

AP42 Section:	10.3. Pulp Bleaching
Title:	Emission Factor Documentation for AP-42 Section 10.3 July 1992 – Draft Inactive section

EMISSION FACTOR DOCUMENTATION FOR AP-42 SECTION 10.3
Pulp Bleaching Processes

1. INTRODUCTION

The document Compilation of Air Pollutant Emissions Factors (AP-42) has been published by the U.S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by EPA to respond to new emission factor needs of EPA, State and local air pollution control programs, and industry.

An emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. The end uses for the emission factors reported in AP-42 include:

1. Estimating areawide emissions;
2. Estimating emissions for a specific facility; and
3. Evaluating emissions relative to ambient air quality.

The purpose of this report is to provide background information from test reports and other information to support preparation of AP-42 Section 10.3, Pulp Bleaching Processes.

This background report consists of five sections. Section 1 includes the introduction to the report. Section 2 gives a description of the pulp bleaching industry. It includes a characterization of the industry, an overview of the different process types, a description of emissions, and a description of the technology used to control emissions resulting from pulp bleaching. Section 3 is a review of process/emissions data collection and laboratory analysis procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Section 4 details pollutant emission factor development and includes the review of specific data sets and the results of data analysis. Section 5 presents the AP-42 Section 10.3, Pulp Bleaching Processes.

2. INDUSTRY DESCRIPTION

Bleaching enhances the physical and optical qualities of wood pulp. Bleaching whitens or brightens the naturally colored pulp to a desired level of whiteness by removal or decolorization of the lignin. Two approaches, brightening and true bleaching, are used to increase the whiteness of pulp.

Brightening uses selective chemicals to destroy some of the chromophobic groups in the wood fiber while preserving the lignin. Brightening is advantageous because the wood fibers themselves are not attacked; however, the lightening effects are not permanent.

The advantage of bleaching over brightening is that the whiteness of the pulp is longer lasting, if not permanent. Bleaching can weaken the fibers, however, and reduce sheet strength. The most common bleaching chemical is chlorine, which further delignifies the pulp. The chlorinated lignin is then removed and a bleaching chemical is added in a following stage. Typical bleaching chemicals are chlorine, chlorine dioxide, hypochlorite, oxygen, and peroxides.

There are currently no Standard Industrial Classification (SIC) codes for pulp bleaching. However, the XATEF data base lists two emission factors for pulp and paper bleaching under SIC 2611 (pulp mills). There are currently no Source Classification Codes (SCC's) for pulp bleaching processes.

2.1 CHARACTERIZATION OF THE INDUSTRY

2.2 PROCESS DESCRIPTION¹

The industry uses the following notation for the bleaching stages: chlorination (C), extraction (E), hypochlorite (H), chlorine dioxide (D), peroxide (P), oxygen (O), mixtures of chlorine dioxide with chlorine (Dc), and mixtures of chlorine with chlorine dioxide (Cd). Note: The lower case letter in the notations for the mixtures refers to a substitution of some percentage of the primary ingredient with the secondary ingredient. For example, Cd50 = 50 percent of the chlorine in a chlorine stage is

replaced with chlorine dioxide, and $Dc25 = 25$ percent of the chlorine dioxide in a chlorine dioxide stage is replaced with chlorine.

Figure 2-1 presents a typical bleaching sequence used in industry. The sequence is chlorination, extraction, chlorine dioxide, extraction, and chlorine dioxide; or, using the accepted notation, CEDED. The bleaching stages can be ordered in any number of combinations or sequences, and both the types of chemicals selected and the number of stages used depend on the level of pulp quality and brightness desired for the final product.

The first two stages in the bleaching process are typically chlorination and extraction, and a primary function in these first stages is to further delignify the pulp. The pulp is generally pumped into a tower or stage (in the case of the chlorination stage, containing chlorine) where it passes from the top to the bottom of the stage by gravity. The chlorine reacts with the noncarbohydrate constituents in the pulp, rendering them soluble. Some stages now employ a mixture of chlorine and chlorine dioxide where a portion of the chlorine is substituted with chlorine dioxide. This substitution helps minimize the degradation of the chemicals between stages. For example, hydrochloric acid formed in the chlorination stage would have neutralizing effect on the caustic in the following extraction stage.

The effluent from one washing stage is often recycled to another washer in the bleaching line. Countercurrent washing systems are used to reduce fresh water demand. Recycle of bleaching washer effluent has many advantages, such as chemical savings, heat conservation, and reduction in effluent volume. The two potential problems are the corrosion in the washers from the build-up of chlorinated compounds and variable pH. Most new mills are designed for this type of countercurrent washing and utilize suitable building materials to withstand corrosion. Washing with effluent from the previous stage with the addition of fresh water at some or all the stages is practiced by most mills, with the exception of effluent from the extraction stage. The extraction stage washing effluent contains solubilized chlorolignin compounds. Mixing of the extraction effluent in the chlorination stage could result in precipitation of the chlorolignin compounds, so a small amount may be recycled and the remaining effluent sewered.

The extraction stage, which typically employs caustic, but may use oxygen or peroxide, removes the chlorinated and oxidized lignin by solubilization. The pulp is washed after this stage to remove

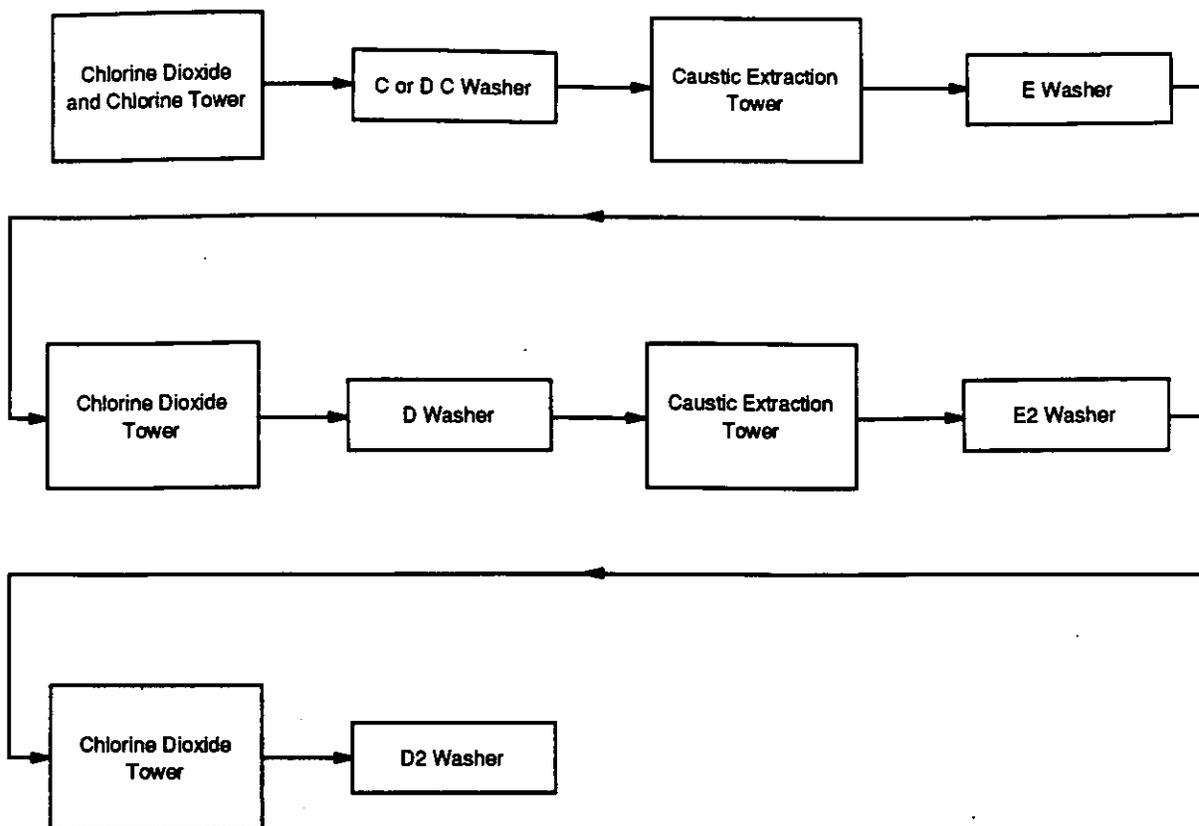


Figure 2-1. Flow diagram of CEDED bleaching sequence.

the excess chemicals and solubilized lignin. As discussed above, a portion of the effluent may be recycled and the remaining effluent sewerred to prevent precipitation of the solubilized chlorolignin compounds.

The remaining stages in the overall bleaching sequence serve to bleach and whiten the delignified pulp. A common bleaching stage is hypochlorite. The pH plays a key role in the attack on cellulose, and a pH of 9 is typically favored to prevent such attack. Some sites have begun using hot hypochlorite stages for faster satisfactory bleaching results.

2.3 EMISSIONS¹⁻⁷

The bleaching chemicals are commonly applied to pulp in bleaching stages or towers. Emission sources for each stage are located at the tower vent, the washer vent, and the seal tank vent. Figure 2-2 presents a typical bleaching stage, indicating these emission locations. Another potential source of air pollutant emissions is the wastewater effluent. Primary wastewater treatment typically includes screening to remove large particles and gravity sedimentation to remove smaller solids. Secondary treatment usually consists of aerobic biological oxidation in an oxidation lagoon. In some cases, a color removal system follows secondary treatment. The remaining sludge is concentrated before disposal in a landfill or by incineration.

The expected pollutants formed in the various bleaching stages are potentially emitted from vents and wastewater streams. Of these pollutants, only chlorine, chloroform, and carbon tetrachloride are documented as HAP releases from vents. Chlorine and carbon tetrachloride are emitted from the chlorination stage tower vent while chloroform is emitted from the chlorination, hypochlorite, and extraction stages. These three pollutants may be emitted from other stages as well. The remaining pollutants are suspected air releases due to their presence in the bleach line wastewater effluent.

The HAP emissions from each bleaching stage vary depending on the bleaching chemical used and the amount applied. For example, chloroform, chlorinated phenolics, dioxins, furans, and other chlorinated organics are formed when chlorine is used as a bleaching agent. In addition, a single, relatively large dose of chlorine may drive the reactions producing these compounds more so than a number of smaller additions because of concentration gradient.

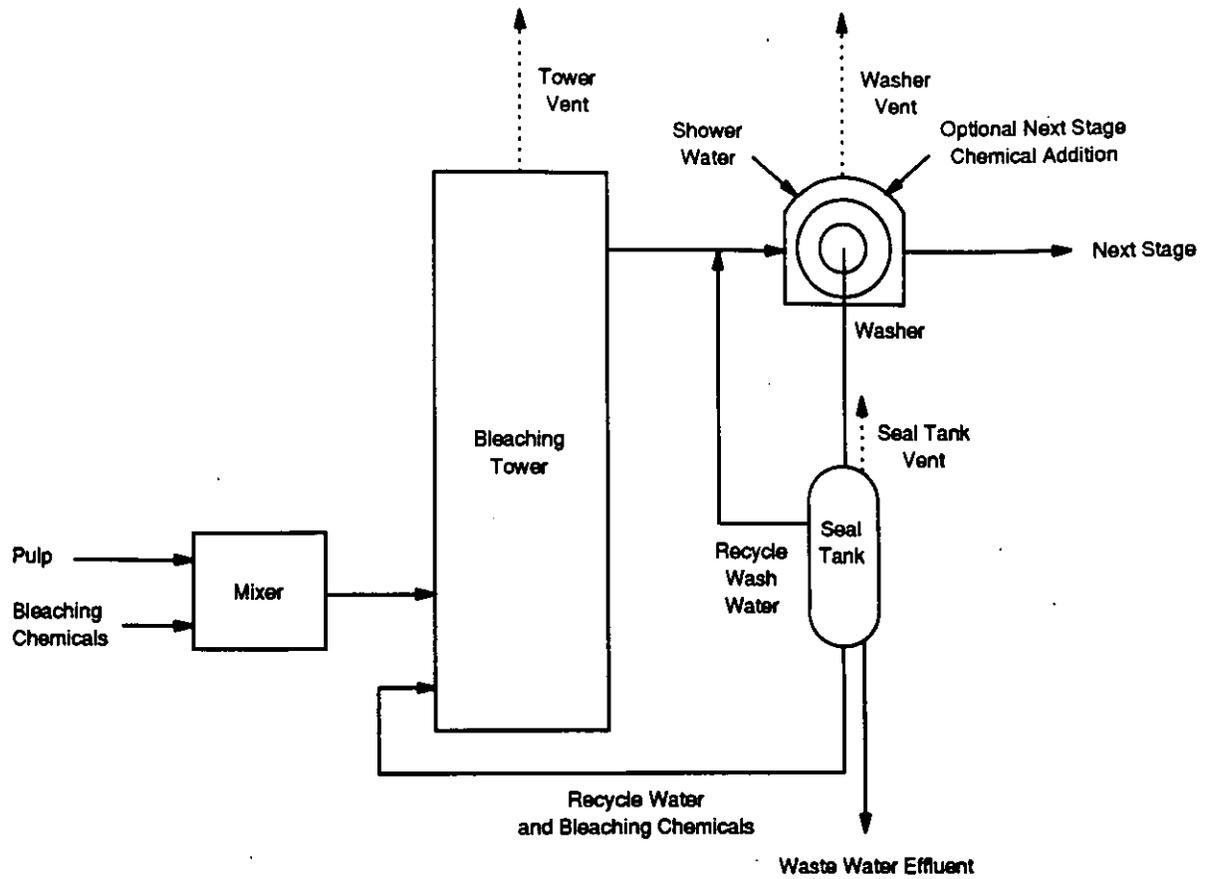


Figure 2-2. Typical venting from a bleaching stage.

Chlorination and extraction stages. In the chlorination stage, pulp is treated with chlorine in a water solution to continue the delignification process begun during the pulping process. The chlorine reacts with the lignin through substitution and oxidation reactions, producing byproducts which include chloroform, phenol, benzene, chlorinated phenolics, dioxins and furans, and other chlorinated organics. These byproduct emissions, as well as unreacted chlorine, may be vented from the chlorination stage tower, the washer, and the seal tank.

The extraction stage removes the chlorinated and oxidized lignin with a caustic solution. The final pH in the stage should be above 10.8 for complete solubilization. The largest amount of the unwanted lignin remaining from the pulping process is removed in these two stages. The majority of the dioxins, furans, chlorinated phenolics, and other chlorinated organics are formed and discharged from these two stages into the wastewater effluent.

Chlorine dioxide stage. Bleach plants often practice bleaching with chlorine dioxide substitution in the chlorination stage or with chlorine dioxide stages. The chlorine dioxide stage is similar to the chlorination stage and has similar emission points. One of the benefits of using chlorine dioxide is a reduction in the formation of chlorinated organics.

Other bleaching stages. Three other common stages are the hypochlorite stage, oxygen stage, and peroxide stage. The hypochlorite stage, along with the chlorination and extraction stages, has been identified as one of the most significant sources of chloroform emissions. Air emissions of other HAP compounds are not documented.

The oxygen stage can serve as a delignification stage or as a bleaching stage. Emissions from this stage are not clearly documented. A third potential bleaching stage is the peroxide stage. The emissions from this stage are also not well-documented.

2.4 CONTROL TECHNOLOGY

Maintaining low residual levels of bleaching chemicals in the pulp after it leaves the bleaching tower helps keep washer hood vent and seal tank vent emissions to a minimum. Scrubbers using various scrubbing fluids, including extraction-stage filtrate, sodium hydroxide solution, sodium bisulfite solution, alkaline wash water from causticizing, white liquor, and chilled water, have been

installed for controlling air emissions of chlorine and chlorine dioxide. Smaller scrubbers, designed with chemical recovery in mind, may be installed on the washer hood vent, tower vent, and seal tank vent individually, or a single, larger scrubber may scrub the combined gases from all three vents. Between 10 and 94 percent of the byproduct chloroform is released to the wastewater treatment area, where most of it is stripped or volatilized. Removing hypochlorite from the bleaching sequence may reduce chloroform formation.

REFERENCES FOR SECTION 2

1. G. A. Smook, Handbook for Pulp and Paper Technologists, TAPPI, Atlanta, GA, 1987.
2. M. A. Hannah, "Reaction Engineering Analysis of Oxygen-Bicarbonate Delignification," Northwest Regional Conference, The Institute of Paper Chemistry, Appleton, WI, November 12, 1979.
3. Environmental Protection Control, Pulp and Paper Industry, Part I, Air, EPA-625/7-76-001, U.S. Environmental Protection Agency, Technology Transfer, October 1976.
4. Summary of Technologies for the Control and Reduction of Chlorinated Organics from the Bleached Chemical Subcategories of the Pulp and Paper Industry, U.S. Environmental Protection Agency, Office of Water, Washington, D.C., April 27, 1990.
5. Industrial Wastewater Volatile Organic Compounds Emissions--Background Information for BACT/LAER Determinations, Control Technology Center, EPA-450/3-90-004, January 1990.
6. Results of Field Measurements of Chloroform Formation and Release from Pulp Bleaching, Technical Bulletin No. 558, National Council of the Paper Industry for Air and Stream Improvement, New York, 1988.
7. NCASI Handbook of Chemical Specific Information for SARA Section 313 Form R Reporting, National Council of the Paper Industry for Air and Stream Improvement, New York, April 1990.

3. GENERAL DATA REVIEW AND ANALYSIS

3.1 LITERATURE SEARCH AND SCREENING

Data for this investigation were obtained from a number of sources within the Office of Air Quality Planning and Standards (OAQPS) and from outside organizations. The Crosswalk/Air Toxic Emission Factor Data Base Management System (XATEF) and VOC/PM Speciation Data Base Management System (SPECIATE) were searched by SCC code for identification of the potential pollutants emitted and emission factors for those pollutants. A general search of the Air CHIEF CD-ROM also was conducted to supplement the information from these two data bases.

Information on the industry, including number of plants, plant location, and annual production capacities, was obtained from the 1990 DFPI Directory of the Forest Products Industry and the 1987 Census of Manufactures. The Aerometric Information Retrieval System (AIRS) data base also was searched for data on the number of plants, plant location, and estimated annual emissions of criteria pollutants.

Numerous sources of information were investigated specifically for emission test reports and data. A search of the Test Method Storage and Retrieval (TSAR) data base revealed no test reports for sources within the pulp bleaching industry. The EPA library was searched for additional test reports. (Using this information and information obtained on plant location from the 1990 DFPI Directory of the Forest Products Industry and the 1987 Census of Manufactures, State and Regional air offices were contacted about the availability of test reports. However, the information obtained from these offices was limited.) Publications lists from the Office of Research and Development (ORD) and Control Technology Center (CTC) were also searched for reports on emissions from the pulp bleaching industry. In addition, representative trade associations, including the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), were contacted for assistance in obtaining information about the industry and emissions.

To screen out unusable test reports, documents, and information from which emission factors could not be developed, the following general criteria were used:

1. Emissions data must be from a primary reference:
 - a. Source testing must be from a referenced study that does not reiterate information from previous studies.
 - b. The document must constitute the original source of test data. For example, a technical paper was not included if the original study was contained in the previous document. If the exact source of the data could not be determined, the document was eliminated.
2. The referenced study must contain test results based on more than one test run.
3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions (e.g., 1-page reports were generally rejected).

A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria.

3.2 EMISSION DATA QUALITY RATING SYSTEM^{1,2}

As part of the analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were excluded from consideration:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (i.e., comparison of EPA Method 5 front half with EPA Method 5 front and back half);
3. Test series of controlled emissions for which the control device is not specified;
4. Test series in which the source process is not clearly identified and described; and

5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Test data sets that were not excluded were assigned a quality rating. The rating system used was that specified by EIB for preparing AP-42 sections. The data were rated as follows:

A--Multiple tests that were performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in EPA reference test methods, although these methods were used as a guide for the methodology actually used.

B--Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C--Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D--Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented in the report. The source was operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent to which such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data are documented in the report, and any variations in the sampling and process operation are noted. If a large spread between

test results cannot be explained by information contained in the test report, the data are suspect and are given a lower rating.

4. Laboratory analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM^{1,2}

The quality of the emission factors developed from analysis of the test data was rated using the following general criteria:

A--Excellent: Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B--Above average: Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. The source category is specific enough so that variability within the source category population may be minimized.

C--Average: Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. In addition, the source category is specific enough so that variability within the source category population may be minimized.

D--Below average: The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E--Poor: The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent upon the individual reviewer. Details of the rating of each candidate emission factor are provided in Chapter 4 of this report.

REFERENCES FOR SECTION 3

1. Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections (Draft), Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 6, 1992.
2. Midwest Research Institute, Emission Factor Documentation for AP-42 Section 2.5, Sewage Sludge Incineration, EPA-40/4-90-017, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, August 1990.

4. AP-42 SECTION DEVELOPMENT

4.1 DEVELOPMENT OF SECTION NARRATIVE

The draft AP-42 section is a new section addressing pulp bleaching processes. The new section is based on information gathered from the references cited, and includes a description of the industry, a process flow diagram, and emission factors for specific process emission points.

Occurring simultaneously with the revision of AP-42 Chapter 10, the Chemicals and Petroleum Branch (CPB) is developing maximum achievable control technology (MACT) standards for the pulp and paper industry. As part of the MACT development effort, EPA is conducting tests of various sources within the pulping and pulp bleaching industries. When these new data become available, they could be incorporated into the appropriate sections of AP-42. Additionally, since the new data gathered for the MACT standards will be forthcoming, only those data readily available were evaluated.

4.2 POLLUTANT EMISSION FACTOR DEVELOPMENT

Only a single reference was documented and reviewed in the process of developing the emission factors for the section on pulp bleaching.

4.2.1 Review of Specific Data Sets

4.2.1.1 Reference 1. This information document provides background information on the pulp and paper industry, including bleaching processes, for assisting EPA's OAQPS in evaluating the need for standards or guidelines addressing air emissions from pulping, bleaching, and paper-making processes. The document focuses on HAP and VOC emissions and control technologies.

This document gives emission factors for a number of HAP's and VOC's from bleach line vents, wastewater effluents, and chlorine dioxide generation. Although this document is a secondary reference, it is the sole source of emission factors for the included HAP's and VOC's that is readily available for review. Because of the emphasis on including noncriteria pollutants in AP-42, these

HAP and VOC emission factors were not rejected, but instead were given a data rating of D and incorporated into AP-42.

4.2.2 Review of XATEF and SPECIATE Data Base Emission Factors

The SPECIATE data base includes no emission factors for pulp bleaching processes.

The XATEF data base includes two emission factors for chlorine emissions from pulp and paper bleaching, one for chlorine dioxide generation and one for the entire bleaching process. The reference cited for both of these emission factors (M. G. Johnston, Preliminary Source Assessment for Chloride, Final Report, U. S. Environmental Protection Agency, Research Triangle Park, NC, 1986) could not be obtained. For that reason, these emission factors have not been incorporated into the draft of AP-42, Section 10.2.

4.2.3 Results of Data Analysis

Emission data have been identified for the following pulp bleaching sources:

- | | |
|-----------------------------------|---|
| Bleach line vents | - Carbon tetrachloride, chlorine, chloroform |
| Bleach line wastewater effluents | - Benzene, carbon tetrachloride, chloroform, methanol, methyl chloroform, pentachlorophenol, phenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,7,8-TCDD, 2,3,7,8-TCDF |
| Chlorine dioxide generation vents | - Chlorine |

These data appear in Tables 4-1 through 4-3.

Based on the data summarized in Tables 4-1 through 4-3, a number of emission factors were developed for pulp bleaching. Emission factors for pulp bleaching were developed from the emission data for the following pollutants from the emission points given.

Carbon tetrachloride	-- bleach line vents, chlorination stage -- bleach line wastewater, chlorination stage
Chlorine	-- bleach line vents, no hypochlorite use -- bleach line vents, less than 0.5 percent hypochlorite use -- bleach line vents, between 0.5 and 2 percent hypochlorite use -- bleach line vents, greater than 2 percent hypochlorite use -- chlorine dioxide generation vents
Benzene	-- bleach line wastewater -- bleach line wastewater, sulfite pulping
Chloroform	-- bleach line vents, no hypochlorite use -- bleach line vents, less than 0.5 percent hypochlorite use -- bleach line vents, between 0.5 and 2 percent hypochlorite use -- bleach line vents, greater than 2 percent hypochlorite use -- bleach line wastewater, no hypochlorite use -- bleach line wastewater, less than 0.5 percent hypochlorite use -- bleach line wastewater, between 0.5 and 2 percent hypochlorite use -- bleach line wastewater, greater than 2 percent hypochlorite use
Methanol	-- bleach line wastewater, softwood pulp -- bleach line wastewater, hardwood pulp
Methyl chloroform	-- bleach line wastewater -- bleach line wastewater, sulfite pulping
Pentachlorophenol	-- bleach line wastewater
Phenol	-- bleach line wastewater
2,4,5-Trichlorophenol	-- bleach line wastewater -- bleach line wastewater, with slimicide
2,4,6-Trichlorophenol	-- bleach line wastewater -- bleach line wastewater, sulfite pulping

2,3,7,8-TCDD -- bleach line wastewater

2,3,7,8-TCDF -- bleach line wastewater

The emission factors discussed above were extracted from a secondary reference and appear to be based on material balance data, as opposed to test data. Because of the questionable nature of these emission factors, the lack of any corroborating data, and the emphasis on including noncriteria pollutants in AP-42, these emission factors were incorporated into AP-42 with ratings of E.

REFERENCES FOR SECTION 4

1. General Information Document for the Pulp and Paper Industry, Draft, U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, March 1991.

TABLE 4-1. SUMMARY OF TEST DATA FOR BLEACHING LINE VENTS

Type of control	Pollutant	No. of test runs	Data rating	Emission factor		Ref. No.
				Range, kg/Mg, lb/ton	Average, kg/Mg, lb/ton	
N/K	Carbon tetrachloride ^a	NA	D	NA ^b	4.80E-04 (9.6E-04)	1
N/K	Chlorine ^a	NA	D	NA ^b	3.50E-01 (7.0E-01)	1
N/K	Chlorine ^c	NA	D	NA ^b	5.00E-04 (1.0E-03)	1
N/K	Chloroform ^d	NA	D	NA ^b	8.50E-02 (1.7E-01)	1
N/K	Chloroform ^e	NA	D	NA ^b	1.45E-01 (2.9E-01)	1
N/K	Chloroform ^f	NA	D	NA ^b	2.90E-01 (5.8E-01)	1
N/K	Chloroform ^g	NA	D	NA ^b	4.35E-01 (8.7E-01)	1

N/K = not known

NA = not available

kg/Mg = kg of pollutant per Mg of pulp produced

lb/ton = lb of pollutant per ton of pulp produced

E = exponent, e.g., 5.8E-05 = 5.8 x 10⁻⁵

^aChlorination stage emissions.

^bOnly individual figures were reported for these emissions. They appear in the average column.

^cFugitive emissions.

^dNo hypochlorite use.

^eLess than 0.5 percent hypochlorite use.

^fBetween 0.5 and 2 percent hypochlorite use.

^gGreater than 2 percent hypochlorite use.

TABLE 4-2. SUMMARY OF TEST DATA FOR AIR EMISSIONS FROM BLEACHING LINE WASTEWATER EFFLUENTS

Type of control	Pollutant	No. of test runs	Data rating	Emission factor		Ref. No.
				Range, kg/Mg, lb/ton	Average, kg/Mg, lb/ton	
N/K	Benzene	NA	D	NA ^a	7.00E-04 (1.4E-03)	1
N/K	Benzene ^b	NA	D	NA ^a	4.45E-03 (8.9E-03)	1
N/K	Carbon tetrachloride ^c	NA	D	NA ^a	2.49E-05 (4.98E-05)	1
N/K	Chloroform ^d	NA	D	NA ^a	4.48E-02 (8.96E-02)	1
N/K	Chloroform ^e	NA	D	NA ^a	7.23E-02 (1.446E-01)	1
N/K	Chloroform ^f	NA	D	NA ^a	1.45E-01 (2.9E-01)	1
N/K	Chloroform ^g	NA	D	NA ^a	2.17E-01 (4.34E-01)	1
N/K	Methanol ^h	NA	D	NA ^a	1.01E+00 (2.02E+00)	1
N/K	Methanol ⁱ	NA	D	NA ^a	4.43E-01 (8.86E-01)	1
N/K	Methyl chloroform	NA	D	NA ^a	5.80E-03 (1.16E-02)	1
N/K	Methyl chloroform ^b	NA	D	NA ^a	1.07E-01 (2.14E-01)	1
N/K	Pentachlorophenol	NA	D	NA ^a	1.75E-03 (3.5E-03)	1
N/K	Phenol	NA	D	NA ^a	2.60E-03 (5.2E-03)	1
N/K	2,4,5-Trichlorophenol	NA	D	NA ^a	3.74E-04 (7.48E-04)	1
N/K	2,4,5-Trichlorophenol ^j	NA	D	NA ^a	1.02E-03 (2.04E-03)	1
N/K	2,4,6-Trichlorophenol	NA	D	NA ^a	7.50E-04 (1.5E-03)	1
N/K	2,4,6-Trichlorophenol ^b	NA	D	NA ^a	2.86E-02 (5.72E-02)	1

TABLE 4-2. (Continued)

Type of control	Pollutant	No. of test runs	Data rating	Emission factor		Ref. No.
				Range, kg/Mg, lb/ton	Average, kg/Mg, lb/ton	
N/K	2,3,7,8-TCDD	NA	D	NA ^a	3.10E-07 (6.2E-07)	1
N/K	2,3,7,8-TCDF	NA	D	NA ^a	1.74E-06 (3.48E-06)	1

N/K = not known

NA = data not available

kg/Mg = kg of pollutant per Mg of pulp produced

lb/ton = lb of pollutant per ton of pulp produced

E = exponent, e.g., 5.8E-05 = 5.8×10^{-5}

^aOnly individual figures were reported for these emission. They appear in the average column.

^bSulfite pulping.

^cChlorination stage.

^dNo hypochlorite use.

^eLess than 0.5 percent hypochlorite use.

^fBetween 0.5 and 2 percent hypochlorite use.

^gGreater than 2 percent hypochlorite use.

^hSoftwood pulp.

ⁱHardwood pulp.

^jWith slimicide.

TABLE 4-3. SUMMARY OF TEST DATA FOR CHLORINE DIOXIDE GENERATION VENTS

Type of control	Pollutant	No. of test runs	Data rating	Emission factor		Ref. No.
				Range, kg/Mg, lb/ton	Average, kg/Mg, lb/ton	
N/K	Chlorine	NA	D	NA ^a	3.04E-01 (6.08E-01)	1

N/K = not known

NA = data not available

kg/Mg = kg of pollutant per Mg of pulp produced

lb/ton = lb of pollutant per ton of pulp produced

E = exponent, e.g., 5.8E-05 = 5.8×10^{-5}

^aOnly individual figures were reported for these emissions. They appear in the average column.

5. DRAFT AP-42 SECTION 10.3

10.3 Pulp Bleaching Processes

10.3.1 General¹

Bleaching enhances the physical and optical qualities of wood pulp. Bleaching whitens or brightens the naturally colored pulp to a desired level of whiteness by removing or decolorizing the lignin. Two approaches, brightening and true bleaching, are used to increase the whiteness of pulp.

Brightening uses selective chemicals to destroy some of the chromophobic groups in the wood fiber while preserving the lignin. Brightening is advantageous because the wood fibers themselves are not attacked; however, the lightening effects are not permanent.

The advantage of bleaching over brightening is that the whiteness of the pulp is longer lasting, if not permanent. Bleaching can weaken the fibers, however, and reduce sheet strength in the finished paper product. The most common bleaching chemical is chlorine, which further delignifies the pulp. The chlorinated lignin is then removed and a bleaching chemical is added in a subsequent stage. Typical bleaching chemicals are chlorine, chlorine dioxide, hypochlorite, oxygen, and peroxide. Concern over chlorinated compounds such as dioxins and furans has prompted the pulp bleaching industry to shift away from chlorine to other bleaching chemicals for delignification and bleaching.

10.3.2 Process Description¹

The pulp bleaching industry uses the following notation for bleaching stages: chlorination (C), extraction (E), hypochlorite (H), chlorine dioxide (D), peroxide (P), oxygen (O), mixtures of chlorine dioxide with chlorine (Dc), and mixtures of chlorine with chlorine dioxide (Cd). Note: The lower case letter in the notations for the mixtures refers to a substitution of some percentage of the primary ingredient with the secondary ingredient. For example, Cd₅₀ = 50% of the chlorine in a chlorine stage is replaced with chlorine dioxide, and Dc₂₅ = 25% of the chlorine dioxide in a chlorine dioxide stage is replaced with chlorine.

Figure 10.3-1 presents a typical bleaching sequence. The sequence is chlorination, extraction, chlorine dioxide, extraction, and chlorine dioxide; or, using the accepted notation, CEDED. The

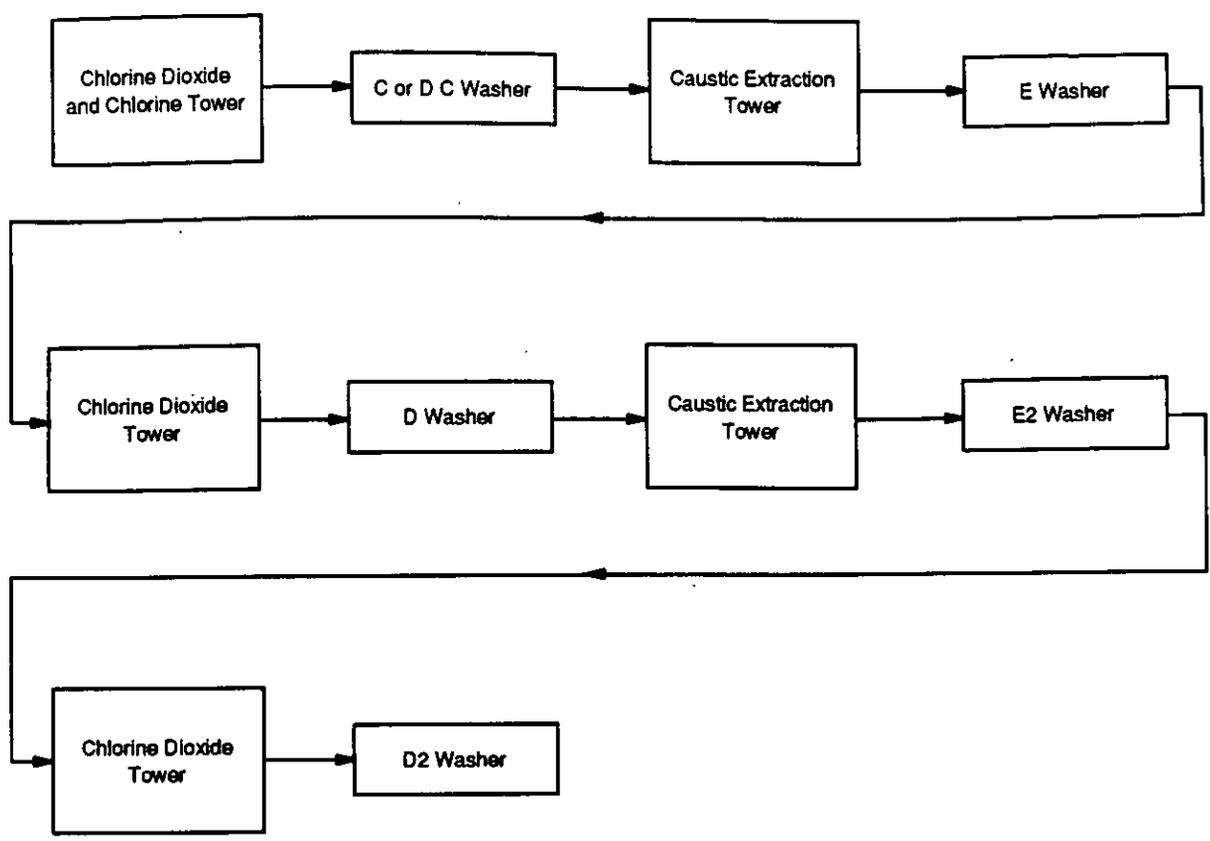


Figure 10.3-1. Flow diagram of CEDED bleaching sequence.

bleaching stages can be ordered in a wide variety of combinations or sequences, and both the types of chemicals selected and the number of stages used depend on the level of pulp quality and brightness required for the final product.

The primary function of the first two stages of the bleaching process, typically chlorination and extraction, is to further delignify the pulp. The pulp is generally pumped into a tower or stage (in the case of the chlorination stage, containing chlorine) where it passes from the top to the bottom of the stage by gravity. The chlorine reacts with the noncarbohydrate constituents in the pulp, rendering them soluble. Some stages now use a mixture of chlorine and chlorine dioxide where a portion of the chlorine is substituted with chlorine dioxide. This substitution helps minimize the degradation of the chemicals between stages. For example, hydrochloric acid formed in the chlorination stage would have a neutralizing effect on the caustic in the following extraction stage.

The effluent from one washing stage is often reused in another washer in the bleaching line. Countercurrent washing systems are used to reduce fresh water demand. Bleach washer effluent recycling has several advantages, including chemical savings, heat conservation, and reduction of effluent volume. The two potential problems with effluent recycling are corrosion in the washers from the build-up of chlorinated compounds and variable Ph. Most new mills are designed for this type of countercurrent washing and are constructed to withstand corrosion. Washing with effluent from the previous stage with the addition of fresh water at some or all the stages is practiced by most mills, with the exception of effluent from the extraction stage. The extraction stage washing effluent contains solubilized chlorolignin compounds. Mixing the extraction effluent in the chlorination stage could result in precipitation of the chlorolignin compounds, so only a small amount may be recycled and the remaining effluent must be sewered.

The extraction stage, which typically uses caustic, but may use oxygen or peroxide, removes the chlorinated and oxidized lignin by solubilization. The pulp is washed after this stage to remove excess chemicals and solubilized lignin. As discussed above, a portion of the effluent may be recycled but the remaining effluent must be sewered to prevent precipitation of the solubilized chlorolignin compounds.

The remaining stages in the bleaching sequence serve to bleach and whiten the delignified pulp. A common bleaching stage is the hypochlorite stage. The pH plays a key role in the attack on

cellulose, and a pH of 9 is generally favored to prevent such attack. Some sites are using hot hypochlorite stages for faster satisfactory bleaching results.

10.3.3 Emissions¹⁻⁷

Bleaching chemicals are typically applied to pulp in bleaching stages or towers. Emission points for each stage are located at the tower vent, the washer vent, and the seal tank vent. Figure 10.3-2 presents a typical bleaching stage, indicating the location of these emission points. Another potential source of air pollutant emissions is the wastewater effluent.

Primary wastewater treatment typically includes screening to remove large particles and gravity sedimentation to remove smaller solids. Secondary treatment usually consists of aerobic biological oxidation in an oxidation lagoon. In some cases, a color removal system follows secondary treatment. The remaining sludge is concentrated before disposal in a landfill or by incineration.

The expected pollutants formed in the various bleaching stages are potentially emitted from vents and wastewater streams. Of these pollutants, only chlorine, chloroform, and carbon tetrachloride are documented as HAP releases from vents. Chlorine and carbon tetrachloride are emitted from the chlorination stage tower vent while chloroform is emitted from the chlorination, hypochlorite, and extraction stages. These three pollutants may be emitted from other stages as well. The remaining pollutants are suspected air releases due to their presence in the bleach line wastewater effluent. Table 10.3-1 presents emission factors for organic and inorganic pollutant emissions from pulp bleaching.

The HAP emissions from each bleaching stage vary depending on the bleaching chemical used and the amount applied. For example, chloroform, chlorinated phenolics, dioxins, furans, and other chlorinated organics are formed when chlorine is used as a bleaching agent. In addition, a single, relatively large dose of chlorine may drive the reactions producing these compounds more so than a number of smaller additions because of concentration gradient.

Chlorination and extraction stages. In the chlorination stage, pulp is treated with chlorine in a water solution to continue the delignification process begun during the pulping process. The chlorine reacts with the lignin through substitution and oxidation reactions, producing byproducts which

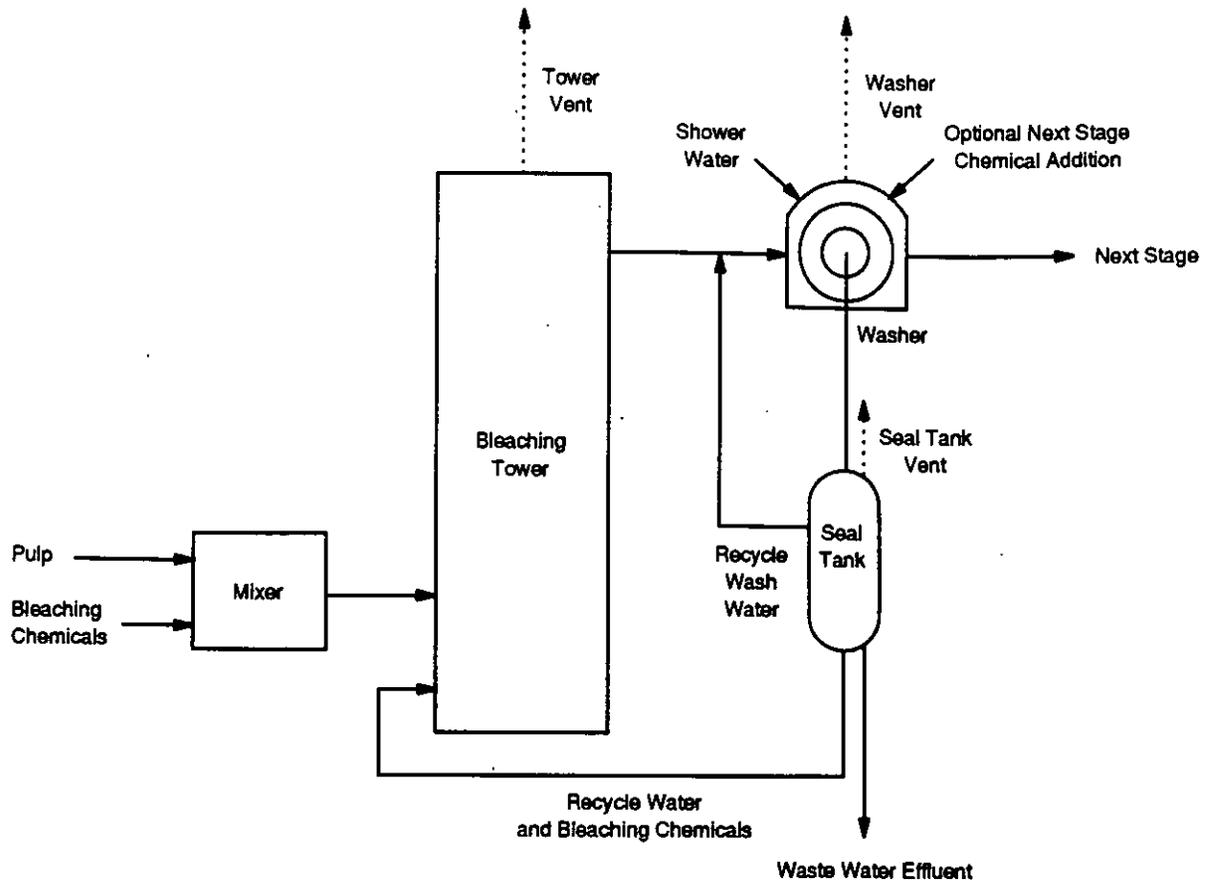


Figure 10.3-2. Typical venting from a bleaching stage.

TABLE 10.3-1. EMISSION FACTORS FOR ORGANIC AND INORGANIC
POLLUTANT EMISSIONS FROM PULP BLEACHING PROCESSES

(Uncontrolled emissions unless otherwise noted)

Source (SCC)	Pollutant		Emission factor		Rating	Ref.
	CASRN*	Name	kg/Mg	lb/ton		
Bleach line vents	56-23-5	Carbon tetrachloride ^a	4.80E-04	9.6E-04	E	7
	67-66-3	Chloroform ^b	8.50E-02	1.7E-01	E	7
	67-66-3	Chloroform ^c	1.45E-01	2.9E-01	E	7
	67-66-3	Chloroform ^d	2.90E-01	5.8E-01	E	7
	67-66-3	Chloroform ^e	4.35E-01	8.7E-01	E	7
	71-43-2	Benzene	NA	NA		
	71-55-6	1,1,1-Trichloroethane	NA	NA		
	87-86-5	Pentachlorophenol	NA	NA		
	88-06-2	2,4,6-Trichlorophenol	NA	NA		
	95-95-4	2,4,5-Trichlorophenol	NA	NA		
	108-95-2	Phenol	NA	NA		
	1746-01-6	TCDD	NA	NA		
		TCDF	NA	NA		
	7647-01-0	Hydrochloric acid	NA	NA		
	7782-50-5	Chlorine ^a	3.50E-01	7.0E-01	E	7
	7782-50-5	Chlorine ^f	5.00E-04	1.0E-03	E	7
10049-04-4	Chlorine dioxide	NA	NA			
Wastewater	56-23-5	Carbon tetrachloride ^a	2.49E-05	4.98E-05	E	7
	67-56-1	Methanol ^g	1.01E+00	2.02E+00	E	7
	67-56-1	Methanol ^h	4.43E-01	8.86E-01	E	7
	67-66-3	Chloroform ^b	4.48E-02	8.96E-02	E	7
	67-66-3	Chloroform ^c	7.23E-02	1.446E-01	E	7
	67-66-3	Chloroform ^d	1.45E-01	2.9E-01	E	7
	67-66-3	Chloroform ^e	2.17E-01	4.34E-01	E	7
	71-43-2	Benzene	7.00E-04	1.4E-03	E	7
	71-43-2	Benzene ⁱ	4.45E-03	8.9E-03	E	7
	71-55-6	Methyl chloroform	5.80E-03	1.16E-02	E	7
	71-55-6	Methyl chloroform ⁱ	1.07E-01	2.14E-01	E	7
	87-86-5	Pentachlorophenol	1.75E-03	3.5E-03	E	7
	88-06-2	2,4,6-Trichlorophenol	7.50E-04	1.5E-03	E	7
	88-06-2	2,4,6-Trichlorophenol ^l	2.86E-02	5.72E-02	E	7
	95-95-4	2,4,5-Trichlorophenol	3.74E-04	7.48E-04	E	7
	95-95-4	2,4,5-Trichlorophenol ^l	1.02E-03	2.04E-03	E	7
	108-95-2	Phenol	2.60E-03	5.2E-03	E	7
	1746-01-6	2,3,7,8-TCDD	3.10E-07	6.2E-07	E	7
		2,3,7,8-TCDF	1.74E-06	3.48E-06	E	7
	10049-04-4	Chlorine dioxide	NA	NA		

TABLE 10.3-1 (Continued)

Source (SCC)	Pollutant		Emission factor		Rating	Ref.
	CASRN*	Name	kg/Mg	lb/ton		
Chlorine dioxide manufacture	7782-50-5	Chlorine	3.04E-01	6.08E-01	E	7
	10049-04-4	Chlorine dioxide	NA	NA		

*CASRN = Chemical Abstracts Service Registry Number

NA = Data not available (this pollutant is expected to be released from the source shown but an emission factor is not currently available)

SCC = Source Classification Code, in parentheses immediately following classified sources

kg/Mg = kg of pollutant per Mg of pulp produced

lb/ton = lb of pollutant per ton of pulp produced

E = exponent, e.g., 5.8E-05 = 5.8×10^{-5}

^aChlorination stage emissions.

^bNo hypochlorite use.

^cLess than 0.5 percent hypochlorite use.

^dBetween 0.5 and 2 percent hypochlorite use.

^eGreater than 2 percent hypochlorite use.

^fFugitive emissions.

^gSoftwood pulp.

^hHardwood pulp.

ⁱSulfite pulping.

^jWith slimicide.

include chloroform, phenol, benzene, chlorinated phenolics, dioxins and furans, and other chlorinated organics. These byproduct emissions, as well as unreacted chlorine, may be vented from the chlorination stage tower, the washer, and the seal tank.

The extraction stage removes the chlorinated and oxidized lignin with a caustic solution. The final pH in the stage should be above 10.8 for complete solubilization. The largest amount of the unwanted lignin remaining from the pulping process is removed in these two stages. The majority of the dioxins, furans, chlorinated phenolics, and other chlorinated organics are formed and discharged from these two stages into the wastewater effluent.

Chlorine dioxide stage. Bleach plants often practice bleaching with chlorine dioxide substitution in the chlorination stage or with chlorine dioxide stages. The chlorine dioxide stage is similar to the chlorination stage and has similar emission points. One of the benefits of using chlorine dioxide is a reduction in the formation of chlorinated organics.

Other bleaching stages. Three other common stages are the hypochlorite stage, oxygen stage, and peroxide stage. The hypochlorite stage, along with the chlorination and extraction stages, has been identified as one of the most significant sources of chloroform emissions. Air emissions of other HAP compounds are not documented.

The oxygen stage can serve as a delignification stage or as a bleaching stage. Emissions from this stage are not clearly documented. A third potential bleaching stage is the peroxide stage. The emissions from this stage are also not well-documented.

10.3.4 Controls⁸

Maintaining low residual levels of bleaching chemicals in the pulp after it leaves the bleaching tower helps keep washer hood vent and seal tank vent emissions to a minimum. Scrubbers using various scrubbing fluids, including extraction-stage filtrate, sodium hydroxide solution, sodium bisulfite solution, alkaline wash water from causticizing, white liquor, and chilled water, have been installed for controlling air emissions of chlorine and chlorine dioxide. Smaller scrubbers, designed with chemical recovery in mind, may be installed on the washer hood vent, tower vent, and seal tank vent individually, or a single, larger scrubber may scrub the combined gases from all three vents.

Between 10 and 94 percent of the byproduct chloroform is released to the wastewater treatment area, where most of it is stripped or volatilized. Removing hypochlorite from the bleaching sequence may reduce chloroform formation.

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