PCDFs.

Field work for the five-mill study was conducted during the period June 1986-January 1987 through the combined efforts of four USEPA regional offices, five state environmental control agencies, the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), and the participating paper companies. The analytical methods development program and analyses of samples for selected PCDDs and PCDFs were conducted at the Brehm Laboratory, Wright State University. Selected samples were analyzed for certain chlorinated phenolics by NCASI. Conventional pollutants (total suspended solids (TSS) and five-day biochemical oxygen demand (BOD₅)) were determined for selected samples by mill laboratories for three mills, by a USEPA laboratory for one mill, and by a local water authority for the remaining mill.

This report is limited to presentation of the complete data and the scientific and technical findings resulting from the cooperative study. Consideration of public and occupational health, environmental, consumer product, and regulatory issues that may be associated with study findings is beyond the scope of this report. At this writing, additional research is being planned and implemented by both government and industry to deal with such issues.

II. STUDY DESIGN

To accomplish the first study objective, it was necessary to design a general comprehensive study plan of all major and minor mill inputs, intermediates, and mill exports. The general plan was modified as necessary to conform to the specific circumstances of each mill. Because chlorine and chlorine derivatives are first introduced in substantial quantities in the bleaching process, emphasis was placed on detailed process sampling in bleacheries. Mill inputs include wood chips, treated river waters used for processing, and numerous process additives including pulping chemicals, bleaching chemicals and paper mill additives (clays, alums, dyes, slimicides, etc.). Intermediates include river and well water supply treatment residuals, chemical recovery muds, brown pulps, untreated process wastewaters, and certain wastewater sludges. The principal mill exports include bleached pulps, treated process wastewater effluents, and wastewater sludges dewatered for disposal. Although bleached pulps are converted into paper products at each mill studied, bleached pulps were considered mill exports for purposes of this study. This eliminated the need to sample and quantify mass outputs of numerous paper machines which were not always related to bleachery operations during field sampling. At some mills wastewater sludge landfill leachates are also mill exports. They were sampled but assumed to be minor sources compared to bleached pulps, effluents, and sludges.

The second objective was addressed by sampling combined untreated wastewaters, intermediate and final wastewater sludges, and treated process wastewater effluents. Evaluation of noncontact cooling waters and possible atmospheric emissions were not included in the study design.

Initially, the analytical program required, where possible, for each sample, isomer-specific analyses of tetrachloro dibenzo-p-dioxins (TCDDs) and tetrachloro dibenzofurans (TCDFs) and, where possible, for selected samples, isomer-specific analyses of 2378-substituted penta- through hepta- CDDs and CDFs, and OCDD and OCDF. However, based upon analysis of a limited number of preliminary samples and a limited number of USEPA analyses of samples from other mills, the scope of the analytical program was reduced. The preliminary analyses indicate that 2378-TCDD and 2378-TCDF are the principal PCDDs and PCDFs found in the pulp and paper mill matrices, particularly when considered in light of USEPA's 2378-TCDD toxicity equivalents approach.² Accordingly, all samples were analyzed for 2378-TCDD and 2378-TCDF, since the extensive analytical methods development work required for isomer-specific analysis of the other compounds did not appear warranted.

A considerable effort was expended to develop the analytical protocol used in this study for isomer-specific 2378-TCDD and 2378-TCDF determinations. The results from field, laboratory and native spike duplicate, and native spike recovery experiments are presented herein. Sample analyses were conducted on a priority basis to minimize the total analytical burden. Limited experiments were conducted to develop analytical methods for isomer-specific determinations of 2378-substituted penta- through hepta- CDDs and CDFs, and OCDD and OCDF. Limited inter-laboratory method comparisons were conducted for four samples.

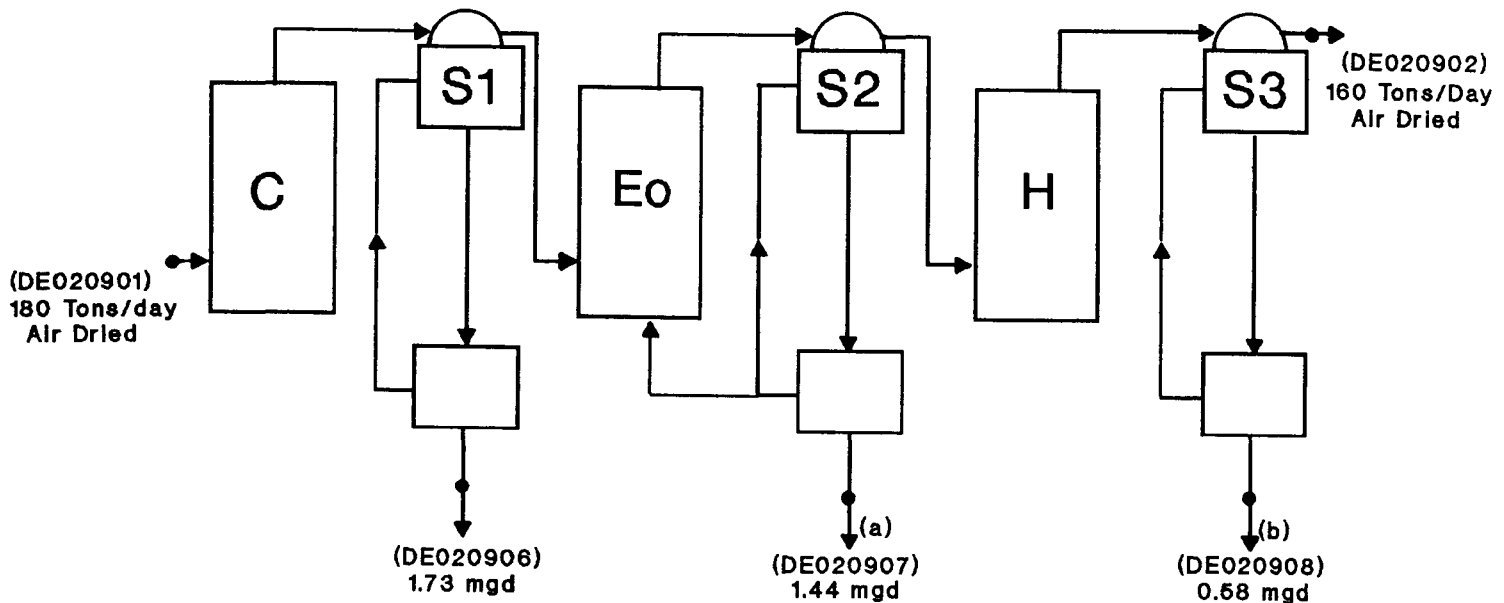
Selected samples were analyzed for chlorinated phenolics, total suspended solids (TSS), and biochemical oxygen demand (BOD₅). The chlorinated phenolics analyses were conducted to determine whether there is any relationship between the presence of those compounds and the presence of PCDDs and PCDFs. The TSS and BOD₅ analyses were conducted principally to determine whether there were any abnormal wastewater treatment system operations during the surveys.

III. THE FIVE BLEACHED KRAFT PULP AND PAPER MILLS

A. Mill A

Mill A is an integrated bleached kraft mill with a capacity of 580 tons per day of fine papers. Products include bond, business forms, coating base, envelope, ledger, reprographic, and tablet papers. Four batch digestors are used to pulp 400 tons per day of hardwood and softwood chips with a typical mix of 70% hardwood and 30% softwood. Pulping capacity exists for 365 tons per day bleached kraft (400 tons per day unbleached kraft).

The hardwood and softwood pulps are bleached separately in three lines. The softwood line consists of a CE₀H sequence while the hardwood line is split following common C and E₀ stages. One hardwood line has a single H stage while the other consists of two H stages followed by a peroxide (P) stage. All three bleaching lines are schematically shown in Figures III-1 and III-2. Sample identification codes and flow rates at the time of sampling are noted next to each sampling location. Nominal operating conditions and chemical usages are listed in Table III-1. It is significant to note that chlorine use at this mill was estimated from monthly inventory reports.



- a) Possible Over Flow to S1 Seal Box
b) Possible Over Flow to S2 Seal Box

FIGURE III-1. Mill A Softwood Bleaching Line Schematic

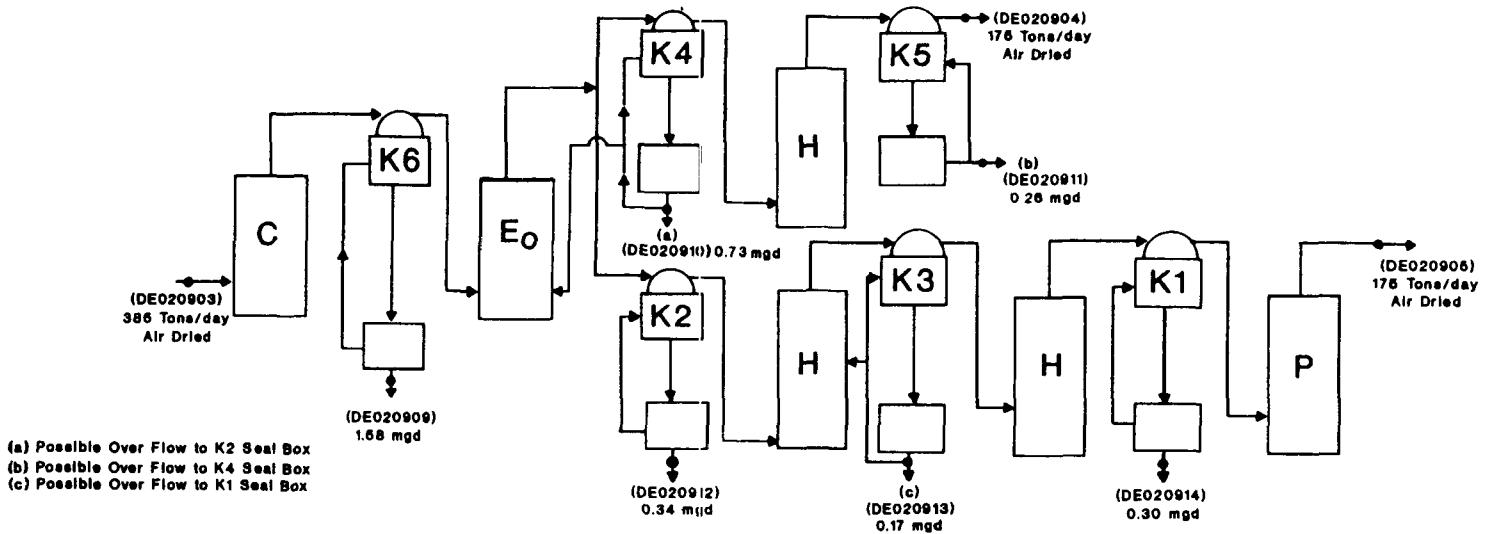


FIGURE III-2. Mill A Hardwood Bleaching Line Schematic

The power boiler burns gas and approximately 350 tons per day of bark to produce 650,000 lbs of steam per hour. Fly ash from the boiler is collected by electrostatic precipitation, combined with the wastewater treatment plant sludge and disposed of in a landfill. There is no contact of the boiler ash with the general mill sewer.

Raw water to the mill is pumped from a nearby river, treated with caustic, chlorine, alum, and mixed media filtration prior to use in the mill. Residues from this treatment are sewered. Approximately 20 MGD of treated process water are used. In addition, another 5.0 MGD is used for noncontact cooling water on the turbine condensers. A general schematic of the mill sewer system is shown in Figure III-3. This figure provides identification codes and flow rates associated with each sample location. The measurements or estimates were the best available at the time of sampling.

TABLE III-1

MILL A BLEACH PLANT OPERATING CONDITIONS AND CHEMICAL USAGES

Parameter	Bleaching Stage				
	C	E ₀	H	H	P
<u>Softwood</u>					
Throughput (BDT/day)	--	--	--	184	
Residence Time (hours)	1	1.3	1	1	
pH	1.9	10.5	9.0	8.4	
Temperature (°F)	99	145	95	95	
Chemical Usage (lb/ton)					
Cl ₂	80		--	--	
NaOH	--	30	--	--	
O ₂	--	10-12	--	--	
NaOCl	--	30	110	--	
Residual Cl ₂ (%Cl ₂)	0.24		1.1	0.85	
Wet Brightness	38.3	55.5	77.5-79.5	79.0-81.0	
Permanganate No.	20.2	2.5-3.0	--	--	
<u>Hardwood 1</u>					
*Throughput (BDT/day)	--	303	--	151.5	
Residence Time (hours)	0.6	0.8	1.2	1.2	
pH	2.4	10.5	8.9	--	
Temperature (°F)	104	148	104	--	
Chemical Usage (lb/ton)					
Cl ₂	60	--	--	--	
NaOH	--	25.3	--	--	
O ₂	--	8	--	--	
NaOCl	--	--	70	--	
Residual Cl ₂ (%Cl ₂)	0.23	--	1.1	0	
Wet Brightness	34	54	79	79.5-80.5	
Permanganate No.	11.4	2.9	--	--	
<u>Hardwood 2</u>					
*Throughput (BDT/day)	--	303	--	--	151.5
Residence Time (hours)	0.6	0.8	1.5	1.5	1.5
pH	2.4	10.5	9.0	8.4	9.8
Temperature (°F)	104	148	100	96	150
Chemical Usage (lb/ton)					
Cl ₂	60	--	--	--	--
NaOH	--	25.3	3.8	--	--
O ₂	--	8	--	--	--
NaOCl	--	--	70	--	--
H ₂ O ₂	--	--	--	--	10
Residual Cl ₂ (%Cl ₂)	--	--	0.53	0.14	0.35 (H ₂ O ₂)
Wet Brightness	34	54	75.7	--	78.5-79.5
Permanganate No.	11.4	2.9	--	--	--

*303 BDT through E₀ Stage, then split into two equal flows.

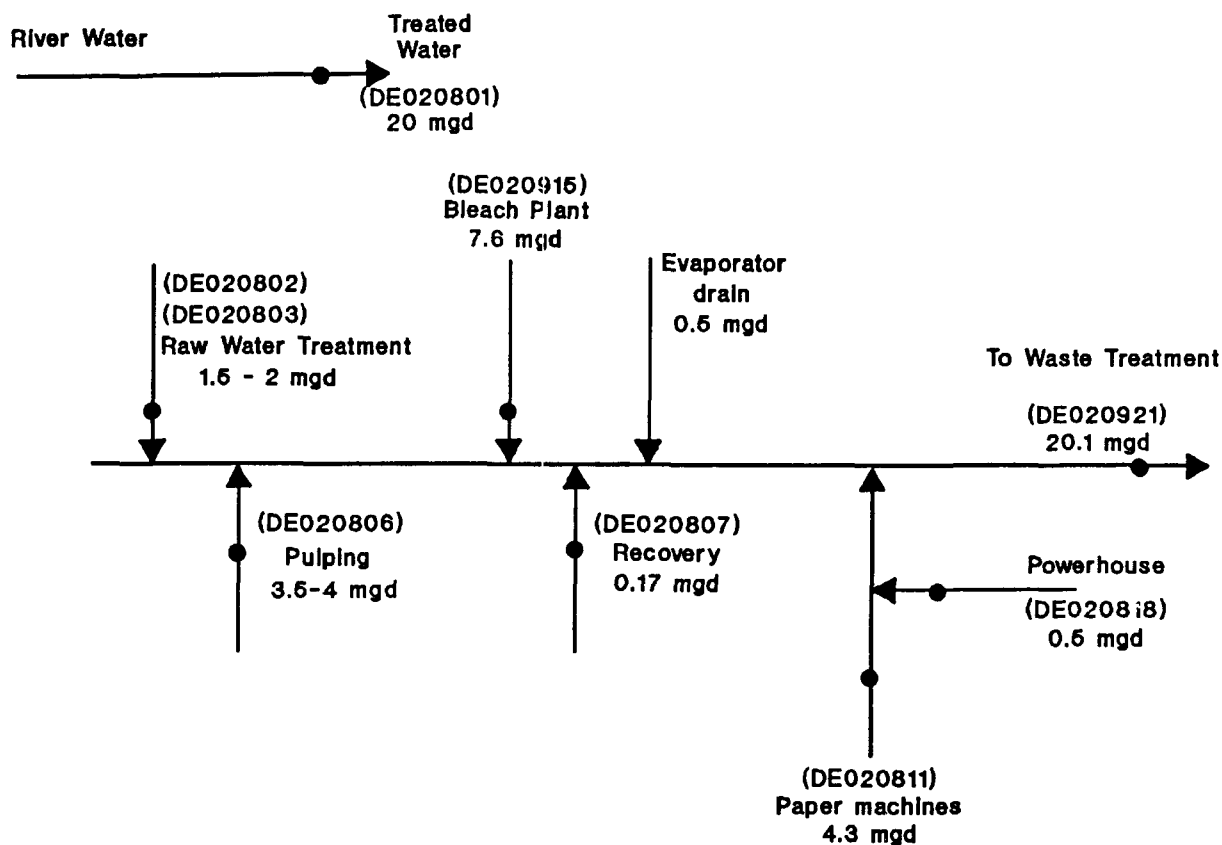


FIGURE III-3. Mill A Sewer System Schematic

The wastewater treatment system consists of primary clarification and oxygen activated sludge (UNOX) with 8.4 hours aeration time. All mill wastewaters go to the primary clarifier with no bypass. Combined primary and secondary sludge are dewatered with belt filter presses prior to landfill disposal. The noncontact cooling water mixes with the secondary effluent prior to river discharge. The wastewater treatment plant schematic is shown in Figure III-4. Identification codes and flow rates at the time of sampling are noted next to each sampling location. Typical operating conditions and performance are shown in Tables III-2 and III-3. These data reflect average operating conditions for both winter and summer months.

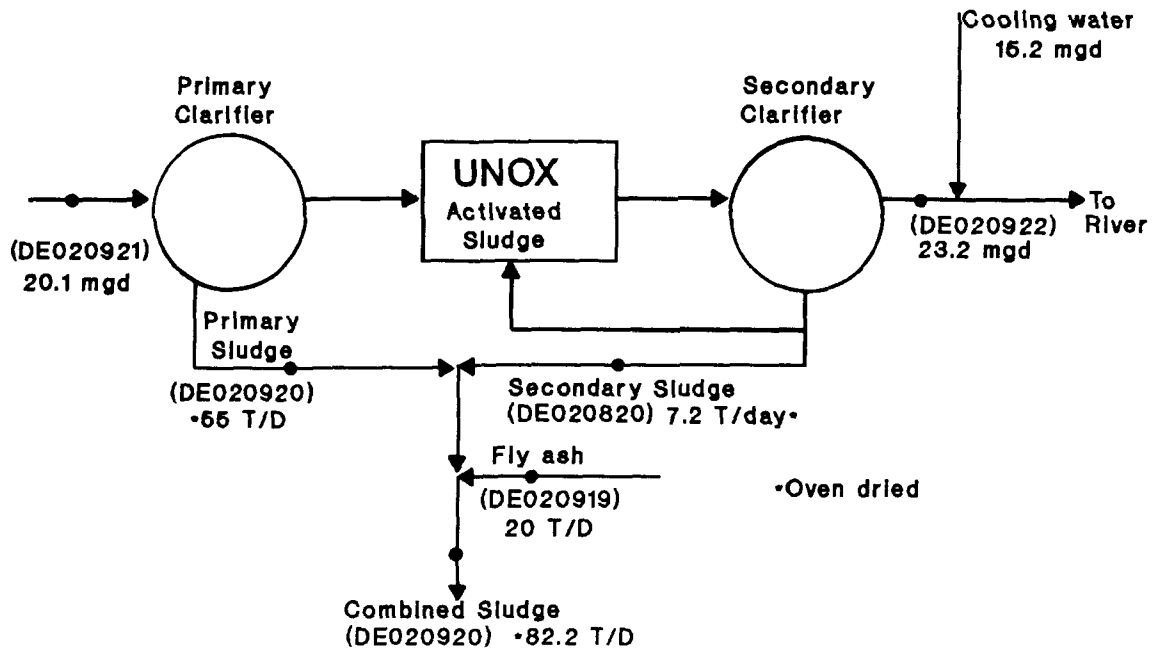


FIGURE III-4. Mill A Wastewater Treatment Plant Schematic

TABLE III-2

MILL A WASTEWATER TREATMENT PLANT OPERATING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Flow (MGD)	21-25
Residence Time (days)	0.5
Mixed Liquor Suspended Solids (mg/L)	3200
Return Sludge Recycle (%)	73
Aeration Horsepower (HP/million gallons)	33

TABLE III-3

MILL A WASTEWATER TREATMENT PLANT PERFORMANCE DATA

<u>Parameter</u>	<u>Winter</u>	<u>Summer</u>
BOD ₅ Loading (lbs/day)	20,000	18,800
BOD ₅ Removal (%)	94	83
Suspended Solids Loading (lbs/day)	18,800	20,700
Suspended Solids Removal (%)	68	58
Primary Sludge Production (tons/day)		55*
Consistency (%)		unknown
Waste Activated Sludge Production (tons/day)		7.2*
Consistency (%)		1.6
Combined Dewatered		
Sludge Production (dry tons/day)	59	65
Consistency (%)	37	39

*Oven dried basis

B. Mill B

Mill B is an integrated bleached kraft mill with a capacity for 875 tons per day of miscellaneous papers plus 150 tons per day of market pulp. Major paper products include bond, facial tissue, toilet tissue, napkin tissue, freezer paper, toweling, and newsprint. Two continuous digestors (Kamyr, Bauer) are used to pulp both hardwoods and softwoods with a typical mix of 20% hardwood and 80% softwood. The bleached/semi-bleached kraft pulp capacity is 775 tons per day with an additional 300 tons per day of pulp generated by refiner mechanical groundwood. The latter is used primarily for the newsprint production.

The bleach plant consists of a single line with a CEHED sequence; however, during the survey, the line was operated in a C_DEHHD sequence. The bleach plant is shown schematically in Figure III-5. Sample identification codes and flow rates of both pulp and washer filtrates are listed next to each sampling location. Nominal operating conditions and chemical usages are listed in Table III-4.

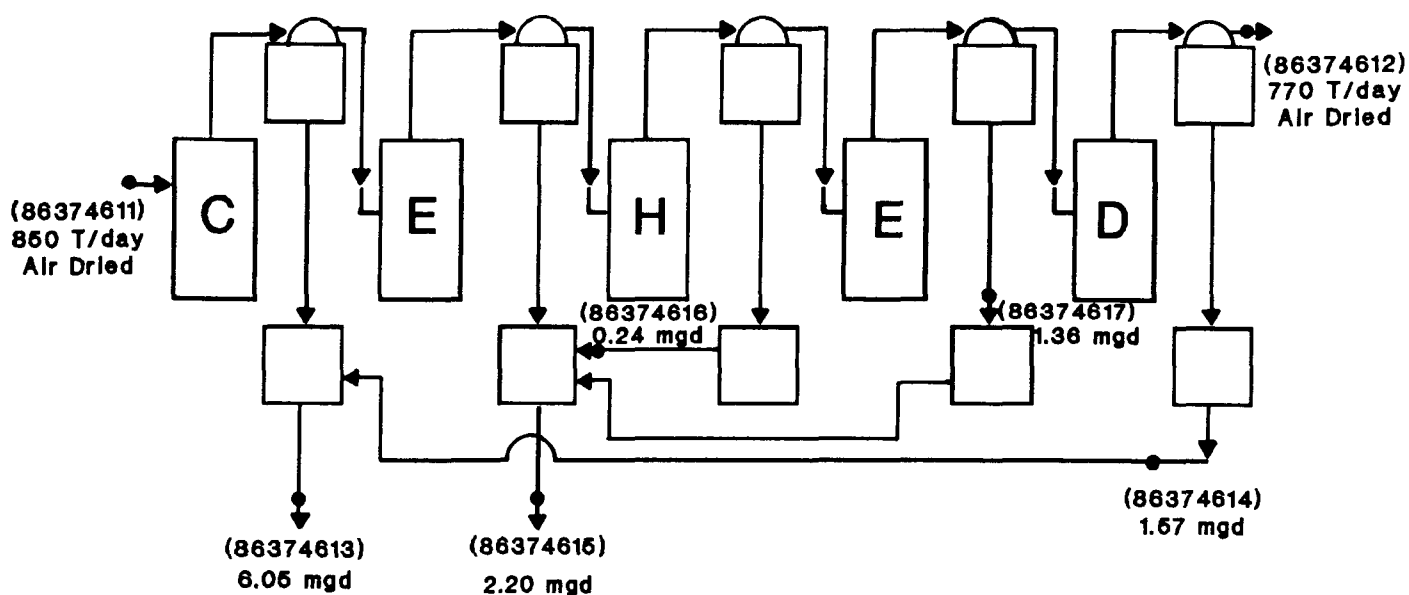


FIGURE III-5. Mill B Bleaching Line Schematic

TABLE III-4

MILL B BLEACH PLANT OPERATING CONDITIONS AND CHEMICAL USAGES

Parameter	Bleaching Stage				
	C	E	H	E	D
Throughput (ADT/hours)	34.5	34.5	34.5	34.5	34.5
Residence Time (hours)	0.23	0.70	0.15	0.08	2.80
pH	--	10.2	9.1	--	2.1
Temperature (°F)	102	150	150	150	150
Chemical Usage (lbs/ton)					
Cl ₂	100	--	--	--	--
NaOH	--	58	--	--	--
NaOCl (as available Cl ₂)	--	--	34	--	--
ClO ₂	--	--	--	--	10
Residual Cl ₂ (lbs/ton)	3.5	--	Trace	--	Trace
Permanganate No.	19.8	4.5	--	--	--
Brightness	--	--	59	61	83

The power boiler at the mill uses both gas and oil to produce 200,000 lbs/hour of steam. There is no significant contact of residues from this operation with the mill general sewer.

Raw water to the mill is taken from a nearby river, treated with filtration, and chlorinated prior to use in the mill. Approximately 40 MGD of treated water are used in the process. Filter plant backwash from this process is returned to the river. The general mill sewer is shown schematically in Figure III-6. This figure provides identification codes and flow rates associated with each sample location. These flow values represent measurements or estimates where flow is not routinely monitored.

The wastewater treatment system consists of primary clarification and a holding pond with 8 hours detention time. The pond is followed by an activated sludge system with an additional 8 hours aeration time. The acid sewer from the bleach plant bypasses primary treatment and is put directly into the holding pond. Primary sludge is dewatered on a coil filter, while the waste activated secondary sludge is dewatered with a Winkle press. Polymer is used as an aid in dewatering this sludge. Primary sludge is landfilled on site while secondary sludge is disposed off site. The wastewater treatment plant is shown schematically in Figure III-7. Identification codes and flow rates at the time of sampling are noted next to each sample location. Typical operating conditions and performance during both winter and summer months are shown in Tables III-5 and III-6.

TABLE III-5

MILL B WASTEWATER TREATMENT PLANT OPERATING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Flow (MGD)	40.8
Residence Time (days)	0.8-0.9
Mixed Liquor Suspended Solids (mg/L)	3100
Return Sludge Recycle (%)	97
Aeration Horsepower (HP/million gallons)	208

TABLE III-6

MILL B WASTEWATER TREATMENT PLANT PERFORMANCE DATA

<u>Parameter</u>	<u>Winter</u>	<u>Summer</u>
BOD ₅ Loading (lbs/day)	55,000	55,000
BOD ₅ Removal (%)	93	94
Suspended Solids Loading (lbs/day)	98,000	98,000
Suspended Solids Removal (%)	88	88
Primary Sludge Production (tons/day)	40	40
Consistency (%)	17	17
Secondary Sludge Production (tons/day)	3	15
Consistency (%)	13	13

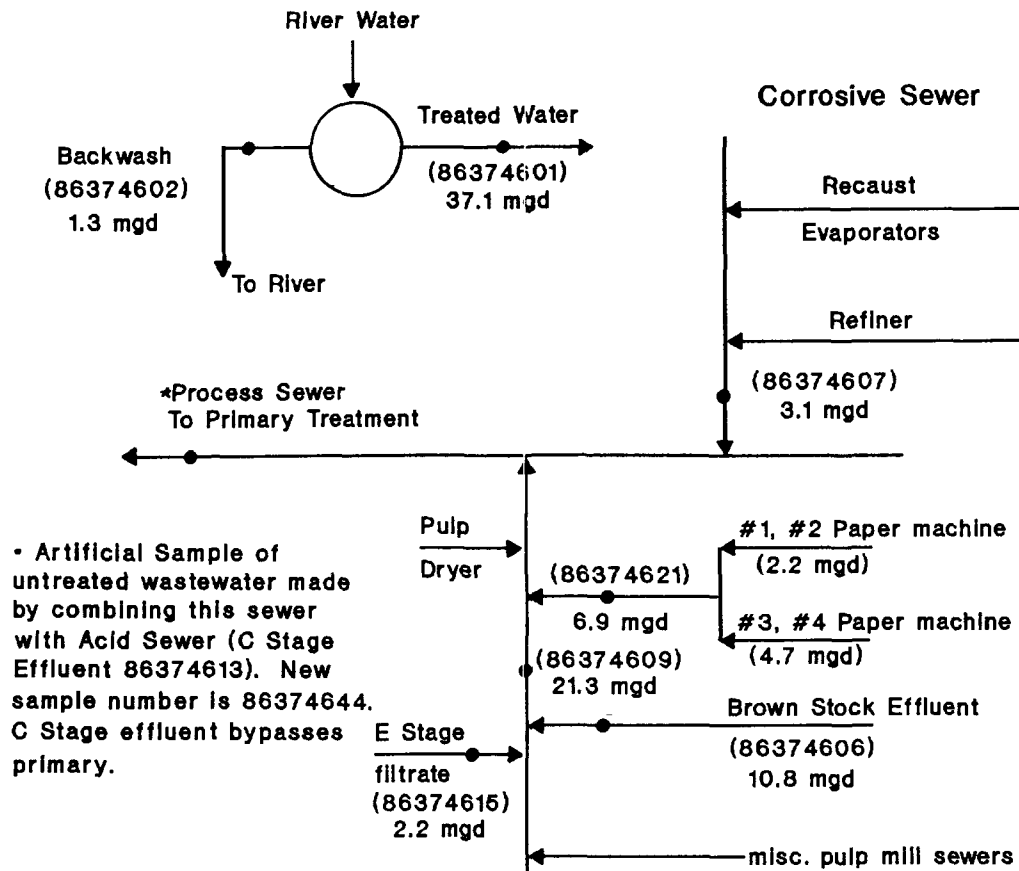


FIGURE III-6. Mill B Sewer System Schematic

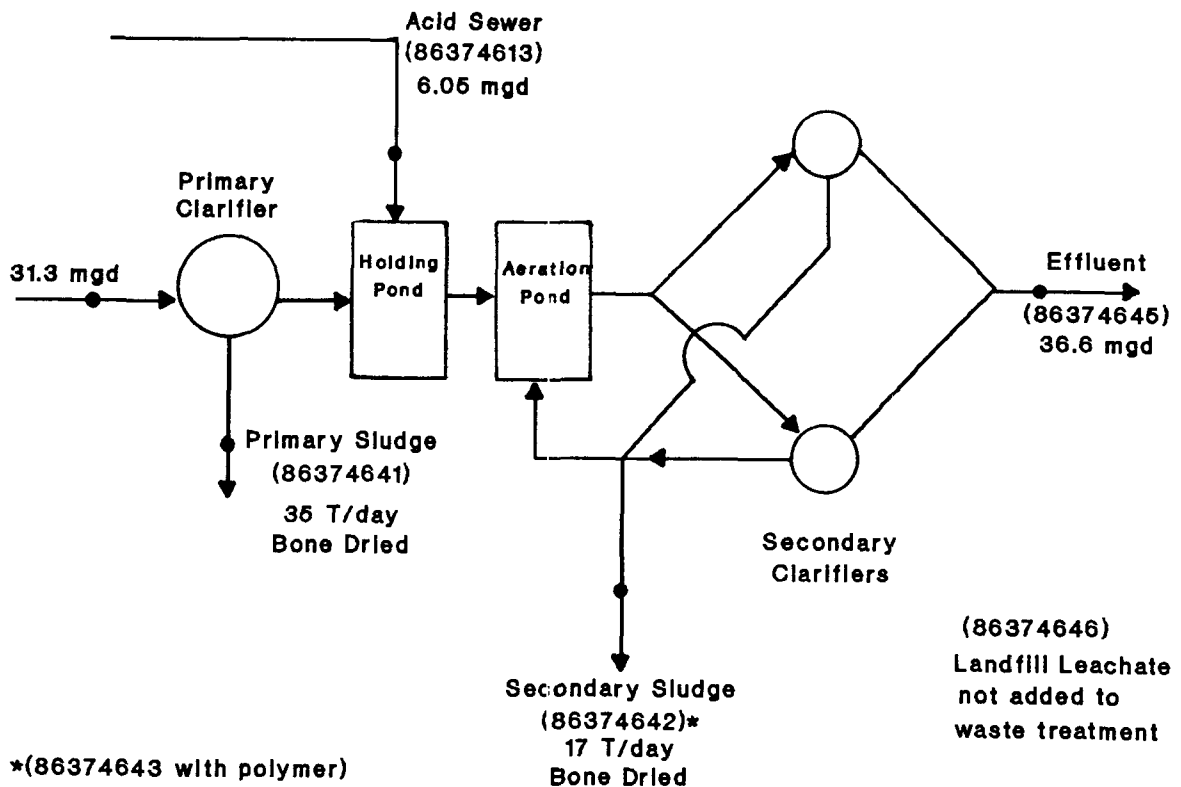


FIGURE III-7. Mill B Wastewater Treatment Plant Schematic

C. Mill C

Mill C is an integrated bleached kraft mill with a capacity for 1170 tons per day of printing and writing papers. Products include business form paper, carbonless copy paper, cover paper, and tablet grade paper. Eight batch digestors are used to pulp 2200 tons per day of hardwood chips. Pulping capacity exists for 1000 tons per day of bleached kraft, although current production is 800 tons per day.

The brownstock pulp is bleached with a single C/DE₀D sequence. The bleach plant is shown schematically in Figure III-8. Sample identification codes and flow rates are noted next to each sampling location. Nominal operating conditions and chemical usages are listed in Table III-7.

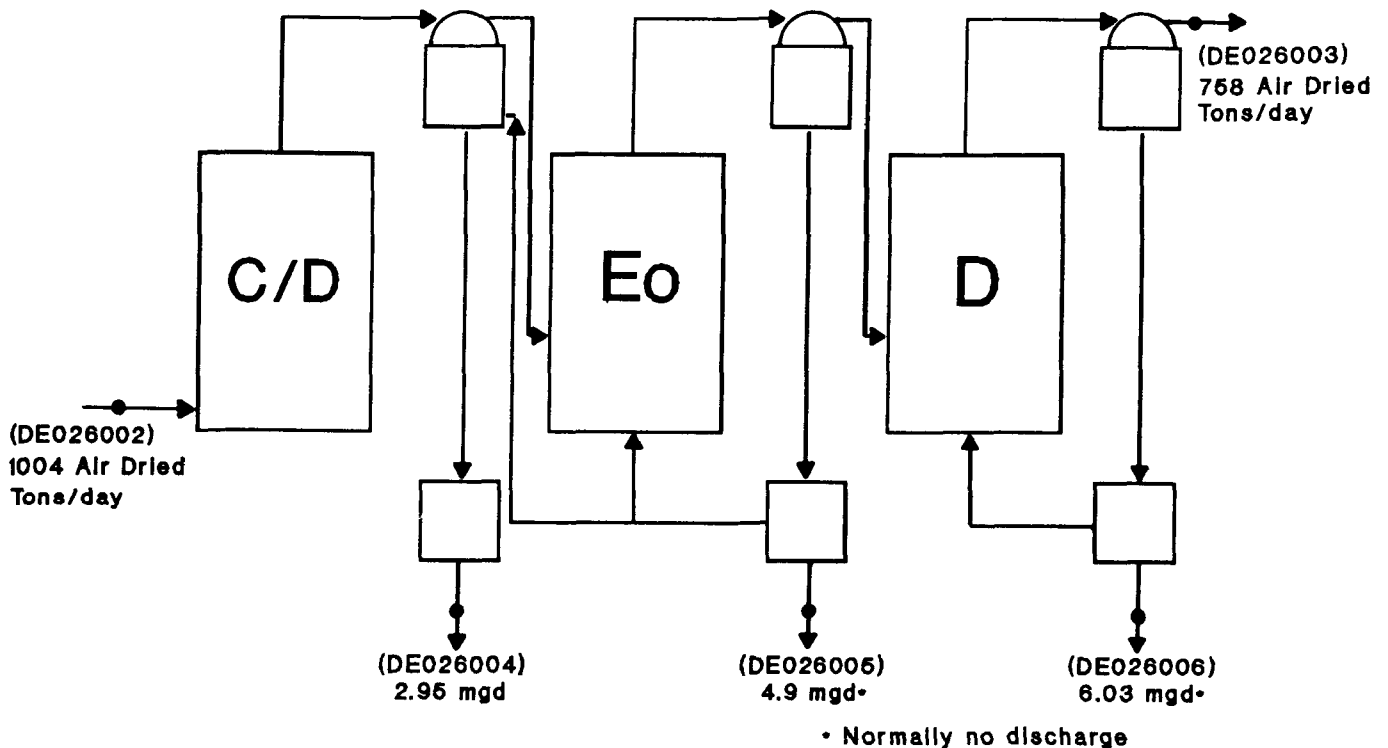


FIGURE III-8. Mill C Bleaching Line Schematic

TABLE III-7

MILL C BLEACH PLANT NOMINAL OPERATING CONDITIONS AND CHEMICAL USAGES

Parameter	Bleaching Stage		
	C/D	E ₀	D
Throughput (ADT/day)	1000	--	--
Residence Time (hours)	0.3	0.62	4.5
pH	1.7	11.5	4.0
Temperature (°F)	130	170	170
Chemical Usage (lbs/ton)			
Cl ₂	60	--	--
ClO ₂	5	--	18
O ₂	--	12.5	--
NaOH	--	20	--
Other (SO ₂)	--	--	50
Residual Cl ₂	Trace	--	--
Brightness	--	47	>88

Four power boilers are used to produce 1.3 million lbs of steam/hour. Three burn coal while the fourth burns wood wastes (800 tons per day). Fly ash from the three coal boilers is collected by electrostatic precipitators while ash from the wood waste boiler is collected by a wet scrubber. All ash including bottom ash is landfilled. Wastewater is used to convey some of these ashes and is then sewered.

Raw water to the mill is supplied from two sources including river water and wells. Portions of the total (30 MGD) receive treatment with either sand filtration or lime softening prior to use in specific parts of the mill. Residues from both processes are sewered. The general mill sewer system is shown schematically in Figure III-9. Identification codes and flow rates for each sample location are provided.

FIGURE III-9. Mill C Sewer System Schematic

The wastewater treatment system consists of primary clarification followed by a 10-acre aerated stabilization basin (ASB) and a 7-acre activated sludge (AST) system. Excess solids from the two secondary clarifiers are returned to both the primary clarifier and the sludge thickener. Thickened secondary sludge and primary sludge are combined prior to dewatering. Dewatered solids are utilized commercially and/or sent to a landfill. Nearly 2 MGD of the secondary effluent is recycled back into the mill and used in the woodwaste boiler scrubber. The remaining portion is discharged to a river.

The wastewater treatment plant is shown schematically in Figure III-10. Identification codes and flow rates at the time of sampling are noted next to each sample location. Typical operating conditions and performance are shown in Tables III-8 and III-9. These data reflect average operating conditions for both winter and summer months.

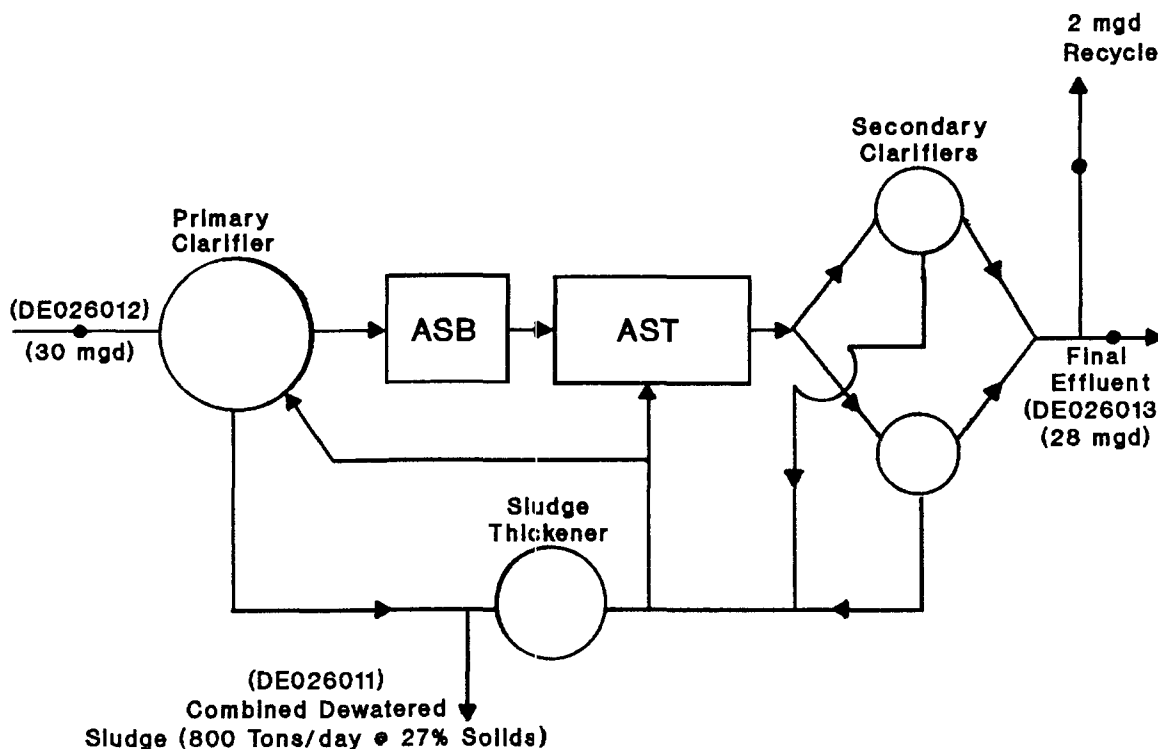


FIGURE III-10. Mill C Wastewater Treatment Plant Schematic

TABLE III-8

MILL C WASTEWATER TREATMENT PLANT OPERATING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Flow (MGD)	28
Residence Time (days)	1.5
Mixed Liquor Suspended Solids (mg/L)	2400
Return Sludge Recycle (%)	50
Aeration Horsepower (HP/million gallons)	38

TABLE III-9

MILL C WASTEWATER TREATMENT PLANT PERFORMANCE DATA

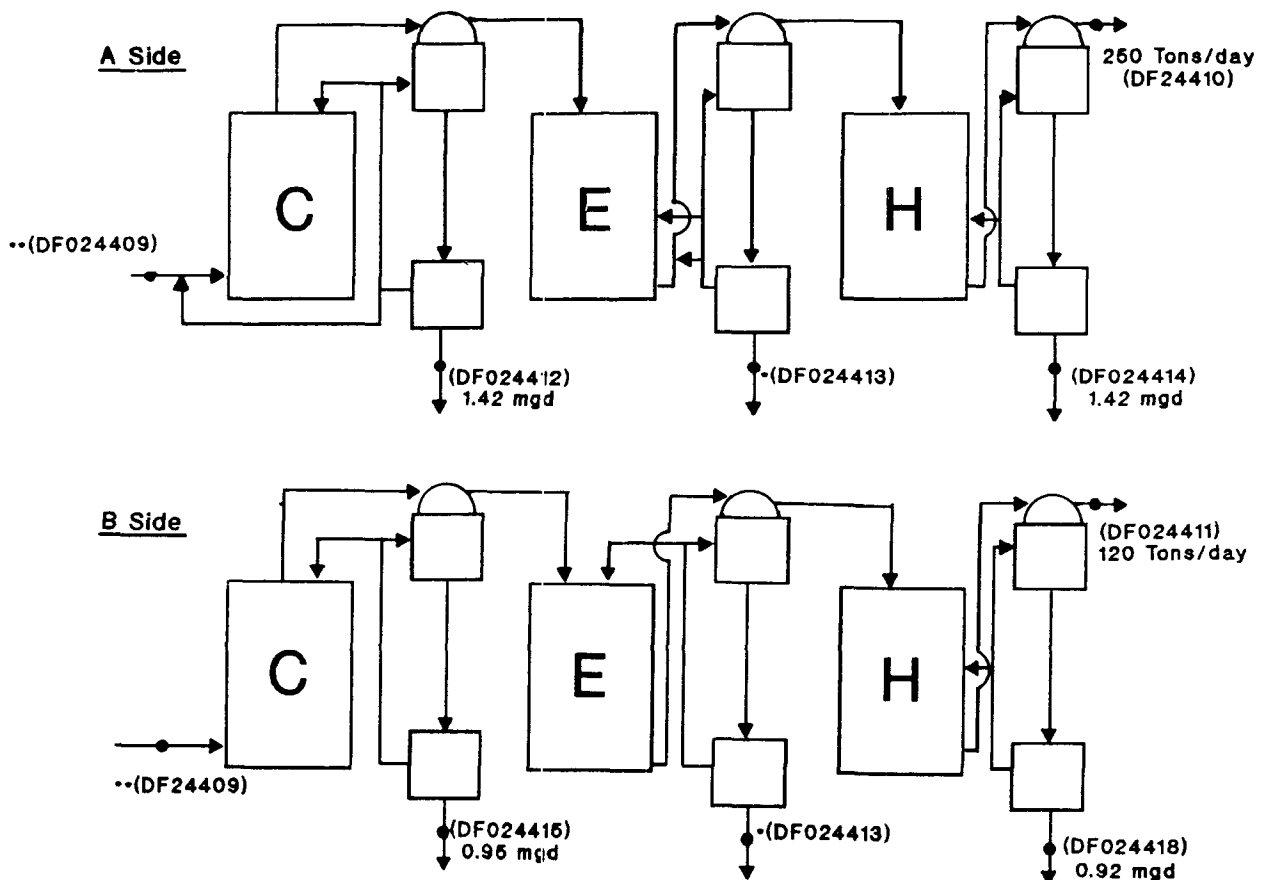
<u>Parameter</u>	
BOD ₅ Loading (lbs/day)	100,000-150,000
BOD ₅ Removal (%)	97
Suspended Solids Loading (lbs/day)	409,000
Suspended Solids Removal (%)	96
Primary Sludge Production (wet tons/day)	2500
Consistency (%)	8
Waste Activated Sludge Production (tons/day)	5800
Consistency (%)	0.6
Combined Dewatered Sludge Production (wet tons/day)	800
Consistency (%)	27%

No significant differences between winter and summer operations.

D. Mill D

Mill D is an integrated bleached kraft mill with a capacity for 1105 tons per day of paper products. Major products are newsprint and telephone directory paper. Six batch digestors are used to pulp softwood chips. Pulping capacity exists for 460 tons per day bleached kraft (425 tons per day unbleached kraft). In addition there is capacity for 830 tons per day groundwood production.

The bleach plant consists of two lines, each utilizing a CEH sequence. The bleach plant is shown schematically in Figure III-11. Sample identification codes and flow rates of both pulp and washer filtrates are listed next to each sampling location. Nominal operating conditions and chemical usages are listed in Table III-10. The relatively high hypochlorite use in the B bleach line hypochlorite stage is related to high caustic carryover from an undersized E-stage washer. Chlorine use on the B bleach line was computed from tank car inventories.



- Combined Caustic Sewer 2.72 mgd
- Combined brownstock pulp 423 air dried Tons/day

FIGURE III-11. Mill D Bleaching Line Schematics

TABLE III-10

MILL D BLEACH PLANT OPERATING CONDITIONS AND CHEMICAL USAGES

<u>SOFTWOOD LINE A</u>	<u>Bleaching Stage</u>		
<u>Parameter</u>	<u>C</u>	<u>E</u>	<u>H</u>
Throughput (dry tons/hour)	13.3	13.3	13.3
Residence Time (hours)	0.91	0.30	1.16
pH	2.3	10.5	8.5
Temperature (°F)	--	--	--
Chemical Usage (lbs/ton)			
Cl ₂	67.1	0	0
NaOH	0	46	0
NaOCl	0	0	90
Monoethanolamine	0.25	0	0.14
Residual Cl ₂	2.0	--	14.9
Semi-bleached Brightness	--	--	69

<u>SOFTWOOD LINE B</u>	<u>Bleaching Stage</u>		
<u>Parameter</u>	<u>C</u>	<u>E</u>	<u>H</u>
Throughput (dry tons/hour)	5.8	5.8	5.8
Residence Time (hours)	2.0	0.5	2.5
pH			
Temperature (°F)	--	--	--
Chemical Usage (lbs/ton)			
Cl ₂	76.5	0	0
NaOH	0	53	0
NaOCl	0	0	227
Monoethanolamine	--	0	0.39
Residual Cl ₂	4.0	--	9.9
Semi-bleached Brightness	--	--	69

NOTE: Brownstock pulp permanganate number for both bleach lines is typically 24.5.

Power boilers at the mill burn gas and approximately 600 tons per day of bark to produce 550,000 lbs per hour of steam. Black liquor is burned in a recovery boiler. Fly ash from the bark boiler is collected with a mechanical dust collector and a wet scrubber. Both fly ash and bottom ash are landfilled. The scrubber water is sewered.

Raw water to the mill is taken from a nearby lake and from wells. Water from both sources is chlorinated prior to use in the mill. Approximately 22 MGD are used in the process. The general mill sewer is shown in Figure III-12. This figure provides identification codes and flow rates associated with each sample location. These flow values represent measurements or estimates where flow is not routinely monitored.

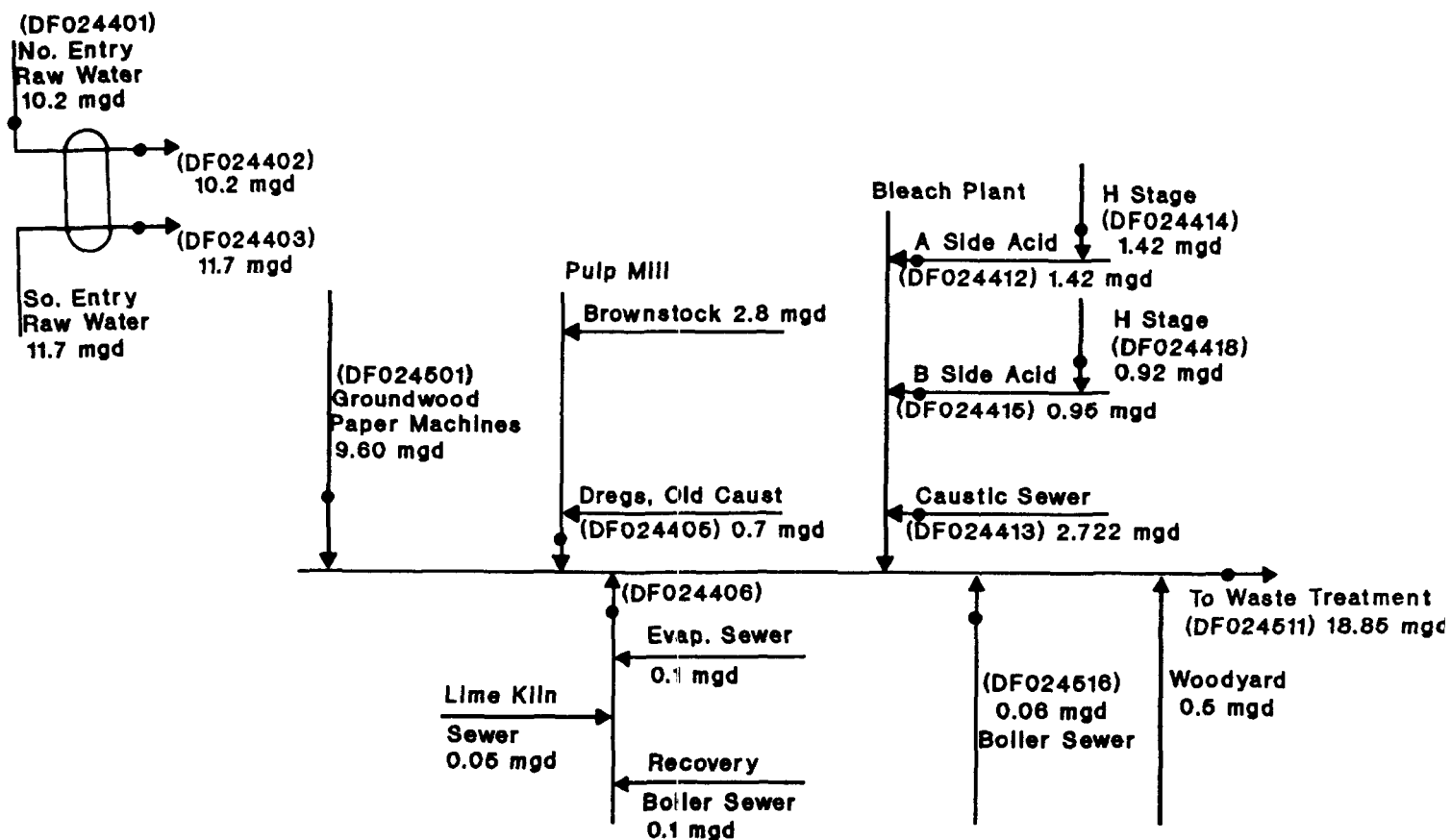


FIGURE III-12. Mill D General Mill Sewer Schematic

The wastewater treatment system consists of primary clarification followed by activated sludge with 2 to 3 hours detention time. A dissolved air flotation system is used to control suspended solids prior to the secondary clarifiers. Waste solids are returned to the lagoon. Waste activated sludge is returned to the primary clarifier. The combined sludge is dewatered and sent to landfill for disposal. Chlorine (1000 lbs/day) is regularly used to control secondary sludge bulking. The waste treatment plant is shown schematically in Figure III-13. Identification codes and flow rates at the time of sampling are noted next to each sample location. Typical operating conditions and performance during both winter and summer months are shown in Tables III-11 and III-12.

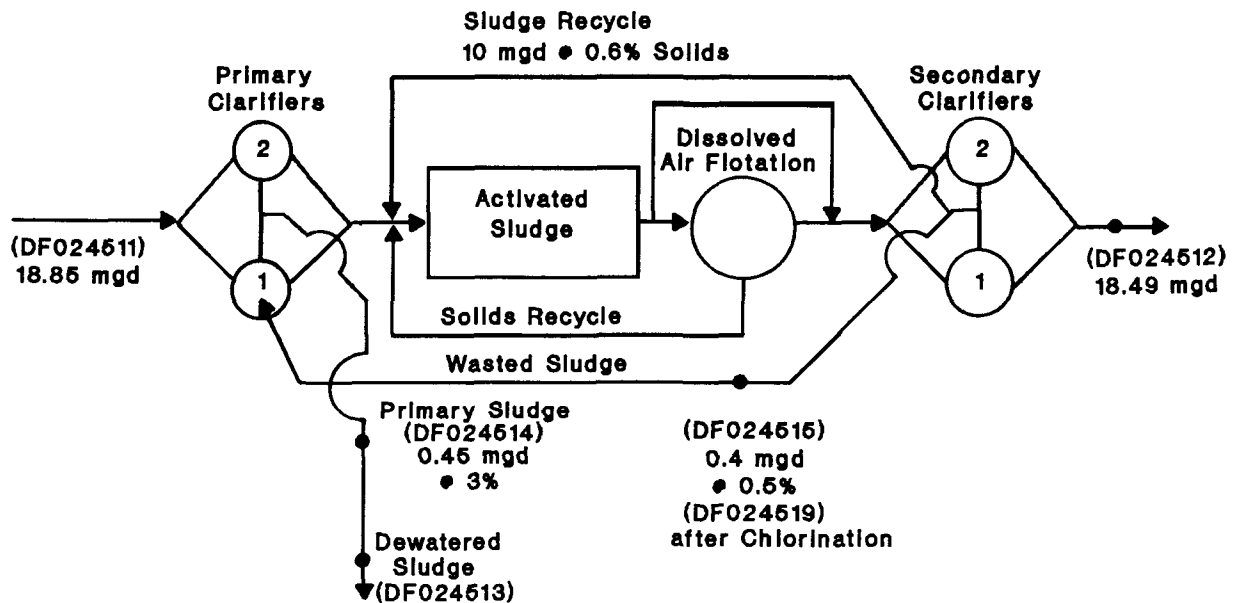


FIGURE III-13. Mill D Wastewater Treatment Plant Schematic

TABLE III-11

MILL D WASTEWATER TREATMENT PLANT OPERATING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Flow (MGD)	20
Residence Time (days)	0.75
Mixed Liquor Suspended Solids (mg/L)	1200-1500
Sludge Age	2-2.5 days
Return Sludge Recycle (%)	50
Aeration Horsepower (HP/million gallons)	30
Primary Sludge Production (gal/day)	600,000
Consistency (%)	2-2.5
Waste Activated Sludge Production (gal/day)	400,000
Consistency (%)	0.50

TABLE III-12

MILL D WASTEWATER TREATMENT PLANT PERFORMANCE DATA

<u>Parameter</u>	<u>Winter</u>	<u>Summer</u>
BOD ₅ Loading (lbs/day)	15,000-30,000	15,000-30,000
BOD ₅ Removal (%)	85-90	90-93
Suspended Solids Loading (lbs/day)	100,000-200,000	100,000-200,000
Suspended Solids Removal (%)	90-98	95-99
Combined Dewatered		
Dry Sludge Production (tons/day)	50-100	50-100
Consistency (%)	15-18	15-18

E. Mill E

Mill E is an integrated bleached kraft mill with a capacity for 1330 tons per day of miscellaneous papers. Major products include bond, business form paper, carbonizing, envelope, ledger, offset paper, coated publication paper, and tablet. Two continuous Kamyr digestors are used to pulp both hardwood and softwood chips with a typical mix of 30% hardwood and 70% softwood. The kraft pulp capacity is 1200 tons per day with an additional 130 tons per day groundwood production.

The bleach plant consists of two lines both with a $C_D E_O H/D$ sequence. One of the lines alternately bleaches hardwood and softwood pulp. The bleach plant is shown schematically in Figure III-14. Sample identification codes and flow rates of both pulp and washer filtrates are listed next to each sampling location. Nominal operating conditions and chemical usages are listed in Table III-13.

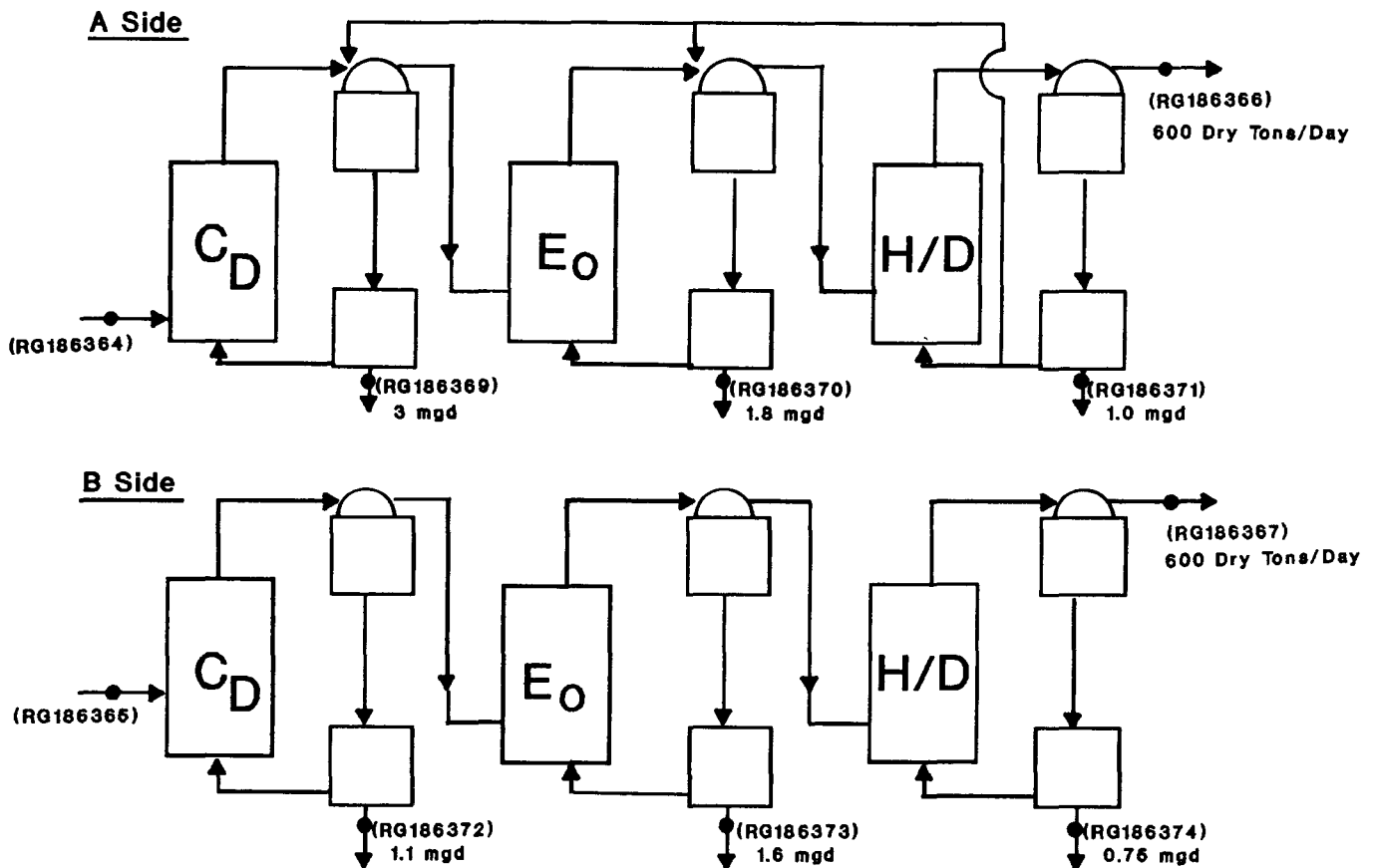


FIGURE III-14. Mill E Bleaching Line Schematics

TABLE III-13

MILL E BLEACH PLANT OPERATING CONDITIONS AND CHEMICAL USAGES

Parameter	Bleaching Stage			
	C _D	E _O	H	D
<u>LINE A - SOFTWOOD</u>				
Throughput (tons/hours)	25	25	25	25
Residence Time (hours)	0.67	1.7	0.20	1.5-2.0
pH	1.8	10.7	9.4	6.7
Temperature (°F)	110	160	185	180
Chemical Usage (lbs/ton)				
Cl ₂	120	--	--	--
ClO ₂	3.3	--	--	11.17
NaOH	--	81	2.65	2.71
O ₂	--	7.85	--	--
NaOCl	--	2.97	17.2	--
Residual Cl ₂ (gm/L)	0.019	--	0.0	0.06
Brightness	--	--	66.3	84.2
<u>LINE B - HARDWOOD</u>				
Throughput (tons/hours)	25	25	25	25
Residence Time (hours)	0.33	1.50	0.20	1.5-2.0
pH	1.80	11.2	10.1	7.0
Temperature (°F)	130	155	185	180
Chemical Usage (lbs/ton)				
Cl ₂	80.4	--	--	--
ClO ₂	2.03	--	--	14.9
NaOH	--	116.5	0.35	4.05
O ₂	--	4.7	--	--
NaOCl	--	--	24.6	--
Residual Cl ₂ (gm/L)	0.022	--	0.0	0.0
Brightness	--	--	64.5	85.8
<u>LINE B - SOFTWOOD</u>				
Throughput (tons/hours)	21	21	21	21
Residence Time (hours)	0.33	1.50	0.20	1.5-2.0
pH	1.80	11.2	10.1	7.0
Temperature (°F)	130	155	185	180
Chemical Usage (lbs/ton)				
Cl ₂	80.4	--	--	--
ClO ₂	2.03	--	--	14.9
NaOH	--	116.5	0.35	4.05
O ₂	--	4.7	--	--
NaOCl	--	--	24.6	--
Residual Cl ₂ (gm/L)	0.022	--	0.0	0.09
Brightness	--	--	66.1	84.8

The power boiler at the mill burns oil and approximately 250 bone dry tons per day of bark to produce 1.1 million pounds of steam per hour. Both bottom and fly ash are sewered directly.

Raw water to the mill is taken from a nearby river, treated with alum flocculation, sand filtration, and chlorination prior to use in the mill. Residues from the alum flocculation are sewered. Approximately 38 MGD of treated water are used in the process. The general mill sewer is shown schematically in Figure III-15. This figure also provides identification codes and flow rates associated with each sample location. These flow values represent measurements or estimates when flow is not routinely monitored.

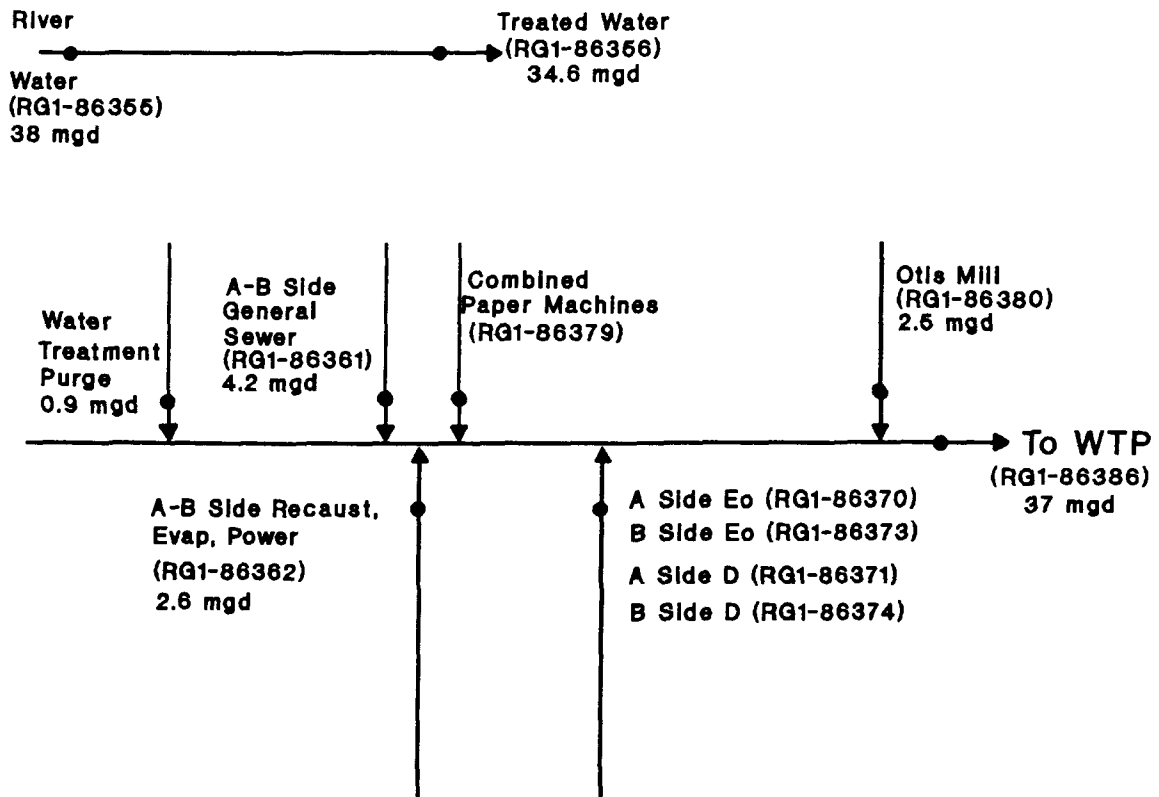


FIGURE III-15. Mill E Sewer System Schematic

The wastewater treatment system consists of primary clarification followed by an activated sludge system with 1.1 day aeration time. The acid sewer bypasses primary treatment and is put directly into the aeration lagoon. Secondary sludge is gravity thickened prior to dewatering with the primary sludge on sludge presses. Overflow from the gravity thickener is recycled to the primary clarifier.

The wastewater treatment plant is shown schematically in Figure III-16. Identification codes and flow rates at the time of sampling are noted next to each sample location. Typical operating conditions and performance during both winter and summer months are shown in Tables III-14 and III-15.

TABLE III-14

MILL E WASTEWATER TREATMENT PLANT OPERATING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Flow (MGD)	40
Residence Time (days)	1.2
Mixed Liquor Suspended Solids (mg/L)	1300-1400
Return Sludge Recycle (%)	53
Aeration Horsepower (HP/million gallons)	44

TABLE III-15

MILL E WASTEWATER TREATMENT PLANT PERFORMANCE DATA

<u>Parameter</u>	
BOD ₅ Loading (lbs/day)	80,000-120,000
BOD ₅ Removal (%)	93-94
Suspended Solids Loading (lbs/day)	430,000
Suspended Solids Removal (%)	93-95
Secondary Sludge Production (dry tons/day)	35
Combined Sludge Production (dry tons/day)	200

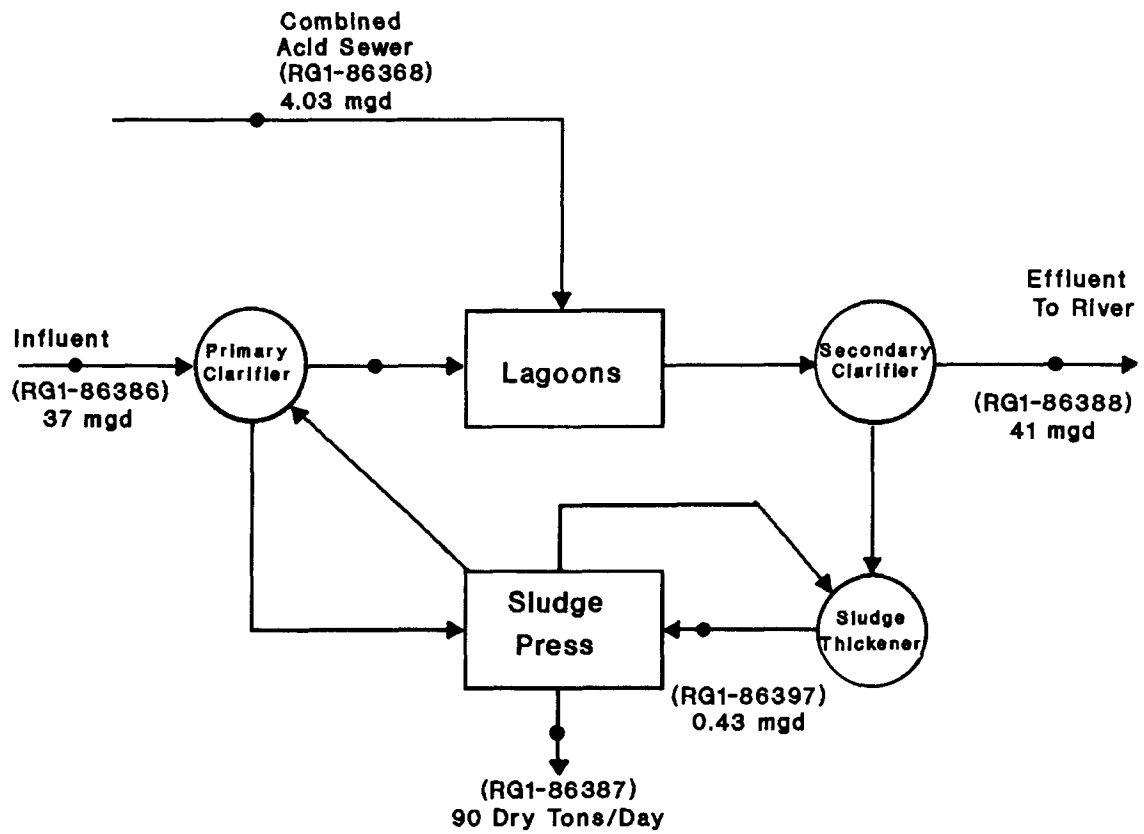


FIGURE III-16. Mill E Wastewater Treatment Plant Schematic

IV. FIELD PROGRAM

The field program for this study was conducted according to the schedule shown below:

Mill A	June 24-25, 1986
Mill B	September 8-10, 1986
Mill C	October 15-18, 1986
Mill D	December 2-3, 1986
Mill E	January 13-15, 1987

In addition, preliminary grab samples were collected from Mill A in March 1986 for analytical methods development and prescreening of selected samples including wood chips, unbleached and bleached pulps, selected untreated wastewaters, paper machine additives, wastewater sludges, and treated process wastewater effluents.

A. Sampling Plan

The study design called for sampling all mill inputs thought to be significant; intermediate process materials and untreated process wastewaters; and mill exports including bleached pulps, wastewater sludges, and treated process wastewater effluents. Table IV-1 presents the detailed sampling plan for Mill A. Similar plans were developed for each mill after site reconnaissance visits to review process water treatment systems, process operations, sewerage systems, and wastewater treatment systems.

Based upon the results of the reconnaissance visits, specific sampling locations were selected to determine mass flow rates of process waters, wastewaters, and process materials. The sampling plans were reviewed in detail by USEPA, NCASI, and mill personnel prior to implementation. Arrangements were made to acquire pulp mill, bleach plant, and wastewater treatment system operating logs during each sampling survey. Note that primary flow monitoring devices have not been installed on most internal plant process wastewater streams. Accordingly, crude measurements or best engineering estimates of flow were developed for these streams. This is particularly common for the individual bleach plant pulp washing stages between chemical applications. Mass flow rates of pulps and final treated process wastewater effluents were generally determined with primary monitoring devices and are considered to be more accurate. Also, the determination of chemical applications in the bleach plants from the operating logs was found to be difficult due to differences in reporting, solution strength measurement methods, and mill-specific data recording procedures.

TABLE IV-1

MILL A - DETAILED SAMPLING PLAN

<u>SAMPLE NUMBER</u>	<u>SAMPLE DESCRIPTION</u>	<u>SAMPLE NUMBER</u>	<u>SAMPLE DESCRIPTION</u>
<u>A. Background Samples</u>		<u>E. Paper Machines</u>	
DE020801	Treated River Water	DE020811	Combined Process WW Process Additives
DE020802	Water Treatment Precip. Sludge	DE020812	Alum
DE020803	Water Treatment Sandfilter Sludge	DE020813	Clay-1
DE020804	Softwood Chips	DE020814	Clay-2
DE020805	Hardwood Chips	DE020916	Dye-1
<u>B. Pulping Process</u>		DE020917	Dye-2
DE020806	Combined Pulping & Recaust WWS	DE020815	Resin Size Emulsion
<u>C. Chemical Recovery Plant</u>		DE020816	High Brightness Filter
DE020807	Combined Process Wastewater	DE020817	Slimicide
DE020808	Lime Mud	DE020822	Soda Ash
<u>D. Bleach Plant</u>		DE020823	Sodium Thiosulfate
DE020901	Unbleached Softwood Pulp	DE021001	White Water - Clean
DE020902	Bleached Softwood Pulp	DE021002	White Water - Dirty
DE020903	Unbleached Hardwood Pulp	<u>F. Utilities, Wastewater Treatment</u>	
DE020904	Hypo Hardwood Pulp	DE020818	Powerhouse Wastewater
DE020905	Peroxide Hardwood Pulp	DE020918	Bottom Ash
<u>Softwood Bleach Line</u>		DE020919	Fly Ash
DE020906	S-1 Washer, C Stage	DE020819	WWTP Primary Sludge
DE020907	S-2 Washer, E _o Stage	DE020820	WWTP Secondary Sludge
DE020908	S-3 Washer, H Stage	DE020920	WWTP Composite Sludge
<u>Hardwood Bleach Lines</u>		DE020921	Combined Untreated Wastewater
DE020909	K-6 Washer, C Stage	DE020922	Final Wastewater Effluent
DE020910	K-4 Washer, E _o Stage (Hypo line)	DE020821	Landfill Leachate
DE020911	K-5 Washer, H Stage (Hypo line)	<u>G. Other</u>	
DE020912	K-2 Washer, E _o Stage (Per line)	DE020923	Sludge - not from Mill A
DE020913	K-3 Washer, H Stage (Per Line)	DE020824	Thiosulfate & H ₂ SO ₄ Reagent Blank
DE020914	K-1 Washer, H Stage (Per Line)		
DE020915	Combined Process Wastewater		
DE020809	Hypo Solution		
DE020810	Caustic Solution		

The sampling plan for each mill called for 24-hour composite sampling of mill inputs, intermediates, and exports, except for paper machine additives (alum, clays, dyes, slimicides) and, for some mills, power boiler ashes and landfill leachates. Discrete grab samples of those materials were collected during or immediately after the 24-hour sampling period. At most mills where multiple dyes are used, samples were collected of at least two dyes used at the time of the survey and of one or two dyes most heavily used throughout the prior year. For four of the mills, final process wastewater effluent sampling was delayed to account for the estimated time-of-travel or residence time of the wastewater through the respective wastewater treatment systems. Mill-specific field sampling is described in Section IV.C.

B. Sample Collection, Sample Handling, and Sample Custody

Attachment B presents the field protocols followed for the five-mill study. Precleaned sample collection devices and sample containers (one gallon or one quart glass bottles) were used throughout the study. The cleaning procedures are outlined in Attachment B. For liquid samples (treated process water, untreated and treated wastewaters, liquid or slurry sludges, and dilute process additive solutions) one gallon samples were collected. For solids and semi-solids (wood chips, clays, dewatered sludges, ashes, and pulps) and concentrated liquid additives (slimicides, dyes, and certain paper machine additives) one quart samples were collected. The pulp samples were partially dewatered in the field at the time of collection by manually squeezing individual grab samples used to make up the 24-hour composite samples. The analytical data for solid and semi-solid samples including liquid sludges were determined on a dry weight basis. All other samples were analyzed on a wet weight basis. At most mills, individual or combined paper machine wastewaters were sampled at convenient sewer locations and combined on a flow-proportioned basis with other paper machine wastewaters to form one composite paper machine wastewater sample from the mill.

The 24-hour composite samples were manually collected and comprised of eight discrete grab samples obtained at approximate three-hour intervals.

All samples were iced during the collection period and secured in locked ice chests or in ice chests secured with custody seals or tape. With few exceptions, individual or multiple ice chests were specifically assigned to a sampling location to minimize chances of sampling errors. Wastewater samples suspected of containing chlorine were checked for total residual chlorine at the time of collection. Total residual chlorine was neutralized

with a slight excess of sodium thiosulfate in solution or in crystalline form at the time of collection. Also, samples collected for chlorinated phenolics were adjusted to pH <2 with 6M sulfuric acid upon collection for sample preservation.

C. Site Specific Sampling

The sampling at each mill was conducted according to the sampling plans and protocols described above and in Attachment B. Unique sampling and deviations from the sampling protocols at each mill are described below:

1. Mill A

Sample Number DE020818 - Due to minimal wastewater flows, the powerhouse wastewater was grab sampled.

Sample Number DE020821 - The landfill leachate and runoff sample was a grab sample vs. a 24-hour composite sample since the leachate and runoff collected in a pond with long retention time. The wastewaters are discharged on an intermittent basis to the wastewater treatment facilities.

Sample Number DE020922 - The final effluent 24-hour composite sample was collected concurrently with samples from the mill. Hence, the estimated residence time in the wastewater treatment system was not taken into account in the sampling program as was the case for the other four mills included in the study.

2. Mill B

Sample Number 86374621 - The first aliquots for the individual 24-hour field composite samples from the newsprint machine #3 (station E-2A) and forms bond machine (station E-2B) were not taken due to sampling error.

Sample Number 86374646 - The landfill leachate sample was a short term composite sample vs. a 24-hour composite sample since the discharge flow rate was minimal and the discharge was direct rather than to the wastewater treatment system.

3. Mill C

Sample Number DE026006 - Only one aliquot of D-stage filtrate was collected during the first 12 hours of the survey due to a plugged sample port. Sampling resumed as normal for the balance of the survey. The D-stage filtrate was not sewered during the survey.

Sample Number DE026011 - Due to minimal wastewater volume and remote location, the wastewater sludge landfill leachate was grab sampled.

Sample Numbers DE026013 and DE026206 - 24-Hour composite samples of secondary wastewater effluent were collected during the 24-hour sampling period for the mill (0-24 hours) and on a delayed basis (36-72 hours) to account for residence time in the wastewater treatment facilities. The 0-24-hour sample was collected to characterize about 2 MGD of treated effluent returned to the mill during the survey period.

4. Mill D

No significant changes from the sampling protocols.

5. Mill E

Sample Number RG1-86357 - A two gallon concentrated sample of river intake water filter backwash was obtained by decanting one gallon samples from six separate filter backwashes.

Sample Numbers RG1-86367, 72, 73, and 74 - Due to production scheduling at the mill, the B bleach line was sampled for a 4-hour period after the 24-hour sampling period for the mill and after a change from softwood to hardwood production. Precautions were taken in the field to insure hardwood pulp was being sampled on this line. However, based upon a review of process operating logs, the short-term bleached pulp composite sample obtained was comprised of undetermined amounts of both softwood and hardwood pulps.

Sample Numbers RG1-86380/92 - An untreated paper machine wastewater from a nonintegrated paper mill located near Mill E was sampled as it entered the Mill E wastewater treatment system.

V. ANALYTICAL PROGRAM

A. Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs)

1. Compounds Selected for Analyses

Analyses of preliminary samples from two mills indicated that 2378-TCDD and 2378-TCDF are the principal PCDDs and PCDFs found in various pulp and paper mill matrices. Samples from other pulp and paper mills analyzed by USEPA reveal similar patterns.³

Tables V-1 to V-3 present data for six mills for isomer specific determinations of 2378-TCDD, data for the determination of 2378-TCDF plus possible co-eluting isomers, and data for higher chlorinated PCDDs and PCDFs. Each of these mills process primarily virgin fiber. Mills A and E (Tables V-1 and V-2) are among the five mills included in the cooperative study. Mill 1 (Table V-1) and Mills 2, 3, and 4 (Table V-3) are other bleached kraft mills not included in this study. Data for Mill E were developed using procedures previously demonstrated to be isomer specific for 2378-TCDF. Also summarized are the 2378-TCDD toxic equivalents computed to the extent possible for all detected PCDDs and PCDFs. Very few of the higher congener measurements were made using procedures which have been demonstrated to be isomer specific for the 2378-substituted isomer. Accordingly, the results must be qualified as possibly reflecting the presence of co-eluting isomers. Nevertheless, conservative calculations of the toxic equivalents (TEQs) were made assuming the concentrations reported for the 2378-substituted isomers were all the most toxic isomer.

Note that the analyses were completed by three laboratories (Dow Chemical (Table V-1); Wright State University (Table V-2); and USEPA-ERL Duluth (Table V-3)) using different sample cleanup, extraction, and analytical protocols. Accordingly, the results may not be fully comparable. Nonetheless, the data are consistent in the relative absence of the higher chlorinated PCDDs and PCDFs.

The 2378-TCDF concentrations measured as part of a full congener analysis for Mill A and Mill 1 (Table V-1) were shown to be substantially correct based upon split sample analyses using procedures which were isomer specific for this compound. It should also be noted that only the 2378-substituted isomers were quantitated in the Mill A and Mill 1 analyses. However, the comparatively low relative toxicity equivalency factors for the higher congener non-2378-substituted isomers indicate that this data limitation does not substantially alter the conclusion that virtually all the TEQs are associated with 2378-TCDD and 2378-TCDF.

TABLE V-1

PCDDs and PCDFs IN BLEACHED KRAFT PAPER MILL MATRICES
USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY
DOW CHEMICAL ANALYSES

PCDDs	Mill A Bleachery Wastewaters ^a	Mill A Final Effluent ^a	Mill A Wastewater Sludge ^b	Mill 1 Combined Wastewater Sludge ^b	Notes
2378-TCDD	150 ppq	73 ppq	17 ppt	240 ppt	
12378-PeCDD	6 (6)	ND (7)	ND (1)	25	d
123789-HxCDD	ND (20) ^c	ND (20)	ND (7)	6 (3)	
123678-HxCDD	ND (15)	ND (15)	ND (7)	} 9 (5)	
123478-HxCDD	ND (15)	ND (15)	ND (7)		
1234678-HpCDD	45 (10)	30 (15)	ND (6)	150	
OCDD	220 (40)	220 (30)	59 (9)	1400	
<u>PCDFs</u>					
2378-TCDF	2500 ppq	1000 ppq	300 ppt	2300 ppt	d
23478-PeCDF	23 (3)	16 (3)	3 (1)	53	d
12378-PeCDF	27 (3)	16 (2)	3 (1)	140	d
234678-HxCDF	ND (5)	ND (5)	2 (2)	3 (1)	d
123789-HxCDF	ND (7)	ND (5)	ND (2)	<4	d,e
123678-HxCDF } 123478-HxCDF	9 (2)	5 (3)	1 (1)	20	d
1234789-HpCDF	ND (10)	ND (10)	ND (3)	5 (2)	
1234678-HpCDF	10 (5)	7 (7)	2 (2)	11	
OCDF	30 (15)	20 (10)	5 (5)	43	
SAMPLE TEQ ^f	410 ppq	180 ppq	48 ppt	500 ppt	
% TEQ from 2378-TCDD & 2378-TCDF	98%	98%	99%	94%	

- NOTES: (a) Concentrations in liquid samples determined on the basis of the total weight of the samples.
(b) Concentrations in sludge samples determined on dry weight basis.
(c) ND - Not detected at stated detection level; detection level is reported in parentheses (). Detection level reported in parentheses () when analytical result is less than 10 times detection level.
(d) Data may reflect presence of co-eluting isomers.
(e) Maximum possible concentration.
(f) Sample TEQ computed assuming isomer-specific analyses for listed compounds. Sample TEQ computed by USEPA (see Reference 2).

TABLE V-2

PCDDs and PCDFs IN BLEACHED KRAFT PAPER MILL MATRICES
USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY
WRIGHT STATE UNIVERSITY ANALYSES

<u>PCDDs</u>	<u>Mill E Bleachery Wastewaters</u>	<u>Mill E Final Effluent</u>	<u>Mill E Combined Wastewater Sludge</u>
2378-TCDD	970 ppq	80 ppq	190 ppt
12378-PeCDD	ND (70)	ND (12)	12
123789-HxCDD	ND (70)	ND (100)	ND (13)
123678-HxCDD	ND (30)	ND (50)	ND (23)
123478-HxCDD	ND (30)	ND (120)	ND (1.9)
1234678-HpCDD	130	80	26
OCDD	1800	990	298
<u>PCDFs</u>			
2378-TCDF	4600 ppq	360 ppq	760 ppt
23478-PeCDF	ND (20)	ND (15)	ND (12)
12378-PeCDF	ND (90)	ND (5)	ND (19)
234678-HxCDF	ND (870)	ND (410)	ND (68)
123789-HxCDF	ND (130)	ND (450)	ND (29)
123678-HxCDF	ND (150)	ND (340)	ND (19)
123478-HxCDF	ND (70)	ND (130)	ND (11)
1234789-HpCDF	ND (40)	ND (90)	ND (4)
1234678-HpCDF	ND (10)	ND (20)	ND (2)
OCDF	70	86	ND (9)
SAMPLE TEQ	1400 ppq (1500) ^c	120 ppq (150) ^c	270 ppt (280) ^c
% TEQ from 2378-TCDD & 2378-TCDF	>99% (96%) ^c	>99% (78%) ^c	98% (96%) ^c

- NOTES:
- (a) ND - Not detected at stated detection level; detection level is reported in parenthesis ().
 - (b) Data for 2378-TCDD, 2378-TCDF, OCDD, OCDF are isomer specific. Data for other compounds may reflect the presence of co-eluting isomers.
 - (c) Sample TEQ and percentage attributable to 2378-TCDD and 2378-TCDF shown in () were computed assuming all compounds present at stated analytical detection levels.

TABLE V-3

PCDDs and PCDFs IN BLEACHED KRAFT
PAPER MILL WASTEWATER SLUDGES
USEPA-ERL DULUTH ANALYSES

	Mill 2 Combined Wastewater Sludge	Mill 3 Combined Wastewater Sludge	Mill 4 Combined Wastewater Sludge
2378-TCDD	150 ppt	37 ppt	53 ppt
TCDD-Other	ND (10)	ND (5)	ND (1)
12378-PeCDD	ND (5)	ND (5)	ND (5)
PeCDD-Other	ND (5)	ND (5)	ND (5)
123678-HxCDD	17	2	2 (2)
HxCDD-Other	62	21	10
1234678-HpCDD	110	1380	33
1234679-HpCDD	82	1240	29
OCDD	1860	14000	710
2378-TCDF	880 ppt	200 ppt	280 ppt
TCDF-Other	640	310	220
12378-PeCDF	29	2	ND (5)
PeCDF-Other	140	15	ND (5)
123678-HxCDF	5	31	ND (5)
HxCDF-Other	30	240	ND (5)
HpCDF-Total	5	360	22
OCDF	53	310	ND (20)
SAMPLE TEQ	260 ppt	61 ppt	81 ppt
% TEQ from 2378-TCDD & 2378-TCDF	93%	94%	>99%

- NOTES:
- (a) ND - Not detected at stated detection level; detection level is reported in parentheses ().
 - (b) Data for 2378-TCDD, OCDD, and OCDF are isomer specific. Data for other 2378-substituted compounds may reflect the presence of co-eluting isomers.
 - (c) Mills 2, 3, and 4 were not among the five mills included in this study.

Note that for Mill E (Table V-2), TEQs were computed in two ways: (1) assuming that compounds not detected were present at the stated analytical detection level; and (2) that compounds not detected were not present, i.e., concentration of zero. This was done because of the relatively high analytical detection levels observed for several higher chlorinated 2378-substituted PCDDs and PCDFs in the bleachery wastewater and final effluent samples. For the bleachery wastewater there is no significant difference in the proportion of the TEQ associated with 2378-TCDD and 2378-TCDF with either of the methods described above. For the final effluent only 78% of the TEQ would be associated with 2378-TCDD and 2378-TCDF, if it were assumed that all of the higher chlorinated compounds not detected were present at the stated analytical detection levels. However, this is unlikely given the findings in wastewater sludge from that mill. The conservative calculations have the tendency to overstate the TEQs associated with the higher congeners. Despite this bias, the 2378-TCDD and 2378-TCDF concentrations for the remaining mills clearly represent the major portion of the total PCDD/PCDF toxic equivalents (TEQ). Based upon these data, the principal focus of the analytical program for this study was directed at isomer-specific analyses for 2378-TCDD and 2378-TCDF.

Each of the mills listed in Tables V-1 to V-3 and each of the five mills included in this study are reported to produce virgin hardwood or softwood pulps. Extraneous sources of fiber that might include wood treated with chemical preservatives are not used at these mills. Hence, the introduction of higher chlorinated dioxins and furans associated with pentachlorophenol is not likely.

2. Preliminary Sampling - March 1986

As part of the analytical methods development for this study preliminary grab samples of selected matrices were collected from Mill A in March 1986. The analytical results for the process samples are presented in Table V-4, while the results for wastewater and sludge samples and process additives are presented in Tables V-5 and V-6, respectively. The sample preparation, sample extract processing, and GC/MS analytical methods used for analyses of these samples were not the final methods selected for the five-mill study. The data for 2378-TCDF were not isomer-specific and only total homologue data were developed for penta-octa CDDs and CDFs. In some cases, the analytical detection levels attained were not consistent with the study objectives. Finally, since the samples were grab samples, the representativeness of the results with respect to mass flow rates is questionable. Nonetheless, the results provide some insight to the formation of PCDDs and PCDFs in this bleached kraft pulp and paper mill and to the relative distribution of 2378-TCDD and 2378-TCDF versus other PCDDs and PCDFs.

In Table V-4, 2378-TCDD and 2378-TCDF were not found in softwood chips, weak liquor, or recovery system mud, all samples obtained prior to pulp bleaching; neither were TCDDs, PeCDDs, HxCDDs, or TCDFs, PeCDFs, HxCDFs, HpCDFs, or OCDF at detection levels in the 0.5 to 12 ppt range. Total HpCDDs and OCDD were found in the softwood chips (37 and 154 ppt, respectively) and in the recovery mud (3.3 and 10.7 ppt, respectively). The brownstock pulp contained only OCDD at 1.2 ppt while the bleached pulp contained 2378-TCDD and 2378-TCDF plus possible co-eluting isomers at 8 and 70 ppt, respectively. Other TCDDs and TCDFs were not found at significantly higher levels in the bleached pulp, and penta-hepta CDDs and CDFs and OCDF were not found at detection levels of less than 1 ppt. OCDD was found in the bleached pulp at nearly 1 ppt. These data indicate that 2378-TCDD and 2378-TCDF plus possible co-eluting isomers are formed in the bleaching of softwood pulp and these compounds are preferentially formed over higher chlorinated PCDDs and PCDFs.

The wastewater and sludge results presented in Table V-5 show similar trends. Wastewater samples obtained prior to pulp bleaching show no detectable PCDDs and PCDFs at detection levels in the 0.01 to 0.02 ppt range, except for OCDD at 0.04 ppt. The combined untreated bleach plant wastewaters contained 1.1 ppt of 2378-TCDD and 3.9 ppt of 2378-TCDF plus possible co-eluting isomers. While no other TCDDs were found, about 3 ppt of TCDFs other than 2378-TCDF were found. Considerably lower levels of 2378-TCDD (0.09 ppt) and 2378-TCDF plus possible co-eluting isomers (0.45 ppt) were detected in the paper machine wastewaters. Penta-octa CDDs and CDFs were not analyzed in the bleach plant and paper machine wastewaters. The treated final process wastewater effluent contained both 2378-TCDD (0.25 ppt) and 2378-TCDF plus possible co-eluting isomers (1.0 ppt). Higher chlorinated PCDDs and PCDFs were not found in the treated effluent in the 0.01 to 0.05 ppt range. The combined wastewater treatment sludge sample contained about 65 ppt of 2378-TCDD (average of two analyses) and 280 ppt of 2378-TCDF plus possible co-eluting isomers. Except for OCDD, higher chlorinated PCDDs and PCDFs were not detected in the sludge.

TCDDs and TCDFs were not detected in samples of slimicide, alum, clays, and a yellow dye at detection levels of less than 1 ppt (Table V-6). However 2378-TCDD and other TCDDs were found in a sample of blue dye at 3.4 ppt and 53 ppt, respectively. TCDFs were not found in the blue dye.

The distribution of PCDDs and PCDFs in these samples were also considered in the decision to focus the analytical program on 2378-TCDD and 2378-TCDF.

TABLE V-4

MILL A
PRELIMINARY SAMPLING - MARCH 18, 1986
PROCESS SAMPLES

Laboratory Report: August 29, 1986
August 9, 1986
(Results in parts per trillion.)

Sample:	Softwood Chips	Weak Liquor	Recovery Mud	Brownstock Softwood Pulp	Bleached Softwood Pulp	Bleached*
Sample No.: Field ID:	5-89651 S01B	5-89652 S02B	5-89654 S03B	5-89655 S04B	5-89658 S05B	5-89658 S05B
Iso-2378-TCDD	ND (1.5)	ND (0.41)	ND (0.33)	ND (0.10)	8.3	8.4
% Rec ¹³ C ₁₂ -2378-TCDD	67%	67%	73%	61%	73%	103%
% Rec Surrogate	89%	96%	96%	102%	92%	100%
Ion Ratio 320/322	NA	NA	NA	NA	0.80	0.84
Total TCDDs	ND (1.6)	ND (0.52)	ND (0.33)	ND (0.11)	9.0	8.4
Total PeCDDs	ND (4.2)	ND (1.1)	ND (0.97)	ND (0.13)	ND (0.16)	ND (1.0)
Total HxCDDs	ND (8.1)	ND (5.1)	ND (2.7)	ND (0.21)	ND (0.13)	ND (0.7)
Total HpCDDs	37.2	ND (1.4)	3.3	ND (0.30)	ND (0.20)	ND (0.9)
OCDD	154	ND (1.4)	10.7	1.2	0.88	2.1
% Rec ¹³ C ₁₂ -OCDD	101%	71%	40%	19%	86%	77%
2378-TCDF**	ND (1.2)	ND (0.40)	ND (0.44)	0.25	72	62
% Rec ³⁷ Cl ₄ 2378-TCDF	66%	73%	75%	69%	52%	96%
Ion Ratio 304/306	NA	NA	NA	0.73	0.71	0.83
Total TCDFs	ND (1.4)	ND (0.44)	ND (0.44)	0.39	104	90
Total PeCDFs	ND (4.1)	ND (0.59)	ND (0.62)	ND (0.09)	ND (0.48)	ND (1.3)
Total HxCDFs	ND (6.6)	ND (1.6)	ND (1.0)	ND (0.12)	ND (0.22)	ND (1.4)
Total HpCDFs	ND (5.9)	ND (1.1)	ND (1.5)	ND (0.20)	ND (0.14)	ND (0.8)
OCDF	ND (12)	ND (1.3)	ND (3.1)	ND (0.59)	ND (0.49)	ND (1.0)

*From August 9, 1986, laboratory report; duplicate laboratory analysis.

**2378-TCDF plus co-eluting isomers.

NA - Not applicable.

ND - Not detected at stated detection level ().

TABLE V-5

MILL A
PRELIMINARY SAMPLING - MARCH 18, 1986
WASTEWATERS AND SLUDGES

Laboratory Report: August 9, 1986
(Results in parts per trillion.)

Sample:	Station 6 Kraft Recovery	Station 5 Bleach Plant	Station 2 Paper Machines	Treated Final Process Wastewater Effluent	Wastewater* Composite Sludge	Wastewater* Composite Sludge
Sample No.: Field ID:	5-89660 S06	5-89687 S07	5-89669 S08	5-89700 S10	5-89671 S09	5-89671 S09
Iso-2378-TCDD	ND(0.019)	1.1	ND(0.093)	0.25	71	59
% Rec 13C12-2378-TCDD	61%	73%	61%	47%	65%	78%
% Rec Surrogate	99%	120%	100%	98%	107%	95%
Ion Ratio 320/322	NA	0.84	NA	0.86	0.85	0.77
Total TCDDs	ND(0.015)	1.1	ND(0.007)	0.32	72	59
Total PeCDDs	ND(0.008)	--	--	ND(0.019)	ND(9.1)	ND(7.0)
Total HxCDDs	ND(0.015)	--	--	ND(0.021)	ND(14)	ND(6.0)
Total HpCDDs	ND(0.019)	--	--	ND(0.024)	ND(4.2)	ND(6.6)
OCDD	0.043	--	--	0.15	34	61
% Rec 13C12-OCDD	100%	--	--	81%	195%	42%
2378-TCDF**	ND(0.016)	3.9	0.45	1.0	276	278
% Rec 37C14-2378-TCDF	72%	71%	64%	49%	80%	86%
Ion Ratio 304/306	NA	0.82	0.81	0.77	0.75	0.80
Total TCDFs	ND(0.016)	6.6	0.80	1.5	384	418
Total PeCDFs	ND(0.007)	--	--	ND(0.11)	ND(23)	ND(34)
Total HxCDFs	ND(0.012)	--	--	ND(0.13)	ND(22)	ND(24)
Total HpCDFs	ND(0.018)	--	--	ND(0.034)	ND(4.5)	ND(6.9)
OCDF	ND(0.017)	--	--	ND(0.049)	ND(42)	ND(34)

*Duplicate laboratory analyses.

**2378-TCDF plus co-eluting isomers.

NA - Not applicable.

ND - Not detected at stated detection level ().

TABLE V-6

MILL A
PRELIMINARY SAMPLING - MARCH 18, 1986
PROCESS ADDITIVES

Laboratory Report: August 9, 1986
(Results in parts per trillion.)

Sample:	Blue Dye	Slimicide	Alum	Clay	Yellow Dye
Sample No.:	5-89676	5-89677	5-89679	5-89680	5-89689
Field ID:	S11	S12	S13	S14	S15
Iso-2378-TCDD	3.4	ND(0.71)	ND(0.68)	ND(0.52)	ND(0.45)
% Rec 13 Cl ₂ -2378-TCDD	61%	53%	53%	73%	51%
% Rec Surrogate	91%	90%	98%	95%	90%
Ion Ratio 320/322	0.86	NA	NA	NA	NA
Total TCDDs	53	ND(0.62)	ND(0.49)	ND(0.43)	ND(0.43)
2378-TCDF*	ND(0.50)	ND(0.68)	ND(0.44)	ND(0.55)	ND(0.77)
% Rec 37 Cl ₄ 2378-TCDF	64%	47%	51%	72%	46%
Ion Ratio 304/306	NA	NA	NA	NA	NA
Total TCDFs	ND(0.56)	ND(0.69)	ND(0.44)	ND(0.50)	ND(0.58)

*2378-TCDF plus co-eluting isomers.

NA - Not applicable.

ND - Not detected at stated detection level ().

3. Analytical Methods for 2378-TCDD and 2378-TCDF

As noted above, in the initial phase of the assessment of paper mill process samples and waste products, attention was focused on accurate quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF). Target detection limits of 1-2 parts per trillion (ppt) for these isomers in solid media were established, while the target limits for these isomers in aqueous media were set at 0.001 to 0.010 ppt (1-10 parts per quadrillion (ppq)). Analyses of the preliminary samples at Wright State University indicated that achieving these detection levels was not practical using the traditionally applied sample extraction and cleanup techniques. Moreover, an extensive evaluation of the separation capabilities of the several capillary gas chromatography columns which are usually employed in such analyses (DB-5, SP-2330, SP-2340), using all 38 TCDF isomers, revealed that 2378-TCDF co-elutes with one or more of the other TCDF isomers on all of these columns. Therefore, 2378-TCDF could not be uniquely determined by using any of these columns. Accordingly, Wright State, in consultation with USEPA and NCASI, undertook the development and validation of sample extract cleanup procedures which utilized a multiple silica, alumina, and carbon column liquid-chromatographic cleanup sequence which has the capacity to remove larger quantities of matrix constituents and other chemical residues. These methods also utilize modified alumina column elution procedures, in which the strength of the eluting solvent mixtures is more critically adjusted in order to optimize separation of 2378-TCDD and 2378-TCDF from other extraneous chemicals in the sample extract. Finally, gas chromatographic studies were accomplished which led to the development of a hybrid phase DB-225/DB-5 capillary GC column, which was demonstrated to completely resolve 2378-TCDF (<10% to <25% valley) from the other 37 TCDF isomers. This column was applied routinely for definitive 2378-TCDF analyses. A brief summary of the overall analytical procedures applied to determine 2378-TCDD and 2378-TCDF in the samples characterized in this study follows. The final analytical protocol is presented as Attachment C.

a. Sample preparation

Sludge samples were mixed thoroughly to achieve uniformity and two aliquots were withdrawn. One aliquot was subjected to oven drying at 105°C until the sample attained constant weight. This aliquot was then discarded. The percent solids determined on this basis was used for determining the concentration of the analytes in the second aliquot, which was the portion of the sample actually analyzed for 2378-TCDD and 2378-TCDF. The second

sample aliquot was dried on a stainless steel screen which was supported within a desiccator. The dried sample was homogenized in a laboratory blender and an aliquot was removed for analysis.

Wood chip samples were reduced to a particle size of 1 cm diameter or less using a laboratory mill. The pulverized wood was then dried, homogenized, and subsampled in the same manner as the sludge samples just described.

Ash samples were prepared in the same manner as sludge samples, except that they were dried in a shallow flat dish placed in a desiccator.

Pulp samples were manually compressed to removed the bulk of water contained therein and the sample was broken up to small pieces (2 cm or less in diameter) which were then dried, homogenized, and subsampled in the same manner as the sludge samples.

Slurries (secondary sludge and similar materials) were stirred to suspend particulate matter and an aliquot was removed for total suspended solids determination (Standard Methods for the Examination of Water and Wastewater, 17th Edition, APHA, AWWA, WPCF, 1986, Method 209C). The remainder of the sample was allowed to settle, under refrigeration, and the supernatant was removed and filtered through a tared Gelman Type A/E filter. The solids thus recovered were dried, homogenized and subsampled, in the same manner as described for sludge samples.

Water and wastewater samples were agitated in the original sample vessel to resuspend solids contained therein, and the sample was split into four portions, each portion being placed in a new sample bottle. One of the split samples was spiked with isotopically labelled $^{13}\text{C}_{12}$ -2378-TCDD and TCDF internal standards in an acetone solution and the sample was stirred vigorously for 15 minutes to disperse the spiking standards. The aqueous sample was then filtered through a Whatman 42 filter and the filtrate was retained for analysis. The filter and solids recovered were dried in a desiccator to constant weight and the solids were retained for analysis.

Exceptional samples which were too wet to dry efficiently in a desiccator but could not be filtered were first air dried at ambient temperature, then desiccated.

b. Extraction of 2378-TCDD and 2378-TCDF from the sample matrices

Methylene chloride was added to internal-standard spiked aqueous filtrates (1 liter, typically) and the sample was stirred for 16 hours. The aqueous and organic phases were allowed to separate and the organic phase was removed and retained for analysis. The aqueous sample was reextracted sequentially with two additional portions of methylene chloride and those were pooled with the original extract. This extract solution was concentrated and combined with the benzene:acetone solvent in the Soxhlet apparatus used to extract the solid portion of each filtered aqueous sample, as described below.

Portions (typically 7-10 grams) of the solid samples (dried sludges, ash, wood chips, pulp, solids from water and wastewater) were placed in a Soxhlet apparatus, spiked with $^{13}\text{C}_{12}$ -2378-TCDD and TCDF internal standards, and extracted with a 50:50 solution of benzene:acetone for a period of 16 hours. Extracts were concentrated to a volume of about 15 mL using a Snyder column. These extracts were cleaned up as described below.

c. Preliminary fractionation of sample extracts to separate 2378-TCDD and 2378-TCDF from other extract constituents

Organic extracts prepared as described above were subjected to a series of sequential washes with 20% aqueous potassium hydroxide, concentrated sulfuric acid and double-distilled water, discarding the aqueous portions and retaining the organic phase in each case.

Each washed organic extract was subjected to a sequence of liquid chromatographic column separations, including, (a) passage through a composite column of silica gel, base-modified and acid-modified silica gel, eluting the column with hexane and retaining the eluate; (b) passage through a Woelm basic alumina column, eluting sequentially with 3% methylene chloride-in-hexane, 20% methylene chloride-in-hexane and 50% methylene chloride-in-hexane, retaining only the last eluate fraction; (c) passage through a second basic alumina column, as just described; (d) passage through a carbon/celite column, eluting with hexane, 50% methylene chloride/50% cyclohexane, then with 50% benzene/50% ethyl acetate, and finally reverse eluting with toluene, retaining only the last eluate fraction; and (e) passage through a third basic alumina column, just as described earlier. The final eluate fraction collected was concentrated just to dryness, and was reconstituted with 10 micro liters of tridecane containing other appropriate standards, prior to GC/MS analysis.

d. Gas chromatographic-mass spectrometric (GC/MS) analyses of sample extracts

Sample extracts prepared by the procedures described in the foregoing were analyzed by GC/MS utilizing an appropriate capillary GC column (temperature-programmed) while the MS is operated in the selected ion monitoring (SIM) mode, monitoring simultaneously the ion masses appropriate for detection of 2378-TCDD, 2378-TCDF, and the $^{13}\text{C}_{12}$ -labelled internal standards of these. Typically, 1 to 5 uL portions of the extract are injected into the GC. Sample extracts were initially analyzed using a 60 meter DB-5 capillary GC column at a typical mass spectral resolution of 1:600 to obtain data on the concentration of 2378-TCDD and to determine if 2378-TCDF or other isomers which co-elute with 2378-TCDF are present. If the latter were detected in this analysis, then another aliquot of the sample extract was analyzed in a separate run, using a newly developed hybrid column which consists of a 10 meter section of a 0.25 mm I.D. fused silica open tubular DB-5 capillary column coupled with a 30 meter section of a 0.25 mm I.D. DB-225 column. Again, the mass spectrometer was operated at low resolution (typically 1:600) in the first analysis with this column. The hybrid column uniquely separates 2378-TCDF from the other 37 TCDF isomers and therefore yields definite data on the concentration of 2378-TCDF in the extract which is analyzed. However, in some instances compounds are present in the sample extract which give rise to ion masses which, at low mass resolution (1:600), interfere with the quantitation of 2378-TCDF. In these instances the analysis of the sample extract was repeated, using the DB-5/DB-225 hybrid column, but this time at a mass spectral resolution of 1:6,500 or higher.

The analytical procedures summarized here are fully described in Attachment C.

4. Identification and Quantitation of 2378-TCDD and 2378-TCDF

The following criteria were established for positive identification and quantitation of the target analytes:

- (1) Mass spectral responses must be observed for the following ions monitored, i.e.:

	TCDD:	320, 322, and 257
$^{13}\text{C}_{12}$ -TCDD:		332 and 334
	TCDF:	304, 306, and 241
$^{13}\text{C}_{12}$ -TCDF:		314 and 316

- (2) The signal to noise ratio of the molecular ions (2378-TCDD -- 320 and 322; 2378-TCDF -- 304 and 306) must be greater than 2.5:1 for the ions to be considered detectable.

- (3) The molecular ions for a given analyte should co-maximize within no more than plus or minus one scan of each other.
- (4) The ratio of the $[M]^+$ to $[M + 2]^+$ intensities must be at or within $\pm 15\%$ of the theoretically expected ratio of 0.77; i.e., 0.65 to 0.89 for 2378-TCDD and 2378-TCDF.
- (5) The chromatographic retention time of the unlabelled 2378-TCDD or 2378-TCDF must be within five seconds of the corresponding ^{13}C -labelled internal standard.
- (6) The GC column resolution must be demonstrated to provide a 25% valley or less between 2378-TCDD and its closest eluting isomers on the DB-5 column or between 2378-TCDF and its closest eluting isomers on the DB-5/DB-225 column.
- (7) If responses are detected for the molecular ions of 2378-TCDF on the DB-5 column, the sample extract must be re-injected and reanalyzed on the DB-5/DB-225 column to ensure isomer specific quantitation.
- (8) No response must be seen at $M/Z = 374$, the $[M]^+$ ion for hexachlorodiphenyl ether, at the same retention time as 2378-TCDF. This ether would give fragment ions identical to 2378-TCDF, and hence cause false positives.
- (9) The target percent recoveries of the ^{13}C -labeled analogs for 2378-TCDD and 2378-TCDF were set at 40%-120%.

5. Intra-Laboratory Method Validation Experiments

This study was one of the first large-scale attempts at quantifying 2378-TCDD and 2378-TCDF on an isomer-specific basis, at ppt and ppq levels, in pulp and paper mill matrices. These matrices were expected to provide considerable difficulties in cleanup and isolation of the target analytes due to the high levels of particulate matter, dissolved organics and other chemicals. It was also felt that the variability of feedstock, in-plant processes, chemical application rates, etc., could cause problems that were specific to samples from particular mills. Therefore, method validation experiments were carried out on selected matrices. These analyses were to characterize any inherent deficiencies in the analytical methodology that would result in inter-mill data comparability problems. Since virtually all of the samples were to be analyzed by a single laboratory for 2378-TCDD and 2378-TCDF, the primary goal was to validate the method internally within the scope of the study.

Method validation studies were carried out on three distinctly different matrices that are the primary exports from pulp and paper mills. The three matrices were bleached pulp, wastewater treatment sludge, and treated process wastewater effluent. The cleanup and the last would be demanding because of the relatively low target detection limit of 0.010 ppt. A restricted study was carried out on a fourth matrix, namely an artificial composite caustic extraction stage effluent made up of equal volumes of caustic extraction stage effluents from the five mills. Samples for each matrix from four of the five mills surveyed in this screening study were analyzed in duplicate. . Additional sample aliquots were spiked with 2378-TCDD and 2378-TCDF at concentration levels two to three times the native concentrations. In general, 16 determinations each were made for 2378-TCDD and 2378-TCDF in these selected matrices. An exception was the caustic extraction stage wastewater where a composite sample made up of equal volumes from all five mills was used for the method validation experiment. A single sample spike and spike duplicate analytical sequence was carried out for this composite sample.

The analytical results obtained, i.e., concentrations, native spike recoveries, and relative percent differences in the detected levels are presented in Tables V-7 to V-10. Examination of these results indicate that with the exception of one treated process wastewater, that gave an elevated recovery, these experiments were an unqualified success. These data indicate that the analytical method is relatively insensitive to the variations in sample composition or chemical loading that exist from mill to mill due to variations in manufacturing processes. While not every sample matrix has undergone this type of method validation study, these data provide experimental documentation of the overall method performance for the matrices tested.

TABLE V-7
METHOD VALIDATION EXPERIMENT
BLEACHED KRAFT PULPS

	Concentration (ppt,pg/gm)	2378-TCDD		Concentration (ppt,pg/gm)	2378-TCDF	
		RPD	% Spike Recovery		RPD	% Spike Recovery
<u>Pulp 1</u> (DE020902)	15.2			--		
Duplicate	16.3	7		333		
Matrix Spike	47.5		105	1064		121
Spike Duplicate	51.7	9	118	912	15	96
<u>Pulp 2</u> (86374612)	10.2			54.3		
Duplicate	11.0	8		64.4	17	
Matrix Spike	37.5		99	211		112
Spike Duplicate	38.0	1	102	203	4	107
<u>Pulp 3</u> (DF024411)	3.89			7.68		
Duplicate	3.99	3		7.9	3	
Matrix Spike	15.9		110	21.5		84
Spike Duplicate	15.8	1	109	21.6	0	84
<u>Pulp 4</u> (RG1-86367)	55.7			181		
Duplicate	46.7	18		183	1	
Matrix Spike	161		92	575		92
Spike Duplicate	171	6	100	559	3	87

NOTE: (1) RPD - Relative Percent Difference.
(2) Each analysis (original, duplicate, matrix spike, and matrix spike duplicate) was conducted on a separate aliquot of unprocessed sample.

TABLE V-8
METHOD VALIDATION EXPERIMENT
WASTEWATER TREATMENT SLUDGES

	Concentration (ppt,pg/gm)	2378-TCDD		Concentration (ppt,pg/gm)	2378-TCDF	
		RPD	% Spike Recovery		RPD	% Spike Recovery
<u>Sludge 1</u> (DE026011)	3.37			42.6		
Duplicate	3.27	3		34.5	21	
Matrix Spike	13.0		97	142		104
Spike Duplicate	11.8	10	86	148	4	111
<u>Sludge 2</u> (RG1-86387)	193			879		
Duplicate	168	14		670	27	
Matrix Spike	552		88	2641		99
Spike Duplicate	576	4	95	3023	13	119
<u>Sludge 3</u> (DF024606)	19.2			35.7		
Duplicate	17.4	10		31.9	11	
Matrix Spike	71.2		106	129		95
Spike Duplicate	64.0	11	91	125	3	91
<u>Sludge 4</u> (DE020920)	37.4			624		
Duplicate	35.8	4		732	16	
Matrix Spike	119		104	2023		113
Spike Duplicate	127	7	115	1883	7	101

NOTES: (1) RPD - Relative Percent Difference.
(2) Each analysis (original, duplicate, matrix spike, and matrix spike duplicate) was conducted on a separate aliquot of unprocessed sample.

TABLE V-9
METHOD VALIDATION EXPERIMENT
TREATED PROCESS WASTEWATER

	Concentration (ppt,pg/gm)	2378-TCDD		Concentration (ppt,pg/gm)	2378-TCDF	
		RPD	% Spike Recovery		RPD	% Spike Recovery
<u>Effluent 1 (86374645)</u>	0.0157			0.133		
Duplicate	0.0145	8		0.110	19	
Matrix Spike	0.0550		95	0.376		97
Spike Duplicate	(2)	--		(2)	--	
<u>Effluent 2 (DE026006)</u>	ND(0.0034)			0.0085		
Duplicate	ND(0.0042)	--		0.0140	49	
Matrix Spike	0.0156		158	0.0279		84
Spike Duplicate	0.0125	22	125	0.0365	27	126
<u>Effluent 3 (DF024512)</u>	ND(0.0075)			ND(0.0069)		
Duplicate	ND(0.0072)	--		ND(0.0066)	--	
Matrix Spike	0.0203		115	0.0187		106
Spike Duplicate	0.0178	13	101	0.0253	30	143
<u>Effluent 4 (RG1-86388)</u>	0.0881			0.447		
Duplicate	0.0953	8		0.441	1	
Matrix Spike	0.538		112	2.140		85
Spike Duplicate	(2)	--		(2)	--	

NOTES: (1) RPD - Relative Percent Difference.
(2) Not analyzed due to insufficient sample volume.
(3) Each analysis (original, duplicate, matrix spike, and matrix spike duplicate) was conducted on a separate aliquot of unprocessed sample.

TABLE V-10

METHOD VALIDATION EXPERIMENT

COMPOSITE CAUSTIC EXTRACTION STAGE WASTEWATER SAMPLE

	Concentration (ppt,pg/gm)	2378-TCDD		Concentration (ppt,pg/gm)	2378-TCDF	
		RPD	% Spike Recovery		RPD	% Spike Recovery
Sample	961			7080		
Matrix Spike	2774		87	20,312		85
Spike Duplicate	3010	8	94	23,301	14	99

- NOTE: (1) RPD - Relative Percent Difference.
 (2) Sample consisted of a composite of equal volumes of the caustic extraction stage samples collected at each of the five mills. Sample was not run in duplicate.
 (3) Each analysis (original, matrix spike, and matrix spike duplicate) was conducted on a separate aliquot of the composite sample.

6. Inter-Laboratory Method Comparison

A limited inter-laboratory method comparison study was attempted involving Dow Chemical and Brehm Laboratory, Wright State University (WSU). At the outset of the study, two wastewater and two sludge samples were analyzed by both laboratories. The data and the relative percent difference (RPD) are presented below:

		<u>Concentrations (ppt)</u>			
<u>Sample Number</u>		<u>Dow*</u>	<u>WSU</u>	<u>RPD</u>	
			<u>Range</u>		<u>Mean</u>
DE020915	2378-TCDD	0.150	--	0.296	65
Wastewater	2378-TCDF	2.50	--	NA**	--
DE020922	2378-TCDD	0.073	(0.111-0.150)	0.124	52
Wastewater	2378-TCDF	1.00	--	2.18	74
DE020920	2378-TCDD	17.0	(35.8-37.4)	36.6	73
Sludge	2378-TCDF	300	(624-732)	678	77
DE020923	2378-TCDD	240	(317-470)	394	49
Sludge	2378-TCDF	2300	(3270-4190)	3730	47

* The Dow Chemical analytical results for 2378-TCDF may reflect the presence of co-eluting isomers.

** NA - Sample consumed in analytical method development experiments.

The Dow Chemical results confirm the presence of 2378-TCDD and 2378-TCDF in these samples. However, the mean RPD of 62% indicates notable differences in reported concentrations when compared to the high degree of precision achieved for intra-laboratory and field duplicate samples. The bias observed in the data is consistent in both direction and magnitude. These differences can be attributed to variations in extraction and cleanup procedures and to the fact that different calibration standards were used. Additional inter-laboratory method comparisons have not been conducted as part of this study. The above data clearly indicate the need for further inter-laboratory studies involving these atypical sample matrices.

B. Chlorinated Phenolics

Selected water and wastewater samples were analyzed for the following chlorinated phenolics using NCASI GC/MS analytical methods (Technical Bulletin No. 498, July 1986):

<u>Chlorophenols</u>	<u>Chloroguaiacols</u>	<u>Chlorovanillins</u>
2-Chlorophenol	4,5-Dichloroguaiacol	5-Chlorovanillin
2,6-Dichlorophenol	3,4,5-Trichloroguaiacol	6-Chlorovanillin
2,4-Dichlorophenol	4,5,6-Trichloroguaiacol	5,6-Dichlorovanillin
1,4/2,5-Dichlorophenol	Tetrachloroguaiacol	
3,4-Dichlorophenol		
2,5-Dichlorophenol		
2,3-Dichlorophenol		
2,4,5-Trichlorophenol		
Pentachlorophenol		

A revised quantitation procedure (May 1987) incorporating stable isotope internal standards was used in the analysis of samples from Mills C, D, and E. All analyses were completed by NCASI at its West Coast Regional Center located at Corvallis, Oregon. The NCASI methods are fully described in Attachment D.

C. Total Suspended Solids and Biochemical Oxygen Demand

Selected water and wastewater samples were analyzed for total suspended solids and five-day biochemical oxygen demand by mill laboratories for four mills and by a local water authority for one mill. The analytical methods used were those contained in Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980 (APHA, AWWA, WPCF); or, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, March 1979, USEPA, EMSL-Cincinnati, Ohio.

VI. QUALITY ASSURANCE

A. 2378-TCDD and 2378-TCDF

1. Quality Assurance Objectives

Prior to undertaking the five-mill screening study, data quality objectives for precision, accuracy, and completeness were established. The primary goal was to provide reliable measurements of the concentrations of 2378-TCDD and 2378-TCDF at low ppt levels in solids and low ppq levels in liquids. The approach included the isotope dilution analytical methodology used in the National Dioxin Study. An isotopically labelled analogue (^{13}C labelled) for each of the target compounds was added as early as possible in the sample preparation process. This labelled compound would then be present throughout the entire extraction, cleanup, and instrumental analysis. Any losses of the unlabelled naturally occurring TCDD or TCDF would be mimicked by the labelled TCDD or TCDF. Therefore, operational problems would be compensated for and final recoveries of the labelled analogues would serve as indicators of overall method efficiencies.

In this discussion, 2378-TCDD and 2378-TCDF results are evaluated as two separate analyses on the same sample even though the sample extraction, multi-column cleanup, and concentration steps were common to both compounds. The only divergence in analytical methodology occurs at the gas chromatographic stage where capillary columns of different polarities were utilized to ensure isomer specificity for both 2378-TCDD and 2378-TCDF.

a. Laboratory precision

As noted in the analytical methods section, a considerable amount of sample processing, i.e., drying, blending, filtering, splitting, etc., takes place before the extraction and cleanup stages. Therefore, documenting laboratory precision was of paramount importance. This was done by carrying out replicate analyses of sample aliquots and calculating the relative percent difference (RPD). In cases where multiple determinations were made, the percent relative standard deviation (% RSD) was calculated. Duplicate aliquots of samples were also spiked with 2378-TCDD and 2378-TCDF and the precision evaluated by comparison of these concentrations. A QA objective of precision $\leq 50\%$ RPD was established for this study.

b. Field precision

Field precision targets were not established prior to initiating this screening study due to the wide range of matrix types, variability of solids content, and the collection of both grab and multi-hour composite samples. However, a selected number of field duplicate samples for each type of sample matrix were collected and analyzed to provide an indication of field sampling precision.

c. Accuracy

The accuracy of the analytical process was evaluated by analyzing samples spiked with known amounts of 2378-TCDD and 2378-TCDF. Subsequently, percent recoveries of the spiked compounds were calculated. This was done in addition to calculating the percent recoveries of the labelled dioxin and furan to provide an estimate of the accuracy of the analytical system. Since valid measurements of accuracy require reasonable spike levels, samples were analyzed once, to determine the native concentration, and then reextracted and reanalyzed after spiking at a level of 2 to 3 times the native concentrations.

d. Completeness

A target of 80%-100% completeness was established at the beginning of the study. This was the percentage of sample analyses that met all other QA objectives. Since a substantially larger number of samples, particularly background and chemical additives, were collected than were essential to characterize mill operations, completeness is a measure of the percentage of the samples analyzed deemed critical by the project manager that were subjected to analysis.

e. Internal standard recovery

One of the quality assurance targets established at the beginning of the screening study was that the recoveries of the isotopically labeled internal standards should be in the range of 40%-120%. As mentioned in the analytical protocol, the internal standards $^{13}\text{C}_{12}$ -2378-TCDD, $^{13}\text{C}_{12}$ -2378-TCDF, and $^{37}\text{Cl}_4$ -1278-TCDF are added to the samples before sample processing, carried through the entire extraction and cleanup process, and finally quantified against $^{13}\text{C}_{12}$ -1234-TCDD and $^{37}\text{Cl}_4$ -1278-TCDF added prior to injection on the GC/MS.

2. Quality Assurance Results for 2378-TCDD and 2378-TCDF

Table VI-1 provides a tabulated summary of how well the QA objectives were met in the course of the study. As indicated in the previous section concerning the methods validation experiments (V.A.5), three matrices believed to be the most environmentally significant were selected for extensive laboratory duplicate, spike and spike duplicate analyses. In addition, a similar group of analyses were carried out on a five-mill caustic extraction stage composite sample. These results are presented in detail in Tables V-7 to V-10.

In the course of carrying out the analytical portion of the study, it was noted that certain samples had internal standard recoveries of less than 40%, primarily for the 2378-TCDF internal standard. For the majority of these instances, the recoveries were in the 30%-40% range and gave acceptable signal to noise (S/N) ratios. In addition, the samples in which 2378-TCDD or 2378-TCDF were not detected, had detection limits that were judged acceptable for the purposes of the study.

In order to better assess any possible impact that internal standard recoveries less than 40% may have on data quality or usability, leading chemists in the field of dioxin/furan analyses, in both the public and private sectors, were polled. These reviewers were in general agreement that internal standard recoveries of less than 40% could produce usable data. Several commented that the analytical system would have to meet criteria regarding adequate S/N, correct isotope ratios, and correct mass measurements. The possible impact of decreased S/N would be questionable extraction or cleanup efficiency, elevated detection limits, and decreasing precision.

Careful examination of the analytical data acquired in this study showed 11 samples that had pairs of positive results with internal standard recoveries bracketing the 40% criterion. Calculation of the relative percent difference (RPD) between the two concentrations for each sample resulted in RPDs less than 50% for 10 of the 11 samples. The one outlier had an RPD of 62%. The mean RPD for the 11 samples was 20%. These data clearly suggest that internal standard recoveries of between 10% and 40% do not significantly impact quantitation of the target analytes in this study. Accordingly, for purposes of the mass balance calculations, the mean of the duplicate results, including results with low internal standard recoveries, was used to characterize the sample, provided all other QA criteria were met.

TABLE VI-1

QUALITY ASSURANCE SUMMARY

<u>Laboratory Precision as RPD</u>	<u>2378-TCDD</u>	<u>2378-TCDF</u>
Quality Assurance Objectives	≤ 50	≤ 50
Number of Determinations ¹	35	33
Range (mean)	1-138 (15)	0-62 (16)
Percent Meeting QA Objectives	97	97
 <u>Field Precision as RPD</u>		
Quality Assurance Objectives	NA	NA
Number of Determinations	8	9
Range (mean)	4-19 (14)	0-99 (22)
 <u>Accuracy as % Spike Recovery</u>		
Quality Assurance Objectives	50-150%	50-150%
Number of Determinations ¹	35	35
Range (mean)	66-160 (103)	58-153 (102)
Percent Meeting QA Objectives	97	97
 <u>Completeness</u>		
Quality Assurance Objectives	80-100%	80-100%
Number of Determinations	133	133
Percent Meeting QA Objectives	95%	95%

NOTE: (1) The number of determinations for laboratory precision and accuracy include those from intralaboratory method validation experiments (Section V.A.5). Thus, the percents meeting QA objectives are weighted toward the mill exports (bleached pulp, treated wastewater effluent, and wastewater sludge). Refer to the text for discussion of other sample matrices.

Analysis of the field duplicates indicated excellent field sampling reproducibility in the great majority of the cases. Two dioxin field duplicate pairs and one furan pair gave inconclusive results as one analysis gave a positive result and the other a nondetect. An evaluation of these results and their use within the scope of this study are presented Section VII.

QA results on a matrix-specific basis are presented below for the main matrices of interest.

a. Bleached and unbleached pulps

Bleached pulp was one of the matrices selected for intra-laboratory method validation experiments. Bleached pulp samples from four of the five mills were analyzed in duplicate before and after spiking with 2378-TCDD and 2378-TCDF (see Table V-7). Fifteen of the sixteen determinations gave RPDs less than 18, with one analysis being rejected due to a high peak ratio for m/m+2 for 2378-TCDF in the unspiked sample. This indicates excellent precision in laboratory operations as these samples were dried, blended, homogenized, and subsampled prior to analysis. All spike recoveries ranged between 84% and 121% indicating acceptable accuracy. Spike recoveries were comparable (81%-108%) with those for unbleached pulp. When field duplicates were analyzed for both the bleached and unbleached pulps, the RPDs ranged from 0 to 33. Clearly, the pulp matrix is one that can be accommodated by the field and laboratory protocols and the data generated are of high quality.

b. Bleach plant wastewaters

Since caustic extraction stage filtrates were determined to be critical process samples, with high levels of organic materials and high pH, a composite sample was prepared by blending equal amounts of the E-stage samples from all five mills. This sample was analyzed in duplicate after spiking with twice the estimated concentrations of 2378-TCDD and 2378-TCDF. The results presented in Table V-10 indicate good precision and accuracy. One additional laboratory duplicate and two field duplicate determinations for actual field samples had RPDs of 0 to 5. Note that many of the initial analyses for caustic extraction stage filtrates had very low internal standard recoveries and/or high detection limits. Reanalyses using medium or high resolution were conducted on a number of these samples to confirm the initial results or improve detection limits.

The chlorination stage samples had considerable variation in both spike recoveries and RPDs. Four sample spikes gave recoveries ranging from 94% to 160%. The one sample spike recovery of 160% is out of the QA range of 50-150%. It is probable that this high recovery is due to sample inhomogeneity rather than method inaccuracies as the same sample also gave a high RPD of 138. The five laboratory duplicates covered an RPD range of 3 to 138. The two field duplicate pairs also gave anomalous results with 2378-TCDF RPDs covering a range from 13 to 99 and 2378-TCDD giving one positive result and one nondetect in each case. These samples were not subjected to additional cleanup and analysis with a view to lowering the levels of interfering compounds and possibly confirming the presence of 2378-TCDD. While these analytical data point to problems in field and laboratory precision for chlorination stage wastewaters, they were judged not so significant as to render the data unusable.

In contrast, analyses of D-stage and H-stage wastewaters gave good QC results, with one elevated recovery of 153% for a matrix spike of 2378-TCDF as the only outlier. The other three matrix spike results ranged from 99% to 124% recovery. The same sample that was used for matrix spikes was also analyzed as a field duplicate, gave acceptable results for 2378-TCDD, and a positive at 0.0272 ppt and an ND at 0.0056 ppt for 2378-TCDF. This is no clear reason for the discrepancy in the 2378-TCDF results. One additional laboratory duplicate gave an RPD of 12 for 2378-TCDF.

c. Wastewater treatment sludges

Composite sludges from four of the five mills were analyzed as part of the method validation experiments and gave excellent results for all sixteen precision and accuracy determinations. These results are presented in detail in Table V-8. One composite sludge was analyzed in quadruplicate using both the routine protocol and a modified procedure being developed for isomer-specific determinations of all 2378-substituted PCDDs and PCDFs. The results gave a 9% RSD for 2378-TCDD and a 12% RSD for 2378-TCDF. These results demonstrate good sample homogenization and a high degree of analytical precision. One additional matrix spike experiment on a primary sludge gave a 90% recovery for 2378-TCDD and 95% recovery for 2378-TCDF.

d. Treated wastewaters

Since these wastewaters are discharged into streams and rivers, they are of particular environmental significance. Every attempt was made to achieve the lowest possible detection limits. A method validation study was undertaken to determine if any mill-

specific processing could affect the analytical method performance. Laboratory duplicates and matrix spike analyses were carried out on samples from four mills. Matrix spike duplicate results could only be obtained on samples from two mills due to the lack of sufficient sample volume from the other two mills. These results are presented in detail in Table V-9 and indicate good precision and accuracy with one outlier, i.e., a recovery of 158% for a 2378-TCDD matrix spike, slightly above the upper bound of the acceptable range of 50% to 150%. The duplicate analyses for this sample (DE026006) resulted in no detectable 2378-TCDD at detection levels of 0.003 and 0.004 ppt, respectively; and the spike level was about 0.010 ppt. Given that 2378-TCDD might be present in this sample at less than detectable levels, the computation of percent spike recovery may be influenced by trace levels of native 2378-TCDD present. In retrospect, slightly higher spike levels (e.g., 0.015 or 0.020 ppt) should have been chosen. Samples from three mills were run in triplicate with results ranging from 0 to 18% RSD. One sample run in triplicate for 2378-TCDF gave an RSD of 12%. Overall this indicates good laboratory precision in splitting the effluent samples into multiple aliquots and in carrying out the analyses.

B. Chlorinated Phenolics

Since chlorinated phenols are known to be produced in the bleaching process, it was thought that chlorination in the bleaching stage could be followed by cyclization forming chlorinated dibenzodioxin and dibenzofuran products. In order to determine the amounts and species of chlorinated phenols produced, selected background, bleach plant, and wastewater samples from all five mills were analyzed for chlorinated phenols, vanillins, and guaiacols.

The analytical methodology underwent slight alterations in the course of this survey in order to utilize procedures more comparable with the isotope dilution quantitation used for 2378-TCDD and 2378-TCDF. The samples from Mill A were acetylated, extracted, and quantitated against 3,4,5-trichlorophenol as the internal standard. Two stable labelled internal standards, namely $^2\text{H}_3$ -2,4-dichlorophenol and $^{13}\text{C}_6$ -pentachlorophenol, were added to the samples from Mill B prior to derivatization. The samples from the last three mills were treated in a similar fashion except for the inclusion of two additional deuterium labelled compounds, $^2\text{H}_4$ -chlorophenol and $^2\text{H}_2$ -2,4,5-trichlorophenol.

Table VI-2 provides a summary of the results obtained for duplicate and spike samples analyzed from each of the five mills. Overall, the data obtained met established quality assurance objectives.

TABLE VI-2

QUALITY ASSURANCE SUMMARY FOR CHLORINATED PHENOLICS

Mill:	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
<u>Precision as RPD</u>					
QA Objectives	<40	<40	<40	<40	<40
No. of determinations	24	8	18	22	1
Range	0-70	2-53	1-93	3-40	5.4
Mean	13	16	18	16	5
% meeting QA objectives	96	88	94	100	100
<u>Accuracy as % Recovery</u>					
QA Objectives	60-140	60-140	60-140	60-140	60-140
No. of determinations	65	28	42	42	14
Range	52-149	82-127	71-122	63-125	66-98
Mean	93	108	99	99	85
% meeting QA objectives	95	100	100	100	100
<u>Completeness</u>					
QA Objectives	80-100	80-100	80-100	80-100	80-100
No. of determinations	98	126	112	112	154
% meeting QA objectives	96	99	99	100	100

NOTE: (1) For Mill A, the quality assurance summary includes one sample analyzed by GC/EC. The data for Mill A do not include spike recoveries for spike levels less than twice the background.

VII. RESULTS AND DISCUSSION

Attachment E contains the master sample lists for the field surveys conducted at each of the five mills. All samples collected at each mill are identified by a unique sample number and a brief description. For those samples analyzed, the following information is displayed: 2378-TCDD and 2378-TCDF concentrations in ppt; ratio of monitored molecular ion clusters for identification of 2378-TCDD and 2378-TCDF; percent recoveries of the internal standards used to quantitate 2378-TCDD and 2378-TCDF; and, for those samples where both 2378-TCDD and 2378-TCDF were found, the 2378-TCDF/2378-TCDD ratio. Where detectable quantities of 2378-TCDD or 2378-TCDF were not found, the analytical detection level is presented with the percent recovery of the respective internal standard. Positive findings are reported for only those samples where criteria established for identification of 2378-TCDD and 2378-TCDF were achieved (i.e., 2378-TCDD, 320/322 ratio (0.65 to 0.89); 2378-TCDF, 304/306 ratio (0.65-0.89)). For reference purposes, the date of the laboratory report for each analysis is also presented.

The following protocols were followed to establish the 2378-TCDD and 2378-TCDF concentrations used in this report for mass balance calculations:

1. For samples with no detectable levels of 2378-TCDD or 2378-TCDF, concentrations of zero were assigned.
2. For samples with multiple analyses (blind or known field duplicates and laboratory duplicates), the mean values of the multiple analyses were used to characterize the samples, with nondetects counted as zero.

There were three field duplicate sample pairs where duplicate 2378-TCDD analyses yielded a nondetect and a positive finding. For one of those pairs (Mill D, sample numbers DF024511/604) the positive finding was used in the mass balance calculations based upon consideration of findings in tributary streams and the 2378-TCDF/2378-TCDD ratio characteristic of that mill (see Section VII.A). There was reasonably good agreement between 2378-TCDF analyses for this sample pair. For the second sample pair (Mill B, sample numbers 86374613/73), the average of the 2378-TCDD results was used based upon consideration of the 2378-TCDF/2378-TCDD ratio characteristic of that mill. The 2378-TCDF analyses were in good agreement. For the third sample pair (Mill D, sample numbers DF024412/605), agreements between the field duplicate analyses and the laboratory duplicate analyses for sample DF024605 were poor, as was agreement for the corresponding 2378-TCDF analyses. Lacking any suitable criteria to evaluate these data,

all results were averaged to characterize this stream. The resulting 2378-TCDF/2378-TCDD ratio fell in the mid-range of other samples from Mill D. Finally, there was one field duplicate sample pair (Mill C sample numbers DE026003/013) where analyses for 2378-TCDF yield a nondetect and a positive finding. The average value of these analyses was assigned to this sample. This had no impact on mass balance calculations since there was no discharge of wastewater to the mill wastewater treatment system from this source during the survey. Aside from these four sample pairs, agreement between analyses of field duplicate samples and agreement between laboratory duplicate analyses for the remaining 28 sample pairs was considered good (generally within $\pm 15\%$). The impact on mass balance calculations would not be significant had either of the duplicate analytical results been used for the remaining samples.

The data contained in Attachment E are presented as received from the laboratory with no editing of significant figures. These data were used with the mass flow rates of pulps, untreated and treated wastewaters, and sludges and ashes to compute the mass flow rates of 2378-TCDD and 2378-TCDF for each mill. The concentration data, mass flow data, and mass flow rates of 2378-TCDD and 2378-TCDF are presented by mill for each sample in Attachment F. The mass flows of process waters, treated and untreated wastewaters, pulps, and sludges and ashes were obtained for the survey periods from primary measurement devices or from best engineering estimates by mill personnel. As noted earlier, the mass flow rates of treated process water, treated effluents, pulps and, to a lesser extent, sludges are considered to be fairly accurate. However, in most cases, the mass flow rates of untreated wastewater streams, particularly bleach plant filtrates, can only be characterized as reasonable estimates. The mass flow data were not edited as to significant figures for the calculation of mass flow rates of 2378-TCDD and 2378-TCDF. For purposes of reporting in this section, the computed mass flow rates of 2378-TCDD and 2378-TCDF were generally rounded to two significant figures.

A. Observation on 2378-TCDF/2378-TCDD Ratio

In the course of obtaining and reviewing analytical results from the laboratory over a period of several months, certain trends in the data began to emerge. Among these was the observation that the ratio of the concentration of 2378-TCDF to that of 2378-TCDD for samples where both were detected appeared to be somewhat uniform within mills or within bleach lines. The data for individual bleach lines for all five mills are presented in Table VII-1. These data demonstrate considerable variations in the mean 2378-TCDF/2378-TCDD ratio across the seven bleach lines. However, for the softwood bleach lines at Mills A, B, D, and E, and

TABLE VII-1

2378-TCDF/2378-TCDD RATIO
BLEACH LINE SUMMARY

MILL:	<u>A</u>		<u>B</u>	<u>D</u>		<u>E</u>
<u>Softwood Lines</u>				<u>A</u>	<u>B</u>	
Bleached Pulp	21.1		5.4	ND	2.0	5.4
Filtrates	C	16.0	C _D 2.9	C 1.8	C 3.3	C/D 3.9
	E _O	17.9	E 4.7	E 1.8	E 1.8	E 4.5
	H ₁	16.9	H 4.4	H 1.6	H 1.8	D 5.2
	H		H 6.9			
			D 4.5			
Range	16.0-21.1		2.9-6.9	1.6-3.3		3.9-5.4
Mean	18.0		4.8	2.0		4.8

MILL:	<u>A</u>		<u>C</u>	<u>E</u>
<u>Hardwood Lines</u>	<u>Hypochlorite</u>	<u>Peroxide</u>		
Bleached Pulp	9.7	16.8	ND	3.6
Filtrates	C 14.4	C 14.4	C/D ND	C/D 4.9
	E _O ND	E _O 7.0	E _O ND	E _O 3.9
	H ND	H 4.2	D ND	D 4.8
		H 7.0		
		P --		
Range	9.7-14.4	4.2-16.8	--	3.6-4.9
Mean	--	9.9	--	4.3

- NOTES:
- (1) ND - 2378-TCDD not detected.
 - (2) Mill D - A and B softwood bleach lines with combined E-stage filtrates.
 - (3) Mill A - Hardwood bleach lines - common C and E_O-stages; separate E_O-stage washers and filtrates.

for the hardwood bleach line at Mill E, the ratios were remarkably uniform. The ranges of ratios computed for the hardwood bleach lines at Mill A and the softwood bleach line at Mill B were somewhat larger. The 2378-TCDF/2378-TCDD ratio could not be computed for Mill C because 2378-TCDD was not detected in the bleached hardwood pulp or bleach plant filtrates from that mill.

Table VII-2 presents 2378-TCDF/2378-TCDD ratios for paper machine wastewaters, combined untreated wastewaters, final effluents, wastewater sludges, and landfill leachates for the five mills. The characteristic high ratio for the softwood bleach line at Mill A was in evidence for all other samples at Mill A except for the landfill leachate. In similar manner, the bleach line ratios observed at Mills D and E were also observed in other samples from those mills with little variation. For Mill B, the final effluent and secondary wastewater treatment sludge exhibited somewhat higher ratios than the bleach plant samples, while the ratio for the primary wastewater treatment sludge was more in line with the bleach plant ratio. This possibly suggests preferential partitioning of 2378-TCDF in biological solids at Mill B. The limited data preclude a more definitive statement.

Factors accounting for the differences in 2378-TCDF/2378-TCDD ratios across bleach lines and across mills have not been determined nor has the possible process significance been formulated. Controlled laboratory or bench scale research studies would be necessary to provide insight into the mechanisms of formation of 2378-TCDD and 2378-TCDF.

B. Background Samples

1. Treated Intake Process Waters and Residuals

Table VII-3 presents analytical results for the treated intake process waters at the five mills. Intake process waters are obtained from surface waters at three mills and from a combination of surface water and ground water at two mills. In each case, the untreated intake process waters are treated by coagulation and sedimentation or filtration followed by chlorination (residual chlorine about 1 mg/L) prior to use in the pulp and papermaking processes. The samples obtained were after chlorination but prior to any uses. The data indicate no 2378-TCDD or 2378-TCDF contamination of treated intake process waters at or below the desired analytical detection level of 0.01 ppt.

For Mill E, a concentrated sample of river water filter backwash was obtained and analyzed. The solids in this sample are comprised principally of river sediment and coagulants used

TABLE VII-2
2378-TCDF/2378-TCDD RATIO
MILL SUMMARY

<u>Bleached Pulp</u>	MILL:	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Softwood		21.1	5.4	--	ND, 2.0	5.4
Hardwood		9.7, 15.8	--	ND	--	3.6
<u>Bleach Plant Filtrates</u>						
Softwood Line		16.0-17.9	2.9-6.9	--	1.6-3.3	3.9-5.2
Hardwood Line		4.2-14.4	--	ND	--	3.9-4.9
<u>Paper Machine Wastewaters</u>		9.3	ND	18.6	ND	3.3, 3.5
<u>Combined Untreated Wastewaters</u>		14.1	ND	ND	2.1	4.7
<u>Final Effluents</u>		17.6	8.1	ND	ND	4.7
<u>Wastewater Sludges</u>						
Primary		16.3	5.3	--	1.8	--
Secondary		15.4	9.1	6.7	2.2	4.3
Combined		18.5	--	11.6	1.9	4.2
<u>Landfill Leachates</u>		4.4	ND	ND	ND	ND
Number		17	9	3	11	14
Range		4.2-21.1	2.9-9.1	6.7-18.6	1.6-3.3	3.3-5.4
Mean		13.3	5.7	12.3	2.0	4.4
Std. Dev.		5.3	2.0	--	0.5	0.6

NOTE: ND - 2378-TCDD not detected.

TABLE VII-3

MILL INPUTS

TREATED INTAKE PROCESS WATERS

[Concentrations in parts per trillion (ppt) or pg/gm.]

	<u>2378-TCDD</u>	<u>2378-TCDF</u>
MILL A	ND (0.005)	ND (0.011)
MILL B	ND (0.007)	ND (0.010)
MILL C	ND (0.005)	ND (0.007)
MILL D	ND (0.005)	ND (0.005)
MILL E	ND (0.006)	ND (0.007)

NOTE: ND - Not detected; analytical detection level in parentheses ().

for water treatment prior to chlorination. There are two bleached kraft pulp and paper mills located upstream from Mill E. 2378-TCDD was not found in the solids fraction of the Mill E filter backwash at a detection level of 1.8 ppt. 2378-TCDF was found at about 8 ppt. However, due to low recovery of the internal standard for the 2378-TCDF analysis (13%), quantitation at that level is questionable. A second analysis of a much smaller mass of remaining solid filter residue confirmed the presence of 2378-TCDF; however, quantitation is again questionable because of the low mass of sample analyzed. Nonetheless, these data indicate 2378-TCDF is present in the river system upstream of Mill E. The source or sources cannot be identified from this information, nor can the amount removed in the Mill E water treatment process or the mass amount contributed to the Mill E wastewater treatment system. Based upon the results obtained for major wastewater flows at Mill E, the amount of 2378-TCDF contributed to the wastewater treatment system from the river water filter backwash system is believed to be a relatively small fraction of the untreated process wastewater loading.

2. Kraft Pulping Process

Seven unbleached kraft (brownstock) pulps from the five mills were analyzed for 2378-TCDD and 2378-TCDF. The data are displayed in Table VII-4. 2378-TCDD was not detected in any of the unbleached pulps at detection levels ranging from 0.3 to about 1.0 ppt. 2378-TCDF was not found in the unbleached pulps from Mills A, C, and D at detection levels less than 0.3 ppt.

2378-TCDF was found in the unbleached softwood pulp at Mill B at 1.5 ppt and in the unbleached softwood and hardwood pulps at Mill E at 1.1 and 2.3 ppt, respectively. These findings may be accounted for by reuse of paper machine white waters for brownstock pulp washing or dilution at both mills. As shown later (Section VII.D.1, Table VII-16), paper machine white waters contain 0.11 ppt and 0.17 ppt of 2378-TCDF at Mills B and E, respectively. It is theorized that the 2378-TCDF is transferred to the brownstock pulp during pulp washing and dilution. The mass amounts of 2378-TCDF found in the brownstock pulps at Mills B and E are substantially less than the mass amounts contained in the respective paper machine white waters discharged to the wastewater treatment systems. This suggests that the 2378-TCDF found in the brownstock pulps may be accounted for by the volume of paper machine white waters reused at these mills. Representatives from Mills C and D report no reuse or recycle of paper machine white waters to the respective pulping processes, while reuse of paper machine white waters for brownstock pulp dilution is practiced at Mill A. More detailed mass balance studies would be necessary to determine

TABLE VII-4

UNBLEACHED KRAFT PULPS

[Concentrations in parts per trillion (ppt) or pg/gm.]

	<u>2378-TCDD</u>	<u>2378-TCDF</u>
<u>MILL A</u>		
Softwood	ND (0.74)	ND (0.27)
Hardwood	ND (0.31)	ND (0.23)
<u>MILL B</u>		
Softwood	ND (0.95)	1.5
<u>MILL C</u>		
Hardwood	ND (0.56)	ND (0.16)
<u>MILL D</u>		
Softwood	ND (0.70)	ND (0.20)
<u>MILL E</u>		
Softwood	ND (0.44)	1.1
Hardwood	ND (0.98)	2.3

NOTE: ND - Not detected; analytical detection level in parentheses ().

the extent to which the brownstock pulp findings can be attributed to this practice. The 2378-TCDF data and the 2378-TCDF/2378-TCDD ratio for other mill streams also suggest that the brownstock pulps at Mills B and E may contain 2378-TCDD at less than detectable levels.

Based upon the negative 2378-TCDD findings and the intermittent and relatively low level contamination of unbleached pulps with 2378-TCDF, analyses of pulping process and chemical recovery system wastewaters and lime muds were not conducted in order to conserve analytical resources. Analyses of preliminary samples from Mill A (Section V.A.2) indicate no detectable levels of 2378-TCDD or 2378-TCDF in pulping process wastewaters or lime mud at that mill.

C. Bleach Plant Findings

1. Bleach Plant Chemical Applications

As noted earlier, bleach plant process operating logs were obtained from the respective mills during the weeks of the field surveys. The data for the 24-hour sampling periods were reduced and are presented in Table VII-5 for each bleach line. A significant finding from this exercise is that interpretation of the process operating logs from different mills is not straightforward. Mill personnel sometimes record data entries on log sheets that are different than called for by the headings on the logs (e.g., % valve opening vs. gpm of chemical solution); NaOCl solution strength and flow may not be monitored routinely; and mass flow rates of chlorine may not be monitored with a reasonable degree of accuracy. In many cases, these practices have evolved over a number of years. They are the reported process control information most useful for bleach plant operators. However, these practices created considerable difficulty in determining reasonably accurate chemical application rates for the sampling periods for this study. Accordingly, it is strongly recommended that further mill scale research or monitoring efforts be preceded by a thorough review of existing bleach plant process operating monitoring systems and data reporting procedures.

Notwithstanding, the data reported on Table VII-5 are believed to be fair representations of chemical applications during the survey periods for most of the five mills. Data for Mill D are rough engineering estimates of typical chemical usages determined from inventories over a monthly period encompassing the field program for that mill. Deficiencies in monitoring equipment in the bleach plant precluded collection of more reliable chemical application rate data for the survey period. Data for the other mills were developed in large measure directly from the bleach plant operating logs with adjustments suggested by mill personnel

TABLE VII-5

BLEACH PLANT CHEMICAL APPLICATIONS
(lbs/ton of Air Dried Unbleached Pulp)

Mill A - Softwood Bleach Line (June 24-25, 1986)

	<u>Unbleached Pulp</u>	<u>C</u>	<u>E₀</u>	<u>H</u>	<u>H</u>
Cl ₂		64/75/89			
NaOH			25/29/32		
O ₂					
NaOCl			91.4	76.9	--
pH		1.8/1.9	10.3/10.8	8.6/8.8	8.3/8.6
PN:	19.0/19.6/20.3	CEK:	2.9/3.0/3.2		

Mill A - Hardwood Bleach Line (June 24-25, 1986)

	<u>Unbleached Pulp</u>	<u>C</u>	<u>E₀</u>	<u>I</u>	<u>H</u>	<u>H</u>	<u>H</u>	<u>P</u>
Cl ₂		55/66/73						
NaOH			22/23/24					
O ₂								
NaOCl					61.3	69.5	--	
H ₂ O ₂								NA
pH		2.5/2.8	9.7/10.7	8.2/9.4	8.3/9.3	7.7/8.7	--	--
PN:	11.6/11.8/12.2	CEK:	2.7/2.9/3.0					

Mill B - Softwood Bleach Line (September 8-9, 1986)

	<u>Unbleached Pulp</u>	<u>C_D</u>	<u>E</u>	<u>H</u>	<u>H</u>	<u>D</u>
Cl ₂		50/82/117				
ClO ₂		0/0.6/1.5				8.6/11/12
NaOH			38/54/72			
NaOCl				19/33/52	0/2.7/4.4	
pH		NA	10.2/10.7	8.5/8.9	NA	1.9/2.6
PN:	11.1/19.6/26.4	CEK:	2.2/4.6/5.9			

- NOTES:
- (1) Minimum/Average/Maximum (lbs/ton).
 - (2) pH - Minimum/Maximum standard units.
 - (3) PN - Permanganate number or K number for unbleached kraft pulp - minimum/average/maximum.
 - (4) NA - Data not available.
 - (5) NM - Not measured.
 - (6) CEK - Caustic extraction stage pulp permanganate number or K number - minimum/average/maximum.

TABLE VII-5 (continued)

BLEACH PLANT CHEMICAL APPLICATIONS
(lbs/ton of Air Dried Unbleached Pulp)

Mill C - Hardwood Bleach Line (October 15-16, 1986)

	Unbleached Pulp	C _D	E _O	D
Cl ₂		42/50/65		
ClO ₂		3.7/4.3/5.0		14/15/17
NaOH			15/19/22	
O ₂			12/12/14	
pH		1.5/1.9	10.5/11.6	NA
PN:	12.9/13.7/14.4	CEK:	2.1/2.3/2.5	

Mill D - Softwood Bleach Line - A (December 2-3, 1986)

	Unbleached Pulp	C	E	H
Cl ₂		69		
NaOH			46	
NaOCl				89
pH		2.3	9.5/10.6	7.8/9.1
PN:	22.0/24.3/26.9	CEK:	NM	

Mill D - Softwood Bleach Line - B (December 2-3, 1986)

	Unbleached Pulp	C	E	H
Cl ₂		73		
NaOH			53	
NaOCl				226
pH		2.3/2.4	9.7/10.6	7.5/8.8
PN:	22.0/24.3/26.9	CEK:	NM	

Mill E - Softwood Bleach Line (January 13-14, 1987)

	Unbleached Pulp	C _D	E _O	H	D
Cl ₂		120/147/191			
ClO ₂		3.4			12/13/13
NaOH			108/139/187	2.4	2.4
O ₂			7.1		
NaOCl				12/19/28	
pH		1.8	10.5/11.3	8.2/9.9	3.9/9.0
PN:	10.1/18.8/24.5	CEK:	2.5/3.0/3.3		

TABLE VII-5 (continued)

BLEACH PLANT CHEMICAL APPLICATIONS
(lbs/ton of Air Dried Unbleached Pulp)

Mill E - Hardwood Bleach Line (January 14, 1987)

	<u>Unbleached Pulp</u>	<u>C_D</u>	<u>E_O</u>	<u>H</u>	<u>D</u>
Cl ₂		76/93/107			
ClO ₂		1.8/1.9/2.2			13/15/16
NaOH			90/93/97		
O ₂			4.2		
NaOCl				14/23/38	
pH		1.8	11.4/11.5	9.9/10.7	6.5/7.3
PN:	11/16.7/22.4	CEK:	2.1/2.8/3.7		

in certain cases. The permanganate numbers for the unbleached kraft pulps fed to the chlorination stages and the minimum and maximum pH values recorded at each stage of bleaching are also presented in Table VII-5.

The bleaching practices at the five mills cover a fairly broad spectrum of bleaching sequences and chemical application rates. However, these plants do not represent the full range of bleaching sequences, bleaching tower configurations, or chemical application rates in United States bleached kraft pulp and paper mills. For the five mills, first stage chlorination rates range from 50 to 108 lbs Cl_2 /ton of air dried brownstock pulp, or 2.5% to 5.4%. Chlorine dioxide is added in the chlorination stage at four of eight bleach lines at rates of 0.6 to 4.3 lbs/ton. Sodium hydroxide is applied from 19 to 139 lbs/ton in caustic extraction stages. Oxygen is added in five of eight caustic extraction stages. Sodium hypochlorite is also applied in two of eight caustic extraction stages, both with oxygen. For the four mills with hypochlorite stages, the range of sodium hypochlorite application rates is 19 to 227 lbs/ton. These data are used and discussed in subsequent sections.

2. Unbleached and Bleached Kraft Pulps

The unbleached pulp 2378-TCDD and 2378-TCDF data from Table VII-4 are presented in Table VII-6 with the corresponding bleached pulp data for the five mills. Nine samples of bleached pulp were collected vs. seven samples of unbleached pulp. At Mill A, the unbleached hardwood pulp is bleached using CE_0HH and CE_0HHP bleaching sequences. At Mill D, the unbleached softwood pulp is bleached in parallel CEH sequences.

These data clearly show the effect of bleaching kraft pulps on the formation of 2378-TCDD and 2378-TCDF. 2378-TCDD was found in seven of nine bleached pulps at concentrations ranging from 3 to 51 ppt and 2378-TCDF was found in eight of nine pulps at levels ranging from 8 to 330 ppt. The median and mean concentrations are presented below with nondetects counted as zero:

	<u>2378-TCDD</u>	<u>2378-TCDF</u>
Median	5 ppt	50 ppt
Mean	13 ppt	93 ppt

There does not appear to be a clear relationship between the type of wood pulp processed and the concentrations of 2378-TCDD or 2378-TCDF found in the fully bleached pulps. At the outset of

TABLE VII-6

UNBLEACHED AND BLEACHED KRAFT PULPS

[Concentrations in parts per trillion (ppt) or pg/gm.]

MILL A	2378-TCDD		2378-TCDF	
	Unbleached Pulp	Bleached Pulp	Unbleached Pulp	Bleached Pulp
Softwood	ND (0.74)	16	ND (0.27)	330
Hardwood	ND (0.31)	{ 4.9 (H) 3.0 (P)	ND (0.23)	{ 47 (H) 50 (P)
<u>MILL B</u>				
Softwood	ND (0.95)	11	1.5	61
<u>MILL C</u>				
Hardwood	ND (0.56)	ND (0.62)	ND (0.16)	15
<u>MILL D</u>				
Softwood A	ND (0.70)	ND (1.0)	ND (0.20)	ND (1.2)
Softwood B	ND (0.70)	3.9	ND (0.20)	7.8
<u>MILL E</u>				
Softwood	ND (0.44)	26	1.1	140
Hardwood	ND (0.98)	51	2.3	180

NOTES: (1) ND - Not detected; analytical detection level in parentheses ().

(2) Mill A - H = Bleached pulp from CE₀HH sequence.
P = Bleached pulp from CE₀HHP sequence.
Unbleached kraft hardwood pulp is processed in common C and E₀ stages.

(3) Mill D - A common unbleached kraft pulp is supplied to both bleach lines at Mill D.

(4) Mill E - The hardwood line bleached pulp sample contained an unknown amount of softwood pulp.

this study, it was hypothesized that bleaching of softwood pulps may result in higher levels of 2378-TCDD and 2378-TCDF based upon the higher lignin content typically found in softwoods. However, the data displayed in Table VII-6 do not support that hypothesis. Note that although precautions were taken in the field to insure that hardwood pulp was sampled on the B bleach line at Mill E after a change over from softwood pulp bleaching, a review of process operating logs indicates the pulp sample designated as hardwood contains undetermined amounts of both hardwood and softwood pulp. The relatively high concentrations of 2378-TCDD and 2378-TCDF in that sample and the uncertainty surrounding its actual composition confuses this analysis. Variables other than the general wood type furnished to the bleach plant would appear to have more influence on the formation of 2378-TCDD and 2378-TCDF. It should be noted that the results presented in Table VII-6 may not account for either sampling or process variability and it would be inappropriate to generalize further on the effect of wood species with this limited data base. This question is examined further in Section VII.C.5. in the context of the relative amounts of lignin removed during bleaching.

The pulp samples were squeezed during collection to remove any loose water in the pulp mat and the pulps were analyzed on dry weight basis. Hence, the 2378-TCDD and 2378-TCDF concentrations reflect findings on the bleached pulp carried over to the paper machine areas. The next section presents the findings for bleach plant filtrates (wastewaters).

3. Bleach Plant Wastewaters

The bleach plant sampling plan for each mill was focused on the collection of wastewater samples as close to the individual bleaching stages as possible. In every mill, seal tank overflows or seal tank contents were sampled following each stage in the respective bleaching sequence. While sampling in this manner yielded analytical results for 2378-TCDD and 2378-TCDF close to process, the computation of mass discharges was confounded by the overall lack of primary flow measuring devices on these streams. In some cases, these flows were not continuous. For every bleach line, best engineering estimates by mill personnel served as the basis for the wastewater flow rates from each pulp washing stage. For Mill A, the estimates were refined after the field survey by mill personnel through supplemental field testing. Although the accuracy of the flow estimates could not easily be verified at most mills, they are considered reasonable for computing the mass discharges of 2378-TCDD and 2378-TCDF in these streams. Often the mills relied upon prior special study situations in which water balances were estimated for the bleach plant and other process areas.

The computation of mass flow rates of 2378-TCDD and 2378-TCDF from the bleacheries is also affected by the reliability of the analytical results. As described in Section VI, the analytical results are considered to be highly reliable with few exceptions. Analyses of field duplicate samples and duplicate laboratory analyses for bleach plant samples yielded agreement within $\pm 15\%$ and recovery of labeled spiked compounds were within acceptable ranges. Data for two C-stage samples with duplicate field or laboratory analyses (Mill B - 86374613/73; Mill D - DF024412/605) did not yield good agreement as discussed above. These data suggest the possibility of field sampling problems (e.g., collection of nonrepresentative duplicate samples) or laboratory-related issues (e.g., nonhomogeneity of sample aliquots analyzed). Analytical difficulties peculiar to C-stage filtrates may be possible.

As described earlier, the analytical results for 2378-TCDD and 2378-TCDF presented in Attachment E were combined with the wastewater flow estimates and pulp production rates to compute the mass flow rates of 2378-TCDD and 2378-TCDF presented in Attachment F. While the data contained in Attachment F were generated with a computer program to more than two significant figures, the resultant mass flow rates are considered accurate at most to only two significant figures.

Table VII-7 presents a summary of the bleach line wastewater data for 2378-TCDD and 2378-TCDF. 2378-TCDD was detected in bleach line wastewaters from four of five mills, Mill C being the exception. 2378-TCDF was found in every bleach line wastewater sampled. Although 2378-TCDD was not found in the bleached pulp or in bleach line wastewaters from Mill C, it is probably present at less than analytical detection levels since it was found in combined paper machine wastewaters and wastewater sludges from that mill. (Another possible source of 2378-TCDD in the wastewater sludge at Mill C is purchased bleached softwood pulp from outside sources.) Generally the highest concentrations and mass discharges of 2378-TCDD and 2378-TCDF were found in caustic extraction stage (E or E₀) wastewaters with lesser amounts in hypochlorite (H, H/D) and chlorination stage wastewaters (C, C_D, and C/D).

Individual bleach line summaries are presented in Tables VII-8 to VII-12. The summaries include concentrations and estimated mass loadings of 2378-TCDD and 2378-TCDF in unbleached and bleached kraft pulps and individual bleach line wastewaters. The estimated total daily bleach line generation rates of 2378-TCDD and 2378-TCDF were determined as the sum of the mass flow rates in bleached kraft pulps and bleach line wastewaters (bleaching stage filtrates). The relatively minor amounts of 2378-TCDF found in unbleached kraft pulps at Mills B and E were not discounted from the bleached pulp results for purposes of estimating the amount

TABLE VII-7
2378-TCDD and 2378-TCDF IN BLEACH PLANT WASTEWATERS

2378-TCDD	Number	Concentrations (ppt, pg/gm)			Mass Loadings (lbs/day (kg/day) x 10 ⁻⁶)		
		Range	Median	Mean	Range	Median	Mean
C Stages (C,Cd,C/D)	8	ND(0.006)-0.24	0.05	0.07	0-3.4 (0-1.5)	0.53 (0.24)	0.89 (0.40)
E Stages (E,Eo)	8	ND(0.006)-3.6	0.26	1.1	0-48 (0-22)	3.5 (1.6)	14 (6.3)
H Stages (H,H/D)	10	ND(0.017)-1.9	0.19	0.40	0-12 (0-5.4)	1.1 (0.5)	2.7 (1.2)
D Stages (D)	2	ND(0.003)-0.03	--	0.015	0.4a (0.18)	-- (--)	-- (--)
<u>2378-TCDF</u>							
C Stages (C,Cd,C/D)	8	0.068- 3.8	0.24	0.65	0.8-55 (0.36-25)	3.1 (1.4)	9.4 (4.3)
E Stages (E,Eo)	8	0.056-14	0.51	3.3	0.9-390 (0.41-180)	5.8 (2.6)	93 (42)
H Stages (H,H/D)	10	0.086- 9.2	0.59	2.3	0.2-57 (0.10-26)	3.5 (1.6)	14 (6.3)
D Stages (D)	2	0.014- 0.13	--	0.072	1.7a (0.77)	-- (--)	-- (--)

NOTE: (a) Only one data point. D-stage flow at Mill C zero during survey.

TABLE VII-8

BLEACH PLANT SUMMARY - MILL A

SOFTWOOD BLEACH LINE

<u>2378-TCDD</u>				<u>2378-TCDF</u>		
<u>Pulp</u>	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution
Unbleached Pulp	ND(0.74)	--		ND(0.27)	--	
Bleached Pulp	16	4.5(2.0)	14%	330	94 (43)	17%
<u>Wastewater</u>						
C Stage	0.24	3.4		3.8	55	
E ₀ Stage	1.8	21.9		33	391	
H Stage	0.34	1.7		5.8	28	
	Subtotal	27.0(12.2)	86%	Subtotal	474 (215)	83%
<u>Bleach Line Total</u>		31.5(14.2)			568 (258)	

TABLE VII-8
(continued)

BLEACH PLANT SUMMARY - MILL A

HARDWOOD BLEACH LINE

Pulp	2378-TCDD			2378-TCDF		
	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution
Unbleached Pulp	ND(0.31)	--		ND(0.23)	--	
Bleached Pulp-H	4.9	1.56		47	15.1	
Bleached Pulp-P	3.0	0.95		50	16.0	
	Subtotal	2.51(1.14)	78%	Subtotal	31.1(14.1)	80%
<u>Wastewater</u>						
C Stage	0.02	0.28		0.31	4.0	
E ₀ Stage	ND(0.033)	--		0.25	1.5	
H Stage	ND(0.017)	--		0.11	0.2	
E ₀ Stage	0.045	0.13		0.32	0.9	
H Stage	0.040	0.21		0.17	0.9	
H Stage	0.025	0.06		0.17	0.4	
	Subtotal	0.68 (0.31)	22%	Subtotal	7.9 (3.6)	20%
<u>Bleach Line Total</u>		3.2 (1.4)			39.0 (17.7)	

NOTES: (1) Bleached Pulp-H from CE₀HH sequence.
(2) Bleached Pulp-P from CE₀HHP sequence.

TABLE VII-9

BLEACH PLANT SUMMARY - MILL B

SOFTWOOD BLEACH LINE

<u>Pulp</u>	<u>2378-TCDD</u>			<u>2378-TCDF</u>		
	<u>Concentration</u> (ppt,pg/gm)	<u>Mass</u> lbs/day(kg/day) x 10 ⁻⁶	<u>Distribution</u>	<u>Concentration</u> (ppt,pg/gm)	<u>Mass</u> lbs/day(kg/day) x 10 ⁻⁶	<u>Distribution</u>
Unbleached Pulp	ND(0.95)	--		1.5	2.7(1.2)	
Bleached Pulp	11	17.4 (7.9)	79%	61	93.8(42.5)	81%
<u>Wastewater</u>						
C _D Stage ^a	0.02	1.2		0.068	3.4	
E Stage ^b	0.22	4.1		1.0	19.1	
H-1 Stage ^b	0.26	0.5		1.1	2.3	
H-2 Stage ^b	0.13	1.5		0.58	6.6	
D Stage ^a	0.03	0.4		0.13	1.7	
	Subtotal	5.3 (2.4) ^{a,b}	21%	Subtotal	22.5 (10.2) ^{a,b}	19%
<u>Bleach Line Total</u>		22.7 (10.3)			116.3 (52.9)	

Notes: (a) D stage recycled to C stage; D stage mass presented for C stage.
(b) H-1 and H-2 stages recycled to E stage.

TABLE VII-10
BLEACH PLANT SUMMARY - MILL C

		HARDWOOD BLEACH LINE		
		2378-TCDD		2378-TCDF
Pulp		Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution
Unbleached Pulp		ND(0.56)	--	
Bleached Pulp		ND(0.62)	--	--
Wastewater				
C _D Stage		ND(0.006)	--	
E _O Stage		ND(0.011)	--	
D Stage		ND(0.003)	--	
	Subtotal		--	--
Bleach Line Total			--(--)	
		Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution
		ND(0.16)	--	
		15	27.7(12.6)	86%
		0.093	2.3	
		0.056	2.3	
		0.014	--a	
		Subtotal	4.6 (2.1)	14%
			32.3(14.7)	

NOTES: (a) D Stage flow zero during sampling.

TABLE VII-11

BLEACH PLANT SUMMARY - MILL D

2378-TCDD			2378-TCDF			
	Mass		Distribution	Mass		Distribution
	Concentration (ppt,pg/gm)	lbs/day(kg/day) x 10 ⁶		Concentration (ppt,pg/gm)	lbs/day(kg/day) x 10 ⁻⁶	
SOFTWOOD BLEACH LINE - A LINE						
Pulp						
Unbleached Pulp ^a	ND(0.70)	--	0%	ND(0.20)	--	0%
Bleached Pulp	ND(1.0)	--		ND(1.2)	--	
Wastewater						
C Stage	0.04	0.45	100%	0.069	0.8	100%
E ^b Stage	0.26	2.9		0.51	5.8	
H Stage	0.05	0.65		0.086	1.0	
	Subtotal	4.0 (1.8)		Subtotal	7.6 (3.4)	
Bleach Line Total		4.0 (1.8)			7.6 (3.4)	
SOFTWOOD BLEACH LINE - B LINE						
Pulp						
Unbleached Pulp ^a	ND(0.70)	--	13%	ND(0.20)	--	12%
Bleached Pulp	3.9	0.9 (0.4)		7.8	1.9 (0.9)	
Wastewater						
C Stage	0.12	0.9	87%	0.39	3.1	88%
E ^b Stage	0.26	2.9		0.51	5.8	
H Stage	0.33	2.5		0.60	4.6	
	Subtotal	6.3 (2.9)		Subtotal	13.5 (6.1)	
Bleach Line Total		7.2 (3.3)			15.4 (7.0)	

NOTES: (a) A common unbleached kraft pulp is supplied to each bleach line.

(b) Combined E stage mass loading allocated equally to A and B lines.

TABLE VII-12

BLEACH PLANT SUMMARY - MILL E

	2378-TCDD			2378-TCDF		
	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution	Concentration (ppt,pg/gm)	Mass lbs/day(kg/day) x 10 ⁻⁶	Distribution
<u>Pulp</u>						
Unbleached Pulp	ND(0.44)	--		1.1	1.2(0.54)	
Bleached Pulp	26	24.7(11.2)	36%	140	134 (61)	40%
<u>Wastewater</u>						
C _D Stage	0.05	1.1		0.17	4	
E _O Stage	2.3	34.4		10	152	
D Stage	0.91	7.6		5.0	42	
				Subtotal	198 (89)	60%
<u>Bleach Line Total</u>			64%		332 (150)	
<u>Pulp</u>						
Unbleached Pulp	ND(0.98)	--		2.3	2.8(1.3)	
Bleached Pulp	51	57.5(26.1)	49%	180	204 (93)	45%
<u>Wastewater</u>						
C _D Stage	0.07	0.6		0.33	3	
E _O Stage	3.6	48.0		14	189	
D Stage	1.9	12.0		9.2	57	
				Subtotal	249 (113)	55%
<u>Bleach Line Total</u>			51%		453 (206)	

HARDWOOD BLEACH LINE^aNOTE: ^aThe Mill E hardwood line bleached pulp sample contained an unknown amount of softwood pulp.

of 2378-TCDF produced in bleach lines at those mills. Also, recycle of paper machine white waters practiced at some mills was not taken into account in these calculations owing to the relatively low-level contamination found in paper machine wastewaters (see Section D below). The practice of recirculating white waters may be intermittent depending upon the availability of warm process water for pulp transport or dilution.

The wastewater data for the softwood bleach line at Mill A (Table VII-8), the softwood and hardwood lines at Mill E (Table VII-12), and, to a lesser extent, the softwood lines at Mills B and D (Tables VII-9 and VII-11) show similar patterns in that the greatest amounts of 2378-TCDD and 2378-TCDF were found in caustic extraction stage effluents. That trend is not evident in the hardwood bleach line at Mill A. At Mill C 2378-TCDD was not detected in bleach line wastewaters. The 2378-TCDF data at Mill C show an even distribution in C_D-stage and E_O-stage wastewaters. As noted above, the C-stage and H-stage wastewaters generally contain significantly less 2378-TCDD and 2378-TCDF than the E-stage wastewaters.

The bleach plant wastewater data do not clearly distinguish the point or points of dioxin formation in the bleacheries. However, these data indicate formation in the C stages and possibly in the E stages. It is not possible with these data to determine whether 2378-TCDD and 2378-TCDF are formed in the highly acidic C stage and extracted from the pulp in the E stage, or, whether there is additional formation in the highly alkaline environment of the E stage. The data also suggest formation of 2378-TCDD and 2378-TCDF in subsequent bleaching stages. This point is particularly evident from the Mill D data which show that 2378-TCDD and 2378-TCDF can be found in the final hypochlorite bleaching stage. Rigorous mass balance studies around each bleaching stage in several bleach lines are necessary to fully investigate this question. Recent data from other researchers where inter-stage pulp samples were collected in bleach lines suggests that 2378-TCDD and 2378-TCDF formation is concentrated in the chlorine stage.^{4,5}

4. Distributions of 2378-TCDD and 2378-TCDF

Total bleach line exports of 2378-TCDD and 2378-TCDF are presented in Table VII-13 with the distribution between pulp and wastewater from each line. Within each bleach line the distributions of 2378-TCDD and 2378-TCDF agree within 4%, which is substantially less than the sampling and analytical error and uncertainty in wastewater flow measurements expected in this study. These data indicate the partitioning of 2378-TCDD and 2378-TCDF between bleached pulp and wastewaters within bleach lines is essentially the same. There is considerable variability

TABLE VII-13

DISTRIBUTIONS OF 2378-TCDD AND 2378-TCDF
IN BLEACH LINE EXPORTS

Bleach Line	2378-TCDD			2378-TCDF		
	Bleach Line Total (lbs/day)(kg/day)x10 ⁻⁶	Pulp	Waste- water	Bleach Line Total (lbs/day)(kg/day)x10 ⁻⁶	Pulp	Waste- water
<u>Mill A</u>						
Softwood	32 (14)	14%	86%	570 (260)	17%	83%
Hardwood	3.2 (1.4)	78%	22%	39 (18)	80%	20%
<u>Mill B</u>						
Softwood	23 (10)	79%	21%	120 (53)	81%	19%
<u>Mill C</u>						
Hardwood	-- (--)	ND	ND	32 (15)	86%	14%
<u>Mill D</u>						
Softwood A	4.0 (1.8)	ND	~100%	7.6 (3.4)	ND	~100%
Softwood B	7.2 (3.3)	13%	87%	15 (7.0)	12%	88%
<u>Mill E</u>						
Softwood	68 (31)	36%	64%	330 (150)	40%	60%
Hardwood	120 (54)	49%	51%	450 (210)	45%	55%

NOTES: (1) ND - 2378-TCDD or 2378-TCDF not detected.

(2) The Mill E hardwood line bleached pulp sample contained an unknown amount of softwood pulp.

in the distributions between pulp and wastewaters across the eight bleach lines. There is no obvious pattern associated with the type of pulp bleached or the degree of application of bleaching chemicals. Factors accounting for these differences are not known, but may be related to the efficiency of chemical mixing within the bleaching reactors, bleach tower pH or temperature, the efficiency of pulp washing between bleaching stages, or some mechanism associated with the chemical or physical characteristics of the partially bleached pulps.

5. Formation of 2378-TCDD and 2378-TCDF

The rates of formation of 2378-TCDD and 2378-TCDF for the five mills are presented in Table VII-14 computed as follows:

1. From individual bleach line exports - the sum of the bleached pulp and bleach line wastewater loadings was divided by the respective brownstock pulp inputs to the respective bleach lines; and
2. From total mill exports - the sum of the bleached pulp, treated wastewater effluent, and wastewater sludge loadings was divided by the sum of brownstock pulp inputs to the bleach lines.

This method of presenting the data was initially selected because it was hypothesized that the major source of 2378-TCDD and 2378-TCDF was the bleaching process. Thus, reducing the data based upon the brownstock pulp entering the bleach plant was considered logical.

For Mills A, B, and C the rates of formation computed from the total mill exports fall within the range or are close to the rates computed from the individual bleach line exports. The rates of formation computed from the total mill exports at Mills D and E are less than those computed from the individual bleach line exports. Agreement between the rates of formation computed from bleach line and total mill exports is considered reasonably good. The extent to which formation of 2378-TCDD and 2378-TCDF determined for the bleach lines at the five mills and from the total mill exports is representative of long-term average conditions at these mills is not known. The extent to which the data from these mills are representative of the industry is also not known.

Although the scope of this study was limited to screening for sources of dioxins at five bleached kraft pulp and paper mills, there were several hypotheses that developed during the course of the study regarding the formation of 2378-TCDD and 2378-TCDF. At the outset, the principal hypothesis was that bleaching of kraft

TABLE VII-14

FORMATION OF 2378-TCDD AND 2378-TCDF

[10⁻⁸ lbs/ton (kg/kkg) of brownstock pulp bleached]

<u>MILL</u>	<u>From Bleach Line Exports</u>		<u>From Total Mill Exports</u>	
	<u>2378-TCDD</u>	<u>2378-TCDF</u>	<u>2378-TCDD</u>	<u>2378-TCDF</u>
A - Softwood	20	360	7.2	130
A - Hardwood	0.9	11		
B - Softwood	2.6	13	3.0	19
C - Hardwood	ND	3.2	0.14	4.7
D - Softwood A	1.4	2.6	0.76	1.5
D - Softwood B	5.7	12		
E - Softwood	13	63	11	51
E - Hardwood	20	76		
MEDIAN	4.1(2.0)	12.5(6.3)	3.0(1.5)	19(9.5)
MEAN	8.0(4.0)	68 (34)	4.4(2.2)	41(21)

- NOTES: (1) ND - 2378-TCDD not detected.
 (2) Bleach line exports include bleached pulp and bleach line wastewater streams discharged from the process at each bleach line.
 (3) Paper mill exports include bleached pulp from all bleach lines, treated wastewater effluent, and combined wastewater sludge. The formation of 2378-TCDD and 2378-TCDF was computed on a production weighted basis for mills with multiple bleach lines.
 (4) The Mill E hardwood line bleached pulp sample contained an unknown amount of softwood pulp.

pulps with chlorine and chlorine derivatives would, in some manner, give rise to formation of 2378-TCDD and 2378-TCDF. This was clearly indicated by the results from preliminary sampling at Mill A (Section V) and was confirmed by the data from full-scale sampling at the five mills. With that hypothesis confirmed, attention was directed at using the available data and recorded process information to explore other relevant hypotheses beyond the principal one noted above. The data obtained from this limited study are clearly not sufficient to establish any of the following hypotheses. However, some useful insights can be gained from the analyses presented below:

a. Bleaching softwood vs. hardwood kraft pulps

As noted earlier, it was theorized that bleaching softwood kraft pulps might result in higher rates of formation of 2378-TCDD and 2378-TCDF than bleaching of hardwood kraft pulps due to the higher lignin content of softwoods. The data presented in Table VII-14 do not indicate a clear trend with respect to wood types. While the formation rates for 2378-TCDD for all of the softwood bleach lines are higher than those for the hardwood bleach lines at Mills A and C, the hardwood bleach line at Mill E generated 2378-TCDD at a rate equivalent to the highest softwood bleach line (Mill A). (Note the bleached pulp sampled at the Mill E hardwood bleach line on a short-term basis was a combination of hardwood and softwood pulps resulting from a process change.) For 2378-TCDF, the softwood bleach line at Mill A generated more 2378-TCDF per ton of brownstock pulp bleached than did any other bleach line. (The 2378-TCDF/2378-TCDD ratio for this bleach line was the highest among all bleach lines sampled). The softwood and hardwood bleach lines at Mill E also generated considerably more 2378-TCDF, as well as 2378-TCDD than all other bleach lines except the softwood line at Mill A. Analysis of particular wood species beyond the general hardwood/softwood classifications has not been attempted here but may prove to be worthwhile.

To investigate bleaching of hardwood pulps vs. softwood pulps further, estimates of lignin removal in the chlorination and caustic extraction stages in each bleach line were made. The average CEK number (permanganate number of the partially bleached pulp after caustic extraction) was subtracted from the average K-number (permanganate number) of the brownstock pulp for each bleach line. K-CEK for Mill D was not determined since CEK is not monitored at the bleach lines at Mill D. The K-CEK values are uniformly higher for partially bleached softwood pulps.

Figures VII-1 and VII-2 are plots of 2378-TCDD and 2378-TCDF formation for each bleach line vs. the difference in permanganate number from brownstock pulp to partially bleached pulp after the caustic extraction stages (K-CEK). The bleach lines are designated by mill and by "h" or "s" for hardwood or softwood, respectively. These graphs show, generally, with increasing lignin removal as estimated by K-CEK, there is increasing formation of 2378-TCDD and 2378-TCDF. The data for the hardwood bleach line at Mill E (Figure VII-1) does not fall within the general trend observed for most of the other bleach lines. If more softwood pulp had been sampled during the short-term, 4-hour composite sample at this line, than was estimated from a review of the log sheets, the actual K-CEK for the pulp sampled would have been greater, thus causing the plotted point for that bleach line to fall closer to those for the softwood bleach lines for Mills A and E. The same type of change would occur in Figure VII-2 for 2378-TCDF. The limited data were evaluated with a curve fitting program to determine whether any linear, exponential, log, or power functions might describe the results. For Figure VII-1 (2378-TCDD vs. K-CEK), the r^2 value (coefficient of determination) for each function was less than 0.5, indicating the data do not fit any of the functions. For Figure VII-2 (2378-TCDF vs. K-CEK) the results were about the same. Clearly, substantial additional data from other mills are needed to examine these relationships.

Nonetheless, these limited data appear to provide some support to the hypothesis that bleaching of kraft softwood pulps results in greater formation of 2378-TCDD and 2378-TCDF than bleaching of kraft hardwood pulps. Because of the possible significance of the results, additional research into this question through full-scale sampling at other mills is warranted. Care should be taken to insure that the sampling programs are conducted in a manner to clearly isolate samples of hardwood and softwood pulps on bleach lines that process both types of pulps.

b. Degree of chlorination

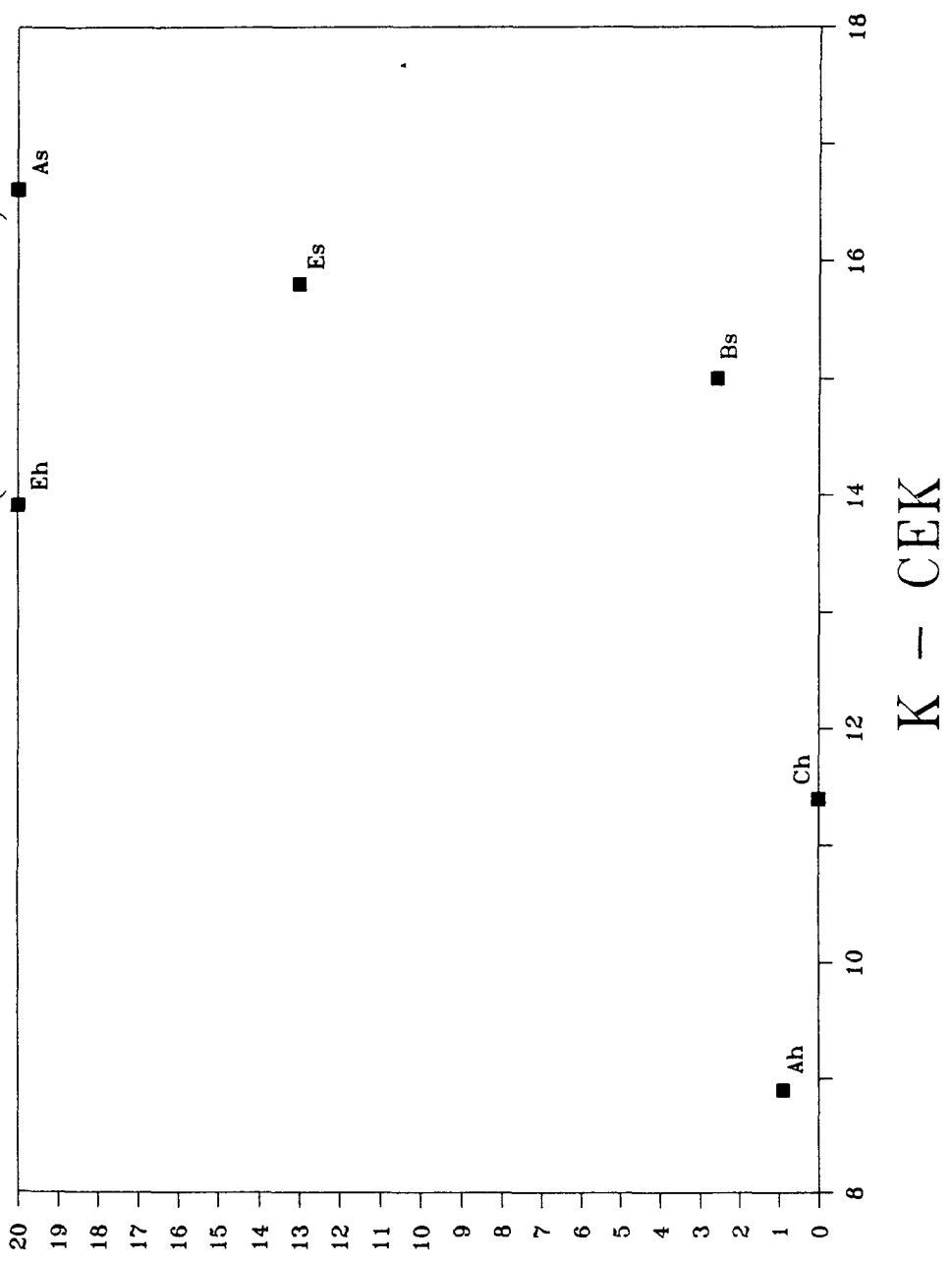
The amount of lignin remaining in the brownstock pulp is a major determinant of the amount of chlorine required in the first stage chlorination reactor. It was also theorized that the gross amount of chlorine applied to the pulp may have a substantial effect on the amounts of 2378-TCDD and 2378-TCDF formed. The formation of 2378-TCDD and 2378-TCDF at the five mills was evaluated with respect to applications of chlorine and chlorine derivatives as follows:

- (1) The rate of application of chlorine and chlorine equivalents (lbs/ton air dried of brownstock pulp) in the first stage chlorination reactor.

2378-TCDD

LBS E-08 / TON A.D.B.S. PULP
BLEACH LINE EXPORTS

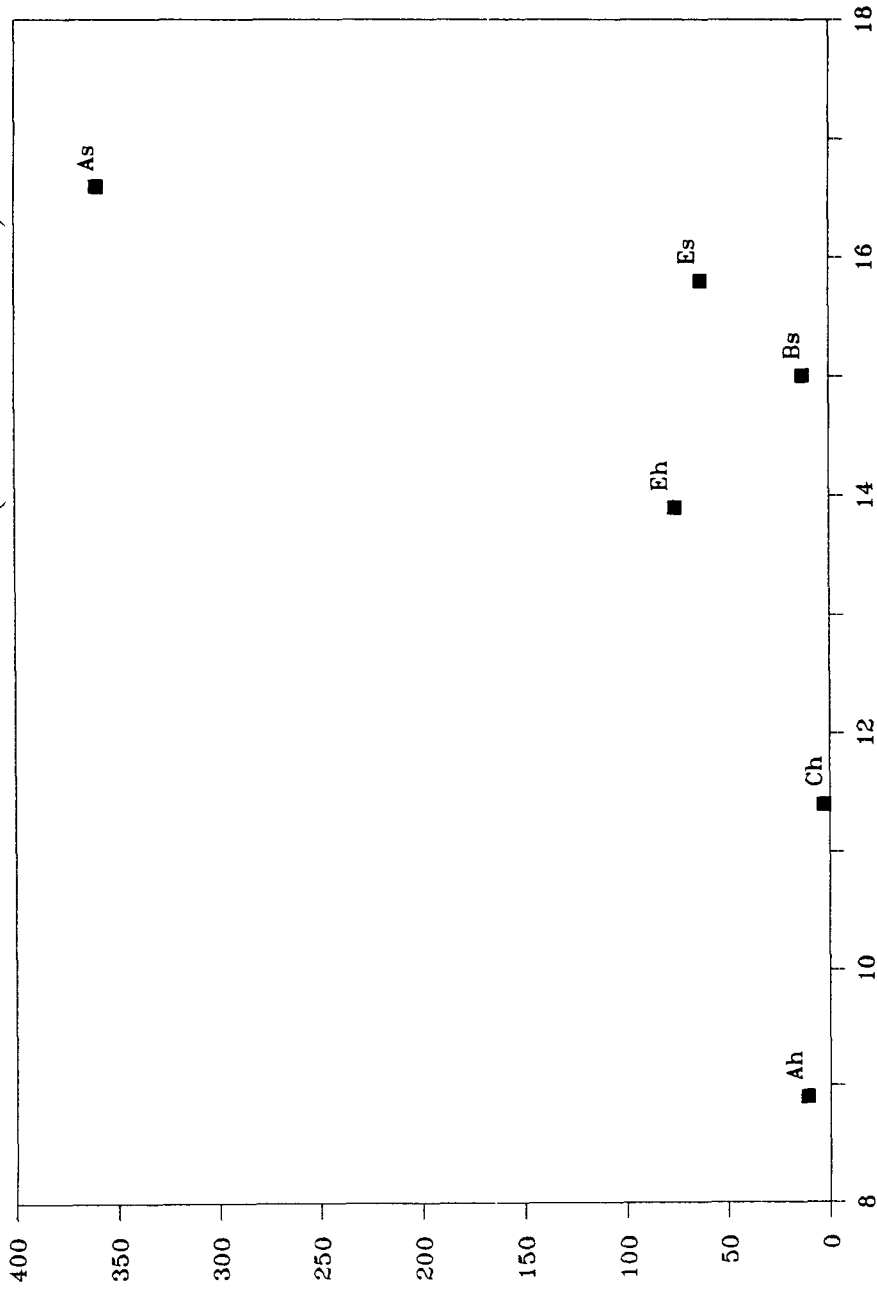
FIGURE VII-1
2378-TCDD VS (K - CEK)



A - E			K		
h			Brownstock Pulp		
s			Permanganate Number		
A.D.B.S.			Caustic Extraction Stage		
Air-Dried Brownstock			Permanganate Number		

2378-TCDF
 LBS E-08 / TON A.D.B.S. PULP
 BLEACH LINE EXPORTS

FIGURE VII-2
 2378-TCDF VS (K - CEK)



K - CEK

A - E h s A.D.B.S.	Mill Code	Brownstock Pulp	
		Permananate Number	Caustic Extraction Stage
	Hardwood	CEK	Permananate Number
	Softwood		
	Air-Dried Brownstock		

- (2) The rate of application of chlorine and chlorine equivalents (lbs/ton air dried of brownstock pulp) in the entire bleaching sequence.

The chlorine equivalents were computed on the basis of the weight percent composition of chlorine in chlorine dioxide and sodium hypochlorite (Cl_2EQWT), and on the basis of the chlorine equivalent oxidizing power of chlorine dioxide and sodium hypochlorite (Cl_2EQOX).⁶ Table VII-15 presents a summary of the chemical application rates derived as described above for the chlorination stage at each bleach line and the total for all stages of bleaching at each bleach line. The chlorine dioxide and sodium hypochlorite application rates presented in Table VII-5 were used to compute the chlorine equivalents presented in Table VII-15. Note that chemical application data presented in Table VII-15 are averages over the sampling period for each bleach line. Reference is made to Table VII-5 for the range of values recorded during the surveys. For the hardwood bleach line at Mill E, the residence time in the bleach line was taken into account to the extent possible when computing chemical application rates to adjust for the short-term (4-hour) sampling period. This was judged not necessary at the other bleach lines where 24-hour sampling was conducted and the production grades did not change during the sampling surveys. A two-hour gap in the process data for the Mill E hardwood bleach line occurred just prior to the change over. This made determination of actual chemical application rates during that period impossible.

Figures VII-3 and VII-4 are plots of 2378-TCDD and 2378-TCDF formed in each bleach line (lbs $\times 10^{-8}$ /ton of air dried brownstock pulp) vs. the degree of chlorination in the first stage bleaching tower (lbs Cl_2 applied per ton of air dried brownstock pulp). Figures VII-5 and VII-6 are similar plots of the formation of 2378-TCDD and 2378-TCDF vs. the equivalent chlorine oxidizing power (Cl_2EQOX) applied in the first stage chlorination reactor, thus taking into account the oxidizing power of chlorine dioxide applied in the chlorination stages at certain bleach lines. Plots of the equivalent chlorine applied in the C-stages on a weight composition basis (Cl_2EQWT) were also prepared, but are similar to Figures VII-3 and VII-4 and are not presented here.

The data presented in Figures VII-3 through VII-6 show to a limited extent, that the bleach lines with higher rates of chlorination in the C stages produce more 2378-TCDD and 2378-TCDF in the entire bleach lines. However, there are no quantitative relationships evident (r^2 values for linear, exponential, log, and power functions were less than 0.5 for Figures VII-3 through VII-6). Note that these plots deal with the chemical applications

TABLE VII-15

CHLORINATION STAGE AND BLEACH LINE CHLORINE APPLICATIONS
(lbs/ton of Air Dried Brownstock Pulp)

Mill	Wood Type	Bleaching Sequence	Chlorination Stage			Bleach Line	
			Cl ₂	Cl ₂ EQWT	Cl ₂ EQOX	Cl ₂ EQWT	Cl ₂ EQOX
A	Softwood	CE ₀ HH	75	75	75	115	235
	Hardwood	CE ₀ H	66	66	66	81	125
		↓-->HHP	66	66	66	83	132
B	Softwood	C _D EHHD	82	83	84	98	147
C	Hardwood	C _D E ₀ D	50	51	61	55	100
D	Softwood	CEH	69	69	69	90	154
	Softwood	CEH	73	73	73	127 ⁴	289 ⁴
E	Softwood	C _D E ₀ D	148	149	157	157	208
	Hardwood	C _D E ₀ D	93	93	98	102	156

- NOTES:
- (1) Cl₂ - Chlorine
 - (2) Cl₂EQWT - Equivalent chlorine applied based upon the weight percent composition of Cl₂ in ClO₂ and NaOCl:
(ClO₂ x 0.256) and (NaOCl x 0.238)
 - (3) Cl₂EQOX - Equivalent chlorine oxidizing power applied based upon oxidizing power of ClO₂ and NaOCl:
(ClO₂ x 2.63) and (NaOCl x 0.952)
 - [Reference 6]
 - (4) For the Mill D second softwood bleach line, H stage sodium hypochlorite usage is unusually high due to caustic carryover from an undersized caustic washer. Mill personnel estimate that roughly one-half of the sodium hypochlorite applied may be consumed to neutralize excess alkalinity. Accordingly, the following chlorine equivalents were estimated for this bleach line and used in subsequent analyses:

Cl₂EQWT - 102 lbs/ADT

CL₂EQOX - 181 lbs/ADT

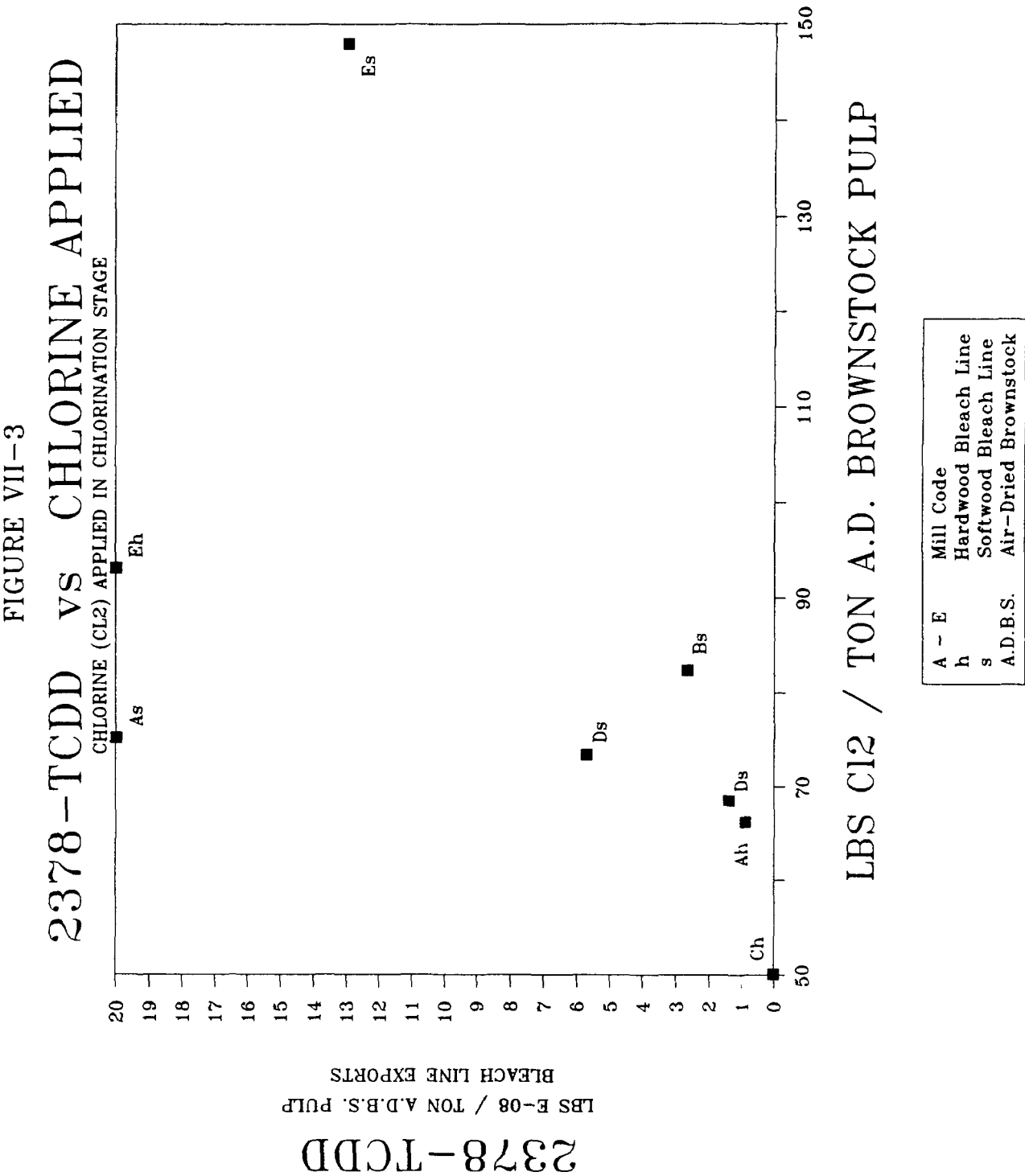
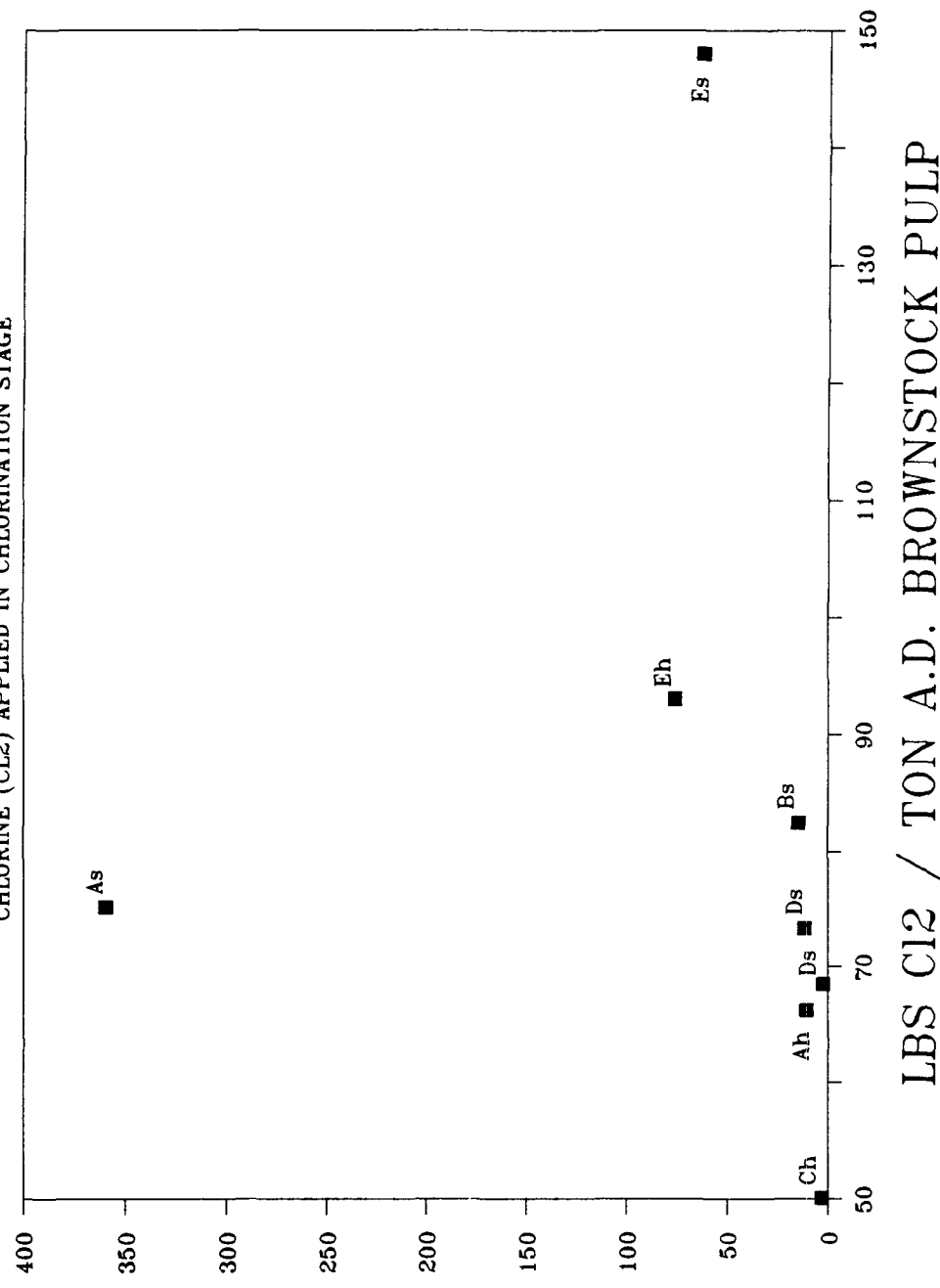


FIGURE VII-4
2378-TCDF VS CHLORINE APPLIED
CHLORINE (CL2) APPLIED IN CHLORINATION STAGE

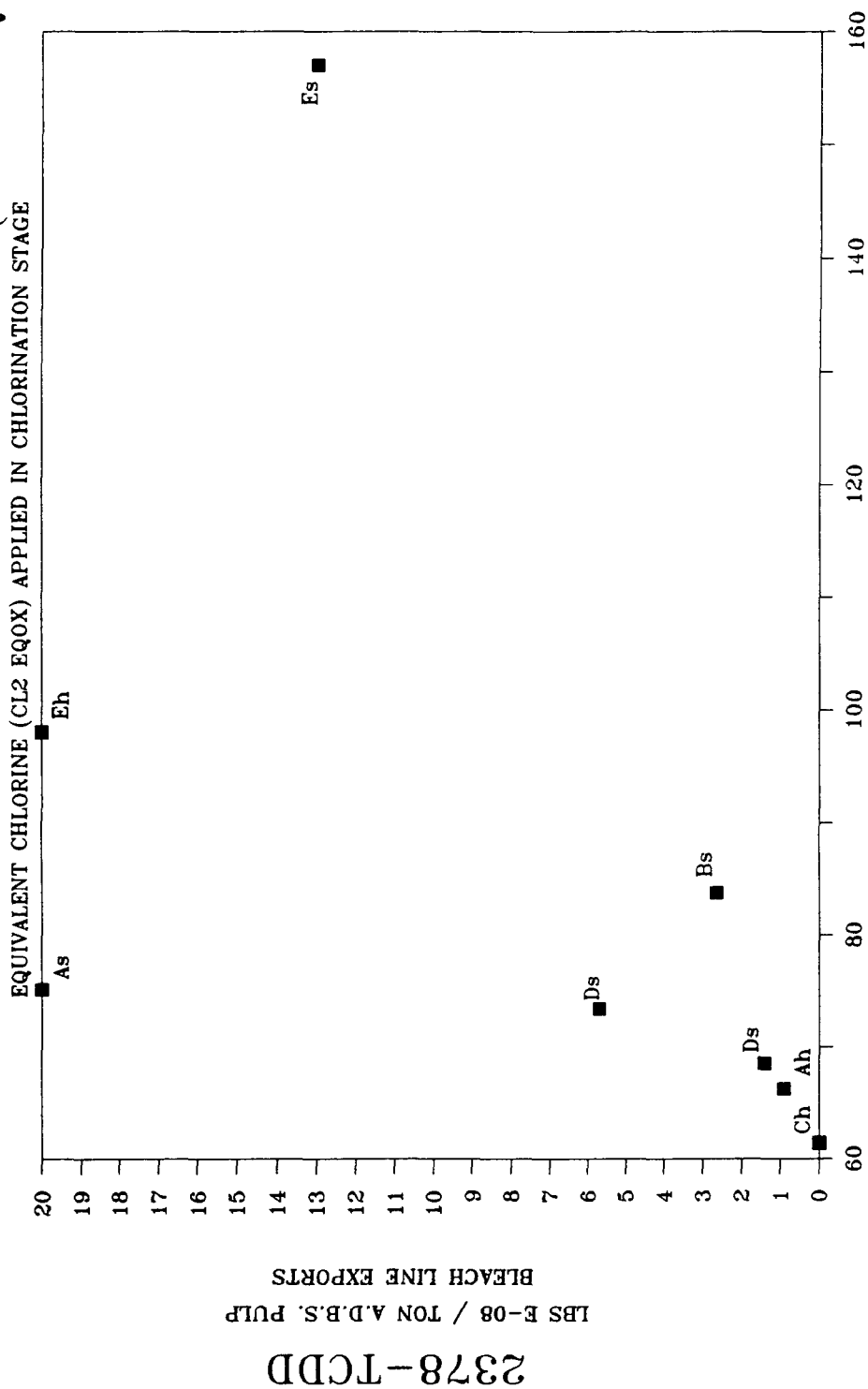


2378-TCDF
LBS E-08 / TON A.D.B.S. PULP
BLEACH LINE EXPORTS

LBS CL2 / TON A.D. BROWNSTOCK PULP

A - E	Mill Code
h	Hardwood Bleach Line
s	Softwood Bleach Line
A.D.B.S.	Air-Dried Brownstock

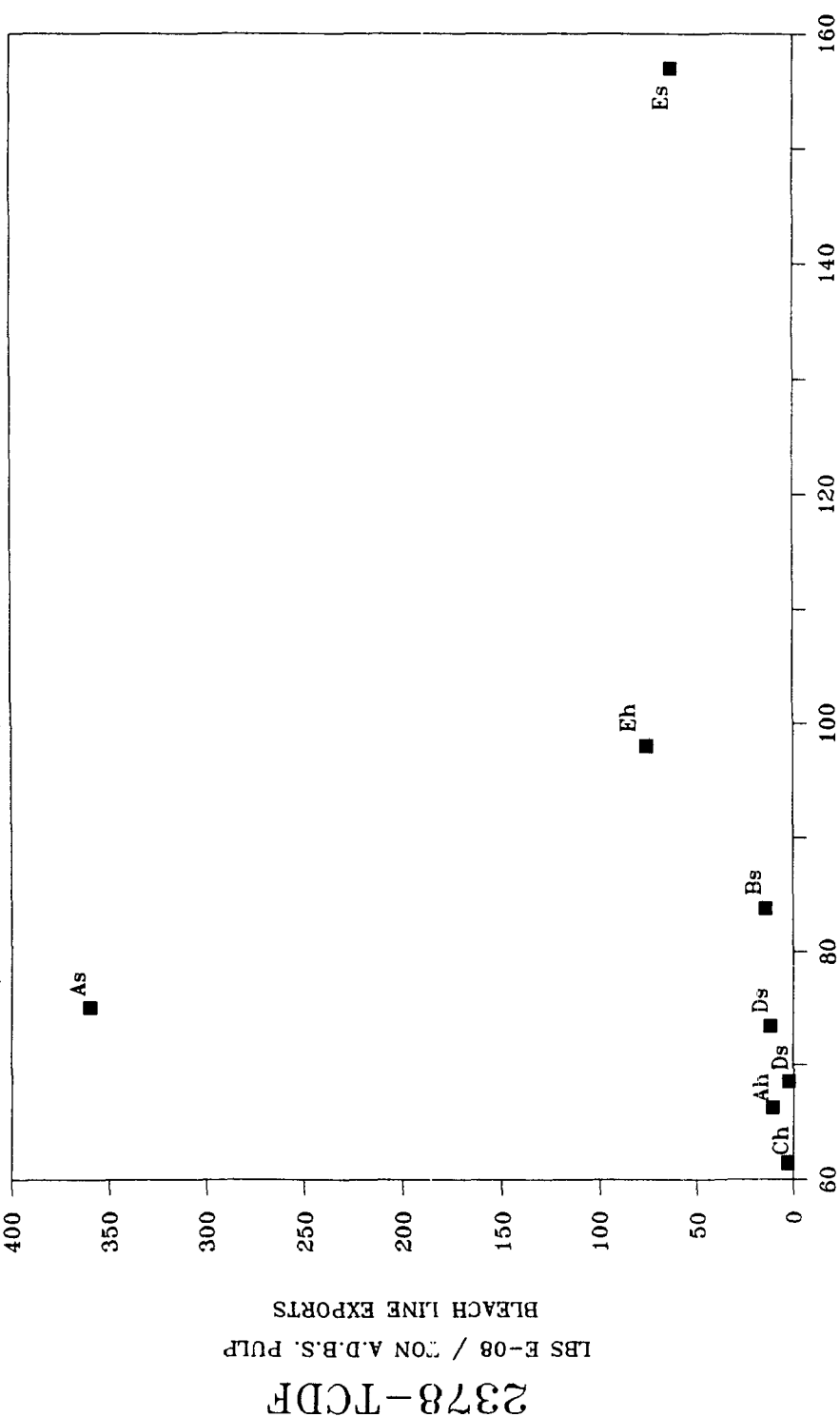
FIGURE VII-5
 2378-TCDD VS CHLORINE APPLIED (CL2 EQOX) (CL2 EQOX)



LBS CL2 EQOX / TON A.D. BROWNSTOCK PULP

A - E	Mill Code
h	Hardwood Bleach Line
s	Softwood Bleach Line
A.D.B.S.	Air-Dried Brownstock

FIGURE VII-6
 2378-TCDF VS CHLORINE APPLIED (CL2 EQOX)
 EQUIVALENT CHLORINE (CL2 EQOX) APPLIED IN CHLORINATION STAGE



LBS CL2 EQOX / TON A.D. BROWNSTOCK PULP

A - E	Mill Code
h	Hardwood Bleach Line
s	Softwood Bleach Line
A.D.B.S.	Air-Dried Brownstock

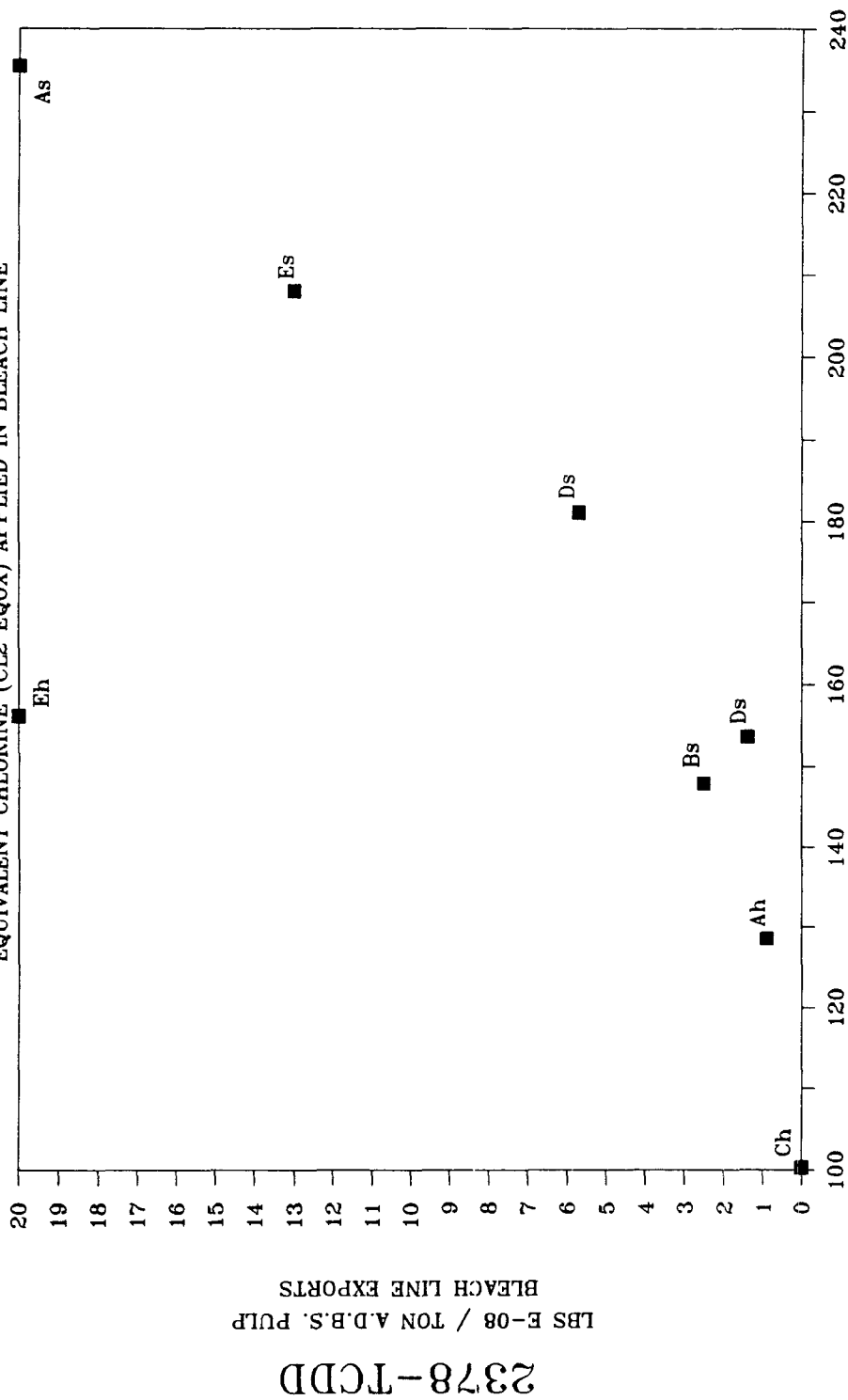
2378-TCDF
 LBS E-08 / TON A.D.B.S. PULP
 BLEACH LINE EXPORTS

in chlorination stages only while the 2378-TCDD and 2378-TCDF data are for each bleach line as a whole. Rigorous mass balance studies around the C and E stages at a number of mills would be necessary to determine to what extent there is a direct relationship between first stage chlorination and formation of 2378-TCDD and 2378-TCDF.

Figures VII-7 and VII-8 are plots of formation of 2378-TCDD and 2378-TCDF vs. the chlorine equivalents (Cl_2EQOX) for the entire bleaching sequence at each mill. Figure VII-7 shows a much clearer relationship between the application of chlorine and chlorine derivatives and formation of 2378-TCDD (r^2 0.60 for exponential function; r^2 0.72 for power function). The Mill E hardwood line appears as the only outlier in Figure VII-7. As noted earlier, sampling at that mill was conducted for only a short time after a change over from softwood to hardwood pulp bleaching. Thus, the pulp sample obtained was a mixture of undetermined amounts of softwood and hardwood pulp. Also, the log sheet for that line had a two-hour gap in data just prior to the change over, making a determination of actual chemical application rates for the pulp sampled impossible. Discounting data from that line, the r^2 values for the remaining data are 0.87 (linear function); 0.70 (exponential function); 0.78 (log function); and 0.80 (power function). These data suggest the possibility of a quantitative linear relationship between dioxin formation and the rate of chlorine equivalents applied across entire bleach lines. In Figure VII-8, the plot for 2378-TCDF is somewhat skewed by the data for the hardwood line at Mill E and the softwood line at Mill A. The latter line had the highest rate of formation of 2378-TCDF. Those data do not fit any of the above cited functions particularly well (r^2 0.45-0.63).

The data presented earlier (Tables VII-8 through VII-12) and in Figures VII-3 through VII-8, indicate that although most of the formation of 2378-TCDD and 2378-TCDF may be occurring in the first stage of chlorination, the formation of 2378-TCDD and 2378-TCDF across the bleach lines is more closely correlated to the application of chlorine and chlorine derivatives across entire bleach lines rather than chemical application in the first stage of chlorination.

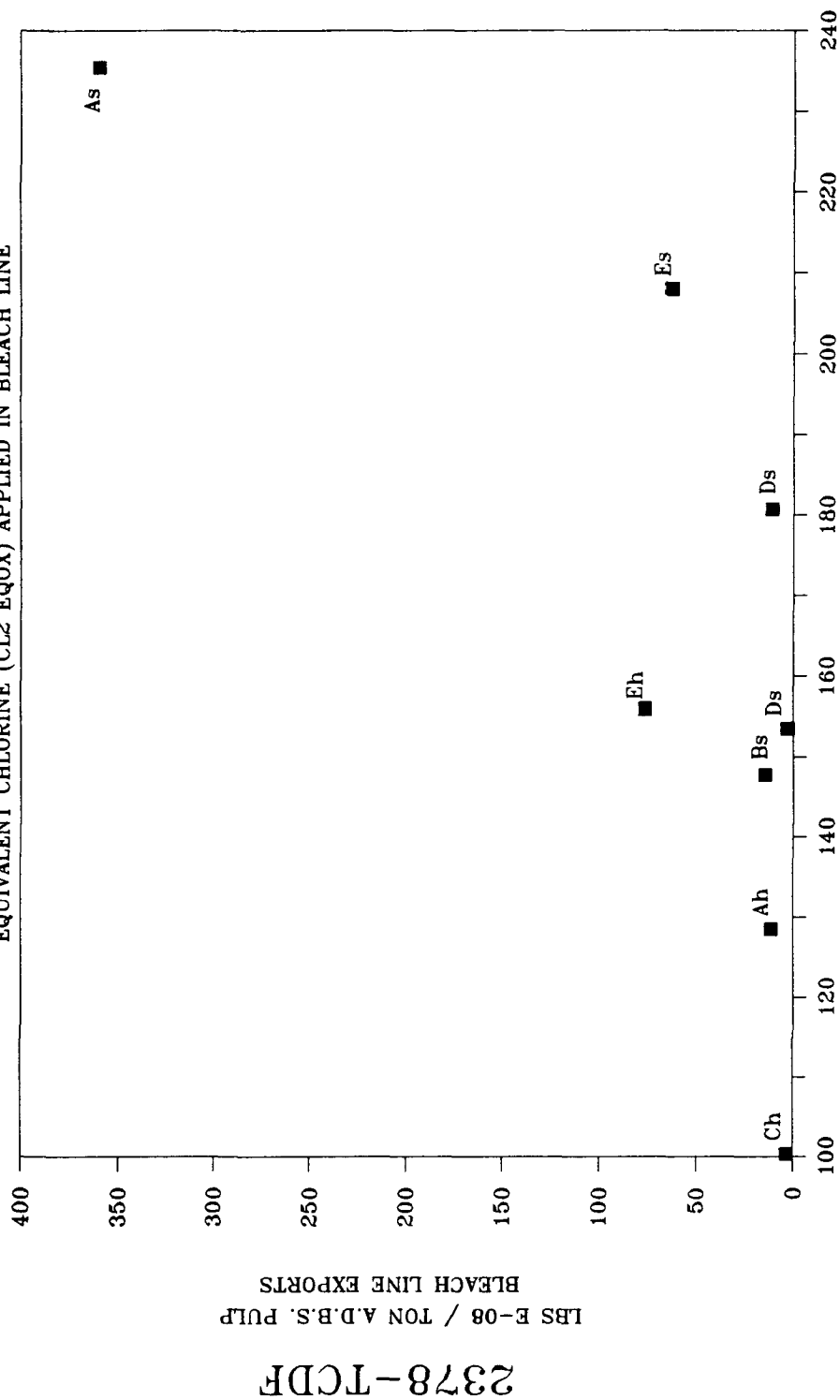
FIGURE VII-7
 2378-TCDD VS CHLORINE APPLIED (CL2 EQOX)
 EQUIVALENT CHLORINE (CL2 EQOX) APPLIED IN BLEACH LINE



LBS CL2 EQOX / TON A.D. BROWNSTOCK PULP

A - E	Mill Code
h	Hardwood Bleach Line
s	Softwood Bleach Line
A.D.B.S.	Air-Dried Brownstock

FIGURE VII-8
 2378-TCDF VS CHLORINE APPLIED (CL2 EQOX)
 EQUIVALENT CHLORINE (CL2 EQOX) APPLIED IN BLEACH LINE



LBS CL2 EQOX / TON A.D. BROWNSTOCK PULP

A - E	Mill Code
h	Hardwood Bleach Line
s	Softwood Bleach Line
A.D.B.S.	Air-Dried Brownstock

c. Chlorine dioxide substitution in chlorination stage

In a survey of United States pulp mills, it is reported that ClO_2 is substituted for some fraction of the chlorine in C-stages at 82 of 95 bleach lines.⁷ The rates of application were reported to be above 10 lbs/ton for 16 mills and below 10 lbs/ton for 66 mills.

Reproduced below is a summary of chlorine dioxide (ClO_2) substitution practiced at Mills B, C, and E during the field surveys at each mill. Chlorine dioxide is not used at Mills A and D.

Mill	Bleach Line	C-Stage Chemical Application		Chlorine Dioxide Substitution
		lbs/ton Air Dried BS Pulp		
		Chlorine	Chlorine Dioxide	
B	Softwood	84	0.6	1.8%
C	Hardwood	50	4.3	18.4%
E	Softwood	147	3.4	5.7%
	Hardwood	93	1.9	5.1%

Another hypothesis is that substantial substitution of ClO_2 in C-stages would give rise to lower rates of formation of 2378-TCDD and 2378-TCDF. The data from this survey are far too limited to validate or disprove this hypothesis. However, it is noteworthy that 2378-TCDD was not detected in bleached pulp or bleach line wastewaters at Mill C, with the highest ClO_2 substitution (and overall lowest chlorine usage in the C-stage). The rates of formation of 2378-TCDD and 2378-TCDF at Mill E are substantially higher than at Mill B despite ClO_2 substitution about three times greater. However, chlorination rates at Mill E were both 11% higher (Mill E hardwood) and 75% higher (Mill E softwood) than at Mill B. While data from other mills might be helpful in reviewing this question, the impact of ClO_2 substitution on formation of 2378-TCDD and 2378-TCDF can best be studied with controlled laboratory experiments.

d. Oxidative extraction

Nationally, out of 95 bleach lines for which data were reported, 49 include oxygen addition to caustic extraction stages.⁷ Of the eight bleach lines included in this study, oxidative extraction is practiced at Mill A (softwood and hardwood), Mill C (hardwood), and Mill E (softwood and hardwood). Sodium hypochlorite is also added to the caustic extraction stage at the Mill A softwood bleach line. There are no discernible relationships regarding formation of 2378-TCDD and 2378-TCDF among the bleach lines at

these mills or between those bleach lines with or without oxidative extraction. Since it appears that 2378-TCDD and 2378-TCDF are principally formed in the C-stages, the impact of different downstream processes such as oxidative extraction may be of lesser significance than chemical reactions and environmental conditions in the C-stages. Here again the impact of oxidative extraction can best be studied with controlled laboratory or mill experiments.

e. Recycle of bleach line filtrates

For the five mills included in this study, recycle of bleach line wash waters is practiced to a significant extent only at Mill B. As shown in Figure III-5, the D-stage filtrate is recycled to the C-stage seal tank and the first and second hypochlorite stage filtrates are recycled to the E-stage seal tank. The impact of this practice on formation of 2378-TCDD and 2378-TCDF at Mill B is not known, but thought to be not significant. It is possible, however, that recycle of bleach line filtrates in certain circumstances might be significant. For example, should minor amounts of E-stage filtrates be used for shower water additions on C-stage washers, process conditions at the point of addition (high pH with free chlorine and potential dioxin precursor compounds present) might be conducive to formation of 2378-TCDD and 2378-TCDF. Review of data from other mills and laboratory scale research are needed to further explore this question.

Based upon these analyses, it is apparent that the formation of 2378-TCDD and 2378-TCDF is in some manner related to the degree of chlorination and lignin content of the brownstock pulp. However, the limited data and limitations regarding the accuracy of chemical application data preclude a more rigorous analysis here. There are undoubtedly other factors that may affect formation of 2378-TCDD and 2378-TCDF in the bleaching of kraft pulp. Following is a limited list of possible factors:

- (1) Process conditions in the chlorination stage (pH, temperature, residence time, pulp consistency, and viscosity).
- (2) Presence of specific precursor compounds in unbleached pulp that may be attributable to certain wood species or pulping practices.
- (3) Efficiency of brownstock and partially bleached pulp washing.

- (4) Efficiency of chemical mixing with unbleached or partially bleached pulp.
- (5) Bleach plant filtrate recycle(s) used for shower water, vat dilution, or stock dilution.
- (6) Delignification with chemicals other than chlorine prior to chlorine bleaching.

An analysis of total mill exports of 2378-TCDD and 2378-TCDF is presented later in this section. Total mill exports are comprised of 2378-TCDD and 2378-TCDF contained in bleached pulp, treated wastewater effluent, and wastewater treatment sludges.

D. Paper Machine Wastewaters, Utility Ashes, and Landfill Leachates

1. Paper Machine Wastewaters

Paper machine wastewaters were sampled at each mill at locations of combined wastewater flow or at individual paper machine wastewater discharges which were flow-composited into one sample for analysis after collection. Mill E receives paper machine wastewaters from a nearby nonintegrated paper mill for treatment. The data from that mill are included in this section. Paper machine wastewater flows were obtained from primary flow measuring devices or from estimates by mill personnel.

Table VII-16 presents a summary of combined paper machine wastewater concentrations and mass flow rates for 2378-TCDD and 2378-TCDF. 2378-TCDD was detected in four of six combined paper machine wastewater samples, ranging from 0.053-0.10 ppt. 2378-TCDF was detected in each combined paper machine wastewater sample ranging from 0.015-0.35 ppt. The source of 2378-TCDD and 2378-TCDF in these wastewaters is assumed to be the bleached pulp slurry fed to the paper machines. The 2378-TCDD and 2378-TCDF on fine particulates or in solution is passed from the pulp slurry to the wastewaters. Except for Mill C where 2378-TCDD was not detected in bleach line wastewaters, the concentrations and mass discharges of 2378-TCDD and 2378-TCDF from paper machine wastewaters are quite small when compared to combined bleach plant wastewaters. As noted earlier, a possible contributing source of 2378-TCDD found in wastewater sludges at Mill C may be purchased bleached softwood pulp used at that mill.

2. Utility Ashes

A selected number of utility samples were analyzed for 2378-TCDD and 2378-TCDF. These data are presented in Attachments E and F. 2378-TCDD was not detected in fly ash from Mill A or in bottom ash and fly ash at Mill E at detection levels ranging from 0.28-0.66 ppt. 2378-TCDF was not detected in these samples at detection levels ranging from 0.18-0.35 ppt. Ash samples from the other mills were not analyzed. At some mills, primary and/or secondary wastewater sludges are disposed of by incineration in hog fuel boilers. However, this is not practiced at any of the five mills included in this study.

3. Landfill Leachates

Landfill leachate samples were collected at four mills and a sludge lagoon effluent sample was collected at Mill D. The landfill leachate at Mill A is a noncontinuous flow and is composed of sludge landfill leachate, landfill surface runoff, and ground

TABLE VII-16

COMBINED PAPER MACHINE WASTEWATERS

<u>Mill</u>	<u>2378-TCDD</u>		<u>2378-TCDF</u>	
	<u>Concentration</u> <u>(ppt,pg/gm)</u>	<u>Mass Loading</u> <u>lbs/day</u> <u>(kg/day)x10⁻⁶</u>	<u>Concentration</u> <u>(ppt,pg/gm)</u>	<u>Mass Loading</u> <u>lbs/day</u> <u>(kg/day)x10⁻⁶</u>
A	0.021	0.73(0.33)	0.19	6.9(3.1)
B	ND(0.0051)	--	0.11	6.2(2.8)
C	0.011	0.73(0.33)	0.20	14 (6.1)
D	ND(0.0060)	--	0.015	1.2(0.53)
E	0.053 0.10 ^a	8.3(3.8) 2.1(0.93)	0.17 0.35	27 (12) 7.2(3.3)
MEAN	0.031	2.0(0.91)	0.17	10 (4.5)
MEDIAN	0.016	0.73(0.33)	0.18	7.1(3.2)

NOTES: (a) Nonintegrated paper mill wastewater discharged to Mill E for treatment.
(b) ND - Not detected at stated analytical detection level ().

water. Leachate wastewater streams are returned for wastewater treatment at Mills A, C, and E. The sludge lagoon sample from Mill D and the leachate sample from Mill B are discharged directly to surface waters. Table VII-17 presents a summary of 2378-TCDD and 2378-TCDF concentrations and mass loadings for landfill leachates. The data show that only one sample, Mill A, had a detectable level of 2378-TCDD (0.025 ppt). The other 2378-TCDD results were not detected at detection levels ranging from 0.003-0.008 ppt. 2378-TCDF was detected in all but one sample (Mill C). Positive 2378-TCDF findings ranged from 0.011-0.11 ppt for the leachate samples. The mass discharges are not significant when compared to the untreated wastewater loadings from other pulp and paper mill sources, and relatively small when compared to treated process wastewater effluent discharges for those mills with detected levels of 2378-TCDD or 2378-TCDF in treated effluents.

TABLE VII-17

LANDFILL LEACHATES

Mill	2378-TCDD		2378-TCDF	
	Concentration (ppt,pg/gm)	Mass Loadings lbs/day (kg/day) x10 ⁻⁸	Concentration (ppt,pg/gm)	Mass Loadings lbs/day (kg/day) x10 ⁻⁸
A	0.025	3.8 (1.7)	0.11	17 (7.5)
B	ND (0.004) ^a	--	0.011	-- ^b
C	ND (0.006)	--	ND (0.009)	--
D ^c	ND (0.003)	--	0.016	7.9 (3.6)
E	ND (0.008)	--	0.064	3.8 (1.7)

NOTES: (a) ND - Not detected at stated analytical detection levels ().
 (b) Flow negligible at time of survey (est. <50 gal/day).
 (c) Sludge lagoon effluent.

E. Wastewater Treatment System Findings

A principle objective of this study was to (a) quantify the loadings of 2378-TCDD, 2378-TCDF, and other PCDDs and PCDFs to the general wastewater sewer; (b) determine the removal efficiency in wastewater treatment; and (c) examine their distribution in the three wastewater treatment plant export vectors (treated effluents, combined dewatered sludges, and landfill leachates).

Because of the prolonged residence time in wastewater treatment systems compared to the general mill sewer flows, the wastewater treatment system effluents were sampled over a different time frame to account for the time lag in wastewater treatment. The specific time lags incorporated into the effluent sampling programs were as follows:

Mill A	None
Mill B	~12 hours
Mill C	36 hours
Mill D	~16 hours
Mill E	~24 hours

The sampling locations selected for the wastewater treatment systems are identified in Figures III-4, III-7, III-10, III-13, and III-16. In general the sampling plan for each mill included the following locations:

1. influent to primary clarifiers or treatment system,
2. effluent discharged to receiving stream, and
3. dewatered sludge (combined or separate).

All five of the mills have activated sludge treatment. Hence, both primary and secondary sludges were designated as sampling locations. Discrete sampling of these sludges was physically possible at Mills A, B, and D. Mill B did not have a combined dewatered sludge but did add polymer to the secondary sludge to aid dewatering. The sludge was sampled prior to and after polymer addition. The sample without polymer was analyzed.

A number of other special conditions were identified and incorporated into the sampling plan. The acid sewer from the bleach plants at Mills B and E bypassed primary clarification. The influent to wastewater treatment was defined as the sum of the acid sewer plus the general mill sewer. At Mill B a composite

sample was generated by combining both streams based upon flows. At Mill C, a 2 MGD portion of the final effluent was recycled back into the mill as process water. This particular flow was sampled in the same time frame as the mill process sewers.

Mill D chlorinated a portion of the secondary sludge recycled to the primary clarifier. This sludge was sampled before and after chlorination. Mill E treated the wastewater from a nearby nonintegrated paper mill. This 2.5 MGD flow was also sampled. Landfill leachates were sampled from four mills and included in the mass balance for those flows that were returned to the wastewater treatment.

During and immediately preceeding the sampling program, Mill A was experiencing upset conditions in the wastewater treatment system which resulted in significantly higher effluent suspended solids discharges.

The major results of these analyses are noted in the following tables. They are grouped according to sample type. The concentrations (ppt, pg/gm) presented represent the average of all analyses (laboratory duplicates and/or field duplicates). The mass numbers (lbs/day, kg/day) are based upon the sewer flows and/or sludge tonnages noted in Attachment F.

1. Influents to Wastewater Treatment

The 2378-TCDD and 2378-TCDF results for influents to wastewater treatment are shown in Table VII-18. The data are presented for actual treatment system influents as monitored during the sampling surveys and as a summary of mass loadings from individual wastewater sources at the mills. Note that in two cases the influent analysis resulted in nondetectable 2378-TCDD concentrations at low (ppq) detection limits. However, when individual flows that make up this flow were analyzed, detectable concentrations were found. It is hypothesized that dilution in the combined influent sewer sample was responsible for reducing the 2378-TCDD concentrations to levels either at or below the established detection limits for this matrix. In further use of these values for mass balance calculations, the influent sample analysis was used unless this analysis resulted in a nondetectable concentration. In this case, the influent mass loading to the wastewater treatment plant (WWTP) was assumed equal to the sum of the loading found in tributary process sewers. Detection limits were not used or assumed to be equal to the WWTP influent sample concentration. Nondetected (ND) concentrations were treated as 0.0 ppt in the mass balance calculations.

TABLE VII-18

SUMMARY OF RESULTS FOR
INFLUENT TO WASTEWATER TREATMENT

	<u>2378-TCDD</u>		<u>2378-TCDF</u>	
	<u>Concentration</u> <u>(ppt or pg/gm)</u>	<u>Mass Loading</u> <u>lbs/day (kg/day)</u>	<u>Concentration</u> <u>(ppt or pg/gm)</u>	<u>Mass Loading</u> <u>lbs/day (kg/day)</u>
<u>Mill A</u>				
Influent to WWTP ¹	0.14	2.3(1.0) x 10 ⁻⁵	1.9	3.2(1.5) x 10 ⁻⁴
Sum of Sources	--	2.8(1.3) x 10 ⁻⁵	--	4.9(2.2) x 10 ⁻⁴
<u>Mill B</u>				
Influent to WWTP ²	ND(0.006)	--	0.11	3.4(1.5) x 10 ⁻⁵
Sum of Sources	--	5.3(2.4) x 10 ⁻⁶	--	2.9(1.3) x 10 ⁻⁵
<u>Mill C</u>				
Influent to WWTP	ND(0.003)	--	0.036	9.5(4.3) x 10 ⁻⁶
Sum of Sources	--	7.2(3.3) x 10 ⁻⁷	--	3.0(1.4) x 10 ⁻⁵
<u>Mill D</u>				
Influent to WWTP	0.028	4.4(2.0) x 10 ⁻⁶	0.063	1.0(0.45) x 10 ⁻⁵
Sum of Sources	--	1.0(0.47) x 10 ⁻⁵	--	2.1(0.97) x 10 ⁻⁵
<u>Mill E</u>				
Influent to WWTP ³	--	2.1(0.95) x 10 ⁻⁴	--	10.3(4.7) x 10 ⁻⁴
Sum of Sources	--	1.1(0.52) x 10 ⁻⁴	--	4.8(2.2) x 10 ⁻⁴

NOTES:

- (1) Mass loading from influent to WWTP at primary clarifier (DE020921). Negligible mass loading from landfill leachate (DE020821) discharged to UNOX system not included.
- (2) Synthetic flow weighted sample created from process sewer and acid sewer.
- (3) Mass loading includes combined acid sewer (RG1-86388) which bypasses primary treatment and primary treatment influent (RG1-86386/02).

2. Wastewater Treatment Sludges

The combined dewatered sludge, primary sludge, and secondary sludge concentrations and mass loadings for both 2378-TCDD and 2378-TCDF are shown in Table VII-19. In all cases where both primary and secondary sludges were analyzed, the secondary sludges, comprised principally of biological solids, contained much higher concentrations of 2378-TCDD and 2378-TCDF than primary sludges. The secondary sludges, which are lower in volume than primary sludges, also contained the greater mass of 2378-TCDD and 2378-TCDF.

3. Treated Process Wastewater Effluents

The final treated effluent concentrations and mass loadings for both 2378-TCDD and 2378-TCDF are presented in Table VII-20. With few exceptions, the effluent mass loadings are less than the estimates of untreated wastewater loadings presented in Table VII-18. There is no evidence to suggest that 2378-TCDD and 2378-TCDF are destroyed in the wastewater treatment systems. Rather, it appears that any removal across the treatment systems is simply mass transfer to the wastewater treatment sludges (Table VII-19). Estimates of wastewater treatment system removals (transfer to sludges) for 2378-TCDD and 2378-TCDF were made by comparing the treated effluent mass loadings with the greater of the influent mass loadings determined from monitoring at a central wastewater collection point prior to treatment, or the influent mass loadings determined from summing the mass loadings from individual bleach plant streams and other sources such as paper machine wastewaters (see Table VII-18). The results are presented in Table VII-20. As noted above, 2378-TCDD and 2378-TCDF treatment system removals constitute mass transfer from the wastewaters to the sludges rather than destruction or degradation to other compounds.

These data show variable results for the five mills. At Mill A, where effluent suspended solids during the sampling survey were higher than normal, about 15% of the detected 2378-TCDD and 2378-TCDF were removed or transferred to the sludges. The data for Mill B show about 13% removal of the detected 2378-TCDD and about a 10% increase in 2378-TCDF across the treatment system. At Mills C and D, where untreated wastewater loadings of 2378-TCDD and 2378-TCDF were relatively low and effluent suspended solids were relatively low, nearly all of the detected influent 2378-TCDD and 2378-TCDF were removed across the treatment systems. Finally at Mill E, with the highest influent loadings of 2378-TCDD and 2378-TCDF, treatment system removals were estimated at 86%.

TABLE VII-19

SUMMARY OF RESULTS FOR
WASTEWATER TREATMENT SLUDGES

	2378-TCDD		2378-TCDF	
	Concentration (ppt or pg/gm)	Mass Loading lbs/day (kg/day) (x 10 ⁻⁶)	Concentration (ppt or pg/gm)	Mass Loading lbs/day (kg/day) (x 10 ⁻⁶)
<u>Mill A</u>				
Primary Sludge	24	2.6 (1.2)	380	42 (19)
Secondary Sludge	710	10.2 (4.6)	10,900	160 (71)
Combined Dewatered Sludge	37	6.0 (2.7)	680	110 (51)
<u>Mill B</u>				
Primary Dewatered Sludge	19	1.3 (0.60)	100	7.1 (3.2)
Secondary Sludge (1)	89	3.0 (1.4)	810	27 (13)
TOTAL	42 (2)	4.3 (2.0)	330 (2)	34 (16)
<u>Mill C (3)</u>				
Secondary Sludge	11	0.49 (0.22)	75	3.3 (1.5)
Combined Dewatered Sludge	3.3	1.4 (0.65)	39	17 (7.6)
<u>Mill D</u>				
Primary Sludge	17	1.9 (0.85)	32	3.4 (1.6)
Secondary Sludge	36	0.58 (0.26)	78	1.3 (0.57)
Secondary Sludge-Chlorinated (4)	36	--	73	--
Combined Dewatered Sludge	18	2.2 (1.0)	34	4.2 (1.9)
<u>Mill E (3)</u>				
Secondary Sludge	500	34 (15)	2100	146 (66)
Combined Dewatered Sludge	180	32 (14)	760	136 (62)

NOTES:

- (1) Secondary sludge sampled before polymer addition.
- (2) Computed concentrations based upon mass balance. Primary and secondary sludges from Mill B are disposed of separately.
- (3) The primary sludge could not be safely collected at Mills C and E.
- (4) Chlorinated secondary sludge is returned to the aeration basins.

TABLE VII-20

SUMMARY OF RESULTS FOR
TREATED EFFLUENTS FROM WASTEWATER TREATMENT

	2378-TCDD			2378-TCDF		
	Concentration (ppt, pg/gm)	Mass Loading lbs/day (kg/day)	Wastewater Treatment System Removal	Concentration (ppt, pg/gm)	Mass Loading lbs/day (kg/day)	Wastewater Treatment System Removal
Mill A	0.12	2.4 (1.1) x10 ⁻⁵	15%	2.2	4.2 (1.9) x10 ⁻⁴	14%
Mill B	0.015	4.6 (2.1) x10 ⁻⁶	13%	0.12	3.7 (1.7) x10 ⁻⁵	Increase
Mill C	ND (0.003)	--	~100%	0.011	2.8 (1.3) x10 ⁻⁶	91%
Mill D	ND (0.007)	--	~100%	ND (0.007)	--	~100%
Mill E	0.088	3.0 (1.4) x10 ⁻⁵	86%	0.42	1.4 (0.65) x10 ⁻⁴	86%

NOTE: (1) There is no evidence to suggest that 2378-TCDD and 2378-TCDF are destroyed in wastewater treatment systems. Wastewater treatment system removal constitutes mass transfer from untreated wastewaters to wastewater sludges.

4. Wastewater Treatment System Mass Balances

The mass balances for the wastewater treatment systems are summarized in Tables VII-21 and VII-22 for 2378-TCDD and 2378-TCDF, respectively. The mass balances were based upon the influent to the wastewater treatment system, the combined dewatered sludge (primary plus secondary for Mill B), and the final treated effluent.

TABLE VII-21

SUMMARY OF WASTEWATER TREATMENT MASS BALANCES FOR 2378-TCDD

<u>2378-TCDD Mass</u>			
	<u>Input</u> <u>(lbs/day)</u>	<u>Exports</u> <u>(lbs/day)</u>	<u>% Exports</u> <u>Accounted for</u> <u>by Inputs</u>
Mill A ¹	2.8 x10 ⁻⁵	3.0x10 ⁻⁵	95%
Mill B ¹	5.3 x10 ⁻⁶	9.0x10 ⁻⁶	59%
Mill C ¹	0.72x10 ⁻⁶	1.4x10 ⁻⁶	51%
Mill D	4.4 x10 ⁻⁶	2.2x10 ⁻⁶	200%
Mill E	2.1 x10 ⁻⁴	6.2x10 ⁻⁵	340%

NOTES: (1) Influent based upon sum of individual process sewer mass loadings to wastewater treatment.

TABLE VII-22

SUMMARY OF WASTEWATER TREATMENT MASS BALANCES FOR 2378-TCDF

<u>2378-TCDF Mass</u>			
	<u>Input</u> <u>(lbs/day)</u>	<u>Exports</u> <u>(lbs/day)</u>	<u>% Exports</u> <u>Accounted for</u> <u>by Inputs</u>
Mill A ¹	4.9 x10 ⁻⁴	5.3 x10 ⁻⁴	92%
Mill B ¹	3.4 x10 ⁻⁵	7.2 x10 ⁻⁵	47%
Mill C ¹	3.1 x10 ⁻⁵	1.9 x10 ⁻⁵	160%
Mill D	1.0 x10 ⁻⁵	4.2 x10 ⁻⁶	240%
Mill E	1.0 x10 ⁻³	2.8 x10 ⁻⁴	370%

NOTES: (1) Influent based upon sum of individual process sewer mass loadings to wastewater treatment.

The significance of the mass balance calculations shown in Tables VII-21 and VII-22 should be reviewed in the context of both the precision in the 2378-TCDD and 2378-TCDF measurements and the process sewer flow rates and sludge tonnage values. Section VI of this report provides a detailed discussion of the quality assurance/quality control results for each of the major matrices included in this study. For the sludge and final treated effluent matrices, the measurement precision estimates were $\pm 15\%$ and $\pm 20\%$, respectively. The uncertainty associated with the sludge, effluent, and influent flow rates could not be quantified. The effluent flow estimates, however, are probably fairly reliable ($< \pm 10\%$) since the mills are required to monitor flow for NPDES reporting purposes. The sludge tonnage data, however, are likely the least reliable and could easily be in error by another $\pm 10\%$ to 15% .

Furthermore, two of the wastewater treatment influents (Mills B and C) and two of the treated effluents (Mills C and D) had nondetectable (ND) 2378-TCDD concentrations. Mill D also had a nondetected 2378-TCDF concentration in the treated effluent. In all of these cases, the effluent ND was treated as 0 ppt for the purposes of the mass balance calculations. The influent masses for Mills B and C were computed from the sum of less dilute internal process flows that entered the sewers going to primary treatment. These flows included both bleach plant and paper machine white water sources. The large discrepancy at Mill E may also have been due to the sample collection timing sequence. At this mill, the influent streams to wastewater treatment were sampled over a 0 to 24-hour period while the effluent sample collection was lagged by 24 hours to account for the residence time in wastewater treatment and collected during the 24- to 48-hour time frame. During the initial 24-hour period, however, significant process changes occurred relating to the wood species being bleached. The hardwood bleach line was sampled over a 4-hour period after the 24-hour mill composite sample period for the balance of the bleach plant and the internal process sewers. During the 24-hour composite sampling period for the mill, both softwood and hardwood pulps were bleached on the hardwood bleach line. The hardwood bleach line filtrates were not sampled during that period. Thus, the data used for mass balances from the short-term composite samples obtained on the hardwood line may not be representative of effluent and sludge conditions during the 24-hour mill sampling.

In summary, the various possible sources of error noted above could easily account for the generally poor mass balance calculations observed for all five mills. Given the low concentrations

and inherent measurement difficulties at these levels, the mass balance calculations for both 2378-TCDD and 2378-TCDF were judged reasonable.

As noted in Table VII-19, the final wastewater effluent concentrations of 2378-TCDD ranged from ND in two samples (0.003, 0.007 ppt) to 0.12 ppt; and 2378-TCDF ranged from ND (0.007 ppt) to 2.20 ppt. Because of the significance of this vector, these values were further examined in the context of a mass balance between the final effluent and the concentrations of both isomers of dioxin and furan in the secondary sludges.

It was assumed that the 2378-TCDD and 2378-TCDF associated with the final treated effluent comes from the unsettled mixed liquor suspended solids (MLSS) and is partitioned primarily to the solid phase. An estimate of the final effluent concentration can, therefore, be calculated from a knowledge of the effluent suspended solids and the secondary sludge concentrations. The results of these calculations are summarized in Tables VII-23 and VII-24. Suspended solids levels in the final effluents ranged from 14 to 104 ppm (mg/l) and represented nominal wastewater treatment plant performance at each of the five mills, with the exception of Mill A which had higher than normal suspended solids discharges during the sampling survey.

It is interesting to note that the calculated effluent 2378-TCDD and 2378-TCDF concentrations were lower than the measured concentrations in seven cases but of similar order of magnitude. In three other cases, nondetectable concentrations of both compounds were observed and the calculated values were lower than the reported detection limits and also of similar order of magnitude. Within the limits of the analytical capability for these measurements (both GC/MS and suspended solids), these calculations suggest that the unsettled mixed liquor suspended solids (MLSS) could be the major source of 2378-TCDD and 2378-TCDF in the final treated effluents. Furthermore, since the calculated concentrations were always lower than the corresponding measured values, the liquid phase must also contribute some mass to this export vector. This observation was judged reasonable based upon the fact that random experimental errors in both suspended solids and 2378-TCDD and 2378-TCDF measurements would likely produce a less biased result with some calculated 2378-TCDD and 2378-TCDF concentrations higher than the measured values.

TABLE VII-23

APPROXIMATION OF TREATED EFFLUENT 2378-TCDD
CONCENTRATIONS USING SECONDARY SLUDGE ASSUMPTION

	Effluent Suspended Solids (ppm)	Secondary Sludge 2378-TCDD (ppt)	Calculated Effluent 2378-TCDD (ppt)	Measured Effluent 2378-TCDD (ppt)
Mill A	104	710	0.074	0.12
Mill B	40	90	0.004	0.015
Mill C	26	11	0.0003	ND(0.003)
Mill D	14	36	0.0005	ND(0.007)
Mill E	89	500	0.045	0.088

TABLE VII-24

APPROXIMATION OF TREATED EFFLUENT 2378-TCDF
CONCENTRATIONS USING SECONDARY SLUDGE ASSUMPTION

	Effluent Suspended Solids (ppm)	Secondary Sludge 2378-TCDF (ppt)	Calculated Effluent 2378-TCDF (ppt)	Measured Effluent 2378-TCDF (ppt)
Mill A	104	10,900	1.1	2.2
Mill B	40	810	0.032	0.12
Mill C	26	75	0.002	0.011
Mill D	14	78	0.0011	ND(0.007)
Mill E	89	2,100	0.188	0.42

5. Distribution of 2378-TCDD and 2378-TCDF in Wastewater
Treatment System Effluents and Sludges

A final observation on the distribution of 2378-TCDD and 2378-TCDF in the wastewater treatment plant export vectors is illustrated in Table VII-25. These data indicate that both compounds are distributed differently in the sludge and effluent vectors from mill to mill but consistently within each mill. The reasons for these differences are not understood. Activated sludge wastewater treatment with fairly conventional residence times, aeration capacity, and secondary sludge recycles is provided at each mill.

TABLE VII-25

DISTRIBUTION OF 2378-TCDD and 2378-TCDF
IN WASTEWATER TREATMENT EXPORT VECTORS

	<u>2378-TCDD</u>		<u>2378-TCDF</u>	
	<u>% Effluent</u>	<u>% Sludge</u>	<u>% Effluent</u>	<u>% Sludge</u>
Mill A	80%	20%	79%	21%
Mill B	51%	49%	52%	48%
Mill C	~0%	~100%	14%	86%
Mill D	~0%	~100%	~0%	~100%
Mill E	48%	52%	51%	49%

F. Pulp and Paper Mill Exports

For purposes of this study, export vectors were defined as the final treated effluent, dewatered sludges, and the final bleached pulp. At some mills landfill leachates are discharged separately from the treated process wastewater effluents. The mass discharges from leachates were not significant compared to those from other vectors and thus were not considered in this analysis. In one pathway or another, these materials enter the environment. Summaries of the results for each mill are presented in Tables VII-26 and VII-27 for 2378-TCDD and 2378-TCDF, respectively. The most obvious feature of the data shown in these tables is the variable distribution of 2378-TCDD and 2378-TCDF in the three export vectors across the mills. The distributions of 2378-TCDD and 2378-TCDF were consistent within each mill.

The distributions in the treated effluents were apparently related to the final effluent suspended solids content as noted in Table VII-28. The data in this table suggest a casual relationship between the effluent suspended solids concentration and the relative distribution of 2378-TCDD and 2378-TCDF in the wastewater treatment plant export vectors (treated effluent, wastewater sludge). Generally, higher suspended solids contents resulted in a greater fraction of the 2378-TCDD and 2378-TCDF associated with the effluent rather than the sludge.

TABLE VII-26

MASS AND DISTRIBUTION OF 2378-TCDD IN TOTAL MILL EXPORT VECTORS

	<u>Dewatered Sludges % of Total</u>	<u>Final Effluent % of Total</u>	<u>Bleached Pulp % of Total</u>	<u>Total Mass in Export Vectors lbs/day (kg/day)</u>
Mill A	16	65	19	$3.7 (1.7) \times 10^{-5}$
Mill B	17	17	66	$2.6 (1.2) \times 10^{-5}$
Mill C	~100	~0	~0	$1.4 (0.64) \times 10^{-6}$
Mill D	~70	~0	~30	$3.2 (1.5) \times 10^{-6}$
Mill E	28	26	46	$1.1 (0.51) \times 10^{-4}$

TABLE VII-27

MASS AND DISTRIBUTION OF 2378-TCDF IN TOTAL MILL EXPORT VECTORS

	<u>Dewatered Sludges % of Total</u>	<u>Final Effluent % of Total</u>	<u>Bleached Pulp % of Total</u>	<u>Total Mass in Export Vectors lbs/day (kg/day)</u>
Mill A	17	64	19	$6.6 (3.0) \times 10^{-4}$
Mill B	20	23	57	$1.7 (0.75) \times 10^{-4}$
Mill C	35	6	59	$4.7 (2.1) \times 10^{-5}$
Mill D	~69	~0	~31	$6.1 (2.8) \times 10^{-6}$
Mill E	27	28	45	$5.1 (2.3) \times 10^{-4}$

TABLE VII-28

FINAL TREATED EFFLUENT TCDD/TCDF DISTRIBUTION IN EXPORT VECTORS
VS. EFFLUENT SUSPENDED SOLIDS CONCENTRATION

	<u>Effluent Suspended Solids (ppm)</u>	<u>% of Total TCDD in Effluent Export Vector</u>	<u>% of Total TCDF in Effluent Export Vector</u>
Mill D	15	~0	~0
Mill C	36	~0	6
Mill B	40	17	23
Mill E	89	26	28
Mill A	104	65	64

The total mass of 2378-TCDD and 2378-TCDF in the export vectors (Tables VII-26 and VII-27) can be accounted for by those process sewers related to the bleach plant. The summaries shown in Tables VII-29 and VII-30 illustrate the results of these mass balances. Note that at Mill C, 2378-TCDD was not detected in any bleach plant samples, although it may be present at less than detectable levels. The positive findings in paper machine wastewaters at this mill may be due to papermaking with purchased bleached softwood pulp.

TABLE VII-29

FRACTION OF 2378-TCDD FOUND IN
TOTAL MILL EXPORT VECTORS ATTRIBUTED TO
BLEACH PLANT SOURCES

	<u>2378-TCDD from Bleach Plant lbs/day(kg/day)</u>	<u>2378-TCDD in Export Vectors lbs/day(kg/day)</u>	<u>% Accounted for by Bleach Plant Sources</u>
Mill A	3.5(1.6) x10 ⁻⁵	3.7(1.7) x10 ⁻⁵	94%
Mill B	2.3(1.0) x10 ⁻⁵	2.6(1.2) x10 ⁻⁵	86%
Mill C	7.3(3.3) x10 ⁻⁷ (1)	1.4(0.64) x10 ⁻⁶	0%
Mill D	1.1(0.50) x10 ⁻⁵	3.2(1.5) x10 ⁻⁶ (2)	360%
Mill E	1.7(0.77) x10 ⁻⁴ (3)	1.2(0.51) x10 ⁻⁴	140%

- NOTES:
- (1) 2378-TCDD was not found in bleached pulp or bleach plant wastewater streams. This mass was found in paper machine wastewaters and may be associated with purchased bleached softwood pulp used for paper making.
 - (2) 2378-TCDD was found in the wastewater treatment plant influent and sludge but not in the effluent. Hence, the effluent ND(0.007) ppt was assumed to be 0.0 ppt. 2378-TCDD was not found in one bleach line bleached pulp ND(1.2). This export vector source was also assumed to be 0.0 ppt.
 - (3) Sampling was not done at the same time on hardwood and softwood bleach lines but the bleach line masses were assumed to be additive to reflect mix of total mill production during the sampling survey.

TABLE VII-30

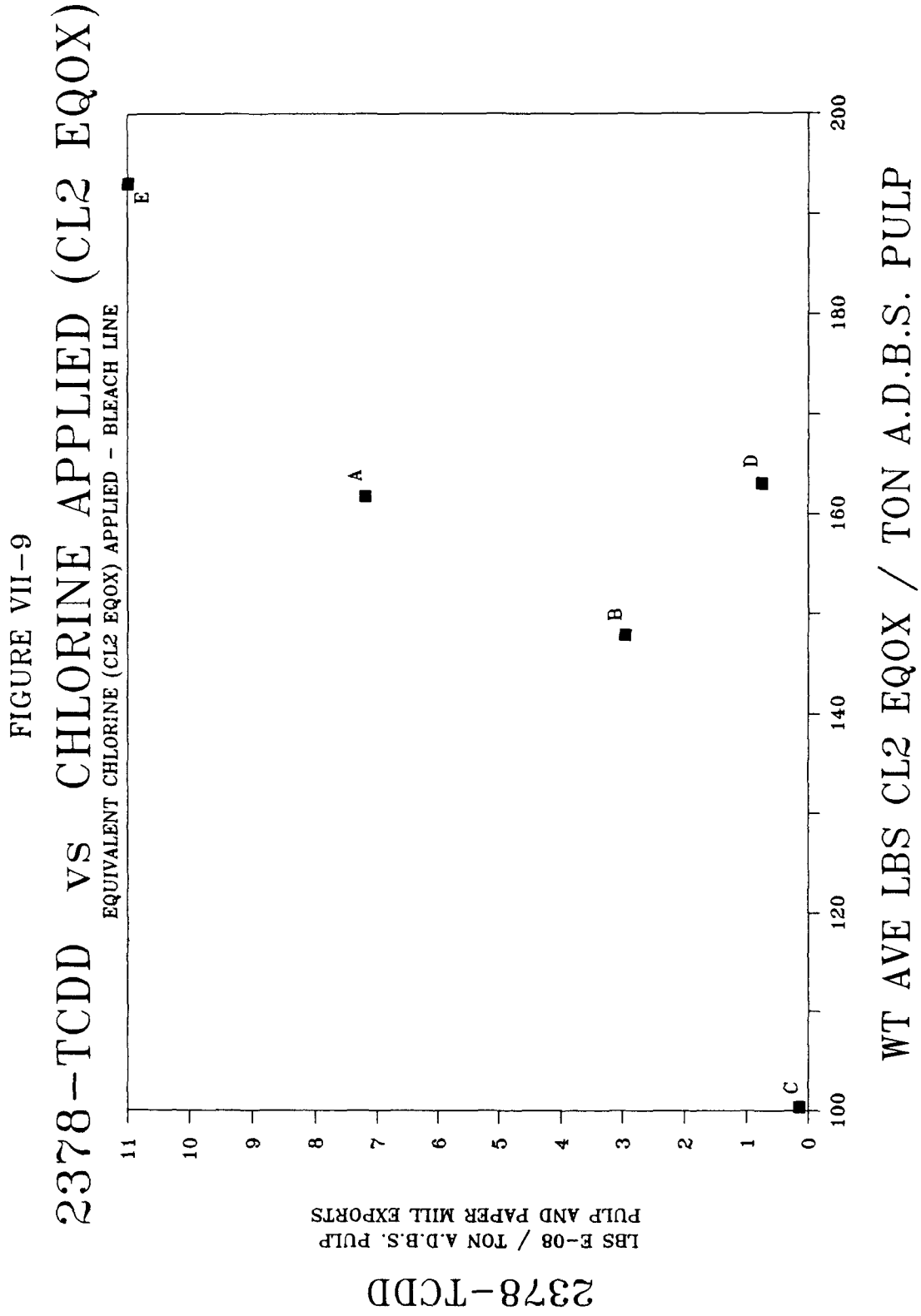
FRACTION OF 2378-TCDF FOUND IN
TOTAL MILL EXPORT VECTORS ATTRIBUTED TO
BLEACH PLANT SOURCES

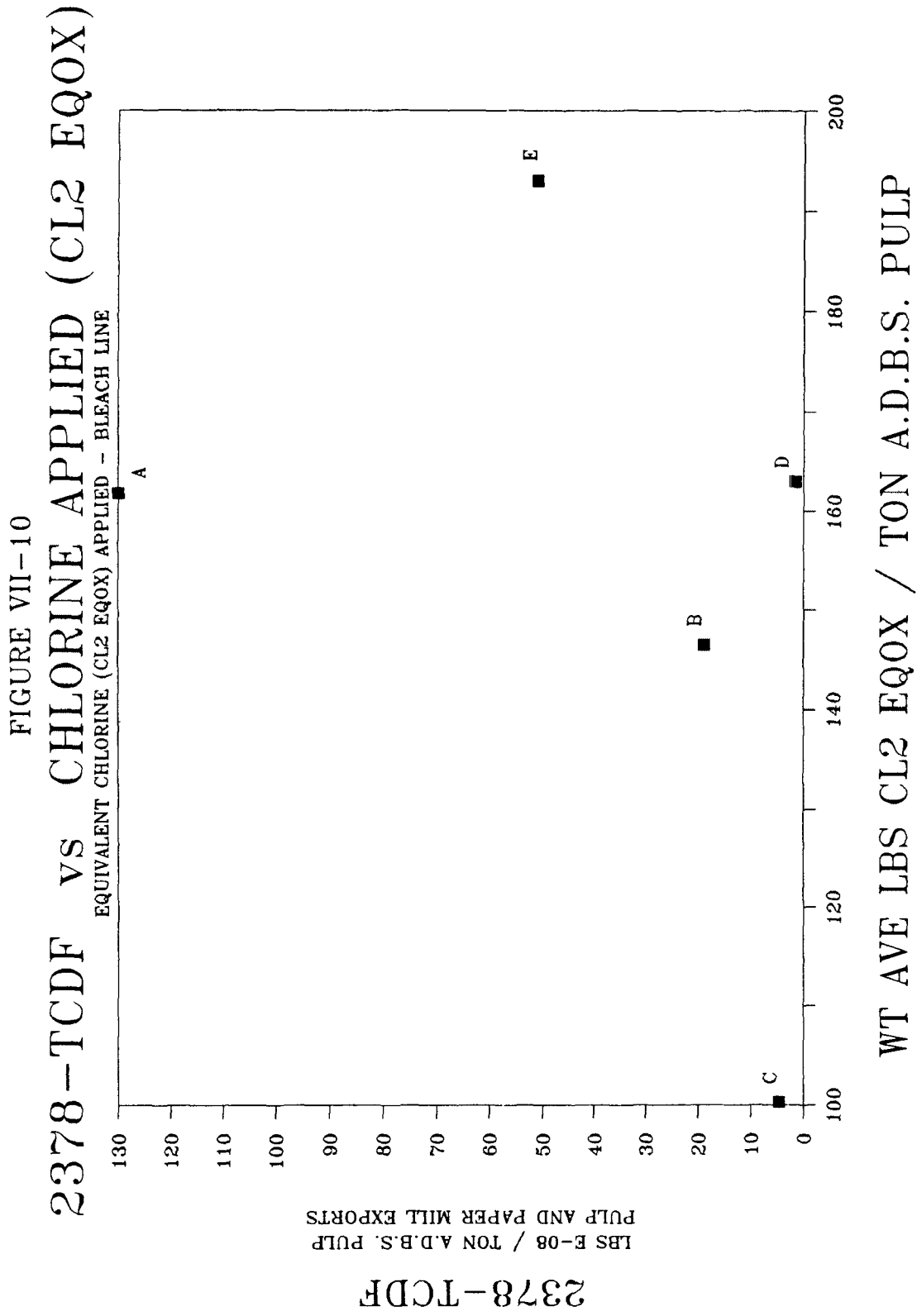
	<u>2378-TCDF from Bleach Plant lbs/day(kg/day)</u>	<u>2378-TCDF in Export Vectors lbs/day(kg/day)</u>	<u>% Accounted for by Bleach Plant Sources</u>
Mill A	6.1 (2.8) x10 ⁻⁴	6.6 (3.0) x10 ⁻⁴	92%
Mill B	1.2 (0.54) x10 ⁻⁴	1.7 (0.75) x10 ⁻⁴	70%
Mill C	3.2 (1.4) x10 ⁻⁵	4.7 (2.1) x10 ⁻⁵	68%
Mill D	2.2 (1.0) x10 ⁻⁵	6.1 (2.7) x10 ⁻⁶	360%
Mill E	7.3 (3.3) x10 ⁻⁴ (1)	5.6 (2.5) x10 ⁻⁴	130%

NOTES: (1) Sampling was not done at the same time on hardwood and softwood bleach lines but the bleach line masses were assumed to be additive to reflect total mill production during the sampling period.

The footnotes to the tables qualify a number of the sampling and calculation assumptions made in computing the mass balances. Given the various possible sources of error discussed earlier in this section, it is reasonable to conclude that the 2378-TCDD and 2378-TCDF formed are attributable to bleach plant sources in each mill. The small amounts of 2378-TCDF found in unbleached pulp from two mills were not significant.

As noted earlier in Section VII.C., the mass formation rates for both 2378-TCDD and 2378-TCDF in the bleach plants were related in some manner to the mass amounts of equivalent chlorine (Cl₂EQOX) applied to the brownstock pulp. Higher chlorine application rates in the bleach plant generally resulted in greater amounts of 2378-TCDD and 2378-TCDF formed. Similar correlations are presented for the total mill export vectors (pulp, sludge, and treated effluent) in Figures VII-9 and VII-10 for 2378-TCDD and 2378-TCDF, respectively. The y-axis represents the mass of each isomer found in all three export vectors divided by the brownstock pulp production. The x-axis represents the total mass amount of chlorine and chlorine derivatives expressed as equivalent chlorine (Cl₂EQOX) used in all stages of bleaching. The computations of





2378-TCDD and 2378-TCDF formed and chemical use were based upon a production weighted basis for mills with multiple bleach lines. Since 2378-TCDD and 2378-TCDF are not destroyed or eliminated in the wastewater treatment systems, these two graphs basically repeat the correlations shown in Figures VII-7 and VII-8. This observation is consistent with the fact that the formation of 2378-TCDD and 2378-TCDF is principally attributed to bleach plant sources.

G. Chlorinated Phenolics

At each of the five mills, samples were taken at selected background, bleach plant, and WWTP locations to be analyzed for chlorinated phenols, guaiacols, and vanillins. A list of the chlorinated phenolics is found in Table VII-31. Analytical data for these samples are presented in Attachment G along with several data summary sheets tabulated by sample type.

TABLE VII-31

CHLORINATED PHENOLIC ANALYTES

<u>Chlorophenols</u>	<u>Chloroguaiacols</u>	<u>Chlorovanillins</u>
2-Chlorophenol	4,5-Dichloroguaiacol	5-Chlorovanillin
2,6-Dichlorophenol	3,4,5-Trichloroguaiacol	6-Chlorovanillin
2,4-Dichlorophenol	4,5,6-Trichloroguaiacol	5,6-Dichlorovanillin
1,4/2,5-Dichlorophenol	Tetrachloroguaiacol	
3,4-Dichlorophenol		
2,5-Dichlorophenol		
2,3-Dichlorophenol		
2,4,5-Trichlorophenol		
Pentachlorophenol		

Table VII-32 presents chlorinated phenolics mass loading summaries based upon the analytical results for treated intake process waters, WWTP influents, and WWTP effluents for the five mills. Table VII-33 presents a summary of chlorinated phenolics mass loadings in the bleach plant wastewaters sampled in the five-mill study. Tables VII-34 and VII-35 present wastewater treatment system and bleach plant mass loadings normalized to production on the basis of air-dried brownstock pulp.

The data indicate that none of the chlorinated phenols were detected in any of the five mill treated intake process waters at detection levels estimated to be in the 1 to 3 ppb range.

TABLE VII-32

CHLORINATED PHENOLICS SUMMARY
Mass Loadings - lbs/day (kg/day)

<u>Intake Process Water</u>		<u>Sum of Chlorophenols</u>	<u>Sum of Chloroguaiacols</u>	<u>Sum of Chlorovanillins</u>	<u>Sum of All Analytes</u>
Number of Sources	5				5
Range	ND			ND	ND
Median	--			--	--
Mean	--			--	--
<u>WWTP Influent</u>					
Number of Sources	5				5
Range	ND-3.6 (ND-1.6)	3.6-34 (1.6-15)	0.77-8.0 (0.35-3.6)	4.9-46 (2.2-21)	
Median	0.99 (0.45)	7.2 (3.3)	4.1 (1.9)	14 (6.3)	
Mean	1.6 (0.73)	11 (5.0)	4.3 (1.9)	17 (7.7)	
<u>WWTP Effluent</u>					
Number of Sources	5				5
Range	ND-0.91 (ND-0.41)	ND-3.8 (ND-1.7)	ND-2.8 (ND-1.3)	0.17-5.6 (0.077-2.5)	
Median	0.17 (0.077)	2.1 (0.95)	ND	3.3 (1.5)	
Mean	0.39 (0.18)	2.1 (0.95)	0.75 (0.34)	3.2 (1.5)	

TABLE VII-33

CHLORINATED PHENOLICS IN BLEACH PLANT WASTEWATERS
Mass Loadings - lbs/day (kg/day)

	<u>Number of Sources</u>	<u>Range</u>	<u>Median</u>	<u>Mean</u>
<u>Sum of Chlorophenols</u>				
C-Stages	8	ND-0.53 (ND-0.24)	0.09 (0.41)	0.17 (0.077)
E-Stages	7	0.16-2.8 (0.073-1.3)	0.63 (0.29)	0.92 (0.42)
H-Stages	4	ND-0.06 (ND-0.027)	0.02 (0.009)	0.03 (0.014)
D-Stages	4	ND	ND	ND
<u>Sum of Chloroguaiacols</u>				
C-Stages	8	0.09-2.1 (0.041-0.95)	0.25 (0.11)	0.69 (0.31)
E-Stages	7	2.1-26 (0.95-12)	16 (7.3)	13 (5.9)
H-Stages	4	0.40-0.67 (0.18-0.30)	0.50 (0.23)	0.52 (0.24)
D-Stages	4	ND-0.18 (ND-0.081)	0.025 (0.011)	0.06 (0.027)
<u>Sum of Chlorovanillins</u>				
C-Stages	8	ND-1.9 (ND-0.86)	0.18 (0.082)	0.39 (0.18)
E-Stages	7	0.57-13 (0.26-5.9)	5.2 (2.4)	5.5 (2.5)
H-Stages	4	0.20-0.43 (0.091-0.19)	0.34 (0.15)	0.33 (0.15)
D-Stages	4	ND-0.01 (ND-0.005)	--	0.003 (0.0014)
<u>Sum of All Analytes</u>				
C-Stages	8	0.13-4.0 (0.059-1.8)	0.61 (0.28)	1.2 (0.54)
E-Stages	7	3.1-41 (1.4-19)	22 (10)	20 (9.1)
H-Stages	4	0.61-1.1 (0.28-0.50)	0.85 (0.39)	0.87 (0.39)
D-Stages	4	ND-0.18 (ND-0.082)	0.03 (0.014)	0.06 (0.027)

TABLE VII-34

WWTP MASS LOADINGS - SUM OF CHLORINATED PHENOLICS
[10⁻³ lbs/ton (kg/kg) of brownstock pulp bleached]

<u>Mill</u>	<u>Influent</u>	<u>Effluent</u>
A	9.4	6.4
B	15	5.6
C	9.1	0.17
D	33	13
E	45	1.9
Range	9.1-45	0.17-6.4
Mean	22(11)	5.4(2.7)
Median	15(7.5)	5.6(1.3)

NOTE: Sum of chlorinated phenolics includes chlorinated phenols, chlorinated guaiacols, and chlorinated vanillins.

TABLE VII-35

BLEACH PLANT MASS LOADINGS - SUM OF CHLORINATED PHENOLICS
C-STAGE AND E-STAGE FILTRATES
[10⁻³ lbs/ton (kg/kg) of brownstock pulp bleached]

<u>Mill</u>	<u>C-Stage</u>	<u>E-Stage</u>	<u>Sum of C and E Stages</u>
A-HW	0.51	8.8	9.3
A-SW	0.81	29	30
B-SW	3.6	25	29
C-HW	4.0	34	38
D-SW-A	2.1	49(2)	51
D-SW-B	4.6	49(2)	54
E-SW	1.8	46	48
E-HW(3)	0.55	20	21
Range	0.51-4.6	8.8-49	9.3-54
Mean	2.2 (1.1)	33 (17)	35 (17)
Median	1.9 (0.95)	32 (16)	34 (17)

NOTE: (1) Sum of chlorinated phenolics includes chlorinated phenols, chlorinated guaiacols, and chlorinated vanillins.
(2) Common E-stage mass loading allocated equally to A and B lines.
(3) The Mill E hardwood bleach line filtrate samples were obtained when an undetermined amount of softwood pulp was being processed on the line.

The wastewater treatment plant influent data for chlorophenols show three chlorophenols were detected at four of the five mills. with 2,4-dichlorophenol (and 2,4/2,5-dichlorophenol coelution) making up 99% of the combined five-mill influent chlorophenols mass loadings. Pentachlorophenol was detected at one mill. Of the three chlorovanillins analyzed, 6-chlorovanillin was predominant and detected at each mill, accounting for about 63% of the combined five-mill chlorovanillin influent mass loading. Chloroguaiacols were found at each mill in more evenly distributed patterns than the chlorophenols or chlorovanillins. From Table VII-34, the mean of all chlorinated phenolic influent mass loadings was 22×10^{-3} lbs/ton of air-dried brownstock pulp bleached.

Chlorinated phenolic effluent data presented in Table VII-32 show a similar distribution between the various analytes. The overall reduction of the sum of all chlorinated phenolics across the wastewater treatment facilities at the five mills was about 82%. From Table VII-34 the mean of all chlorinated phenolic effluent mass loadings was 5.4×10^{-3} lbs/ton of air-dried brownstock pulp bleached.

With respect to internal bleach plant sources of chlorinated phenolic wastewater streams, the data summarized in Tables VII-33, VII-35, and G-10 in Attachment G show that the E-stages accounted for most of the mass loadings of chlorinated phenolics in the bleachery samples analyzed in the five-mill study. These findings are similar to those for 2378-TCDD and 2378-TCDF. (see Section VII.C.3). The distribution of chlorophenols in the E-stage wastewater streams generally was similar to that for the WWTP influents. 2-Chlorophenol was detected in the E-stage wastewaters at one mill (Mill E, A side) in a trace amount.

With the limited data correlations were not attempted between chlorinated phenolics and levels of 2378-TCDD and 2378-TCDF present in wastewater treatment system influents or effluents. Since chlorinated phenolics were only analyzed on the water matrix, an evaluation of chlorinated phenolics in bleach plant or total mill exports could not be made. With the limited and incomplete wastewater data, mass balance calculations between internal bleach plant filtrates and wastewater treatment system influents were not attempted.

H. Total Suspended Solids and Biochemical Oxygen Demand

Selected samples were analyzed for total suspended solids (TSS) and biochemical oxygen demand (BOD₅). The TSS and BOD₅ analyses were conducted primarily to determine whether there were any abnormal wastewater treatment system operations during the sampling

events. Analytical results for TSS and BOD₅ for the five mills are presented in Attachment G. Tables VII-36 and VII-37 summarize TSS and BOD data for the wastewater treatment plant influents and effluents.

The effluent mass loading data from the five-mill study were reviewed with respect to typical loadings and percent removals presented in Section III (Tables III-3, 6, 9, 12, and 15). Effluent mass loadings for TSS generally were within typical ranges with the exception of Mill A. As noted in Section VII.E., during and immediately preceding the sampling period, Mill A was experiencing upset conditions in the wastewater treatment system which resulted in higher than normal mass loadings in the effluent. Monthly sewer and WWTP operating reports for Mill A were obtained for the sampling period and reviewed. According to Mill A personnel, failure of the white liquor clarifier and disposal of lime mud into the primary clarifier resulted in an overload of solids in the wastewater treatment system which took months to recover a suitable balance in the system. Based upon Mill A sewer operating reports, fiber losses during the sampling period were about 30% higher than the yearly average prior to the date of sampling.

TABLE VII-36

WASTEWATER TREATMENT PLANT
TOTAL SUSPENDED SOLIDS SUMMARY

Mill	Influent		Effluent		% Removal
	Conc. mg/L	Mass Loading lbs/day (kg/day)	Conc. mg/L	Mass Loading lbs/day (kg/day)	
A	654	109,700 (49,800)	104	20,100 (9100)	82%
B	--	52,800 ¹ (23,900)	40	12,800 (5800)	76%
C	540	141,900 (64,400)	36	8,900 (4000)	94%
D	875	137,600 (62,400)	15	2,200 (1000)	98%
E	680	210,000 (95,200)	89	30,500 (13,800)	86%

TABLE VII-37

WASTEWATER TREATMENT PLANT
BOD₅ SUMMARY

Mill	Influent		Effluent		% Removal
	Conc. mg/L	Mass Loading lbs/day (kg/day)	Conc. mg/L	Mass Loading lbs/day (kg/day)	
A	175	29,300 (13,300)	29	5,600 (2500)	81%
B	--	48,100 ¹ (21,800)	5	1,500 (680)	97%
C	301	79,100 (35,900)	9	2,200 (1000)	97%
D	232	36,500 (16,600)	13	2,000 (910)	95%
E	340	105,000 (47,600)	16	5,500 (2500)	95%

NOTES: (1) Mill B influent mass loadings calculated from data from two process sewers.

VIII. FINDINGS AND CONCLUSIONS

A. Data Quality and Data Limitations

1. The analytical protocol for 2378-TCDD and 2378-TCDF developed for this study was found to be satisfactory for isomer-specific determinations of 2378-TCDD and 2378-TCDF in selected pulp and paper mill sample matrices. Intra-laboratory method validation experiments for pulp, sludge, and wastewater effluent samples indicate the performance of the analytical method with respect to precision and spike recovery is demonstrably uniform. The method performance does not appear to be sensitive to any specific matrix or chemical effects which might be associated with the manufacturing processes at a given mill. Limited inter-laboratory comparisons incorporating different sample preparation, calibration standards, and analytical methods confirmed the presence of 2378-TCDD and 2378-TCDF in selected samples. However, a consistent bias was observed for quantitation of both 2378-TCDD and 2378-TCDF.

2. With few exceptions, the data quality assurance objectives established for this study for 2378-TCDD and 2378-TCDF were achieved.

- (a) Laboratory precision expressed as relative percent difference between duplicate analyses for thirty-five 2378-TCDD determinations was 15 percent mean (range 1-138 percent); and for thirty-three 2378-TCDF determinations, 16 percent mean (range 0-62 percent).
- (b) Field precision for eight 2378-TCDD determinations was 14 percent mean (range 4-19 percent); and for nine 2378-TCDF determinations, 22 percent mean (range 0-99 percent).
- (c) For thirty-five 2378-TCDD determinations, accuracy expressed as percent spike recovery was 103 percent mean (range 66-168 percent); and for thirty-five 2378-TCDF determinations, 102 percent mean (range 58-153 percent).
- (d) Including results from intra-laboratory method validation experiments, 97 percent of the analyses met the quality assurance objectives for laboratory precision and accuracy. Ninety-five percent of 133 determinations for 2378-TCDD and for 2378-TCDF resulted in analytical data suitable for project objectives.

- (e) Target analytical detection levels of 1 ppt for solid samples were achieved for all but one sample for 2378-TCDD and all but one sample for 2378-TCDF (different samples). Target analytical detection levels of 0.01 ppt for liquid samples were achieved for all but three samples for 2378-TCDD and all but two samples for 2378-TCDF (different samples).

3. Mass flow calculations for 2378-TCDD and 2378-TCDF combine analytical results with mass flow rates of solid materials (pulp, sludges) and liquids (waters, wastewaters). The mass flow rates for pulps and final treated wastewater effluents are considered to be accurate within less than $\pm 10\%$ while mass flow rates for sludges, within less than $\pm 10\%$ to 15% . Mass flow rates for internal plant wastewaters were generally based upon best engineering estimates and are considered accurate to less than $\pm 20\%$ to 25% . The reliability of reported bleach plant chemical application rates varied considerably from mill to mill, and in two cases, were best engineering estimates. The calculations and analyses presented in this report should be viewed accordingly.

B. PCDDs and PCDFs Found in Pulp and Paper Mill Matrices

1. Analyses of samples obtained at a number of bleached kraft pulp and paper mills for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) uniformly show that 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF) are the principal PCDDs and PCDFs found. This is particularly evident when the data are considered in light of USEPA's 2378-TCDD toxic equivalents approach for dealing with mixtures of PCDDs and PCDFs.

2. Data for the five mills included in this study show there is a characteristic 2378-TCDF/2378-TCDD ratio associated with individual bleach lines and individual mills, ranging from about 2 to about 18. This observation suggests that once 2378-TCDD and 2378-TCDF are formed, they are not altered in further processing or in wastewater treatment. Factors accounting for the differences in 2378-TCDF/ 2378-TCDD ratios across bleach lines and across mills have not been determined, nor has the possible process significance been formulated.

C. Sources of 2378-TCDD and 2378-TCDF

1. 2378-TCDD and 2378-TCDF are formed during the bleaching of kraft hardwood and softwood pulps with chlorine and chlorine derivatives at mills included in this study.

2. 2378-TCDD was not detected in seven unbleached kraft pulps collected at the five mills at detection levels ranging from 0.3 ppt to 1.0 ppt. 2378-TCDF was not detected in four of seven unbleached pulps at detection levels less than 0.3 ppt, but was found in three pulps collected at two mills at levels ranging from 1.1 to 2.3 ppt. The positive 2378-TCDF findings in unbleached pulps may be attributed to reuse of contaminated paper machine white waters for brownstock pulp washing or dilution.

3. 2378-TCDD was found in seven of nine bleached pulps collected at the five mills at concentrations ranging from 3 to 51 ppt and 2378-TCDF was found in eight of nine bleached pulps at levels ranging from 8 to 330 ppt. The median and mean concentrations are presented below with nondetects counted as zero:

	<u>2378-TCDD</u>	<u>2378-TCDF</u>
Median	5 ppt	50 ppt
Mean	13 ppt	93 ppt

4. 2378-TCDD and 2378-TCDF were found in most untreated bleach line filtrates sampled from the five mills. Wastewaters from caustic extraction stages (E and E₀) generally contained the highest concentrations and mass discharges from the bleach lines sampled.

5. The distributions of 2378-TCDD and 2378-TCDF in bleach line exports (bleached pulp and bleach plant wastewaters) were found to be highly variable from bleach line to bleach line. However, 2378-TCDD and 2378-TCDF were partitioned similarly to bleached pulps and bleach plant wastewaters within each bleach line.

6. 2378-TCDD was found in paper machine wastewaters from three of five mills and 2378-TCDF was found in paper machine wastewaters from each mill. The levels of 2378-TCDD and 2378-TCDF found in paper machine wastewaters were significantly less than found in the respective bleach plant wastewaters at four of five mills. The source of 2378-TCDD and 2378-TCDF in paper machine wastewaters at these mills is believed to be the bleaching operations. At one mill, 2378-TCDD was not detected in any bleach plant sources but was found in paper machine wastewaters. Purchased bleached pulp used at that mill may be a possible source.

7. 2378-TCDD was found in one of five sludge landfill leachate or runoff samples at 0.025 ppt, while 2378-TCDF was found in four of five samples at levels ranging from 0.01 to 0.11 ppt. 2378-TCDD and 2378-TCDF were not detected in coal-fired power boiler ash samples from two mills at detection levels less than 1.0 ppt.

8. 2378-TCDD and other TCDDs were detected in a blue dye collected during preliminary sampling at Mill A at levels of 3.4 and 53 ppt, respectively. 2378-TCDF and other TCDFs were not detected in that sample.

D. Formation of 2378-TCDD and 2378-TCDF

1. The rates of formation of 2378-TCDD and 2378-TCDF were normalized on a production basis to lbs/ton (kg/kkg) of air dried brownstock pulp. The rates of formation computed from bleach line exports (bleached pulps and bleach plant wastewaters) and from total mill exports (bleached pulp, treated wastewater effluents, and combined wastewater sludges) are summarized below:

10 ⁻⁸ lbs/ton (kg/kkg) of Brownstock Pulp		
	<u>Bleach Line Exports</u> (eight bleach lines)	<u>Total Mill Exports</u> (five mills)
<u>2378-TCDD</u>		
Range	ND-20(10)	0.14(0.07)-11(5.5)
Median	4.1(2.0)	3.0(1.5)
Mean	8.0(4.0)	4.4(2.2)
<u>2378-TCDF</u>		
Range	2.6(1.3)-360(180)	1.5(0.75)-130(65)
Median	12.5(6.3)	19(9.5)
Mean	68 (34)	41(21)

The range computed from bleach plant exports exceeds that computed from total mill exports because of the integration of results from mills with multiple bleach lines in the mill export calculations. For three out of five mills, the calculations using export vectors resulted in values less than computed from individual bleach lines. The extent to which these data are representative of long-term operations at the five mills, or are representative of the bleached kraft industry as a whole is not known.

2. Although the data from this study are limited, the results suggest casual relationships between the formation of 2378-TCDD and 2378-TCDF and (1) the degree of bleaching across bleach lines as estimated by the chlorine and chlorine equivalents applied to the unbleached pulp, and (2) the amount of lignin removed in the pulp across chlorination and caustic extraction stages as estimated by

the difference in permanganate number (K) and CEK (permanganate number after caustic extraction). Attempts were made to develop statistical correlations with the limited data. However, the results were generally poor. Data from several additional mills would be necessary to confirm these relationships.

3. Bleach lines processing exclusively softwood pulps had higher rates of formation of 2378-TCDD and 2378-TCDF than bleach lines processing exclusively hardwood pulps. However, bleaching conditions on the softwood and hardwood bleach lines were different, and thus, it is not possible to conclude that the general wood species bleached is the determinant variable in formation of 2378-TCDD and 2378-TCDF.

E. Wastewater Treatment System Findings

1. 2378-TCDD was found in treated wastewater effluents from three of five mills at levels ranging from 0.015 to 0.12 ppt and 2378-TCDF was found in four of five effluents at levels from 0.011 to 2.2 ppt. The mass discharges are summarized below:

10 ⁻⁵ lbs/day (kg/day)			
2378-TCDD		2378-TCDF	
Range	Median	Range	Median
ND-3.0 (1.4)	0.46 (0.21)	ND-42 (19)	3.7 (1.7)

2. 2378-TCDD and 2378-TCDF were found in wastewater treatment sludges collected from each of the five mills at the following levels:

	2378-TCDD		2378-TCDF	
	Range	Median	Range	Median
Primary Sludges	17 - 24 ppt	19 ppt	32- 380 ppt	100 ppt
Secondary Sludges	11 -710 ppt	89 ppt	75-10,900 ppt	810 ppt
Combined Sludges	3.3-180 ppt	37 ppt	34- 760 ppt	330 ppt

3. Mass balance calculations around the wastewater treatment systems for three mills showed that about 50% to 80% of the 2378-TCDD and 40% to 60% of the 2378-TCDF found in treatment system exports (treated effluent, wastewater sludge) can be accounted for by treatment system inputs. For two mills the treatment

system input loadings exceeded the export loadings by more than 200%. The poor mass balances are attributed to uncertainties in sludge, influent, and effluent flow rates, the sequencing of sampling at certain mills, and, to some extent, analytical variability associated with trace level analyses near method detection limits.

4. There is no evidence to suggest that 2378-TCDD and 2378-TCDF are destroyed in wastewater treatment systems. Rather, they are transferred, to varying degrees, to wastewater treatment sludges. At two mills, about 10% to 15% of the 2378-TCDD and 2378-TCDF contained in untreated wastewater streams was transferred to the sludges in the wastewater treatment systems, while at the remaining three mills more than 80% transfer to sludges is indicated.

5. The distributions of 2378-TCDD and 2378-TCDF between wastewater treatment exports (treated effluents and wastewater sludges) were highly variable from mill to mill. However, the partitioning of 2378-TCDD and 2378-TCDF between treated effluents and wastewater sludges was consistent within each mill. Mills with higher total suspended solids in effluents had higher levels of 2378-TCDD and 2378-TCDF partitioned to the effluent rather than to the sludge.

F. Pulp and Paper Mill Exports

1. The distributions of 2378-TCDD and 2378-TCDF among pulp and paper mill exports (bleached pulp, treated effluents, wastewater sludges) were highly variable from mill to mill, but the partitioning of 2378-TCDD and 2378-TCDF to the exports was consistent within each mill.

2. Mass balance calculations indicate that bleach plant sources accounted for about 90% to 140% of 2378-TCDD measured in mill exports at three mills and more than 300% at another mill. 2378-TCDD was not detected at bleach plant sources at one mill. For 2378-TCDF, bleach plant sources were found to account for 70% to 130% of the amount measured in mill exports at four mills, and more than 300% in the last mill. The poor mass balance results at some mills are attributed to uncertainties in mass flow rates of wastewater, sludge, and pulp, and, to some extent, analytical variability associated with trace level analyses near method detection limits.

G. Chlorinated Phenolics

1. For this study, chlorinated phenolics include selected chlorinated phenols, chlorinated guaiacols, and chlorinated vanillins. Chlorinated phenolics were formed in the bleaching process at each of the five mills. These compounds were not detected in treated intake process waters but were found in bleach plant filtrates and wastewater treatment system influents and effluents. Chlorinated phenolics were distributed differently at each mill.

2. Wastewaters from caustic extraction stage (E and E₀) washers accounted for most of the chlorinated phenolics. This finding is similar to findings for 2378-TCDD and 2378-TCDF in bleach line filtrates.

3. The amounts of chlorinated phenolics found in C-stage and E-stage filtrates were normalized to lbs/ton (kg/kg) of air-dried brownstock pulp and are summarized below:

10⁻³ lbs/ton (kg/kg) of Air-Dried Brownstock Pulp

<u>Sum of Chlorinated Phenolics</u>	<u>Sum of C-Stage and E-Stage Filtrates (eight bleach lines)</u>
Range	9.3-54 (4.2-24)
Mean	35 (17)
Median	34 (17)

4. With the limited data available, correlations between the presence of chlorinated phenolics and 2378-TCDD or 2378-TCDF in wastewater treatment system influents or effluents were not attempted. Because chlorinated phenolics were analyzed only for the water matrix, an evaluation of total chlorinated phenolics exports from bleach plants (i.e., pulp and wastewaters) could not be made. With the limited and incomplete wastewater data available, mass balance calculations between internal bleach plant filtrates and wastewater treatment system influents were not attempted.

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GLOSSARY

A. Chemical Terminology, Abbreviations, Units

BOD--Biochemical oxygen demand is a measure of biological decomposition of organic matter in a water sample. It is determined by measuring the oxygen required by microorganisms to oxidize the organic contaminants of a water sample under standard laboratory conditions. The standard conditions include incubation for five days at 20°C. BOD₅--Biochemical oxygen demand, measured after five-days.

CDDs--Chlorinated dibenzo-p-dioxins; chemical family consisting of eight homologues (monochlorinated through octachlorinated) and 75 congeners. PCDDs--Polychlorinated dibenzo-p-dioxins.

2378-TCDD--2,3,7,8-Tetrachlorodibenzo-p-dioxin.

TCDDs--Tetrachlorodibenzo-p-dioxins; homologue comprised of 22 isomers of TCDDs.

PeCDDs--Pentachlorodibenzo-p-dioxins; homologue comprised of 14 isomers of PeCDDs.

HxCDDs--Hexachlorodibenzo-p-dioxins; homologue comprised of 10 isomers of HxCDDs.

HpCDDs--Heptachlorodibenzo-p-dioxins; homologue comprised of 2 isomers of HpCDDs.

OCDD--Octachlorodibenzo-p-dioxin; homologue consisting of a single isomer.

CDFs--Chlorinated dibenzofurans; chemical family consisting of eight homologues (monochlorinated through octachlorinated) and 135 congeners. PCDFs--Polychlorinated dibenzofurans.

2378-TCDF--2,3,7,8-Tetrachlorodibenzofuran.

TCDFs--Tetrachlorodibenzofurans; homologue comprised of 38 isomers of TCDFs.

PeCDFs--Pentachlorodibenzofurans; homologue comprised of 28 isomers of PeCDFs.

HxCDFs--Hexachlorodibenzofurans; homologue comprised of 16 isomers of HxCDFs.

HpCDFs--Heptachlorodibenzofurans; homologue comprised of 4 isomers of HpCDFs.

OCDF--Octachlorodibenzofuran; homologue consisting of a single isomer.

Congener--Any one particular member of the same chemical family; e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins. A specific congener is denoted by unique chemical notation. For example, 2,3,7,8-tetrachlorodibenzofuran is referred to as 2,3,7,8-TCDF or, in this report, 2378-TCDF.

GC--Gas chromatograph.

GC/MS--Gas chromatography/mass spectrometry.

Homologue--A group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDDs, monochlorinated through octochlorinated.

Isomer--Substances that belong to the same homologous class. For example, there are 22 isomers that constitute the homologues of TCDDs.

ppm--Parts per million (equal to milligrams per liter, mg/l, when the specific gravity is one for aqueous samples; and equal to micrograms per gram, ug/gm, for solid samples).

ppb--Parts per billion (equal to micrograms per liter, ug/l, when the specific gravity is one for aqueous samples; and equal to nanograms per gram, ng/gm, for solid samples).

ppt--Parts per trillion (equal to nanograms per liter, ng/l, when the specific gravity is one for aqueous samples; and equal to picograms per gram, pg/gm, for solid samples).

ppq--Parts per quadrillion (equal to picograms per liter, pg/l, when the specific gravity is one for aqueous samples; and equal to femtograms per gram, fg/gm, for solid samples).

B. Pulp and Paper Industry Terms

Active Chlorine--That portion of chlorine in chemical compounds available to do useful work in the chlorination of mill water supply and in the bleaching of pulp. (See also Available Chlorine)

Additives--Chemicals or any other materials added to pulp stock slurry to impart special physical and visual properties to the paper sheet or board made from it. (See Paper Additive)

Air Dried--Reference to pulp and paper when dried artificially with the use of heated air in appropriate type dryers.

Air Dry (AD)--Refers to weight of moisture-free pulp or paper plus 10% moisture based on a traditional assumption that this amount of moisture exists when they come into equilibrium with the atmosphere, which in actuality is dependent on the conditions of the atmosphere to which it is exposed. Air-dried weight is determined by dividing the oven-dried weight by a factor of 0.9.

Alkali Extraction--The second stage in a pulp bleaching sequence where the first stage is chlorination (in which chlorine is added and allowed to react with the pulp slurry). The resulting chlorinated fiber residuals and other alkali-soluble constituents are then dissolved in the second or "alkali" extraction stage; also, caustic extraction stage, or "E"-stage.

Alum--A papermaking chemical, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ or a mixture of these hydrates, commonly used for precipitating rosin size onto the pulp fibers to impart water-resistant properties (when used for water treatment) to the paper made from it. Also called aluminum sulfate or papermaker's alum.

Available Chlorine--A term used in rating chlorinated lime, hypochlorites, chlorine dioxide, and other chlorine derived chemicals (usually used in water treatment and pulp bleaching operations) as to their total oxidizing power; $\text{Cl}_2\text{-EQOX}$, as used in this report. (See also Active Chlorine)

Backwashing--The operation of cleaning a rapid sand or mechanical filter by reversing the flow of water or liquid that is being filtered.

Bark--The rind covering of stems, branches, and roots of trees and plants. Technically, all tissues of woody plants which are outside the cambium layer.

Bark Boiler--A furnace designed especially to burn bark as a fuel. It is usually equipped with Dutch ovens.

Batch Digester--A cooking vessel, usually pressurized, in which predetermined, specific amounts of wood and cooking liquors are heated so that the wood conversion to pulp is completed and removed before the cycle repeats, as opposed to a continuous digester.

Batch System--A pulp and paper manufacturing unit process consisting of a series of operating units which processes predetermined specific amounts of materials and carries the process to completion before starting another cycle.

Black Liquor--Liquor from the digester to the point of its incineration in the recovery furnace of a sulfate chemical recovery process. It contains dissolved organic wood substances and residual active alkali compounds from the cook.

Black Liquor Evaporators--Multiple-effect combination of steam pressure and vacuum vessels in which black liquor is concentrated. They are arranged in such a way as to minimize the amount of steam used to carry on the process of water evaporation.

Black Liquor Recovery Boiler--A boiler designed especially to recover heat by burning concentrated black liquor (from the cooking of wood by the sulfate process) and to use the heat for steam generation.

Black Liquor Recovery Furnace--A furnace or combustion chamber especially designed to recover desirable chemicals from burning concentrated spent black liquor from the cooking of wood by the sulfate process.

Bleach--(1) A chemical used to purify and whiten pulp. It is usually of the oxidizing or reducing type, such as chlorine-based solution, oxygen, and similar chemicals. (2) The process of purifying and whitening pulp by chemically treating it to alter the coloring matter and to impart a higher brightness to the pulp.

Bleach Plant--That portion of a pulp mill where the bleaching process is performed. It usually adjoins the brownstock washing operation but sometimes is contained in a separate building. Occasionally, this area is referred to as a bleachery or the bleaching plant. It also refers to the area where hypochlorite bleach solutions are prepared.

Bleach Tower--A tall, cylindrical retention chest where pulp, mixed with the bleaching agent, is retained the required time for the bleaching action to be completed in a continuous system of pulp bleaching. An upflow-type is used when bleaching low consistency pulp, and a downflow-type is used when bleaching medium and higher consistency pulp. Also referred to as bleaching tower.

Bleach Washer--A filter (washer) located after a bleach tower in the bleaching sequence of pulp where the pulp is washed free of the residual bleaching agent and the products of the bleaching action.

Bleached Pulp--Pulp that has been purified or whitened by chemical treatment to alter coloring matter and has taken on a higher brightness characteristic.

Bleaching--The process of purifying and whitening pulp by chemical treatment to remove or change existing coloring material so that the pulp takes on a higher brightness characteristic. It is usually carried out in a single stage or a sequence of several stages. Chlorine, peroxides, calcium hypochlorite, carbon dioxide, and, lately, oxygen are most generally used to bleach chemical pulps. For groundwood pulp, sulfur dioxide and sodium peroxide are used.

Bleaching Agent--A variety of chemicals used in the bleaching of wood pulp such as chlorine (Cl_2), sodium hypochlorite (NaOCl), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], chlorine dioxide (ClO_2), peroxide (H_2O_2), sodium chlorite (NaClO_2), oxygen (O_2), and others. Also referred to as bleaching chemical.

Bleaching Stage--One of the unit process operations in which one of the bleaching chemicals is added in the sequence of a continuous system of bleaching pulp.

Bone Dry (B.D.)--(1) A descriptive term for the moisture-free conditions of pulp and paper. See Oven Dry (O.D.). (2) Refers to air containing absolutely no vapor.

Caustic Extraction--A stage in the pulp bleaching sequence (E) that normally follows the chlorination stages to remove alkali-soluble, chlorinated lignins. (See Alkaline Extraction and Extraction Stage)

Caustic Extracted K. No. (CEK)--A measure of the bleachability of pulp tested immediately after the caustic extraction stage in a pulp bleaching process. (See Permanganate Number and K Number)

Causticizing--Converting green liquor to white liquor by the use of slaked lime $[\text{Ca}(\text{OH})_2]$ which reacts with the sodium carbonate (Na_2CO_3) in the green liquor to form active sodium hydroxide (NaOH) in the white liquor. Also called recausticizing.

Cellulose--The chief substance in the cell walls of plants used in pulp manufacturing. It is the fibrous substance that remains after the nonfibrous portions, such as lignin and some carbohydrates, are removed during the cooking and bleaching operations of a pulp mill.

Chemical Pulp--The mass of fibers resulting from the reduction of wood or other fibrous raw material into its component parts during the cooking phases with various chemical liquors, in such processes as sulfate, sulfite, soda, NSSC, etc.

Chemical Recovery--The recovery of chemicals in sulfate cooking liquor after it is used to cook wood in the digester (spent liquor). It is expressed as a percentage determined by dividing the total alkali to the digesters, minus the sodium sulfate added to liquor, by the total alkali in the cooking liquor going to the digester after correcting for any change in liquor inventory.

Chip Pile--Chips that are stored outside in a mound type of structure usually located near the pulp mill so that chips can be conveniently conveyed from it to the digester storage.

Chipper--A piece of equipment in the woodyard/pulp mill area used to "chip" whole logs. It consists of an enclosed, rapidly revolving disk fitted with surface-mounted knives against which the logs are dropped in an endwise direction in such a manner that they are reduced to chips, diagonally to the grain.

Chlorination--(1) The mixing and reacting of chlorine water or gas with pulp in the bleaching operation. (2) The application of chlorine to mill water supply and sewage for disinfection or oxidation of undesirable compounds.

Chlorination Stage--The step in a multi-stage bleaching process ("C" stage) where chlorine water or gas is mixed, allowed to react, and then washed as an initial operation in a complete pulp bleaching system.

Chlorinator--A device for adding a chlorine-containing gas or liquid to mill wastewater. Sometimes the term is also used to refer to the chlorine mixer in the bleach plant.

Chlorine--A greenish-yellow, poisonous, gaseous chemical element (Cl_2) used in bleaching pulp and water purification in a pulp and paper mill.

Chlorine Consumption--Actual amount of chlorine consumed to bleach pulp, expressed as pounds of chlorine used per air dry ton of pulp bleached, or a percentage on the same basis. It may also be expressed on a bone dry basis.

Chlorine Dioxide Solution--A very unstable water solution of chlorine dioxide gas (ClO_2) produced in the chemical preparation area of a pulp mill. It is used in the pulp bleaching process.

Chlorine Dioxide Stage--The step or steps in a multi-stage bleaching process ("D"-stages) where chlorine dioxide solution is mixed with pulp, allowed to react, and then washed as one of the operations making up a complete pulp bleaching system.

Chlorine Evaporator--A specially constructed, thermostatically controlled vessel using hot water or steam to vaporize liquid chlorine transferred from tank cars to a pulp mill bleach plant. This vaporized product is used in the chlorination stage of a bleaching process, as well as to make up hypochlorite bleaching liquor. Also called chlorine vaporizer.

Chlorine Mixer--A mixing device used in the bleach plant to mix chlorine water or gas with unbleached pulp.

Chlorine Requirement--The amount of elemental chlorine (Cl_2) required to achieve a specified final brightness level of pulp in the bleaching process. It is supplied in the form of elemental chlorine and/or bleaching agents such as hypochlorites, chlorine dioxide, etc.

Chlorolignin--The product of reaction between lignin in unbleached pulp and chlorine in the chlorination stage of a multi-stage pulp bleaching system.

Clay--A naturally occurring, earthy, fine-grain material composed of a group of crystalline clay minerals with a natural basic structure of aluminosilicates whose hydrous chemical form is $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. It is commonly used in the paper industry to make up paper filling and coating materials. Clays are sometimes altered by further refining, heat treatment, etc., to enhance or extend their end uses, eg., calcined clay and delaminated clay.

Coated Paper--A term applied to any type of paper whose surface has been treated in such a way as to apply a coating in order to enhance its finish characteristics.

Coating--(1) The process of treating a sheet of paper or paperboard so that a coating material layer of a clear film is applied to its surface. (2) Refers to the coating material or film substance before coating. (3) The coating layer that is formed on the paper and paperboard sheet.

Consistency--(1) A measure of the fibrous material in pulp solutions, e.g., pulp and water, or stock (pulp and additives) and water. It is expressed as a percentage of this material in the solution, in terms of bone dry (BD), oven dry (OD), or air dry (AD) weight. (2) That property of adhesives or other coating material related to viscosity, plasticity, etc., that makes it resistant to deformation or flow.

Continuous Digester--A wood-cooking vessel in which chips are reduced to their fiber components in suitable chemicals under controlled temperature and pressure in a continuous operation.

Continuous Pulping Processes--Any pulping process in which the fibrous raw material and cooking chemicals move through the successive processing phases in a continuous fashion.

Converting Mill--A name sometimes applied to a paper or paperboard mill which does not produce the pulp it uses on site.

Countercurrent Washing--(1) method of washing pulp by running the wash water countercurrent to the flow of pulp through the process. Examples include countercurrent intra-stage washing in a multi-stage bleaching process (to minimize effluent) and the countercurrent flow of wash water to pulp flow on vacuum-type brownstock washers (to minimize water use and maximize black liquor recovery). (2) The washing of pulp within a Kamyr continuous digester (before blowing) in which the wash water flows countercurrent to the pulp flow in the process.

Delignification--The separation of the lignin component from the cellulose and carbohydrate materials of wood and woody materials by chemical treatment, such as the cooking of chips and the bleaching of pulp.

Dewater--(1) The tendency of solids in a slurry to aggregate and cause the draining of water from standing or flowing sludge or pulp slurry in a pipeline, sometimes to the point where the remaining solids become thick enough to make removal difficult, or to obstruct free flow through the line or a restriction such as a valve. (2) The process by which some of the water is removed from the pulp stock, increasing the consistency.

Digester--(1) A pressure vessel used to chemically treat chips and other cellulosic fibrous materials such as straw, bagasse, rags, etc., under elevated temperature and pressure in order to separate fibers from each other. It produces pulp. (2) In a waste treatment plant, it is a closed tank that decreases the volume of solids and stabilizes raw sludge by bacterial action.

Dye--(1) A natural or synthetic, organic or inorganic substance used to make up materials to impart a color to pulp slurries or the paper or paperboard sheet in papermaking, or to make up coating material to color their surfaces. The name is used interchangeably with the common paper mill term, dyestuff. (2) The act of coloring (or changing the color of) any material (stock, paper, etc.) by bringing it into contact with another material (dye) of a different color in such a manner that the resulting color will be more or less permanent.

Extraction Stage--That stage in a multi-stage pulp bleaching operation ("E"-stage), usually following the chlorination stage, in which sodium hydroxide (NaOH) is used to remove water insoluble chlorinated lignin and other colored components not removed in an intermediate washing operation. Also referred to as the caustic stage or alkaline extraction stage.

Fine Papers--High-quality writing, printing, and cover-type papers having excellent pen and ink writing surface characteristics.

First Stage--A pulp mill reference to the chlorination stage (C-stage) of a multistage pulp bleaching operation, which traditionally has been the first step. Recent technological developments have introduced other chemicals for use in the first step.

Free Chlorine--Elemental chlorine in the pulp bleaching process which is in solution and not compounded with lignin elements in chlorinated pulp slurries.

Green Liquor--A liquid that is formed during the sulfate chemical recovery process by dissolving smelt from the recovery furnace in a dissolving tank. The clear liquid takes on a greenish tinge.

Green Liquor Clarification--The removal of suspended solids (dregs) from green liquor, prior to causticizing in a pulp mill, by settling it in any one of several types of sedimentation units after flocculation.

Groundwood--Pulp and paper made up of mechanical fibers produced by the grinding of pulpwood.

Groundwood Pulp--A fibrous slurry produced by mechanically abrading the fibers from barked logs through forced contact with the surface of a revolving grindstone. It is used extensively in the manufacture of newsprint and publication papers.

Hardwood--Pulpwood from broad-leaved dicotyledonous deciduous trees.

Hardwood Pulp--Pulp produced from the wood of broad-leaved dicotyledonous deciduous trees.

High Density Storage--The storage of pulp slurries in a high consistency condition, usually after the bleaching process and just prior to the stock preparation.

High Temperature Bleaching--Operating the bleaching stages (hypochlorite or chlorine dioxide) of a multistage pulp bleaching system at temperatures higher than considered conventional.

High Temperature Chlorination--Operating the first bleaching stage (chlorination) of a multistage pulp bleaching process at higher temperatures (usually 110°F to 120°F) than considered conventional (less than 80°F).

Hog Fuel--Raw bark, wood waste, and other extraneous materials which are pulverized and used as a fuel for power boilers in a mill.

Hydrated Lime (CaOH₂)--Partially slaked lime produced by adding water to lime (CaO).

Hypochlorite--Reducing-type of bleaching chemical, usually in the form of calcium hypochlorite or sodium hypochlorite, used extensively in the bleaching of chemical pulps.

Hypochlorite Stage--The step or steps ("H"-stages) in a multistage bleaching process in which hypochlorite bleaching chemicals (usually calcium or sodium hypochlorite) are mixed, allowed to react, and washed.

K Number--A value, also called permanganate number, which is the result of a laboratory test for indirectly indicating the lignin content, relative hardness, and bleachability of pulps usually having lignin contents below 6 percent. It is determined by the number of milliliters of tenth normal permanganate solution (0.1 KMnO₄) which is absorbed by 1 gram of oven dry pulp under specified conditions.

Kappa Number--A value obtained by a laboratory test procedure for indirectly indicating the lignin content, relative hardness, or bleachability of higher lignin content pulps, usually with yields of 70 percent or more. It is determined by the number of milliliters of tenth normal permanganate solution (0.1 KMnO_4) which is absorbed by 1 gram of oven dry pulp under specified conditions, and is then corrected to 50 percent consumption of permanganate.

Kraft Process--The sulfate chemical pulping process. Also any equipment used as well as any intermediate or final products derived from the process. It means "strength" in German, and is a common pulp mill name for the sulfate process.

Kraft Cooking Liquor--A chemical mixture consisting primarily of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). It is used to cook wood chips and convert them into wood pulp. Sometimes called sulfate cooking liquor.

Kraft Digester--A pulpwood cooking vessel in which sulfate cooking liquor, consisting of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) active chemicals, is used as the cooking medium.

Kraft Paper--High-strength paper made from sulfate pulp. It is usually made with a naturally brown color using unbleached pulp, but it can also be made of bleached pulp and dyed to other colors. Also known as sulfate paper.

Kraft Pulp--Wood pulp produced by the sulfate chemical process using cooking liquor. It is made up primarily of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), using basically softwood species of pulpwood. Also known as sulfate pulp.

Kraft Pulping Liquor--A cooking chemical solution made up of sodium-based chemicals such as NaOH , Na_2S , Na_2CO_3 , and $\text{Na}_2\text{S}_2\text{O}_3$.

Kraft Recovery Cycle--The series of unit processes in a sulfate pulp mill in which the spent cooking liquor is separated from the pulp by washing, concentrated by evaporation, supplemented to make up for lost chemicals, and burned to recover other chemicals. These recovered chemicals are converted to new cooking liquor by reacting them with fresh and recovered lime in a causticizing operation.

Lignin--A brown-colored organic substance which acts as an interfiber bond in woody materials. It is chemically separated during the cooking process to release the cellulose fibers to form pulp, and is removed along with other organic materials in the spent cooking liquor during subsequent washing and bleaching stages.

Lignin Content--The amount of lignin present in the composition of the raw fibrous materials used in pulping and in the pulp after cooking and washing.

Lime (CaO)--A pulp mill chemical obtained by burning limestone (CaCO_3) and used to prepare cooking and bleaching liquors. It is also used in causticizing sulfate and soda cooking liquors, and to make up milk of lime [Ca(OH)_2] for the sulfite cooking process. See also Limestone.

Lime Kiln--A refractory lined, open-end, inclined steel cylinder located in the lime recovery area of a pulp mill and mounted on rollers. It is rotated about its longitudinal axis as lime mud (CaCO_3) is fed in the higher end, and burned to form lime (CaO) as it travels to the lower discharge end.

Lime Milk--The calcium hydroxide [Ca(OH)_2] formed by the reaction of lime (CaO) with water (H_2O).

Lime Mud--The sludge which is primarily calcium carbonate (CaCO_3) that settles out and is separated from the white liquor during the clarification operation in the causticizing process in a pulp mill recovery cycle prior to pumping over to the lime recovery area. Also called white mud.

Limestone (CaCO_3)--A naturally occurring mineral which is heated to form lime. It is used by pulp mills in preparing cooking and bleaching liquors, causticizing of sulfate and soda cooking liquors, and other uses. See also Lime.

Mechanical Pulp--Pulp produced by reducing pulpwood logs and chips into their fiber components by the use of mechanical energy, via grinding stones, refiners, etc.

Medium Consistency--A generalized reference used to describe pulp slurries having consistencies within the approximate range of 6 to 15 percent, although it may vary somewhat depending on where in the pulp and papermaking process the reference is made.

Multistage Bleaching--Any pulp-bleaching process consisting of two or more stages of operation in continuous series, rather than in one single step.

Oven Dry (OD)--Moisture-free conditions of pulp and paper and other materials used in the pulp and paper industry. It is usually determined by drying a known sample to a constant weight in a completely dry atmosphere at a temperature of 100°C to 105°C (212°F to 221°F). Also called bone dry (BD).

Paper--A homogeneous sheet of felted cellulose fibers, bound together by interweaving and by the use of bonding agents, and made in a variety of types. It is used for a multitude of purposes such as writing, printing, wrapping, clothing, industrial, domestic, sanitary, etc.

Paper Additive--Chemical or other material added to paper, paperboard, or their stock slurries to impart specific physical and visual properties to the sheet, such as wet strength, water repellency, and fire resistance. See also Additives.

Paper Machine--The primary machine in a paper mill on which slurries containing fibers and other constituents are formed into a sheet by the drainage of water, pressing, drying, winding into rolls, and sometimes coating.

Paper Mill--A factory or plant location where various pulps in slurry form are mechanically treated, mixed with the proper dyes, additives, and chemicals, and converted into a sheet of paper by the processes of drainage, formation, and drying on a paper machine. Some paper mills also finish the paper in various ways.

Permanganate Number--A value, also known as K number, that indicates the relative hardness or bleachability of chemical pulp usually having lignin contents below 6 percent. It is determined by the number of milliliters of one-tenth normal potassium permanganate solution (KMnO_4) that is absorbed by 1 gram of oven dry pulp under specified and carefully controlled conditions.

Peroxide--A short name for sodium peroxide (Na_2O_2) or hydrogen peroxide (H_2O_2) which are used to make up bleach liquor for bleaching mechanical-type pulps.

Peroxide Bleaching Stage--A sodium or hydrogen peroxide bleaching step or steps ("P"-stages) sometimes used in the later part of the multi-stage chemical-bleaching sequence as one of the operations making up the complete pulp-bleaching system.

Process Water--Any water in a pulp and paper mill that is used to dilute, wash, or carry raw materials, pulp, and any other materials used in the process of making pulp and paper.

Pulp--A fibrous material produced by mechanically or chemically reducing woody plants into their component parts from which pulp, paper, and paperboard sheets are formed after proper slushing and treatment, or used for dissolving purposes (dissolving pulp or chemical cellulose) to make rayon, plastics, and other synthetic products. Sometimes called wood pulp.

Pulp Bleaching--The process of purifying and whitening pulp in a pulp mill by chemically treating it to alter the coloring matter and to impart a higher brightness to the pulp.

Pulp Cooking--The process of reacting fiber-containing materials with suitable chemicals, usually under high temperature and pressure, in order to reduce them into their component parts with the fiber portion separated in the form of pulp. More commonly known as pulping.

Pulp Mill--A plant in which pulp is mechanically or chemically produced from fibrous materials such as woody plants, together with other associated processes such as pulp washing and bleaching. Chemical preparation and cooking chemical recovery operations are also conducted there.

Pulp Washer--A piece of pulp mill equipment designed to separate soluble, undesirable components in a pulp slurry from the acceptable fibers, usually by some type of screening method combined with diffusion and displacement with wash liquids, utilizing vacuum or the natural force of gravity.

Pulping Processes--Processes for converting fibrous raw material into pulp. They are usually classified by either the nature or degree of the chemical and/or mechanical treatments used in the pulping action.

Recovery Boiler--A combination unit in a pulp mill used to recover the spent chemicals from cooking liquor and to produce steam.

Recovery Furnace--The unit in a sulfate pulp mill in which concentrated spent cooking liquor (black Liquor) is burnt to a smelt to recover inorganic sodium salts and to generate steam.

Recovery Plant--The area, building, or buildings where all of the process units considered to be included in the chemical recovery cycle of a pulp mill are located.

Rosin--A material made up of a suspension and used for internal sizing of paper and paperboard. It is obtained as a residue from the distillation of gum from resinous southern pines. Sometimes called colophony.

Rosin Size--Rosin made up as a suspension and used for internal sizing of paper and paperboard to enhance its ability to repel moisture and water.

Salt Cake--A form of natural sodium sulfate (Na_2SO_4) added to the thick black liquor just prior to incineration in a sulfate recovery furnace where it is converted to sodium sulfide (Na_2S) to provide one of the active chemicals in the subsequent makeup of raw cooking liquor in the sulfate pulping process. Also referred to as glauher's salt.

Seal Tank--A receiving tank located beneath vacuum-type washers and filters. The water drops into it through a pipeline and forms a seal to create a vacuum in the sheet-forming cylinder portion of the unit. Sometimes referred to as a seal pit.

Sediment--Any material that settles out of pulp slurries, liquid solution, treated water, wastewater, and other fluids.

Semibleached Kraft (SBK)--Pulp made by the sulfate process which has not been bleached to the extent that normally fully bleached pulp has. It is used to make up end products considered of lower quality.

Semibleached Pulp--Pulp which has been only lightly bleached to what is ordinarily considered a very low brightness range.

Showers--Water jets or sprays used throughout pulp and paper mills to wash wire mesh screens, wires, wet felts, and pulp pads on paper machines, cylindrical-type washers, pulp screens, pulp drainers, etc.

Slaking/Causticizing--A two-stage chemical process in the causticizing plant of an alkaline pulp mill in which the sodium carbonate (Na_2CO_3) in the green liquor is converted to sodium hydroxide (NaOH) to produce white liquor. The first stage is slaking, which consists of the addition of lime (CaO) to green liquor where it reacts with water to form calcium hydroxide [$\text{Ca}(\text{OH})_2$]. The second stage is causticizing, in which the calcium hydroxide reacts with the sodium carbonate to form sodium hydroxide. Both stages overlap.

Slime--An undesirable slippery, glutinous film formed by microorganisms and the agglomeration of nonbiological matter. It is found throughout the pulp and paper stock flow and storage system.

Slimicide--Toxic chemical substance added to the pulp and paper process to inhibit the growth of undesirable microorganisms that cause slime.

Sodium Hydroxide (NaOH)--A strong alkali-type chemical used in making up cooking liquor in alkaline pulp mills. It is commonly referred to in the mill as caustic, caustic soda, or lye.

Sodium Hypochlorite (NaOCl)--A chemical used as one of the bleaching agents in multi-stage pulp mill bleach plants.

Softwood--Wood obtained from evergreen, cone-bearing species of trees, such as the pines, spruces, hemlocks, etc., which are characterized by having needles.

Softwood Pulp--Pulp produced from the wood of evergreen coniferous species of trees, such as pines, spruces, hemlocks, etc.

Spent Liquor (SL)--Used cooking liquor in a chemical pulp mill which is separated from the pulp after the cooking process. It contains the lignins, resins, carbohydrates, and other extracted substances from the material being cooked. Usually, this liquor is processed through a recovery cycle to produce fresh cooking liquor and steam for process use and/or power generation.

Sulfate Process--An alkaline pulp manufacturing process in which the active components of the liquor used in cooking chips in a pressurized vessel are primarily sodium sulfide (Na_2S) and sodium hydroxide (NaOH) with sodium sulfate (Na_2SO_4) and lime (CaO) being used to replenish these chemicals in recovery operations. Sometimes referred to as the kraft process.

Sulfate Pulp--Fibrous material used in pulp, paper, and paperboard manufacture, produced by chemically reducing wood chips into their component parts by cooking in a vessel under pressure using an alkaline cooking liquor. This liquor consists primarily of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). Also referred to as kraft pulp.

Unbleached Pulp--Pulp that has not been treated in a bleaching process and can be used as is in inferior grades of paper and paperboard.

Washer--Pulp mill equipment designed to separate soluble, undesirable components in a pulp slurry from the acceptable fibers. It usually consists of some type of screening method combined with diffusion and displacement with wash liquid, utilizing vacuum, or the natural force of gravity.

Water Supply--The primary source of natural water used in a pulp and paper mill, such as streams, rivers, lakes, and wells.

White Liquor--Cooking liquor formed by refortifying green liquor in the causticizing operation of an alkaline-type pulp mill so that it contains the active chemicals that will reduce chips into their fiber components by dissolving the lignin cementing material during the digester operation, thereby producing pulp.

White Liquor Clarification--The removal of calcium carbonate (CaCO_3) and other impurities from the causticizing liquor, usually by gravity sedimentation in units called clarifiers. This takes place in the liquor recausticizing process of a pulp mill in order to obtain a clear liquor for cooking wood.

White Water--Mill waters which have a white, cloudy appearance due to a very fine dispersion of fibers picked up when separated from pulp suspension on paper machines, washers, thickeners, save-alls, and other pulp-filtering equipment. It may also contain fine suspensions of sizing, dyestuffs, and filling materials, and it is reused in the papermaking process or it is refiltered to reclaim the suspended fibers.

Wood--That part of the stem of a plant, located between the bark and the pith, which is one of the primary sources for fiber used in the manufacture of pulp and paper.

All definitions for Section B and some definitions in Section C were obtained from Pulp and Paper Dictionary, Lavigne, John R., Miller Freeman Publications, 1936.

C. Utilities and Wastewater Treatment

Activated Sludge--The settled solids after treatment of pulp and paper mill effluent by aeration with microorganisms. The solids are collected at the bottom of a clarifier tank after mixing with oxygen in an aeration tank. Part of the sludge is recycled back to the aeration tank to maintain high solids concentrations and efficient treatment.

Activated Sludge Process--The treatment of pulp and paper mill effluent with air to oxygenate the biological mass. See Activated Sludge.

Aerated Lagoon--A natural or artificial wastewater treatment pond in which mechanical or diffused-air aeration is used to supplement the oxygen supply.

Biological Effluent Treatment--Process in which living microorganisms are mixed with incoming wastewater to a paper mill wastewater treatment plant, and use the biologically degradable organics in waste as food-stuffs or an energy source, thus effectively removing them from applied wastewater.

Biological Oxidation--Breaking down (oxidizing) organic carbon by bacteria that utilize free dissolved oxygen (aerobic) or "chemically bound" oxygen (anaerobic).

Boiler--Broad or general term for a steam-generating unit. It is referred to as an industrial boiler when primarily used to generate steam for process requirements such as in a pulp and paper mill, or as a recovery boiler when used in the chemical recovery cycle of a pulp mill.

Boiler Blowdown--Periodic or continuous drains from the drum and/or waterwall headers to remove spent precipitated feedwater treatment chemicals from the unit.

Clarification--(1) The removal of turbidity and suspended solids by settling in mill wastewater treatment. (2) In the causticizing plant in a pulp mill, it refers to the settling out of suspended materials from green and white liquors.

Clarifiers--Storage tanks in which suspended solids are allowed to settle and be removed from green and white liquors in the causticizing areas of a pulp mill. Tank used in wastewater treatment for separation of settleable solids.

Effluent--Pulp or paper mill wastewater discharges to receiving waters including streams, lakes, and other bodies of water.

Fly Ash--Entrained, partially burned dust, soot, and other materials and chemicals that are carried over with the flue gases emitted from the smoke stacks of power and recovery furnaces.

gpm--Gallon per minute.

Influent--Mill wastes, water, and other liquids, which can be raw or partially treated, flowing into a treatment plant, reservoir, basin, or holding pond.

Leachate--Liquid containing dissolved chemicals picked up by flowing the liquid through a material, such as water through the contents of a landfill.

MGD--Million gallons per day.

MLSS--Mixed-liquor suspended solids.

MLVSS--Mixed-liquor volatile suspended solids.

Outfall--The mouth of conduit drains and other conduits from which a mill effluent discharges into receiving waters.

Primary Sludge--The settlings removed from the first stage of a wastewater treatment plant which consists of a sludge settling tank. The sludge is normally dried over vacuum filters and disposed of in landfills or dried and burned in the power furnace.

Primary Treatment--The removal of suspended matter from mill wastewater by sedimentation. It is usually the first stage in a multistage wastewater treatment process, where substantially all floating or settleable solids are mechanically removed by screening and sedimentation.

Secondary Wastewater Treatment--Biological treatment of some pulp and paper mill effluents after sedimentation in a primary wastewater treatment plant.

Sedimentation--The settling of suspended solids from pulp slurries, liquid solutions, treated water, wastewater, and other fluids. It is usually accomplished by reducing the velocity of the liquid below the point where it can transport the suspended material.

Sedimentation Basin--A large container in which wastewater is retained so that any suspended solids will settle by gravity and then can be removed.

Sludge--Solid material filtered out of mill wastewater which is either disposed of in landfill operations or burned in power boilers.

Vacuum Filter--Any type of slurry filter in which suction is employed to deposit and form a pad of solids on the surface of a separating material (screen) with the liquid flowing through it.

Wastewater--Water carrying waste materials from a mill. It is a mixture of water, chemicals, and dissolved or suspended solids.

Water Softener--Apparatus designed to remove the dissolved calcium and magnesium minerals that produce hardness from water to prevent scaling in power and recovery boilers.

Water Treatment--The processing of mill source waters from rivers, lakes, and streams to remove impurities by sedimentation, filtration, and the addition of chemicals including alum, sodium carbonate and chlorine.

ATTACHMENT A

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY

JUNE 20, 1986

6/20/86

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY

Background and Project Introduction

Results from the National Dioxin Study indicate that 2378-TCDD has been detected in fish and river sediments collected downstream from some pulp and paper mills located in various parts of the country. The Peterwell Flowage in Wisconsin, the Rainy River in Minnesota, and the Androscoggin River in Maine have been identified as areas containing levels of dioxin to date. Current wastewater treatment plant sludges from some Maine, Minnesota, and Wisconsin mills contain parts per trillion (ppt) levels of 2378-TCDD and other PCDDs and PCDFs. Available EPA data indicate that, within the paper industry, bleached kraft mills have the highest levels of 2378-TCDD in wastewater sludge. This would indicate that current process operations may be responsible. However, there are currently no data to document potential process sources of dioxins nor to explain the wide range of sludge concentrations at bleach kraft mills. The paper industry has initiated a sampling program for paper mill wastewater treatment plant sludges. At this writing, paper industry data are not available.

The U.S. Environmental Protection Agency (USEPA), the American Paper Institute (API) and the National Council of the Paper Industry for Air and Stream Improvement (NCASI), have decided to conduct a cooperative screening study of five bleached kraft mills to determine possible process sources of PCDDs and PCDFs and quantify raw waste, sludge, and final effluent loadings of PCDDs and PCDFs. The cooperative screening study is being conducted to determine the formation and fate of PCDDs and PCDFs in bleached kraft pulp and paper making operations and respective wastewater treatment facilities. The cooperating parties believe a screening study of this nature can most efficiently be conducted by combining the knowledge and resources of federal and state governments and industry.

On March 5, 1986, the USEPA sent a formal request for information and cooperation to the Boise-Cascade Corporation with respect to its International Falls, Minnesota, mill. Since this cooperative screening study is expected to generate information fully satisfying that asked for in USEPA's March 5, 1986, request, USEPA hereby agrees to withdraw that request pending satisfactory execution of the cooperative screening study.

Screening Study Objectives

1. Determine, if present, the source or sources of 2378-TCDD and other PCDDs and PCDFs at five bleached kraft pulp and paper mills.
2. Quantify the untreated wastewater discharge loadings, final effluent discharge loadings, sludge concentrations, and wastewater treatment system efficiency for 2378-TCDD and other PCDDs and PCDFs. Determine raw wastewater and final effluent levels of selected other organic compounds.

General Project Organization and Responsibilities

1. Joint USEPA and Industry Responsibilities

Responsible for: (1) study design; (2) field coordination of sampling collection program; (3) providing personnel and equipment for sampling; (4) providing quality assurance review of analytical data from all samples; (5) development of final report; (6) public, local government, and media relations.

2. USEPA

Responsible for: (1) approval of sampling locations; (2) contract analytical support; (3) coordination of field sampling with participating State Agencies; (4) selection and prioritization of samples for analysis; (5) providing confidential treatment of process related information in accordance with Agency regulations; (6) preparation of final report, and (7) public, local government, and media relations as necessary. For USEPA the study will be directed through the Office of Water Regulations and Standards, Industrial Technology Division and Monitoring and Data Support Division.

3. Industry

API and NCASI will each direct portions of the industry efforts, with the assistance of the five mills participating in the study.

Responsible for:

- (1) providing study sites and a proposed sampling plan for each site; (Participating Mills and NCASI)
- (2) contracting for analytical support; (NCASI)
- (3) providing access to facilities, processes and production information to USEPA; (Participating Mills)
- (4) public, local government, and media relations as necessary. (API and Participating Mills)
- (5) Should a step in the kraft pulp and papermaking process be isolated as a major source of dioxin, the industry agrees to undertake a further investigation in attempt to determine its source and formation.

General Field Sampling Plan

A complete set of samples at each mill will be obtained during a single sampling event. Individual samples will be collected over a 24-hour period or other suitable composite sampling period. Where appropriate, process additives may be grab sampled. The approximate level of detail of sampling to be conducted at each mill is presented in Table 1 along with analytical requirements. The

outline presented in Table 1 will be used as a guide for developing specific sampling plans for each mill. All samples will be collected with appropriate documentation, coding, and custody procedures. Samples will be kept chilled during collection and shipment to the analytical laboratory. Process operating conditions and production records during the survey will be recorded and made available to study participants at the conclusion of each mill-specific sampling event.

General Analytical Plan

Table 1 also presents a general analytical plan, and Table 2 presents additional detail on sample prioritization. Samples and analyses are prioritized to conserve analytical resources. Priority 1 analyses will be conducted and reviewed prior to initiating Priority 2 analyses. USEPA, NCASI, and industry participants will consult to select Priority 2 samples and analyses. Analytical costs for each mill will be shared on the basis of 25 percent funding by USEPA and 75 percent funding by industry for all Priority 1 samples and up to a maximum of 15 Priority 2 samples. Industry's share of the total analytical cost for the screening study shall not exceed \$150,000.

Quality Assurance Review

The coded analytical data will be forwarded from the contract laboratory simultaneously to the EPA and the NCASI quality assurance managers. The quality assurance managers will complete timely reviews of the data, consult with each other and transmit the data to the EPA and NCASI project managers. Should the quality assurance managers disagree as to whether certain samples require reanalyses or followup analyses, the matter will be referred to the USEPA and NCASI project managers for resolution. Analytical costs associated with further analyses beyond that normally conducted by the analytical laboratory to resolve analytical problems will be shared by USEPA and industry on the same basis noted above. An outline of the Quality Assurance Project Plan for this screening study is presented as Attachment 1.

Confidentiality

Section 308(b) of the Clean Water Act, 33 USC § 1318(b), provides that confidential treatment may be afforded to trade secrets which are contained in information collected by, or submitted to, USEPA except that confidential treatment is precluded for "effluent data." Information collected pursuant to this dioxin screening study can be afforded such confidential treatment in accordance with 40 CFR Part 2. The participating companies may make claims of confidentiality on information submitted to USEPA as specified in 40 CFR § 2.203(b). USEPA will treat such submitted information in accordance with its regulations found at 40 CFR Part 2.

USEPA shall choose the appropriate manner in which to release the report for this dioxin screening study after considering the confidentiality provisions in the Clean Water Act and Agency regulations and after consultation with the participating mills, NCASI, and API.

Other Matters

Any other matters regarding study design, study implementation, analytical issues, etc., will be referred to the USEPA and industry project managers in a timely fashion as they arise for resolution with other parties.

Final Report

The cooperating parties agree that the final report of this screening study will be limited to a technical document responsive to study objectives. USEPA will have primary responsibility for preparation of the final report. NCASI and API will provide input to the development of the final report and have the opportunity to provide comments on review drafts. In the event industry participants do not agree with EPA's evaluation and conclusions regarding the data resulting from this screening study, NCASI and API may provide separate views regarding the data for inclusion in the final report.

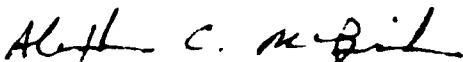
The undersigned signatories consent to, and approve this USEPA/Paper Industry Cooperative Dioxin Screening Study:



Michael C. Farrar
Vice President
Environment and Health
American Paper Institute



Isaiah Gellman
Executive Vice President
National Council
of the Paper Industry for
Air and Stream Improvement



Alexander C. McBride, Chief
Water Quality Analysis Branch
Monitoring and Data Support Division

TABLE 1

GENERAL SAMPLING PLAN AND ANALYTICAL REQUIREMENTS

	<u>ANALYTICAL PACKAGE</u>
A. Background Samples	
Treated River Water	2,3,4,5,6
Treated River Water Sludge	1
Wood Chips	1
B. Pulping Process	
Combined Process Wastewaters	2,5
C. Chemical Recovery Plant	
Recovery Plant Combined Wastewaters	2
Recovery Plant Waste Solids (Lime Mud)	1
D. Bleach Plant	
Pulp (Bleached and Unbleached)	1 or 2
Individual Sewered Streams from Bleachines	1 or 2
Combined Bleach Plant Process Wastewaters	2,5
Bleaching Agents Or Solutions	1
E. Paper Machines	
Combined Paper Machine Wastewaters	2,5
Process Additives (Alum, Clay, Dyes, Other Chemicals)	1
Slimeicides	1 or 2
F. Utilities, Wastewater Treatment	
Powerhouse Wastewater	2,5
Powerhouse Ash to Treatment	2
Wastewater Treatment Primary Sludge	2
Wastewater Treatment Secondary Sludge	2
Wastewater Treatment Composite Sludge	2
Combined Untreated Process Wastewater	2,3,4,5,6
Final Treated Process Wastewater Effluent	2,3,4,5,6
Other Wastewater Streams to Treatment (e.g. Landfill Leachates)	1,5

Analytical Packages

1. Isomer specific analyses for TCDDs and TCDFs
2. Package 1 plus 2378-substituted and selected bioaccumulative PCDDs and PCDFs
3. Suspected precursor compounds: Chlorinated phenols, vanillins, and guaiacols
4. Non-polar compounds: HRGC scan for non-polar compounds
5. TSS: Total suspended solids
6. BOD₅: Five-Day biochemical oxygen demand

TABLE 2

ANALYTICAL PRIORITIES

<u>PRIORITY 1 - Samples to be analyzed at all plants</u>	<u>Estimated Number of Samples</u>
a. Process Related	
Pulp (in - out)	2-6
Bleach Plant Wastewaters	4-12
Powerhouse Ash to Treatment	1
Selected Additives	2
b. Effluent Related	
Combined Bleach Plant Wastewaters	1
Combined Untreated Process Wastewaters	1
Final Treated Process Wastewater Effluent	1
Composite Wastewater Sludge	1
<u>Priority 2 - Samples to be selected from Table 1 for analysis based upon Priority 1 results</u>	15



A7
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 16 1986

OFFICE OF
WATER

Michael C. Farrar
Vice President
American Paper Institute
1250 Connecticut Avenue, N.W.
Washington, D.C. 20036

Dear Mr. Farrar:

This letter is to inform you of a minor modification to the analytical scope of our cooperative dioxin screening study. Specifically, EPA and NCASI participants in the study have agreed to eliminate the analyses for certain selected bioaccumulative PCDFs and for the non-polar compounds, both of which were listed in the agreement. The reasons for eliminating these analyses were 1) they were not directly related to the objectives of the study, 2) they would require additional analytical methods development and resulting costs, and 3) they could delay completion of the analytical efforts which are directly related to the study objectives. Attached is an amended version of Table 1 from the agreement showing the changes.

The study appears to be progressing well. Jim McKeown and Ray Whittemore of NCASI attended a meeting of our regional coordinators for the study on July 8, 1986, in Boston. At this meeting we were able to review what we had learned from the Boise Cascade sampling effort and to develop a tentative schedule for the remainder of the study. We hope to be able to complete the field work this calendar year and the analytical work within two or three months after that.

Sincerely,

Alec McBride

Alec McBride, Chief
Water Quality Analysis
Branch (WH-553)

Attachment

cc: Russ Blosser, NCASI
Gary Amendola
Tom O'Farrell

7/16/86

TABLE 1

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Wood Chips	1
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Combined Process Wastewaters	2,5
C. Chemical Recovery Plant	
Recovery Plant Combined Wastewaters	2
Recovery Plant Waste Solids (Lime Mud)	1
D. Bleach Plant	
Pulp (Bleached and Unbleached)	1 or 2
Individual Sewered Streams from Bleachines	1 or 2
Combined Bleach Plant Process Wastewaters	2,5
Bleaching Agents Or Solutions	1
E. Paper Machines	
Combined Paper Machine Wastewaters	2,5
Process Additives (Alum, Clay, Dyes, Other Chemicals)	1
Slimicides	1 or 2
F. Utilities, Wastewater Treatment	
Powerhouse Wastewater	2,5
Powerhouse Ash to Treatment	2
Wastewater Treatment Primary Sludge	2
Wastewater Treatment Secondary Sludge	2
Wastewater Treatment Composite Sludge	2
Combined Untreated Process Wastewater	2,3, X 5,6
Final Treated Process Wastewater Effluent	2,3, X 5,6
Other Wastewater Streams to Treatment (e.g. Landfill Leachates)	1,5

Analytical Packages

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2. Package 1 plus 2378-substituted ~~and selected bioaccumulative~~ PCDDs and PCDFs
3. Suspected precursor compounds: Chlorinated phenols, vanillins, and guaiacols
- ~~4. Non-polar compounds. HPCG scan for non-polar compounds~~
5. TSS: Total suspended solids
6. BOD₅: Five-Day biochemical oxygen demand



A9

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 16 1986

OFFICE OF
WATER

Isaiah Gellman
Executive Vice President
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
260 Madison Avenue
New York, N.Y. 10016

Dear Mr. Gellman:

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Attachment

cc: Russ Blosser, NCASI
Gary Amendola
Tom O'Farrell

A10
TABLE 1

~~6/20/86~~
7/16/86

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Wastewater Treatment Composite Sludge	2
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Other Wastewater Streams to Treatment (e.g. Landfill Leachates)	1,5

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- ~~4. Non-polar compounds: HPCG con for non-polar compounds~~
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A9

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 16 1986

OFFICE OF
WATER

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Executive Vice President
National Council of the Paper Industry
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Powerhouse Wastewater	2,5
Powerhouse Ash to Treatment	2
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Wastewater Treatment Composite Sludge	2
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ATTACHMENT B

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY
SAMPLING PROCEDURES, SAMPLE PRESERVATION, AND SAMPLE HANDLING

ATTACHMENT B

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN SCREENING STUDY SAMPLING PROCEDURES, SAMPLE PRESERVATION, AND SAMPLE HANDLING

A. Waters, Wastewaters, Pulps, High Moisture (Liquid) Sludges

1. Definitions

Grab Sample - A discrete sample collected manually over a period of time not to exceed 15 minutes.

Composite Sample - A sample formed by combining grab samples taken at periodic time intervals over a specified sampling period. In order to form a representative composite, the volumes of the individual grabs may be proportioned according to the time intervals or according to the total flows occurring during the time intervals.

Sampling Container - The precleaned stainless steel or glass container used to obtain grab samples from the flow of material at the sampling site.

Sampling Device - The apparatus to which the sampling container is attached to collect grab samples. One gallon for liquids and slurries and one quart for solids.

Composite Sample Bottle - The precleaned glass bottle which becomes the final repository of the composite sample for shipment to the analytical laboratory.

Aliquot Bottles - Precleaned glass containers into which grab samples are apportioned for the purpose of providing the appropriate volumes of the grab sample for preparing composite samples where more than one composite sample bottle is required at a sampling site.

2. Precleaning of Sampling Containers, Aliquot Bottles, Composite Sample Bottles, and Sampling Devices

Prior to the survey, the sampling containers, aliquot bottles, composite sample bottles, and that portion of the sampling device that will contact the sample shall be cleaned as follows:

Water and Detergent Wash
Water Rinse (deionized)
Methylene Chloride Rinse or Hexane Rinse
Oven Dry or Air Dry

For transport to the field, sampling devices shall be wrapped in aluminum foil, shiny side in. Precleaning of aluminum foil is not required. Any cleaning in the field shall be in accordance with the above.

3. Passivation of Sampling Containers, Aliquot Bottles, and Composite Sample Bottles

Prior to initiation of sampling, each sampling container, aliquot bottle, and composite sample bottle must be prerinsed with the material to be sampled to passivate any adsorptive sites on the containers or bottles. This shall be done at the outset of the survey and prior to use of any new sampling containers or aliquot bottles that are introduced due to breakage or modification of the sampling plan. Passivation of sampling containers or sample bottles is not necessary for solids samples.

4. Pretreatment and Preservation of Selected Samples

During reconnaissance prior to the survey, sites containing or having the potential to contain total residual chlorine and pH values outside the neutral range shall be identified. An additional portion of each sample suspected of having a chlorine residual or requiring pH adjustment shall be transported to a field laboratory for analysis of chlorine residual and/or pH. For each grab sample at such sites, the total residual chlorine shall be determined amperometrically or by wet chemical methods and recorded. The residual chlorine shall then be neutralized as soon as practical with crystalline, reagent grade sodium or potassium thiosulfate (35 mg/ppm Cl₂/liter) prior to adjustment of pH with 6 M sulfuric acid.

For composite samples designated for analysis of selected chlorinated phenolic compounds the pH of each grab sample shall be adjusted to less than 2 standard units, using 6 M sulfuric acid, prior to addition to the composite sample bottle. The pH of the composite sample shall be checked at the conclusion of the survey to insure that a pH less than 2 has been achieved. All samples shall be chilled from time of collection through delivery to the analytical laboratory.

5. Sampling Procedures

Prior to obtaining each grab sample, the sampling container and sampling device shall be rinsed twice with the material to be sampled. Sufficient volume of grab sample shall be obtained at one time to fill the aliquot bottles for all composite sample bottles at a sampling site. For liquid samples, the grab sample must be thoroughly mixed (manually shaken) while preparing the aliquots. Each aliquot bottle shall be filled from the sampling container in quarter-volume increments on a rotating basis to insure that each composite sample bottle receives a representative portion of the grab sample. For pulp samples, each sample shall be collected manually with a rubber or latex glove and dewatered by manual squeezing upon collection prior to introduction to the sample container. Where necessary, for safety reasons a pulp sampling device such as a stainless steel spoon or wooden paddle dedicated to that site may be used to collect the individual grab samples.

If it is not feasible to obtain sufficient volume of liquid sample with one grab sample, multiple grab samples may be obtained. In these cases, the aliquot bottles shall be filled with equal portions of each grab sample obtained. When not in use, the sampling container and aliquot bottles shall be kept in the ice chest designated for that site or otherwise secured and protected from contamination.

6. Sample Identification and Coding

Each composite sample bottle shall be identified with a gummed label bearing a sample identification number unique to the sampling site. The composite sample bottles shall be placed in ice chests which shall be clearly identified by sample number and sample site name for the duration of the sampling survey. Samples from a given sampling station shall be retained in an ice chest or ice chests dedicated to that sampling station only. Each composite sample bottle for analysis of selected chlorinated phenolic compounds shall be distinguished with a bright yellow tag for identification during the sampling event. Sample identification by site shall not be provided to the analytical laboratory.

7. Sample Handling and Shipping

Upon completion of the survey, a second tag bearing the sample identification number and the analytical package required shall be attached to each composite sample bottle. The composite sample bottles shall be sorted by site into Priority 1 and Priority 2 analysis groups and packaged in ice chests accordingly. The ice chests shall be clearly marked as Priority 1 or Priority 2. The ice chests shall be packed to prevent sample breakage and iced to maintain low sample temperatures.

B. Composite Wastewater Sludge (Semi-Solid)

1. Definitions

Grab Sample - A discrete sample collected manually over a period of time not to exceed 15 minutes.

Composite Sample - A sample formed by mixing grab samples taken at periodic time intervals.

Sampling Device - Precleaned stainless steel spoon, attached to a pole, if necessary.

Grab Sample Preparation Pan - Precleaned aluminum pan used for field homogenization of sludge grab samples prior to introduction of aliquots into the composite sample bottles.

Composite Sample Bottle - The precleaned glass bottle which becomes the final repository of the composite sample for shipment to the analytical laboratory.

2. Precleaning of Composite Sample bottles and Sampling Devices

Prior to the survey, the composite sample bottles, the grab sample preparation pans, and the sampling devices shall be cleaned as follows:

Water and Detergent Wash
Water Rinse (deionized)
Methylene Chloride Rinse or Hexane Rinse
Oven Dry or Air Dry

For transport to the field, sampling devices shall be wrapped in aluminum foil, shiny side in. Precleaning of aluminum foil is not required. Any cleaning in the field shall be in accordance with the above.

3. Passivation of Composite Sample Bottles and Sampling Devices

Passivation of composite sample bottles and sampling devices for sludges is not essential. Prior to initiation of sampling, composite sample bottles, grab sample preparation pans, and sampling devices may be prerinsed with final treated wastewater effluent to passivate any adsorptive sites on the containers or devices. This may be done at the outset of the survey and prior to use of any new containers or sampling devices that are introduced due to breakage or modification of the sampling plan.

4. Preservation of Samples

Composite samples shall be iced from collection to delivery to the analytical laboratories.

5. Sampling Procedures

The stainless steel spoon shall be used to obtain a sludge grab sample of sufficient volume to make up aliquots for all composite samples at a given site. The sludge shall be placed in the grab sample preparation pan and mixed with the stainless steel spoon until a uniform appearance is evident. The mass shall be quartered and requartered. A rotating system shall be used to add the proper volume aliquot to each composite sample bottle.

6. Sample Identification and Coding

Each composite sample bottle shall be identified with a gummed label bearing a sample identification number unique to the sampling site. The composite sample bottles shall be placed in ice chests which shall be clearly identified by sample number and sample site name for the duration of the sampling survey. Sample identification by site shall not be provided to the analytical laboratory.

7. Sample Handling and Shipping

Upon completion of the survey, a second tag bearing the sample identification number and the analytical package required shall be attached to each composite sample bottle. The composite sample bottles shall be sorted by site into Priority 1 and Priority 2 analysis groups and packaged in ice chests accordingly. The ice chests shall be clearly marked as Priority 1 or Priority 2. The ice chests shall be packed to prevent sample breakage and iced to maintain low sample temperatures.

C. Process Additives

1. Definitions

Grab Sample - A discrete sample collected manually over a period of time not to exceed 15 minutes.

Grab Sampling Container - The precleaned glass or stainless steel container used to obtain the grab sample. In many cases a glass sampling container may be the final grab sample bottle.

Sampling Device - The apparatus to which the sampling container is attached to collect grab samples. One gallon for liquids and slurries and one quart for solids.

Final Grab Sample Bottle - The precleaned glass bottle which becomes the final repository of the grab sample for shipment to the analytical laboratory.

2. Precleaning of Grab Sampling Containers, Final Grab Sample Bottles, and Sampling Devices

Prior to the survey, the grab sampling containers, final grab sample bottles, and that portion of the sampling device that will contact the sample shall be cleaned as follows:

Water and Detergent Wash
Water Rinse (deionized)
Methylene Chloride Rinse or Hexane Rinse
Oven Dry or Air Dry

For transport to the field, sampling devices shall be wrapped in aluminum foil, shiny side in. Precleaning of aluminum foil is not required. Any cleaning in the field shall be in accordance with the above.

3. Passivation of Grab Sampling Containers and Final Grab Sample Bottles

Passivation of grab sampling containers and final grab sample bottles for liquid samples shall consist of a rinse with the material to be sampled. Grab sampling containers and final grab sample bottles for solid samples shall not be passivated.

4. Pretreatment and Preservation of Samples

Samples shall not be pretreated or chemically preserved, except that any samples with residual chlorine shall be treated with sodium or potassium thiosulfate as soon as practical to neutralize the chlorine. Samples shall be kept chilled from collection to delivery to the analytical laboratory.

5. Sampling Procedures

Representative grab samples shall be obtained as appropriate.

6. Sample Identification and Coding

Each final grab sample bottle shall be identified with a gummed label bearing a sample identification number unique to the sampling site. The final grab sample bottles shall be placed in ice chests which shall be clearly identified by sample number and sample site name for the duration of the sampling survey. Sample identification by site shall not be provided to the analytical laboratory.

7. Sample Handling and Shipping

Upon completion of the survey, a second tag bearing the sample identification number and the analytical package required shall be attached to each final grab sample bottle. The final grab sample bottles shall be sorted by site into Priority 1 and Priority 2 groups for analysis and packaged in ice chests accordingly. The ice chests shall be clearly marked as Priority 1 or Priority 2. The ice chests shall be packed to prevent sample breakage and iced to maintain low sample temperatures.

ATTACHMENT C

ANALYTICAL PROTOCOL FOR THE DETERMINATION OF
2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN AND
2,3,7,8-TETRACHLORODIBENZOFURAN IN
PAPER MILL PROCESS SAMPLES AND PAPER MILL EFFLUENTS

June 12, 1987
REV June 22, 1987

WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

ANALYTICAL PROTOCOL FOR THE DETERMINATION
OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN AND
2,3,7,8-TETRACHLORODIBENZOFURAN IN PAPER MILL PROCESS SAMPLES
(WOODCHIPS AND PAPER PULP) AND PAPER MILL EFFLUENTS
(SLUDGE, ASH, MUD, TREATED AND UNTREATED WASTEWATER):
DIOXIN I ANALYSES

I. SUMMARY OF SAMPLE RECEIPT AND HANDLING PROCEDURES

Samples are shipped to Wright State University (WSU), Dayton, Ohio, via Priority Carrier (such as Federal Express or UPS Overnight) or are delivered by U.S. EPA personnel and upon arrival at the WSU Central Receiving Area, the Laboratory Sample Custodian or his designate is notified. The Sample Custodian proceeds to Central Receiving, signs the carrier's shipping documents, and any Chain-of-Custody documentation received with the samples, takes custody of the shipment, and transports the shipment to the Laboratory. The samples are then carefully unpacked within a hood located in a secure room, the condition of each sample is noted and the individual sample numbers assigned by the person(s) who collected the samples in the field and the accompanying descriptions of the samples are recorded in a Laboratory Sample Log-In Book. Also, at this time, an Intralaboratory Control Number is assigned to each sample by the Laboratory Sample Custodian, and this identifying number is entered in the Laboratory Sample Log Book and is also recorded on a label affixed to the sample vessel. Subsequently, a Receipt Memorandum is prepared by the Laboratory Sample Custodian, which provides a detailed listing and description of the samples received, and this is forwarded to the Laboratory Director.

Accompanying this Sample Receipt Memorandum are Chain-of-Custody documents and any other pertinent shipping documents which accompanied the samples. The original Sample Receipt Memorandum and associated documentation become a permanent component of the appropriate contract folder which is maintained in this Laboratory. Copies of the Sample Receipt Memorandum and associated documentation are ultimately appended to reports issued by this Laboratory which summarize analytical results obtained for the samples. If requested by U.S. EPA, signed chain-of-custody documentation establishing receipt of the samples by Wright State is provided to the requesting organization.

Samples are stored in locked refrigerators if appropriate, and samples not requiring refrigeration are stored in locked cabinets which are located in secure, locked rooms. The Sample Custodian controls access to the samples, and only authorized personnel are permitted access to the samples, for the purpose of obtaining aliquots of the samples for analysis. All Laboratory Personnel who handle the samples are required to sign the Intralaboratory Sample Tracking Form which accompanies the samples and extracts prepared therefrom, throughout the Laboratory, during all phases of preparation and analysis.

II. PROCEDURES UTILIZED FOR STORING AND PREPARING SAMPLES FOR ANALYSIS, INCLUDING DRYING SOLID SAMPLES AND FILTERING AQUEOUS SAMPLES

A. Storage of Samples

1. Refrigerate all of the samples (at 5°C) upon receipt in the Laboratory and proceed with the procedures outlined below as soon as practical.

B. Sample Preparation

1. Sludge Samples

a. Open the sample container and using a spatula, break the sludge into small particles (about 2 cm diameter or less) and stir the sample vigorously to make it as homogeneous as possible. Remove an aliquot of this sample (approximately 5 g) for an "oven-dried solids as-received" determination, using the procedures described below (Section II.B.1.d.). Remove the remaining sample from the container and distribute it uniformly on a stainless steel screen which is supported at a distance of about 1 cm above a sheet of aluminum foil, both the foil and the screen being contained within a desiccator containing an appropriate water sorbent. To minimize the possibility of contamination or cross-contamination of the sample, only one sample at a time is dried in a given desiccator. Allow the sample to remain in the desiccator until it is essentially dry, as indicated by the sample color, consistency, and ease of mixing. For each group of five sludge samples which are desiccated, prepare a laboratory blank as follows. Place a 15 cm Whatman #42 filter on a stainless steel screen supported at a distance of 1 cm above a sheet of aluminum foil contained in a desiccator and allow the filter to remain in the desiccator for the same period as that which was used for that sample of the five which required the longest drying time. Subsequently remove the filter from the desiccator and continue with the homogenization, drying, and other sample preparative steps described below.

b. When the sample has been dried sufficiently, remove it from the desiccator and transfer it to a laboratory blender which is housed within a glove box or similar enclosure. Following homogenization in the blender, remove an aliquot (approximately 5 g) of the blended solids, accurately weigh this sample aliquot, and subject it to an oven-dried solids determination, as described in Section II.B.1.d. of this protocol.

c. Place the remaining desiccated, blended sample into a clean sample bottle fitted with a Teflon-lined screw cap, and store the bottle in a refrigerator (5°C). An aliquot of this desiccated, blended sample is subsequently analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF by applying the extraction and analysis procedures which are described in Sections IV. and V., respectively, of this protocol.

d. Determination of oven-dried-solids on a sample aliquot is accomplished by placing the weighed aliquot into a tared aluminum boat which is then placed in an oven maintained at 105°C. After heating for a period of twenty-four hours, the aluminum boat containing the sample is removed from the oven, allowed to cool for 30 minutes in a desiccator, and then weighed. The boat and sample are then returned to the oven for an additional four-hour period, after which, the boat is again removed from the oven, allowed to cool and weighed again. The latter procedure is repeated until the weight of the sample as indicated by two successive weighings is observed to be constant. From the observed weight loss upon drying, the percentage of oven-dried-solids in the original sample can be determined. This result, as determined for an aliquot of the sample as received,

is reported as the "initial oven-dried solids as received." The oven-dried weight loss, as determined for an aliquot of the previously desiccated sample (a separate aliquot of which is subsequently analyzed for TCDD/TCDF) is used only to determine the actual weight of the sample aliquot which is analyzed on the oven-dried solids basis.

2. Wood Chip Samples

a. Samples of wood chips in which the chips are relatively large (typically 1-1.5 inches in length) are initially reduced to smaller particle size (2 cm diameter or less) using a laboratory mill. This mill is cleaned thoroughly before each sample is introduced. The pulverized wood sample resulting from this operation is subsampled and dried using exactly the same procedures described for sludge samples in the foregoing Section II.B.1.

3. Ash Samples

a. Ash Samples are prepared using the same procedures as described above for sludge (Section II.B.1.), with the exception that these samples cannot be supported on a screen to dry, and are therefore placed into a shallow, flat dish in order to dry them in the desiccator. The ash is spread as a thin layer over the bottom of the dish and is gently stirred periodically during the drying period.

4. Paper Pulp Samples

a. Remove the pulp sample from the container, and then express as much water from the sample as possible by compressing it with a spatula after wrapping the sample in aluminum foil.

Using the spatula, separate the sample mass into pieces which are about 2 cm or less in diameter, and distribute these pieces uniformly on a stainless steel screen supported about 1 cm above a sheet of aluminum foil, both the screen and the foil being placed in a desiccator. Allow the sample to remain in the desiccator until it is essentially dry, as gauged by color and consistency. For each group of five pulp samples, prepare a laboratory blank using the procedures described in II.B.1. Proceed with the subsampling and other drying procedures, as described for sludge samples, beginning with Section II.B.1.b.

5. Slurry-Type Samples (Secondary Sludge, etc.)

a. Shake the sample bottle vigorously so as to obtain a uniform suspension of the sample and when the sample is homogeneous throughout, as judged by visual inspection, remove an aliquot of the sample and subject it to a Total Suspended Solids Determination, as described in Standard Methods For the Examination of Water and Wastewater, 17th Edition, APHA, AWWA, WPCF, 1986, Method 209C. Allow the remainder of the sample to stand under refrigeration and when the solids appear to have totally settled to the bottom of the container, filter the supernatant using a previously desiccated and tared Gelman Type A/E filter contained in a glass filtering funnel. Remove the solids from the sample container using a clean spatula and utilize three 100 mL aliquots of HPLC water to accomplish three successive rinses of the sample container, and to effect a quantitative transfer of the solids from the sample container to the filter. Following separation of the water from the solid remove the solid along with the filter paper from the funnel and

distribute the solids and the filter paper on a stainless steel screen supported about 1 cm above a sheet of aluminum foil, both the screen and the foil being placed in a desiccator. Allow the sample to dry until it is friable. For each group of five samples, prepare a laboratory blank using the procedures described in II.B.1. Proceed with the subsampling and other drying procedures described for sludge samples, beginning with Section II.B.1.b. Note that the tare weights of all filters used in the separation of the liquid and solid phases of these samples must be subtracted from the combined solids-filter weight to determine the actual weights of the solids samples prepared, since the filter and solids cannot be readily separated.

6. Water and Wastewater Samples

a. Clean and prepare four new 2 L bottles fitted with Teflon-lined caps. Mark the 1 gallon bottle containing the aqueous sample, as received, to show the original level of the liquid in the bottle. Shake the bottle vigorously until all solids in the bottle (which may have settled to the bottom of the bottle if the sample was undisturbed for some time prior to analysis) are suspended, as visually estimated. Pour approximately equal portions of the resuspended aqueous sample from the 1 gallon bottle into each of the four 2 L bottles using a funnel. To accomplish this transfer, pour small portions from the 1 gallon bottle into each of the 2 L bottles in succession, repeating this cycle as many times as necessary to dispense all of the contents of the 1 gallon container. Following each pouring step, recap the 1 gallon bottle and shake it vigorously

to ensure that any particulate in the liquid remains suspended.

b. After all of the contents of the 1 gallon bottle have been transferred to the four 2 L bottles, rinse the 1 gallon bottle successively with two 50 mL portions of HPLC grade water, accumulating these rinses in a 250 mL graduated beaker. Transfer one-fourth of each of these accumulated water rinses to each of the four 2 L bottles. Rinse the 250 mL beaker successively with two 40 mL portions of HPLC water, transferring one-fourth of these rinses to each of the four 2 L bottles. Recap all four 2 L bottles and retain for subsequent extraction and analysis.

c. Rinse the original 1 gallon empty sample bottle successively with two 50 mL portions of methylene chloride, accumulating these in the 250 mL beaker used earlier. Transfer these methylene chloride rinses to a clean 250 mL bottle fitted with a Teflon-lined cap. Rinse the 250 mL beaker successively with two 50 mL portions of methylene chloride, and pool these rinses with the other accumulated methylene chloride rinses in the 250 mL bottle. Reserve the pooled methylene chloride rinses for later splitting and combination with the methylene chloride rinses collected as described in Section III.B. below.

d. Select one of the 2 L bottles containing the split water/wastewater sample, and add to this bottle a solution of the $^{13}\text{C}_{12}$ -labelled TCDD and TCDF internal standards, prepared by combining the 20 μL of Standard 4310-1 with 1.0 mL of acetone in a glass test tube. Rinse the test tube with 0.5 mL acetone, followed by a second 0.5 mL portion of acetone, and transfer these rinses to the aqueous sample.

e. Place a Teflon-coated, magnetic stirring bar in the

sample container, and stir the aqueous sample using a magnetic stirplate for 15 minutes to disperse the spiking solution. Position the stem of a glass filtering funnel to discharge into a pre-cleaned 5 L round bottom flask and place a filter (Whatman 42 filter, fluted fold) into the funnel.

f. Decant and/or pour the internal standard-spiked water sample from the 2 L bottle into the filter and collect the filtrate in the 5 L flask.

g. Rinse the empty 2 L sample container sequentially with three 100 mL aliquots of HPLC grade water, pouring each rinse through the filter, and collecting the filtrate in the 5 L vessel. Check to ensure that all residual particulates and sediments are removed from the original sample container by the aqueous rinsing procedure. Retain this filtrate for subsequent extraction using the procedures described in Section III.

h. Transfer the combined filter and particulate to a clean Petri dish and place them into a desiccator. Allow these solids to dry completely (as indicated by constant weight upon successive weighings). Retain these solids for subsequent extraction as described in Section IV.B.

i. Rinse the original 2 L sample container sequentially with three 50 mL aliquots of methylene chloride. Pour the rinsates through the empty funnel and collect in a clean 1000 mL glass bottle fitted with a Teflon-lined lid. Retain this for subsequent combination with the methylene chloride extract of the aqueous filtrate, obtained as described in Section III.

7. Exceptional Samples

Some of the samples received may be too wet to dry efficiently in a desiccator, but may still not contain sufficient liquid to permit separation of the phases by filtering or other such means. Such samples will be distributed on sheets of aluminum foil and allowed to air-dry at ambient temperature on a bench top. For such samples, the surface area will be recorded, so that a correction can be made, if this is necessary, for contamination or cross-contamination of the samples. The extent of contamination of such samples will be estimated by placing a filter paper blank in the same area where these samples are air-dried and this blank will subsequently be analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF. If the blank is found to be positive for these compounds, the corresponding levels of these compounds in the samples will be corrected for the levels detected in the blank.

III. PROCEDURES FOR EXTRACTING 2,3,7,8-TCDD AND 2,3,7,8-TCDF FROM AQUEOUS FILTRATE

The internal-standard-spiked, aqueous filtrate resulting from application of the procedures described in Section II.B.6. is extracted utilizing the following procedures.

A. Add 400 mL of methylene chloride to the aqueous filtrate contained in the 5 L flask (from the step described in Section II.B.6.g.). Place a magnetic stirring bar into the 5 L flask, place the flask on a stir-plate, and stir the liquid in the flask for 16 hours.

B. Discontinue stirring of the contents of the 5 L flask, allow the aqueous and organic phases to separate, then remove the

organic layer using a pipette, and place it in the 1000 mL bottle containing the accumulated methylene chloride rinsates collected as described in Section II.B.6.i. At this point, also add to the contents of this same 1000 mL bottle, one-fourth of the methylene chloride rinsates collected as described in Section II.B.6.c. Retain the rest of the latter rinsate for subsequent splitting among the extracts of the other three splits of the original aqueous sample, if these are subsequently analyzed.

C. Sequentially, repeat the extraction of the aqueous filtrate two additional times using a 100 mL portion of methylene chloride each time, and combine each extract with the original extract in the 1000 mL bottle. Reserve this pooled extract for later combination with the Soxhlet extract of the particulate and filter, as described in Section IV.

IV. PROCEDURES FOR SOXHLET-EXTRACTING 2,3,7,8-TCDD AND 2,3,7,8-TCDF FROM DRIED BULK SOLIDS AND FILTERED WASTEWATER SOLIDS

A. Dried Sludges, Ash Samples, Wood Chips and Paper Pulp

Solid samples of these types, prepared as described in Section II, are extracted using the following procedures.

1. Prepare a glass Soxhlet extraction thimble (90 mm by 35 mm) for use by rinsing it sequentially with methanol, acetone and methylene chloride. Add silica to form a 3-6 mm layer on the surface of the glass frit at the bottom of the thimble, and place a 10 mm layer of glass wool over the layer of silica.

2. Prepare a Soxhlet extraction apparatus, consisting of a Soxhlet extraction tube, a 250 mL Erlenmeyer flask and a water-cooled condenser, for use by rinsing it sequentially with

methanol, acetone, and methylene chloride, and allowing it to air-dry. Place 175 mL of a solution consisting of 50% benzene and 50% acetone (by volume), along with about 10 pre-cleaned 2 mm glass beads, into the Erlenmeyer flask. Place the Soxhlet thimble (prepared as described in Step IV.A.1.) into the Soxhlet extraction tube, assemble the Soxhlet-extraction apparatus, heat the contents of the Erlenmeyer flask to reflux temperature, and continue the Soxhlet extraction procedure for a period of 3 hours.

3. Remove the heat source from the Soxhlet apparatus, allow the apparatus to cool, and then decant the benzene/acetone solution into a clean, 250 mL flint glass bottle and seal the bottle with a Teflon-lined screw cap. This solution is retained in case additional analyses are required to check the cleanliness of the Soxhlet apparatus, as a QC measure.

4. Place a fresh 175 mL aliquot of 50:50 (volume/volume) benzene/acetone into the Erlenmeyer flask of the Soxhlet extraction apparatus and re-connect the Soxhlet extraction tube to the Erlenmeyer flask. Remove the layer of glass wool from the glass thimble. Transfer an accurately weighed aliquot (approximately 7-10 grams, depending upon the sample type) of the previously desiccated solid sample, prepared as described in Section II, from the sample bottle containing the dried sample to the Soxhlet extraction thimble.

5. Using a microsyringe, add the appropriate internal standard solution (Standard Solution 4610-1, described in Section IV.D.1.) to the solid sample in the Soxhlet extraction thimble.

Place the previously removed glass wool (Step IV.A.4.) on top of the sample in the glass thimble. Place the condenser on the Soxhlet extraction tube and heat the solvent reservoir so that the extraction solvent refluxes. Soxhlet extract the sample for a period of 16 hours, then discontinue heating the apparatus and allow it to cool to ambient temperature.

6. Remove the Soxhlet extractor from the Erlenmeyer flask reservoir and replace the extractor with a 3-ball Snyder column. Resume heating the reservoir and concentrate the benzene/acetone extract to a volume of about 15 mL. Rinse the Snyder column twice with small quantities of hexane, then continue heating and concentrating the solution in the reservoir with the column in place until a final volume of 10 mL is attained.

7. Using a 10 mL disposable pipette, transfer the concentrated solution obtained in Step IV.A.6. to a pre-rinsed, 125 mL flint glass bottle fitted with a Teflon-lined screw cap. Rinse the Erlenmeyer flask four times using 10 mL aliquots of hexane, transferring each rinse solution to the 125 mL bottle, to effect a quantitative transfer of the concentrate from the Erlenmeyer flask to the bottle.

8. Proceed with the remainder of the clean-up and analytical procedures described in Section V.

B. Soxhlet Extraction of Water and Filtered Wastewater Solids

1. Remove the desiccated filter and associated solids resulting from filtration of a water/wastewater sample containing particulates, as described in Section II, from its sample container, and immediately place the filter and solids into a Soxhlet extraction thimble which has been pre-cleaned, as

described above in Step IV.A.1.

2. Pre-clean a Soxhlet extraction apparatus as described in Steps IV.A.2 through IV.A.4.

3. Concentrate the methylene chloride extract resulting from extraction of the aqueous filtrate which has been pooled with other methylene chloride rinsates (obtained as described in Section III.B.) by transferring about 150 mL of the methylene chloride extract to a 250 mL Erlenmeyer flask, attaching a 3-ball Snyder column to the flask and heating the flask to concentrate the methylene chloride. Continue to transfer 150 mL aliquots of the methylene chloride extract to the Erlenmeyer flask as each portion is reduced in volume by concentration, until the volume of the extract is reduced to about 25 mL. Then add 150 mL of 50:50 volume:volume benzene-acetone to the Erlenmeyer flask containing the residue from the methylene chloride concentration and reconnect the flask to the Soxhlet extractor. Note that it is not necessary to spike this sample with internal standards since the wastewater sample was previously spiked with internal standards prior to filtering.

4. Heat the Soxhlet apparatus and extract the filter and solids for a period of 16 hours, then discontinue heating and allow the apparatus to cool. Remove and concentrate the extract as described in Section IV.A.6. Transfer the concentrate to a new sample bottle, as described in Section IV.A.7.

5. Proceed with the remainder of the clean-up and analytical procedures described in Section V.

V. PROCEDURES FOR ISOLATING AND QUANTITATING 2,3,7,8-TCDD
AND 2,3,7,8-TCDF PRESENT IN ORGANIC EXTRACTS
OF PAPER MILL PROCESS AND EFFLUENT SAMPLES

A. Preliminary Separation of 2,3,7,8-TCDD and 2,3,7,8-TCDF
From Other Chemical Residues in the Extracts Obtained As
Described in Sections III. and IV.

Organic extracts obtained utilizing the procedures described in Sections III. and IV. are subjected to the fractionation procedures which follow.

1. Add 30 mL of aqueous potassium hydroxide (20% w/v) to the bottle containing the sample extract, seal the bottle and agitate it for a period of 10 minutes. Aspirate and discard the aqueous phase, retaining the organic phase.

2. If the aqueous layer from the previous step appears to be colored following the base extraction procedure, then repeat this operation (Step V.A.1.).

3. Add 30 mL of double-distilled water to the organic phase from Step V.A.1., seal the bottle, and agitate the mixture for a period of 1 minute. Again, aspirate and discard the aqueous phase, retaining the organic phase.

4. Add 30 mL of concentrated sulfuric acid to the residual hexane extract from the previous step, seal the bottle, and agitate it for a period of 10 seconds. If emulsions form, centrifuge the bottle to achieve separation of the organic and acidic aqueous phases. Remove and discard the aqueous acidic layer, retaining the organic layer.

5. Repeat the concentrated sulfuric acid wash (the foregoing step) this time adding 30 mL of sulfuric acid to the sample extract, and agitating the acidified sample for 10 minutes. Again, aspirate and discard the aqueous layer. Repeat

this step until the acid layer is visibly colorless.

6. Repeat Step V.A.3.

7. Add 5 g of anhydrous sodium sulfate to the organic extract and allow the mixture to stand for at least 15 minutes.

8. Quantitatively transfer the organic extract, using hexane to rinse the sample bottle, to a clean test tube, and reduce the volume to approximately 5 mL by passing a stream of pre-purified nitrogen over the extract, while maintaining the test tube at 55°C in a water bath.

9. Proceed with the liquid column chromatographic procedures described in Section V.B.

B. Liquid Column Chromatographic Procedures for Isolating 2,3,7,8-TCDD and 2,3,7,8-TCDF From Extracts Previously Washed with Acids and Bases

1. Fabricate a glass chromatography-column (20 mm OD x 230 mm long) tapered to 6 mm OD on one end. Pack the column, in succession, with a plug of glass wool (silanized), 1.0 g silica, 2.0 g silica containing 28% (w/w) 1 M NaOH, 1.0 g silica, 4.0 g silica containing 30% (w/w) sulfuric acid, and 2.0 g silica.

2. Quantitatively transfer the concentrated extract obtained in Step V.A.8., along with two rinsings of the sample container, using 1 mL portions of hexane each time, to the column and elute the column with 90 mL of hexane. Collect the entire eluate and concentrate to a volume of 1-2 mL in a centrifuge tube.

3. If any layer of the silica gel column implemented in Step V.B.2. becomes visibly colored as the column is eluted, repeat Steps V.B.1. and V.B.2.

4. Prepare a liquid chromatography column (11 mm OD x 120 mm) by packing the constricted end with a plug of silanized glass wool and then adding three grams of Woelm basic alumina (previously activated overnight at 600°C in a muffle furnace and placed in a desiccator for 30 minutes just prior to use).

5. Aspirate the concentrated extract obtained in Step V.B.2. and transfer it onto the alumina column prepared in Step V.B.4. Rinse the test tube which contained the concentrate successively with two 1 mL portions of hexane, each time transferring the rinse solution to the alumina column.

6. Elute the alumina column as follows: (a) Elute the alumina column with 10 mL of 3% (v/v) methylene chloride-in-hexane, taking care not to let the column become completely dry during the elution, and discard the entire eluate. (b) Elute the column with 15 mL of 20% (v/v) methylene chloride-in-hexane and discard the entire eluate. (c) Elute the column with 15 mL of 50% (v/v) methylene chloride-in-hexane, retain this entire eluate, and reduce the volume to about 1.0 mL by passing a stream of pre-purified nitrogen over the solution while heating the solution in a 55°C water bath.

7. Prepare a second alumina column as described in Step V.B.4., transfer the concentrated eluate obtained in Step V.B.6. to the column, and elute the column as described in Step V.B.6. Collect the column eluate and concentrate it to a volume of about 1 mL.

8. Prepare a liquid chromatography column by cutting off a 9-inch disposable Pasteur pipette 1.25 cm above the tip constriction leaving a straight glass tube with an indentation

approximately 2.5 cm inch from the top. Insert a filter paper disk in the tube and position the disk 2.5 cm below the indentation. Add a sufficient quantity of PX-21 Carbon/Celite 545 (prepared as described in Section V.C. of this Protocol) to the tube to form a 2 cm length of the Carbon/Celite. Insert a glass wool plug on top of the Carbon/Celite. Pre-elute the column sequentially with 2 mL of a 50% benzene/50% ethyl acetate solution (v/v), 2 mL of 50% methylene chloride/50% cyclohexane, and 2 mL of hexane, and discard these eluates. Transfer the residual sample extract (in 1 mL of hexane) resulting from the alumina column cleanup (Step V.B.7.) onto the top of the Carbon/Celite column, along with 1 mL of a hexane rinse of the original sample vessel. Elute the column with 2 mL of 50% methylene chloride/50% cyclohexane solution and 2 mL of 50% benzene/50% ethyl acetate and discard these eluates. Invert the column and elute it in the reverse direction with 4 mL of toluene, retaining this eluate. Concentrate the collected column effluent to a volume of about 1 mL using a stream of pre-purified nitrogen.

9. Prepare a third alumina column as described in Step V.B.4., transfer the concentrated eluate from the second alumina column sequence to this column, elute the column, and collect the eluate as already described in Step V.B.6, in a test tube. Concentrate the collected eluate to a volume of about 1 mL, then quantitatively transfer the concentrate to a 3 mL micro-reaction vessel (Reacti-vial), using two 1 mL portions of methylene chloride to rinse the test tube, and also transferring these to

the micro-reaction vessel. Concentrate the solution in the latter vessel just to dryness, using a stream of dry N₂, as described previously. Rinse the walls of the micro-reaction vessel using 0.5 mL of methylene chloride, and again concentrate just to dryness. Seal the vessel and store it in a freezer (-15°C). Just prior to GC-MS analysis, remove the vessel from the freezer, allow it to warm to ambient temperature, and reconstitute the residue in the vessel by adding 10 µL of Standard 4643-1 to the vial.

C. Reagents and Chemicals

Reagents and chemicals used in implementing the procedures described herein and the sources of these are described in the following.

1. Potassium hydroxide, anhydrous, granular sodium sulfate and sulfuric acid (all Reagent Grade): J.T. Baker Chemical Co., Glen Ellyn, IL, or Fisher Scientific Co., Cincinnati, OH. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for four hours, then removing the beaker and allowing it to cool in a desiccator. Store the purified sodium sulfate in a bottle equipped with a Teflon-lined screw cap.

2. Acetone, hexane, methylene chloride, benzene, ethyl acetate, methanol, toluene, cyclohexane, isooctane: "Distilled in Glass" Burdick and Jackson, Muskegon, MI.

3. Dodecane and Tridecane (Reagent Grade): Sigma Chemical Co., St. Louis, MO.

4. Basic Alumina (Activity Grade 1): ICN Pharmaceuticals,

Cleveland, OH. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowing to cool in a desiccator for 30 minutes prior to use.

5. Silica (Bio-Sil A 100/200 mesh): Bio-Rad, Rockville Centre, NY. the Bio-Sil A is conditioned prior to use by initially placing a 200 g portion of the silica in a 30 mm x 30 cm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a pre-purified nitrogen cylinder through a series of four traps (stainless steel tubes, 1.0 cm OD x 10 cm long)*. Trap Number 1 contains a mixture composed of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), graphite (100 mesh, 1-M-USP), and activated carbon (50 to 200 mesh), in a 7:1.5:1.5 ratio. Chromosorb W/AW and Apiezon L were obtained from Supelco, Inc., Bellefonte, Pennsylvania; graphite was obtained from Ultracarbon Corporation, Bay City, Michigan; activated carbon was obtained from Fisher Scientific Co., Cincinnati, Ohio. Trap Number 2 contains Molecular Sieve 13X (60/80 mesh, obtained from Supelco, Inc., Bellefonte, Pennsylvania). Trap Number 3 contains silica gel impregnated with 30% (w/w) sulfuric acid (prepared as described in V.C.6. below). Trap Number 4 contains Carbosieve S 80/100 mesh, (obtained from Supelco, Inc., Bellefonte, Pennsylvania). The first step in conditioning the Bio-Sil A entails heating the glass tube containing the 200 g aliquot of silica for 30 minutes at 180°C while purging with nitrogen (flow

*. See T. J. Nestrick and L. L. Lamparski, Anal. Chem 53, 122 (1981) for additional details and rationale regarding use of these traps.

rate 50-100 mL/minute), subsequently the tube is removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50 to 100 mL/minute flow), the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 180°C over a period of 25 minutes and maintained at 180°C for 90 minutes. Heating is then discontinued but the nitrogen purge is maintained until the tube cools to room temperature. Finally, the silica is transferred to a clean, dry, glass bottle and capped with a Teflon-lined screw cap for storage in a desiccator.

6. Silica Gel Impregnated with Sulfuric Acid (30% w/w): Concentrated sulfuric acid (4.4 g) is combined with 10.0 g silica gel (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H₂SO₄-silica gel is stored in a screw-capped bottle (equipped with a Teflon-lined cap).

7. Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (30 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

8. Carbon/Celite: A 10.7 g aliquot of PX-21 carbon (Anderson Development Co., Adrian, Michigan) is combined with 125

g of Celite 545 (Fisher Scientific Co.) in a 250 mL glass bottle, fitted with a Teflon-lined cap, and the mixture is shaken to obtain a uniform mixture. The Carbon/Celite mixture is stored in the screw-capped bottle.

9. Nitrogen (Pre-purified) and Hydrogen (Ultra High Purity): Airco, Inc., Montvale, NJ.

D. Calibration and Spiking Standards

Stock standard solutions of the appropriate TCDD and TCDF isomers, and mixtures thereof, are prepared in a glovebox, using weighed quantities of the authentic isomers. These stock solutions are contained in appropriate amber bottles and are stored tightly stoppered in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly (by comparing instrument response factors for them over a period of time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The standard solutions which may be required to perform the quantitative analyses of 2,3,7,8-TCDD and 2,3,7,8-TCDF are listed below.

1. Internal Standard Solution 4610-1. An aliquot of this solution is added to samples which are to be analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF. Prepare a stock solution containing the following isotopically-labelled TCDD and TCDF compounds in isooctane at the indicated concentrations: 0.05 ng/ μ L $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, 0.02 ng/ μ L $^{37}\text{Cl}_4$ -2,3,7,8-TCDD, 0.05 ng/ μ L $^{13}\text{C}_{12}$ -2,3,7,8-TCDF, and 0.02 ng/ μ L $^{37}\text{Cl}_4$ -2,3,7,8-TCDF. Typically a twenty microliter aliquot of this standard solution

is added to each sample aliquot prior to preparation and the $^{13}\text{C}_{12}$ -labelled materials serve as internal standards for use in quantitation. Recovery of these standards is also used to gauge the overall efficacy of the analytical procedure.

2. Standard Solution 4643-1. Prepare a stock solution containing 0.05 ng of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and 0.10 ng of $^{37}\text{Cl}_4$ -1,2,7,8-TCDF/ μL tridecane. A 10 microliter aliquot of this standard is added to the final extract obtained for each sample just prior to GC-MS analysis. When the DB-5 capillary column is employed, the $^{13}\text{C}_{12}$ -1,2,3,4-TCDD is used as an external standard in the quantitation of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and the $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standards present in the final extract, and the percent recovery of each of these $^{13}\text{C}_{12}$ -labelled internal standards is calculated on the basis of this quantitative analysis. The $^{37}\text{Cl}_4$ -1,2,7,8-TCDF external standard is employed in quantitating the concentration of $^{13}\text{C}_{12}$ -2,3,7,8-TCDF when the hybrid DB-5/DB-225 capillary column is implemented in quantitating 2,3,7,8-TCDF. These latter results are subsequently implemented in calculating the percent recovery of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard achieved during the analysis performed using the hybrid column.

3. Standard Solutions 4616-1, 4616-2, 4617-1, and 4617-2. Prepare four separate calibration standards as follows: (a) Standard 4616-1, 0.2 ng/ μL 2,3,7,8-TCDD, 0.2 ng/ μL 2,3,7,8-TCDF, 0.05 ng/ μL $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, 0.05 ng/ μL $^{13}\text{C}_{12}$ -2,3,7,8-TCDF, 0.02 ng/ μL $^{37}\text{Cl}_4$ -2,3,7,8-TCDD, 0.02 ng/ μL $^{37}\text{Cl}_4$ -2,3,7,8-TCDF, 0.05 ng/ μL $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and 0.10 ng/ μL $^{37}\text{Cl}_4$ -1,2,7,8-TCDF;

(b) Standard 4616-2, 0.05 ng/ μ L 2,3,7,8-TCDD, 0.05 ng/ μ L 2,3,7,8-TCDF plus the same concentration of isotopically-labelled standards included in 4616-1; (c) Standard 4617-1, 0.01 ng/ μ L 2,3,7,8-TCDD, 0.01 ng/ μ L 2,3,7,8-TCDF plus the same concentration of isotopically-labelled standards included in 4616-1; (d) Standard 4617-2, 0.0025 ng/ μ L 2,3,7,8-TCDD, 0.0025 ng/ μ L 2,3,7,8-TCDF plus the same concentration of isotopically-labelled standards included in 4616-1; (e) Standard 4636-1, 2.0 ng/ μ L 2,3,7,8-TCDD, 2.0 ng 2,3,7,8-TCDF plus the same concentrations of isotopically-labelled standards included in 4616-1. Aliquots of these standards are injected to obtain data which is implemented in constructing the calibration curve used in quantitating 2,3,7,8-TCDD and 2,3,7,8-TCDF.

4. Standard Mixture 109071-1. Prepare an isooctane solution containing 0.05 ng/ μ L concentrations of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; 1,2,3,4-TCDD and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the DB-5 GC column). The remaining isomers serve to demonstrate that the 2,3,7,8-TCDD isomer is resolved from the other nearest eluting TCDD isomers, and that the column therefore yields quantitative data for the 2,3,7,8-TCDD isomer alone.

5. Standard Mixture 4612-2. Prepare a solution containing 0.250 ng/ μ L 2,3,7,8-TCDF in tridecane. This standard is implemented when it is desired to add only native 2,3,7,8-TCDF

to a sample.

6. Standard Mixture 76179-1. Prepare a solution containing approximately 0.250 ng/ μ L of each of the 37 TCDF isomers (exclusive of 2,3,7,8-TCDF) in isooctane. This standard is used when it is desired to add all of the TCDF isomers except 2,3,7,8-TCDF to a sample. This standard is also implemented to determine the relative retention times of the TCDF isomers and, when this standard is co-injected with an aliquot of standard 4612-2, the efficacy of a particular gas chromatographic column for separating 2,3,7,8-TCDF from each of the 37 other TCDF isomers can be ascertained.

7. Standard Mixtures 4614-1 and 4614-2. For Mixture 4614-1, prepare a solution containing 0.025 ng 2,3,7,8-TCDD and 0.025 ng 2,3,7,8-TCDF per microliter of tridecane. For mixture 4614-2, prepare a solution containing 0.005 ng 2,3,7,8-TCDD and 0.005 ng 2,3,7,8-TCDF. These standards are employed when it is desired to simultaneously add both native 2,3,7,8-TCDD and native 2,3,7,8-TCDF to a sample.

E. Gas Chromatographic-Mass Spectrometric (GC-MS) Procedures for Quantitating 2,3,7,8-TCDD and 2,3,7,8-TCDF Present in Sample Extracts

Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the instrumentation and operating parameters listed below. Typically, 1 to 5 μ L portions of the extract are injected into the GC. Sample extracts are initially analyzed using the DB-5 capillary GC column at a mass spectral resolution of 1:600 to obtain data on the concentration of 2,3,7,8-TCDD and to ascertain if 2,3,7,8-TCDF or other isomers

which coelute with 2,3,7,8-TCDF are present. If the latter are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using a newly developed hybrid column which consists of a 10 meter length of a 0.25 mm I.D. fused silica open tubular DB-5 capillary column coupled with a 30 meter section of a 0.25 mm I.D. DB-225 column. Again, the mass spectrometer is operated at low resolution (1:600). The hybrid column uniquely separates 2,3,7,8-TCDF from the other 37 TCDF isomers and therefore yields definitive data on the concentration of 2,3,7,8-TCDF in the extract which is analyzed. However, in some instances compounds are present in the sample extract which give rise to ion masses which, at low (1:600) mass resolution, interfere with the quantitation of 2,3,7,8-TCDF. In these instances the analysis of the sample extract can be repeated, at the option of USEPA/NCASI, using the DB-5/DB-225 hybrid column, but this time at a mass spectral resolution of 1:6,500. The instrumentation and operating parameters utilized in these analyses are as follows.

1. Gas Chromatograph: Perkin-Elmer Sigma III or Varian 3740

a. Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection): injector temperature, 280°C.

b. Carrier gas:

- i) For DB-5 column: Hydrogen, 30 lb. head pressure (MS-25 jet separator); 18 lb. head pressure (MS-30 direct coupled)

- ii) For DB-5/DB-225 column: Hydrogen, 30 lb. head pressure (MS-25 jet separator); 18 lb. head pressure (MS-30 direct coupled)

c. Capillary Column 1: For quantitation of 2,3,7,8-TCDD (isomer specific) and 2,3,7,8-TCDF (non-isomer specific), 60 M x 0.25 mm ID fused silica coated with a 0.25 micron film of DB-5, temperature programmed, see Table 1 for temperature program.

Capillary Column 2: For quantitation of 2,3,7,8-TCDF (isomer specific), 10 M x 0.25 mm ID fused silica column coated with a 0.25 micron film of DB-5 coupled with a 30 M x 0.25 mm I.D. fused silica column coated with a 0.25 micron film of DB-225. This column is temperature programmed as indicated in Table 2.

d. Interface Temperature: 250°C

2. Mass Spectrometer: Kratos MS-30 or Kratos MS-25

a. Ionization Mode: Electron impact (70 eV)

b. Static Resolution: 1:600 (10% valley) or 1:6,500 depending upon instrumentation.

c. Source Temperature: 250°C

d. Accelerating Voltage: 2KV or 4KV, depending upon instrument.

e. Ions Monitored: Computer controlled Selected Ion Monitoring, See Tables 1 and 2 for list of ion masses monitored and time intervals during which ions characteristic of 2,3,7,8-TCDD and 2,3,7,8-TCDF are monitored. Note that in the case of quantitation of the 2,3,7,8-TCDF, the hexachlorinated diphenylether molecular ion, which could give rise to an interference at m/z 304 and 306, is also monitored as indicated in Table 2.

3. Calibration Procedures:

a. Calibrating the MS Mass Scale: Perfluorokerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 350. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

b. Table 1 shows the GC temperature program typically used to resolve 2,3,7,8-TCDD from each of the 21 other TCDD isomers and indicates the ion-masses monitored and the time analytical sequence implemented for isomer specific quantitation of 2,3,7,8-TCDD and non-isomer specific quantitation of 2,3,7,8-TCDF. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixture 109071-1, as well as the calibration mixtures (4616-1, 4616-2, 4617-1, and 4617-2) into the GC-MS. It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

c. Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize Standard Mixture 109071-1 to check the DB-5 column resolution for 2,3,7,8-TCDD, and utilize a combination of Standards 4612-2 and 76179-1 to verify that 2,3,7,8-TCDF is separated from all of the other TCDF isomers on the hybrid DB-5/DB-225 column. A 25% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers and similar separation of

2,3,7,8-TCDF from other neighboring TCDFs is required. Analyze the column performance standards using the instrumental parameters specified above and in Table 1 and 2. The column performance evaluation must be accomplished each time a new column is installed in the gas chromatograph, and at the beginning and conclusion of each 8 hour operating period. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new DB-5 and/or DB-5/DB-225 hybrid GC column must be installed.

d. Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF contained in the sample extract is accomplished by analyzing a series of at least three working calibration standards. Each of these standards is prepared to contain the same concentration of each of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standards used here but a different concentration of the native 2,3,7,8-TCDD and 2,3,7,8-TCDF. Typically, mixtures will be prepared so that the ratio of the native 2,3,7,8-TCDD and 2,3,7,8-TCDF to the isotopically-labelled TCDD/TCDF ranges between 0.05 and 4.0 in the four working calibration mixtures. Prior to injecting aliquots of actual sample extracts, an aliquot of a standard containing typically 0.2 ng of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and 0.4 ng of $^{37}\text{Cl}_4$ -1,2,7,8-TCDF (Standard 4643-1) is used to dilute the extract in the sample vials and is therefore co-injected along with the sample extract, in order to obtain data

permitting calculation of the percent recovery of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standards. When the analysis of the extract is performed using the DB-5 capillary column, the $^{13}\text{C}_{12}$ -1,2,3,4-TCDD standard is implemented as the external standard in quantitating both $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF. However, when the hybrid DB-5/DB-225 column is employed in analyzing the 2,3,7,8-TCDF, the $^{37}\text{Cl}_4$ -1,2,7,8-TCDF is implemented in quantitating the $^{13}\text{C}_{12}$ -labelled TCDF internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF, as well as the concentration of native 2,3,7,8-TCDD and 2,3,7,8-TCDF in the sample (from the extract analysis), are summarized below.

Daily checks of the instrument performance will be accomplished using Standard 4617-1. This standard will be injected at the beginning of each work-day (or the beginning of each 8-hour shift) and RRF values for 2,3,7,8-TCDD and 2,3,7,8-TCDF will be calculated. If either of these RRF values deviate from the values contained in the calibration curve by more than $\pm 20\%$, then a second injection will be made and RRF values for the two compounds will be again calculated. If either of these RRF values also fail to agree with the calibration curve by more than $\pm 20\%$, then the entire series of calibration standards will be analyzed, new RRF values will be calculated, and a new calibration curve will be constructed and applied in subsequent analyses.

4. Equations Used for Calculating Analytical Results from the GC-MS Data

- a. Equation 1: Calculation of Relative Response Factor for native 2,3,7,8-TCDD (RRF₂) using ¹³C₁₂-2,3,7,8-TCDD as an internal standard.

$$RRF_2 = (A_s C_{is} / A_{is} C_s)$$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for ¹³C₁₂-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

C_{is} = Concentration of the internal standard (pg./μL.)

C_s = Concentration of the 2,3,7,8-TCDD (pg./μL.)

- b. Equation 2: Calculation of Relative Response Factor for ¹³C₁₂-2,3,7,8-TCDD (RRF_b)

$$RRF_b = (A_{is} C_{es} / A_{es} C_{is})$$

where: A_{is} = SIM response for ¹³C₁₂-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

A_{es} = SIM response for ¹³C₁₂-1,2,3,4-TCDD external standard at m/z 332 + 334

C_{is} = Concentration of the ¹³C₁₂-2,3,7,8-TCDD internal standard (pg./μL.)

C_{es} = Concentration of the ¹³C₁₂-1,2,3,4-TCDD standard (pg./μL.)

- c. Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}\text{C}_{12}$ -2,3,7,8-TCDD as internal standard

$$\text{Concentration, pg./g.} = (A_s) (I_s) / (A_{is}) (RRF_2) (W)$$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD internal standard ion at m/z 332 + 334

I_s = Amount of internal standard added to each sample (pg.)

W = Weight of sample in grams

RRF_2 = Relative response factor from Equation 1

- d. Equation 4: Calculation of % recovery of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD internal standard

$$\% \text{ Recovery} = 100 (A_{is}) (E_s) / (A_{es}) (I_1) (RRF_b)$$

A_{is} = SIM response for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD internal standard ion at m/z 332 + 334

A_{es} = SIM response for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD external standard ion at m/z 332 + 334

E_s = Amount of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD external standard co-injected with sample extract

I_1 = Theoretical amount of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD internal standard in injection

RRF_b = Relative response factor from Equation 2

- e. Equation 5: Calculation of Relative Response Factor for native 2,3,7,8-TCDF (RRF_c) using ¹³C₁₂-2,3,7,8-TCDF as an internal standard.

$$RRF_c = (A_s C_{is} / A_{is} C_s)$$

where: A_s = SIM response for 2,3,7,8-TCDF ion at m/z 304 + 306

A_{is} = SIM response for ¹³C₁₂-2,3,7,8-TCDF internal standard ion at m/z 316 + 318

C_{is} = Concentration of the internal standard (pg./μL.)

C_s = Concentration of the 2,3,7,8-TCDF (pg./μL.)

- f. Equation 6: Calculation of Relative Response Factor for ¹³C₁₂-2,3,7,8-TCDF (RRF_d) (When analysis is performed using DB-5 Column)

$$RRF_d = (A_{is} C_{es} / A_{es} C_{is})$$

where: A_{is} = SIM response for ¹³C₁₂-2,3,7,8-TCDF internal standard ion at m/z 316 + 318

A_{es} = SIM response for ¹³C₁₂-1,2,3,4-TCDD external standard at m/z 332 + 334

C_{is} = Concentration of the ¹³C₁₂-2,3,7,8-TCDF internal standard (pg./μL.)

C_{es} = Concentration of the ¹³C₁₂-1,2,3,4-TCDD external standard (pg./μL.)

- g. Equation 7: Calculation of Relative Response Factor for ¹³C₁₂-2,3,7,8-TCDF (RRF_e) (When analysis is performed using DB-5/DB-225 Hybrid Column)

$$RRF_e = (A_{is} C_{es} / A_{es} C_{is})$$

where A_{is} = SIM response for ¹³C₁₂-2,3,7,8-TCDF internal standard ion at m/z 316 + 318

A_{es} = SIM response for ³⁷Cl₄-1,2,7,8-TCDF external standard at m/z 312

C_{is} = Concentration of the ¹³C₁₂-2,3,7,8-TCDF internal standard (pg/μL)

C_{es} = Concentration of the ³⁷Cl₄-1,2,7,8-TCDF external standard (pg/μL)

- h. Equation 8: Calculation of concentration of native 2,3,7,8-TCDF using $^{13}\text{C}_{12}$ -2,3,7,8-TCDF as internal standard

$$\text{Concentration, pg./g.} = (A_s) (I_s) / (A_{I_s}) (RRF_c) (W)$$

where: A_s = SIM response for 2,3,7,8-TCDF ion at m/z 304 + 306

A_{I_s} = SIM response for the $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard ion at m/z 316 + 318

I_s = Amount of internal standard added to each sample (pg.)

W = Weight of sample in grams

RRF_c = Relative response factor from Equation 5

- i. Equation 9: Calculation of % recovery of $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard (When analysis is performed using DB-5 Column)

$$\% \text{ Recovery} = 100 (A_{I_s}) (E_s) / (A_{E_s}) (I_1) (RRF_d)$$

A_{I_s} = SIM response for $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard ion at m/z 316 + 318

A_{E_s} = SIM response for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD external standard ion at m/z 332 + 334

E_s = Amount of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD external standard co-injected with sample extract

I_1 = Theoretical amount of $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard in injection

RRF_d = Relative response factor from Equation 6

- j. Equation 10: Calculation of % recovery of $^{13}\text{C}_{12}$ -2,3,7,8-TCDF internal standard (when analysis is performed using hybrid DB-5/DB-225 column)

$$\% \text{ Recovery} = 100 (A_{I_s}) (E_s) / (A_{E_s}) (I_1) (RRF_e)$$

A_{I_s} = SIM response for $^{13}\text{C}_{12}$ -TCDF internal standard ion at m/z 316 + 318

A_{E_s} = SIM response for $^{37}\text{Cl}_4$ -1,2,7,8-TCDF external standard ion at m/z 312

E_s = Amount of $^{37}\text{Cl}_4$ -1,2,7,8-TCDF external standard in injection

RRF_e = Relative response factor from Equation 7

5. Criteria Applied for Qualitative Identification of
2,3,7,8-TCDD and 2,3,7,8-TCDF

a. Mass Spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of TCDD and TCDF (see Tables 1 and 2) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chromatographic retention times observed for 2,3,7,8-TCDD and 2,3,7,8-TCDF must be correct relative to the appropriate stable-isotopically labelled internal standard.

b. The ratio of the intensity of the response for the molecular ion, $[M]^+$, to the response for the $[M+2]^+$ ion must be within $\pm 15\%$ of the theoretically expected ratio for both the native TCDD and native TCDF signals (for example, 0.77 in the case of TCDD and TCDF; therefore, the acceptable range for this ratio is 0.65 to 0.89).

c. The intensities of the ion signals for either 2,3,7,8-TCDD or 2,3,7,8-TCDF are considered to be detectable if each exceeds the baseline noise by a factor of at least 2.5:1.

d. For reliable detection and quantitation of 2,3,7,8-TCDF, it is also necessary to monitor the molecular ion of hexachlorinated diphenyl ether which, if present, could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the TCDF. Accordingly, in Tables 1 and 2, the appropriate ion-mass for hexachlorinated diphenyl ether is specified and this ion-mass must be monitored simultaneously with the 2,3,7,8-TCDF ion-masses. Only when the

response for the diphenyl ether ion-mass is not detected at the same time as the 2,3,7,8-TCDF ion mass can the signal obtained for 2,3,7,8-TCDF be considered unique.

F. Quality Assurance/Quality Control Procedures

1. The Quality Assurance and Quality Control procedures itemized below will be implemented throughout the course of the Dioxin I analyses:

a. Each sample analyzed is spiked with stable isotopically-labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 40-120%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native 2,3,7,8-TCDD and 2,3,7,8-TCDF, but may result in higher detection limits than are desired.

b. Processing and analysis of at least one method blank sample is generally accomplished for each set of samples.

c. It is desirable to analyze at least one sample spiked with representative native TCDD/TCDF for each set of samples. The results of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of the native 2,3,7,8-TCDD and 2,3,7,8-TCDF added to the sample is within $\pm 50\%$ of the known concentration.

d. At least one of the samples analyzed out of each set is usually analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

2. A report describing the results of the analyses

discussed above will, at a minimum, include copies of original mass chromatograms obtained during analyses of the sample extracts and associated calibration standards, a description of the analytical methodology employed, and tabulations of calculated results. Calculations and manipulation of data are most efficaciously accomplished using computerized data reduction techniques. The tabulations of calculated results provided in the report will include a set of tables showing the concentrations of 2,3,7,8-TCDD and an additional set of tables showing the concentrations of 2,3,7,8-TCDF which were measured in each sample. Also shown in the tables are the quantity of each sample analyzed; the detection limits for those samples which were found to contain no 2,3,7,8-TCDD or 2,3,7,8-TCDF; the GC-MS instrument implemented in the analysis; the date and time of the analysis; the ratio of the intensities of m/z 320 vs. m/z 322 and m/z 332 vs. m/z 334 for TCDD and the ratio of the intensities of m/z 304 vs. m/z 306 and m/z 316 vs. m/z 318 for TCDF; the percent recovery of the internal standard ($^{13}\text{C}_{12}$ -2,3,7,8-TCDD or $^{13}\text{C}_{12}$ -2,3,7,8-TCDF); and the ion intensities for the following m/z's: 320, 322, 257, 332 and 334 for TCDD, and 304, 306, 241, 316 and 318 for TCDF. Examples of typical tables of the type described above are provided in Attachment A. Other tabulations of data shown in Attachment A which will be provided in the report include a table showing a summary of the calibration data obtained for 2,3,7,8-TCDD and 2,3,7,8-TCDF, which show the date of the calibration; the GC-MS instrument implemented; the WSU identification number of the calibration solution; the calculated

response factors and the mean response factors obtained for native 2,3,7,8-TCDD, native 2,3,7,8-TCDF, $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF; and the % valley observed for the GC separation of the 2,3,7,8-TCDD from adjacent-eluting TCDD isomers and of the 2,3,7,8-TCDF from adjacent-eluting TCDF isomers. A typical calibration summary presentation is provided in Attachment A. Additional tables which present calibration data and results obtained for each individual sample in a more detailed manner than that given in the summary tables mentioned earlier are also shown in Attachment A.

TABLE 1

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF 2,3,7,8-TCDF AND 2,3,7,8-TCDD
IN ENVIRONMENTAL SAMPLES USING A 60 M DB-5 COLUMN

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of of [M]:[M+2]*
0.00	Injection, Splitless	180					
	Start Tetra Program: sweep = 350 ppm; time/mass = 0.08 sec.						
				240.9378	[M-COCl]*	TCDF	
				256.9328	[M-COCl]*	TCDD	
				303.9016	[M]*	TCDF	
				305.8996	[M+2]*	TCDF	
				315.9418	[M]*	¹³ C ₁₂ -2,3,7,8-TCDF	0.77
				317.9388	[M+2]*	¹³ C ₁₂ -2,3,7,8-TCDF	0.77
				319.8965	[M]*	TCDD	
				321.8935	[M+2]*	TCDD	
				331.9367	[M]*	¹³ C ₁₂ -2,3,7,8-TCDD,	0.77
						¹³ C ₁₂ -1,2,3,4-TCDD	
						¹³ C ₁₂ -2,3,7,8-TCDD,	
				333.9337	[M+2]*	¹³ C ₁₂ -1,2,3,4-TCDD	
						¹³ C ₁₂ -2,3,7,8-TCDD,	
						¹³ C ₁₂ -1,2,3,4-TCDD	0.77
				373.8207	[M]*	Hexachlorodiphenyl Ether	
1.00	Turn on split valve:	180					
	Begin Temp Program to 240°C	180	2				
31.00	Stop Tetra Program	240					
31.00	Increase Column Temp Ballistically Program to 300°	240					
45.00	Commence Cooling GC Column Oven Temperature to 180°	300					

TABLE 2

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF 2,3,7,8-TCDF
IN ENVIRONMENTAL SAMPLES USING A HYBRID DB-5/DB-225 COLUMN

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of of (M) ⁺ : (M+2) ⁺
0.00	Injection, Splitless	180					
	Start Tetra Program: sweep = 350 ppm; time/mass = 0.08 sec.			240.9378 303.9016 305.8996 311.8897 315.9418 317.9388 331.9367 333.9337 373.8207	[M-COC1] ⁺ [M] ⁺ [M+2] ⁺ [M] ⁺ [M] ⁺ [M+2] ⁺ [M] ⁺ [M+2] ⁺ [M] ⁺	TCDF TCDF TCDF 1,2,3,7,8-TCDF 1,2,3,7,8-TCDF 1,2,3,7,8-TCDF 1,2,3,4-TCDD 1,2,3,4-TCDD Hexachlorodiphenyl Ether	0.77 0.77
1.00	Turn on split valve; Begin Temp Program to 220°C;	180	2				
41.00	Stop Tetra Program	220					
71.00	Commence Cooling Column to 180°	220					

ATTACHMENT A

REPRESENTATIVE TABLES OF DATA OBTAINED IN DIOXIN I ANALYSES

TABLE 1

Wright State University, Dayton, Ohio 45435

Results of GC/MS Analyses of Extracts for 2,3,7,8-TetraChloroDibenzo-p-Dioxin
 Concentrations Found (picograms per gram of sample or parts-per-trillion)
 DBS Column(Isomer Specific for 2,3,7,8 TCDD)

EPA(Paper) Sample Number	Weight g. a.	Conc. Found		Instr. ID	Date	Time	Ion Int. Ratios		% C. Rec.	Ion Intensities a.e.				
		meas.	MDC b.				320/312	332/334		320	322	257	332	334
DE222026	850.0	ND	0.0112	MS25A	031287	18:45	0.73	49.1	-1.3E+04	-1.7E+04	-2.2E+04	3.20E+05	4.31E+05	
86374615	1070	ND	0.0098	MS25A	031087	13:18	0.78	39.3	-1.1E+04	-1.7E+04	-3.8E+04	2.88E+05	3.53E+05	
DE222037	950.0	1.32		MS25A	031087	15:27	0.85	0.81	58.1	5.78E+05	6.77E+05	3.42E+05	3.50E+05	4.47E+05
RG1-25386	970.0	0.531		MS25A	031187	12:19	0.76	0.92	79.3	2.15E+05	2.55E+05	1.20E+05	3.76E+05	4.53E+05
RG1-25353	950.0	ND	0.0225	MS25A	031187	13:23	0.85	39.1	-1.8E+04	-1.7E+04	-3.2E+04	1.73E+05	2.03E+05	
86374613	875.0	ND	0.0327	MS25A	031187	19:31	0.65	42.1	-2.8E+04	5.24E+04	-5.7E+04	1.37E+05	2.12E+05	
L2B BLANK	1000	ND	0.0152	MS25A	031187	17:25	0.93	52.5	-3.6E+04	-2.7E+04	-5.7E+04	3.88E+05	4.58E+05	
DF22-603	8.790	52.6		MS25A	031187	14:20	0.76	0.90	83.5	8.01E+05	1.03E+07	4.96E+05	1.11E+07	1.33E+07
DE222092	7.420	15.2		MS25A	031987	11:07	0.76	0.79	76.0	1.85E+04	2.16E+04	1.23E+04	1.65E+05	2.03E+05
DE222030	9.120	37.4		MS25A	031287	14:32	0.72	0.76	86.9	1.05E+05	1.45E+05	5.13E+05	3.53E+05	4.54E+05
DE222003	5.520	ND	3.02	MS25A	031187	18:27	0.81	68.7	-1.8E+04	-2.2E+04	-4.7E+04	2.84E+05	3.56E+05	
L2B BLANK	10.00	ND	0.878	MS25A	031187	20:29	0.79	59.4	-1.9E+04	-1.3E+04	-5.6E+04	3.13E+05	3.35E+05	
DF22-513	9.550	17.6		MS25A	031287	10:42	0.63	0.75	71.6	4.83E+05	5.54E+05	3.38E+05	3.03E+05	4.14E+05
RG1-25357	7.770	ND	1.82	MS25A	031287	12:35	0.78	64.9	-2.2E+04	-2.4E+04	-3.8E+04	3.67E+05	4.53E+05	
L2B BLANK	10.00	ND	0.635	MS25A	031287	13:32	0.73	64.9	-1.3E+04	-9.3E+03	-1.5E+04	3.28E+05	4.03E+05	
L2B BLANK	10.00	ND	1.84	MS25A	031287	11:39	0.85	56.4	-1.0E+04	-1.3E+04	-2.7E+04	1.64E+05	1.34E+05	

- For water samples the weight of the sample aliquot was calculated by multiplying the volume of water analyzed by 1.0000. The weight of each aliquot of sludge and silt was obtained after oven-drying the solid (see Analytical Protocol for Oven-Dried Solids Determination). Samples received as slurries were filtered, the solids oven-dried (see Analytical Protocol for reference to Total Suspended Solids Determination), an aliquot of the dried solid was then removed and weighed prior to analysis.
- MDC = Minimum Detectable Concentration
- % Rec. = Percent recovery for 13C12-2,3,7,8-TCDD internal standard
- The notation used here to designate ion intensities is exponential notation. The number preceding E should be multiplied by a factor of 10 raised to the power of the number following E. Therefore the designation 7.60E+05 indicates 760,000.
- A negative sign preceding the peak intensity value cited indicates that no response was observed at that m/z which exceeds the noise level by a factor of 2.5 or greater. The number following the negative sign is the observed noise level at that m/z.

TABLE 2

Wright State University, Dayton, Ohio *5435

Results of GC/MS Analyses of Extracts for 2,3,7,8-TetraChlorodibenzofuran
Concentrations Found (picograms per gram of sample or parts-per-trillion)
DBS Column

ET-40/Carbowax Sample Number	Weight g. a.	Conc. Found pg/g Meas. c. MDC c.	Instr. ID Date	Time	Ion Int. 304/305	Ratio 315/318	% c. Rec.	Ion Intensities a.f.						
								304	305	241	315	318		
DE322026	868.3	ND	0.0055	MS25A	031287	13:45	0.40	0.81	52.1	3.34E+04	8.43E+04	-5.2E+04	6.39E+05	3.56E+05
DE37-213	1070	ND	0.0054	MS25A	031387	13:18	1.25	0.85	38.8	4.54E+04	3.64E+04	-3.6E+04	5.08E+05	5.95E+05
DE322037	950.0	25.3		MS25A	031087	15:27	0.77	0.75	98.3	2.03E+07	2.63E+07	6.18E+06	8.13E+05	1.24E+06
RS1-36365	970.0	3.18		MS25A	031187	12:19	0.80	0.85	82.5	2.13E+07	2.67E+07	5.26E+06	7.05E+05	5.33E+05
RS1-36366	950.0	ND	0.0155	MS25A	031187	13:23		0.93	35.2	-1.5E+04	-2.1E+04	-4.1E+04	2.91E+05	3.14E+05
DE37-213	870.0	0.0039		MS25A	031167	19:31	0.99	0.77	51.5	1.44E+05	2.07E+05	8.69E+04	3.21E+05	4.15E+05
LFB BLANK	1000	ND	0.0065	MS25A	031187	17:25		0.91	57.1	-1.9E+04	-3.7E+04	-4.2E+04	7.23E+05	8.90E+05
DE32-203	8.790	955		MS25A	031167	15:22	0.74	0.86	100.0	1.52E+07	2.52E+07	8.34E+06	2.39E+06	2.77E+06
DE322032	7.450	229		MS25A	031587	11:07	0.75	0.82	84.5	5.32E+05	7.13E+05	1.46E+05	3.23E+05	3.97E+05
DE322030	9.100	565		MS25A	031287	14:32	0.80	0.83	78.8	3.14E+07	3.91E+07	8.12E+06	5.83E+05	7.01E+05
DE322033	5.600	15.1		MS25A	031187	18:27	0.64	0.80	64.3	3.47E+05	5.43E+05	9.67E+04	4.61E+05	5.77E+05
LFB BLANK	10.00	ND	0.684	MS25A	031187	20:29		0.84	55.3	-1.6E+04	-1.9E+04	-4.5E+04	5.22E+05	6.23E+05
DE32-213	9.530	33.1		MS25A	031287	10:42	0.85	0.78	79.7	2.00E+05	2.35E+05	4.70E+05	5.93E+05	7.64E+05
RS1-36387	7.770	7.12		MS25A	031287	12:35	0.71	0.73	67.4	3.50E+05	4.33E+05	1.63E+05	6.36E+05	8.55E+05
LFB BLANK	10.00	ND	0.492	MS25A	031287	13:32		0.82	60.5	-3.9E+03	-1.6E+04	-4.1E+04	5.26E+05	5.42E+05
LFB BLANK	10.00	ND	0.518	MS25A	031287	11:39		0.88	55.4	-5.6E+03	-8.4E+03	6.21E+04	2.85E+05	3.24E+05

- For water samples the weight of the sample aliquot was calculated by multiplying the volume of water analyzed by 1.0000. The weight of each aliquot of sludge and oil was obtained after oven-drying the solid (see Analytical Protocol for Oven-Dried Solids Determination). Samples received as slurries were filtered, the solids oven-dried (see Analytical Protocol for reference to Total Suspended Solids Determination), an aliquot of the dried solid was then removed and weighed prior to analysis.
- The concentrations listed for 2,3,7,8-TCDF could include contributions from co-eluting TCDF isomers.
- MDC = Minimum Detectable Concentration
- % Rec. = Percent recovery for 13C12-2,3,7,8-TCDF internal standard
- The notation used here to designate ion intensities is exponential notation. The number preceding E should be multiplied by a factor of 10 raised to the power of the number following E. Therefore the designation 7.30E+05 indicates 730,000.
- A negative sign preceding the peak intensity value cited indicates that no response was observed at that m/z which exceeds the noise level by a factor of 2.5 or greater. The number following the negative sign is the observed noise level at that m/z.

TABLE 3

Wright State University, Dayton, Ohio 45435

Results of GC/MS Analyses of Extracts for 2,3,7,8-TetraChlorodibenzo-p-dioxin
 Concentrations Found (picograms per gram of sample or parts-per-trillion)
 DBS/DBPIS Column/Isomer Specific for 2,3,7,8 TCDF

GC/MS Sample Number	Weight g. a.	Conc. Found ppt res.	MDL p.	Inscr. ID	Date	Time	Ion Int. Ratios 304/305 316/318	% Rec.	Ion Intensities c.e.					
									304	305	241	316	318	
8637-510	875.3	0.2535		MS25A	031587	11:37	0.83	0.79	38.6	7.19E+03	9.14E+03	4.81E+03	1.21E+05	1.53E+05
DE228023	5.520	14.9		MS25A	031587	15:20	0.83	0.83	62.6	2.21E+04	2.46E+04	5.36E+03	2.52E+05	3.25E+05
RG1-86357	7.770	8.61		MS25A	031687	13:33	0.81	0.73	12.8	5.29E+03	6.33E+03	8.82E+02	7.24E+04	5.14E+04
DF22-513	3.550	33.7		MS25A	031587	16:13	0.83	0.75	57.5	1.17E+05	1.34E+05	3.44E+04	3.29E+05	4.41E+05
DE228022	7.450	317		MS25A	031687	17:31	0.82	0.77	49.7	5.37E+05	5.53E+05	1.41E+05	1.93E+06	2.51E+06
RG1-86356	970.0	3.53		MS25A	031787	12:54	0.83	0.79	31.7	4.68E+05	5.30E+05	1.07E+05	1.27E+05	1.58E+05
DE228020	9.130	62-		MS25A	031787	14:25	0.83	0.71	74.6	1.64E+06	2.26E+06	4.62E+05	2.82E+06	3.54E+06
DF22-511	8.750	975		MS25A	031787	15:18	0.85	0.81	100.4	3.11E+06	1.07E+06	2.05E+05	1.22E+06	1.28E+06
DE228027	950.3	32.5		MS25A	031787	15:42	0.88	0.68	72.5	4.83E+05	5.51E+05	1.14E+05	1.33E+05	1.56E+05
LAR BLANK	10.20	ND	0.875	MS25A	031787	16:42		0.83	46.2	-2.5E+03	-1.3E+03	-3.1E+03	2.86E+05	3.44E+05

- For water samples the weight of the sample aliquot was calculated by multiplying the volume of water analyzed by 1.0000. The weight of each aliquot of sludge and silt was obtained after oven-drying the solids (see Analytical Protocol for Oven-Dried Solids Determination). Samples received as slurries were filtered, the solids oven dried (see Analytical Protocol for reference to Total Suspended Solids Determination), an aliquot of the dried solid was then removed and weighed prior to analysis.
- MDL = Minimum Detectable Concentration
- % Rec. = Percent recovery for 13C12-2,3,7,8-TCDF internal standard
- The notation used here to designate ion intensities is exponential notation. The number preceding E should be multiplied by a factor of 10 raised to the power of the number following E. Therefore the designation 7.26E+05 indicates 726,000.
- A negative sign preceding the peak intensity value cited indicates that no response was observed at that m/z which exceeds the noise level by a factor of 2.5 or greater. The number following the negative sign is the observed noise level at that m/z.

TABLE 4

Wright State University, Dayton, Ohio 45435

Summary of 2,3,7,8-TCDD, TCDF Calibration and Resolution Standards for GC-MS MS25A

Date	Std ID	Measured RF		Mean RF		A Valley
		TCDD Native	TCDF Native	TCDD Native	TCDF Native	
03/10/87	TCDD PEMIX					13
03/13/87	2.5 co	0.94	0.87	0.90	1.01	
03/13/87	2 no	0.96	1.04	0.90	1.01	
03/13/87	TCDD PEMIX					15
03/11/87	TCDD PEMIX					14
03/11/87	2.5 co	0.92	0.92	0.90	1.01	
03/11/87	TCDD PEMIX					13
03/12/87	TCDD PEMIX					15
03/12/87	2.5 co	0.98	0.95	0.90	1.01	
03/12/87	TCDD PEMIX					11
03/15/87	TCDF PEMIX					4
03/15/87	10 co	0.80	1.01	0.90	1.01	
03/15/87	TCDF PEMIX					4
03/17/87	TCDF PEMIX					5
03/17/87	10 co	0.80	1.05	0.90	1.01	
03/17/87	TCDF PEMIX					3
03/19/87	TCDD PEMIX					14
03/19/87	2.5 co	0.94	0.95	0.90	1.01	
03/19/87	TCDD PEMIX					10

TABLE 5

Wright State University, Dayton, Ohio 45435

Standard summary for Dioxins & Furans

Standard ID 2 ng

Date: 03/10/87 Time: 11:02

GC/MS Run No. TDF4-89 File # 27

Standard curve # 1

Injection amount 3.000 UL OF STANDARD

Instrument ID #5154

Internal Standard Levels - ng/ul

13012 TCDF 13012 TCDD 13012 1234

0.05 ng 0.05 ng 0.05 ng

Native levels ng/ul

TCDF TCDD

0.00000.0000

Internal Standards

M/I	Max Tic	% Tic	Ratio	Region	Measured RF	Mean RF
316	53577	99	0.77	13012 TCDF	2.19*	2.09
318	68457	99				
332	383-0	98	0.74	13012 TCDD		
334	48550	99				
332	383-0	77	0.74	13012 1234	38339200.20	1683572.50
334	48550	78				

Native Regions

M/I	Max Tic	% Tic	Ratio	Region	Measured RF	Mean RF
241	1454	80				
324	2353	95				
326	3131	95	0.74	TCDF	0.87	1.01
257	1724	80				
320	1553	95				
322	1934	95	0.94	TCDD	0.94	0.90

TABLE 6

Wright State University, Dayton, Ohio 45435

Standard summary for Dioxins & Furans

Standard ID 2 ng

Date: 03/10/87 Time: 16:26

GC/MS Run No. TDF4-80104 File # 29

Standard curve # 1

Injection amount 0.500 UL OF STANDARD

Instrument ID #5257

Internal Standard Levels - ng/ul

13012 TCDF 13012 TCDD 13012 1234

0.05 ng 0.05 ng 0.05 ng

Native levels ng/ul

TCDF TCDD

2.000002.0000

Internal Standards

M/I	Max Tic	% Tic	Ratio	Region	Measured RF	Mean RF
316	3421	98	0.89	13012 TCDF	2.11*	2.09
318	3819	98				
332	2214	97	0.89	13012 TCDD		
334	2457	98				
332	2214	74	0.95	13012 1234	13432040.00	1683572.50
334	2457	70				

Native Regions

M/I	Max Tic	% Tic	Ratio	Region	Measured RF	Mean RF
241	36355	100				
304	131093	100				
326	164633	100	0.60	TCDF	1.04	1.01
257	36670	100				
320	66364	100				
322	90580	100	0.73	TCDD	0.85	0.90

TABLE 12

Customer ID DE209226 WSD ID C-LS-27A
 Sample analysis for 2378 TCDF,TCDD only(285)
 Date: 03/10/87 Time: 18:46
 Run No. TCF4-2103 File # 31
 Sample Size 820.0 µl Injection Amount 0.250 of Sample
 Instrument ID MS25A
 Spike Levels 13012 TCDF 13012 TCDD 1234 TCDD
 1.00 NG 1.00 NG 0.50 NG

Internal Standard Summary

M/Z	Max TIC	% TIC Ratio	Region	Recovery
315	85824	100	0.61 13012 TCDF	52.1
318	85812	100		
332	36753	99	0.73 13012 TCDD	49.1
334	50263	99		
332	36753	91	0.87 1234 TCDD	335.1
334	50263	77		

2378 Isomers Summary PPT Levels

M/Z	Max TIC	% TIC Ratio	Region	Value	MDQ
241	5189	-10			
324	418	80			
326	1054	80	0.40* TCDF	0.2000	0.2050
257	1105	-20			
323	323	-40			
322	418	-40	0.00* TCDD	0.2000	0.2112

TABLE 13

Customer ID 85374518 WSD ID FWC6-27A
 Sample analysis for 2378 TCDF,TCDD only(285)
 Date: 03/10/87 Time: 13:18
 Run No. TCF4-2101 File # 32
 Sample Size 1070 µl Injection Amount 0.250 of Sample
 Instrument ID MS25A
 Spike Levels 13012 TCDF 13012 TCDD 1234 TCDD
 1.00 NG 1.00 NG 0.50 NG

Internal Standard Summary

M/Z	Max TIC	% TIC Ratio	Region	Recovery
315	50840	100	0.85 13012 TCDF	38.8
318	59831	100		
332	38991	93	0.78 13012 TCDD	39.9
334	38039	97		
332	38991	99	0.81 1234 TCDD	218.5
334	38039	99		

2378 Isomers Summary PPT Levels

M/Z	Max TIC	% TIC Ratio	Region	Value	MDQ
241	1202	-30			
324	757	60			
326	520	70	1.25* TCDF	0.2000	0.2054
257	1258	-30			
323	351	-30			
322	576	-30	0.00* TCDD	0.2000	0.2098

TABLE 29

Customer ID 0827-013 WSJ ID 0-16-89
 Sample analysis for 2378 TCDF (08265/082)
 Date: 03/15/97 Time: 11:37
 Run No. TDF=115 File # 47
 Sample Size 573.0 ml Injection Amount 0.200 of Sample
 Instrument ID 08253
 Spike Levels 13012 TCDF
 1.20 NG

Internal Standard Summary

M/Z	Max TIC % TIC	Ratio	Region	Recovery	
316	1271	95	0.79	13012 TCDF	32.5
318	1553	99			

2378 Isomers Summary PPT Levels

M/Z	MAX TIC % TIC	RATIO	REGION	VALUE	MDQ
241	535	9			
324	78	92			
326	87	94	0.83	TCDF	0.2635 0.2000

TABLE 30

Customer ID 08225203 WSJ ID 0-16-92
 Sample analysis for 2378 TCDF (08215/085)
 Date: 03/15/97 Time: 15:20
 Run No. TDF=133 File # 43
 Sample Size 5.500 gram Injection Amount 0.200 of Sample
 Instrument ID 08354
 Spike Levels 13012 TCDF
 1.20 NG

Internal Standard Summary

M/Z	Max TIC % TIC	Ratio	Region	Recovery	
316	2527	96	0.93	13012 TCDF	62.5
318	3334	99			

2378 Isomers Summary PPT Levels

M/Z	MAX TIC % TIC	RATIO	REGION	VALUE	MDQ
241	303	21			
324	239	97			
326	256	97	0.89	TCDF	14.9 0.2000

TABLE 39

WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435
ADDITIONAL DATA RESULTING FROM ANALYSES OF SAMPLES
FOR EPA/NCASI PAPER MILL STUDY

EPA I.D.	Sample Type	% Moisture As Received	Total Suspended Solid
DF024603	Sludge	5.8	--
DE020920	Sludge	61.7	--
DF024513	Sludge	83.3	--
RGI-86357	Slurry	--	5188 mg/L

ATTACHMENT D

NCASI METHODS FOR THE ANALYSIS OF
CHLORINATED PHENOLICS IN PULP INDUSTRY WASTEWATERS



technical bulletin

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 10016

NCASI METHODS FOR THE ANALYSIS OF CHLORINATED PHENOLICS
IN PULP INDUSTRY WASTEWATERS

TECHNICAL BULETIN NO. 498

JULY 1986

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
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July 25, 1986

TECHNICAL BULLETIN NO. 498

NCASI METHODS FOR THE ANALYSIS OF CHLORINATED PHENOLICS
IN PULP INDUSTRY WASTEWATERS

Analytical measurement method development and evaluation represents a significant portion of the National Council program. The attached technical bulletin is another on this subject and deals with methods for analysis of chlorinated phenolics in pulp industry wastewaters.

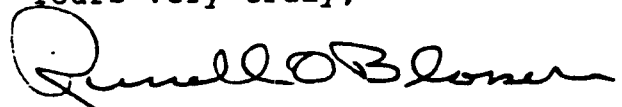
The first technical bulletin on this subject was issued as Stream Improvement Technical Bulletin No. 347. This technical bulletin reflects the improvements in the method made since then. It discusses the modifications made to the original procedures and why these were required.

The bulletin includes (a) the revised gas chromatographic procedure for analysis of chlorophenols in water and (b) an improved gas chromatographic/mass spectrometer procedure which permits identification of six additional compounds of interest.

The laboratory investigation of these procedures and preparation of the technical bulletin was carried out by Lawrence E. LaFleur, Organic Analytical Program Manager. He was assisted by Mr. Kenneth Ramage. Both are located at the West Coast Regional Center.

Your comments and questions on the contents of this bulletin are solicited and should be directed to this office or to Mr. LaFleur, NCASI West Coast Regional Center, P.O. Box 458, Corvallis, OR 97339, telephone 503-754-2015.

Yours very truly,



Russell O. Blosser
Technical Director

ROB:mh

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NCASI METHODS FOR THE ANALYSIS OF CHLORINATED PHENOLICS
IN PULP INDUSTRY WASTEWATERS

I INTRODUCTION

As part of NCASI's ongoing methods development and evaluation program, the procedures used for the analysis of chlorinated phenolic compounds characteristic of bleached pulp mill effluents have been continually improved and refined since the original method evaluations were reported in Technical Bulletin No. 347 (1). The purpose of this report is to provide analysts with a revised method which reflects the improvements which have been incorporated into the earlier procedure, thereby bringing them up to date with current practices. The following section highlights some of the changes. Appendix A presents NCASI Method CP-85.01 in standard methodology format.

It also became apparent that a GC/MS confirmation method would be desirable, particularly when NCASI Method CP-85.01 was applied to new matrices. Section III of this report discusses the modifications to the in situ acetylation which were required to adapt the method for GC/MS analysis. The procedure, NCASI Method CP-86.01, is presented in standard methodology format in Appendix B.

II DISCUSSION OF NCASI METHOD CP-85.01

A. Scope and Application

NCASI Method CP-85.01 reflects an expansion in scope and application both in terms of the number of analytes and the types of matrices to which it has been applied. The increased number and diversity of analytes was in part due to the availability of standards (initially by in-house synthesis, more recently through commercial suppliers) but mostly to provide data necessary to evaluate and monitor the environmental significance of the wider array of sample matrices being analyzed. Information needs pertaining to environmental samples which have undergone anaerobic degradation prompted inclusion of certain chlorinated phenols which aren't normally found in bleach pulp mill effluents. The additional chlorinated guaiacols and catechols and the chlorinated benzaldehydes resulted from a desire to better characterize bleach pulp mill effluents. The specific method modifications or adaptations required to accommodate the expanded scope are discussed below.

B. Reagents

The chlorinated benzaldehyde compounds (i.e. chlorovanillins, chlorohydroxybenzaldehyde and chlorosyringaldehyde) were found to form hemi-acetals when stored for prolonged periods in alcohol solvents such as methanol. Thus, Method CP-85.01 calls for preparation of stock solutions of these analytes in acetone

and that working solutions be made up fresh just prior to use and be subsequently discarded. This short exposure to methanol has not presented any problems.

C. Sample Preservation

Sample and extract preservation studies showed that with acidification to a pH of two with H_2SO_4 , samples stored refrigerated for up to 30 days showed no significant changes in analyte concentrations. The data documented storage up to that length of time but did not indicate 30 days was an upper limit. Storage beyond this time would have to be supported with additional information. Similarly, refrigerated extracts were found to be stable over a 30 day period.

D. Procedure Modifications Due To Matrix Effects

One problem encountered with some of the different matrices resulted from the inherent buffering capacity of the sample. The normal carbonate buffer added to the sample failed to raise the pH adequately enough to insure ionization of some of the weakly acidic analytes resulting in low recoveries. To resolve this problem, the pH of the sample is adjusted to 11.6 with 5 percent NaOH following the addition of the carbonate buffer. This provides both the desired final pH and buffering capacity.

Other matrix problems can be minimized by using a smaller aliquot of the sample and adjusting to the final volume with reagent water. This is required when the concentrations of analytes exceed the linear range of the GC-ECD but also is an option to minimize matrix effects. It should be recognized that this directly influences detection limits.

The sample preservation requirements had to be modified to include addition of sodium thiosulfate to remove residual chlorine, particularly in bleach plant process stream samples.

E. Calibration

The single point calibration procedure described in Technical Bulletin No. 347 was abandoned in favor of a six point calibration curve. Although the calibration procedure is definitely more time consuming, it substantially improved the accuracy. A daily calibration check was added to the quality control plan to test the validity of the calibration curve.

F. Quality Control

A table summarizing NCASI quality control (QC) data has been included to provide guidelines of what method performance might be anticipated. Many of the replicate analyses in the QC data set were at or near the detection limit, so the reported relative percent differences reflect method performance over the entire

working range of the procedure. Generally, relative percent differences of less than 15 to 20 percent can be expected with 35 percent being a suggested upper control limit.

The replicate determination requires that the analyte be at measurable levels in order to provide the data to estimate the precision, so, for many compounds which are not commonly encountered (i.e. 3,5-dichlorophenol, 3,4-dichlorophenol, 2,3,6-trichlorophenol, etc.) there is little data available. Recovery determinations do not suffer from this limitation and the summary data provided in the method gives a much better estimate due to the larger number of data points. In general, recoveries of 90 to 100 percent can be expected for chlorophenols, chloroguaiacols and chlorinated benzaldehyde type compounds with the relative standard deviations of the recoveries of these compounds ranging from 15 to 25 percent. Chlorocatechol recoveries are more in the range of 70 to 80 percent with relative standard deviations of 22 to 37 percent.

Both the replicate data and the recovery summaries show that the chlorocatechols remain the most difficult group of compounds to quantify. The chlorovanillins also seem to cause problems, but this may be due to lesser experience since they were the last group of analytes incorporated into NCASI Method CP-85.01. The lower sensitivity of the monochloro- and dichloro-compounds of all classes of compounds makes their detection and quantification more difficult thus giving rise to generally lower precision and recovery.

III DISCUSSION OF NCASI METHOD CP-86.01

A. Scope and Application

NCASI Method CP-86.01 was developed to provide a means of qualitatively confirming compound identifications while semi-quantifying the concentrations. The method as presented has not been used as extensively as NCASI Method CP-85.01 and therefore the performance characteristics are not as well documented. For this reason, the scope of the method has been limited to semi-quantitative. This does not imply that the concentration data obtained by NCASI Method CP-86.01 is inaccurate, just that the precision and accuracy of the method has not been well documented.

The lower sensitivity of the electron capture detector for compounds with a single chlorine atom prevents their analysis by NCASI Method CP-85.01. The higher selectivity of a GC/MS analysis and adjustments made to make up for the inherently lower sensitivity of the mass spectrometer operated in the full scan mode allows the scope of NCASI Method CP-86.01 to be extended to include mono-chloro compounds. The ability to quantify compounds which are not chromatographically separated through the use of extracted ion current techniques further allows the scope of the method to be expanded. Thus, six addi-

tional compounds can be detected and semi-quantified by NCASI Method CP-86.01.

B. Acetylation Procedure

The lower sensitivity of a GC/MS compared to an ECD required that the sample volume be increased in order to achieve similar detection limits. Thus, three 100 mL portions were acetylated in situ, extracted with three portions of hexane and the hexane extracts were combined and concentrated prior to analysis. It was felt that this approach more closely approximated the acetylation procedure used in NCASI Method CP-85.01 and would be less likely to cause problems due to unforeseen difficulties. It also provided a simple means for the analyst to increase or decrease the sample size to accommodate individual sensitivity requirements without raising questions about the applicability of the in situ acetylation and/or extraction on larger sample volumes.

The quantitation technique used in NCASI Method CP-85.01 does not require quantitative recovery of the analytes since the internal standard is spiked into the sample prior to acetylation and extraction. This effectively corrects for recovery. However, in the case of the GC/MS procedure, it was considered beneficial to improve the absolute recovery of the analytes to further help improve sensitivity. This was accomplished by combining three sequential hexane extracts from each acetylated sample aliquot prior to concentration.

Since the quantitation technique still relies on the calibration procedure mimicking the sample analysis procedure, appropriate modifications in the procedures for the preparation of the GC/MS calibration standards were incorporated into the method.

C. GC/MS Analysis Procedure

A 30m DB-5 fused silica column was used for the analysis, not because of improved chromatography, but as a compromise to minimize overhead time required to change columns. All other in-house GC/MS analyses routinely performed in our laboratory utilize a DB-5 column and since relatively few chlorophenolic conformational analyses are required and the DB-5 column provided adequate separations, there seemed to be no reason not to use it. Therefore, for at least those analytes listed in NCASI Method CP-85.01 which are chromatographically separated, either a DB-5 or a DB-1 column could be used for GC/MS analysis. A less sophisticated gas chromatograph temperature program had to be used due to the software limitations of the HP-5993 GC/MS data system. Analysts should use their own judgement in making any changes in the recommended temperature program. Any changes deemed appropriate should be relatively straightforward and, with appropriate documentation through quality assurance, should not alter the applicability of the method.

IV SUMMARY AND FUTURE STUDIES

NCASI Methods CP-85.01 and CP-86.01 as presented in Appendices A and B represent the culmination of NCASI laboratory method evaluations and refinements. Although vigorous or formalized ruggedness testing has not been conducted, analysts skilled in trace environmental analyses should be able to conduct the procedure and, with appropriate quality assurance documentation, generate reliable data.

The Methods have essentially been subjected to single laboratory validation studies. It is hoped that through distribution of these procedures that other laboratories will become familiar with the methods. The inevitable positive feedback can be incorporated into improved protocols. This will set the stage for critical interlaboratory validation studies. Upon completion of those studies, the performance characteristics of the Methods should be fully determined.

The results of such an intercalibration study were recently described by Starck, et.al.(2). The procedure used was quite similar to NCASI Method CP-85.01. The authors reported that recoveries of greater than 80 percent were generally achievable for analyte concentrations above 20 ppb. Below this concentration, the recoveries ranged from 60 to 70 percent. As is consistent with NCASI Method CP-85.01 performance characteristics, the chlorocatechols were found to exhibit the highest variabilities in the recoveries reported. However, this study relied heavily on spiked water (presumably reagent water) data. The relative standard deviation of the chlorocatechol results for the waste water sample was 40 to 54 percent and the recoveries of these analytes were 0 to 10 percent. Thus, there remain significant matrix effects which have not been resolved by their methodology.

Future interlaboratory studies should cover a wider range of analytes (the study mentioned above only discussed six compounds), address the preparation and accuracy of calibration standards and cover as wide a range of matrices and concentrations as possible. The resulting data will then complement the study described above and complete the documentation of the methods performance characteristics.

V LITERATURE REFERENCES

- (1) "Experience With the Analysis of Pulp Mill Effluents for Chlorinated Phenols Using an Acetic Anhydride Derivatization Procedure," NCASI Technical Bulletin No. 347 (June 1981).
- (2) Starck, B., Bethge, P.O., Gergov, M., Talka, E., "Determination of Chlorinated Phenols in Pulp Mill Effluents - An Intercalibration Study," Paperi ja Puu - Papper och Tra, 12, 745-749 (1985).

D9

APPENDIX A

NCASI

METHOD CP-85.01

CHLORINATED PHENOLICS IN WATER BY
IN SITU ACETYLATION/GC-ECD DETERMINATION

NCASIMETHOD CP-85.01CHLORINATED PHENOLICS IN WATER BY
IN SITU ACETYLATION/GC-ECD DETERMINATION1.0 Scope and Application

1.1 Method CP-85.01 is used to determine the concentration of chlorinated phenols, chlorinated guaiacols, chlorinated catechols and chlorinated benzaldehydes (i.e. vanillins, and syringaldehyde) in water samples. Specifically, Method CP-85.01 can be used to determine:

Chlorinated Phenols

3,5-dichlorophenol
3,4-dichlorophenol
2,6-dichlorophenol
2,4-dichlorophenol
2,3,6-trichlorophenol
2,4,6-trichlorophenol
2,4,5-trichlorophenol
2,3,4,6-tetrachlorophenol
pentachlorophenol

Chlorinated Guaiacols

4,6-dichloroguaiacol
4,5-dichloroguaiacol
3,4,5-trichloroguaiacol
4,5,6-trichloroguaiacol
tetrachloroguaiacol

Chlorinated Catechols

3,6-dichlorocatechol
3,4-dichlorocatechol
4,5-dichlorocatechol
3,4,6-trichlorocatechol
3,4,5-trichlorocatechol
tetrachlorocatechol

Chlorinated Benzaldehydes

6-chlorovanillin
5,6-dichlorovanillin
chlorosyringaldehyde

Miscellaneous Compounds

trichlorosyringol

1.2 This method has been used to analyze untreated and biologically treated pulp mill effluents, landfill leachates and receiving waters and bleach plant effluents.

1.3 The method has been found unsuitable for groundwater samples which contain high levels of non-chlorinated phenols (i.e. creosote contamination) or samples where pentachlorophenol and/or 2,3,4,5-tetrachlorophenol are present and are suspected to have undergone anaerobic degradation.

1.4 When Method CP-85.01 is used to analyze unfamiliar samples, quality assurance duplicates and recovery samples should be run and compound identifications should be supported by qualitative GC/MS.

2.0 Summary of Method

2.1 Method CP-85.01 provides in situ derivatization, extraction and gas chromatographic conditions for the detection of ppb levels of chlorinated phenolics. Samples are neutralized, spiked with the Internal Standard, then buffered with K_2CO_3 in order to form the phenolate ions which are then converted in situ (i.e. in the aqueous matrix) to their acetate derivatives by the addition of acetic anhydride. The chlorophenolic acetates thus formed are extracted with hexane. A 1 μ L to 2 μ L portion of the hexane extract is injected into a gas chromatograph using a Grob type splitless injection technique and is chromatographed on a fused silica capillary column using electron capture detection. The standards used to determine the calibration curve are prepared by spiking the Internal Standard and the appropriate levels of analytes into blank water and then analyzing in the same manner as the sample.

2.2 The Internal Standard used in the method 3,4,5-trichlorophenol has been identified as a persistent anaerobic degradation product of 2,3,4,5-tetrachlorophenol and/or pentachlorophenol. Other workers analyzing samples containing these compounds which have been subjected to anaerobic conditions have substituted 2,6-dibromophenol as the Internal Standard.

2.3 The sensitivity of Method CP-85.01 usually depends on the level of interferences rather than on instrumental limitations. The lower detection (LDL) and lower quantitation limits (LQL) listed in Table 1 represent sensitivities that generally can be achieved in biologically treated effluent with some degree of reliability and confidence. Actual detection limits would have to be determined on each sample.

2.4 Additional compounds can be determined by CP-85.01 but have not been validated on the above mentioned sample matrices. Chromatographic data for these compounds is given in Table 2.

3.0 Interferences

3.1 When Method CP-85.01 was applied to groundwater samples collected in the vicinity of a source of creosote, (i.e. wood preservation plant) the high levels of non-chlorinated phenols caused poor recoveries and the method was unsatisfactory.

3.2 The Internal Standard, 3,4,5-trichlorophenol, has been shown by some researchers to be a persistent anaerobic degradation product of 2,3,4,5-tetrachlorophenol and pentachlorophenol.

TABLE 1
CHROMATOGRAPHIC CONDITIONS, DETECTION
LIMITS AND QUANTITATION LIMITS FOR
METHOD CP-85.01 IN TREATED PULP MILL EFFLUENTS

<u>Compound</u>	<u>Relative Retention Time^{a,b}</u>	<u>LDL^c (µg/L)</u>	<u>LQL^d (µg/L)</u>
2,6-dichlorophenol	0.526	ND	ND
2,4-dichlorophenol	0.564	3.0	5.0
3,5-dichlorophenol	0.592	ND	ND
3,4-dichlorophenol	0.661	ND	ND
2,4,6-trichlorophenol	0.738	1.2	2.4
2,4,5-trichlorophenol	0.864	1.2	ND
2,3,6-trichlorophenol	0.818	ND	ND
2,3,4,6-tetrachlorophenol	1.164	0.8	1.5
pentachlorophenol	1.646	0.6	1.0
4,6-dichloroguaiacol	0.956	3.5	7.0
4,5-dichloroguaiacol	1.086	3.5	7.0
3,4,5-trichloroguaiacol	1.380	0.6	1.5
4,5,6-trichloroguaiacol	1.469	0.6	1.0
tetrachloroguaiacol	1.723	0.6	1.0
3,6-dichlorocatechol	1.109	ND	ND
3,4-dichlorocatechol	1.262	ND	ND
4,5-dichlorocatechol	1.337	3.0	5.0
3,4,6-trichlorocatechol	1.494	ND	ND
3,4,5-trichlorocatechol	1.673	1.5	4.0
tetrachlorocatechol	1.991	1.0	2.5
6-chlorovanillin	1.207	ND	ND
5,6-dichlorovanillin	1.567	ND	ND
chlorosyringaldehyde	1.636	ND	ND
trichlorosyringol	1.777	ND	ND

ND = Not Determined

a Retention times of acetate derivatives relative to

3,4,5-trichlorophenol acetate

b 15 m x 0.25 mm I.D. fused silica DB-1, 0.25 micron film thickness. Helium carrier (μ = 31 cm/sec at 125°C) 90 percent argon/10 percent methane detector make-up gas (30 mL/min).

Oven programed from 45°C after a one minute hold at 15°C/min to 100°C and then at 2°C/min to 165° then 20°C/min to 230°C. Under these conditions the retention time of 3,4,5-trichlorophenol acetate is 17.080 minutes.

c LDL Lower Detection Limit

d LQL Lower Quantitation Limit

Method CP-85.01 would have to be modified appropriately when applied to samples suspected of containing these compounds and having undergone anaerobic degradation. Other workers have used 2,6-dibromophenol as an alternative Internal Standard.

TABLE 2 ADDITIONAL CHROMATOGRAPHIC DATA

<u>Compound</u>	<u>Relative Retention Time</u>
4-chlorophenol	0.415
2,5-dichlorophenol	0.564
2,3-dichlorophenol	0.612
5-chlorovanillin	1.160
2,6-dibromophenol	0.826
trichloro-3-methyl catechol	1.877
4-chlorocatechol	0.924
3,4-dichloroguaiacol	0.973
3,5-dichloro-4-hydroxybenzaldehyde	1.456

3.3 Blanks most frequently are contaminated with penta-chlorophenol. Generally this has been traced to the K_2CO_3 and has been removed by baking the reagent at 400°C+ overnight. All reagents should be tested for contamination prior to use.

3.4 All glassware should be washed with hot detergent water, air dried and then baked at 400°C for 6-8 hours. Volumetric pipets should be washed in an alcoholic - KOH bath and then rinsed thoroughly with tap water before air drying.

4.0 Apparatus and Materials

4.1 Glassware:

125 mL separatory funnel
 100 mL beaker
 50 mL graduated cylinder
 Volumetric pipets (TD)
 2 dram vials with Teflon-lined screw caps
 Centrifuge tubes with Teflon-lined screw caps

4.2 pH Meter: Calibrated using two point procedure

4.3 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for splitless capillary injection, electron capture detector, electronic integrator and recording device.

4.4 Chromatography Column: 15m x 0.25 mm I.D. fused silica DB-1 (0.25 μ film thickness).

4.5 Centrifuge

5.0 Reagents

5.1 Hexane: Distilled in glass; Methanol: Distilled reagent grade.

5.2 Acetic anhydride: Redistilled reagent grade.

5.3 Reagent water: Organic free such as produced by a Barnstead Model D2798 NANOpure-A water purification system.

5.4 Sodium Hydroxide: 5 percent w/w in reagent water.

5.5 Sulfuric Acid: Mix one part concentrated H_2SO_4 with four parts reagent water.

5.6 Potassium Carbonate: Dissolve 150g K_2CO_3 (purified by heating at 400°C for 6 to 8 hours in a shallow tray) in 250 mL reagent water.

5.7 Internal Standard Stock Solution: Weigh (to the nearest 0.1 mg) 25 \pm 3 mg of 3,4,5-trichlorophenol and dissolve to volume with methanol in a 50 mL ground-glass-stoppered volumetric flask. Transfer the stock solution into an amber bottle with a Teflon-lined screw cap and store under refrigeration (4°C).

5.8 Internal Standard Spiking Solution: Pipet 5.0 mL of the stock solution into a 100 mL ground-glass-stoppered volumetric flask and dilute to volume with methanol. Transfer the spiking solution into five ca 20 mL portions in separate Teflon-lined screw capped vials, number 1-5 and store under refrigeration (4°C).

5.9 Calibration standard stock solutions: Individual stocks are prepared by dissolving the amounts of the analyte indicated in either Table 3 or 4 (\pm 3 mg weighed to the nearest 0.1 mg) in the indicated solvent in 50 mL ground-glass-stoppered volumetric flasks. Combined secondary dilution stocks are prepared by pipetting the volumes of the individual stock solutions indicated in Table 3 and 4 into separate 50 mL ground-glass-stoppered volumetric flasks and diluting to volume with the solvents indicated. The final working solution of the calibration standard is prepared by pipetting 5.0 mL of each of the secondary dilution stock into a 25 mL ground-glass-stoppered volumetric flask and diluting to volume with methanol. All stock solutions and secondary dilutions are transferred into amber bottles with Teflon-lined screw caps and are stored under refrigeration (4°C). The working solutions are discarded after use.

5.10 Calibration Curve Standards: The calibration curve standards are prepared by spiking separate 50.0 mL portions of reagent water with 25 μ L of the Internal Standard spiking solution and 25, 50, 75, 100, 125, and 150 μ L portions of the final calibration working solution. The resulting solutions are then acetylated and extracted in a manner exactly analogous to the samples.

TABLE 3 METHANOL STOCK SOLUTIONS

<u>Compound</u>	<u>mg in 50 mL Stock</u>	<u>mL in Secondary Dilution</u>	<u>Secondary Solution ng/μL</u>
2,6-dichlorophenol	40	2	32.0
2,4-dichlorophenol	40	2	32.0
3,5-dichlorophenol	40	2	32.0
3,4-dichlorophenol	40	2	32.0
2,4,6-trichlorophenol	40	1	16.0
2,4,5-trichlorophenol	40	1	16.0
2,3,6-trichlorophenol	40	1	16.0
2,3,4,6-tetrachlorophenol	40	1	16.0
pentachlorophenol	10	1	2.0
4,6-dichloroguaiacol	40	2	32.0
4,5-dichloroguaiacol	40	2	32.0
3,4,5-trichloroguaiacol	40	2	32.0
4,5,6-trichloroguaiacol	40	2	32.0
tetrachloroguaiacol	40	2	32.0
3,6-dichlorocatechol	40	2	32.0
3,4-dichlorocatechol	40	2	32.0
4,5-dichlorocatechol	40	2	32.0
3,4,6-trichlorocatechol	40	2	32.0
3,4,5-trichlorocatechol	40	2	32.0
tetrachlorocatechol	40	2	32.0
trichlorosyringol	40	2	32.0

TABLE 4 ACETONE STOCK SOLUTIONS

<u>Compound</u>	<u>mg in 50 mL Stock</u>	<u>mL in Secondary Dilution</u>	<u>Secondary Solution ng/μL</u>
6-chlorovanillin	40	2	32.0
5,6-dichlorovanillin	40	2	32.0
chlorosyringaldehyde	40	2	32.0

6.0 Sample Collection, Handling and Preservation

6.1 Samples should be collected in glass containers and all portions of automatic sampling equipment which come in contact with the sample should be constructed of glass, Teflon or stainless steel. Composite samples should be refrigerated during the sampling period.

6.2 The samples must be iced or refrigerated from the time of collection until acetylated.

6.3 A portion of the sample should be tested for free or residual chlorine. Add 35 mg of sodium thiosulfate per ppm free chlorine per liter. Adjust the sample pH to approximately two using sulfuric acid. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

6.4 All samples must be acetylated within 30 days and be completely analyzed within 30 days after acetylation.

7.0 Procedures

7.1 Sample Preparation

7.1.1 In Situ Acetylation: Remove the sample from the refrigerator and allow it to come to room temperature. Shake the sample vigorously to insure it is homogeneous and then measure out an appropriate aliquot. If less than 50 mL of sample is used, bring the final volume up to 50 mL with reagent water. Neutralize the sample to pH 7.0 to 7.1 using 5 percent NaOH and 1:4 sulfuric acid. Add 1.3 mL of the potassium carbonate solution and adjust the pH to 11.6 \pm 0.1 with 5 percent NaOH if necessary.

Transfer the sample to a 125 mL separatory funnel and spike it with 25 μ L of the Internal Standard spiking solution. Shake the sample to insure thorough mixing. Add 1.0 mL of acetic anhydride and shake the sample with frequent venting for 30 seconds. Let the sample stand for 5 minutes then shake and vent.

Add 5 mL of hexane and shake vigorously for 1 to 2 minutes with frequent venting. Allow the phases to separate and drain and discard the aqueous portion. If there is an emulsion problem, drain the organic layer into a centrifuge tube, cap and centrifuge for two to three minutes or until the emulsion is broken. Transfer as much of the hexane as possible into a vial with Teflon-lined screw cap, label and refrigerate until analyzed.

7.2 The recommended gas chromatographic column and operating conditions for the instrument are: 15m x 0.25 mm I.D. fused silica DB-1, 0.25 micron film thickness. Helium carrier gas ($\mu = 31$ cm/sec at 125°C), 90 percent argon/10 percent methane detector make-up gas (30 mL/min). The injection port temperature is 210°C and the oven is programed from an initial temperature of 45°C after a 1 minute hold at 15°C/min to 100°C and then 2°C/min to 165°C then 20°C/min to 230°C. The Ni⁶³ detector is operated at 300°C.

The injection port is configured for a Grob type splitless injection with a 30 second purge activation delay.

7.3 Calibration

7.3.1 Calibration Curve: Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.2. Using 1 μ L splitless injections of the calibration curve standards, tabulate the ratio of the area of the analyte divided by the area of the Internal Standard data against the concentration of the analyte. Using these data, calculate the linear regression and tabulate the slope and intercept data.

This procedure should be repeated whenever the daily calibration check is out of range, the instrument has not been used or has been down, a new column has been installed, etc.

7.3.2 Daily Calibration Check: The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the concentration of any analyte based on the current calibration curve varies by more than ± 20 percent, the test must be repeated at a different concentration level. If this value is also out of range, a new calibration curve must be prepared.

7.4 Sample Analysis

7.4.1 Sample extracts are analyzed using the gas chromatographic operating conditions indicated in Section 7.2. Peak integration parameters and area reject thresholds should be set such that the sensitivities indicated in Table 1 (Section 2.3) can be achieved.

7.4.2 Inject 1 μ L of the sample extract using the Grob type purged splitless injection technique. If the peak areas of the identified analytes exceed the linear range of the instrument, a separate smaller aliquot of the sample should be acetylated, extracted and analyzed.

7.4.3 Calculate the concentration of the analytes using the following equation:

$$\text{Concentration} = \frac{(A_S) (V_o) (m_S)}{(A_{IS}) \times 50} + b_S$$

where: A_S = area of the analyte
 A_{IS} = area of the internal standard
 V_o = volume of sample acetylated (in mL)
 m_S = slope from calibration curve for analyte
 b_S = intercept from calibration curve for analyte.

8.0 Quality Control

8.1 Blanks: Before processing any samples or whenever a new reagent is prepared, the analyst should demonstrate through the analysis of a reagent water blank that utilizes all glassware and reagents required for sample analyses that all materials are interference free. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Frequency: Approximately 12 to 15 percent of routine samples should be allocated for quality control. In addition to this, representative samples from each new or untested source or sample matrix should be treated as a quality control sample. Laboratory replicates and fortification should be conducted on each QC sample to document method performance as indicated by precision and recovery.

8.3 Replicates: Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. The range and mean concentration of the replicates are determined from the results. The relative percent difference is calculated as follows:

$$\text{Relative Percent Difference} = 100 \left(\frac{\text{range}}{\text{mean}} \right)$$

Table 5 summarizes the relative percent differences measured by the NCASI laboratory and gives an indication of the precision of the method.

8.4 Recovery: Using the mean concentration determined by the replicate analyses, determine a spiking level which will give a minimum of three times the background. Spike an aliquot of the sample with the determined amount of the calibration standard working solution and proceed to analyze the sample in the normal manner. Using the results of that analysis, calculate

the percent recovery as follows:

$$\text{Percent Recovery} = \frac{\text{Level Measured} - \text{Background}}{\text{Level Spiked}} \times 100$$

where the background is the mean of the replicate determinations described above.

Table 5 summarizes the percent recoveries measured by the NCASI laboratory and gives an indication of the accuracy of the method.

TABLE 5 SUMMARY OF THE NCASI LABORATORY QA/QC DATA^a

<u>Compound</u>	<u>Relative Percent Difference</u>			<u>Percent Recovery</u>	
	<u>\bar{x}</u>	<u>(n)^b</u>	<u>Maximum</u>	<u>\bar{x}</u>	<u>Rel.S.D.</u>
2,6-dichlorophenol	2.1	(5)	8.3	108	13.3
2,4-dichlorophenol	7.6	(22)	27.2	106	14.1
3,5-dichlorophenol	2.8	(3)	8.3	108	10.6
3,4-dichlorophenol	10	(2)	20.0	104	14.8
2,4,6-trichlorophenol	4.7	(26)	17.5	98	21.7
2,3,6-trichlorophenol	-	(1)	-	106	10.4
2,4,5-trichlorophenol	5.8	(4)	13.3	114	17.5
2,3,4,6-tetrachlorophenol	10.5	(26)	31.3	96	15.8
pentachlorophenol	7.8	(18)	30.0	104	18.5
4,6-dichloroguaiacol	13.2	(12)	27.7	104	19.0
4,5-dichloroguaiacol	8.2	(12)	31.9	103	18.6
3,4,5-trichloroguaiacol	5.9	(32)	28.1	95	19.6
4,5,6-trichloroguaiacol	7.1	(28)	27.3	95	10.6
tetrachloroguaiacol	6.3	(33)	28.0	91	18.1
3,6-dichlorocatechol	11.4	(4)	16.7	83	37.7
3,4-dichlorocatechol	-	(1)	-	91	35.9
4,5-dichlorocatechol	12.6	(21)	32.2	80	31.0
3,4,6-trichlorocatechol	10.3	(12)	24.0	70	22.3
3,4,5-trichlorocatechol	9.5	(29)	34.1	78	36.9
tetrachlorocatechol	11.5	(24)	26.7	76	36.0
6-chlorovanillin	11.7	(14)	33.3	108	25.5
5,6-dichlorovanillin	13.4	(17)	33.3	94	14.6
chlorosyringaldehyde	18.9	(5)	30.0	98	25.6
trichlorosyringol	5.5	(31)	31.0	91	24.6

^a QA/QC data up to 6/86 included in summary

^b n = number of determinations

8.5 Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectrometry (e.g. NCASI Method CP-86.01) should be used.

D20

APPENDIX B

NCASI

METHOD CP-86.01

CHLORINATED PHENOLICS IN WATER BY IN SITU
ACETYLATION/GC/MS DETERMINATION

NCASIMETHOD CP-86.01CHLORINATED PHENOLICS IN WATER BY IN SITU
ACETYLATION/GC/MS DETERMINATION1.0 Scope and Application

1.1 Method CP-86.01 is used to qualitatively confirm and semi-quantitate the concentration of chlorinated phenols, chlorinated guaiacols, chlorinated catechols, and chlorinated benzaldehydes (i.e. vanillins and syringaldehydes) in water samples. Specifically, Method CP-86.01 can be used to confirm or determine:

Chlorinated Phenols

2-chlorophenol
4-chlorophenol
3,5-dichlorophenol
3,4-dichlorophenol
2,6-dichlorophenol
2,4-dichlorophenol
2,3,6-trichlorophenol
2,4,6-trichlorophenol
2,4,5-trichlorophenol
2,3,4,6-tetrachlorophenol
pentachlorophenol

Chlorinated Guaiacols

4-chloroguaiacol
4,5-dichloroguaiacol
4,6-dichloroguaiacol
3,4,5-trichloroguaiacol
4,5,6-trichloroguaiacol
tetrachloroguaiacol

Chlorinated Catechols

4-chlorocatechol
3,6-dichlorocatechol
3,4-dichlorocatechol
4,5-dichlorocatechol
3,4,5-trichlorocatechol
3,4,6-trichlorocatechol
tetrachlorocatechol

Chlorinated Benzaldehydes

6-chlorovanillin
5-chlorovanillin
5,6-dichlorovanillin
chlorosyringaldehyde
3,5-dichloro-4-hydroxy-
benzaldehyde

Miscellaneous Compounds

trichlorosyringol

1.2 This method has been used to analyze untreated and biologically treated pulp mill effluents and bleach plant process streams.

1.3 When CP-86.01 is used to analyze unfamiliar samples, quality assurance duplicate and recovery samples should be run. Method CP-86.01 is intended to complement Method CP-85.01, Chlorinated Phenolics In Water By In Situ Acetylation/GC-ECD Determination.

2.0 Summary of Method

2.1 Method CP-86.01 provides in situ derivitization, extraction and gas chromatographic conditions for the detection of ppb levels of chlorinated phenolics. Samples are neutralized, spiked with the Internal Standard, then buffered with potassium carbonate in order to form the phenolate ions which are then converted in situ (i.e. in the aqueous matrix) to their acetate derivatives by the addition of acetic anhydride. The chlorophenolic acetates thus formed are extracted with hexane. A 1 to 2 μ L portion of the hexane extract is injected into a gas chromatograph using a Grob type splitless injection technique and is chromatographed on a fused silica capillary column using mass spectrometric determination. The standards used to determine the calibration curve are prepared by spiking the Internal Standard and the appropriate levels of analytes into blank water and then derivatizing in the same manner as the sample.

2.2 The Internal Standard used in the method 3,4,5-trichlorophenol has been identified as a persistent anaerobic degradation product of 2,3,4,5-tetrachlorophenol and/or pentachlorophenol. Other workers analyzing samples containing these compounds which have been subjected to anaerobic conditions and are using a similar in situ acetylation GC-ECD procedure have substituted 2,6-dibromophenol as the Internal Standard.

2.3 The sensitivity of Method CP-86.01 depends on both the level of interferences in the matrix and on the sensitivity of the GC/MS. Generally, low ppb detection limits can be achieved in most samples. Actual detection limits would have to be determined on each type of matrix.

3.0 Interferences

3.1 When a similar procedure (NCASI Method CP-85.01) was applied to groundwater samples collected in the vicinity of a source of creosote, (i.e. wood preservation plant) the high levels of non-chlorinated phenols caused poor recoveries and the method was found unsatisfactory. It is likely that Method CP-86.01 would be subject to the same limitation, although no tests have been run to confirm this.

3.2 The Internal Standard, 3,4,5-trichlorophenol, has been shown by some researchers to be a persistent anaerobic degradation product of 2,3,4,5-tetrachlorophenol and/or pentachlorophenol. Thus, Method CP-86.01 would have to be modified appropriately when applied to samples suspected of containing these compounds and having undergone anaerobic degradation. Other workers have used 2,6-dibromophenol as an alternative Internal Standard in similar in situ acetylation GC-ECD procedures.

3.3 Blanks most frequently are contaminated with penta-chlorophenol. Generally this has been traced to the potassium carbonate and has been removed by baking the reagent at 400°C overnight. All reagents should be tested for contamination prior to use.

3.4 All glassware should be washed with hot detergent water, rinsed, air dried and then baked at 400°C for 6-8 hours. Volumetric pipets should be washed in an alcoholic KOH bath and then rinsed thoroughly with tap water before air drying.

4.0 Apparatus and Equipment

4.1 Glassware

250 mL Separatory funnel with Teflon stopcock
 250 mL beaker
 100 mL graduated cylinder
 Volumetric pipets (TD)
 Centrifuge tubes: 35 mL with Teflon lined screw cap
 Centrifuge tube: 15 mL graduated conical with ground glass stopper
 2 dram vials with Teflon-lined screw caps
 Concentrator tube, Kuderna-Danish: 15 mL
 Evaporative flask, Kuderna-Danish: 250 mL, attach to concentrator tube with springs
 Snyder column, Kuderna-Danish: three-ball macro

4.2 pH Meter: Calibrated using two point procedure

4.3 Centrifuge: Bench top model

4.4 Evaporation/concentration assembly: Pierce 19797 Uni-Vap Evaporator or equivalent.

4.5 Water bath: Constant temperature capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

4.6 Gas Chromatograph/Detector System

4.6.1 Column: 30 m x 0.25 mm bonded-phase fused silica DB-5 capillary column (J&W Scientific DB-5 or equivalent).

4.6.2 Mass Spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. A computer system must be interfaced to the mass spectrometer capable of allowing the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic

program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software capabilities must also allow integrating the abundance in any EICP between specified time or scan number limits.

5.0 Reagents

5.1 Non-spectrograde hexane distilled in glass (Burdick and Jackson)

5.2 Acetic anhydride: Redistilled reagent grade

5.3 Reagent water: Organic free such as produced by a Barnstead Model D2798 NANO-pure-A water purification system

5.4 Sodium hydroxide: 5 percent w/w in reagent water

5.5 Sulfuric acid: Mix one part conc. H_2SO_4 with four parts reagent water

5.6 Potassium Carbonate: Dissolve 150 g K_2CO_3 (purified by heating at 400°C for 6 to 8 hours in a shallow tray) in 250 mL reagent water

5.7 Internal Standard Stock Solution: Weigh (to the nearest 0.1 mg) 25 ± 3 mg of 3,4,5-trichlorophenol and dissolve to volume with methanol in a 50 mL volumetric flask. Transfer the stock solution into an amber bottle with a Teflon-lined screw cap and store under refrigeration.

5.8 Internal Standard Spiking Solution: Pipet 5.0 mL of the stock solution into a 100 mL ground-glass-stoppered volumetric flask and dilute to volume with methanol. Transfer the spiking solution into five ca 20 mL portions in separate Teflon-lined screw capped vials, number 1 to 5 and store under refrigeration (4°C).

5.9 Calibration Standard Stock Solutions: Prepare stock solutions of individual compounds by weighing (to the nearest 0.1 mg) 25 ± 1 mg of each compound of a known purity. Dissolve the material in methanol (acetone must be used for the chlorinated benzaldehydes) and bring to volume in a 25 mL ground-glass-stoppered volumetric flask. Transfer the individual stock solutions to 25 mL scintillation vials with Teflon-lined screw caps and refrigerate at 4°C . Prepare the working solution by pipeting 1.0 mL of each stock solution into a 50 mL ground-glass-stoppered volumetric flask. Bring to volume with methanol. This working solution is discarded after use.

5.10 Calibration Curve Standards: The calibration curve standards are prepared by spiking separate 100 mL portions of reagent water with 150 μ L of the Internal Standard spiking solution and 50, 750, 1500 μ L portions of the calibration standard working solution. The resulting solutions are then acetylated, extracted and concentrated in a manner analogous to a 100 mL sample aliquot.

6.0 Sample Collection, Preservation and Storage

6.1 Collection: Grab samples must be collected in glass containers having a Teflon-lined screw cap. Automatic sampling equipment which comes in contact with the sample should be constructed of glass, Teflon, or stainless steel. Composite samples should be refrigerated during the sampling period.

6.2 Preservation: All samples must be preserved by adjusting to pH two, with H_2SO_4 , and refrigerating. This should be done as soon as possible after sample collection. Samples must be shipped in iced containers as quickly as possible.

6.3 A portion of the sample should be tested for free or residual chlorine. Add 35 mg of sodium thiosulfate per ppm free chlorine per liter.

6.4 Storage: Samples may be stored in the refrigerator (4°C) for up to 30 days. Acetylated extracts must be analyzed within 30 days after acetylation.

7.0 Procedures

7.1 Sample Preparation:

7.1.1 In Situ Acetylation: Remove the sample from the refrigerator and allow it to come to room temperature. Shake the sample vigorously to insure it is homogeneous and then measure out three 100 mL aliquots. Neutralize the sample to pH 7.0 to 7.1 using 5 percent NaOH and 1:4 sulfuric acid. Add 2.6 mL of the potassium carbonate solution and adjust the pH to 11.6 ± 0.1 with 5 percent NaOH if necessary.

Transfer the sample to a 250 mL separatory funnel and spike it with 50 μ L of the Internal Standard spiking solution. Shake the sample to insure thorough mixing. Add 2.0 mL of acetic anhydride and shake the sample with frequent venting for 30 seconds. Let the sample stand for 5 minutes then shake and vent.

Add 10 mL of hexane and shake vigorously for 1 to 2 minutes with frequent venting. Allow the phases to separate and drain off the aqueous portion into the beaker. If there is

an emulsion problem, drain the organic layer into a centrifuge tube, cap and centrifuge for 2 to 3 minutes or until the emulsion is broken. Transfer as much of the hexane as possible into the Kuderna-Danish (K-D) assembly. Transfer the aqueous portions back to the separatory funnel and extract two more times with 10 mL hexane, combining the extracts in the K-D. Repeat this process with the remaining two 100 mL sample aliquots, combining all hexane extracts and rinses into the one K-D assembly. Add 1 or 2 carborundum boiling chips and secure the assembly in the water bath. Watch the sample carefully and remove when the K-D receiving tube is about 1/4 full. Do not allow the sample to go to dryness. Transfer the concentrated extract to a 15 mL centrifuge tube using three 1 mL hexane rinses. Concentrate to a final volume of ca 0.2 mL. Cap and store in the refrigerator until analyzed. After analysis has been completed, transfer the sample using three 1 mL hexane rinses to a labeled 2-dram Teflon-lined screw cap vial and refrigerate.

7.2 The recommended gas chromatographic column and operating conditions for the instrument are : 30 m x 0.25 mm id fused silica DB-5, 0.25 micron film thickness. Helium carrier gas (36 cm/sec at 200°C). Injection port temperature 210°C. Column temperature, isothermal at 45°C for one minute then temperature programmed at 6°C/min to 280°C holding for 25 minutes.

7.3 The recommended mass spectrometer operating conditions are: mass scan range m/e 42 to 336 with a scan speed of 216.7 amu/sec.

7.4 Calibration

7.4.1 Prior to any analysis of standards or samples, the mass spectrometer must be tuned in such a manner that a mass spectrum of DFTPP meeting all criteria in Table 1 can be obtained.

7.4.2 Calibration Curve: Establish GC/MS operating parameters equivalent to those described in Sections 7.2 and 7.3. Analyze 1 μ L splitless injection of the calibration curve standards and integrate the extracted ion current areas for each of the characteristic ions shown in Table 2. Tabulate the ratio of the area of the analyte quantitation ions divided by the area of the Internal Standard. Using this data and the concentrations of the analytes, assuming a 300 mL sample volume, calculate the linear regressions and tabulate the calibration slope and intercept data.

TABLE 1 DFTPP KEY MASSES AND ABUNDANCE CRITERIA^{a,b}

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30 to 60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40 to 60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 to 23% of mass 442

^a J.W. Eichelberger, L.E. Harris, and W.L. Budde, "Reference Compound To Calibrate Ion Abundance Measurement In Gas Chromatography-Mass Spectrometry." Analytical Chemistry 47,995 (1975).

^b 50 ng DFTPP injected using a Grob type splitless injection and the following gas chromatographic conditions:
Injection port temperature 210°C, oven programmed from 160°C after a one minute hold at 6°C/minute to 210°C.
Mass spectrometer conditions are set to scan from 45 to 445 amu at 216.7 amu/sec.

7.4.3 Daily Calibration Check: The working calibration curve must be verified on each working day by the analysis of one or more calibration curve standards. If the recovery of any analyte varies by more than ± 20 percent, the test must be repeated at a different concentration level. If this value is also out of range, a new calibration curve must be prepared.

7.5 Sample Analysis

7.5.1 The sample extract is analyzed using the conditions described in Sections 7.2 and 7.3. The extracted ion current profile areas for each of the ions listed in Table 2 are tabulated.

TABLE 2 CHARACTERISTIC IONS AND RELATIVE RETENTION TIMES

Compound	Characteristic Ions		Relative Retention Time ^a
	Primary	Secondary	
2-chlorophenol	128	130, 170	0.598
4-chlorophenol	128	130, 170	0.637
2,6-dichlorophenol	162	164, 204	0.747
2,4-dichlorophenol	162	164, 204	0.771
3,5-dichlorophenol	162	164, 204	0.784
3,4-dichlorophenol	162	164, 204	0.835
4-chloroguaiacol	158	160, 200	0.863
2,4,6-trichlorophenol	196	198, 238	0.877
2,3,6-trichlorophenol	196	198, 238	0.923
2,4,5-trichlorophenol	196	198, 238	0.939
4,6-dichloroguaiacol	192	194, 234	0.987
3,4,5-trichlorophenol(IS)	196		1.00
3,5-dichloro-4-hydroxybenzaldehyde	189	191, 232	1.001
4,5-dichloroguaiacol	192	194, 234	1.041
3,5-dichlorocatechol	178	180, 262	1.053
2,3,4,6-tetrachlorophenol	230	232, 272	1.066
5-chlorovanillin	186	188, 228	1.086
6-chlorovanillin	186	188, 228	1.094
3,4-dichlorocatechol	178	180, 232	1.108
4,5-dichlorocatechol	178	180, 232	1.130
3,4,5-trichloroguaiacol	226	228, 268	1.143
4,5,6-trichloroguaiacol	226	228, 268	1.180
3,4,6-trichlorocatechol	212	214, 296	1.184
5,6-dichlorovanillin	220	222, 262	1.220
pentachlorophenol	266	268, 308	1.231
chlorosyringaldehyde	216	218, 258	1.231
3,4,5-trichlorocatechol	212	214, 296	1.243
tetrachloroguaiacol	260	262, 302	1.258
trichlorosyringol	256	258, 298	1.272
tetrachlorocatechol	246	248, 330	1.338

^a Retention times of acetate derivatives relative to 3,4,5-trichlorophenol acetate. Under the chromatographic conditions in Section 7.2, the retention time for 3,4,5-trichlorophenol acetate is 20.92 minutes.

7.5.2 Qualitative criteria: Obtain EICPs for the primary ions and the two secondary ions listed in Table 2. The following criteria must be met in order to make a qualitative identification. The characteristic ions of each compound of interest must maximize within two scans of each other and the retention time must fall within 20

seconds of the authentic compound. The relative peak areas of the characteristic ions must fall within 20 percent of the relative intensities as determined in the reference compound obtained from the previously analyzed calibration standards.

7.5.3 Quantitation: Calculate the concentration of the analytes using the following equation:

$$\text{Concentration} = \left(\frac{A_S}{A_{IS}} \right) (m_S) + b_S$$

where: A_S = area of the analyte ion

A_{IS} = area of the internal standard ion

m_S = slope from calibration curve for analyte ion

b_S = intercept from calibration curve for analyte ion

If the sample produces an interference for the primary ion, use a secondary characteristic ion to quantitate.

8.0 Quality Control

8.1 Blanks: Before processing any samples or whenever a new reagent is prepared, the analyst should demonstrate through the analysis of a blank that utilizes all glassware and reagents required for sample analyses that all materials are interference free. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Frequency: A minimum of 5 percent of routine samples should be allocated for quality control. In addition to this, representative samples from each new or untested source or sample matrix should be treated as a quality control sample. Laboratory replicates and fortification should be conducted on each QC sample to document method performance as indicated by precision and recovery.

8.3 Replicates: Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. The range and mean concentration of the replicates are determined from the results and the relative percent difference is calculated as follows:

$$\text{Rel. Percent Difference} = 100 \left(\frac{\text{range}}{\text{mean}} \right)$$

8.4 Recovery: Using the mean concentration determined by

the replicate analyses, determine the spiking level which will give a minimum of three times the background. Spike the sample with the determined amount of the calibration standard working solution and proceed to analyze the sample in the normal manner. Calculate and record the percent recovery as follows:

$$\text{Percent Recovery} = \frac{\text{Level Measured-Background}}{\text{Level Spiked}} \times 100$$

where the Background is the mean of the replicate determinations described above.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

May 8, 1987

MEMO TO: Frank Thomas

FROM: Larry LaFleur *LL*

SUBJECT: Revised Isotopic Dilution Quantitation Procedures for
Chlorinated Phenolics Analysis Procedures

Attached is a summary of the revised quantitation procedures we have discussed in the past and agreed to incorporate into the analysis of the Cooperative Study chlorinated phenolics analysis procedures. Essentially, stable isotope internal standards have been incorporated wherever possible. The standards were obtained and details were worked out before we began the analysis of the samples from the final three mills. Thus, as indicated in the reports I have already sent out, NCASI Method CP-86.01 was used for the first two mills and this revised quantification procedure was used for the last three mills.

**REVISED QUANTIFICATION PROCEDURE
FOR CHLORINATED PHENOLICS ANALYSIS**

The compounds are quantified using multiple internal standards, with the internal standard to be used designated as the one closest in retention time to that of a given analyte. When a labelled analog exists for an analyte, isotopic dilution is the quantitation method used. The internal standards and the corresponding analytes are listed below:

$^2\text{H}_4$ -4-chlorophenol	2-chlorophenol
$^2\text{H}_3$ -2,4-dichlorophenol	2,6-dichlorophenol
	2,3-dichlorophenol
	3,4-dichlorophenol
	2,4-dichlorophenol
$^2\text{H}_2$ -2,4,5-trichlorophenol	2,4,5-trichlorophenol
3,4,5-trichlorophenol	4,5-dichloroguaiacol
	3,4,5-trichloroguaiacol
	4,5,6-trichloroguaiacol
	5-chlorovanillin
	6-chlorovanillin
$^{13}\text{C}_6$ -pentachlorophenol	pentachlorophenol
	5,6-dichlorovanillin
	tetrachloroguaiacol

A four-point (including the origin) calibration curve is established by analyzing three levels of analytes using a constant amount of the internal standards in each. The ratios of the EICP area of the analyte quantitation ion divided by the EICP area of the appropriate internal standard quantitation ion are plotted against analyte concentration. The slope and intercept are calculated using a linear regression equation and these values are used to calculate sample concentrations as follows:

$$\text{Concentration} = \text{slope} \times \frac{A_x}{A_I} + \text{intercept}$$

where: A_x = EICP area of the analyte primary quantitation ion

A_I = EICP area of the internal standard primary quantitation ion

For those compounds (2,4 dichlorophenol, 2,3,5-trichlorophenol, and pentachlorophenol) where a labeled analog is present, quantitation is performed using the relative responses of analyte to labeled analog to create a calibration curve as previously mentioned for the internal standard quantitation. The relative responses (RR) are calculated using the equation:

$$RR = \frac{(R_Y - R_m) (R_X + 1)}{(R_m - R_X) (R_Y + 1)}$$

where:

R_X = the isotope ratio measured for the native analyte

R_Y = the isotope ratio of an analytical mixture of the native analyte and labelled analog

The R_X and R_Y values are calculated from the EICP data of the specified quantitation ion obtained by analyzing separate aliquots of the native analytes and the labelled analogs. This need only be done once at the beginning of the project. The R_m values are generated over the range of concentrations which will be measured and are the ratios of the EICP areas of the analyte quantitation ion divided by the EICP areas of the labelled analog quantitation ion. The calibration curve is established by plotting RR against analyte concentration. As before, the slope and intercept are calculated and values are used to calculate sample concentrations as follows:

$$\text{Concentration} = \text{slope (RR)} + \text{intercept}$$

where: RR = relative response factor defined above

$$RR = \frac{A_X}{A_I}$$

A_X = EICP area of the analyte quantitation ion

A_I = EICP area of the labelled analog quantitation ion.

The following table presents the pertinent data for all compounds used to establish the calibration curves.

COMPOUND	QUANTITATION ION	RETENTION TIME	CALIBRATION CURVE WEIGHT FACTORS(ug)			
			100ul STD	500ul STD	1000ul STD	
2-Chlorophenol	128	14.8	3.91	19.55	39.10	
4-Chlorophenol-d4(IS)	132	15.6	6.10	6.10	6.10	
2,6-Dichlorophenol	162	18.0	3.51	17.55	35.10	
2,4-Dichlorophenol	162	18.5	2.74	13.70	27.40	
2,3-Dichlorophenol	162	19.3	3.50	17.50	35.00	
3,4-Dichlorophenol	162	19.8	3.14	15.70	31.40	
2,4-Dichlorophenol-d3(IS)	165	18.5				
2,4,5-Trichlorophenol	196	22.1	3.18	15.90	31.80	
2,4,5-Trichlorophenol-d2(IS)	200	22.1	5.12	5.12	5.12	
4,5-Dichloroguaiacol	192	24.2	2.77	13.85	27.70	
3,4,5-Trichloroguaiacol	226	26.4	1.90	9.50	19.00	
4,5,6-Trichloroguaiacol	226	27.1	3.25	16.25	32.50	
5-Chlorovanillin	186	25.0	2.25	11.25	22.50	
6-Chlorovanillin	186	25.2	3.12	15.60	31.20	
3,4,5-Trichlorophenol(IS)	196	23.3	5.93	5.93	5.93	
Pentachlorophenol	266	28.4	3.22	16.10	32.20	
5,6-Dichlorovanillin	220	27.9	2.68	13.40	26.80	
Tetrachloroguaiacol	260	28.8	2.07	10.35	20.70	
Pentachlorophenol-Cl3(IS)	272	28.4	5.35	5.35	5.35	

ATTACHMENT E

ANALYTICAL RESULTS FOR 2378-TCDD and 2378-TCDF
(Master Sample Lists)

25-Feb-88

Mill A
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
A. BACKGROUND SAMPLES											
DE020801	Treated River Water	ND(0.00514)	**	61.0	11-16-87		ND(0.0107)	**	51.9	11-16-87	ERR
DE020802	Water Treatment Precip. Sludge										ERR
DE020803	Water Treatment Sandfilter Sludge										ERR
DE020804	Softwood Chips										ERR
DE020805	Hardwood Chips										ERR
B. PULPING PROCESS											
DE020806	Combined Pulping & Recaust WWs										ERR
C. CHEMICAL RECOVERY PLANT											
DE020807	Combined Process Wastewater										ERR
DE020808	Lime Mud										ERR
D. BLEACH PLANT											
DE020901	Unbleached Softwood Pulp	ND(0.738)	**	69.7	9-25-87		ND(0.271)	**	57.1	9-25-87	ERR
DE020902	Bleached Softwood Pulp	15.2	0.76	76.0	3-19-87						
DE020902	Bleached Softwood Pulp	16.3	0.79	82.3	4-21-87		333	0.78	74.8	4-21-87	
	AVERAGE	15.8					333				21.08
DE020903	Unbleached Hardwood Pulp	ND(0.309)	**	70.4	9-25-87		ND(0.231)	**	64.3	9-25-87	ERR
DE020904	Hypo Hardwood Pulp	4.89	0.79	64.1	4-21-87		47.3	0.78	54.6	7-17-87	9.67
DE020905	Peroxide Hardwood Pulp	2.98	0.85	77.1	4-21-87		50.1	0.67	54.3	7-17-87	16.81
Softwood Bleach Line											
DE020906	S-1 Washer, C Stage	0.238	0.81	72.0	4-28-87		3.806	0.82 ->	37.8	4-28-87	15.99
DE020907	S-2 Washer, Eo Stage	1.82	0.85	68.1	3-19-87		32.6	0.88	72.5	3-19-87	17.91
DE020908	S-3 Washer, H Stage	0.342	0.80	65.6	5-22-87		5.778	0.82	75.3	5-22-87	16.89
Hardwood Bleach Lines											
DE020909	K-6 Washer, C Stage	0.0212	0.84	78.9	4-28-87		0.305	0.88	50.2	6-15-87	14.39
DE020910	K-4 Washer, Eo Stage (Hypo line)	ND(0.0326)	**	51.7	5-22-87		0.247	0.82 ->	39.9	6-15-87	UNDEFINED
DE020911	K-5 Washer, H Stage (Hypo line)	ND(0.0168)	**	56.4	6-19-87		0.114	0.68	61.4	7-17-87	UNDEFINED
DE020912	K-2 Washer, Eo Stage (Per line)	0.0453	0.82	91.0	5-22-87		0.318	0.84	59.4	6-15-87	7.02
DE020913	K-3 Washer, H Stage (Per line)	0.0403	0.83	52.5	6-19-87		0.170	0.77	53.5	7-17-87	4.22
DE020914	K-1 Washer, H Stage (Per line)	0.0247	0.79	60.1	5-12-87		0.174	0.85	57.0	6-15-87	7.04
DE020809	Hypo Solution										ERR
DE020810	Caustic Solution										ERR
DE020915	Combined Process Wastewater	0.296	0.81	106	1-16-87						

09-Mar-88

Mill A
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
E. PAPER MACHINES											
DE020811	Combined Process Wastewaters Process Additives	0.0205	0.81	52.4	8-19-87		0.191	0.80	52.5	8-19-87	9.32
DE020812	Alum										ERR
DE020813	Filler Clay										ERR
DE020814	Coater Clay										ERR
DE020916	Dye-1 (Helmerco Blue MGW)										ERR
DE020917	Dye-2 (Cartosol Brill. Paper Yellow)										ERR
DE020815	Resin Size Emulsion (Neuphor)										ERR
DE020816	High Brightness Filter (Hycal)										ERR
DE020817	Slimicide (Dearborn 6202)										ERR
DE020822	Soda Ash										ERR
DE020823	Sodium Thiosulfate										ERR
DE021001	Whitewater - Clean										ERR
DE021002	Whitewater - Dirty										ERR
F. UTILITIES, WASTEWATER TREATMENT											
DE020818	Powerhouse Wastewater										ERR
DE020918	Bottom Ash										ERR
DE020919	Fly Ash	ND(0.660)	**	77.9	9-21-87		ND(0.349)	**	61.2	9-21-87	ERR
DE020819	WWTP Primary Sludge	23.5	0.76	96.2	9-21-87		362	0.81	60.1	9-21-87	16.26
DE020820	WWTP Secondary Sludge	709	0.82	77.8	9-21-87		10532	0.80	48.2	9-21-87	15.42
DE020920	WWTP Composite Sludge	37.4	0.72	86.9	3-19-87		624	0.89	74.6	3-19-87	
DE020920	WWTP Composite Sludge	35.8	0.80	80.3	4-21-87		732	0.76	72.5	4-21-87	
	AVERAGE	36.6					678				18.52
DE020921	Combined Untreated Wastewater	0.136	0.79	71.1	6-18-87		1.916	0.78	64.8	6-18-87	14.09
DE020922	Final Wastewater Effluent	0.111	0.72	89.8	1-16-87		2.18	0.74	42.6	2-12-87	
DE020922	Final Wastewater Effluent	0.150	0.86	44.5	2-12-87						
DE020922	Final Wastewater Effluent	0.111	0.85	63.2	2-12-87						
	AVERAGE	0.124					2.18				17.58
DE020821	Landfill Leachate	0.0309	0.78	59.1	7-9-87		0.124	0.78	48.7	7-9-87	
DE020821	Landfill Leachate	0.0196	0.86	52.7	9-11-87		0.095	0.79	52.6	9-11-87	
	AVERAGE	0.0253					0.110				4.36
G. OTHER											
DE020923	Sludge (not from Mill A)	470	0.79	64.6	4-21-87		4186	0.72	47.4	4-21-87	8.91
DE020824	Thiosulfate & H2SO4 Reagent Blank	ND(0.0102)	**	->	35.8	9-21-87	ND(0.0293)	**	42.7	9-21-87	ERR
DE020924	Field Blank										

16-Feb-88

Mill B
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
A. BACKGROUND SAMPLES											
86374601	Treated Intake	ND(0.00693)	**	54.5	11-16-87		ND(0.00950)	**	47.1	11-16-87	ERR
86374602	Filter Backwash										ERR
86374603	Softwood Chips										ERR
86374604	Hardwood Chips										ERR
86374605	Softwood Sawdust										ERR
86374671	Softwood Sawdust										ERR
B. PULPING PROCESS											
86374606	Brownstock Filtrate (Int./Ext.)										
86374607	Pulp Mill										ERR
86374609	Recovery, Evap, Recaust										ERR
86374672	Recovery, Evap, Recaust										ERR
C. CHEMICAL RECOVERY PLANT											
86374610	Lime Mud										ERR
D. BLEACH PLANT											
86374611	Unbleached Pulp	ND(0.949)	**	41.4	9-25-87		1.54	0.68 ->	39.0	9-25-87	ERR
86374612	Bleached Pulp	10.2	0.83	54.6	4-21-87		54.3	0.65	67.1	4-21-87	
86374612	Bleached Pulp	11.0	0.77	60.2	8-19-87		64.4	0.73 ->	10.3	8-19-87	
86374661	Bleached Pulp	12.6	0.69	67.0	4-21-87		63.9	0.77	55.4	4-21-87	
	AVERAGE (612/661)	11.3					60.9				5.40
86374613	Chlorination Stage (C)	ND(0.0327)	**	42.1	3-19-87		0.0635	0.88 ->	30.6	3-19-87	ERR
86374673	Chlorination Stage (C)	0.0463	0.84	57.6	11-16-87		0.0722	0.70	48.2	11-16-87	
	AVERAGE (613/673)	0.0232					0.0679				2.93
86374674	Chlorination Stage (Grab)										ERR
86374614	Dioxide Stage (D)	0.0298	0.80	78.6	5-12-87		0.133	0.68	62.5	5-12-87	4.46
86374615	Caustic Stage (E)	0.229	0.81	59.8	6-19-87		1.254	0.67	44.1	6-19-87	
86374615	Caustic Stage (E)	0.219	0.81	69.2	7-7-87		0.834	0.70	49.4	7-17-87	
	AVERAGE	0.224					1.044				4.66
86374616	First Hypo Stage (H)	0.258	0.83	50.9	5-22-87		1.129	0.71	59.7	5-22-87	4.38
86374617	Second Hypo Stage (H)	0.132	0.78	51.4	6-19-87		0.913	0.84	80.8	11-16-87	6.92
86374618	Hypo Solution	ND(0.0098)	** ->	39.9	3-19-87		ND(0.0054)	** ->	38.8	3-19-87	UNDEFINED
86374619	Caustic Solution										ERR
86374620	Chlorine Dioxide Solution										ERR

16-Feb-88

Mill B
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%EC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
E. PAPER MACHINES											
86374621	Paper Machine	ND(0.00514)	** ->	35.9	8-19-87		0.108	0.69 ->	36.9	8-19-87	ERR
86374623	Slimicide (CB 210)										
86374624	Dye (Yellow)										
86374625	Slimicide (D3TA)										
86374626	Dye (Violet)										
86374627	HTI 6440										
86374628	Perez 631										
86374629	Santo Rez										
F. UTILITIES, WASTEWATER TREATMENT											
86374641	Primary Sludge	18.9	0.79	102.1	9-21-87		101	0.80	90.1	9-21-87	5.34
86374642	Secondary Sludge (No/Poly)	88.9	0.80	78.2	4-21-87		808	0.72	84.8	4-21-87	9.09
86374643	Secondary Sludge (W/Poly)										ERR
86374644	Untreated Wastewaters	ND(.0129)	**	52.4	6-18-87		0.092	0.68	49.8	6-18-87	UNDEFINED
86374644	Untreated Wastewaters	ND(0.00644)	** ->	27.5	9-21-87		0.124	0.67 ->	27.9	9-21-87	UNDEFINED
	AVERAGE	0					0.108				UNDEFINED
86374646	Leachate	ND(0.00405)	**	43.7	9-11-87		0.0105	0.64	40.9	9-11-87	ERR
86374645	Final Effluent	0.0157	0.86	69.7	7-9-87		0.133	0.65 ->	30.5	7-9-87	
86374645	Final Effluent	0.0145	0.66	69.0	11-16-87		0.110	0.72	57.8	9-30-87	
	AVERAGE	0.0151					0.122				8.08
G. OTHER											
86374681	Field Blank										

16-Feb-88

Mill C
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C127CDD	LAB REPORT DATE	**	TCDF (ppt)	304/306 RATIO	% REC 13C127CDD	LAB REPORT DATE	TCDF/TCDD RATIO
A. BACKGROUND SAMPLES											
DE026001	Treated River Water	ND(0.00531)	**	41.9	8-19-87		ND(0.00694)	**	41.0	11-16-87	ERR
DE026101	Water Soft. Sludge										ERR
DE026102	Sandfilter Backwash										ERR
DE026103	Hardwood Chips										ERR
DE026104	Raw Water Comp										ERR
B. PULPING PROCESS											
DE026107	Combined Pulping Comp										ERR
DE026111	Recaust And Lime Kiln										ERR
C. BLEACH PLANT											
DE026002	Unbleached Pulp	ND(0.564)	**	60.2	9-25-87		ND(0.162)	**	44.6	9-25-87	ERR
DE026003	Bleached Pulp	ND(0.620)	**	91.1	11-16-87		14.9	0.89	62.5	3-19-87	UNDEFINED
DE026004	C/D Filtrate	ND(0.00593)	**	63.4	4-28-87		0.0929	0.73	53.7	4-28-87	UNDEFINED
C/D-1	C/D Filtrate (Grab-1)										
C/D-2	C/D Filtrate (Grab-2)										
C/D-3	C/D Filtrate (Grab-3)										
C/D-4	C/D Filtrate (Grab-4)										
DE026005	E/O Filtrate	ND(0.0106)	**	52.2	6-19-87		0.0573	0.87 ->	24.8	7-17-87	
DE026211	E/O Filtrate	ND(0.0154)	**	48.3	6-19-87		0.0543	0.83 ->	13.1	7-17-87	
	AVERAGE (005/211)	0					0.0558				UNDEFINED
DE026212	E/O Filtrate										ERR
E/O-1	E/O Filtrate (Grab-1)										
E/O-2	E/O Filtrate (Grab-2)										
E/O-3	E/O Filtrate (Grab-3)										
E/O-4	E/O Filtrate (Grab-4)										
DE026006	D Filtrate	ND(0.0112)	**	49.1	3-19-87		ND(0.0056)	**	52.1	3-19-87	UNDEFINED
DE026213	D Filtrate	ND(0.00341)	**	80.3	5-12-87		0.0272	0.69	68.3	5-12-87	
	AVERAGE (006/213)	0					0.0136				UNDEFINED
DE026214	D Filtrate										ERR
D-1	D Filtrate (Grab-1)										
D-2	D Filtrate (Grab-2)										
D-3	D Filtrate (Grab-3)										
D-4	D Filtrate (Grab-4)										
DE026114	Scrubber	ND(0.00912)	**	68.4	9-21-87		0.429	0.76	54.8	9-21-87	
DE026116	ClO2 Solution										ERR
DE026117	Caustic Solution										ERR

09-Mar-88

Mill C
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
D. PAPER MACHINES											
DE026118	Combined Process Water	0.0106	0.70	60.1	6-19-87		0.197	0.73	56.5	8-19-87	16.58
DE026123	Dye (Mobay Pont. Brill. Blue A)										ERR
DE026124	Dye (Pergasol Yellow 5RA Extra-6)										ERR
DE026201	Dye (Anthosin Red 21P-BASF)										ERR
DE026202	Biocide (Betz RX-41)										ERR
DE026203	Defoamer (Fleetcol 9170)										ERR
DE026204	Dye (Mobay Pont. Bond Yellow 303)										ERR
E. UTILITIES, WASTEWATER TREATMENT											
DE026205	Station 15 Woodboiler										ERR
DE026007	Coal Ash - Sluiced										ERR
DE026008	Coal Ash - ESP										ERR
DE026009	Mechanical Coal Ash										ERR
DE026010	Wood Waste Ash Water										ERR
DE026215	Wood Waste Ash Water										ERR
DE026011	Combined Dewatered Sludge	3.37	0.80	77.7	4-21-87		42.6	0.76	53.3	4-21-87	
DE026011	Combined Dewatered Sludge	3.27	0.70	68.2	8-19-87		34.5	0.71	63.8	8-19-87	
	AVERAGE	3.32					36.6				11.61
DE026012	Primary Influent	ND(0.00278)	**	51.4	6-18-87		0.0362	0.72	46.2	6-18-87	UNDEFINED
DE026013	Secondary Effluent (0-24 hrs)	ND(0.00281)	**	62.6	7-9-87		0.0128	0.67	57.1	7-9-87	UNDEFINED
DE026014	Landfill Leachate	ND(0.00595)	**	50.8	9-11-87		ND(0.00869)	** ->	31.4	9-11-87	ERR
DE026207	Thickened Secondary Sludge	11.2	0.81 ->	22.4	1-20-88		75.4	0.8	55.5	1-20-88	6.73
DE026216	Thickened Secondary Sludge										ERR
DE026206	Secondary Effluent (36-72 hrs)	ND(0.00339)	**	50.7	7-9-87		0.00848	0.79	54.0	7-9-87	UNDEFINED
DE026206	Secondary Effluent (36-72 hrs)	ND(0.00424)	**	61.7	9-30-87		0.0140	0.65	42.1	11-16-87	
	AVERAGE	0					0.01124				UNDEFINED
F. OTHER											
DE026220	Sludge (not from Mill C)	317	0.82	63.2	9-21-87		3266	0.81	47.7	9-21-87	10.3
DE026208	Reagent Blank										
DE026209	Field Blank										

16-Feb-88

Mill D
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
A. BACKGROUND SAMPLES											
DF024401	Unchlorinated Water										ERR
DF024402	Chlorinated North Entry	ND(0.00456)	** ->	36.9	7-9-87		ND(0.00521)	** ->	28.5	7-9-87	ERR
DF024402	Chlorinated North Entry	ND(0.00773)	**	46.9	8-19-87		ND(0.00469)	**	51.1	8-19-87	UNDEFINED
	AVERAGE	0					0				
DF024403	Chlorinated South Entry										ERR
DF024404	Softwood Chips										ERR
B. PULPING PROCESS											
DF024405	Brownstock Sewer										ERR
C. CHEMICAL RECOVERY PLANT											
DF024406	Evap.,Recov.,Lime Kiln Sewer										ERR
DF024407	Lime Mud										ERR
DF024408	Wet Lime										ERR
D. BLEACH PLANT											
DF024409	Combined Brownstock Pulp	ND(0.695)	**	47.4	9-25-87		ND(0.203)	** ->	35.2	9-25-87	ERR
DF024410	Bleached Pulp - A	ND(1.03)	**	54.6	4-21-87		ND(1.23)	**	41.4	4-21-87	ERR
DF024411	Bleached Pulp - B	3.89	0.80	75.8	4-21-87		7.68	0.69	66.4	4-21-87	
DF024411	Bleached Pulp - B	3.99	0.75	67.6	8-19-87		7.90	0.81 ->	28.3	8-19-87	
	AVERAGE	3.94					7.79				1.98
DF024412	A Side Chlorination (C)	ND(0.0132)	**	80.3	4-28-87		0.123	0.80 ->	12.1	4-28-87	
DF024605	A Side Chlorination (C)	0.0174	0.77	90.8	4-28-87		0.0286	0.77	55.1	4-28-87	
DF024605	A Side Chlorination (C)	0.0955	0.79	40.3	7-7-87		0.0542	0.71 ->	37.6	7-7-87	
	AVERAGE (412/605)	0.0376					0.0686				1.82
DF024701	A Side Chlorination (Grab-1)										
DF024702	A Side Chlorination (Grab-2)										
DF024703	A Side Chlorination (Grab-3)										
DF024704	A Side Chlorination (Grab-4)										
DF024705	A + B Side Caustic (Grab-1)										
DF024706	A + B Side Caustic (Grab-2)										
DF024707	A + B Side Caustic (Grab-3)										
DF024708	A + B Side Caustic (Grab-4)										
DF024413	Caustic Combined (E)	0.257	0.76	45.3	6-19-87		0.509	0.81 ->	34.9	6-19-87	
DF024413	Caustic Combined (E)						0.434	0.74 ->	32.2	11-16-87	
	AVERAGE (413)	0.257					0.472				1.83

16-Feb-88

Mill D
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
D. BLEACH PLANT (cont.)											
DF024414	A Side Hypo (H)	0.0551	0.77	42.6	5-22-87		0.0857	0.71	50.7	5-22-87	1.56
DF024709	A Side Hypo (Grab-1)										
DF024710	A Side Hypo (Grab-2)										
DF024711	A Side Hypo (Grab-3)										
DF024712	A Side Hypo (Grab-4)										
DF024415	B Side Chlorination (C)	0.119	0.70	102.6	4-28-87		0.394*	0.79	41.5	4-28-87	3.31
DF024713	B Side Chlorination (Grab-1)										
DF024714	B Side Chlorination (Grab-2)										
DF024715	B Side Chlorination (Grab-3)										
DF024716	B Side Chlorination (Grab-4)										
DF024418	B Side Hypo (H)	0.331	0.82	75.4	5-22-87		0.602	0.80	67.3	5-22-87	1.82
DF024717	B Side Hypo (Grab-1)										
DF024718	B Side Hypo (Grab-2)										
DF024719	B Side Hypo (Grab-3)										
DF024720	B Side Hypo (Grab-4)										
DF024416	Hypo Solution										ERR
DF024417	Caustic Solution										ERR
E. PAPER MACHINES											
DF024501	Paper Machine	ND(0.00590)	**	53.1	8-19-87		0.0146	0.65	56.7	8-19-87	ERR
DF024502	Acid Regeneration										ERR
DF024503	Caustic Regeneration										ERR
DF024504	Size Emulsion										ERR
DF024505	Methyl Violet										ERR
DF024506	Yellow 9G										ERR
DF024507	Biocide										ERR

09-Mar-88

Mill E
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TODD (ppt)	320/322 RATIO	%REC 13012TODD	LAB REPORT DATE	** **	TODF (ppt)	304/306 RATIO	% REC 13012TODF	LAB REPORT DATE	TODF/TODD RATIO
F. UTILITIES, WASTEWATER TREATMENT											
DF024511	WWTP Influent						0.0684	0.81 -	35.4	6-18-87	ERR
DF024604	WWTP Influent	0.0283	0.86	61.0	11-16-87		0.0583	0.76	73.5	11-16-87	2.06
	AVERAGE (511/604)						0.0634				
DF024512	WWTP Effluent	ND(0.00746)	**	50.1	7-9-87		ND(0.00688)	** -	34.6	7-9-87	UNDEFINED
DF024512	WWTP Effluent	ND(0.00716)	**	55.6	9-30-87		ND(0.00663)	**	49.1	9-30-87	UNDEFINED
DF024512	WWTP Effluent	ND(0.00908)	**	56.7	11-16-87						
	AVERAGE	0					0				
DF024513	Dewatered Sludge	17.6	0.83	71.8	3-19-87		33.7	0.88	57.5	3-19-87	
DF024606	Dewatered Sludge	19.2	0.78	69.6	4-21-87		35.7	0.81	55.6	4-21-87	
DF024606	Dewatered Sludge	17.4	0.74	66.5	8-19-87		31.9	0.71	47.8	6-19-87	
	AVERAGE (513/606)	18.1					33.8				1.87
DF024514	#2 Clarifier Primary Sludge	17.4	0.84 -	18.1	1-20-88		31.9	0.79	77.2	1-20-88	1.83
DF024515	Secondary Sludge Before Chlorination	36.1	0.77	89.0	9-21-87		77.9	0.68	82.4	9-21-87	2.16
DF024607	Secondary Sludge Before Chlorination										ERR
DF024516	#11 Boiler Scrubber										ERR
DF024517	Sludge Lagoon	ND(0.00317)	**	42.2	9-11-87		0.0156	0.67	48.5	9-11-87	ERR
DF024518	#11 Boiler Bottom Ash										ERR
DF024519	Secondary Sludge After Chlorination	35.8	0.80	83.6	9-21-87		73.2	0.75	87.0	9-21-87	2.04
G. OTHER											
DF024601	Bottle Blank										
DF024602	Reagent Blank										
DF024603	Sludge (not from Mill D)	92.6	0.78	83.5	3-19-87		976	0.85	100.4	3-19-87	10.54

12-Feb-88

Mill E
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
A. BACKGROUND SAMPLES											
RG186355	Upstream River Water										ERR
RG186356	Chlorinated Process Water	ND(0.0226)	** ->	39.1	3-19-87		ND(0.0155)	** ->	36.2	3-19-87	UNDEFINED
RG186356	Chlorinated Process Water	ND(0.00632)	**	43.1	8-19-87		ND(0.00660)	** ->	33.3	8-19-87	UNDEFINED
	AVERAGE	0					0				UNDEFINED
RG186389	Chlorinated Process Water										
RG186357	Filter Backwash	ND(1.82)	**	64.9	3-19-87		8.61	0.81 ->	12.8	3-19-87	UNDEFINED
RG186357	Filter Backwash	ND(8.21)	** ->	33.1	11-16-87		49.6	0.77	60.7	11-16-87	
RG186390	Filter Backwash										ERR
RG186358	Hardwood Chips										ERR
RG186359	Softwood Chips										ERR
RG186360	Groundwood Pulp										ERR
B. PULPING PROCESS											
RG186361	A&B Side General Sewers										ERR
RG186362	Recaust.A&B Power Groups w/Evap										ERR
RG186363	Lime Mud										ERR
C. BLEACH PLANT											
RG186364	Unbleached Pulp A Side	ND(0.568)	**	76.0	9-25-87		1.32	0.66	66.7	9-25-87	ERR
RG186391	Unbleached Pulp A Side	ND(0.441)	**	81.9	9-25-87		0.946	0.65	79.4	9-25-87	ERR
	AVERAGE (364/391)	0					1.133				
RG186385	Unbleached Pulp B Side	ND(0.984)	**	71.7	9-25-87		2.32	0.65	68.6	9-25-87	ERR
RG186366	Bleached Pulp A Side	25.6	0.77	76	4-21-87		139	0.85	78.3	4-21-87	5.43
RG186367	Bleached Pulp B Side	55.7	0.79	68.5	4-21-87		181	0.84	78.5	4-21-87	
RG186367	Bleached Pulp B Side	46.7	0.78	59.6	8-19-87		183	0.73	53.7	8-19-87	
	AVERAGE	51.2					182				3.55
RG186368	Combined Acid Sever	0.270	0.84	71.7	9-21-87		2.693	0.72	57.0	9-21-87	
RG186368	Combined Acid Sewer	0.277	0.80	73.6	11-16-87						
	AVERAGE (368)	0.274					2.693				9.85
RG186369	A Side C Seal Box	0.0449	0.80	77.1	4-28-87		0.173	0.78	59.3	4-28-87	3.85
RG186370	A Side E Seal Box	2.292	0.77	64.9	6-19-87		10.102	0.74 ->	13.6	7-17-87	
RG186370	A Side E Seal Box						10.526	0.82	73.2	11-16-87	
	AVERAGE (370)	2.292					10.314				4.50
RG186371	A Side D Seal Box	0.910	0.81	67.5	5-12-87		4.993	0.88 ->	24.7	5-12-87	
RG186371	A Side D Seal Box						4.437	0.81	57.9	11-16-87	
	AVERAGE (371)	0.910					4.715				5.18
RG186372	B Side C Seal Box	0.0669	0.85	60.7	4-28-87		0.326	0.86	52.6	4-28-87	4.87
RG186373	B Side E Seal Box	3.597	0.80	66.3	6-19-87		14.128	0.75	59.1	6-19-87	3.93
RG186374	B Side D Seal Box	1.92	0.77	77.7	5-12-87		9.158	0.80	68.1	5-12-87	4.77
RG186375	Caustic Solution										ERR
RG186376	Hypo Solution										ERR
RG186377	Dioxide Solution										ERR
RG186378	A Side Caustic										ERR

12-Feb-88

Mill E
Laboratory Data

SAMPLE NUMBER	SAMPLE DESCRIPTION	TCDD (ppt)	320/322 RATIO	%REC 13C12TCDD	LAB REPORT DATE	** **	TCDF (ppt)	304/306 RATIO	% REC 13C12TCDF	LAB REPORT DATE	TCDF/TCDD RATIO
D. PAPER MACHINES											
RG186379	Nos 1,2,3,4 & 5 Machines	0.0522	0.84	77.4	7-9-87		0.170	0.72	60.7	7-9-87	
RG186379	Nos 1,2,3,4 & 5 Machines	0.0528	0.82	49.0	8-19-87		0.176	0.75	65.3	8-19-87	
	AVERAGE	0.0525					0.173				3.3
RG186380	Otis Mill Return	0.0908	0.75	63.7	8-19-87		0.332	0.74	63.1	8-19-87	
RG186392	Otis Mill Return	0.106	0.78	67.4	8-19-87		0.361	0.73	66.2	8-19-87	
	AVERAGE (380/392)	0.0984					0.346				3.52
RG186381	Titanium Dioxide										ERR
RG186382	Slimicide RX-36										ERR
RG186383	Slimicide RX-31										ERR
RG186384	Pontamine Brilliant Paper										ERR
RG186385	Pontamine Fast Scarlet										ERR
E. UTILITIES, WASTEWATER TREATMENT											
RG186402	Primary Influent	0.680	0.78	68.1	11-16-87		3.117	0.76	73.8	11-16-87	
RG186402	Primary Influent	0.743	0.84 ->	15.8	6-18-87		3.228	0.75 ->	15.1	6-18-87	
RG186386	Primary Influent	0.681	0.76	79.3	3-19-87		3.530	0.88 ->	31.7	3-19-87	
RG186386	Primary Influent	0.497	0.79	41.0	6-18-87		2.267	0.76	46.0	6-18-87	
	AVERAGE (402/386)	0.650					3.036				4.67
RG186387	Combined Dewatered Sludge	193	0.81	82.4	4-21-87		879	0.76	70.1	4-21-87	
RG186387	Combined Dewatered Sludge	168	0.79	64.5	8-19-87		670	0.75	79.0	8-19-87	
RG186387A	Combined Dewatered Sludge	191	0.84	78.9	8-26-87		762	0.78	75.7	8-26-87	
RG186387B	Combined Dewatered Sludge	161	0.79	87.9	8-26-87		713	0.70	106.0	8-26-87	
	AVERAGE (387/387A/387B)	178					756				4.24
RG186388	Final Effluent	0.0881	0.77	71.5	7-7-87		0.447	0.76	65.8	7-7-87	
RG186388	Final Effluent	0.0953	0.70	65.9	9-30-87		0.441	0.74	65.7	9-30-87	
RG186388A	Final Effluent	0.0804	0.65 ->	37.4	8-26-87		0.359	0.78 ->	30.4	8-26-87	
RG186394	Final Effluent										ERR
	AVERAGE (388/388A)	0.0879					0.416				4.73
RG186405	Final Effluent (Grab)										
RG186395	Bottom Ash	ND(0.276)	**	53.4	9-21-87		ND(0.183)	**	42.1	9-21-87	ERR
RG186396	Fly Ash	ND(0.461)	**	66.5	9-21-87		ND(0.310)	**	56.2	9-21-87	ERR
RG186397	Grav. Thick. Secondary Sludge	498	0.77	101.1	9-21-87		2147	0.76	92.5	9-21-87	4.31
RG186404	Grav. Thick. Secondary Sludge										ERR
RG186398	Landfill Leachate	ND(0.00817)	** ->	39.6	9-11-87		0.0636	0.71 ->	37.2	9-11-87	ERR
RG186399	Combined Bleach Plant Eff.										ERR
F. OTHER											
RG186400	Reagent Blank										
RG186401	Bottle Blank										

ATTACHMENT F

MASS FLOW RATES OF 2378-TCDD and 2378-TCDF

ATTACHMENT F

NOTES

- (1) ND - Not detected. Analytical detection level in parentheses.
- (2) Ave - Concentration used for mass flow determinations is an average of multiple analyses of the same sample or of duplicate field samples.
- (3) QA - Percent recoveries of internal standards less than 40% are indicated. See Sections VI and VII for discussion of the significance of these recoveries.

Mill A

08-Feb-88

Mill A

Mass Balance [ND assumed 0.0]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated River Water	DE 020801	20	0	0.000E+00	0.000E+00	ND(0.00514)		27.9 %
2. HW Chips	DE 020805	595		0.000E+00	0.000E+00			
3. SW Chips	DE 020804	105		0.000E+00	0.000E+00			
4. Landfill Leachate	DE 020821	0.18	0.0253	1.724E-05	3.797E-08		X	
			TOTAL	1.724E-05	3.797E-08			
B1. General Sewer Inputs								
1. Water Treatment Sludge	DE 020802	0.8		0.000E+00	0.000E+00			
2. Water Treatment Backwash	DE 020803	0.8		0.000E+00	0.000E+00			
3. Bleach Plant Total		7.6		1.254E-02	2.762E-05			
4. Combined Pulping	DE 020806	5.5		0.000E+00	0.000E+00			
5. Combined Recovery	DE 020807	0.17		0.000E+00	0.000E+00			
6. Power House	DE 020818	0.5		0.000E+00	0.000E+00			
7. Combined Paper Machines	DE 020811	4.3	0.0205	3.336E-04	7.349E-07			
	Flow Total	19.7	TOTAL	1.287E-02	2.836E-05			
C1a. Bleach Plant Inputs								
1. HW Brownstock Pulp	DE 020903	355	0	0.000E+00	0.000E+00	ND(0.309)		
2. SW Brownstock Pulp	DE 020901	160	0	0.000E+00	0.000E+00	ND(0.738)		
3. Treated River Water	DE 020801	7	0	0.000E+00	0.000E+00	ND(0.00514)		27.9 %
4. Papermachine Whitewater	DE 021001	1.5		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. SW C Stage Filtrate	DE 020906	1.73	0.238	1.558E-03	3.433E-06			
2. SW Eo Stage Filtrate	DE 020907	1.44	1.82	9.920E-03	2.185E-05			
3. SW H Stage Filtrate	DE 020908	0.58	0.342	7.508E-04	1.654E-06			
Softwood Line Subtotal		3.75		1.223E-02	2.694E-05			
4. HW C Stage Filtrate	DE 020909	1.58	0.0212	1.268E-04	2.793E-07			
5. HW(Hypo Line) Eo Filtrate	DE 020910	0.73	0	0.000E+00	0.000E+00	ND(0.0326)		
6. HW(Hypo Line) H Filtrate	DE 020911	0.26	0	0.000E+00	0.000E+00	ND(0.0168)		
7. HW(Peroxide Line) Eo Filtrate	DE 020912	0.34	0.0453	5.830E-05	1.284E-07			
8. HW(Peroxide Line) H Filtrate	DE 020913	0.64	0.0403	9.762E-05	2.150E-07			
9. HW(Peroxide Line) H Filtrate	DE 020914	0.30	0.0247	2.805E-05	6.178E-08			
Hardwood Line Subtotal		3.85		3.107E-04	6.845E-07			
	Bleach Plant Total	7.60	TOTAL	1.254E-02	2.762E-05			
D1a. WWTP Inputs								
1. Influent To WWTP	DE 020921	20.1	0.136	1.035E-02	2.279E-05			
2. Landfill Leachate	DE 020821	0.18	0.0253	1.724E-05	3.797E-08		X	
3. Fly Ash	DE 020919	20	0	0.000E+00	0.000E+00	ND(0.660)		17.6 %
			TOTAL	1.036E-02	2.283E-05			
D1b. WWTP Sludge Inputs								
1. Fly Ash	DE 020919	20	0	0.000E+00	0.000E+00	ND(0.660)		17.6 %
2. Primary Sludge	DE 020819	55	23.5	1.174E-03	2.585E-06			
3. Secondary Sludge	DE 020820	7.2	709	4.635E-03	1.021E-05			
			TOTAL	5.809E-03	1.279E-05			

Mill A

08-Feb-88

Mill A

Mass Balance (ND assumed 0.0)

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	DE 020922	23.2	0.124	1.089E-02	2.398E-05	64.7%		X	
2. WWTP Composite Sludge	DE 020920	82.2	36.6	2.732E-03	6.017E-06	16.2%		X	
3. HW Hypo Line Pulp	DE 020904	160	4.89	7.104E-04	1.565E-06	4.2%			
4. HW Peroxide Line Pulp	DE 020905	160	2.98	4.329E-04	9.536E-07	2.6%			
5. SW Line Pulp	DE 020902	144	15.8	2.066E-03	4.550E-06	12.3%		X	
6. Bottom Ash	DE 020918	2		0.000E+00	0.000E+00	0.0%			
			TOTAL	1.683E-02	3.707E-05	100.0%			
B2. General Mill Sewer Exports									
1. Influent To WWTP	DE 020921	20.1	0.136	1.035E-02	2.279E-05	100.0%			
			TOTAL	1.035E-02	2.279E-05	100.0%			
C2a. Bleach Plant Exports									
1. Bleached HW Hypo Pulp	DE 020904	160	4.89	7.104E-04	1.565E-06	4.5%			
2. Bleached HW Peroxide Pulp	DE 020905	160	2.98	4.329E-04	9.536E-07	2.7%			
3. Bleached SW Pulp	DE 020902	144	15.8	2.066E-03	4.550E-06	13.1%		X	
4. Combined Process Wastewater (from Clb.)		7.6		1.254E-02	2.762E-05	79.6%			
			TOTAL	1.575E-02	3.469E-05	100.0%			
C2b. Detailed Bleach Plant Exports									
1. Combined Process Wastewater		7.6		1.254E-02	2.762E-05	100.0%			
			TOTAL	1.254E-02	2.762E-05	100.0%			
D2a. WWTP Exports									
1. Effluent	DE 020922	23.2	0.124	1.089E-02	2.398E-05	79.9%		X	
2. WWTP Composite Sludge	DE 020920	82.2	36.6	2.732E-03	6.017E-06	20.1%		X	
			TOTAL	1.362E-02	3.000E-05	100.0%			
D2b. WWTP Sludge Exports									
1. WWTP Composite Sludge	DE 020920	82.2	36.6	2.732E-03	6.017E-06	100.0%		X	
			TOTAL	2.732E-03	6.017E-06	100.0%			

Mill A

08-Feb-88

Mill A

Mass Balance [ND assumed 0.0]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated River Water	DE 020801	20	0	0.000E+00	0.000E+00	ND(0.00107)		20.8 %
2. HW Chips	DE 020805	595		0.000E+00	0.000E+00			
3. SW Chips	DE 020804	105		0.000E+00	0.000E+00			
4. Landfill Leachate	DE 020821	0.18	0.110	7.494E-05	1.651E-07		X	
			TOTAL	7.494E-05	1.651E-07			
B1. General Sewer Inputs								
1. Water Treatment Sludge	DE 020802	0.8		0.000E+00	0.000E+00			
2. Water Treatment Backwash	DE 020803	0.8		0.000E+00	0.000E+00			
3. Bleach Plant Total		7.6		2.189E-01	4.822E-04			
4. Combined Pulping	DE 020806	5.5		0.000E+00	0.000E+00			
5. Combined Recovery	DE 020807	0.17		0.000E+00	0.000E+00			
6. Power House	DE 020818	0.5		0.000E+00	0.000E+00			
7. Combined Paper Machines	DE 020811	4.3	0.191	3.109E-03	6.847E-06			
	Flow Total	19.7	TOTAL	2.220E-01	4.891E-04			
C1a. Bleach Plant Inputs								
1. HW Brownstock Pulp	DE 020903	355	0	0.000E+00	0.000E+00	ND(0.231)		
2. SW Brownstock Pulp	DE 020901	160	0	0.000E+00	0.000E+00	ND(0.271)		
3. Treated River Water	DE 020801	7	0	0.000E+00	0.000E+00	ND(0.00107)		20.8 %
4. Papermachine Whitewater	DE0201001	1.5		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. SW C Stage Filtrate	DE 020906	1.73	3.806	2.492E-02	5.489E-05			37.8%
2. SW Eo Stage Filtrate	DE 020907	1.44	32.6	1.777E-01	3.914E-04			
3. SW H Stage Filtrate	DE 020908	0.58	5.778	1.268E-02	2.794E-05			
Softwood Line Subtotal		3.75		2.153E-01	4.742E-04			
4. HW C Stage Filtrate	DE 020909	1.58	0.305	1.824E-03	4.018E-06			
5. HW(Hypo Line) Eo Filtrate	DE 020910	0.73	0.247	6.825E-04	1.503E-06			
6. HW(Hypo Line) H Filtrate	DE 020911	0.26	0.114	1.122E-04	2.471E-07			
7. HW(Peroxide Line) Eo Filtrate	DE 020912	0.34	0.318	4.092E-04	9.014E-07			
8. HW(Peroxide Line) H Filtrate	DE 020913	0.64	0.17	4.118E-04	9.071E-07			
9. HW(Peroxide Line) H Filtrate	DE 020914	0.30	0.174	1.976E-04	4.352E-07			
Hardwood Line Subtotal		3.85		3.637E-03	8.012E-06			
	Bleach Plant Total	7.60	TOTAL	2.189E-01	4.822E-04			
D1a. WWTP Inputs								
1. Influent To WWTP	DE 020921	20.1	1.916	1.458E-01	3.211E-04			
2. Landfill Leachate	DE 020821	0.18	0.110	7.494E-05	1.651E-07		X	
3. Fly Ash	DE 020919	20	0	0.000E+00	0.000E+00	ND(0.349)		23.9 %
			TOTAL	1.458E-01	3.212E-04			
D1b. WWTP Sludge Inputs								
1. Fly Ash	DE 020919	20	0	0.000E+00	0.000E+00	ND(0.349)		23.9 %
2. Primary Sludge	DE 020819	55	382	1.908E-02	4.202E-05			
3. Secondary Sludge	DE 020820	7.2	10932	7.147E-02	1.574E-04			
			TOTAL	9.055E-02	1.994E-04			

Mill A

08-Feb-88

Mill A

Mass Balance [ND assumed 0.0]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	DE 020922	23.2	2.18	1.914E-01	4.217E-04	63.9%			
2. WWTP Composite Sludge	DE 020920	82.2	678	5.060E-02	1.115E-04	16.9%			X
3. HW Hypo Line Pulp	DE 020904	160	47.3	6.872E-03	1.514E-05	2.3%			
4. HW Peroxide Line Pulp	DE 020905	160	50.1	7.279E-03	1.603E-05	2.4%			
5. SW Line Pulp	DE 020902	144	333	4.354E-02	9.590E-05	14.5%			
6. Bottom Ash	DE 020918	2		0.000E+00	0.000E+00	0.0%			
			TOTAL	2.997E-01	6.602E-04	100.0%			
B2. General Mill Sewer Exports									
1. Influent To WWTP	DE 020921	20.1	1.916	1.458E-01	3.211E-04	100.0%			
			TOTAL	1.458E-01	3.211E-04	100.0%			
C2a. Bleach Plant Exports									
1. Bleached HW Hypo Pulp	DE 020904	160	47.3	6.872E-03	1.514E-05	2.5%			
2. Bleached HW Peroxide Pulp	DE 020905	160	50.1	7.279E-03	1.603E-05	2.6%			
3. Bleached SW Pulp	DE 020902	144	333	4.354E-02	9.590E-05	15.7%			
4. Combined Process Wastewater (from C1b.)		7.6		2.189E-01	4.822E-04	79.1%			
			TOTAL	2.766E-01	6.093E-04	100.0%			
C2b. Detailed Bleach Plant Exports									
1. Combined Process Wastewater (from C1b.)		7.6		2.189E-01	4.822E-04	100.0%			
			TOTAL	2.189E-01	4.822E-04	100.0%			
D2a. WWTP Exports									
1. Effluent	DE 020922	23.2	2.18	1.914E-01	4.217E-04	79.1%			
2. WWTP Composite Sludge	DE 020920	82.2	678	5.060E-02	1.115E-04	20.9%			X
			TOTAL	2.420E-01	5.331E-04	100.0%			
D2b. WWTP Sludge Exports									
1. WWTP Composite Sludge	DE 020920	82.2	678	5.060E-02	1.115E-04	100.0%			X

Mill B

08-Feb-88

Mill B

Mass Balance Basis : 1 Day	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	86374601	37.1	0	0.000E+00	0.000E+00	ND(0.00693)		25.2 %
2. HW Chips	86374604	220		0.000E+00	0.000E+00			
3. SW Chips	86374603	880		0.000E+00	0.000E+00			
4. SW Sawdust	86374605	630		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	86374621	6.9	0	0.000E+00	0.000E+00	ND(0.00514)		35.9 %
2. Caustic Sewer	86374615	2.2	0.224	1.865E-03	4.108E-06		X	
3. Combined Pulping	86374606	10.8		0.000E+00	0.000E+00			
4. Corrosive Sewer	86374607	3.1		0.000E+00	0.000E+00			
	Flow Total	23	TOTAL	1.865E-03	4.108E-06			
C1a. Bleach Plant Inputs								
1. Brownstock Pulp	86374611	883	0	0.000E+00	0.000E+00	ND(0.949)		
2. Process Water	86374601	8.25	0	0.000E+00	0.000E+00	ND(0.00693)		25.2 %
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. C Stage Filtrate	86374673/613	6.05	0.0232	5.313E-04	1.170E-06			
2. E Stage Filtrate	86374615	2.2	0.224	1.865E-03	4.108E-06		X	
3. H-1 Stage Filtrate *	86374616	0.24	0.258	2.344E-04	5.162E-07			
4. H-2 Stage Filtrate *	86374617	1.36	0.132	6.795E-04	1.497E-06			
5. D Stage Filtrate *	86374614	1.57	0.0298	1.771E-04	3.901E-07			
* Recycled Flows	Flow Total	8.25	TOTAL	2.397E-03	5.279E-06			
D1. WWTP Inputs								
1. Influent To WWTP	86374644	37.35	0	0.000E+00	0.000E+00	ND(0.00644)	X	
			TOTAL	0.000E+00	0.000E+00			

*86374614 Recycled To 86374673 [Acid Sewer Assumed To Be Higher Mass]
 86374616 And 86374617 Recycled To 86374615

Mill B

08-Feb-88

Mill B

Mass Balance Basis : 1 Day		Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	86374645	36.6	0.0151	2.092E-03	4.608E-06	17.5%		X	
2. WWTP Primary Sludge	86374641	35	18.9	6.006E-04	1.323E-06	5.0%			
3. WWTP Secondary Sludge	86374642	17	88.9	1.372E-03	3.023E-06	11.5%			
4. Bleached Pulp	86374612/661	770	11.3	7.901E-03	1.740E-05	66.0%		X	
5. Water Treatment Backwash	86374602	1.3		0.000E+00	0.000E+00	0.0%			
6. Landfill Leachate	86374646		0	0.000E+00	0.000E+00	0.0%	ND(0.00405)		
			TOTAL	1.197E-02	2.636E-05	100.0%			
B2. General Mill Sewer Exports									
1. Influent To WWTP	86374644	37.35	0	0.000E+00	0.000E+00		ND(0.00644)	X	
			TOTAL	0.000E+00	0.000E+00				
C2a. Bleach Plant Exports									
1. Bleached Pulp	86374612/661	770	11.3	7.901E-03	1.740E-05	76.7%		X	
*2. Acid Sewer	86374673/613	6.05	0.0232	5.313E-04	1.170E-06	5.2%			
*3. Caustic Sewer	86374615	2.2	0.224	1.865E-03	4.108E-06	18.1%		X	
			TOTAL	1.030E-02	2.268E-05	100.0%			
C2b. Detailed Bleach Plant Exports									
*1. Acid Sewer	86374673/613	6.05	0.0232	5.313E-04	1.170E-06	22.2%			
*2. Caustic Sewer	86374615	2.2	0.224	1.865E-03	4.108E-06	77.8%		X	
	Flow Total	8.25	TOTAL	2.397E-03	5.279E-06	100.0%			
D2. WWTP Exports									
1. Effluent	86374645	36.6	0.0151	2.092E-03	4.608E-06	51.5%		X	
2. WWTP Primary Sludge	86374641	35	18.9	6.006E-04	1.323E-06	14.8%			
3. WWTP Secondary Sludge	86374642	17	88.9	1.372E-03	3.023E-06	33.8%			
			TOTAL	4.065E-03	8.953E-06	100.0%			
*86374614 Recycled To 86374673 [Acid Sewer Assumed To Be Higher Mass]									
86374616 And 86374617 Recycled To 86374615									

Mill B

08-Feb-88

Mill B

Mass Balance

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	86374601	37.1	0	0.000E+00	0.000E+00	ND(0.00950)		13.9 %
2. HW Chips	86374604	220		0.000E+00	0.000E+00			
3. SW Chips	86374603	880		0.000E+00	0.000E+00			
4. SW Sawdust	86374605	630		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	86374621	6.9	0.108	2.821E-03	6.213E-06			36.9 %
2. Caustic Sewer	86374615	2.2	1.044	8.693E-03	1.915E-05		X	
3. Combined Pulping	86374606	10.8		0.000E+00	0.000E+00			
4. Corrosive Sewer	86374607	3.1		0.000E+00	0.000E+00			
	Flow Total	23	TOTAL	1.151E-02	2.536E-05			
C1a. Bleach Plant Inputs								
1. Brownstock Pulp	86374611	883	1.54	1.235E-03	2.720E-06			
2. Process Water	86374601	8.25	0	0.000E+00	0.000E+00	ND(0.00950)		13.9 %
			TOTAL	1.235E-03	2.720E-06			
C1b. Detailed Bleach Plant Filtrate Flows								
1. C Stage Filtrate	86374673/613	6.05	0.0679	1.555E-03	3.425E-06			30.6%
2. E Stage Filtrate	86374615	2.2	1.044	8.693E-03	1.915E-05		X	
3. H-1 Stage Filtrate *	86374616	0.24	1.129	1.026E-03	2.259E-06			
4. H-2 Stage Filtrate *	86374617	1.36	0.913	4.700E-03	1.035E-05			22.2%
5. D Stage Filtrate *	86374614	1.57	0.133	7.903E-04	1.741E-06			
* Recycled Flows	Flow Total	8.25	TOTAL	1.025E-02	2.257E-05			
D1. WWTP Inputs								
1. Influent To WWTP	86374644	37.35	0.108	1.527E-02	3.363E-05		X	49.8 %, 27.9 %
			TOTAL	1.527E-02	3.363E-05			
* 86374614 Recycled To 86374673								
* 86374616 And 86374617 Recycled To 86374615								

Mill B

08-Feb-88

Mill B

Mass Balance

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	86374645	36.6	0.122	1.690E-02	3.723E-05	22.5%			30.5 %
2. WWTP Primary Sludge	86374641	35	101	3.210E-03	7.070E-06	4.3%			
3. WWTP Secondary Sludge	86374642	17	808	1.247E-02	2.747E-05	16.6%			
4. Bleached Pulp	86374612/661	770	60.9	4.258E-02	9.379E-05	56.6%		X	67.1%, 10.3%, 55.4%
5. Water Treatment Backwash	86374602	1.3		0.000E+00	0.000E+00	0.0%			
6. Landfill Leachate	86374646		0.0105	0.000E+00	0.000E+00	0.0%			
			TOTAL	7.516E-02	1.656E-04	100.0%			
B2. General Mill Sewer Exports									
1. Influent To WWTP	86374644	37.35	0.103	1.527E-02	3.363E-05	100.0%		X	49.8 %, 27.9 %
			TOTAL	1.527E-02	3.363E-05	100.0%			
C2a. Bleach Plant Exports									
1. Bleached Pulp	86374612/661	770	60.9	4.258E-02	9.379E-05	80.6%		X	67.1%, 10.3%, 55.4%
*2. Acid Sewer	86374673/613	6.05	0.0679	1.555E-03	3.425E-06	2.9%			30.6%
*3. Caustic Sewer	86374615	2.2	1.044	8.693E-03	1.915E-05	16.5%		X	
			TOTAL	5.283E-02	1.164E-04	100.0%			
C2b. Detailed Bleach Plant Exports									
*1. Acid Sewer	86374673/613	6.05	0.0679	1.555E-03	3.425E-06	15.2%			30.6%
*2. Caustic Sewer	86374615	2.2	1.044	8.693E-03	1.915E-05	84.8%		X	
	Flow Total	8.25	TOTAL	1.025E-02	2.257E-05	100.0%			
D2. WWTP Exports									
1. Effluent	86374645	36.6	0.122	1.690E-02	3.723E-05	51.9%			30.5%
2. WWTP Primary Sludge	86374641	35	101	3.210E-03	7.070E-06	9.9%			
3. WWTP Secondary Sludge	86374642	17	808	1.247E-02	2.747E-05	38.3%			
			TOTAL	3.258E-02	7.177E-05	100.0%			
* 86374614 Recycled To 86374673									
* 86374616 And 86374617 Recycled To 86374615									

Mass Balance Basis : 1 Day		Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	DE 026001	30	0	0.000E+00	0.000E+00	ND(0.00531)		
2. HW Chips	DE 026103	2200		0.000E+00	0.000E+00			
3. Landfill Leachate	DE 026014		0	0.000E+00	0.000E+00	ND(0.00595)		
			TOTAL	0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	DE 026118	8.2	0.0106	3.290E-04	7.247E-07			
2. Misc. Boiler/Scrubber	DE 026205	5		0.000E+00	0.000E+00			
3. Sluiced Coal Bottom Ash	DE 026007							
4. Misc. Pulp Mill/Recovery	DE 026111	1		0.000E+00	0.000E+00			
5. Misc. Pulping	DE 026107	1.6		0.000E+00	0.000E+00			
*6. Bleach Plant/Scrubber Vents	DE 026114	3.5	0	0.000E+00	0.000E+00	ND(0.00912)		
7. No. 2 Softening Sludge	DE 026101	0.3		0.000E+00	0.000E+00			
	Flow Total	19.6	TOTAL	3.290E-04	7.247E-07			
C1a. Bleach Plant Inputs								
1. Brownstock Pulp	DE 026002	1011	0	0.000E+00	0.000E+00	ND(0.564)		
2. Process Water	DE 026001	13	0	0.000E+00	0.000E+00	ND(0.00531)		
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. C Stage Filtrate	DE 026004	2.95	0	0.000E+00	0.000E+00	ND(0.00593)		
2. Eo Stage Filtrate	DE 026005/211	4.9	0	0.000E+00	0.000E+00	ND(0.0106)		X
3. D Stage Filtrate**	DE 026006/213	0	0	0.000E+00	0.000E+00	ND(0.00341)		X
D1a. WWTP Inputs								
1. Influent To WWTP	DE 026012	31.5	0	0.000E+00	0.000E+00	ND(0.00278)		
2. Landfill Leachate	DE 026014		0	0.000E+00	0.000E+00	ND(0.00595)		
			TOTAL	0.000E+00	0.000E+00			
D1b. WWTP Sludge Inputs								
1. Secondary Sludge	DE 026207	22	11.2	2.237E-04	4.928E-07			
* Mainly Sample DE 026004(DE 026005/DE 026006 Possible)								
** Intermittant Flow (Normally Zero)								
DE 026005 Partially Recycled To DE 026004								

Mass Balance		Flow							
Basis : 1 Day		Sample ID	(MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	Percent Total	ND	AVE QA
A2. General Mill Exports									
1. WWTP Effluent (36-72hr)	DE 026206	29.5	0	0.000E+00	0.000E+00	0.0%	ND(0.00339)	X	
2. Combined Dewatered Sludge	DE 026011	216	3.32	6.511E-04	1.434E-06	100.0%		X	
3. Bleached Pulp	DE 026003	930	0	0.000E+00	0.000E+00	0.0%	ND(0.62)		
4. Coal Ash	DE 026007					0.0%			
5. Coal Ash - ESP	DE 026008					0.0%			
6. Coal Mechanical Ash	DE 026009					0.0%			
		TOTAL			6.511E-04	1.434E-06	100.0%		
B2. General Mill Sewer Exports									
1. Influent To WWTP	DE 026012	31.5	0	0.000E+00	0.000E+00		ND(0.00278)		
		TOTAL			0.000E+00	0.000E+00			
C2a. Bleach Plant Exports									
1. Bleached Pulp	DE 026003	930	0	0.000E+00	0.000E+00	0.0%	ND(0.62)		
2. B.P. Effluent/Scrubber Vents	DE 026114	3.5	0	0.000E+00	0.000E+00	0.0%	ND(0.00912)		
3. C/D Filtrate	DE 026004	2.95	0	0.000E+00	0.000E+00	0.0%	ND(0.00593)		
4. Eo Stage Filtrate	DE 026005	4.5	0	0.000E+00	0.000E+00	0.0%	ND(0.0106)		
5. D Stage Filtrate**	DE 026006/213	0	0	0.000E+00	0.000E+00	0.0%	ND(0.00341)	X	
** Intermittant Flow(Normally Zero)									
D2. WWTP Exports									
1. Effluent (36-72hr)	DE 026206	29.5	0	0.000E+00	0.000E+00	0.0%	ND(0.00339)		
2. Combined Dewatered Sludge	DE 026011	216	3.32	6.511E-04	1.434E-06	100.0%		X	
		TOTAL			6.511E-04	1.434E-06	100.0%		
D2b. WWTP Sludge Exports									
1. WWTP Composite Sludge	DE 026011	216	3.32	6.511E-04	1.434E-06	100.0%			X
		TOTAL			6.511E-04	1.434E-06	100.0%		
E2. Other									
1. WWTP Effluent (0-24 hrs) Recycle to Mill	DE 026013	2	0	0.000E+00	0.000E+00		ND(0.00281)		

Mill C

09-Feb-88

Mill C

Mass Balance Basis : 1 Day	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	DE 026001	30	0	0.000E+00	0.000E+00	ND(0.00694)		15.2%
2. HW Chips	DE 026103	2200		0.000E+00	0.000E+00			
3. Landfill Leachate	DE 026014		0	0.000E+00	0.000E+00	ND(0.00869)		
			TOTAL	0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	DE 026118	8.2	0.197	6.114E-03	1.347E-05			
2. Misc. Boiler/Scrubber	DE 026205	5		0.000E+00	0.000E+00			
3. Sluiced Coal Bottom Ash	DE 026007	Incl. 026015						
4. Misc. Pulp Mill/Recovery	DE 026111	1		0.000E+00	0.000E+00			
5. Misc. Pulping	DE 026107	1.6		0.000E+00	0.000E+00			
* 6. Bleach Plant/Scrubber Vents	DE 026114	3.5	0.429	5.683E-03	1.252E-05			
7. No. 2 Softening Sludge	DE 026101	0.3		0.000E+00	0.000E+00			
	Flow Total	19.6	TOTAL	1.180E-02	2.599E-05			
C1a. Bleach Plant Inputs								
1. Brownstock Pulp	DE 026002	1011	0	0.000E+00	0.000E+00	ND(0.162)		
2. Process Water	DE 026001	13	0	0.000E+00	0.000E+00	ND(0.00694)		15.2%
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. C Stage Filtrate	DE 026004	2.95	0.0929	1.037E-03	2.285E-06			
2. Eo Stage Filtrate	DE 026005/211	4.9	0.0558	1.035E-03	2.280E-06		X	25%.13%
3. D Stage Filtrate**	DE 026006/213	0	0.0136	0.000E+00	0.000E+00		X	
D1a. WWTP Inputs								
1. Influent To WWTP	DE 026012	31.5	0.0362	4.316E-03	9.507E-06			
2. Landfill Leachate	DE 026014		0	0.000E+00	0.000E+00	ND(0.00869)		
			TOTAL	4.316E-03	9.507E-06			
D1b. WWTP Sludge Inputs								
1. Secondary Sludge	DE 026207	22	75.4	1.506E-03	3.318E-06			

* Mainly Sample DE 026004(DE 026005/DE 026006 Possible)

** Intermittant Flow (Normally Zero)

DE 026005 Partially Recycled To DE 026004

Mill C

09-Feb-88

Mill C

Mass Balance		Flow				Percent Total	ND	AVE	QA
Basis : 1 Day	Sample ID	(MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)				
A2. General Mill Exports									
1. WWTP Effluent (36-72hr)	DE 026206	29.5	0.01124	1.255E-03	2.764E-06	5.9%		X	
2. Combined Dewatered Sludge	DE 026011	216	38.6	7.571E-03	1.668E-05	35.4%		X	
3. Bleached Pulp	DE 026003	930	14.9	1.258E-02	2.771E-05	58.8%			
4. Coal Ash	DE 026007					0.0%			
5. Coal Ash - ESP	DE 026008					0.0%			
6. Coal Mechanical Ash	DE 026009					0.0%			
			TOTAL	2.141E-02	4.715E-05	100.0%			
B2. General Mill Sewer Exports									
1. Influent To WWTP	DE 026012	31.5	0.0362	4.316E-03	9.507E-06	100.0%			
			TOTAL	4.316E-03	9.507E-06	100.0%			
C2a. Bleach Plant Exports									
1. Bleached Pulp	DE 026003	930	14.9	1.258E-02	2.771E-05	61.8%			
2. B.P. Effluent/Scrubber Vents	DE 026114	3.5	0.429	5.683E-03	1.252E-05	27.9%			
3. C/D Filtrate	DE 026004	2.95	0.0929	1.037E-03	2.285E-06	5.1%			
4. Eo Stage Filtrate	DE 026005	4.9	0.0573	1.063E-03	2.341E-06	5.2%		X	25%, 13%
5. D Stage Filtrate**	DE 026006/213	0	0.0136	0.000E+00	0.000E+00	0.0%		X	
** Intermittent Flow (Normally Zero)			TOTAL	2.037E-02	4.486E-05	100.0%			
D2. WWTP Exports									
1. Effluent (36-72hr)	DE 026206	29.5	0.01124	1.255E-03	2.764E-06	14.2%		X	
2. Combined Dewatered Sludge	DE 026011	216	38.6	7.571E-03	1.668E-05	85.8%		X	
			TOTAL	8.826E-03	1.944E-05	100.0%			
D2b. WWTP Sludge Exports									
1. WWTP Composite Sludge	DE 026011	216	38.6	7.571E-03	1.668E-05	100.0%		X	
			TOTAL	7.571E-03	1.668E-05	100.0%			
E2. Other									
1. WWTP Effluent (0-24 hrs) Recycle to Mill	DE 026013	2	0.0128	9.690E-05	2.134E-07	100.0%			

Mill D

09-Feb-88

Mill D

Mass Balance		Flow							
Basis : 1 Day	Sample ID	(MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)		ND	AVE	QA
A1. General Mill Inputs									
1. Treated Water(North)	DF 024402	10.2	0	0.000E+00	0.000E+00	ND(0.00456)			
2. Treated Water(South)	DF 024403	11.7		0.000E+00	0.000E+00				
3. SW Chips	DF 024404	1712		0.000E+00	0.000E+00				
			TOTAL	0.000E+00	0.000E+00				
B1. General Sewer Inputs									
1. Combined Paper Machines	DF 024501	9.6	0	0.000E+00	0.000E+00	ND(0.0059)			
2. Misc. Pulping	DF 024405	3.5		0.000E+00	0.000E+00				
3. Misc. Evap./Recovery/Kiln	DF 024406	0.25		0.000E+00	0.000E+00				
4. Boiler	DF 024516	0.06		0.000E+00	0.000E+00				
5. A Side Acid Sewer	DF 024412/605	1.42	0.0376	2.021E-04	4.451E-07			X	
6. B Side Acid Sewer	DF 024415	0.95	0.119	4.279E-04	9.425E-07				
7. Combined Caustic Sewer	DF 024413	2.72	0.257	2.646E-03	5.828E-06				
	Flow Total	18.5	TOTAL	3.276E-03	7.216E-06				
C1a. Bleach Plant Inputs									
1. Combined Brownstock Pulp	DF 024409	419	0	0.000E+00	0.000E+00	ND(0.695)			
2. Process Water	DF 024403	5.02		0.000E+00	0.000E+00				
			TOTAL	0.000E+00	0.000E+00				
C1b. Detailed Bleach Plant Filtrate Flows									
1. C Stage Filtrate A Side	DF 024412/605	1.42	0.0376	2.021E-04	4.451E-07			X	
2. Combined E Stage Filtrate	DF 024413	2.72	0.257	2.646E-03	5.828E-06				
3. H Stage Filtrate A Side	DF 024414	1.42	0.0551	2.961E-04	6.523E-07				
4. C Stage Filtrate B Side	DF 024415	0.95	0.119	4.279E-04	9.425E-07				
5. H Stage Filtrate B Side	DF 024418	0.92	0.331	1.153E-03	2.539E-06				
	Flow Total	7.43	TOTAL	4.725E-03	1.041E-05				
D1a. WWTP Inputs									
1. Influent To WWTP	DF 024604	18.85	0.0283	2.019E-03	4.447E-06			X	28.4%
			TOTAL	2.019E-03	4.447E-06				
D1b. WWTP Sludge Inputs									
1. Primary Sludge	DF 024514	54	17.4	8.532E-04	1.879E-06				
2. Secondary Sludge	DF 024515	8	36.1	2.622E-04	5.776E-07				
			TOTAL	1.115E-03	2.457E-06				
3. Secondary Sludge After Chlorination	DF 024519	8	35.8	2.601E-04	5.728E-07				

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	DF 024512	18.49	0	0.000E+00	0.000E+00	0.0%	ND(0.00716)		X
2. Combined Dewatered Sludge	DF 024513/606	62	18.1	1.019E-03	2.244E-06	70.4%			X
3. Bleached Pulp - A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.03)		
4. Bleached Pulp - B Side	DF 024411	120	3.94	4.293E-04	9.456E-07	29.6%			X
			TOTAL	1.448E-03	3.190E-06	100.0%			
B2. General Sewer Exports									
1. WWTP Influent	DF 024604	18.85	0.0283	2.019E-03	4.447E-06				
			TOTAL	2.019E-03	4.447E-06				
C2a. Bleach Plant Exports - General Sewers									
1. Bleached Pulp A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.03)		
2. Bleached Pulp B Side	DF 024411	120	3.94	4.293E-04	9.456E-07	11.6%			X
3. A Side Acid Sewer	DF 024412/605	1.42	0.0376	2.021E-04	4.451E-07	5.5%			X
4. B Side Acid Sewer	DF 024415	0.95	0.119	4.279E-04	9.425E-07	11.5%			
5. Combined Caustic Sewer	DF 024413	2.72	0.257	2.646E-03	5.828E-06	71.4%			
			TOTAL	3.705E-03	8.161E-06	100.0%			
C2b. Detailed Bleach Plant Exports									
1. Bleached Pulp A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.03)		
2. Bleached Pulp B Side	DF 024411	120	3.94	4.293E-04	9.456E-07	8.3%			X
3. Bleach Plant Flows Total (C1b.)		7.43		4.725E-03	1.041E-05	91.7%			
			TOTAL	5.154E-03	1.135E-05	100.0%			
D2a. WWTP Exports									
1. Effluent	DF 024512	18.49	0	0.000E+00	0.000E+00	0.0%	ND(0.00716)		X
2. Combined Dewatered Sludge	DF 024513/606	62	18.1	1.019E-03	2.244E-06	100.0%			X
			TOTAL	1.019E-03	2.244E-06	100.0%			
D2b. WWTP Sludge Exports									
1. Combined Dewatered Sludge	DF 024513/606	62	18.1	1.019E-03	2.244E-06	100.0%			X
			TOTAL	1.019E-03	2.244E-06	100.0%			
D2c. Sludge Lagoon									
1. Sludge Lagoon Effluent	DF 024517	0.603	0	0.000E+00	0.000E+00	ERR	ND(0.00317)		
			TOTAL	0.000E+00	0.000E+00	ERR			

Mill D

09-Feb-88

Mill D

Mass Balance

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(North)	DF 024402	10.2	0	0.000E+00	0.000E+00	ND(0.00469)	X	29%
2. Treated Water(South)	DF 024403	11.7		0.000E+00	0.000E+00			
3. SW Chips	DF 024404	1712		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	DF 024501	9.6	0.0146	5.305E-04	1.169E-06			
2. Misc. Pulping	DF 024405	3.5		0.000E+00	0.000E+00			
3. Misc. Evap./Recovery/Kiln	DF 024406	0.25		0.000E+00	0.000E+00			
4. Boiler	DF 024516	0.06		0.000E+00	0.000E+00			
5. A Side Acid Sewer	DF 024412/605	1.42	0.0686	3.687E-04	8.121E-07		X	12.1%,55.1%,37.6%
6. B Side Acid Sewer	DF 024415	0.95	0.394	1.417E-03	3.121E-06			
7. Combined Caustic Sewer	DF 024413	2.72	0.472	4.859E-03	1.070E-05		X	34.9%
	Flow Total	18.5	TOTAL	7.175E-03	1.580E-05			
C1a. Bleach Plant Inputs								
1. Combined Brownstock Pulp	DF 024409	419	0	0.000E+00	0.000E+00	ND(0.203)		
2. Process Water	DF 024403	5.02		0.000E+00	0.000E+00			
			TOTAL	0.000E+00	0.000E+00			
C1b. Detailed Bleach Plant Filtrate Flows								
1. C Stage Filtrate A Side	DF 024412/605	1.42	0.0686	3.687E-04	8.121E-07		X	12.1%,55.1%,37.6%
2. Combined E Stage Filtrate	DF 024413	2.72	0.472	4.859E-03	1.070E-05		X	34.9%
3. H Stage Filtrate A Side	DF 024414	1.42	0.0857	4.606E-04	1.015E-06			
4. C Stage Filtrate B Side	DF 024415	0.95	0.394	1.417E-03	3.121E-06			
5. H Stage Filtrate B Side	DF 024418	0.92	0.602	2.096E-03	4.617E-06			
	Flow Total	7.43	TOTAL	9.202E-03	2.027E-05			
D1a. WWTP Inputs								
1. Influent To WWTP	DF 024511/604	18.85	0.0634	4.523E-03	9.963E-06		X	35.4%
			TOTAL	4.523E-03	9.963E-06			
D1b. WWTP Sludge Inputs								
1. Primary Sludge	DF 024514	54	31.9	1.564E-03	3.445E-06			
2. Secondary Sludge	DF 024515	8	77.9	5.659E-04	1.246E-06			
			TOTAL	2.130E-03	4.692E-06			
3. Secondary Sludge After Chlorination	DF 024519	8	73.2	5.317E-04	1.171E-06			

Mill D

09-Feb-88

Mill D

Mass Balance
Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	DF 024512	18.49	0	0.000E+00	0.000E+00	0.0%	ND(0.00663)	X	35%
2. Combined Dewatered Sludge	DF 024513/606	62	33.8	1.903E-03	4.191E-06	69.2%		X	
3. Bleached Pulp - A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.23)		
4. Bleached Pulp - B Side	DF 024411	120	7.79	8.488E-04	1.870E-06	30.8%		X	66.4,28.3%
			TOTAL	2.752E-03	6.061E-06	100.0%			
B2. General Sewer Exports									
1. WWTP Influent	DF 024511/604	18.85	0.0634	4.523E-03	9.963E-06	100.0%		X	35.4%
			TOTAL	4.523E-03	9.963E-06	100.0%			
C2a. Bleach Plant Exports - General Sewers									
1. Bleached Pulp A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.23)		41.4%
2. Bleached Pulp B Side	DF 024411	120	7.79	8.488E-04	1.870E-06	11.3%		X	66.4,28.3%
3. A Side Acid Sewer	DF 024412/605	1.42	0.0686	3.687E-04	8.121E-07	4.9%		X	12.1,55.1,37.6%
4. B Side Acid Sewer	DF 024415	0.95	0.394	1.417E-03	3.121E-06	18.9%			
5. Combined Caustic Sewer	DF 024413	2.72	0.472	4.859E-03	1.070E-05	64.8%		X	34.9%
			TOTAL	7.494E-03	1.651E-05	100.0%			
C2b. Detailed Bleach Plant Exports									
1. Bleached Pulp A Side	DF 024410	250	0	0.000E+00	0.000E+00	0.0%	ND(1.23)		41.4%
2. Bleached Pulp B Side	DF 024411	120	7.79	8.488E-04	1.870E-06	8.4%		X	66.4,28.3%
3. Bleach Plant Flows Total (C1b.)		7.43		9.202E-03	2.027E-05	91.6%			
	Flow Total	377.43	TOTAL	1.005E-02	2.214E-05	100.0%			
D2a. WWTP Exports									
1. Effluent	DF 024512	18.49	0	0.000E+00	0.000E+00	0.0%	ND(0.00663)		35%
2. Combined Dewatered Sludge	DF 024513/606	62	33.8	1.903E-03	4.191E-06	100.0%		X	
			TOTAL	1.903E-03	4.191E-06	100.0%			
D2b. WWTP Sludge Exports									
1. Combined Dewatered Sludge	DF 024513/606	62	33.8	1.903E-03	4.191E-06	100.0%		X	
			TOTAL	1.903E-03	4.191E-06	100.0%			
D2c. Sludge Lagoon									
1. Sludge Lagoon Effluent	DF 024517	0.603	0.0156	3.560E-05	7.842E-08	100.0%			
			TOTAL	3.560E-05	7.842E-08	100.0%			

Mill E

16-Feb-88

Mill E

Mass Balance [ND = 0.0 Assumed]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	RG1-86356	34.6	0	0.000E+00	0.000E+00	ND(.00632)	X	
2. HW Chips	RG1-86358	1218		0.000E+00	0.000E+00			
3. SW Chips	RG1-86359	1620		0.000E+00	0.000E+00			
4. Groundwood Pulp	RG1-86360	200		0.000E+00	0.000E+00			
5. Landfill Leachate *	RG1-86398		0	0.000E+00	0.000E+00	ND(0.00817)		39.6%
* Intermittant Flow(50gpm)		TOTAL		0.000E+00	0.000E+00			
B1. General Sewer Inputs								
1. Combined Paper Machines	RG1-86379	18.9	0.0525	3.756E-03	8.272E-06		X	
2. Misc. Pulping	RG1-86361	4.2		0.000E+00	0.000E+00			
3. Misc. Power Groups	RG1-86362	2.6		0.000E+00	0.000E+00			
4. Otis Mill Return	RG1-86380/92	2.5	0.0984	9.311E-04	2.051E-06		X	
5. Water Treatment Backwash	RG1-86357		0	0.000E+00	0.000E+00	ND(1.82)		
6. A Side E Stage Filtrate	RG1-86370	1.8	2.292	1.562E-02	3.440E-05			
7. A Side D Stage Filtrate	RG1-86371	1	0.91	3.444E-03	7.587E-06			
8. B Side E Stage Filtrate	RG1-86373	1.6	3.597	2.178E-02	4.798E-05			
9. B Side D Stage Filtrate	RG1-86374	0.75	1.92	5.450E-03	1.201E-05			
10. Bottom Ash *	RG1-86395		0	0.000E+00	0.000E+00	ND(0.276)		
11. Fly Ash *	RG1-86396		0	0.000E+00	0.000E+00	ND(0.461)		
* Included in 3.	Flow Total	33.35	TOTAL	5.098E-02	1.123E-04			
C1. Bleach Plant Inputs								
1. HW B Side Brownstock Pulp	RG1-86365	289	0	0.000E+00	0.000E+00	ND(0.984)		
2. SW B Side Brownstock Pulp	RG1-86364/91	197	0	0.000E+00	0.000E+00	ND(0.441)		
3. SW A Side Brownstock Pulp	RG1-86364/91	525	0	0.000E+00	0.000E+00	ND(0.441)		
4. Process Water	RG1-86356	9	0	0.000E+00	0.000E+00	ND(.00632)	X	
5. Paper Machine Whitewater	RG1-86379	With Above	0.0525				X	
		TOTAL		0.000E+00	0.000E+00			
C2. Acid Sewer Inputs								
1. A Side C Filtrate	RG1-86369	3	0.0449	5.098E-04	1.123E-06			
2. B Side C Filtrate	RG1-86372	1.1	0.0669	2.785E-04	6.135E-07			
	Flow Total	4.1	TOTAL	7.884E-04	1.737E-06			
D1. WWTP Inputs								
1. Influent To WWTP	RG1-86386/02	37	0.650	9.103E-02	2.005E-04		X	79.3%, 41%, 15.8%
2. Combined Acid Sewer	RG1-86368	4.03	0.274	4.179E-03	9.206E-06		X	
3. Landfill Leachate	RG1-86398		0	0.000E+00	0.000E+00	ND(0.00817)		39.6%
* Intermittant Flow(50gpm)	Flow Total	41.03	TOTAL	9.521E-02	2.097E-04			
D1b. WWTP Sludge Inputs								
1. Gravity Thick. Sec. Sludge	RG1-86397	33.9	498	1.533E-02	3.376E-05			

Mill E

09-Feb-88

Mill E

Mass Balance [ND = 0.0 Assumed]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDD (PPT)	TCDD (Grams)	TCDD (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	RG1-86388/88A	41	0.0879	1.364E-02	3.005E-05	26.2%		X	71.5%, 37.4%
2. Combined Dewatered Sludge	RG1-86387/A/B	90	178	1.455E-02	3.204E-05	27.9%		X	
3. SW Bleached Pulp - A Side	RG1-86366	483	25.6	1.123E-02	2.473E-05	21.6%			
4. HW Bleached Pulp - B Side	RG1-86367	272	51.2	1.265E-02	2.785E-05	24.3%		X	
5. SW Bleached Pulp - B Side	RG1-86366	181	25.6	4.207E-03	9.267E-06	8.1%			
			TOTAL	5.206E-02	1.147E-04	100.0%			
B2. General Sewer Exports									
1. WWTP Influent	RG1-86386/402	37	0.650	9.103E-02	2.005E-04	95.6%		X	79.3, 41, 15.8%
2. Combined Acid Sewer	RG1-86368	4.03	0.274	4.179E-03	9.206E-06	4.4%		X	
			TOTAL	9.521E-02	2.097E-04	100.0%			
C2. Bleach Plant Exports									
1. SW Bleached Pulp A Side	RG1-86366	483	25.6	1.123E-02	2.473E-05	14.9%			
2. HW Bleached Pulp B Side	RG1-86367	272	51.2	1.265E-02	2.785E-05	16.8%		X	
3. SW Bleached Pulp B Side	RG1-86366	181	25.6	4.207E-03	9.267E-06	5.6%			
4. A Side C Filtrate	RG1-86369	3	0.0449	5.098E-04	1.123E-06	0.7%			
5. A Side E Stage Filtrate	RG1-86370	1.8	2.292	1.562E-02	3.440E-05	20.8%			
6. A Side D Stage Filtrate	RG1-86371	1	0.91	3.444E-03	7.587E-06	4.6%			
7. B Side C Filtrate	RG1-86372	1.1	0.0669	2.785E-04	6.135E-07	0.4%			
8. B Side E Stage Filtrate	RG1-86373	1.6	3.597	2.178E-02	4.798E-05	29.0%			
9. B Side D Stage Filtrate	RG1-86374	0.75	1.92	5.450E-03	1.201E-05	7.3%			
			TOTAL	7.516E-02	1.656E-04	100.0%			
D2. WWTP Exports									
1. Effluent	RG1-86388/88A	41	0.0879	1.364E-02	3.005E-05	48.4%		X	71.5%, 37.4%
2. Combined Dewatered Sludge	RG1-86387/A/B	90	178	1.455E-02	3.204E-05	51.6%		X	
			TOTAL	2.819E-02	6.209E-05	100.0%			

Mill E

16-Feb-88

Mill E

Mass Balance (ND = 0.0 Assumed)

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	ND	AVE	QA
A1. General Mill Inputs								
1. Treated Water(River)	RG1-86356	34.6	0	0.000E+00	0.000E+00	ND(0.00660)		33.3%
2. HW Chips	RG1-86358	1218		0.000E+00	0.000E+00			
3. SW Chips	RG1-86359	1620		0.000E+00	0.000E+00			
4. Groundwood Pulp	RG1-86360	200		0.000E+00	0.000E+00			
5. Landfill Leachate *	RG1-86398	0.072	0.0636	1.733E-05	3.818E-08			
* Intermittant Flow(50gpm)			TOTAL	1.733E-05	3.818E-08			
B1. General Sewer Inputs								
1. Combined Paper Machines	RG1-86379	18.9	0.173	1.238E-02	2.726E-05		X	
2. Misc. Pulping	RG1-86361	4.2		0.000E+00	0.000E+00			
3. Misc. Power Groups	RG1-86362	2.6		0.000E+00	0.000E+00			
4. Otis Mill Return	RG1-86380/92	2.5	0.346	3.274E-03	7.212E-06		X	
5. Water Treatment Backwash	RG1-86357		8.61					12.8%
6. A Side E Stage Filtrate	RG1-86370	1.8	10.314	7.027E-02	1.548E-04		X	13.6%
7. A Side D Stage Filtrate	RG1-86371	1	4.715	1.785E-02	3.931E-05		X	24.7%
8. B Side E Stage Filtrate	RG1-86373	1.6	14.128	8.556E-02	1.885E-04			
9. B Side D Stage Filtrate	RG1-86374	0.75	9.158	2.600E-02	5.726E-05			
10. Bottom Ash *	RG1-86395		0			ND(0.183)		
11. Fly Ash *	RG1-86396		0			ND(0.310)		
* Included in 3.	Flow Total	33.35	TOTAL	2.153E-01	4.743E-04			
C1. Bleach Plant Inputs								
1. HW B Side Brownstock Pulp	RG1-86365	289	2.32	6.088E-04	1.341E-06			
2. SW B Side Brownstock Pulp	RG1-86364/91	197	1.133	2.027E-04	4.464E-07			
3. SW A Side Brownstock Pulp	RG1-86364/91	525	1.133	5.401E-04	1.190E-06		X	
4. Process Water	RG1-86356	9	0	0.000E+00	0.000E+00	ND(0.00660)	X	33.3%
5. Paper Machine Whitewater	RG1-86379	With Above	0.173	0.000E+00	0.000E+00		X	
			TOTAL	1.352E-03	2.977E-06			
C2. Acid Sewer inputs								
1. A Side C Filtrate	RG1-86369	3	0.173	1.964E-03	4.327E-06			
2. B Side C Filtrate	RG1-86372	1.1	0.326	1.357E-03	2.990E-06			
	Flow Total	4.1	TOTAL	3.322E-03	7.317E-06			
D1. WWTP Inputs								
1. Influent To WWTP	RG1-86386/02	37	3.036	4.252E-01	9.365E-04		X	31.7%, 46%, 15.1%
2. Combined Acid Sewer	RG1-86368	4.03	2.693	4.108E-02	9.048E-05			
3. Landfill Leachate	RG1-86398	0.072	0.0636	1.733E-05	3.818E-08			
* Intermittant Flow(50gpm)	Flow Total	41.102	TOTAL	4.663E-01	1.027E-03			
D1b. WWTP Sludge Inputs								
1. Gravity Thick. Sec. Sludge	RG1-86397	33.9	2147	6.609E-02	1.456E-04			

Mill E

09-Feb-88

Mill E

Mass Balance [ND = 0.0 Assumed]

Basis : 1 Day

	Sample ID	Flow (MGD or Dry Tons/Day)	TCDF (PPT)	TCDF (Grams)	TCDF (lbs)	Percent Total	ND	AVE	QA
A2. General Mill Exports									
1. WWTP Effluent	RG1-86388/88A	41	0.416	6.456E-02	1.422E-04	27.8%		X	65.8,30.4%
2. Combined Dewatered Sludge	RG1-86387/A/B	90	756	6.178E-02	1.361E-04	26.6%		X	
3. SW Bleached Pulp - A Side	RG1-86366	483	139	6.096E-02	1.343E-04	26.2%			
4. HW Bleached Pulp - B Side	RG1-86367	272	182	4.495E-02	9.901E-05	19.4%		X	
5. SW Bleached Pulp - B Side	RG1-86366	181	139	2.284E-02	5.032E-05	9.8%			
			TOTAL	2.322E-01	5.116E-04	100.0%			
B2. General Sewer Exports									
1. WWTP Influent	RG1-86386/02	37	3.036	4.252E-01	9.365E-04	91.2%		X	31.7%,46%,15.1%
2. Combined Acid Sewer	RG1-86368	4.03	2.693	4.108E-02	9.048E-05	8.8%			
			TOTAL	4.663E-01	1.027E-03	100.0%			
C2. Bleach Plant Exports									
1. SW Bleached Pulp A Side	RG1-86366	483	139	6.096E-02	1.343E-04	18.4%			
2. HW Bleached Pulp B Side	RG1-86367	272	182	4.495E-02	9.901E-05	13.5%		X	
3. SW Bleached Pulp B Side	RG1-86366	181	139	2.284E-02	5.032E-05	6.9%			
4. A Side C Filtrate	RG1-86369	3	0.173	1.964E-03	4.327E-06	0.6%			
5. A Side E Stage Filtrate	RG1-86370	1.8	10.314	7.027E-02	1.548E-04	21.2%		X	13.6%
6. A Side D Stage Filtrate	RG1-86371	1	4.715	1.785E-02	3.931E-05	5.4%		X	24.7%
7. B Side C Filtrate	RG1-86372	1.1	0.326	1.357E-03	2.990E-06	0.4%			
8. B Side E Stage Filtrate	RG1-86373	1.6	14.128	8.556E-02	1.885E-04	25.8%			
9. B Side D Stage Filtrate	RG1-86374	0.75	9.158	2.600E-02	5.726E-05	7.8%			
			TOTAL	3.317E-01	7.307E-04	100.0%			
D2. WWTP Exports									
1. Effluent	RG1-86388/88A	41	0.416	6.456E-02	1.422E-04	51.1%		X	65.8,30.4%
2. Combined Dewatered Sludge	RG1-86387/A/B	90	756	6.178E-02	1.361E-04	48.9%		X	
			TOTAL	1.263E-01	2.783E-04	100.0%			

ATTACHMENT G

ANALYTICAL RESULTS FOR CHLORINATED PHENOLICS,
TOTAL SUSPENDED SOLIDS, AND BIOCHEMICAL OXYGEN DEMAND

TABLE G-1

Chlorinated Phenolics Results Summary
Mill A

Analyte	Concentration Detected (ppb)									
	DEO 20801	DEO 20906	DEO 20909	DEO 20907	DEO 20910	DEO 20922	DEO 20921 ^a	DEO 20801	DEO 20906	DEO 20909
2-Chlorophenol	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND
2,6-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dichlorophenol	ND	3.1	5.3	16.1	26.6	2.1	2.6	ND	ND	ND
3,4-Dichlorophenol	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND
2,5-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	ND	ND	ND	ND	ND	2.0	0.4	ND	ND	ND
4,5-Dichloroguaiacol	ND	ND	3.2	5.1	166	2.7	4.0	ND	ND	ND
3,4,5-Trichloroguaiacol	ND	2.8	3.5	84.0	123	5.0	4.0	ND	ND	ND
4,5,6-Trichloroguaiacol	ND	ND	0.9	54.3	36.5	3.3	0.9	ND	ND	ND
Tetrachloroguaiacol	ND	3.1	0.9	175	19.8	1.9	12.5	ND	ND	ND
5-Chlorovanillin	ND	ND	ND	2.3	16.2	ND	NA	ND	ND	ND
6-Chlorovanillin	ND	ND	ND	6.4	113	ND	3.8	ND	ND	ND
5,6-Dichlorovanillin	ND	ND	ND	38.6	13.2	ND	0.8	ND	ND	ND

ND = Not Detected

NA = Not Analyzed

^a DEO20921 analyzed by GC/ECD (NCASI Method CP-85.01)

TABLE G-2

Chlorinated Phenolics Results Summary
Mill B

Analyte	Concentration Detected (ppb)									
	86-37- 4601	86-37- 4613	86-37- 4614	86-37- 4615	86-37- 4616	86-37- 4617	86-37- 4644	86-37- 4645	86-37- 4646	
2-Chlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,6-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dichlorophenol	ND	9.7	ND	43.6	3.7	ND	9.8	0.2	ND	ND
3,4-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,5-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	ND	0.7	ND	6.1	4.0	1.8	ND	ND	ND	ND
4,5-Dichloroguaiacol	ND	4.8	1.4	196	15.9	5.6	4.8	ND	ND	ND
3,4,5-Trichloroguaiacol	ND	14.3	6.6	351	31.5	11.3	8.9	2.3	ND	ND
4,5,6-Trichloroguaiacol	ND	7.3	0.9	146	68.5	11.8	3.3	1.7	ND	ND
Tetrachloroguaiacol	ND	14.1	4.8	170	81.4	21.0	6.3	2.8	ND	ND
5-Chlorovanillin	ND	ND	ND	24.4	15.0	4.6	2.2	1.9	ND	ND
6-Chlorovanillin	ND	5.6	ND	163	19.6	8.9	6.5	4.2	ND	ND
5,6-Dichlorovanillin	ND	6.1	ND	97.0	64.8	14.7	1.7	3.2	ND	ND
<u>Isotope Percent Recovery</u>										
2H ₃ -2,4-Dichlorophenol	46	77	54	90	95	39	83	99	83	
13C ₆ -Pentachlorophenol	94	137	183	131	103	89	109	101	111	

ND = Not Detected

TABLE G-3

Chlorinated Phenolics Results Summary
Mill C

Analyte	Concentration (ppb)									
	DEO-26 001	DEO-26 004	DEO-26 005	DEO-26 006	DEO-26 [*] 012	DEO-26 013	DEO-26 114	DEO-26 206	DEO-26 206	
2-CHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2,6-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2,4/2,5-DICHLOROPHENOL	ND	ND	7.9	ND	ND	ND	4.2	ND	ND	
2,3-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	
3,4-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2,4,5-TRICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	0.7	
PENTACHLOROPHENOL	ND	ND	7.5	ND	ND	ND	6.7	ND	ND	
4,5-DICHLOROGUAIACOL	ND	54.1	395	4.6	13.8	ND	116	ND	ND	
3,4,5-TRICHLOROGUAIACOL	ND	20.9	86.6	2.1	5.2	ND	43.6	ND	ND	
4,5,6-TRICHLOROGUAIACOL	ND	6.8	39.6	ND	ND	ND	11.9	ND	ND	
TETRACHLOROGUAIACOL	ND	4.5	30.5	ND	0.4	ND	15.6	ND	ND	
5-CHLOROVANILLIN	ND	5.2	15.2	ND	ND	ND	10.8	ND	ND	
6-CHLOROVANILLIN	ND	56.5	209	2.8	13.3	ND	82.2	ND	ND	
5,6-DICHLOROVANILLIN	ND	14.4	40.2	0.7	2.1	ND	32.1	ND	ND	

* - Sample used for duplicate and recovery analyses.
Average values from duplicate analysis reported.

TABLE G-4

Chlorinated Phenolics Results Summary
Mill D

Analyte	Concentrations (ppb)											
	DFO-24 403	DFO-24 511	DFO-24 412	DFO-24 413	DFO-24 414	DFO-24 415	DFO-24 418	DFO-24 512	DFO-24 403	DFO-24 511	DFO-24 412	DFO-24 413
2-CHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,6-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4/2,5-DICHLOROPHENOL	ND	6.3	11.2	117	ND	13.9	4.9	5.9	ND	ND	ND	ND
2,3-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3,4-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-TRICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PENTACHLOROPHENOL	ND	ND	ND	7.1	ND	ND	ND	ND	ND	ND	ND	ND
4,5-DICHLOROGUAIACOL	ND	24.3	14.3	521	22.5	12.9	19.3	3.1	ND	ND	ND	ND
3,4,5-TRICHLOROGUAIACOL	ND	9.0	3.3	314	5.7	6.6	10.7	10.0	ND	ND	ND	ND
4,5,6-TRICHLOROGUAIACOL	ND	7.4	3.1	220	9.7	9.9	22.7	7.2	ND	ND	ND	ND
TETRACHLOROGUAIACOL	ND	4.8	ND	81.5	1.0	3.7	6.1	4.5	ND	ND	ND	ND
5-CHLOROVANILLIN	ND	4.0	ND	37.8	2.4	5.1	12.8	ND	ND	ND	ND	ND
6-CHLOROVANILLIN	ND	21.0	15.3	371	23.6	15.6	22.7	4.8	ND	ND	ND	ND
5,6-DICHLOROVANILLIN	ND	11.3	4.8	146	4.9	6.7	12.4	1.0	ND	ND	ND	ND

* - Sample used for duplicate and recovery analyses.
Average values from duplicate analysis reported.

TABLE G-5

Chlorinated Phenolics Results Summary
Mill E

Analyte	Concentrations (ppb)											
	RG1-86 355	RG1-86 356	RG1-86 368	RG1-86 369	RG1-86 370	RG1-86 371	RG1-86 372	RG1-86 373	RG1-86 374	RG1-86 386	RG1-86 388	
2-CHLOROPHENOL	ND	ND	ND	ND	1.0	ND	ND	ND	ND	ND	ND	
2,6-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2,4/2,5-DICHLOROPHENOL	ND	ND	10.7	15.3	76.0	ND	7.5	33.8	ND	11.7	ND	
2,3-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
3,4-DICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2,4,5-TRICHLOROPHENOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
PENTACHLOROPHENOL	ND	ND	ND	ND	6.8	ND	ND	ND	ND	ND	ND	
4,5-DICHLOROGUAIACOL	ND	ND	1.0	3.7	286	1.7	3.6	106	ND	24.0	ND	
3,4,5-TRICHLOROGUAIACOL	ND	ND	4.5	8.4	422	4.2	7.9	184	ND	30.6	5.6	
4,5,6-TRICHLOROGUAIACOL	ND	ND	ND	ND	60.4	ND	ND	34.8	ND	5.3	ND	
TETRACHLOROGUAIACOL	ND	ND	3.4	5.9	358	ND	6.5	199	ND	50.1	ND	
5-CHLOROVANILLIN	ND	ND	ND	ND	31.4	ND	ND	16.4	ND	ND	ND	
6-CHLOROVANILLIN	ND	ND	ND	4.4	241	1.6	3.5	79.8	ND	13.5	ND	
5,6-DICHLOROVANILLIN	ND	ND	ND	0.7	128	ND	ND	70.5	ND	12.4	ND	

* - Sample used for duplicate and recovery analyses.
Average values from duplicate analysis reported.

Table G-6

Chlorophenol Analyses Summary

(INTAKES)

Analyte	MILL A		B		C		D		E		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
4,5-Dichloroguaiacol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
3,4,5-Trichloroguaiacol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
4,5,6-Trichloroguaiacol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Tetrachloroguaiacol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
5-Chlorovanillin	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
6-Chlorovanillin	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
5,6-Dichlorovanillin	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00

ND - Not detected

	MILL A		B		C		D		E		Sum of All Mills
	Flow (MGD)	20	37.1		30		11.7		34.6		lbs/day
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
Sum of chlorophenols	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of chloroguaiacols	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of chlorovanillins	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of all analytes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 6-7

Chlorophenol Analyses Summary
WWTP INFLUENTS

Analyte	MILL A		B		C		D		E		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
2-Chlorophenol	NA	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	2.6	0.44	9.8	3.05	—	0.00	—	0.00	—	0.00	3.49
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	NA	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	—	0.00	ND	0.00	6.3	0.99	11.7	3.61	4.60
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	0.4	0.07	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.07
4,5-Dichloroguaiacol	4.0	0.67	4.8	1.50	13.8	3.63	24.3	3.82	24.0	7.41	17.03
3,4,5-Trichloroguaiacol	4.0	0.67	8.9	2.77	5.2	1.37	9.0	1.42	30.6	9.45	15.68
4,5,6-Trichloroguaiacol	0.9	0.15	3.3	1.03	ND	0.00	7.4	1.16	5.3	1.64	3.98
Tetrachloroguaiacol	12.5	2.10	6.3	1.96	0.4	0.11	4.8	0.76	50.1	15.47	20.39
5-Chlorovanillin	NA	0.00	2.2	0.69	ND	0.00	4.0	0.63	ND	0.00	1.31
6-Chlorovanillin	3.8	0.64	6.5	2.03	13.3	3.50	21.0	3.30	13.5	4.17	13.63
5,6-Dichlorovanillin	0.8	0.13	1.7	0.53	2.1	0.55	11.3	1.78	12.4	3.83	6.82

ND - Not detected in range of 1 to 3 ug/L (ppb).

NA - Not analyzed

	MILL A		B		C		D		E		Sum of All Mills
	Flow (MGD)										lbs/day
		20.1		37.35		31.5		18.85		37	
		ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day		lbs/day
Sum of chlorophenols		3.00 0.50	9.80 3.05	0.00 0.00	6.30 0.99	11.70 3.61					8.16
Sum of chloroguaiacols		21.40 3.59	23.30 7.26	19.40 5.10	45.50 7.16	110.00 33.96					57.07
Sum of chlorovanillins		4.60 0.77	10.40 3.24	15.40 4.05	36.30 5.71	25.90 8.00					21.77
Sum of all analytes		29.00 4.86	43.50 13.56	34.80 9.15	88.10 13.86	147.60 45.57					87.00

Table G-8

Chlorophenol Analyses Summary
WWTTP EFFLUENTS

Analyte	MILL A		B		C - (36-72 HRS) D				E		Sum of All Mills lbs/day
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	2.1	0.41	0.2	0.06	—	0.00	—	0.00	—	0.00	0.47
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	—	0.00	ND	0.00	5.9	0.91	ND	0.00	0.91
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	0.7	0.17	ND	0.00	ND	0.00	0.17
Pentachlorophenol	2.0	0.39	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.39
4,5-Dichloroguaiacol	2.7	0.52	ND	0.00	ND	0.00	3.1	0.48	ND	0.00	1.00
3,4,5-Trichloroguaiacol	5.0	0.97	2.3	0.70	ND	0.00	10.0	1.54	5.6	1.92	5.13
4,5,6-Trichloroguaiacol	3.3	0.64	1.7	0.52	ND	0.00	7.2	1.11	ND	0.00	2.27
Tetrachloroguaiacol	1.9	0.37	2.8	0.86	ND	0.00	4.5	0.69	ND	0.00	1.92
5-Chlorovanillin	ND	0.00	1.9	0.58	ND	0.00	ND	0.00	ND	0.00	0.58
6-Chlorovanillin	ND	0.00	4.2	1.28	ND	0.00	4.8	0.74	ND	0.00	2.02
5,6-Dichlorovanillin	ND	0.00	3.2	0.98	ND	0.00	1.0	0.15	ND	0.00	1.13

ND - Not detected in range of 1 to 3 ug/L (ppb).

NA - Not analyzed

	MILL A		B		C - (36-72 HRS) D				E		Sum of All Mills lbs/day
	Flow (MGD)										
		23.2		36.6		29.5		18.49		41	
		ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	ppb lbs/day	lbs/day
Sum of chlorophenols		4.10 0.79	0.20 0.06	0.70 0.17	5.90 0.91	0.00 0.00					1.94
Sum of chloroguaiacols		12.90 2.50	6.80 2.08	0.00 0.00	24.80 3.83	5.60 1.92					10.32
Sum of chlorovanillins		0.00 0.00	9.30 2.84	0.00 0.00	5.80 0.89	0.00 0.00					3.74
Sum of all analytes		17.00 3.29	16.30 4.98	0.70 0.17	36.50 5.63	5.60 1.92					15.99

Table G-9

Chlorophenol Analyses Summary
BLEACH PLANT
C STAGES

Analyte	MILL		A - SW		A - HW		B		C		D - A SIDE		D - B SIDE		E - A SIDE		E - B SIDE		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	3.1	0.04	5.3	0.07	9.7	0.49	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	0.60
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	—	0.00	—	0.00	ND	0.00	11.2	0.13	13.9	0.11	15.3	0.38	7.5	0.07			0.69
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	ND	0.00	ND	0.00	0.7	0.04	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.04
4,5-Dichloroguaiacol	ND	0.00	3.2	0.04	4.8	0.24	54.1	1.33	14.3	0.17	12.9	0.10	3.7	0.09	3.6	0.03			2.01
3,4,5-Trichloroguaiacol	2.8	0.04	3.5	0.05	14.3	0.72	20.9	0.51	3.3	0.04	6.6	0.05	8.4	0.21	7.9	0.07			1.70
4,5,6-Trichloroguaiacol	ND	0.00	0.9	0.01	7.3	0.37	6.8	0.17	3.1	0.04	9.9	0.08	ND	0.00	ND	0.00			0.66
Tetrachloroguaiacol	3.1	0.04	0.9	0.01	14.1	0.71	4.5	0.11	ND	0.00	3.7	0.03	5.9	0.15	6.5	0.06			1.12
5-Chlorovanillin	ND	0.00	ND	0.00	ND	0.00	5.2	0.13	ND	0.00	5.1	0.04	ND	0.00	ND	0.00			0.17
6-Chlorovanillin	ND	0.00	ND	0.00	5.6	0.28	56.5	1.39	15.3	0.18	15.6	0.12	4.4	0.11	3.5	0.03			2.12
5,6-Dichlorovanillin	ND	0.00	ND	0.00	6.1	0.31	14.4	0.35	4.8	0.06	6.7	0.05	0.7	0.02	ND	0.00			0.79

ND - Not detected

	MILL	A - SW		A - HW		B		C		D - A SIDE		D - B SIDE		E - A SIDE		E - B SIDE		Sum of All Mills
	Flow (MGD)	1.73		1.58		6.05		2.95		1.42		0.95		3		1.1		
		ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
Sum of chlorophenols		3.10	0.04	5.30	0.07	10.40	0.53	0.00	0.00	11.20	0.13	13.90	0.11	15.30	0.38	7.50	0.07	1.33
Sum of chloroguaiacols		5.90	0.09	8.50	0.11	40.50	2.04	86.30	2.12	20.70	0.25	33.10	0.26	18.00	0.45	18.00	0.17	5.49
Sum of chlorovanillins		0.00	0.00	0.00	0.00	11.70	0.59	76.10	1.87	20.10	0.24	27.40	0.22	5.10	0.13	3.50	0.03	3.08
Sum of all analytes		9.00	0.13	13.80	0.18	62.60	3.16	162.40	4.00	52.00	0.62	74.40	0.59	38.40	0.96	29.00	0.27	9.90

Table 6-10

Chlorophenol Analyses Summary
BLEACH PLANT
E STAGES

Analyte	MILL		A - SW		A - HW		B		C		D		E - A SIDE		E - B SIDE		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	1.0	0.02	ND	0.00	0.02
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	16.1	0.19	26.6	0.16	43.60	0.80	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	1.16
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	—	0.00	—	0.00	7.9	0.32	117	2.66	76.0	1.14	33.8	0.45			4.57
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	ND	0.00	ND	0.00	6.1	0.11	7.5	0.31	7.1	0.16	6.8	0.10	ND	0.00			0.68
4,5-Dichloroguaiacol	5.1	0.06	166	1.01	196	3.60	395	16.15	521	11.83	286	4.30	106	1.42			38.36
3,4,5-Trichloroguaiacol	84.0	1.01	123	0.75	351	6.44	86.6	3.54	314	7.13	422	6.34	184	2.46			27.67
4,5,6-Trichloroguaiacol	54.3	0.65	36.5	0.22	146	2.68	39.6	1.62	220	4.99	60.4	0.91	34.8	0.46			11.54
Tetrachloroguaiacol	175	2.10	19.8	0.12	170	3.12	30.5	1.25	81.5	1.85	358	5.38	199	2.66			16.48
5-Chlorovanillin	2.3	0.03	16.2	0.10	24.4	0.45	15.2	0.62	37.8	0.86	31.4	0.47	16.4	0.22			2.74
6-Chlorovanillin	6.4	0.08	113	0.69	163	2.99	209	8.55	371	8.42	241	3.62	79.8	1.07			25.41
5,6-Dichlorovanillin	38.6	0.46	13.2	0.08	97.0	1.78	40.2	1.64	146	3.31	128	1.92	70.5	0.94			10.15

ND - Not detected

	MILL		A - SW		A - HW		B		C		D		E - A SIDE		E - B SIDE		Sum of All Mills
	Flow (MGD)		1.44		0.73		2.2		4.9		2.72		1.8		1.6		lbs/day
			ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
Sum of chlorophenols			16.10	0.19	26.60	0.16	49.70	0.91	15.40	0.63	124.10	2.82	83.80	1.26	33.80	0.45	6.42
Sum of chloroguaiacols			318.40	3.83	345.30	2.10	863.00	15.84	551.70	22.56	1136.50	25.80	1126.40	16.92	523.80	6.99	94.04
Sum of chlorovanillins			47.30	0.57	142.40	0.87	284.40	5.22	264.40	10.81	554.80	12.59	400.40	6.01	166.70	2.23	38.30
Sum of all analytes			381.80	4.59	514.30	3.13	1197.10	21.98	831.50	34.00	1815.40	41.21	1610.60	24.19	724.30	9.67	138.77

Table 6-11

Chlorophenol Analyses Summary
BLEACH PLANT
D STAGES

Analyte	MILL B		C		E - A SIDE		E - B SIDE		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
4,5-Dichloroguaiacol	1.4	0.02	4.6	0.00	1.7	0.01	ND	0.00	0.03
3,4,5-Trichloroguaiacol	6.6	0.09	2.1	0.00	4.2	0.04	ND	0.00	0.12
4,5,6-Trichloroguaiacol	0.9	0.01	ND	0.00	ND	0.00	ND	0.00	0.01
Tetrachloroguaiacol	4.8	0.06	ND	0.00	ND	0.00	ND	0.00	0.06
5-Chlorovanillin	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
6-Chlorovanillin	ND	0.00	2.8	0.00	1.6	0.01	ND	0.00	0.01
5,6-Dichlorovanillin	ND	0.00	0.7	0.00	ND	0.00	ND	0.00	0.00

ND - Not detected

	MILL B		C		E - A SIDE		E - B SIDE		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
Flow (MGD)	1.57		0		1		0.75		
Sum of chlorophenols	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of chloroguaiacols	13.70	0.18	6.70	0.00	5.90	0.05	0.00	0.00	0.23
Sum of chlorovanillins	0.00	0.00	3.50	0.00	1.60	0.01	0.00	0.00	0.01
Sum of all analytes	13.70	0.18	10.20	0.00	7.50	0.06	0.00	0.00	0.24

Table 6-12

Chlorophenol Analyses Summary
BLEACH PLANT
H STAGES

Analyte	MILL		B (H-1)		B (H-2)		D - A SIDE		D - B SIDE		Sum of All Mills
	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	lbs/day
2-Chlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,6-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4-Dichlorophenol	3.7	0.01	ND	0.00	—	0.00	—	0.00	—	0.00	0.01
3,4-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,5-Dichlorophenol	ND	0.00	ND	0.00	—	0.00	—	0.00	—	0.00	0.00
2,4/2,5-Dichlorophenol	—	0.00	—	0.00	ND	0.00	4.9	0.06			0.06
2,3-Dichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
2,4,5-Trichlorophenol	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	0.00
Pentachlorophenol	4.0	0.01	1.8	0.02	ND	0.00	ND	0.00	ND	0.00	0.03
4,5-Dichloroguaiacol	15.9	0.03	5.6	0.06	22.5	0.26	19.3	0.22			0.57
3,4,5-Trichloroguaiacol	31.5	0.06	11.3	0.13	5.7	0.06	10.7	0.12			0.38
4,5,6-Trichloroguaiacol	68.5	0.14	11.8	0.13	9.7	0.11	22.7	0.26			0.64
Tetrachloroguaiacol	81.4	0.16	21.0	0.24	1.0	0.01	6.1	0.07			0.48
5-Chlorovanillin	15.0	0.03	4.6	0.05	2.4	0.03	2.8	0.03			0.14
6-Chlorovanillin	19.6	0.04	8.9	0.10	23.6	0.27	22.7	0.26			0.67
5,6-Dichlorovanillin	64.8	0.13	14.7	0.17	4.9	0.06	12.4	0.14			0.49

ND - Not detected

	MILL		B (H-1)		B (H-2)		D - A SIDE		D - B SIDE		Sum of All Mills
	Flow (MGD)		0.24		1.36		1.42		0.92		lbs/day
		ppb	lbs/day	ppb	lbs/day	ppb	lbs/day	ppb	lbs/day		lbs/day
Sum of chlorophenols		7.70	0.02	1.80	0.02	0.00	0.00	4.90	0.06		0.09
Sum of chloroguaiacols		197.30	0.40	49.70	0.56	38.90	0.44	58.80	0.67		2.07
Sum of chlorovanillins		99.40	0.20	28.20	0.32	30.90	0.35	37.90	0.43		1.30
Sum of all analytes		304.40	0.61	79.70	0.90	69.80	0.79	101.60	1.15		3.46

Table G-13

Chlorophenol Analyses Summary
LANDFILL LEACHATE

	MILL	B
Analyte	ppb	lbs/day
2-Chlorophenol	ND	0.00
2,6-Dichlorophenol	ND	0.00
2,4-Dichlorophenol	ND	0.00
3,4-Dichlorophenol	ND	0.00
2,5-Dichlorophenol	ND	0.00
2,4/2,5-Dichlorophenol	ND	0.00
2,3-Dichlorophenol	ND	0.00
2,4,5-Trichlorophenol	ND	0.00
Pentachlorophenol	ND	0.00
4,5-Dichloroguaiacol	ND	0.00
3,4,5-Trichloroguaiacol	ND	0.00
4,5,6-Trichloroguaiacol	ND	0.00
Tetrachloroguaiacol	ND	0.00
5-Chlorovanillin	ND	0.00
6-Chlorovanillin	ND	0.00
5,6-Dichlorovanillin	ND	0.00

ND - Not detected

	MILL	B (H-1)
	Flow (MGD)	
	ppb	lbs/day
Sum of chlorophenols	0.00	0.00
Sum of chloroguaiacols	0.00	0.00
Sum of chlorovanillins	0.00	0.00
Sum of all analytes	0.00	0.00

TABLE G-14

BOD₅ and TSS RESULTS SUMMARY
MILL A

<u>Sample I.D.</u>	<u>TSS ppm</u>	<u>5 Day BOD ppm</u>
DE 020818 (Powerhouse Wastewater)	6	0
DE 020801 (Treated river water)	10	0
DE 020921 (combined untreated wastewater)	654	175
DE 020821 (Moonlight Leachate)	94	400
DE 020807 (Recovery #9)	16	119
DE 020915 (Bleach Plant #5)	66	212
DE 020806 (Kraft Mill #6)	1402	291
DE 020811 (Paper Mill #2)	1132	214
DE 020922 (Secondary Clarifier)	104	29

TABLE G-15
BOD₅ and TSS RESULTS SUMMARY
MILL B

<u>SAMPLE CODE</u>	<u>SAMPLE DESCRIPTION</u>	<u>TSS (ppm)</u>	<u>BOD (ppm)</u>
A-1	Treated Water	11	0.5
B-1a	Brown Stock Filtrate Tank	64	115
B-1b	Brown Stock Filtrate Tank o'flow outside Kraft Mill	51	253
B-2a	Corrosive sewer-recovery evaporator, recaust, refiners	144	337
B-3	Kraft sewer - Kraft pulping and Alkaline Bleach	70	226
D-3a	Cl ₂ Seal Tank o'flow	40	253
D-4a	E-1 Seal Tank o'flow	36	240
E-1	Tissue Machine sewer	204	16
F-3a	Combined Acid sewer	49	142
F-3b	Combined Process sewer	193	158
F-4	Secondary Effluent	40	5
F-5	Landfill Leachate	312	71

TABLE G-16

BOD₅ and TSS RESULTS SUMMARY
MILL C

Sample ID	Sample Description	TSS (mg/l)	BOD (mg/l)
DE026 001	Treated River Water	10	2
DE026 105	Untreated Groundwater	6	
DE026 106	Untreated River Water	21	
DE026 108	Station 7	397	
DE026 109	Station 8	1184	
DE026 110	Station 28	25	
DE026 112	Station 9	99	
DE026 113	Station 13	2016	
DE026 119	Station 1	1684	
DE026 120	Station 3	330	
DE026 121	Station 4	768	
DE026 122	Station 5	616	
DE026 012	Primary Influent (Sta 20)	540	301
DE026 013	Secondary Effluent (C-24)	16	11
DE026 014	Sludge Landfill Leachate	66	10
DE026 205	Wood Boiler and Boilerhouse (Sta 15)	1084	
DE026 206	Secondary Effluent (36-72)	36	9

TABLE G-17

BOD₅ and TSS RESULTS SUMMARY
MILL D

<u>Sample ID</u>	<u>Sample Description</u>	<u>TSS (mg/L)</u>	<u>BOD₅ (mg/L)</u>
B1	Brownstock decker sewer	26	180
B2	Dreg wash sewer	1250	
C1	Evaporator sewer	<1	120
C2	Recovery boiler sewer	4.5	
C3	Lime kiln sewer	258	
D4	Chlorination stage - A-side	10.5	
D5	Caustic stage - A-side	12.7	
D6	Hypo stage - A-side	12	
D7	Chlorination stage - B-side	17.5	
D9	Hypo stage - B-side	13	
E1	Ground wood mill/paper machines	1490	305
F1	WWTP influent	875	232
F2	WWTP effluent	14.5	13.2
F7	Sludge lagoon effluent		102 ^a

NOTE: (a) COD value presented.

TABLE G-18

BOD₅ and TSS RESULTS SUMMARY
MILL E

Results:

<u>Sample #</u>	<u>BOD mg/l</u>	<u>TSS mg/l</u>	
A-1	1	2	Upstream River Water
A2	1	*	Chlorinated Process Water
B1.2	220	230	A Side General Sewer
C15	375	600	A Side Caustic
B1.1 D1-1	120	1,100	B Side General Sewer
D2	200	350	Otis Mill Return
E1	340	680	Primary Influent
E3	16	89	Final Effluent
E7	1,400 ⁺	160	Landfill Leachate

* A2 - All sample used for seed. No TSS.