

Final Report

INVENTORY OF CHLOROPHENOL USE IN THE
FOREST PRODUCTS INDUSTRY AND INVESTIGATION OF
RELATED EMISSIONS OF CHLORINATED DIBENZODIOXINS
AND DIBENZOFURANS

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DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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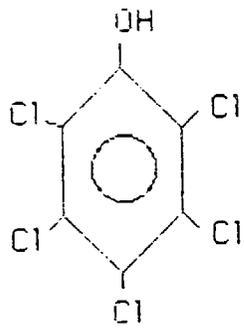
1 INTRODUCTION

Polychlorinated dibenzodioxins and polychlorinated dibenzofurans are chemical species known to be highly toxic and a potential threat to public health. These chemicals are both contaminants in and combustion products of chlorophenols, which are used in the forest products industry as fungicides and wood preservatives. Therefore, extensive efforts have been made by the California State Water Resources Control Board and Regional Water Quality Control Boards to document releases of chlorophenols, dioxins, and furans from forest products industrial sites to ground and surface waters. However, no formal study has been performed to assess potential releases of these substances to the atmosphere. In 1986 the California Air Resources Board (ARB) contracted with Systems Applications, Inc. to perform a thorough survey of statewide emissions of chlorophenol, dioxins, and furans to the atmosphere from forest products industrial operations. This report documents that study.

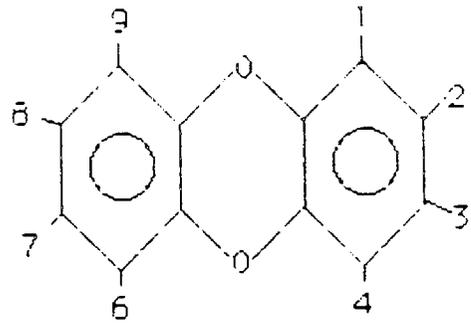
BACKGROUND

Chlorophenols are a class of compounds identified by the ARB as potential toxic air contaminants. The primary use of chlorophenols is currently as a fungicide to preserve wood for outdoor and underground use. Chlorophenols are very effective in inhibiting so-called sapstain problems caused by mold growth, and termite and bacterial action that would shorten the useful life of such products as utility poles, railroad ties, and other structural products exposed to the elements.

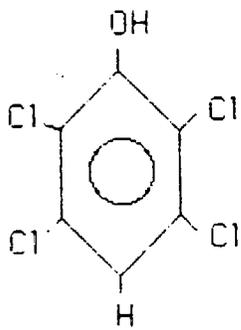
There are two major homologs (chemicals having essentially the same structure) of chlorophenols used in the forest products industry. The most widely used homolog is pentachlorophenol (PCP); PCP is a phenol that has been fully chlorinated without destruction of the benzene ring (see chemical structure at the top left of Figure 1-1) so that all of the benzene ring hydrogen atoms are replaced with chlorine. The wood preservative properties of PCP have been known since the 1930s when the chemical was first commercially produced (Sproule, 1960). The other major chlorophenol homolog is tetrachlorophenol (TCP), which has four, rather than five,



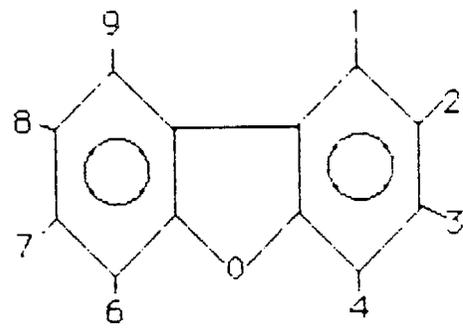
Pentachlorophenol



Dibenzo-p-dioxin



Tetrachlorophenol



Dibenzofuran

Figure 1-1: Principal Chemicals of Interest

chlorine atoms in its chemical structure (see bottom left of Figure 1-1). TCP, like PCP, is a fungicide commonly used in the forest products industry. It is also produced as an inevitable by-product of PCP manufacture.

Commercial chlorophenols are known to contain impurities that include the highly toxic dioxins and furans--polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). These toxic substances are also inevitable by-products of chlorophenol manufacture. They have chemical structures similar to chlorophenols, with two, coupled, chlorinated benzene rings (see chemical structures on the right-hand side of Figure 1-1). There are several isomers of PCDDs and PCDFs of various toxicity as shown in Table 1-1. Strictly speaking, the term isomer refers to only those molecules with the same number of atoms. Tetra, penta, hexa, etc. chlorinated compounds are all "congeners" of each other. However, for this report, for ease of use, we will refer to all congeners and isomers of PCDDs or PCDFs as "isomers." The compounds reported most toxic are 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran. (The numbers refer to the positions of chlorine atoms in the chemical structure; see Figure 1-1.) In addition to their presence as impurities in chlorophenol, PCDD and PCDFs may also be produced as products of combustion when chlorophenol-containing wood or woodwaste is burned. It is also possible that chlorophenols react in the atmosphere, possibly through photochemical reactions, to form PCDDs and PCDFs.

Thus, potential pathways of population exposure to chlorophenols released from forest products industrial sites during wood treatment are of concern to the ARB. The principal use of PCP in California is in the pressure treatment of wood (primarily utility poles). In this process, PCP is dissolved in an organic solvent such as butane and forced deep into the pores of the wood under pressure. TCP is generally used in nonpressure or dip treatments as a salt such as sodium chlorophenolate in an aqueous solution. Dip treatment does not force the chlorophenol as deeply into the wood as does pressure treatment; it does not require large pressure vessels, and is commonly used for surface wood treatment at sawmills.

OBJECTIVES OF THE STUDY

Because of the potential public health risk associated with atmospheric releases of chlorophenol and associated PCDDs and PCDFs from forest product industrial sites, the ARB contracted with Systems Applications, Inc. to perform a statewide survey of chlorophenol use, specific industrial users of wood preservatives, potential pathways of airborne emissions (such as evaporation and combustion), emission factors and release rates, and the resulting atmospheric concentrations and potential population

exposures of toxic chemicals. This nine-month study was initiated in May 1986. Figure 1-2 illustrates the study elements.

The study consisted of the following 6 tasks:

- (1) Development of a statewide inventory of all chlorophenol homologs and derivatives used in industrial wood treatment applications.
- (2) Location of all wood processing and treatment facilities where chlorophenols are currently used in California. This task was, in turn, divided into the development of (a) a statewide mass balance for chlorophenols and (b) facility-specific emission pathways.
- (3) Development of PCDD and PCDF contamination profiles for commercial penta (PCP) and tetra (TCP) chlorophenol.
- (4) Estimation of chlorophenol (and contaminant) emission rates due to evaporation and the probability of the formation of PCDDs and PCDFs both during combustion and in the atmosphere.
- (5) Combination of the results of tasks (2), (3), and (4) to provide facility-specific emission rates for chlorophenols, PCDDs, and PCDFs.
- (6) Assessment of potential atmospheric concentrations and population exposure to these concentrations.

STRUCTURE OF THIS REPORT

This report is divided into six sections and supporting appendixes (A through H). Section 2 describes the survey of statewide and facility-specific chlorophenol use and compares estimates of current chlorophenol use derived from several independent approaches. Section 3 describes chlorophenol treatment methods used in California and the potential pathways for atmospheric releases of chlorophenol and related toxic contaminants. Section 4 develops the technical basis for chlorophenol, PCDD, and PCDF emission factors through a survey of contamination profiles, evaporation rate calculations, and estimates of PCDD and PCDF production during combustion and in the atmosphere. Section 5 presents the statewide mass balance for chlorophenol and the county-specific emission rates of chlorophenol, PCDDs, and PCDFs from the forest products industrial sites. This section also presents the results of human population exposure modeling

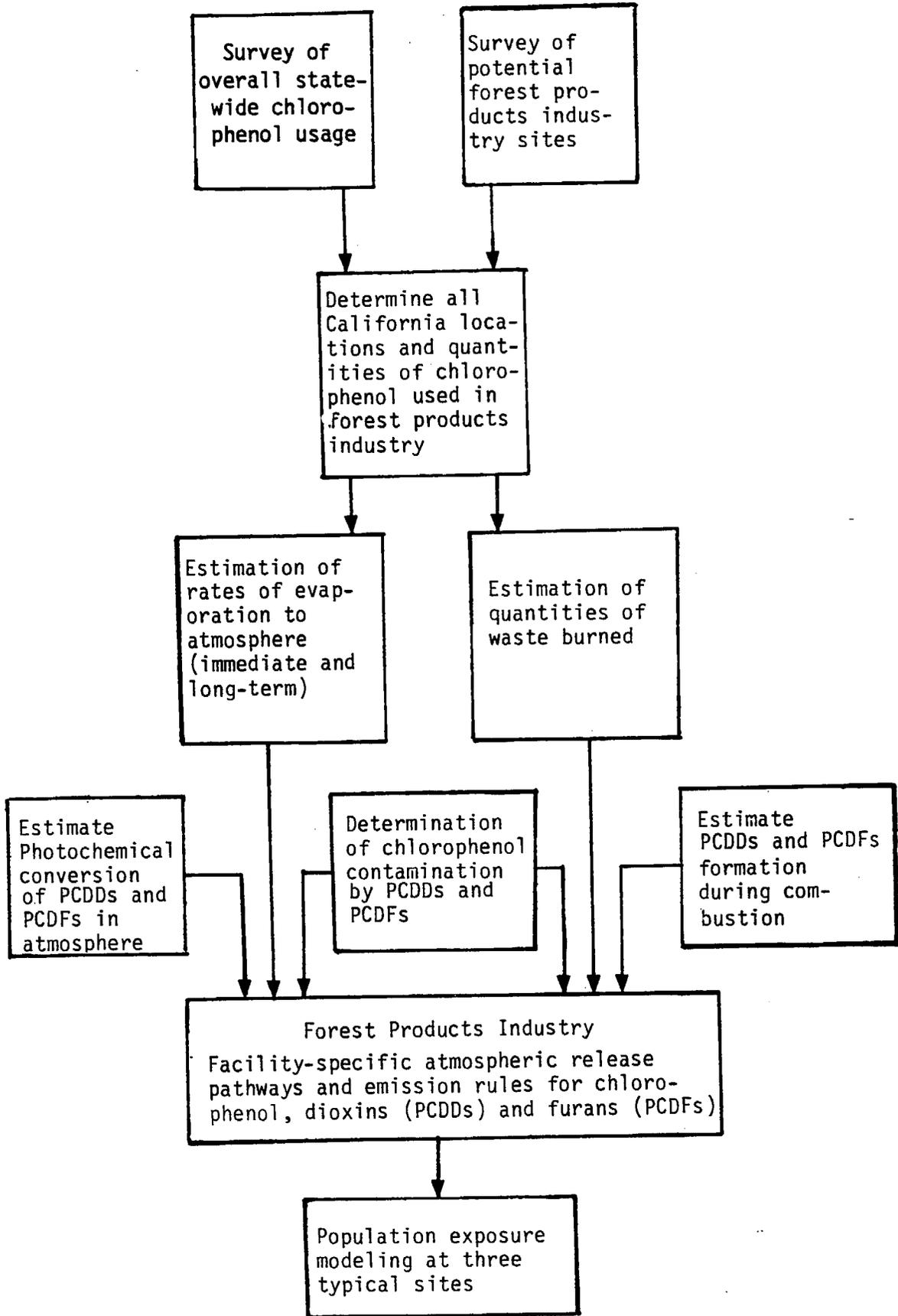


FIGURE 1-2. Study Logic Flow Diagram

for three representative sites. Section 6 summarizes the principal conclusions and uncertainties of this study and provides recommendations regarding future work that may be needed to evaluate the ultimate fate of chlorophenol-treated wood after it has left the forest products industrial sites. Table 1-1 provides a list of the abbreviations used throughout this report.

TABLE 1-1. Congeners of polychlorinated dioxins and furans:
Abbreviations used in this report and number of possible isomers.

Abbreviation Used in this Report	Other Abbreviations	Chemical name	Number of Possible Isomers
PCP	Penta	Pentachlorophenol	1
TCP	Tetra	Tetrachlorophenol	3
4CDD	TCDD, dioxin	Tetrachlorodibenzo-p-dioxin	22
5CDD	PCDD	Pentachlorodibenzo-p-dioxin	14
6CDD	HexCDD, HCDD	Hexachlorodibenzo-p-dioxin	10
7CDD	HepCDD, HpCDD	Heptachlorodibenzo-p-dioxin	2
8CDD	OCDD	Octachlorodibenzo-p-dioxin	1
4CDF	TCDF	Tetrachlorodibenzofuran	38
5CDF	PCDF	Pentachlorodibenzofuran	28
6CDF	HexCDF, HCDF	Hexachlorodibenzofuran	16
7CDF	HepCDF, HpCDF	Heptachlorodibenzofuran	4
8CDF	OCDF	Octachlorodibenzofuran	1
PCDD		Polychlorinated dibenzo-p-dioxins	75
PCDF		Polychlorinated dibenzofurans	135

2 INVENTORY OF CHLOROPHENOL USE IN CALIFORNIA

The use of chemicals to extend the life and usefulness of wood products is an important component of the forest products industry. Chemical preservatives have made it economically possible to use wood in a variety of applications that would be infeasible without such treatment. Chlorophenol is widely used as a wood preservative because it is effective against bacteria and fungi as well as insects (USDA, 1980). It is also used to prevent sapstain, which discolors freshly cut lumber and reduces its value.

The use of chlorophenol and its salts is regulated by the federal Insecticide, Fungicide, and Rodenticide Act, and the standards set by the American Wood Preservers Association. Disposal is regulated under the Resource Conservation and Recovery Act. The U.S. Environmental Protection Agency (EPA) has been tightening its control of chlorophenols because of their potential (along with PCDD and PCDF contaminants) for causing cancer and genetic defects. Regulations currently include (1) classification of chlorophenols as restricted-use pesticides (only registered pesticide applicators may use them), (2) a number of requirements relating to protective measures for their application and situations in which they may not be applied (such as on wood intended for interior use), and (3) limitations on permissible amounts of hexachlorodibenzo-p-dioxin, contained as an impurity in commercial-grade chlorophenol. More detailed information on EPA regulation of chlorophenol is presented in Appendix A.

In this section we present an inventory of chlorophenol use by county for the state of California. The inventory comprises the two homologs* of chlorophenol, pentachlorophenol (PCP), and tetrachlorophenol (TCP), and their derivatives used in the California forest products industry. Chlorophenols are used in California principally as wood preservatives, but are also used in much smaller amounts as herbicides, defoliant, moscidicides, and biocides. This project focuses primarily on chlorophenols used in wood treatment, but includes some information on other uses.

* i.e., species having a common or similar origin.

Chlorophenol is used as a wood preservative to prevent decay and the growth of stain-producing molds on lumber for outdoor use (e.g., construction, railroad ties, marine piling, and highway barriers). The largest use in California involves the treatment of wood used as poles for electric power or telephone transmissions.

Homologs other than the two principal homologs of chlorophenol used in California (PCP and TCP), such as trichlorophenol or dichlorophenol, are not used as wood preservatives. PCP and TCP are usually dissolved in a petroleum solvent, while their principal derivatives--potassium and sodium chlorophenates (salts)--are generally dissolved in water.

STATEWIDE USE

In the remainder of this section we describe (1) the various data bases used to develop the statewide inventory of chlorophenol use by the forest products industry in California; (2) the design and results of the survey of facilities in the state using chlorophenol; and (3) the resulting statewide inventory on a county-by-county basis. Our discussion of these topics includes the following items:

Statewide Use:

Forest products industry needs and regulatory requirements for chlorophenol;

California Department of Food and Agriculture pesticide use and sales reports;

Manufacturers of chlorophenol sales figures; and

Forest products industry use estimates.

Source Identification and Survey of Individual Users:

ARB emissions inventory data base;

State and regional water quality control board assessments;

Forest products industry directories; and

Systems Applications, Inc. survey design and responses.

Inventory of chlorophenol use by county:

Comparison of estimates; and

Uncertainty estimates.

Table 2-1 shows the various sources of information utilized in this study and the types of data obtained from each source. We have attempted to use as many independent sources of data as possible to reduce the likelihood of omitting any important emission sources and to provide a basis for uncertainty estimates. The sources of information contacted ranged from state agencies responsible for air and water quality and pesticide use to forest product industry trade associations. In addition, industrial manufacturers of chlorophenol sold in California were contacted directly. The International Trade Administration was also contacted to determine the quantities of chlorophenol, if any, imported into California from foreign countries. Compilation of data from these various sources of information provided an overall picture of the scope of chlorophenol use in California.

The most recent available data were obtained. In most cases the most recent available data encompass the 12-month period ending December 1985. However, in some cases, sales and use data encompass the 12-month period ending December 1986 or represent estimates of annual use for the 1985/86 timeframe.

California Department of Food and Agriculture Estimates of Statewide Sales and Use

The California Department of Food and Agriculture (CDFA) reports the total sales of chlorophenols in California and also the non-wood-treatment use of chlorophenols on a statewide basis. They do not, however, report wood-treatment use. Tables 2-2 and 2-3 list the CDFA estimates of sales of chlorophenols for both PCP and TCP for 1984 and 1985 and the non-wood use of chlorophenols during 1983 and 1984, the two most recent years for which total sales and non-wood data are available.

There are approximately 500 registered labels for herbicides containing chlorophenol (USDA, 1980). Most herbicides containing chlorophenol are used to control vegetation such as annual grasses and weeds. Some chlorophenol is also used as a mushroom-house biocide to suppress the population levels of pest organisms (fungi and insects) on the surfaces of materials near commercial mushroom beds. The CDFA reports the non-wood use of chlorophenol in California by category of use. CDFA reports indicate that the principal non-wood use in California is structural pest control, with

TABLE 2-1. Source Information Matrix

Source of Information	Type of Information			
	Source Location	Type of Lumber Facility	Chlorophenol Use	Sales
California Dept. of Food & Agriculture			x	x
Vulcan Chemicals				x
Chapman Chemicals				x
American Wood Preservers Association	x	x	x	
National Forest Products Assoc.	x	x		
California Forest Protection Assoc.	x	x		
International Trade Administration				x
International Statistics Council			x	
California State & Regional Water Boards	x			
California Air Resources Board	x	x		

TABLE 2-2. Chlorophenol sales in California reported by the California Department of Food and Agriculture.

Year	Pentachlorophenol (Tons/year)	Tetrachlorophenol (Tons/year)
1984	940	34
1985	902	0

(CDFA 1984; 1985)

TABLE 2-3. Non-wood use of chlorophenols in California reported by the California Department of Food and Agriculture.

Year	Pentachlorophenol (Tons/year)	Tetrachlorophenol (Tons/year)
1983	1.19	0.0
1984	1.22	0.0

(CDFA, 1983; 1984)

small amounts used in landscape maintenance, public health pest control, and industrial areas. Table 2-3 shows the annual non-wood use of chlorophenols in California as reported by the CDFA. No non-wood uses of TCP are reported in the CDFA files after 1981, when only 0.02 lb was used for structural pest control. PCP used annually for non-wood purposes accounts for less than a tenth of a percent of total statewide chlorophenol use. Since the non-wood uses of chlorophenols are extremely small compared to the amounts used in wood treatment and are outside the scope of this study, they are not included in the county-by-county California inventory of chlorophenols presented in this report.

Chlorophenol Manufacturer and Formulator Sales Figures

As of July 1986, the only manufacturer of chlorophenols in the United States is Vulcan Chemicals, a division of Vulcan Materials Company of Birmingham, Alabama. In the recent past, Reichold Chemicals of Tacoma, Washington also manufactured chlorophenols; however, as of July 1986 it was not producing chlorophenols (personal communication, July 1986). It is expected that another manufacturer, Iacon Incorporated of Houston, Texas, will also be producing chlorophenols in the near future (AWPI, 1986). However, Iacon, Inc. plans no sales to California in the foreseeable future (personal communication, December 1986). The only formulator of chlorophenol products in the United States is Chapman Chemical Company of Memphis, Tennessee. Chapman Chemical obtains chlorophenol from Vulcan Chemicals and reformulates it for its own products. Thus, sales of chlorophenol to California users consist of direct purchases from the sole manufacturer as well as sales from the sole reformulator. Table 2-4 shows the most recent sales of chlorophenols in California by Vulcan (12 months ending June 30, 1986) and Chapman (January through December, 1985).

Vulcan Chemical Company produces PCP in a powder or flake form, packaged in bulk tanks or in solid blocks. The PCP is sold directly to pressure treaters and Chapman Chemical Company. Chapman Chemical reformulates it into a liquid preservative (sodium pentachlorophenate). In the past, Chapman Chemical also purchased TCP from Reichold Chemical and reformulated it into sodium or potassium tetrachlorophenate.

International Statistics Council Estimates of Chlorophenol Use

The American Wood Preservers Association and the American Wood Preservers Institute recently sponsored a study performed by J. T. Micklewright of the International Statistics Council (Micklewright, 1986) to report on the activities of the wood preserving industry nationwide during the period of 1983-1984. Micklewright (personal communication, July, 1986) estimates

TABLE 2-4. Annual chlorophenol sales in California as reported by its manufacturer and formulator for 1985/86.

Use	Pentachlorophenol (Tons/year)	Tetrachlorophenol (Tons/year)
Pressure Wood Treatment	913.5	0.0
Nonpressure Wood Treatment and Other	29.2 ¹	28.8 ²

¹ Sold as technical sodium pentachlorophenate.
Also note that all technical sodium pentachlorophenate was sold for non-wood preservative uses.

² Sold as technical sodium tetrachlorophenate (10.1 tons/year) and technical potassium tetrachlorophenate (18.7 tons/year).

the total use of PCP by pressure wood preservers at approximately 1000 tons/year in California during 1984, his most recent available data. His estimate was arrived at by assuming that the 3.894 million cubic feet of lumber treated with PCP during 1984 in California received the industry standard treatment of 0.512 lb/cu ft (3.894×10^6 cu. ft x 0.512 lb/cu. ft x 1 ton/2000 lb = 997 tons).

SOURCE IDENTIFICATION AND SURVEY OF INDIVIDUAL USERS

As noted earlier, we attempted to use as many independent data bases as practical to obtain source information. Different agencies collect data for different reasons, so this approach reduced the likelihood of omitting an important emission source. The principal sources of information were the California Air Resources Board (ARB) emissions data system, site lists provided by Regional Water Quality Control Boards (RWQCBs), a list of wood preservers provided by the International Statistics Council under contract to the American Wood Preservers Institute (AWPI) (Micklewright, 1986), and the 1986 Directory of the Forest Product Industry. We obtained additional facility information from the United States Department of Food and Agriculture, and from first-hand knowledge provided by one of our consultants, W. Dost of the Wood Building Research Center at the University of California.

ARB Source Information

The ARB maintains a detailed data base of sources of air emissions in California. The 1983 data base (the most recent available data) was searched by four-digit Standard Industrial Classification (SIC) codes. The most important SIC codes for this study are 2421 (sawmills and planing mills), 2426 (hardwood dimension and flooring mills), 2429 (special product sawmills), and 2431 (millwork). The technical definitions of the industries that fall into each of these codes are provided in Appendix B. A complete list of these facilities, including their name, facility ID, and city, is provided in Appendix C. Maps showing their distribution throughout the state of California are presented in Figures 2-1 and 2-2.

Source Information Obtained from Regional Water Quality Control Boards (RWQCB)

Various regional water quality control boards have assessed chlorophenol use at sawmills in their jurisdiction. Their concern, of course, was primarily the potential impact of these toxic substances on ground and surface waters. We coordinated our site list development efforts with their

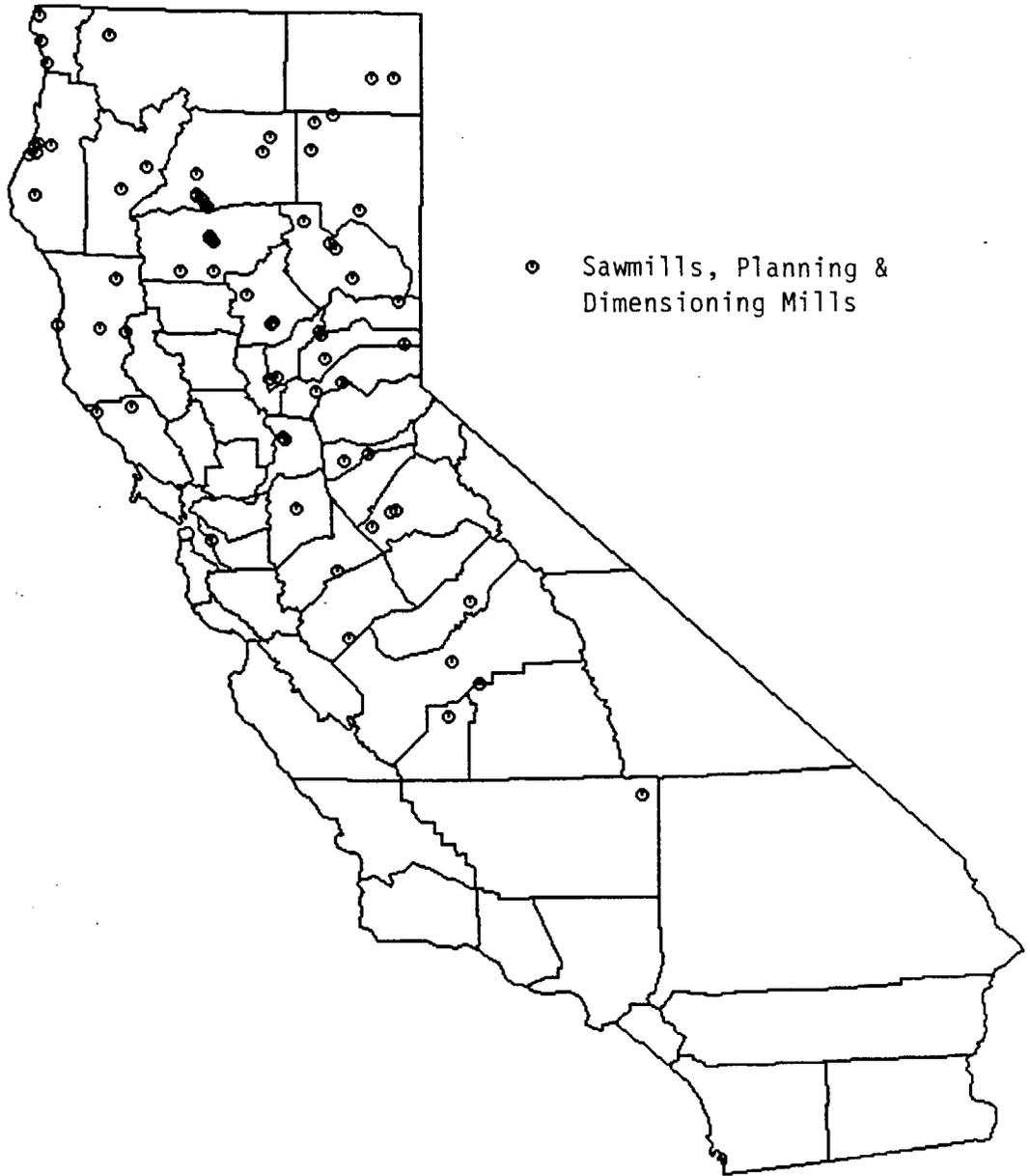


FIGURE 2-1. Sawmills, Planning & Dimensioning Mills.
(Source ARB, 1983)



FIGURE 2-2. Millwork, Plywood & Structural Plants.

assessments by contacting a number of these water quality control boards. These contacts included the California State Water Resources Control Board (F. Palmer), The North Coast RWQCB (A. Wellman), the Central Valley RWQCB (D. Meith), and the Central Coast RWQCB (E. Gobler). The facilities suggested for inclusion in our survey are shown in Tables 2-5 and 2-6.

Source Information From the International Statistics Council

In 1985, the International Statistics Council, under contract to AWPI and also to the American Wood Preservers Association, the Society of American Wood Preservers, the Southern Pressure Treaters Association, the Western Wood Preservers Institute, and the Railway Tie Association, performed a survey-based study to determine the true size and nature of the wood preserving industry and its products. The study identified 547 wood preserving plants nationwide that treated wood in 1984, including 15 in California. Of the 15 identified in California, only 5 are pressure treaters utilizing PCP. The remainder are pressure treaters that use other chemicals such as creosote or inorganic chemicals. Pressure treaters in California that use chlorophenol are listed in Table 2-7.

Survey Design

On the basis of the data sources just described, the advice of W. Dost, and consultation with the various water quality control agency personnel, we compiled a list of known and potential chlorophenol users for our survey. This list is presented in Table 2-8. A survey questionnaire was developed utilizing an iterative process involving staff at the Air Resources Board and Systems Applications. The preliminary form was modeled after the questionnaire used by the International Statistics Council for AWPI because we believed the forms would receive greater response if their appearance was familiar to those responding. The survey was designed to enable us to develop a detailed statewide overview of the use of chlorophenols in the forest products industry. The survey forms were designed to cover questions on the entire wood treatment process, including the quantities of wood treated, amounts of chlorophenol used in treatment, treatment methods, and waste disposal practices. From the survey, we could derive the numbers and locations of treatment facilities that used pressure and nonpressure treatment, as well as the amounts of chlorophenol used in these processes. This information is summarized in Section 5 on statewide mass balance of chlorophenol use in California. The survey and introductory letter are shown as Appendix D.

TABLE 2-5. Potential users of chlorophenol suggested by Central Valley Water Quality Control Board.¹

Facility Name	County
American Forest Prod. ³	Amador
Louisiana Pacific ⁵	Butte
Snyder Lumber ³	Calaveras
Golden St. Bldg. Prod.	El Dorado
American Forest Prod.	Fresno
Hughes Co. ³	Fresno
Louisiana Pacific ⁴	Glenn
Big Valley Lumber Co. ⁶	Lassen
Trin-Co Forest Prod. ⁴	Lassen
American Forest Prod. (Northfork)	Madera
American Forest Prod. (Oakhurst) ⁴	Madera
I'SOT Corp. ³	Modoc
Bohemia Lumber ³	Nevada
Sierra Mountain Mills	Placer
Sierra Pacific Mills ^{3,7}	Plumas
Siskyou Plumas Lumber ³	Plumas
Champion International ⁴	Shasta
Paul Bunyan Lumber ³	Shasta
Sierra Pacific Mill	"
Louisiana Pacific ³	"
Calaran Lumber Co. ⁴	"
Siller Brothers Inc ³	"
Baxter Pole ²	"
Roseburg Lumber ⁶	"
Crane Mills	Tehama
Diamond Lumber ³	Tehama
Louisiana Pacific ⁵	Tehama
Snyder Lumber ³	Tuolumne
Louisiana Pacific (Standard)	"
Louisiana Pacific (Keystone) ⁴	"
Hatler Lumber	"
Erickson Lumber	Yuba

1 Personal communication D. Meith, July, 1986.

2 Proposed facility.

3 Dip system discontinued.

4 Facility discontinued.

5 Dip system using other compounds

6 Spray system in use (March 1987)

7 Dip tanks being used to evaporate remaining supplies of chlorophenol

TABLE 2-6. Potential users of chlorophenol suggested by the North Coast Water Quality Control Board.¹

Facility Name	County
Miller Redwood	Del Norte
North Crest	" "
Pacific Lumber (Carlotta)	Humbolt
Pacific Lumber (Fortuna)	" "
Sympsum Redwood	" "
Eel River Sawmill	" "
Louisiana Pacific (Potter Valley)	Mendocino
Southwest Forest Ind.	Siskiyou
Hi-Ridge Lumber ²	" "
Burnt Ranch	Trinity
Hayfork Mill	" "

¹ Personal communication, A. Wellman, July, 1986.

² Chlorophenol dip system discontinued (F. Palmer, March, 1987)

TABLE 2-7. Chlorophenol pressure treatment facilities in California.

Facility Name	City	County
Koppers Company	Oroville	Butte
Selma Treating Co.	Selma	Fresno
J.H. Baxter & Co.	Long Beach	Los Angeles
San Diego Wood Preserving	National City	San Diego
McCormick & Baxter	Stockton	San Joaquin

TABLE 2-8. Wood treatment survey sites and responses (includes all sites identified in Tables 2-5 through 2-7).

Facility Name	Type	Mailing Address	Response	
			Yes	No
Champion International	Sawmill	Anderson, CA		Closed
Roseburg Lumber Company	Sawmill	Anderson, CA	X	
Siller Bros., Inc.	Sawmill	Anderson, CA	X	
Sympsum Redwood Company	Sawmill	Arcata, CA	X	
Pacific Wood Preserving	Preserver	Bakersfield	X	
Big Valley Lumber Co.	Sawmill	Bieber, CA	X	
Louisiana Pacific, Inc.	Sawmill	Burney, CA	X	
Sierra Pacific Industries	Sawmill	Burney, CA	X	
Southwest Forest Ind.	Sawmill	Burnt Ranch, CA	X	
I'SOT Corporation	Sawmill	Canby, CA		Closed
Pacific Lumber	Sawmill	Carlotta, CA	X	
Crane Mills	Sawmill	Corning, CA	X	
Miller Redwood Company	Sawmill	Crescent City, CA	X	
Northcrest, Inc.	Sawmill	Crescent City, CA	X	
Golden State Building	Sawmill	Folsom, CA		X
Sierra Mountain Mill	Sawmill	Forest Hill, CA	X	
Eel River Sawmills, Inc.	Sawmill	Fortuna, CA	X	
D. P. Hughes Co.	Sawmill	Fowler, CA	X	
American Forest Products	Sawmill	Fresno, CA	X	
Brunswick Timber Corp.	Sawmill	Grass Valley, CA	X	
Southwest Forest Industry	Sawmill	Happy Camp, CA	X	
Sierra Pacific Industries	Sawmill	Hayfork, CA	X	
Fibreboard Corp.	Sawmill	Jamestown, CA	X	

Table 2-8. (Concluded)

Facility Name	Type	Mailing Address	Response	
			Yes	No
American Forest Products	Sawmill	Martell, CA	X	
Erickson Lumber Company	Sawmill	Marysville, CA	X	
San Diego Wood Preserving	Preserver	National City, CA	X	
Sequoia Forest Industries	Sawmill	North Fork, CA	X	
Sequoia Forest Industries	Sawmill	North Fork, CA	X	
American Forest Products	Sawmill	Oakhurst, CA		Closed
Koppers Company	Preserver	Oroville, CA	X	
Louisiana Pacific Corp.	Sawmill	Oroville, CA	X	
Louisiana-Pacific Corp.	Sawmill	Potter Valley, CA	X	
Louisiana-Pacific Corp.	Sawmill	Red Bluff, CA	X	
Louisiana-Pacific Corp.	Sawmill	Redding, CA	X	
Calaran Lumber Company	Sawmill	Redding, CA		Closed
Trin-Co Forest Products	Sawmill	Redding, CA		Closed
J. H. Baxter (Long Beach)	Preserver	San Mateo, CA	X	
Pacific Lumber Co.	Sawmill	Scotia, CA	X	
Selma Treating Company	Preserver	Selma, CA	X	
Sierra Pacific Indust.	Sawmill	Sloat, CA	X	
Hatler & Co., Vernon E.	Sawmill	Sonora, CA	X	
Snyder Lumber Products	Sawmill	Sonora, CA	X	
Louisiana-Pacific Corp.	Sawmill	Standard, CA	X	
McCormick & Baxter	Preserver	Stockton, CA	X	
Snyder Lumber Products	Sawmill	Turlock, CA	X	
Hi-Ridge Lumber Company	Sawmill	Yreka, CA	X	

Survey Responses

As shown in Table 2-8, surveys were sent to 46 facilities in the state and responses for 95 percent of the active facilities on our list were obtained. (Five of the 46 facilities have been closed down.) We classified each plant according to the percentage of total chlorophenol use it accounted for, and the type of treatment used. The most important finding was that only 5 plants account for over 98 percent of the chlorophenol used for wood preservation in California. All 5 of these facilities use pressure treatment. Of the remaining responding facilities, 3 facilities use dip treatment, and only 1 uses spray treatment. Figure 2-3 presents the spatial distribution of the facilities using chlorophenol identified by our survey.

INVENTORY OF CHLOROPHENOL USE BY COUNTY

To develop an inventory by county, we used the results of the survey of wood processing facilities in California, and totaled the results by county. Table 2-9 displays the results of the facility survey by county; Figure 2-4 presents the use of chlorophenols in California during 1986 on a county-by-county basis. As seen in the figure, the areas in which the chlorophenol use is highest are the Central Valley of California and the Los Angeles area. The extreme northern regions of California and San Diego show chlorophenol use on a much smaller scale. TCP is used only in the four northern counties.

COMPARISON AND UNCERTAINTY OF CHLOROPHENOL USE ESTIMATES

Table 2-10 compares the estimates of chlorophenol sold and used in California in recent years by the various sources identified in this study. It is important to note that the CDFA only reports the sales or use of pesticides including chlorophenol if there are more than three registered applicators for that chemical. Therefore, the sales figures may underestimate the true total sales and amount used for non-wood purposes in California. Examination of the 1984 and 1985 CDFA results reveals, on average, that undisclosed sales account for approximately five percent of total statewide sales of a particular class of pesticides such as herbicides. Nevertheless, sales estimates reported by the CDFA of both TCP and PCP are quite close to the amounts reported as sold by Vulcan and Chapman Chemical Companies. The quantities of chlorophenol used, as estimated by the International Statistics Council and our survey, are also in close agreement. Furthermore, the sales estimates are in very good agreement

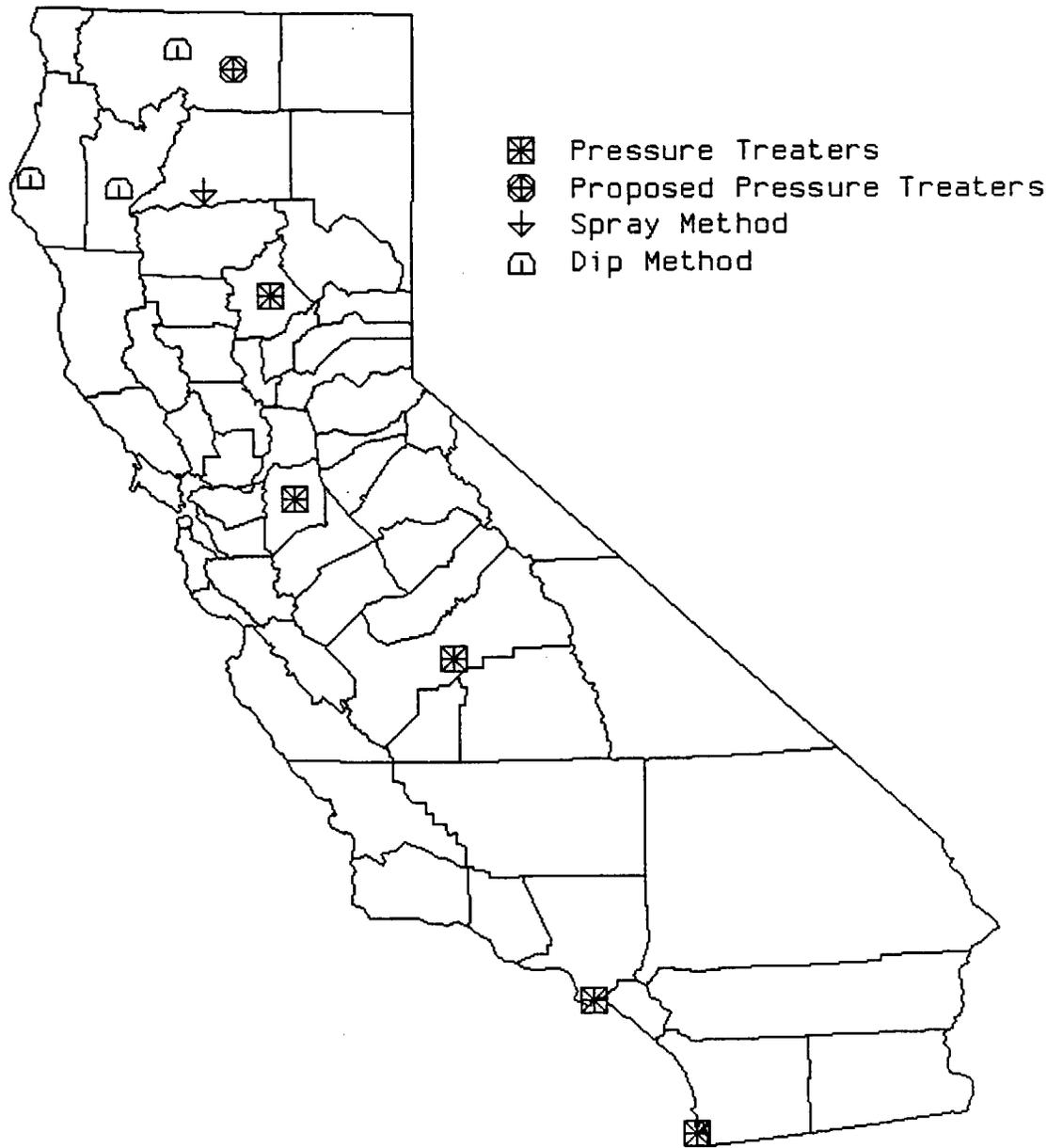


Figure 2-3. Chlorophenol Treatment Facilities
(as of December 1986)

TABLE 2-9. Chlorophenol inventory by county for 1985/1986 in California.

County	Pentachlorophenol (Tons/year)	Tetrachlorophenol (Tons/year)
Butte	425	0
Fresno	60	0
Humboldt	0	2.3
Los Angeles	200	0
San Diego	40	0
San Joaquin	200	0
Siskiyou	0	8.9
Shasta	0	0.2
Trinity	0	0.2
Total	925	11.6

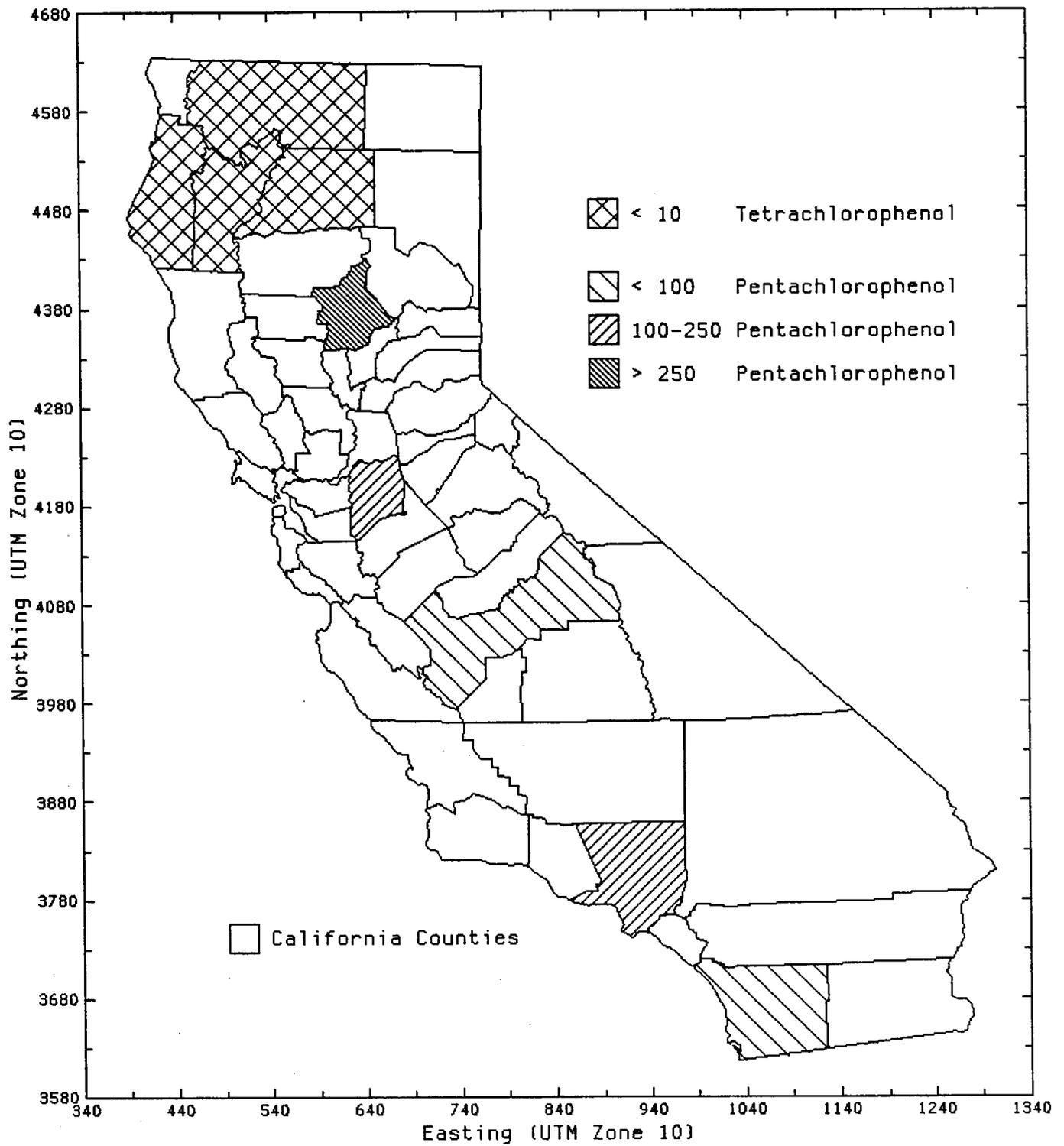


Figure 2-4. Chlorophenol use by county (tons used in 1986)

TABLE 2-10. Comparison of estimates of annual chlorophenol sales and use in California based on independent estimates.

Source	Year	Pentachlorophenol (tons/year)	Tetrachlorophenol (tons/year)
California Department of Food and Agriculture	1984	940	34
	1985	902	0
Vulcan and Chapman Chemical Company Sales	1985/86	943	18
International Statistics Council	1984	997	--
Systems Applications, Inc. survey of wood processing facilities	1985/86	925	12

with the use estimates. Comparison of these sources of information indicates that, on an annual basis, between 900 and 1000 tons of PCP are sold and used in California.

Both the sales and use of TCP are presently undergoing rapid changes. As of July 1986, TCP is no longer being manufactured in the United States. As a result, 1984-1986 annual sales of TCP were abnormally high because wood treatment facilities bought additional supplies. The results of our survey indicate that less than a third of the TCP recently sold has been used during 1985/86. There are two principal explanations for this result. First, treatment facilities are undoubtedly stretching out their supplies in anticipation of a new source of TCP (as yet unidentified). Second, our survey probably did not reach every facility in the state that uses TCP for several reasons. The survey was only sent to those facilities known or thought to be TCP users, as determined by regional water quality boards and pressure treaters. It is possible that some small sawmills, for example, may have been users of TCP without being identified in our survey. However, the amount of TCP used at these unaccounted for facilities must be small since the amounts used and in storage at the facilities responding to our survey account for a large portion of recent sales. Therefore, it is possible that our survey results have somewhat underestimated the current annual use of tetrachlorophenol; however, in the near future TCP use will discontinue entirely because of the cessation of its manufacture.

3 DESCRIPTION OF CHLOROPHENOL TREATMENT METHODS AND POTENTIAL ATMOSPHERIC RELEASES

In this section we describe pressure and nonpressure wood treatment processes and the potential atmospheric pathways for resulting air emissions. The application of chlorophenols as wood preservatives can be accomplished using either pressure or nonpressure techniques. Pressure treatment involves the use of pressure to force the preservative liquid into the wood; nonpressure treatment involves either dip or spray methods. All three of these methods are utilized by the forest product industry in California. To supplement our mail surveys and to gain a more detailed understanding of the treatment processes used in California, we conducted on-site tours of the majority of facilities identified as chlorophenol users. Three of the four nonpressure treatment facilities and four of the five pressure treatment facilities were visited.* As noted earlier, pressure treatment facilities account for more than 98 percent of chlorophenol use in California.

METHODS OF CHLOROPHENOL APPLICATION

Pressure Treatment

Pressure treatment is generally performed at facilities capable of treating large quantities of wood, including poles and lumber. At the facilities visited, nearly all of the wood to be treated was precut at off-site locations, with only minor redimensioning performed at the wood treatment facilities themselves. The redimensioning is always performed prior to treatment and usually consists of cutting off the ends of the poles to provide uniform lengths.

* The only nonpressure treatment facility not visited had "mothballed" its treating equipment during the facility visitation period of this study; the only pressure treater not visited would not permit us to tour the facility.

While variations exist in the treatment method from facility to facility, the following description outlines the general method of pressure application. In the usual application of preservative by pressure processes, wood is loaded on trams, which are then placed in a pressure vessel. Figure 3-1 is a schematic of the treatment schedule followed in the pressure cylinders. In California, the pressure cylinder is filled with preservative and using steam the retort is brought up to pressure, which is maintained until the required absorption of preservative has been achieved. The pressure varies depending upon the type of wood being treated and its planned use. The absorption amount as well as the pressure and time requirements are set forth by the American Wood Preservers' Association. At the end of the pressure cycle, the pressure is reduced to atmospheric level and the preservative solution is returned to storage. The treated wood is then usually placed in a final vacuum vessel to remove excess preservative from the surface. The vacuum is released, the door of the vessel is opened, and the treated wood is removed.

Depending upon the solvent used to apply the preservative, the treated wood may require additional cleaning prior to the completion of the treating process. In particular, after the final vacuum has been applied to the treated wood, if the solvent used was diesel oil, excess oil and preservative may still be present on the wood surface. At each of the facilities toured, a steam cleaning cycle was added at the end of the treating cycle to remove the excess oil and preservative, to recover and reuse the preservative, and to improve the appearance of the treated wood.

Nonpressure Treatment

Nonpressure treatment processes take place under atmospheric conditions. In California, nonpressure treatments include dip and spray processes. The dip method simply entails soaking wood in the preservative for a fixed period of time. At the facilities responding to our survey, the preservative used was tetrachlorophenate dissolved in water. Individual boards or bundles of lumber are submerged in open tanks containing the preservative solution. As the board or bundles are removed from the treatment tank, the excess preservative drains back into the tank. The temporary storage areas for the treated wood are usually lined with concrete so that any subsequent drippage will also drain back into the treatment tank. The spray method entails placing individual boards on a conveyor system that carries them into an enclosed chamber. Within the chamber or spray booth, the lumber is automatically sprayed with preservative. The spray method is designed to use small amounts of liquid so that by the time the treated lumber leaves the spray booth, the preservative has been completely

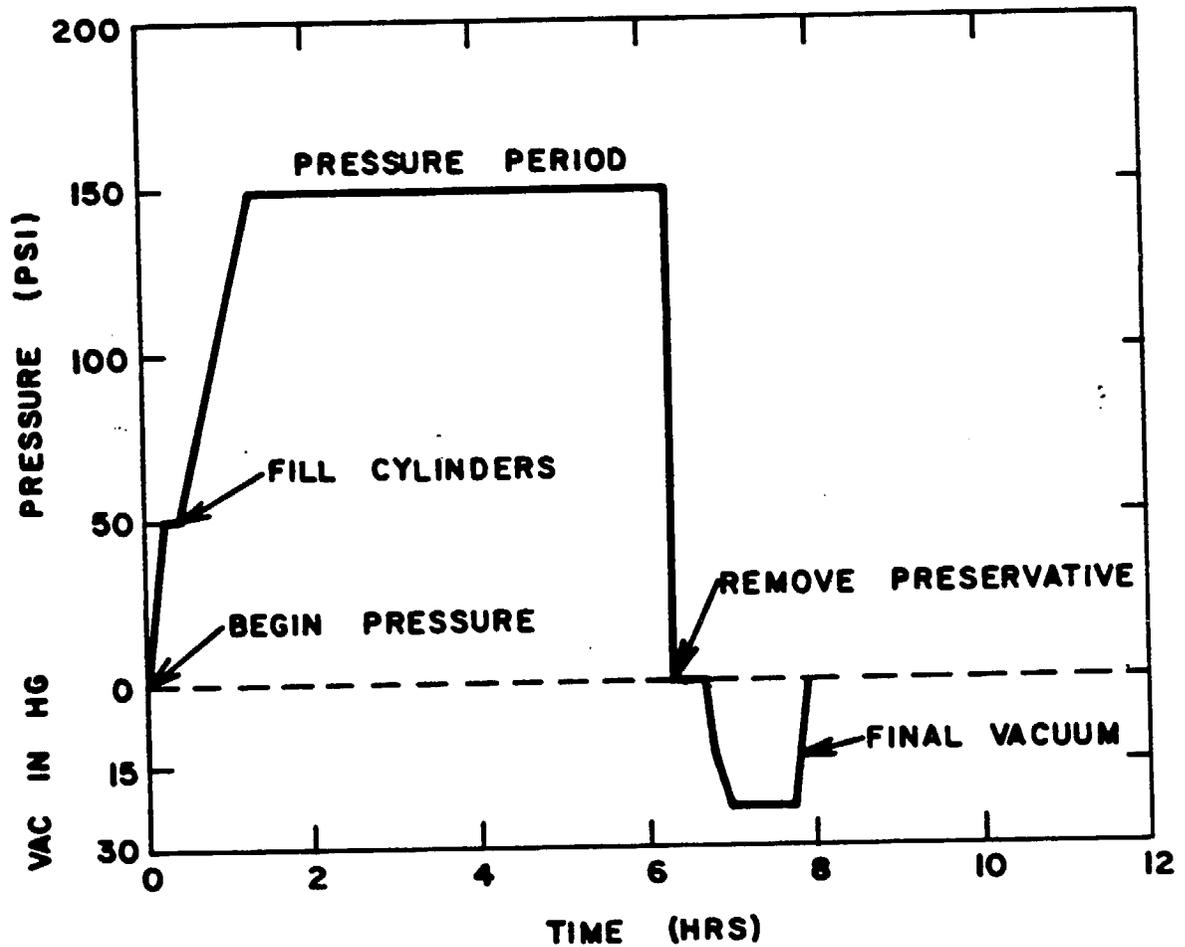


FIGURE 3-1. Schematic showing the treating schedule used in chlorophenol treatment (from USDA, 1980).

absorbed and no surface liquid remains. However, observations by F. Palmer (1987) suggest that some spray method applicators are only partially enclosed and spray sufficient amounts of treating solution to cause the treated wood to leave the chamber wet and dripping.

Lumber treated by nonpressure processes may undergo further dimensioning (e.g., be cut into smaller sizes). This additional cutting produces treated woodwastes in the form of sawdust and wood scraps. The treated woodwastes are generally combined with the facility's other wood wastes and disposed of in various manners, e.g., boiler fuel and raw material for paperpulp mills.

MECHANISMS FOR ATMOSPHERE RELEASE OF CHLOROPHENOL EMISSIONS

Air emissions of chlorophenol and associated dioxin (PCDD) and furan (PCDF) contaminants can occur at various points in the handling of the chlorophenol and during the treating processes at pressure and nonpressure treatment plants. We have defined seven general stages during which releases to the atmosphere may occur, though at a particular facility an individual stage may not actually occur. The seven principal stages are:

- (1) Storage of chlorophenol supplies
- (2) Dispensing of chlorophenol to mixing, storage, and treatment tanks
- (3) Application of preservative to lumber
- (4) Removal of treated lumber from treatment vessel
- (5) Storage of treated lumber
- (6) Cleaning of treatment vessel
- (7) Disposal of treated woodwastes and treatment tank sludge

Pressure Treatment: Air Emission Pathways

Figure 3-2 is a schematic of the devices used in pressure treatment. The principal components are the mixing tank, the storage tank, and the treatment cylinder. Chlorophenol is received from the manufacturer at the pressure treatment plants in 2000 pound blocks sealed in plastic. These penta blocks are placed directly into either the mixing tank or the pressure cylinder, depending on the facility. The pentachlorophenol is exposed to the air only momentarily, when the plastic seal is removed just prior to placing the block in a sealed container. We have not estimated air emissions from this phase of chlorophenol handling since the EPA

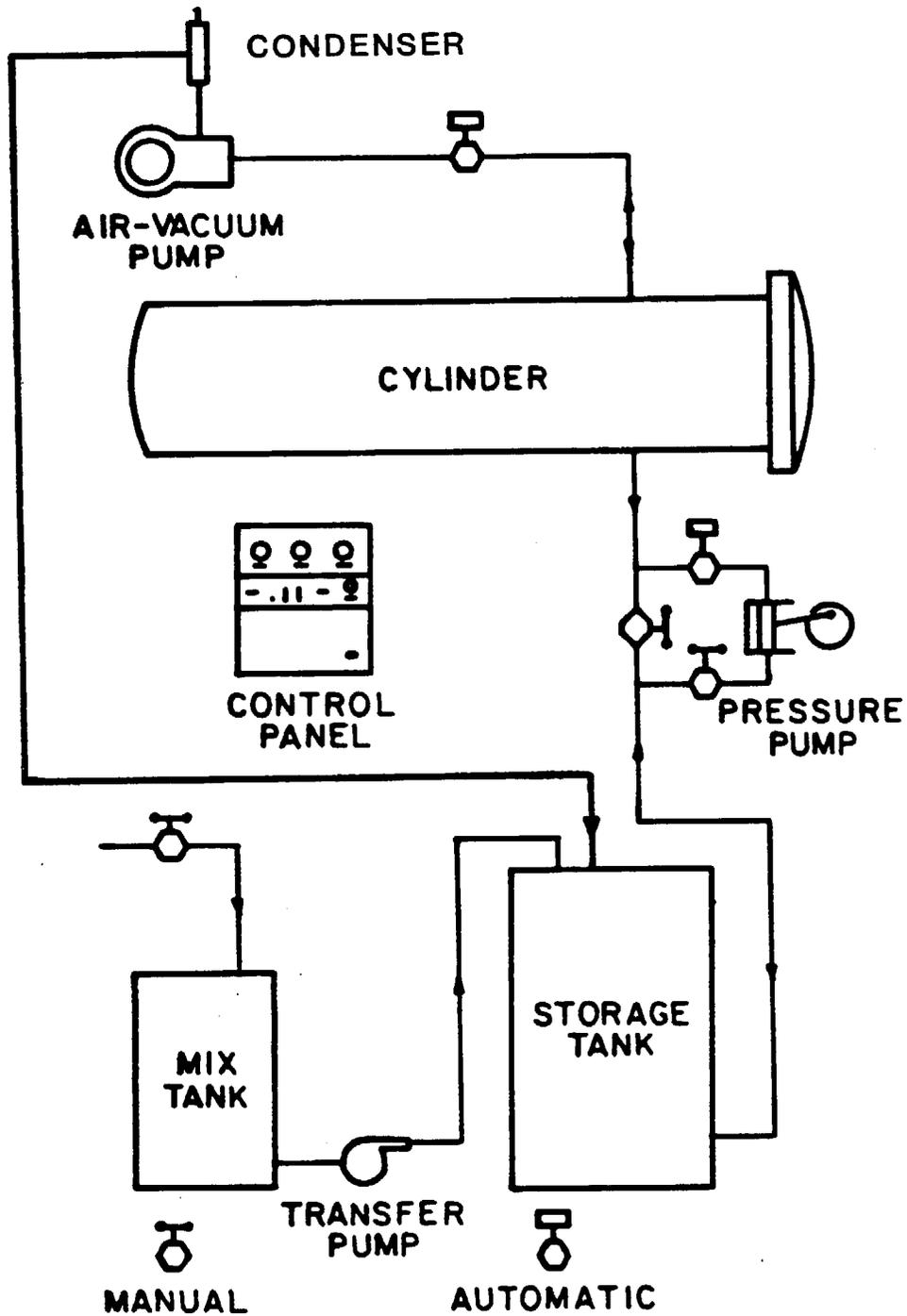


FIGURE 3-2. Schematic drawing of a pressure treating plant. (Source: USDA, 1980.)

definition of a "breach of containment" that requires emissions calculation excludes this type of incidental release (Federal Register 51 FR 1334).

Dispensing of chlorophenol preservative from the mixing tank to the storage tank to the treatment vessel and back to the storage tank involves various pumps, valves, and pipes and fittings. Physical inspection of these components shows that some leakage of the preservative mixture (chlorophenol and oil solvent) is common. The method used to estimate air emissions from these fugitive losses is discussed in Section 4.

The EPA (51 FR 1334) requires that PCP be used in a closed system, which is defined as any containment that prevents the release of the chemical into the surrounding environment. The pressure cylinders in which the lumber is treated are therefore required to be closed systems with no permissible air emissions. However, once the lumber is treated it must be removed from the treatment vessel. The opening of the vessel and removal of treated lumber are unavoidable, but do permit the opportunity for air emissions. In the normal operations of a pressure treatment plant, the treated lumber is removed from the pressure cylinder as quickly as possible following treatment, usually while still quite warm (~120°F), thus emitting significant quantities of steam.

At this stage in the pressure treatment process, two distinct sources of air emissions must be estimated: the evaporative losses from the surface of the treated lumber and the fugitive loss from the air escaping from within the pressure cylinder. Each of these sources of air emissions should be considered short-term periodic releases, since the vessel is generally opened less than once per day and the heated lumber approaches ambient temperatures within a few hours. For the remainder of the time the treated lumber is stored onsite, evaporative losses must be considered as a function of ambient temperatures. For the purposes of this study, treated lumber was assumed to remain in on-site storage for one month prior to shipment. On the basis of our on-site tours, we estimate that the one-month storage period is the upper limit for the time treated lumber is stored onsite.

Pressure cylinders are emptied of solvent and preservative as part of every treatment cycle. The inside surface of the vessel is also cleaned during the post-treatment steam-cleaning of the treated lumber. As noted earlier, each of these processes takes place in a closed system. Therefore no air emissions can be attributed to the cleaning of the pressure vessels. Finally, to our knowledge, all of the poles and lumber treated by the pressure method are pre-cut prior to treatment and undergo no post-treatment redimensioning. Thus, there is no treated woodwaste to dispose of at pressure treatment facilities.

Nonpressure Treatment: Air Emission Pathways

A schematic of operations at a nonpressure treatment plant is presented in Figure 3-3. Principal components are the dip tank or spray booth, air drying, redimensioning, and the combustion of treated woodwaste as boiler fuel. At nonpressure treatment plants, chlorophenol is usually received from the manufacturer in 55 gallon drums. The contents of the drum (usually tetrachlorophenolate) are mixed with water to a 1 percent solution for dip tanks and a 0.3 percent solution for spray booth applications. The solutions are prepared in a closed pumping system that leads to the open dip tank or to the spray nozzles.

The dip tanks are generally open-air steel tanks approximately 30' x 10' x 10'. The tanks are usually contained in a building that is open at two ends. The dip tank is uncovered and thus is exposed to the air within the semi-enclosed structure. During application, air emissions are limited to evaporative losses from the surface of the tank. Treated wood removed from the dip tank is covered with a thin layer of preservative solution, which evaporates or is absorbed into the wood. The spray application takes place in an enclosed chamber, thereby preventing any air emissions from the applications process. Treated wood observed in the spray booth enclosure on our on-site tours did not appear to have any surface moisture. However, observations by F. Palmer (1987) suggest that some spray method applicators are only partially enclosed and spray sufficient amounts of treating solution to cause the treated wood to leave the chamber wet and dripping.

Wood treated by either dip or spray method may undergo additional dimensioning subsequent to treatment. This additional cutting produces small quantities of treated woodwaste such as sawdust and shavings. The amounts of treated woodwaste are discussed in more detail in Section 5, where we present a mass balance of chlorophenol use in California. The treated woodwaste is disposed of in several ways depending on the facility. At some locations, it is used as boiler fuel, while at other locations it is used for other wood products such as raw material for paper pulp mills.

Dip tanks can require periodic cleaning; however, none of the facilities responding to our survey reported cleaning their tanks in the last five years. Upon further questioning, the plant operators stated that when they do clean their dip tanks they plan to place the sludge either in hazardous waste barrels or add it to their boiler fuel supply.

It should be noted that there are a few sawmills which no longer use chlorophenols but probably still have some PCP and TCP remaining in old

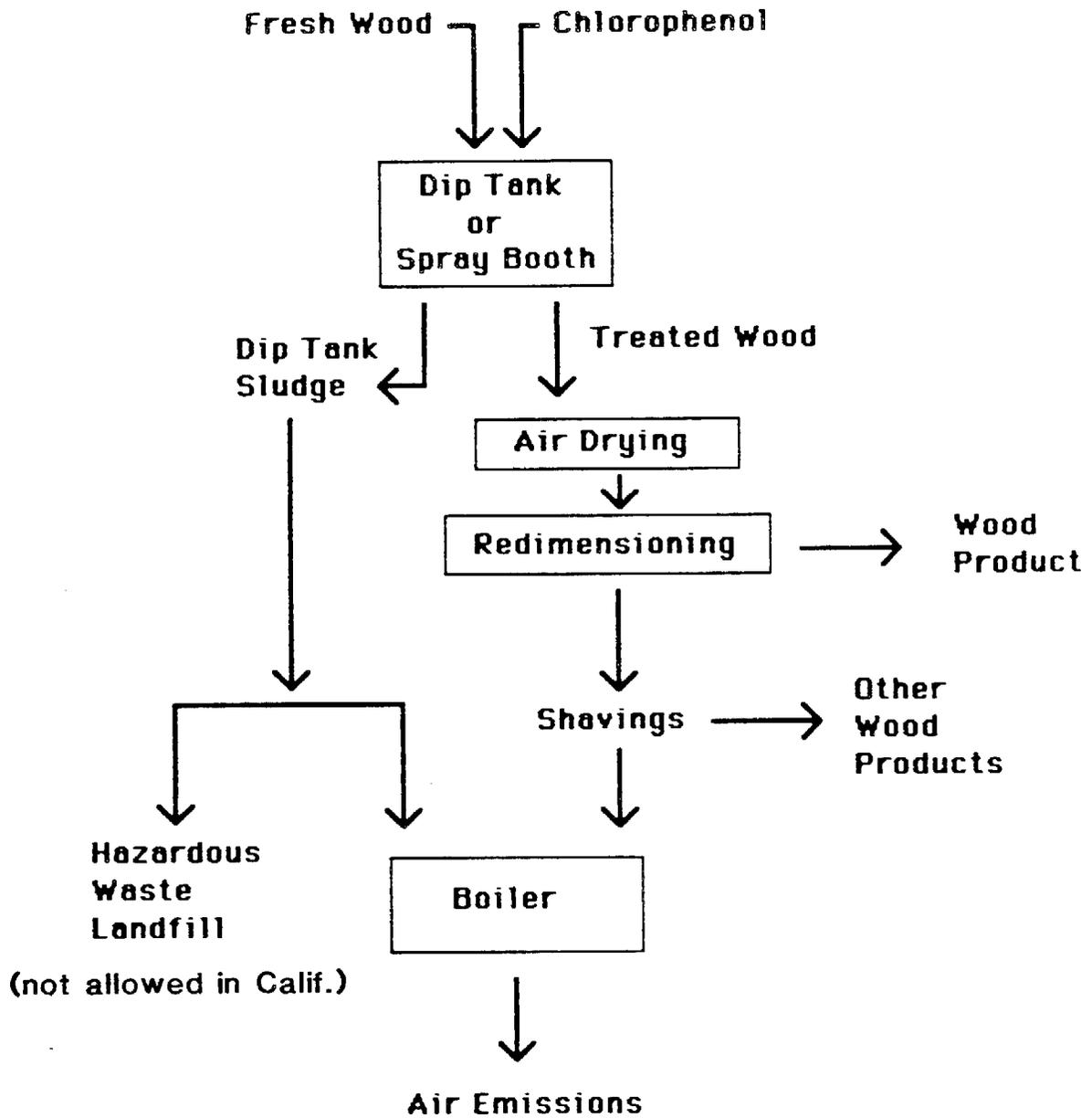


FIGURE 3-3. Operations at a nonpressure wood treatment plant.

dip liquids and sludges. Emissions from these sources could occur, however.

Summary of Air Emission Pathways

Table 3-1 summarizes the air emission pathways at pressure and nonpressure treatment plants. At pressure plants, the principal pathway of concern is the evaporative losses from the surface of the wood immediately following treatment while the wood is still hot. At nonpressure plants there are several stages at which air emissions could be important. Dip tanks themselves are an air emission source. The treated lumber also undergoes further dimensioning, which produces treated woodwastes. There are evaporative emissions from the surface of the treated lumber and there may also be air emissions from the combustion of the treated woodwaste.

TABLE 3-1. Air emission pathways.

Principal Stages	Pressure	Nonpressure	
		Dip Tank	Spray Booth
Storage of chlorophenol	Sealed blocks*	Drum	Drum*
Chlorophenol dispensing to mixing, storage, and treatment tanks	Fugitive*	Evaporative	Closed system*
Application of preservative	Closed system*	Evaporative	Enclosed chamber**
Removal of treated lumber from treatment vessel	Evaporative/fugitive	Evaporative	Enclosed chamber**
Storage of treated product	Evaporative	Evaporative	Evaporative
Cleaning of treatment vessel	Closed system*	Evaporative	N.A.
Disposal of treated wood waste and treatment tank sludge	None	Combustion	Combustion

* No air emissions.

** No air emissions at facilities toured in this study, however, other authors suggest this is a possible source of emission if not completely enclosed or if excessive treating solution is applied.

4 APPROACHES TO THE DEVELOPMENT OF EMISSION ESTIMATES FOR CHLOROPHENOLS, DIOXINS, AND DIBENZOFURANS

In this section we discuss the development of emission estimates for TCP, PCP, PCDDs, and PCDFs. We begin by discussing ways of determining the amount and type of contaminants of PCP and TCP by PCDDs and PCDFs as a basis for understanding the complex chemistry involved in estimating the types and amount of chlorophenol emissions resulting from wood treatment processes. We then discuss the various techniques applicable to the development of estimates of (1) evaporative emissions and (2) emissions from combustion of woodwastes for nonpressure and pressure wood treatment facilities. A final subsection discusses the transformation of these emissions in the atmosphere.

CONTAMINATION OF CHLOROPHENOL PRODUCTS BY PCDDs and PCDFs

The contamination of pentachlorophenol (PCP) and tetrachlorophenol (TCP) by polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is an unavoidable by-product of the manufacturing process; PCDDs and PCDFs are also formed from PCP upon reaction with light (Higgenbotham et al., 1968; Jensen and Renberg, 1972). Technical grade (unrefined) PCP also contains low levels of several other impurities such as chlorodiphenyl and hydroxychlorodiphenyl ethers (Mieure et al., 1977; Cull et al., 1984; Singh, Miles, and Barrette, 1985).

Several different analytical techniques are used to identify the contaminants in PCP; these include gas chromatography (GC) using a variety of different detectors, high-pressure liquid chromatography (HPLC), and gas chromatography coupled with mass spectrometry (GC-MS). There are also several sample workup and extraction procedures. Each technique has its advantages regarding detection limits, precision, speed, amount of sampling required, economics, and quantity of information obtained. Also, the types of columns used for the sample workup, extraction, and detection methods, as well as the stationary and mobile phases used, the standards available for comparison, instrument settings, and number of analyses performed, all contribute to the accuracy of the analysis, its precision, the quantity of information that it provides, and the degree of confidence the reader should place in its results.

One comparative study (Cull et al., 1984) involved three different laboratories and three different workup and detection techniques; one laboratory used HPLC, one used GC with an electron capture detector, and one used a GC-MS system. The results are shown in Table 4-1. As can be seen, the results vary depending on the technique used, and these variations are not consistent; that is, while GC-ECD (gas chromatography using an electron capture detector) identifies most of the PCDDs and PCDFs, the other two techniques (HPLC and GC/MS) vary in reporting either higher or lower concentrations, depending on the isomers. These results indicate the variation that can be expected with these kinds of extremely sensitive techniques.

In addition to simply detecting the presence of PCDDs and PCDFs in PCP, it is important to identify the isomers that are present. The 2,3,7,8-tetrachloro isomer of dibenzo-p-dioxin is by far the most important toxicologically; consequently, it is necessary to identify the positions of the chlorines on the dibenzo-p-dioxin ring.* However, normal analytical procedures are unable to distinguish between positional isomers; therefore, often only the total concentration of all the possible isomers (such as all the 4CDDs) is reported. Sometimes even the different chlorinated isomers are difficult to distinguish, and as shown in Table 4-1, different analytical techniques can give different results. The conclusions to be drawn from these facts are that (1) the variation in reported concentrations of a particular isomer can often be attributed to the precision of the technique used, and (2) the standard deviation of the contamination numbers is usually quite large (though seldom reported).

The contaminants of both technical and research grade PCP are described in several research papers currently in the literature, as well as in notices in the Federal Register (FR, 1978; FR 1985). The literature obtained for this study indicates a wide range of PCDD and PCDF contamination of PCP, which is to be expected given that the analytical methods, sources of PCP, and age and history of the PCP samples differ from study to study. Table 4-2 lists some of the common literature values.

We noted earlier that Vulcan Chemical of Birmingham, Alabama is the only supplier of PCP to California, and that Chapman Chemicals was previously the only supplier of TCP, but will no longer be able to supply it. Accordingly, in the future, all nonpesticide, nonresidential uses of chlorinated phenols will employ products supplied by Vulcan. We obtained from Mr. Dennis Lindsay of Vulcan (personal communication, July 14, 1986) the impurity "profile" for their product. This information is presented

* See Figure 1-1.

TABLE 4-1. Comparison of three different analytical methods for measuring dioxin and furan contamination.

	Method	HpCDF	1,2,3,4, 6,7,9-HpCDD	1,2,3,4, 6,7,8-HpCDD	OCDF	OCDD
Mean ($\mu\text{g g}^{-1}$ Tech PCP)	GC ECD	63.1	35.8	95.8	148	610
	HPLC	34.0	20.2	85.6	106	585
	GC/MS	55.9	22.0	60.3	123	472
Coefficient of variation (%)	GC ECD	33	20	31	29	13
	HPLC	39	18	28	30	13
	GC/MS	35	19	26	27	25

OCDD/F octachlorodibenzo-p-dioxin/furan
 HpCDD/F heptachlorodibenzo-p-dioxin/furan
 HxCDD/F hexachlorodibenzo-p-dioxin/furan
 GC gas chromatography
 HPLC high-pressure liquid chromatography
 MS mass spectrometry
 ECD electron capture detector

* Adapted from Cull et al., 1984.

TABLE 4-2. Sample results of analyses of contaminants in technical pentachlorophenol.*

Polychlorinated Dibenzo-p-dioxins (ppm)			Polychlorinated Dibenzofurans (ppm)			References
Hexa	Hepta	Octa	Hexa	Hepta	Octa	
--	131.6	610	--	63.1	148	Cull et al., 1984
--	105.8	585	--	34.0	106	Cull et al., 1984
--	82.3	472	--	55.9	123	Cull et al., 1984
3.7	150.6	537.1	--	--	--	Singh, Miles, and Barrette, 1985
33.6	465.0	1334.0	--	--	--	Singh, Miles, and Barrette, 1985
2.9	179.2	596.4	--	--	--	Singh, Miles, and Barrette, 1985
1.3	225.2	1262.3	--	--	--	Singh, Miles, and Barrette, 1985
42.0	24.07	10.78	--	--	--	Villanueva, Burse, and Jennings, 1973
42.08	20.37	7.12	--	--	--	Villanueva, Burse, and Jennings, 1973
32.75	19.03	7.52	--	--	--	Villanueva, Burse, and Jennings, 1973
4	125	2500	30	80	80	FR, 1978
1.0	6.5	15.0	< 1	1.8	< 1	FR, 1978
29	524	1306	20	91	18	Lamberton et al., 1979

* Data were not reported for the lower chlorinated isomers.

in Table 4-3. Although this is the analysis of the product as it leaves the factory, it is only an indication of the actual contamination profile of the product as it is used. Since chemical reactions can and will occur within PCP, TCP, and their contaminants, the concentrations of PCDDs and PCDFs will vary considerably over time and as a function of heat, sunlight, and cosolvents.

Fortunately, available data indicate the contamination profile of the PCP and TCP as it is used in California. We obtained unpublished data that provide a complete picture of the contamination of PCP and TCP under the actual conditions of use from the California State Water Resources Control Board (SWRCB) (personal communication, Dr. F. Palmer). These data are presented in Table 4-4 and are used throughout the remainder of this report. Since the data in Table 4-4 are for the solutions used in California as they exist in the field, they are considered to be more representative than the factory data, which are averaged for all states, and are also reported prior to the material's dilution and mixture with cosolvents. Table 4-5 contains analyses of TCP and PCP in the dip tanks used in the sawmills. As can be seen, what is nominally called TCP also contains a significant fraction of PCP. As discussed next, this is important in determining emission values.

POTENTIAL RELEASE MECHANISMS

As discussed in Section 3, there are several potential pathways for PCP, TCP, PCDDs and PCDFs to enter the atmosphere. This report considers only those pathways relevant to the processes used in California wood treatment facilities; facilities in other states may utilize different processes and consequently require different emission factors.

The important pathways for potential release into the atmosphere of PCP, TCP, PCDDs and PCDFs from wood treatment facilities in California are:

- (1) Steam released by the pressure treatment facilities, and evaporation from dip tanks and the treated wood.
- (2) Combustion of wood waste

Each of these important pathways is discussed next. The potential for atmospheric conversion of the emitted chlorophenols, PCDDs and PCDFs to other materials is discussed in a final subsection.

TABLE 4-3. Contamination profile of Vulcan Chemical's pentachlorophenol sold in California.^a

<u>Contaminant</u>	<u>Normal Range (ppm)</u>	<u>Typical Analysis (ppm)</u>
TetraCDD ^b	<0.001 ^c	<0.0001
PentaCDD	<1.0	0.5
HexaCDD	1-10	3.3
HeptaCDD	100-200	175
OctaCDD	1,000-3,000	1700
HexaCDF ^d	5-20	7.1
HeptaCDF	10-100	55
OctaCDF	100-300	140
Hexachlorobenzene	30-60	40

^a D. Lindsay, personal communication, 1986.

^b CDD = chlorodibenzo-p-dioxin.

^c The "<" symbol indicates the detection limit of the method employed.

^d CDF = chlorodibenzofuran.

TABLE 4-4. Concentrations (ppb) of TCP, PCP, PCDD, and PCDF levels in commercial chlorophenol products.*

	Tetrachlorophenolate (Sodium)	Pentachlorophenolate (Sodium)	Pentachlorophenolate (Sodium)	Pentachloropheno1
TCP	140,000,000	140,000,000	77,000,000	§
PCP	31,000,000	170,000,000	150,000,000	
PCDDs				
Tetra	<1.0	<0.5	16	<0.46
Penta	238	11	1,400	220
Hexa	1,100	4,800	14,000	260
Hepta	614	88,000	64,000	5,000
Octa	700	216,000	69,000	170,000
PCDFs				
Tetra	62	2,900	840	180
Penta	3,000	4,100	18,000	4,600
Hexa	17,600	1,900	18,000	5,100
Hepta	22,100	380	3,400	2,300
Octa	11,060	190	2,800	980

* State Water Resources Control Board unpublished data - revised data received after preparation of this report are shown in Appendix H.

§ Not analyzed

TABLE 4-5. PCDD and PCDF levels in soil and product residues related to chlorophenol use.*

	Sawmill, R5		Sawmill, R5A		Sawmill, R5B	Sawmill, R1
	Dip Tank Liquid	Sludge	Dip Tank Wet Sludge	Dip Tank Dry Sludge	Dip Tank Liquid	Dip Tank Sludge
TCP (ppm)	1,700	4,000	300	37,000	11,000	2,300
PCP (ppm)	2,000	5,700	880	160,000	3,700	2,600
PCDDs (ppb)						
Tetra	<0.002	<1.7	0.57	51	<0.34	<0.35
Penta	0.2	16	19	2,000	6.4	84
Hexa	7.7	799	360	13,000	86	2,300
Hepta	112	3,066	1,200	23,000	111	1,300
Octa	352	3,066	3,500	7,400	428	2,600
PCDFs (ppb)						
Tetra	0.84	54	21	5,600	32	110
Penta	3.7	259	92	3,600	106	2,200
Hexa	4.3	1,143	140	12,000	936	1,600
Hepta	0.37	369	350	5,700	90	1,500
Octa	1.3	1,066	17	250	90	65

* State Water Resources Control Board unpublished data.

DEVELOPMENT OF EVAPORATIVE EMISSION ESTIMATES

This section describes the development of evaporative emission estimates for TCP, PCP, PCDDs and PCDFs. As discussed in the previous section, there are significant differences between the nonpressure and pressure methods of wood treatment used in California. Accordingly, they are discussed separately here.

Nonpressure (Dip and Spray) Treatment

The nonpressure (dip and spray) treatment processes are intended only to control surface molding; consequently, only surface application is required. This is done using either a nominally 1 or 0.34 percent solution of TCP (see Table 4-5 for a detailed analysis of the solutions). (As noted in Section 3, all discussion of dip treatment incorporates spray processes as well unless otherwise noted.) The two areas of potential evaporative emissions from dip and spray treatments are the dip tank and from treated wood.

Estimation of Evaporative Emissions from the Dip Tank*

The two means by which volatile compounds can be emitted from an open dip tank are either forced motion on a macroscopic scale (such as occurs when the wood is lowered and then raised from the tank) or diffusion on a molecular or turbulent basis. The factors affecting the evaporation of the TCP (and consequently the contaminants PCP, PCDDs and PCDFs) are the aforementioned macroscopic motion, as well its solubility in water (10.6 mg/l at 25°C), pH (solubility will vary with the pH), vapor pressure (discussed in Appendix E), Henry's law constant (discussed below), the amount and strength of wind over the tank, the temperature of the tank and the outside air, the relative humidity, and the composition of the aqueous solution that it is dissolved in. Although the dip tanks contain a 1 percent solution of TCP (as shown in Table 4-5), "sludge" collected on the bottom of the tanks consists of sawdust, dirt, etc., as well as any other materials that might happen to be on the wood prior to its treatment can affect this percentage. In addition, spills, evaporation, and the wood absorption can deplete the concentration of TCP.

* This discussion is limited to potential dip tank evaporation; a detailed discussion of the various models used to predict losses can be found in Ehrenfeld et al. (1986) and DaRos et al. (1982).

The gas-phase concentration of a volatile substance depends on a number of factors, principally on the vapor pressure of that substance. It also assumes an equilibrium situation, (obviously not the case for an open tank in an open building), and ideal gas behavior. A detailed discussion of the non-ideality corrections and possible ramifications is beyond the scope of this work; the reader is referred to the works of Thibodeaux (1979) and Ehrenfeld et al. (1986) for further discussion. Fortunately, the rate of vaporization of a substance from a solution in a "real world" situation such as an open tank of TCP has been addressed for a number of different scenarios (e.g., aerated and nonaerated lagoons) and for complex mixtures of varying vapor pressures and concentrations. There are a number of air emission release rate (AERR) models for estimating emissions from a large variety of confinements and open areas. A discussion of AERR models for a variety of hazardous waste treatment, storage, and disposal facilities is given in Ehrenfeld et al. (1986).

There are three principal criteria for choosing an appropriate model for estimating emission rates. The model must treat as correctly as possible: the type of chemical, the physical situation that exists in the field, and the availability of the necessary data for the first two criteria. Each of these are discussed below.

Since different chemicals have different volatilities, diffusivities in air and water (a measure of the movement through air or water), and attraction to the solvent (both air and water) and to themselves, a model must correctly treat these factors. The principal rate-limiting factors for a substance volatilizing from an aqueous solution are its diffusivity through air or through water. A model must also be appropriate to the physical site; that is, models appropriate to aerated spray ponds would not be appropriate to a quiescent tank, etc. Atmospheric conditions (temperature, wind speed, relative humidity) also affect the evaporation rate, and different models account for them differently.

The final criterion for the choice of a model is perhaps the most relevant, though the least "esthetically" pleasing. In theory one would not like to be limited by the availability of different parameters and should choose a model based only on the two previous criteria; however, the parameters of all substances are not known. This is especially true for the more esoteric parameters demanded by some of the AERR models for which laboratory determinations are required. Since the scope of this project precludes such effort, other means were used to determine the requisite parameters for the model chosen. Especially for the PCDDs and PCDFs, for which very little physical data have been measured (due to their toxicity and the difficulty in obtaining standards), estimation methods are the only means of obtaining parameters. Lyman et al. (1982) have compiled numerous physical parameter estimation methods and their work was used to derive the diffusivity parameters discussed here.

Given these three criteria, the work of McCord (1981) was chosen as the best model for the evaporation of TCP from the dip tanks used in the saw-mills in California. Other models that might work equally well are discussed in Ehrenfeld et al. (1986) and DaRos (1982); however, the availability of the parameters required, the physical state of the chemical, and the physical layout of the dip tanks led to the choice of the McCord steady-state predictive model for nonaerated surface impoundments.

McCord's model, which was designed for a constantly filling lagoon, has been adapted for this work; this adaptation does not change the basic calculation, only the subsequent calculations that his model requires. Instead of a constantly filled lagoon, we have a tank that is sporadically filled with a TCP solution to achieve an average concentration of one percent. The adaptation assumes that the replenishment is performed in small steps, so that the depletion of the TCP (and contaminants) from the tank does not reduce the concentration below the one percent level and the replenishment does not raise the concentration above the one percent level. This is a reasonable assumption, given that the replenishment rate is unknown, and the evaporation rate is small and directly related to the percent of the chemical in the mixture. Since the average concentration is one percent, an evaporation calculation for an entire year is adequate.

The adapted model of McCord (1981) is as follows:

$$E = 0.53425 A_m (D/L)^{0.22} (\%) (VP) (W)^{0.78} ,$$

where E = Evaporation rate of a compound at steady state (lb/hr)
A_m = Surface area of the tank (m²)
D = Diffusivity coefficient of the compound in air (m²/hr)
L = The shortest tank dimension (m)
% = The weight percent of the compound in the tank solution
VP = The vapor pressure of the pure compound (atm)
W = The average wind velocity (m/s)

Data for all of these parameters, with the exception of the vapor pressure for the PCDDs and PCDFs and the atmospheric diffusivity of all of the compounds, were readily available for the TCP solutions. The vapor pressures for TCP and PCP were estimated as described in Appendix E. The vapor pressure for 4CDD (Firestone, 1977) was estimated from gas chromatography and was used for the other PCDDs and PCDFs as the best available data.

The atmospheric diffusivity of a compound is a measure of how fast it will transport itself through air, given calm conditions and uncontaminated air (obviously, air saturated with a vapor would have a different diffusivity). Since the McCord model assumes that this is a rate-limiting

step, this is a critical parameter; it was estimated for all of the PCDDs, PCDFs, and the tetra and pentachlorophenols using the method of Fuller et al. (1966). This method is considered to be accurate for aromatics (Lyman, 1982) and involves the calculation of several intermediate parameters. A more complete discussion is given in Appendix F. The parameters that were derived using this method were then applied to the adapted McCord model to produce the estimated emissions given in Table 4-6. The contamination levels used were the averaged data given in Table 4-4. Since the adapted model is not a simple one, there are no direct emission factors for the evaporation of the chlorinated phenols and contaminants. A detailed discussion of the model along with an example application is presented in Appendix G.

Evaporative Emissions from the Treated Wood

Since dip treatment using TCP (and its associated contaminants) is conducted outdoors in a covered, but open, shed, and since the wood is stored outdoors in either covered or uncovered piles, it can safely be assumed that whatever TCP that remains on the wood (and is not adsorbed) will eventually evaporate. Morgan and Purslow (1973) studied the evaporation of PCP from pine sap wood blocks treated with a 5 percent solution using a variety of techniques and cosolvents. In their immersion test (similar to the dip treatment used by the sawmills), they reported a 12 percent loss of PCP within one month. Since the treated wood is not kept on-site for a long period of time, the 12 percent loss figure also can be used for the evaporation of TCP from the treated wood.

The alternative to using the data of Morgan and Purslow (1973) is to estimate the emissions with the same model (McCord, 1981) used for evaporation from the dip tanks. Although the wood is certainly not the same as a liquid solvent, the rate-limiting step in the model is the atmospheric diffusivity, so the model should be applicable. The dimensions used are those of the treated wood. Data for both methods of estimation are given in Table 4-7. As can be seen, there is a large difference in the estimated emissions, depending on the method chosen. Since the Morgan and Purslow method does not estimate the vaporization of PCDDs and PCDFs, we could not report such data. However, the theoretical method of McCord (1981) has no such limitation, so these data are presented for all the species. The Morgan and Purslow data are also suspect due to the variability of their reported values, i.e. a value of 12 percent \pm 5 percent can be interpreted to mean 7 or 17 percent. In addition, the authors stated that the 5 percent error was a "reasonable" assumption and was not the result of a statistical analysis. Therefore, these data were not used in the statewide mass balances presented in Section 5. They are presented here for comparison purposes.

TABLE 4-6. Estimated Emissions from TCP dip tanks
Using a Steady-State Model
(McCord, 1981)

Compound	Concentration (%)	Trinity (lbs/yr)	Trinity (g/yr)	Humboldt (lbs/yr)	Humboldt (g/yr)	Siskiyou (lbs/yr)	Siskiyou (lbs/yr)
4CDD	1.71E-05	2.32E-09	1.05E-06	2.50E-09	1.13E-06	8.56E-10	3.88E-07
5CDD	3.30E-04	4.45E-08	2.02E-05	4.79E-08	2.17E-05	1.64E-08	7.44E-06
6CDD	4.69E-03	6.27E-07	2.84E-04	6.75E-07	3.06E-04	2.31E-07	1.05E-04
7CDD	1.12E-02	1.48E-06	6.72E-04	1.59E-06	7.23E-04	5.46E-07	2.48E-04
8CDD	3.90E-02	5.15E-06	2.34E-03	5.54E-06	2.51E-03	1.90E-06	8.61E-04
4CDF	1.64E-03	2.23E-07	1.01E-04	2.40E-07	1.09E-04	8.22E-08	3.73E-05
5CDF	5.49E-03	7.39E-07	3.35E-04	7.96E-07	3.61E-04	2.73E-07	1.24E-04
6CDF	4.70E-02	6.29E-06	2.85E-03	6.77E-06	3.07E-03	2.32E-06	1.05E-03
7CDF	4.52E-03	6.00E-07	2.72E-04	6.46E-07	2.93E-04	2.21E-07	1.00E-04
8CDF	4.57E-03	6.03E-07	2.73E-04	6.49E-07	2.94E-04	2.22E-07	1.01E-04
PentaCP	2.85E-01	1.13E-02	5.11E+00	1.21E-02	5.50E+00	4.15E-03	1.88E+00
TetraCP	6.35E-01	1.91E-01	8.64E+01	2.05E-01	9.30E+01	7.03E-02	3.19E+01

TABLE 4-7

Emissions Estimate using McCord (1981) - Humboldt County

Compound	Atmospheric		Emissions from Lumber	
	Concentration (%)	Diffusivity (m ² /hr)	(lbs/yr)	(g/yr)
4CDD	1.71E-08	1.77E-02	1.99E-09	9.01E-07
5CDD	3.30E-07	1.71E-02	3.81E-08	1.73E-05
6CDD	4.69E-06	1.66E-02	5.36E-07	2.43E-04
7CDD	1.12E-05	1.61E-02	1.27E-06	5.75E-04
8CDD	3.90E-05	1.56E-02	4.41E-06	2.00E-03
4CDF	1.64E-06	1.77E-02	1.91E-07	8.65E-05
5CDF	5.49E-06	1.71E-02	6.32E-07	2.87E-04
6CDF	4.70E-05	1.66E-02	5.38E-06	2.44E-03
7CDF	4.52E-06	1.61E-02	5.14E-07	2.33E-04
8CDF	4.57E-06	1.56E-02	5.16E-07	2.34E-04
PentaCP	2.70E-01	2.07E-02	9.13E+00	4.14E+03
TetraCP	6.50E-01	2.18E-02	1.67E+02	7.57E+04

Emissions Estimate using McCord (1981) - Siskiyou County

Compound	Atmospheric		Emissions from Lumber	
	Concentration (%)	Diffusivity (m ² /hr)	(lbs/yr)	(g/yr)
4CDD	1.71E-08	1.77E-02	7.96E-09	3.61E-06
5CDD	3.30E-07	1.71E-02	1.52E-07	6.92E-05
6CDD	4.69E-06	1.66E-02	2.15E-06	9.75E-04
7CDD	1.12E-05	1.61E-02	5.08E-06	2.30E-03
8CDD	3.90E-05	1.56E-02	1.77E-05	8.01E-03
4CDF	1.64E-06	1.77E-02	7.65E-07	3.47E-04
5CDF	5.49E-06	1.71E-02	2.53E-06	1.15E-03
6CDF	4.70E-05	1.66E-02	2.16E-05	9.78E-03
7CDF	4.52E-06	1.61E-02	2.06E-06	9.34E-04
8CDF	4.57E-06	1.56E-02	2.07E-06	9.38E-04
PentaCP	2.70E-01	2.07E-02	3.66E+01	1.66E+04
TetraCP	6.50E-01	2.18E-02	6.69E+02	3.03E+05

TABLE 4-7. Continued

Emissions Estimate using McCord (1981) - Shasta County

Compound	Atmospheric		Emissions from Lumber	
	Concentration (%)	Diffusivity (m ² /hr)	(lbs/yr)	(g/yr)
4CDD	1.71E-08	1.77E-02	5.01E-10	2.27E-07
5CDD	3.30E-07	1.71E-02	9.59E-09	4.35E-06
6CDD	4.69E-06	1.66E-02	1.35E-07	6.13E-05
7CDD	1.12E-05	1.61E-02	3.20E-07	1.45E-04
8CDD	3.90E-05	1.56E-02	1.11E-06	5.04E-04
4CDF	1.64E-06	1.77E-02	4.81E-08	2.18E-05
5CDF	5.49E-06	1.71E-02	1.59E-07	7.23E-05
6CDF	4.70E-05	1.66E-02	1.36E-06	6.15E-04
7CDF	4.52E-06	1.61E-02	1.30E-07	5.88E-05
8CDF	4.57E-06	1.56E-02	1.30E-07	5.90E-05
PentaCP	2.70E-01	2.07E-02	2.30E+00	1.04E+03
TetraCP	6.50E-01	2.18E-02	4.21E+01	1.91E+04

Emissions Estimate using McCord (1981) - Trinity County

Compound	Atmospheric		Emissions from Lumber	
	Concentration (%)	Diffusivity (m ² /hr)	(lbs/yr)	(g/yr)
4CDD	1.71E-08	1.77E-02	9.27E-11	4.21E-08
5CDD	3.30E-07	1.71E-02	1.78E-09	8.05E-07
6CDD	4.69E-06	1.66E-02	2.50E-08	1.14E-05
7CDD	1.12E-05	1.61E-02	5.92E-08	2.68E-05
8CDD	3.90E-05	1.56E-02	2.06E-07	9.33E-05
4CDF	1.64E-06	1.77E-02	8.90E-09	4.04E-06
5CDF	5.49E-06	1.71E-02	2.95E-08	1.34E-05
6CDF	4.70E-05	1.66E-02	2.51E-07	1.14E-04
7CDF	4.52E-06	1.61E-02	2.40E-08	1.09E-05
8CDF	4.57E-06	1.56E-02	2.41E-08	1.09E-05
PentaCP	2.70E-01	2.07E-02	4.26E-01	1.93E+02
TetraCP	6.50E-01	2.18E-02	7.79E+00	3.53E+03

TABLE 4-7. Concluded

Emissions Estimates using Morgan and Purslow (1973)

County	TCP Used (lbs/yr)	Estimated Evaporative Loss (lbs/yr)	Estimated Evaporative Loss (kg/yr)
Humboldt	4600	552	250
Siskiyou	17800	2136	969
Shasta	459	55	25
Trinity	417	50	23

Pressure Treatment

The principal chlorophenol used in the pressure treatment industry is PCP. The areas of evaporative emissions from the pressure treatment facilities that will be discussed here are

- Fugitive emissions from the treatment vessel
- Fugitive emissions from pipes and fittings
- Evaporation from the wood (hot and cold)

A complete discussion of pressure treatment processes is given in Section 3.

Fugitive Emissions from the Treatment Vessel

As described previously, the pressure treating process involves PCP at elevated temperatures and high pressures. Although a large amount of the PCP is recycled, when the treatment chambers are opened, a steam cloud emerges from the treated wood and the chamber. In their study for the U.S. Environmental Protection Agency, DaRos et al. (1982) measured the concentration of PCP in the steam escaping from the treatment vessel of a commercial PCP pressure treatment facility. The three values they determined (three separate sampling runs) were <0.02, 8.1, and 2.6 milligrams per cubic meter (mg/m^3). These concentrations encompassed the approximately 30 minutes that the treatment vessel was open to the atmosphere. They also stated that "It was not feasible to quantify a mass emission rate due to large fluctuations in ambient air dilution caused by changing wind speed and direction." Averaging these values results in an estimated concentration of $3.6 \text{ mg}/\text{m}^3$ for the escaping air. Multiplying this value times the volume of each cylinder gives an estimated fugitive emission rate for this process. The estimated rate should be used with caution, as it is subject to the limitations discussed.

A more recent study (Engineering Science, 1986) for the U.S. Environmental Protection Agency (EPA) was performed at a pressure treating facility in Washington state. Their calculated emission rate for fugitive emissions of PCP from the opening of the treatment vessel (based on two measurements) was 0.72 lbs for the 30 minutes the cylinder was open. Both of these estimates are presented in Table 4-8. (Emissions by DaRos and Engineering Science).

Because the PCP is at an elevated temperature during this stage, it is reasonable to assume that the lower vapor pressure PCDDs and PCDFs would also be emitted at certainly no higher rate than the PCP, in proportion to

TABLE 4-8. Emissions Estimate - Butte County (6 cylinders)

Compound	Concentration (%)	Total Air Volume (m3)	Emissions (DaRos, 1982) (g/yr)	Emissions (E.Sci., 1986) (g/yr)
4CDD	2.30E-09	1.02E+03	6.22E-06	5.54E-04
5CDD	1.10E-06	1.02E+03	2.97E-03	2.65E-01
6CDD	1.30E-06	1.02E+03	3.51E-03	3.13E-01
7CDD	2.50E-05	1.02E+03	6.76E-02	6.02E+00
8CDD	8.50E-04	1.02E+03	2.30E+00	2.05E+02
4CDF	9.00E-07	1.02E+03	2.43E-03	2.17E-01
5CDF	2.30E-05	1.02E+03	6.22E-02	5.54E+00
6CDF	2.55E-05	1.02E+03	6.89E-02	6.14E+00
7CDF	1.15E-05	1.02E+03	3.11E-02	2.77E+00
8CDF	4.90E-06	1.02E+03	1.32E-02	1.18E+00
PentaCP	8.00E-01	1.02E+03	2.16E+03	1.93E+05
TetraCP	5.45E-01	1.02E+03	1.47E+03	1.31E+05

Emissions Estimate - Fresno County (1 cylinder)

Compound	Concentration (%)	Total Air Volume (m3)	Emissions (DaRos, 1982) (g/yr)	Emissions (E.Sci., 1986) (g/yr)
4CDD	2.30E-09	3.33E+01	1.94E-07	5.29E-04
5CDD	1.10E-06	3.33E+01	9.29E-05	2.53E-01
6CDD	1.30E-06	3.33E+01	1.10E-04	2.99E-01
7CDD	2.50E-05	3.33E+01	2.11E-03	5.75E+00
8CDD	8.50E-04	3.33E+01	7.18E-02	1.95E+02
4CDF	9.00E-07	3.33E+01	7.60E-05	2.07E-01
5CDF	2.30E-05	3.33E+01	1.94E-03	5.29E+00
6CDF	2.55E-05	3.33E+01	2.15E-03	5.86E+00
7CDF	1.15E-05	3.33E+01	9.71E-04	2.64E+00
8CDF	4.90E-06	3.33E+01	4.14E-04	1.13E+00
PentaCP	8.00E-01	3.33E+01	6.76E+01	1.84E+05
TetraCP	5.45E-01	3.33E+01	4.60E+01	1.25E+05

TABLE 4-8. Continued.

Los Angeles County (3 cylinders)

Compound	Concentration (%)	Total Air Volume (m3)	Emissions (DaRos, 1982) (g/yr)	Emissions (E.Sci., 1986) (g/yr)
4CDD	2.30E-09	5.78E+02	1.91E-06	3.00E-04
5CDD	1.10E-06	5.78E+02	9.12E-04	1.43E-01
6CDD	1.30E-06	5.78E+02	1.08E-03	1.69E-01
7CDD	2.50E-05	5.78E+02	2.07E-02	3.26E+00
8CDD	8.50E-04	5.78E+02	7.05E-01	1.11E+02
4CDF	9.00E-07	5.78E+02	7.46E-04	1.17E-01
5CDF	2.30E-05	5.78E+02	1.91E-02	3.00E+00
6CDF	2.55E-05	5.78E+02	2.11E-02	3.32E+00
7CDF	1.15E-05	5.78E+02	9.53E-03	1.50E+00
8CDF	4.90E-06	5.78E+02	4.06E-03	6.38E-01
PentaCP	8.00E-01	5.78E+02	6.63E+02	1.04E+05
TetraCP	5.45E-01	5.78E+02	4.52E+02	7.10E+04

Emissions Estimate - San Diego County (1 cylinder)

Compound	Concentration (%)	Total Air Volume (m3)	Emissions (DaRos, 1982) (g/yr)	Emissions (E.Sci., 1986) (g/yr)
4CDD	2.30E-09	6.00E+01	7.95E-08	1.20E-04
5CDD	1.10E-06	6.00E+01	3.80E-05	5.75E-02
6CDD	1.30E-06	6.00E+01	4.49E-05	6.79E-02
7CDD	2.50E-05	6.00E+01	8.64E-04	1.31E+00
8CDD	8.50E-04	6.00E+01	2.94E-02	4.44E+01
4CDF	9.00E-07	6.00E+01	3.11E-05	4.70E-02
5CDF	2.30E-05	6.00E+01	7.95E-04	1.20E+00
6CDF	2.55E-05	6.00E+01	8.81E-04	1.33E+00
7CDF	1.15E-05	6.00E+01	3.98E-04	6.01E-01
8CDF	4.90E-06	6.00E+01	1.69E-04	2.56E-01
PentaCP	8.00E-01	6.00E+01	2.77E+01	4.18E+04
TetraCP	5.45E-01	6.00E+01	1.88E+01	2.85E+04

TABLE 4-8. Concluded.

San Joaquin (5 cylinders)

Compound	Concentration (%)	Total Air Volume (m3)	Emissions (DaRos, 1982) (g/yr)	Emissions (E.Sci., 1986) (g/yr)
4CDD	2.30E-09	6.82E+02	4.81E-06	6.39E-04
5CDD	1.10E-06	6.82E+02	2.30E-03	3.06E-01
6CDD	1.30E-06	6.82E+02	2.72E-03	3.61E-01
7CDD	2.50E-05	6.82E+02	5.23E-02	6.95E+00
8CDD	8.50E-04	6.82E+02	1.78E+00	2.36E+02
4CDF	9.00E-07	6.82E+02	1.88E-03	2.50E-01
5CDF	2.30E-05	6.82E+02	4.81E-02	6.39E+00
6CDF	2.55E-05	6.82E+02	5.33E-02	7.09E+00
7CDF	1.15E-05	6.82E+02	2.40E-02	3.20E+00
8CDF	4.90E-06	6.82E+02	1.02E-02	1.36E+00
PentaCP	8.00E-01	6.82E+02	1.67E+03	2.22E+05
TetraCP	5.45E-01	6.82E+02	1.14E+03	1.52E+05

their concentration in the PCP. Accordingly, the emissions factors shown in Table 4-8 are based on the contamination data described previously and given in Table 4-4.

Fugitive Emissions from Pipes and Fittings

Fugitive emissions can also occur from valves, pump seals and fittings. Standard emission factors are averaged for different types of apparatus. For the category of petroleum refining, Wetherold (1980) gives emission factors for "heavy liquids" (vapor pressure <0.01 psia @ 100°F) as shown in Table 4-9. These data are the EPA standard estimates for each component. Therefore, an accurate emission estimate requires a component count at each facility. However, for the purposes of this study, we have assumed a total of 6 pumps, 12 valves, and 24 fittings at each facility. Estimated emissions using the data in Table 4-9 are presented in Table 4-10.

Emissions from the Treated Wood

As in TCP treatment, wood treated with PCP will also emit organic material into the atmosphere. Since the wood has been pressure treated, the PCP (as well as TCP, PCDDs and PCDF contaminants) penetrates much deeper into the wood than with dip treatment and there is more of it in the wood. Three separate methods have been used to estimate the quantity of material evaporating from the treated wood:

- (1) Measurement data
- (2) Adapted McCord model
- (3) Morgan and Purslow approach

Method 1. The most relevant estimates of any emissions are based on measurement data. That is, if the amount and rate of emission of a particular substance are measured under the conditions that one is attempting to predict, then the emission calculations are straightforward. The next best data (which seldom exist) are concentration measurements for a given volume of air and a known volume of evaporating material. When averaged over the time the measurements were taken, the data provide an emission rate. The problem with this technique is that the measurement conditions are rarely equivalent to the conditions encountered in the real world. The type of wood, concentration of the material, solvents, cosolvents, contaminants, humidity, temperature, wind speed, nature of the material and solvent (interactions between the two), as well as the physical layout of the facility, all contribute to uncertainty in applying laboratory data to field situations.

TABLE 4-9

FUGITIVE EMISSION FACTORS FOR
HEAVY LIQUIDS (vp <0.1 psia @100 °F)
(Weatherold, 1980)

<u>Emission Source</u>	<u>Emission Factor (lbs/hour/component)</u>	<u>Assumed Daily Operation (hours/cycle)</u>
Valves	0.0005	0.5
Pump seals	0.046	0.5
Fittings	0.00056	0.5

TABLE 4-10

ESTIMATED FUGITIVE EMISSIONS FROM PRESSURE TREATMENT
FACILITY OPERATIONS* (lbs/yr)

<u>County</u>	<u>Chlorophenol</u>	<u>PCDD</u>	<u>PCDF</u>
Butte	0.92	0.60×10^{-3}	0.037×10^{-3}
Fresno	0.53	0.34×10^{-3}	0.021×10^{-3}
Los Angeles	0.61	0.40×10^{-3}	0.024×10^{-3}
San Diego	0.50	0.33×10^{-3}	0.020×10^{-3}
San Joaquin	0.63	0.41×10^{-3}	0.025×10^{-3}

* Assuming 5 percent solution of pentachlorophenol in oil solvent.

Fortunately, studies have been conducted that address the issue of PCP evaporation using a number of different cosolvents. These studies (Ingram, et al., 1981, McGinnis, 1979) were performed at the Mississippi Forest Products Laboratory, Mississippi State University. They consisted of placing treated boards in an enclosed temperature-controlled chamber, allowing them to equilibrate (for 6 to 10 hours), and then measuring the concentration of PCP in the chamber. The boards were treated by a full-cell process to a penta retention of 0.35 to 0.45 pound per cubic foot, using a uniform pressure cycle. A number of solvents and cosolvents were used including methylene chloride, isopropyl alcohol, methanol, mineral spirits, and diesel oil (several different types). The studies showed that the principal factors affecting the air concentration (and consequently the evaporation rate) were the type of solvent and the temperature at which the experiment was conducted. The authors derived several different equations for relating the concentration of PCP in the atmosphere to temperature for each of the solvents that they studied. These equations can be used to derive the concentration data shown in Table 4-11. The assumptions made for this method were that the wood was hot (120°F) for one hour after leaving the chamber and then was ambient (70°F) temperature for one month prior to being shipped out. Also, the time for equilibration was standardized to six hours to assume the highest (most conservative) emission rate.

Method 2. As described in the previous section on dip treatment, the steady-state evaporative model of McCord (1981) can also be used to estimate emissions from treated wood, with some adaptations. Since the rate-limiting step for this model is the atmospheric diffusivity of the material (calculated as shown in Appendix F), the migration of the material through the wood is not considered to be a limiting factor. This model was used for each bundle of wood treated at each facility, and the results summed to give the data in Table 4-11. The results of this model agree surprisingly well with the experimental data of Method 1.

Method 3. Given that the data of Method 1 were for an equilibrium situation and were not measured as a percent lost, but rather as a concentration in a chamber, a different method of estimating these emissions is useful. The only data in the literature applicable to this problem are found in the study by Morgan and Purslow (1973). In that study the authors treated a number of pine sap cubes with different wood preservatives, using different application methods and combinations of solvents and cosolvents, and measured the concentration remaining on the block after a fixed period of time.

TABLE 4-11

Estimate of Emissions from PCP treated wood
Method 2 - Los Angeles County

Compound	Concentration (%)	Atmospheric Diffusivity (m ² /hr)	Poles (lbs/yr)	Lumber (lbs/yr)	Total (lbs/yr)	Total (g/yr)
4CDD	2.30E-09	1.77E-02	3.65E-11	3.12E-12	3.97E-11	1.80E-08
5CDD	1.10E-06	1.71E-02	1.73E-08	1.48E-09	1.88E-08	8.54E-06
6CDD	1.30E-06	1.66E-02	2.03E-08	1.74E-09	2.21E-08	1.00E-05
7CDD	2.50E-05	1.61E-02	3.89E-07	3.32E-08	4.22E-07	1.91E-04
8CDD	8.50E-04	1.56E-02	1.31E-05	1.12E-06	1.42E-05	6.46E-03
4CDF	9.00E-07	1.77E-02	1.43E-08	1.22E-09	1.55E-08	7.04E-06
5CDF	2.30E-05	1.71E-02	3.63E-07	3.09E-08	3.93E-07	1.78E-04
6CDF	2.55E-05	1.66E-02	3.99E-07	3.41E-08	4.33E-07	1.96E-04
7CDF	1.15E-05	1.61E-02	1.79E-07	1.53E-08	1.94E-07	8.80E-05
8CDF	4.90E-06	1.56E-02	7.57E-08	6.46E-09	8.21E-08	3.73E-05
PentaCP	8.00E-01	2.07E-02	3.70E+00	3.16E-01	4.02E+00	1.82E+03
TetraCP	5.45E-01	2.18E-02	1.91E+01	1.63E+00	2.08E+01	9.42E+03

Estimate of Emissions from PCP treated wood
Method 2 - San Diego County

Compound	Concentration (%)	Atmospheric Diffusivity (m ² /hr)	Poles (lbs/yr)	Lumber (lbs/yr)	Total (lbs/yr)	Total (g/yr)
4CDD	2.30E-09	1.77E-02	1.07E-11	1.92E-12	1.26E-11	5.73E-09
5CDD	1.10E-06	1.71E-02	5.09E-09	9.13E-10	6.00E-09	2.72E-06
6CDD	1.30E-06	1.66E-02	5.97E-09	1.07E-09	7.04E-09	3.19E-06
7CDD	2.50E-05	1.61E-02	1.14E-07	2.05E-08	1.34E-07	6.10E-05
8CDD	8.50E-04	1.56E-02	3.85E-06	6.92E-07	4.54E-06	2.06E-03
4CDF	9.00E-07	1.77E-02	4.19E-09	7.53E-10	4.95E-09	2.24E-06
5CDF	2.30E-05	1.71E-02	1.06E-07	1.91E-08	1.25E-07	5.69E-05
6CDF	2.55E-05	1.66E-02	1.17E-07	2.10E-08	1.38E-07	6.26E-05
7CDF	1.15E-05	1.61E-02	5.24E-08	9.42E-09	6.19E-08	2.81E-05
8CDF	4.90E-06	1.56E-02	2.22E-08	3.99E-09	2.62E-08	1.19E-05
PentaCP	8.00E-01	2.07E-02	1.09E+00	1.95E-01	1.28E+00	5.81E+02
TetraCP	5.45E-01	2.18E-02	5.61E+00	1.01E+00	6.62E+00	3.00E+03

TABLE 4-11. Continued.
 Estimate of Emissions from PCP treated wood
 Method 2 - Butte County

Compound	Concentration (%)	Atmospheric Diffusivity (m ² /hr)	Poles (lbs/yr)	Lumber (lbs/yr)	Total (lbs/yr)	Total (g/yr)
4CDD	2.30E-09	1.77E-02	6.75E-11	4.94E-12	7.24E-11	3.29E-08
5CDD	1.10E-06	1.71E-02	3.20E-08	2.34E-09	3.44E-08	1.56E-05
6CDD	1.30E-06	1.66E-02	3.76E-08	2.75E-09	4.03E-08	1.83E-05
7CDD	2.50E-05	1.61E-02	7.18E-07	5.25E-08	7.71E-07	3.50E-04
8CDD	8.50E-04	1.56E-02	2.43E-05	1.77E-06	2.60E-05	1.18E-02
4CDF	9.00E-07	1.77E-02	2.64E-08	1.93E-09	2.83E-08	1.29E-05
5CDF	2.30E-05	1.71E-02	6.70E-07	4.90E-08	7.19E-07	3.26E-04
6CDF	2.55E-05	1.66E-02	7.37E-07	5.39E-08	7.91E-07	3.59E-04
7CDF	1.15E-05	1.61E-02	3.30E-07	2.42E-08	3.54E-07	1.61E-04
8CDF	4.90E-06	1.56E-02	1.40E-07	1.02E-08	1.50E-07	6.81E-05
PentaCP	8.00E-01	2.07E-02	6.84E+00	5.00E-01	7.34E+00	3.33E+03
TetraCP	5.45E-01	2.18E-02	3.54E+01	2.59E+00	3.79E+01	1.72E+04

Estimate of Emissions from PCP treated wood
 Method 2 - Fresno County

Compound	Concentration (%)	Atmospheric Diffusivity (m ² /hr)	Poles (lbs/yr)	Lumber (lbs/yr)	Total (lbs/yr)	Total (g/yr)
4CDD	2.30E-09	1.77E-02	2.69E-11	2.38E-11	5.06E-11	2.30E-08
5CDD	1.10E-06	1.71E-02	1.27E-08	1.13E-08	2.40E-08	1.09E-05
6CDD	1.30E-06	1.66E-02	1.50E-08	1.32E-08	2.82E-08	1.28E-05
7CDD	2.50E-05	1.61E-02	2.86E-07	2.53E-07	5.39E-07	2.44E-04
8CDD	8.50E-04	1.56E-02	9.65E-06	8.55E-06	1.82E-05	8.25E-03
4CDF	9.00E-07	1.77E-02	1.05E-08	9.31E-09	1.98E-08	8.99E-06
5CDF	2.30E-05	1.71E-02	2.67E-07	2.36E-07	5.02E-07	2.28E-04
6CDF	2.55E-05	1.66E-02	2.93E-07	2.60E-07	5.53E-07	2.51E-04
7CDF	1.15E-05	1.61E-02	1.31E-07	1.16E-07	2.48E-07	1.12E-04
8CDF	4.90E-06	1.56E-02	5.56E-08	4.93E-08	1.05E-07	4.76E-05
PentaCP	8.00E-01	2.07E-02	2.72E+00	2.41E+00	5.13E+00	2.33E+03
TetraCP	5.45E-01	2.18E-02	1.41E+01	1.25E+01	2.65E+01	1.20E+04

TABLE 4-11. Concluded.

Estimate of Emissions from PCP treated wood
Method 2 - San Joaquin County

Compound	Concentration (%)	Atmospheric Diffusivity (m ² /hr)	Poles (lbs/yr)	Lumber (lbs/yr)	Total (lbs/yr)	Total (g/yr)
4CDD	2.30E-09	1.77E-02	4.70E-11	1.30E-11	6.00E-11	2.72E-08
5CDD	1.10E-06	1.71E-02	2.23E-08	6.15E-09	2.85E-08	1.29E-05
6CDD	1.30E-06	1.66E-02	2.62E-08	7.21E-09	3.34E-08	1.51E-05
7CDD	2.50E-05	1.61E-02	5.00E-07	1.38E-07	6.38E-07	2.89E-04
8CDD	8.50E-04	1.56E-02	1.69E-05	4.66E-06	2.16E-05	9.77E-03
4CDF	9.00E-07	1.77E-02	1.84E-08	5.07E-09	2.35E-08	1.06E-05
5CDF	2.30E-05	1.71E-02	4.67E-07	1.29E-07	5.95E-07	2.70E-04
6CDF	2.55E-05	1.66E-02	5.14E-07	1.41E-07	6.55E-07	2.97E-04
7CDF	1.15E-05	1.61E-02	2.30E-07	6.34E-08	2.93E-07	1.33E-04
8CDF	4.90E-06	1.56E-02	9.74E-08	2.68E-08	1.24E-07	5.63E-05
PentaCP	8.00E-01	2.07E-02	4.76E+00	1.31E+00	6.07E+00	2.75E+03
TetraCP	5.45E-01	2.18E-02	2.46E+01	6.78E+00	3.14E+01	1.42E+04

The applicable experiment that Morgan and Purslow (1973) performed for this study consisted of treating the wood cubes with a solution of 5 percent PCP, 5 percent gamma-BHC (a contact insecticide), and trixylenyl phosphate (an anti-blooming agent) in a hydrocarbon solvent. The four cubes used in this experiment were treated using a "double vacuum" cycle, which is related to the pressure treatment performed at California facilities. The authors estimate a standard deviation of 5 percent in their determinations, which makes their low estimate of loss (3 percent after one month) suspect. Nonetheless, the 3 percent figure was used to estimate the loss of pentachlorophenol for the California facilities, as shown in Table 4-11. Although this method is uncertain, it does represent the highest data reported in the literature for this effect and therefore must be included.

COMBUSTION OF WOOD WASTE

Although analyses of technical grade PCP have failed to show the presence of the 2,3,7,8-tetrachloro isomer of dibenzo-p-dioxin, that fact does not preclude the subsequent formation of the isomer, either upon reaction to sunlight, or during pyrolysis or combustion. Several studies have shown that when heated, PCP and its contaminants can react to form the 2,3,7,8-tetra isomer, as well as several other less-well-known isomers that were not originally present.

The combustion of wood impregnated with PCP causes both the PCP and the PCDDs and PCDFs to react and isomerize (Olie et al., 1983; Rappe et al., 1978; Langer et al., 1973; Jansson et al., 1978; Langer et al., 1973; Stehl et al., 1973; Bridle et al., 1984). Bridle et al. (1984) estimated that combustion of chlorophenol-contaminated wood wastes converts 0.9 to 1.7 percent of the chlorophenol in the waste to dioxins and furans. The reaction conditions, such as concentrations of the contaminants present, temperature, and form of the PCP, greatly affect the ratios and amounts of the various chlorinated isomers of dibenzo-p-dioxin and dibenzofuran. The actual mechanisms of formation of PCDDs have been postulated to be by dimerization of chlorophenates, dechlorination of higher chlorinated PCDDs, cyclization of predioxins, or by some combination of all these mechanisms (Rappe et al., 1978). When purified tri- and pentachlorophenates are pyrolyzed, they yield large amounts of PCDDs, strongly suggesting a dimerization reaction (Rappe et al., 1978), yet the thermal cyclization of predioxins has also been shown to be a viable pathway (Nilsson et al., 1974). Olie and coworkers (1983) determined that the presence of lignin (found in wood) appears to be essential to the formation of dibenzo-p-dioxins and dibenzofurans.

Differential Thermal Analysis (DTA) of chlorinated phenols (Langer et al., 1973a; Langer et al., 1973b) reveals that, in general, thermal decomposition of chlorinated phenols does not lead to dioxins; however, certain conditions, by themselves or in combination, favor dioxin formation. If PCP is present in the form of a sodium salt, dioxins are formed. If it is present in the form of a silver salt, an exothermic decomposition occurs, yielding higher condensed materials and no dioxins. Along these same lines, Jansson et al. (1978) discovered that the addition of copper salts to the compound being burned drastically reduced the PCDD emissions. They also determined that the combustion of tri- and tetrachlorophenol products produced larger amounts of PCDDs and PCDFs than did the combustion of PCP-treated wood. In addition, insufficient oxygen during the combustion of PCP-treated wood favored the presence of PCDDs and PCDFs. This is interesting in light of the proposed mechanism of Shaub and Tsang (1983) described in the following section on atmospheric reactivity.

These studies all consider the problem of combustion of PCP (and TCP) either in a pure solution, or on treated wood. As described here and in the section on atmospheric reactivity, the critical factors in the formation of PCDDs from PCP during combustion are the combustion conditions. Laboratory studies often do not adequately duplicate actual industrial combustion conditions; however, the EPA has performed an emissions test to determine if PCDDs and PCDFs are formed from the combustion of treated wood in an industrial boiler. In a study for the EPA, DaRos et al. (1982) described an extensive emissions test on a wood-preserving facility's 5 kg/s (40,000 lb/hr) pile-burning water tube boiler co-firing a mixture of woodwaste and penta/cresote wastewater. They measured a PCP concentration of 16 ppm in the treated fuel, as well as a number of other chemicals. The results of their tests showed no detectable PCDD or PCDF air emissions for a detection limit of < 10 micrograms per cubic meter (< 10 ppt/w/v). They did discover PCDDs and PCDFs in the penta treating solution, waste sludge, and bottom ash.

Given the high quantities of penta that were burned in this test, and considering that the study was performed at an industrial site rather than in a laboratory, the results indicate quite strongly that when combusted with sufficient oxygen and at a low enough concentration of PCP in the fuel, PCDDs and PCDFs are not emitted from small-scale combustion of treated wood wastes in industrial boilers using modern pollution control equipment such as baghouses and precipitators. The only instances of TCP-treated wood burned in California that were discovered through the survey and site visits of this project were small amounts in electric power generating facilities. Since the largest amount (nine lbs of TCP/year in Shasta county) is well below the amounts burned in the EPA study (DaRos et al. 1982), it is reasonable to assume that their emissions would also be below detectable limits, given similar operating conditions. Accordingly, the

most realistic estimate would be that given the combustion patterns that now exist in California, there are no PCDD or PCDF emissions.

While the most realistic evaluation of the combustion issue may be that there are no emissions of PCDDs or PCDFs, a more conservative approach is also possible. Laboratory studies (Bridle, et al., 1984 and Jansson, Sundstrom and Ahling, 1978) have shown that the combustion of chlorophenol-treated wood can produce PCDDs and PCDFs. As described previously, the combustion conditions are crucial to determining the destruction and/or formation of the PCDDs and PCDFs. However, using the values of Bridle et al., 1984 for the lowest possible temperature of combustion (700°C) and averaging the destruction efficiencies for the two wood treatment components gives the data shown in Table 4-12. The concentration data were that previously discussed as averaged SWRCB data for chlorophenol formulations as used in California. The amounts of TCP used to produce the emissions estimates in Table 4-12 are discussed in the following section and shown in Table 5-1.

The most conservative emissions values shown in Table 4-12 indicate an annual emission amount of approximately 25 µg/year for the Shasta County facility (the highest value of the three counties). This value is very small. Also, as stated previously, the only field study of a similar operation (DaRos et al. 1982) showed no PCDDs or PCDFs, so it is quite likely that whatever PCDDs and PCDFs are formed are captured in the pollution control equipment (baghouse).

ATMOSPHERIC TRANSFORMATION

It is well known that some chemicals react in the atmosphere. The reactions involved in the formation of ozone from emissions of hydrocarbons and nitrogen oxides are perhaps the most notorious atmospheric reactions and the subject of intense study. Less well known are the atmospheric transformations of molecules not directly associated with ozone formation. The reasons for this are simple: atmospheric chemistry consists of rapid reactions of low concentration gaseous species. This creates more experimental difficulties than are common in traditional "solution" chemical kinetic studies. Experiments designed to simulate the complex reactions of the atmosphere are conducted in large Teflon chambers. They require sophisticated measurement techniques to detect the relatively small concentrations of the reactive materials. These experiments are performed with varying mixtures of other chemicals and different temperature and light conditions for different seasons and times of day. All of these factors combine to make atmospheric chemistry experiments difficult and expensive to perform. Consequently, few data on esoteric chemical reactions in the atmosphere, even ones as potentially important as the formation of PCDDs, are available.

TABLE 4-12. Estimated maximum emissions from combustion of TCP-treated wood.

Compound	Concentration (%)	Destruction Efficiency (%)	Estimated Emissions (%)	Humboldt County Emissions (g/yr)	Siskiyou County Emissions (g/yr)	Shasta County Emissions (g/yr)
4CDD	1.71E-08	64.2	6.12E-09	8.05E-07	5.11E-06	2.55E-05
5CDD	3.30E-07	93.9	2.01E-08	2.65E-06	1.68E-05	8.38E-05
6CDD	4.69E-06	91.2	4.12E-07	5.42E-05	3.44E-04	1.72E-03
7CDD	1.12E-05	93.6	7.14E-07	9.39E-05	5.96E-04	2.97E-03
8CDD	3.90E-05	66.9	1.29E-05	1.70E-03	1.08E-02	5.38E-02
4CDF	1.64E-06	64.2	5.88E-07	7.73E-05	4.91E-04	2.45E-03
5CDF	5.49E-06	93.9	3.35E-07	4.40E-05	2.79E-04	1.39E-03
6CDF	4.70E-05	91.2	4.14E-06	5.44E-04	3.45E-03	1.72E-02
7CDF	4.52E-06	93.6	2.89E-07	3.80E-05	2.41E-04	1.20E-03
8CDF	4.57E-06	66.9	1.51E-06	1.99E-04	1.26E-03	6.29E-03

The formation of PCDDs from PCP and their isomerization have been known to occur upon reaction with sunlight (Arsenault, 1976). Studies have shown that short-term exposure to sunlight results in increases in PCDD concentrations (Lamparski et al., 1980), whereas results of analyses of wood exposed outdoors for long periods suggest no overall formation of octachlorodibenzo-p-dioxin (Dobbs and Grant, 1981). Cull and Dobbs (1984) have also shown that the depth of the block surface, as well as the form of PCP (as either technical PCP or technical sodium pentachlorophenoxide), have an effect on the concentrations and types of isomers that exist in the wood.

The degradation of the various isomers of PCDD upon exposure to sunlight was examined by Stehl and coworkers (1973), who found that the 2,3,7,8-tetra isomer decomposed rapidly. Using artificial sunlight, they discovered that the "half-life" of the 2,3,7,8-tetra isomer ranged from 40 minutes to 3 hours, depending on the intensity of the light. They also determined that the isomer was relatively stable (50 percent remaining) at 700°C for 21 seconds (47 percent remaining after 50 seconds), but was almost totally decomposed (0.05 percent remaining after 21 seconds) at 800°C. This instability can be misleading as the presence of other compounds absorbed onto the PCDD particles would diminish the effect of sunlight and therefore increase the stability of PCDD in the atmosphere.

A theoretical treatment of the formation of PCDDs has been performed (Shaub and Tsang, 1983) for the combustion process, though not for the ambient atmosphere. In this study the authors proposed a detailed mechanism for the formation of PCDDs from chlorinated phenols and calculated several different reaction rate constants based on this mechanism. The mechanism, which is shown in Figure 4-1, has as the rate-limiting step the formation of the molecule polychlorinated 2-phenoxyphenol (PD) (a dioxin precursor shown in Figure 4-2). PD is the intermediate molecule necessary for subsequent formation of PCDDs. PD is formed through the reaction of an oxidized PCP product (P^*) and a second PCP (P) molecule. Although this reaction is possible because of higher temperature and concentrations prior to atmospheric dilution, it will be shown that the atmospheric consequences are nil.

The Shaub and Tsang mechanism was deliberately biased towards the formation of PCDDs to give the most conservative results. In this mechanism, the reactions of P^* , which must be formed in order for PD to be formed, are

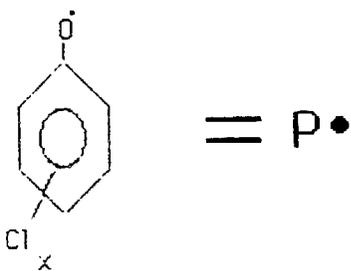
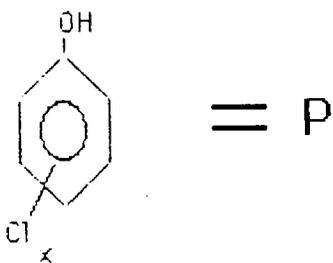
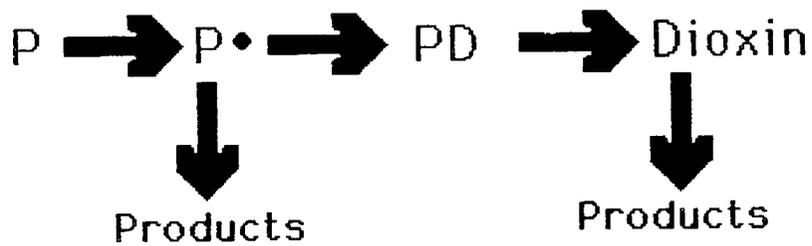
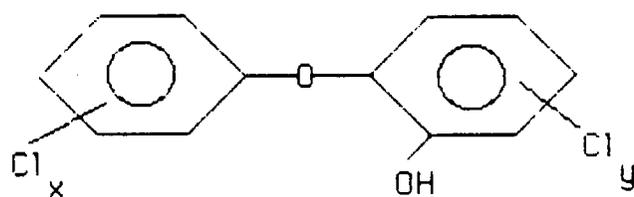


Figure 4-1: Proposed mechanism for the atmospheric transformation of chlorinated phenols to dibenzo-p-dioxins (Shaub and Tsang, 1983)



PD

Figure 4-2: Chemical Intermediate for mechanism of Shaub and Tsang (1983)

<u>Reaction</u>	<u>$K_{loss1}(300, K)$ ($\text{ppm}^{-1}\text{min}^{-1}$)</u>	<u>Equation Number</u>
$P^\bullet \text{ -----> Products}$	"very slow"	(4)
$P + P^\bullet \text{ -----> PD} + \text{Cl}$	2.91×10^{-16}	(5)
$R + P^\bullet \text{ -----> P} + R^\bullet$	2.91×10^{-17}	(6)
$\text{OH} + P^\bullet \text{ -----> Products}$	2453	(7)
$\text{O}_2 + P^\bullet \text{ -----> Products}$	245	(8)
$\text{NO}_2 + P^\bullet \text{ -----> Products}$	20,000	(9)

The equation for the rate of reaction (R_r) for these reactions is

$$R_r = [P^\bullet] [X] K_{loss} \quad \text{(Equation 10)}$$

where

$$[X] = \text{All the reactants (other than P) just listed}$$

$$[P^\bullet] = \text{Concentration of } P^\bullet$$

If the concentration of P and its oxidation product, P^\bullet , are both less than 1 ppm (a most reasonable assumption for any of the pentachlorophenol emission rates described previously), the formation rate of PD (and hence PCDDs) will be even less than the amounts calculated next. However, even assuming a very high concentration (1.0 ppm) of chlorinated phenols in the atmosphere at a given time, the relative rate of PD formation will still be quite small, due to the enormously larger rates of formation of other products, as listed. For example, since oxygen is present at 209,000 ppm (20.9 percent) in the atmosphere, R_f of its reaction would be:

$$R_r (\text{O}_2 \text{ products}) = 245 \times 209,000 \times 1 = 5.12 \times 10^7, \quad \text{(Equation 11)}$$

and NO_2 at 100 ppb (0.1 ppm) would give an R_f of

$$R_r (\text{NO}_2 \text{ products}) = 20,000 \times 0.1 \times 1 = 2000, \quad \text{(Equation 12)}$$

While the R_r of PD would be given by

$$R_r (\text{PD}) = 2.91 \times 10^{-16} \times 1.0 \times 1 = 2.91 \times 10^{-16} \quad \text{(Equation 13)}$$

Comparison of Equations 11 and 13 shows a relative difference of 10^{23} . When the other possible side reactions are also calculated (as shown in Equation 12), the feasibility of PD formation is quite low.

These reaction rate constants were all derived at 300 K (81°F). At 1400 K, the reaction constant (K) for formation of PD is estimated to be 0.1 (instead of 2.91×10^{-16}), which shows why the propensity for PCDD formation appears to be limited to extremely elevated temperature conditions, such as combustion. Even with a difference in K of 10^{15} , the rate of PD formation in combustion is still 10^8 less than the formation of side products (if oxygen is present), since Shaub and Tsang indicate that the oxygen rate constant is relatively temperature-independent.

Given these relationships, which even though strongly conservative (bias towards the formation of PCDDs) still show a 10^{23} skew towards formation of products other than PCDDs, there appears to be little basis for concern regarding the atmospheric transformation of chlorinated phenols from wood product facilities to PCDDs at ambient temperatures and concentrations.

5 SUMMARY OF POTENTIAL ATMOSPHERIC RELEASES OF DIOXINS AND FURANS FROM THE FOREST PRODUCTS INDUSTRY IN CALIFORNIA

In this section we summarize the atmospheric releases of dioxins (PCDDs) and furans (PCDFs) from the forest products industry in California. We first present a statewide mass balance for chlorophenol use that includes the amounts of wood treated with PCP and TCP and the amount of treated woodwastes produced. We then present a summary of air emissions of chlorophenol, PCDDs, and PCDFs broken down by county and release mechanism as defined in Section 3. Last, we present an exposure analysis of three facilities and compare their estimated exposures with current health standards.

CHLOROPHENOL MASS BALANCE

Using the information from our survey and the other data sources described in Section 2 of this report, we constructed a statewide mass balance for annual chlorophenol use in California. Only data for those counties with facilities identified in our survey as chlorophenol users are included. Table 5-1 presents the annual chlorophenol mass balance, quantities of treated wood, and the quantity of chlorophenol contained in treated woodwaste by county for 1985/86 in California. As discussed earlier, pressure treatment facilities use only PCP and produce no treated woodwaste. Approximately 932 tons of PCP are used to treat approximately 3.5 million cubic feet of wood annually. Annual TCP use, which is limited to nonpressure treatment facilities and used to treat nearly 48 million cubic feet of wood annually, was approximately 11.6 tons during 1985/86. Treated woodwastes from non-pressure-treated wood that was subsequently redimensioned contained an annual statewide total of 11.3 lb of TCP.

SUMMARY OF EMISSIONS BY COUNTY AND RELEASE MECHANISM

By combining information on chlorophenol use, the mass balance, potential atmospheric releases, and emission factors, we have compiled a statewide inventory, by county, of air emissions of chlorophenol, PCDDs, and PCDFs. Tables 5-2 through 5-4, respectively, show the estimated air emissions of chlorophenol, PCDD, and PCDFs by county and release mechanism.

TABLE 5-1. Mass balance of annual chlorophenol use for California counties with wood treatment facilities during 1985/86.

	Quantity of Treated Wood (1000 cu ft)	Quantity of Chlorophenol Used in Treatment (tons)		Chlorophenol in Treated Woodwaste (tons)
		Penta	Tetra	
<u>Pressure Treatment</u>				
Butte	1473	426	0	0
Fresno	437	60	0	0
Los Angeles	753	200	0	0
San Diego	165	40	0	0
San Joaquin	<u>701</u>	<u>206</u>	<u>0</u>	<u>0</u>
Subtotal	3,529	932	0	0
<u>Nonpressure Treatment</u>				
Humboldt	3,600	0	2.3	1.5×10^{-4}
Shasta	30,000	0	0.2	4.6×10^{-3}
Siskiyou	13,000	0	8.9	9.0×10^{-4}
Trinity	<u>200</u>	<u>0</u>	<u>0.2</u>	<u>0</u>
Subtotal	46,800	0	11.6	5.65×10^{-3}
State total	50,329	932	11.6	5.65×10^{-3}

TABLE 5-2. Chlorophenol emissions (lbs/yr) by release mechanism.

Principal Stages	Pressure Treatment										Nonpressure Treatment				State Total
	County										County				
	Butte	Fresno	Los Angeles	San Diego	San Joaquin	Humboldt	Siskiyou	Shasta	Trinity						
Storage of chlorophenol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dispensing chlorophenol to mixing, storage, and treatment tanks	9.2×10^{-1}	5.3×10^{-1}	6.1×10^{-1}	5.0×10^{-1}	6.3×10^{-1}	2.2×10^{-1}	7.4×10^{-2}	0	2.0×10^{-1}	0	2.0×10^{-1}	0	4.4×10^0	0	4.4×10^0
Application of preservative	0	0	0	0	0	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a
Removal of treated lumber from treatment vessel	7.8×10^0	2.5×10^{-1}	2.5×10^0	1.0×10^{-1}	6.2×10^0	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	7.7×10^1	0 ^b	7.7×10^1
Storage of treated product	4.5×10^1	3.2×10^1	2.5×10^1	7.9×10^0	3.7×10^1	1.8×10^2	7.0×10^2	4.4×10^1	8.2×10^0	4.4×10^1	7.0×10^2	4.4×10^1	1.0×10^3	8.2×10^0	1.0×10^3
Cleaning of treatment vessel	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Disposal of treated woodwaste and treatment sludge	0	0	0	0	0	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c
	5.3×10^1	3.3×10^1	2.8×10^1	8.5×10^0	4.4×10^1	1.8×10^2	7.0×10^2	4.4×10^1	8.4×10^0	4.4×10^1	7.0×10^2	4.4×10^1	1×10^3	8.4×10^0	1×10^3

^a Included in dispensing of chlorophenol emissions.

^b Included in storage of treated product.

^c Below detectable limits, see discussion of combustion emissions in Section 4.

TABLE 5-3. PCDD emissions (lbs/yr) by release mechanism.

Principal Stages	Pressure Treatment									Nonpressure Treatment											
	County									County											
	Butte	Fresno	Los Angeles	San Diego	San Joaquin	Humboldt	Siskiyou	Shasta	Trinity	State Total	Butte	Fresno	Los Angeles	San Diego	San Joaquin	Humboldt	Siskiyou	Shasta	Trinity	State Total	
Storage of chlorophenol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dispensing chlorophenol to mixing, storage, and treatment tanks	0.60×10^{-3}	0.34×10^{-3}	0.40×10^{-3}	0.33×10^{-3}	0.41×10^{-3}	7.8×10^{-6}	2.7×10^{-6}	0	7.3×10^{-6}	2.1×10^{-3}	0	2.7×10^{-6}	0	0	0	0	0	0	0	0	0
Application of preservative	0	0	0	0	0	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a				
Removal of treated lumber from treatment vessel	5.22×10^{-3}	1.63×10^{-4}	1.61×10^{-3}	6.61×10^{-3}	4.06×10^{-3}	0 ^b	0 ^b	0 ^b	0 ^b	1.1×10^{-2}	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b	0 ^b
Storage of treated product	2.7×10^{-5}	1.9×10^{-5}	1.5×10^{-5}	4.7×10^{-6}	2.2×10^{-5}	6.2×10^{-6}	2.5×10^{-5}	1.6×10^{-6}	2.9×10^{-7}	1.2×10^{-4}	0	0	0	0	0	0	0	0	0	0	0
Cleaning of treatment vessel	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Disposal of treated woodwaste and treatment sludge	0	0	0	0	0	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c				
	5.8×10^{-3}	5.2×10^{-4}	2.0×10^{-3}	0.33×10^{-3}	4.5×10^{-3}	1.4×10^{-5}	2.8×10^{-5}	1.6×10^{-6}	7.6×10^{-6}	1.3×10^{-2}	0	2.8×10^{-5}	1.6×10^{-6}	7.6×10^{-6}	1.3×10^{-2}	0	0	0	0	0	0

* See Section 4 for actual emissions of individual isomers.

a Included in dispensing of chlorophenol emissions.

b Included in storage of treated product.

c Below detectable limits, see discussion of combustion emissions in Section 4.

TABLE 5-4. PCDF emissions (lbs/yr) by release mechanism.

Principal Stages	Pressure Treatment					Nonpressure Treatment				
	County					County				
	Butte	Fresno	Los Angeles	San Diego	San Joaquin	Humboldt	Siskiyou	Shasta	Trinity	State Total
Storage of chlorophenol	0	0	0	0	0	0	0	0	0	0
Dispensing chlorophenol to mixing, storage, and treatment tanks	3.7×10^{-5}	2.1×10^{-5}	2.4×10^{-5}	2.0×10^{-5}	2.5×10^{-5}	9.1×10^{-6}	3.1×10^{-6}	0	8.5×10^{-6}	1.5×10^{-5}
Application of preservative	0	0	0	0	0	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a
Removal of treated lumber from treatment vessel	4.0×10^{-4}	1.2×10^{-4}	1.2×10^{-5}	5.1×10^{-6}	3.1×10^{-4}	0 ^b	0 ^b	0 ^b	0 ^b	8.4×10^{-4}
Storage of treated product	2.0×10^{-6}	1.4×10^{-6}	1.1×10^{-6}	3.6×10^{-7}	1.7×10^{-6}	7.2×10^{-6}	2.9×10^{-5}	1.8×10^{-7}	3.4×10^{-7}	4.3×10^{-5}
Cleaning of treatment vessel	0	0	0	0	0	0	0	0	0	0
Disposal of treated woodwaste and treatment sludge	0	0	0	0	0	0 ^c	0 ^c	0 ^c	0 ^c	0 ^c
Total	4.4×10^{-4}	1.4×10^{-4}	2.7×10^{-5}	2.5×10^{-5}	3.3×10^{-4}	1.6×10^{-5}	3.2×10^{-5}	1.8×10^{-7}	8.8×10^{-6}	9.0×10^{-4}

* See Section 4 for actual emissions of individual isomers.

^a Included in dispensing of chlorophenol emissions.

^b Included in storage of treated product.

^c Below detectable limits, see discussion of combustion emissions in Section 4.

These emissions should be considered as estimates only. No attempt was made to measure emission rates at any of the forest products industry facilities as part of this study. The choice of emission rates used to calculate the values shown in Tables 5-2 through 5-4 has been described in detail in the previous section. The tables provide a means of comparing the air emissions of PCDD, PCDF, and chlorophenol for the various release mechanisms. As shown in the tables, not all of the potential atmospheric pathways are sources of air emissions. For example, no air emissions are shown for the storage of chlorophenol. On the basis of emission factors described in Section 4 and the mass balance of chlorophenol use in California presented here, statewide total emissions of chlorophenols, PCDD, and PCDF were calculated.

Figure 5-1 is a schematic of chlorophenol use and fate. The size of the bars is roughly proportional to the mass of material. The figure shows that about 944 tons of chlorophenol are used annually in California, 932 tons for pressure treatment and 12 tons for nonpressure treatment. Pressure treatment accounts for only 0.08 tons/yr of air emissions of chlorophenols, whereas the significantly smaller use in nonpressure treatment accounts for 0.45 tons/yr of chlorophenol air emissions. The chlorophenol air emissions are further subdivided by release mechanism at pressure and nonpressure treatment facilities. Subsequent emissions of PCDD and PCDF from each type of source and release mechanism are also presented. In summary, the use of chlorophenols by the forest product industry results in the following annual statewide emissions: 0.54 ton/yr of chlorophenol, 6.6×10^{-6} ton/yr of PCDDs, and 4.5×10^{-7} ton/yr of PCDFs.

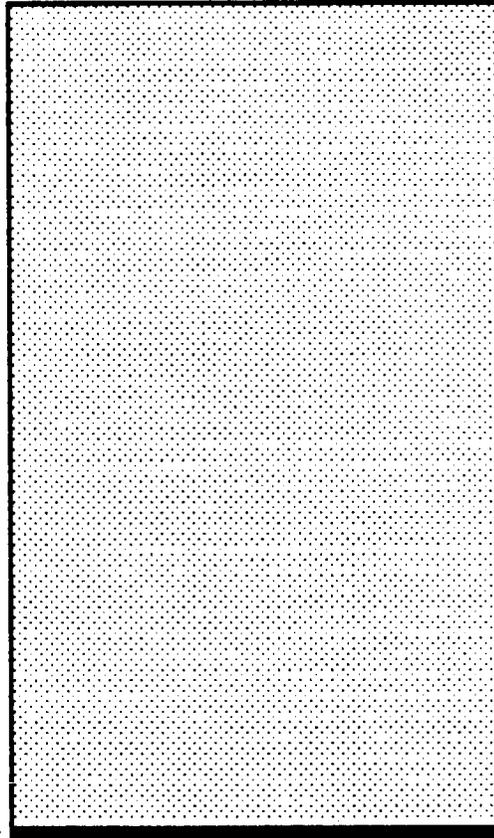
EXPOSURE ANALYSIS

The model used in the exposure analysis of three facilities is the Systems Applications Human Exposure And Risk (SHEAR) model. SHEAR is a set of computer codes and data files designed to estimate patterns of pollutant concentrations and related measures of health risk due to sources of potentially hazardous species in a designated modeling region. It uses a plume dispersion algorithm for individual point sources; for area sources, it acts as a box algorithm. SHEAR predicts annual-average concentration patterns at a set of receptors distributed on a polar grid around the source. Exposure estimates are developed by evaluating the joint occurrence of population density and specific concentration patterns.

Inputs to SHEAR include STAR meteorological data, the frequency distributions of the meteorological data (wind speed, wind direction, and stability) in standard STAR formats, and population resolved on the block-group level. The exposure/dosage algorithms involve interpolation of the

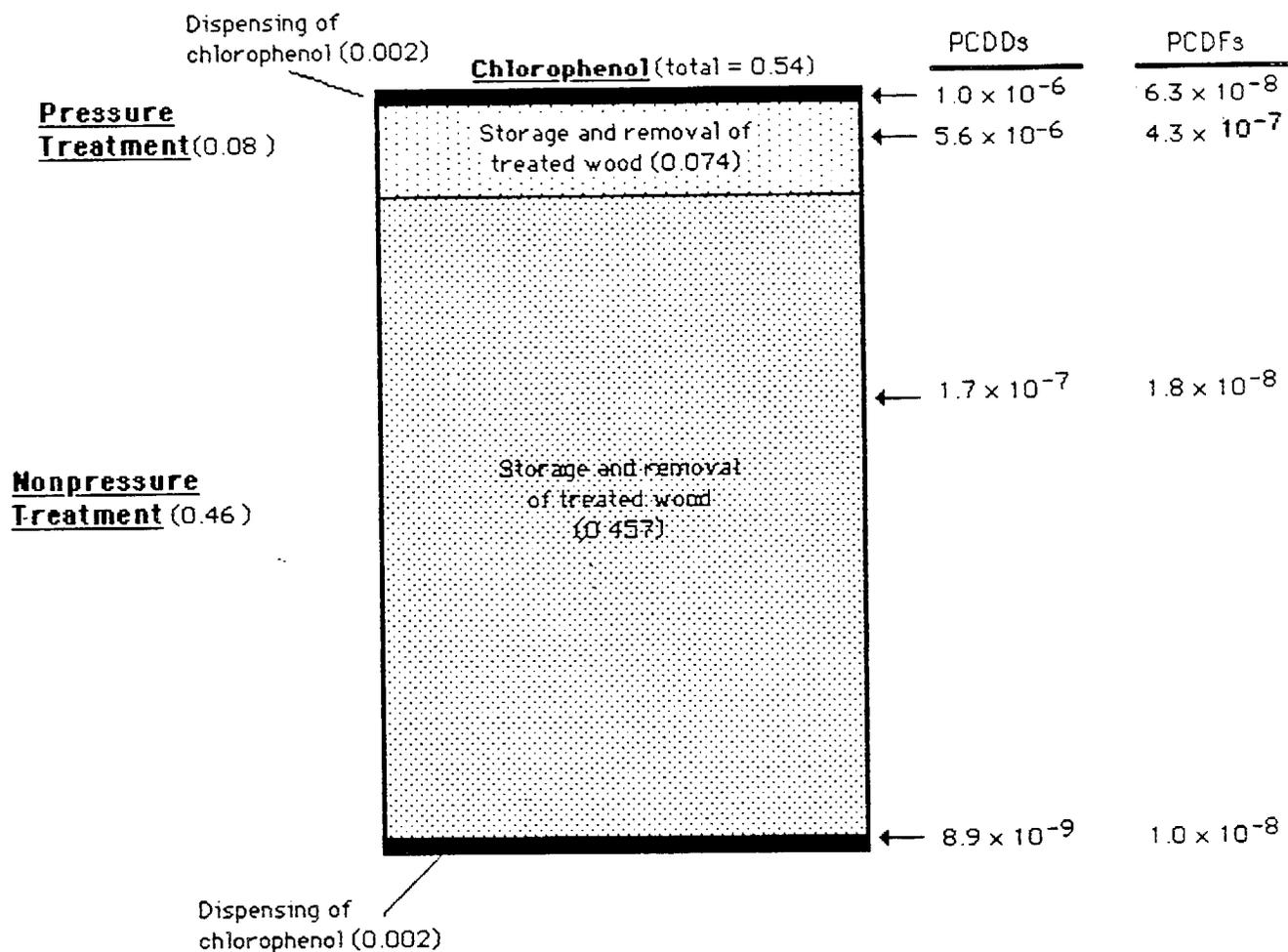
Pressure
Treatment (ton/yr) →
Total Use: 932
Air Emissions: 0.08
Treated Wood Wastes: None

Nonpressure
Treatment (ton/yr) →
Total Use: 12
Air Emissions: 0.46
Treated Wood Waste: 0.0055



(a) Overview of annual chlorophenol use (944 ton/yr)

FIGURE 5-1. Summary of chlorophenol use, air emissions, and woodwaste for the forest products industry in California (1985-1986).



(b) Breakdown of air emissions of chlorophenol and associated dioxins and furans (ton/yr)

FIGURE 5-1. Continued.

Pressure
Treatment: None

Nonpressure
Treatment
(0.0055)

Combustion Fuel 0.0027
Other Uses (no emissions) 0.0027

(c) Amount of chlorophenol in treated wood waste (ton/yr)

FIGURE 5-1. Concluded.

computed concentration patterns and the population data to develop exposure patterns. These exposure patterns are summed to produce specific exposure totals. SHEAR also reports dosage, which is the cumulative product of exposure and concentration.

Site Selection

On the basis of size, type of treatment used, population distribution around the facility, and meteorological characteristics for the area near the chlorophenol emission source, three facilities, one each in Butte, Humboldt, and Los Angeles counties, were selected for exposure modeling. The facilities in Butte and Los Angeles are pressure treaters; the Humboldt facility uses a dip (nonpressure) method. The Butte County source would qualify as a large treatment facility; the Los Angeles County source as medium, and the Humboldt facility as small. All three facilities have population centers within 10-20 km, but the Los Angeles plant is located in the most urban environment of the three.

Model Inputs

The meteorological data were obtained in STAR (STability ARray) format from the National Climatic Center in Asheville, North Carolina. These data consist of climatological frequency distributions of wind speed, wind direction, and atmospheric stability. STAR data collected at stations in Red Bluff, Arcata, and Long Beach, respectively, were used for the Butte, Humboldt, and Los Angeles county facilities.

For modeling purposes, the three facilities were treated as area sources because of the large physical size of their processing facilities. A 16-point polar receptor grid with ring distances at 0.5, 0.7, 1, 2, 5, 10, 15, and 20 km was used. A unit emission rate of one gram per second was used for each plant. The results of the unit emission rate calculations can be multiplied by the actual emission factors to obtain exposure estimates based on those emission estimates.

Model Results

The resulting estimates of annual-average concentration patterns for each plant using the unit emission rate are superimposed on regional terrain maps in Figures 5-2 through 5-4. Block group-enumeration district centroids are plotted as small dots to indicate population patterns. The highest concentrations calculated are generally observed within 100 to 600 m from the source.

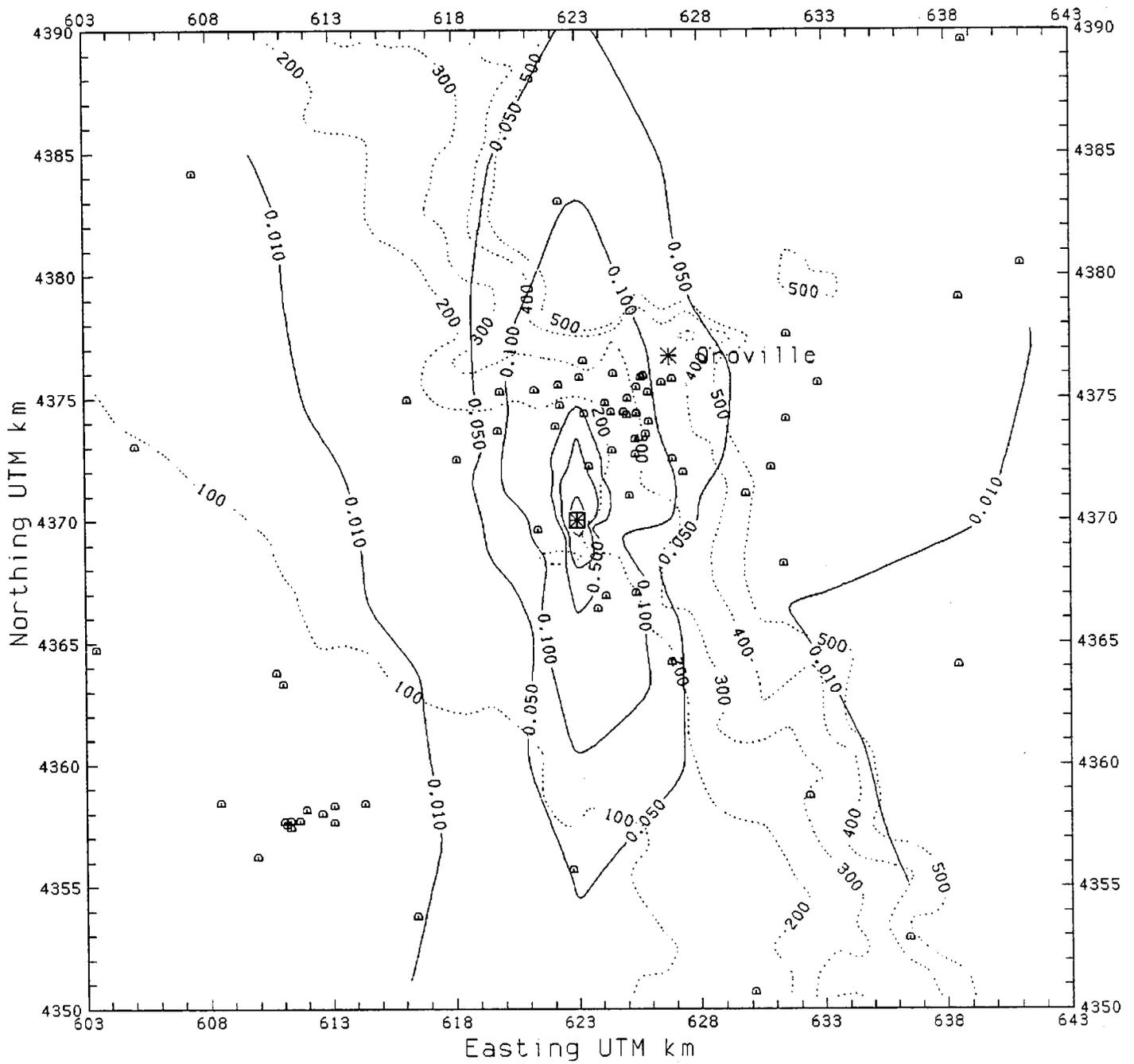


FIGURE 5-2.

Annual Average Pollutant Concentrations ($\mu\text{g}/\text{m}^3$)
 and US Census Enumeration District Centroids
 Large Wood Treatment Plant, Butte County
 (Assuming 1 g/s Emission Rate)

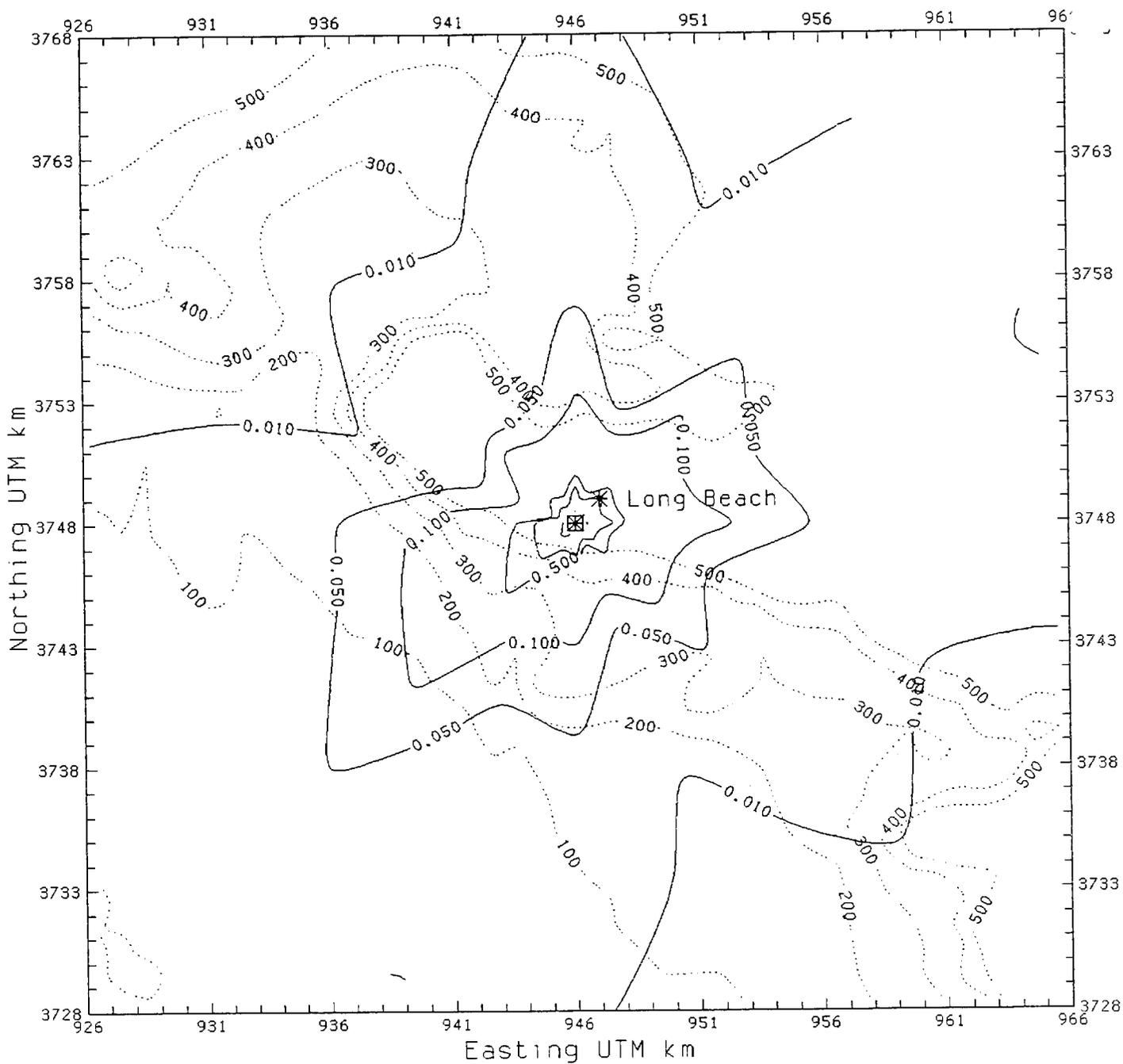


FIGURE 5-3.

Annual Average Pollutant Concentrations ($\mu\text{g}/\text{m}^3$)
 (US Census Enumeration Districts Not Shown)
 Medium Wood Treatment Plant, Los Angeles County
 (Assuming 1 g/s Emission Rate)

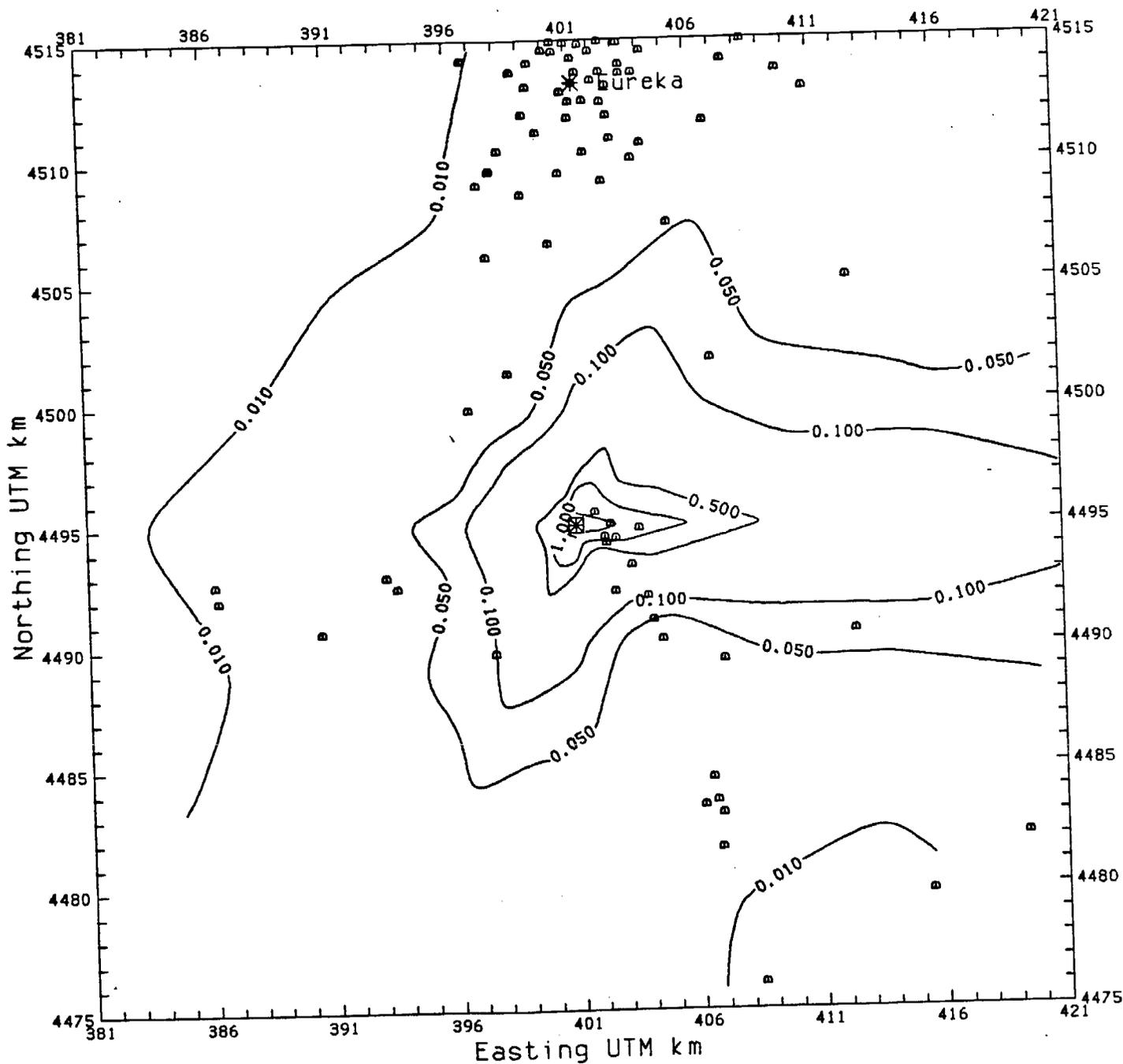


FIGURE 5-3.

Annual Average Pollutant Concentrations ($\mu\text{g}/\text{m}^3$)
 and US Census Enumeration District Centroids
 Small Wood Treatment Plant, Humboldt County
 (Assuming 1 g/s Emission Rate)

Tables 5-5 a, b, and c show summaries of concentration, exposure, and dosage for unit emissions from the three plants. The original computations of these three parameters are made for each population centroid.* SHEAR then orders the BG/EDs by the computed concentrations at each centroid. The first and last rows of the tables present results for the BG/EDs for which the highest and lowest concentrations were computed. All other concentrations in the left column are selected by computer to provide roughly proportional "steps" between the highest and lowest values.

Exposure and dosage entries contain results cumulatively by "bin." That is, the entries in any row provide the number of people exposed or the dose delivered at or above the indicated concentration in the left column. The concentrations thus become "bin" labels; the dose, which is an accumulation over binned BG/EDs, is only approximately the product of the concentration times the exposure from the same row. For any given BG/ED, the dose is exactly the product of the concentration times the exposure.

The reader may scale each of the concentrations listed in Table 5-5 and Figures 5-2 through 5-4 by the appropriately chosen emission rate for each county and for the pollutant of concern. The highest ambient concentration is predicted to occur in a populated area only near the plant in Los Angeles County. The normalized concentrations plotted in the figures must be scaled to the actual concentration by multiplying the normalized concentration by the true emission rate. The concentrations are listed in Table 5-5. For example, the actual concentrations of dioxin resulting from emissions at the Los Angeles County facility can be calculated from the annual emissions of 2.0×10^{-3} lb/yr. First, the annual emissions are converted to an emission rate (2.0×10^{-3} lb/yr \times 1 yr/365 day \times 454 g/lb \times 1 day/24 hr \times 1 hr/60 min \times 1 min/60 s) equal to 2.9×10^{-8} g/s. This emission rate is then used to scale the concentrations plotted in Figure 5-2. Thus, the maximum concentration actually calculated to occur around the Los Angeles County facility is $5.72 \mu\text{g}/\text{m}^3 \times 2.9 \times 10^{-8} = 1.7 \times 10^{-7} \mu\text{g}/\text{m}^3$. Table 5-6(a, b, c) shows the actual concentrations and exposures calculated for the three representative facilities for the PCDD emissions.

For comparison purposes, the state OSHA standard for employee exposure to PCP is $500 \mu\text{g}/\text{m}^3$. It is interesting to note that during our survey we

* Population is defined for each U.S. Census Block Group (BG) or Enumeration District (ED). Population centroids are thus the centroids of the BG/EDs.

TABLE 5-5. Exposure/dose summaries for three facilities calculated with unit emission rate.

Concentration* ($\mu\text{g}/\text{m}^3$)	Exposure (1000's)	Dosage (Con x Exp)
--	----------------------	-----------------------

(a) Facility size: Small
Location: Rural (Humboldt County)

0.88	0.6	0.5
0.50	1.7	1.3
0.25	2.2	1.6
0.10	10.7	3.0
0.05	11.9	3.1
0.025	20.4	3.4
0.010	34.2	3.6
0.008	34.7	3.6

(b) Facility size: Large
Location: Rural (Butte County)

1.66	2.1	3.5
1.00	2.1	3.5
0.50	2.1	3.5
0.25	3.9	4.2
0.10	12.5	5.5
0.05	17.8	5.9
0.025	24.0	6.1
0.010	33.3	6.3
0.005	35.0	6.3
0.0045	35.3	6.3

(c) Facility size: Medium
Location: Urban (Los Angeles County)

5.72	3.1	17.7
5.00	3.1	17.7
2.50	8.2	32.2
1.00	30.2	63.6
0.50	65.5	87.6
0.25	115.4	106.0
0.10	194.3	119.0
0.05	286.7	125.0
0.025	579.8	136.0
0.010	1,627.0	152.0
0.005	2,073.1	156.0
0.0032	2,120.8	156.0

* Based on 1 g/s emission rate of pollutant.

TABLE 5-6. Exposure/dose summaries for three facilities calculated for estimated PCDD emissions.

Concentration ($\mu\text{g}/\text{m}^3$)	Exposure (1000's)	Dosage (Con x Exp)
(a) Facility size: Small		
Location: Rural (Humboldt County)		
1.8×10^{-10}	0.6	1.01×10^{-10}
1.0×10^{-10}	1.7	2.6×10^{-10}
5.1×10^{-11}	2.2	3.2×10^{-10}
2.0×10^{-11}	10.7	6.1×10^{-10}
1.0×10^{-11}	11.9	6.3×10^{-10}
5.1×10^{-12}	20.4	6.9×10^{-10}
2.0×10^{-12}	34.2	7.3×10^{-10}
1.6×10^{-12}	34.7	7.3×10^{-10}
(b) Facility size: Large		
Location: Rural (Butte County)		
1.4×10^{-7}	2.1	2.9×10^{-7}
8.4×10^{-8}	2.1	2.9×10^{-7}
4.2×10^{-8}	2.1	2.9×10^{-7}
2.1×10^{-8}	3.9	3.5×10^{-7}
8.4×10^{-9}	12.5	4.6×10^{-7}
4.2×10^{-9}	17.8	4.9×10^{-7}
2.1×10^{-9}	24.0	5.1×10^{-7}
8.4×10^{-10}	33.3	5.3×10^{-7}
4.2×10^{-10}	35.0	5.3×10^{-7}
3.8×10^{-10}	35.3	5.3×10^{-7}
(c) Facility size: Medium		
Location: Urban (Los Angeles County)		
1.7×10^{-7}	3.1	5.1×10^{-7}
1.4×10^{-7}	3.1	5.1×10^{-7}
7.2×10^{-8}	8.2	9.3×10^{-7}
2.9×10^{-8}	30.2	1.8×10^{-6}
1.44×10^{-8}	65.5	2.5×10^{-6}
7.2×10^{-9}	115.4	3.1×10^{-6}
2.9×10^{-9}	194.3	3.4×10^{-6}
1.4×10^{-9}	286.7	3.4×10^{-6}
7.2×10^{-10}	579.8	3.9×10^{-6}
2.9×10^{-10}	1,627.0	4.4×10^{-6}
1.4×10^{-10}	2,073.1	4.5×10^{-6}
9.2×10^{-11}	2,120.8	4.5×10^{-6}

learned that the concentration of PCP measured at one facility in Fresno County was only $0.14 \mu\text{g}/\text{m}^3$.

The determination of the risk to an individual and to a community for a particular pollutant is a detailed process involving the evaluation of the toxicological data. Such an evaluation has been performed for the PCDDs and PCDFs by the California Department of Health Services (DHS, 1986). In the report, different scenarios are discussed for ranking the various isomers of dioxins and dibenzofurans according to their propensity to cause cancer. The South Coast Air Quality Management District (SCAQMD) requires the use of Scenario 4 (E. Nelson, personal communication) for risk assessments in its region. Since the facility in Los Angeles County has the highest population exposures, due to the large nearby population, we chose it in performing a sample risk assessment. Using the risk estimates from Scenario 4 (DHS, 1986), we calculated the risk due to the emissions of PCDDs and PCDFs from the facility. The results are shown in Table 5-7. These risk estimates are based on the following relationship:

$$IR = Q_i \text{ (g/s)} \cdot E_i \cdot x_i \frac{(\mu\text{g} \cdot \text{s})}{(\text{m}^3 \cdot \text{g})} \cdot \text{URF}_i \frac{(\text{m}^3 \text{ chance})}{(\mu\text{g} \times 70 \text{ yr})} \cdot 70 \text{ yr}$$

where

IR = Aggregate Individual Risk (70-year lifetime)

Q_i = Emission of component (isomer) i

E_i = Proportion (potency ratio) of isomer i (from DHS, 1986)

x_i = Calculated maximum concentration (from Table 5-5c)

URF_i = Unit Risk Factor for TCDD $(38 \mu\text{g}/\text{m}^3)^{-1}$ (from DHS, 1986)

The risk calculations shown in Table 5-7 show that the 3100 persons (as shown in Table 5-5c) that are exposed to the highest concentrations from the facility in Los Angeles County, face an individual aggregate risk of 1.12×10^{-8} due to the PCDD and PCDF emissions. This level is well below the SCAQMD's critical level of concern for individual lifetime toxic risk of 1×10^{-6} .

TABLE 5-7. Emissions Estimate for Los Angeles using Scenario 4 (DHS, 1986) *

Compound	Emissions (DaRos, 1982) (g/yr)	Emissions (DaRos, 1982) (g/s)	Equivalent 2,3,7,8 TCDD Proportion	Risk due to Individual Isomer
4CDD	1.91E-06	6.05E-14	4.50E-02	5.91E-13
5CDD	9.12E-04	2.89E-11	7.10E-02	4.46E-10
6CDD	1.08E-03	3.42E-11	9.00E-03	6.69E-11
7CDD	2.07E-02	6.57E-10	1.50E-02	2.14E-09
8CDD	7.05E-01	2.23E-08	0.00E+00	0.00E+00
4CDF	4.06E-03	1.29E-10	2.60E-02	7.28E-10
5CDF	9.53E-03	3.02E-10	7.20E-02	4.73E-09
6CDF	2.11E-02	6.70E-10	7.56E-03	1.10E-09
7CDF	1.91E-02	6.05E-10	1.50E-02	1.97E-09
8CDF	7.46E-04	2.37E-11	0.00E+00	0.00E+00
Aggregate Risk over 70 years to an individual				1.12E-08

* Based on revised data received subsequent to the completion of the draft report. The composition of the PCDF isomers are reported in Appendix H. This table was changed to reflect the new data and represents the best estimate available at the time of completion of the final report.

6 CONCLUSIONS AND RECOMMENDATIONS

This section summarizes the major conclusions of this study of airborne emissions of chlorophenol and associated polychlorinated dioxins (PCDDs) and furans (PCDFs) resulting from forest products industrial sites in California. Recommendations are also made regarding additional work that would be useful in characterizing the ultimate fate of chlorophenol-treated wood and possible population exposure to toxic airborne substances to supplement this assessment of direct emissions at industrial facilities in California.

CONCLUSIONS

Potential emissions to the atmosphere of polychlorinated PCDD and PCDF, which are highly toxic chemicals, is a public health issue of concern to the ARB. These chemicals are known to be contaminants of chlorophenol, which is used in the forest products industry as a wood preservative. PCDD and PCDF can also be formed when chlorophenol-treated wood is burned. This study is the first detailed assessment of chlorophenol use in the forest products industry in California. The specific sites at which chlorophenols are used were identified as well as the potential pathways by which chlorophenols and their contaminants can be released to the atmosphere. Emission factors were developed and coupled with chlorophenol use and engineering data to derive emission rates. These rates were then used to estimate atmospheric concentrations and potential population exposure.

Chlorophenols are currently used in the forest products industry in California as fungicides to preserve wood used outdoors and to prevent sap-stain, mold growth, and termite and bacterial action. Approximately 900 to 1000 tons of chlorophenols are used in California annually, essentially all of it in the forest products industry. Approximately 98 percent of the chlorophenol used in the state is in the form of PCP, which is applied under pressure to such wood products as utility poles and railroad ties. There are five pressure treatment facilities in the state. Approximately 2 percent of the chlorophenol used is in the form of TCP, which is applied to the wood in dip or spray treatment systems at four sawmills in the state. All PCP sold in California is manufactured by Vulcan Chemicals.

Pressure treaters purchase PCP directly from Vulcan. Historically, non-pressure treaters purchased TCP from Chapman Chemical Company, the sole reformulator of TCP. However, TCP is no longer manufactured; therefore, the currently limited use of TCP is expected to drop to zero when existing supplies are used up.

Four independent means of surveying chlorophenol use in California were used to assess the uncertainty of chlorophenol-use estimates. We used statistics from the California Department of Food and Agriculture, sales data from Vulcan and Chapman Chemical companies, information from the International Statistics Council (sponsored by the American Wood Preservers Institute), and survey data collected by Systems Applications specifically for this study directly from pressure treatment facilities and sawmills in the state. The information obtained from these data was remarkably consistent, suggesting that annual PCP use in the state during 1984 to 1986 is approximately 932 tons. The largest and smallest estimates of PCP use were within 6 percent of this average estimate. Also, the limited data available for subsequent years suggests that PCP use is consistent from one year to the next. TCP annual use was estimated at approximately 12 tons (less than 2 percent of PCP annual use), with upper and lower estimates of 34 and 0 tons, respectively. As noted, TCP is not expected to be used at all in the near future as existing supplies are depleted. When this occurs, there will be only five pressure treaters in the state using PCP; these facilities are located in Butte, Los Angeles, San Joaquin, Fresno, and San Diego counties.

The principal pathway whereby chlorophenol and associated polychlorinated PCDD and PCDF contaminants can be released to the atmosphere was found to be evaporation. Evaporation occurs when treated wood is initially removed from the pressure chamber or dip tank and, over a longer period of time, when the treated product is stored on site. One interesting and unexpected finding of this study was that only miniscule quantities of treated wood are burned in California; thus, combustion does not appear to be a significant pathway for atmospheric emissions. Fugitive emissions from chlorophenol storage, mixing, handling, and treatment facility cleaning operations appear to be quite small compared to estimated evaporative emissions.

The estimation of emission rates of chlorophenols and their polychlorinated PCDD and PCDF contaminants is much more uncertain than the estimation of the quantities of chlorophenols used in the state. It is this step that contributes most to the uncertainty in the emission estimates made in this study. By far, the largest source of airborne chlorophenols from forest products industry sites appears to be the evaporation of chlorophenols from the treated wood, particularly immediately after treatment. Evaporation estimates were made on the basis of various independent

methods. Theoretical models of evaporation were applied for the particular chemical species and ambient conditions representative of California facilities. The results derived from the application of these models were compared with measurements made in the laboratory and the field and were found to be in remarkable agreement in the case of the pressure treaters. Other experimental results were much higher than these two values; however, these values were not used in this study because the experimental conditions were not representative of actual operations in the California forest products industry. The chlorophenol air emission rate is only 0.01 percent of the chlorophenol used by California pressure treaters. The air emission rate from the nonpressure (dip and spray) treatment facilities was found to be higher because of the much larger surface area of the treated wood and because, without pressure treatment to force chlorophenol deep into the wood, more chlorophenol is available for release to the atmosphere. Also, the chlorophenol treating solutions are stored in open tanks, which makes more chlorophenol available for evaporation. Thus, for the dip and spray facilities, we estimate that 3 percent of the chlorophenol used escapes to the atmosphere via evaporation.

Experimental data and standard emission estimation procedures were used to estimate fugitive emissions of chlorophenol to the atmosphere. These calculations indicate that these emissions are much smaller than the evaporative losses.

Estimation of the emission rates of PCDDs and PCDFs is more important for the purposes of this study than estimation of chlorophenol emission rates because of the toxicity of PCDD and PCDF. Emissions of these substances are uncertain because of uncertainties in the estimation of their relative concentration in chlorophenols used by the forest products industry. We obtained information on PCDD and PCDF content from the open literature, Vulcan Chemical Co., and the California State Water Control Board. These contamination values vary considerably on the basis of measurement technique and data source. This variability is understandable considering that (1) analytical techniques such as gas and liquid chromatography are accurate to no more than ± 30 percent, and (2) PCDD and PCDF content would be expected to vary over time depending on the formation and destruction reactions that are a function of heat, sunlight, and the presence of various cosolvents. We have used the California State Water Control Board chlorophenol contamination data because we believe them to be most representative of chlorophenol contamination in the field and because they are more conservative (i.e., have higher PCDD and PCDF content) than the manufacturers' data.

For estimates based on laboratory and field measurements, the emission rates of PCDDs and PCDFs were assumed to be in the same proportion as

their concentrations in the chlorophenols, which is a conservative assumption considering their lower vapor pressures. For estimates based on theoretical evaporation models, the vapor pressures of the PCDDs and PCDFs were explicitly accounted for.

Although our survey indicates that extremely small quantities of chlorophenol-treated wood are burned in the state, we investigated the possible formation of PCDDs and PCDFs during the combustion process. Although there are considerable laboratory data suggesting that chlorophenols react when heated to form PCDDs and PCDFs, the amount formed is a strong function of combustion conditions and the presence of other associated species. One study indicated that approximately 1 to 2 percent of the chlorophenol in treated wood is converted to PCDDs and PCDFs when burned. However, emission tests on chlorophenol-treated wood burned in an industrial boiler found PCDDs and PCDFs in the fly ash and bottom ash collected in the emission control device and the boiler, but none in the flue gas. We believe these results to be most relevant to California; however, to be conservative, we have also estimated PCDD and PCDF emissions based on the less representative laboratory data to provide an upper bound. Regardless of the assumptions regarding PCDD and PCDF production during combustion, this study indicates that combustion is a minor source of PCDD and PCDF emissions from the forest products industry in California compared to potential emissions from evaporative losses.

In addition, a theoretical chemical mechanism was applied to estimate the potential for photochemical reactions in the atmosphere to convert chlorophenols to PCDDs and PCDFs. These calculations indicate that this potential pathway is an insignificant source. One study shows that the highly toxic 2,3,7,8-tetra isomer of PCDD decomposes rapidly when exposed to sunlight.

In summary, approximately 932 tons of PCP are used each year in California by pressure treaters. Only 0.01 percent of the chlorophenol used is estimated to escape to the atmosphere, largely from evaporative losses. This amounts to 0.08 ton/yr or 160 lb/yr total from the five pressure treaters in the state. This amount of chlorophenol use and emissions to the atmosphere is expected to continue in the future. Only approximately 12 tons of TCP are currently used per year by the nonpressure treaters in California, and this use is expected to stop in the near future as the limited stock of tetrachlorophenol is used up. Most of the current chlorophenol emissions to the atmosphere in the state are estimated to result from nonpressure treaters because of the greater surface area of treated wood and because more chlorophenol is available at the surface of the wood for evaporation. Nearly 4 percent of the chlorophenol used by the nonpressure treaters in California is estimated to be released to the atmosphere. Although future emissions will be zero, current chlorophenol emissions

from these sources are nearly 6 times greater than those from the pressure treaters. Only 0.006 ton/yr or 11 lb/yr of chlorophenol is estimated to end up in woodwaste; half of this is disposed of by burning and the remainder by landfill disposal or as feedstock for other products, such as paper pulp.

The use of 944 tons/yr of chlorophenol by the forest products industry in California results in the following statewide annual air emissions: 0.54 tons of chlorophenol, 6.6×10^{-6} tons (0.01 lb) of PCDDs, and 4.5×10^{-7} tons (0.001 lb) of PCDFs.

The risk to the population from estimated PCDD and PCDF emissions for the facility (located in Los Angeles County) with the highest potential for exposing the general population was also examined. Using the Department of Health Services methods, the individual aggregate risk resulting from these air emissions is estimated to be 1.12×10^{-8} . This is well below the action risk level of 1×10^{-6} . Accordingly, no significant risk is projected due to PCDD and PCDF air directly emitted from the chlorophenol wood treatment industry.

Potential Substitutes for Chlorophenol Use in Wood Treatment

Emissions of chlorophenol and its toxic contaminants could be reduced by use of practical chemical substitutes for chlorophenol as a wood preservative. Such substitutes include creosote and inorganic arsenicals, though both substances are also under review by the EPA. Arsenicals are likely substitutes for reasons of cleanliness, freedom from odor, ease of handling, and lower cost. Copper naphthenate, zinc naphthenate, tributyltin-oxide, acid copper chromate, and chromated zinc chloride are also possible substitutes for chlorophenol as a wood preservative. Copper-8-quinolate or rapid kiln drying can replace chlorophenol use for the control of sapstain fungi. (Note: kiln drying cannot be used for export because lumber placed in a ship's holds will become moist and susceptible to sapstain.). A final alternative is replacement of treated wood by untreated wood, concrete, and/or steel.

RECOMMENDATIONS FOR ADDITIONAL RESEARCH

This study was limited to emissions of chlorophenols, PCDDs, and PCDFs directly associated with the application processes and waste disposal practices of the forest products industry in California. However, it is our belief that larger emissions and population exposures may be associated with the ultimate fate of most of the chlorophenol used in California, which remains in the wood products themselves. Therefore, it

is the handling, use, and disposal of these end products that may have the greatest impact on atmospheric emissions of these chemicals. For example, one of the major public utilities in California purchases about 35,000 PCP-pressure-treated utility poles annually. That same utility company disposes of nearly 15,000 treated poles annually. Preliminary investigation has revealed that 50 percent of these treated poles are cut into smaller pieces and reused for outdoor purposes such as fencing and parking barriers. The remaining poles are reportedly placed in land fills. The disposal of the treated poles represents a major uncertainty in the ultimate fate of chlorophenol used in California. The quantification of the disposal practices of treated wood products following their useful lifetime is of paramount importance in better understanding the emission of chlorophenols and associated PCDDs and PCDFs to the atmosphere. If, for example, treated wood is burned in residential fireplaces and wood stoves, this may constitute a significant public health risk. Thus, further study of the ultimate fate and emissions and population exposures resulting from chlorophenol-treated wood may be appropriate.

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Appendix A

REGULATORY STATUS AND POTENTIAL SUBSTITUTES FOR
THE USE OF CHLOROPHENOL IN WOOD TREATMENT

Appendix A

REGULATORY STATUS AND POTENTIAL SUBSTITUTES FOR THE USE OF CHLOROPHENOL IN WOOD TREATMENT

PCP and TCP are regulated under two federal laws. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) regulates use and registration; the Resource Conservation and Recovery Act (RCRA) regulates disposal of these acutely hazardous wastes. The EPA is tightening use requirements in a process begun in 1978. When the EPA determines that the risks of using a product outweigh the benefits, the first step towards reversing this is the issuance of Rebutable Presumptions Against Registration (RPAR).

In 1978 the EPA issued RPARs for products containing chlorophenol. (43 FR 48443). In 1981, after analyzing comments received by registrants, the EPA issued a preliminary Notice of Intent to Conclude the RPAR process for chlorophenol. This notice means that the EPA's next step will be to promulgate specific cases in which registration of the product will be cancelled. In 1984, the EPA issued a Notice of Intent to Cancel chlorophenol registrations. This was amended in 1986 (51 FR 1334). Registration requirements for PCP include the following:

- (1) All uses will be classified as restricted;
- (2) Closed emptying and mixing systems will be required for prilled, flaked, and powdered forms of PCP and pentachlorophenolate;
- (3) Specific requirements regarding the wear and disposal of protective clothing and equipment;
- (4) Prohibitions against eating, drinking, or smoking during application of PCP products;
- (5) Requirements for proper disposal of PCP waste;
- (6) Restrictions against using PCP indoors, or on wood intended for interior use;

- (7) Restrictions against using PCP in a manner that could result in direct exposure to animals or livestock, or in contamination of food, feed, or drinking and irrigation water;
- (8) Requirement for a teratogenicity label warning (teratogenicity means a compound causing developmental malformations and monstrosities in fetuses); and
- (9) Limitation on permissible amounts of hexachlorodibenzo-p-dioxin (HxCDD).

The chlorophenol restricted-use classification applies to all uses of PCP as a wood preservative. These uses include pressurized and nonpressurized treatment of wood products, home use, farm use, repair of railroad ties, groundline treatment of utility poles, and sapstain control. This classification means that the product can only be sold to and used by certified applicators or people under their direct supervision. The applicators are subject to various protective clothing requirements; must not eat, drink, or smoke at times when they could come into contact with the product; and must wash thoroughly after using the product.

In addition, powdered, prilled, or flaked forms of PCP are to be used in closed emptying or mixing systems. A closed system is defined as any containment that prevents the release of the chemical into the surrounding environment. Incidental releases during equipment loading or cleaning or other maintenance operations are not considered to be breaches of containment.

Manufacturers of products containing PCP must either describe the specific PCP product they are using, or state that their products conform to the maximum permissible limits for HxCDD and other contaminants present in their products. Permissible concentrations of HxCDD in PCP are currently set forth in a settlement agreement between manufacturers of PCP and the EPA. This agreement will form the basis of a second amended Federal Register Notice of Intent to Cancel registrations of PCP products. The allowed concentrations are as follows:

Year after Publication of Second Amended Notice	HxCDD Concentrations	
	Maximum Allowed	Average
1	15 ppm	NA
2	6 ppm	3 ppm
3	4 ppm	2 ppm

The average concentration will be calculated on the basis of the average of all shipments during a month. The stated reduction in HxCDD must be achieved without increasing the amount of hexachloro-benzene (HCB) beyond 75 ppm. This is the maximum level currently found in PCP products. Also, PCP products must contain no more than 1 ppb of 2,3,7,8-TCDD (this is the limit of detection). To ensure compliance with these limitations, every batch of a product containing PCP must be sampled and analyzed for HxCDD content using an EPA-approved method. Analysis for HCB and 2,3,7,8-TCDD must be performed monthly. Violations will be dealt with through stop-sale orders. In addition, manufacturers must monitor levels of total tetra-, penta-, hexa-, and hepta-chlorinated dibenzo-p-dioxins (PCDDs), and tetra-, penta-, hexa-, and hepta-chlorinated dibenzofurans (PCDFs). This monitoring must also be performed monthly (or after the the production of 120 batches).

Proper disposal of PCP is covered under regulations governing the disposal of organic pesticides. As a general guideline, the owner of excess pesticides should try to return them to the manufacturer for potential relabeling, recovery, or reprocessing. Under certain conditions, the EPA Administrator may also accept the pesticide for disposal. Recommended procedures for pesticide disposal when the manufacturer will not accept the pesticide are as follows (by order of preference):

- (1) Incineration (as a minimum, all emissions must meet Clean Air Act and other requirements relating to gaseous emissions and disposal of residues);
- (2) Burial in a specially designated landfill;
- (3) Soil injection (with specific guidance from the EPA Regional Administrator);
- (4) Chemical degradation methods (with guidance from the EPA Regional Administrator);
- (5) Temporary storage (if none of the above are available or feasible); and
- (6) Deep-well injection (on proof that reasonable alternative measures have been explored and found less satisfactory in terms of environmental protection).

Finally, the EPA promulgated final regulations on November 7, 1987 regarding restrictions on the land disposal of specific hazardous wastes. In general, solvent wastes and dioxin-containing wastes are prohibited from land disposal except under certain conditions. Unless certain conditions are met, the regulations specifically prohibit the land disposal of the following EPA hazardous wastes after November 8, 1988: F020, F021, F023, F026, F027, and F028. Table A-1 provides descriptions of each of these dioxin-containing wastes.

Land disposal of these wastes can be permitted if one or more of the following conditions are met:

- (1) The wastes are treated to achieve concentrations of the hazardous constituents below amounts stated in the regulations. The concentrations for the hazardous constituents in the dioxin-containing wastes are presented in Table A-2.
- (2) The wastes are disposed of at land disposal units for which petitions from the exemption have been granted by EPA. A petition may be granted only if a demonstration is made to EPA that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the wastes remain hazardous. Such demonstration must contain a "reasonable degree of certainty" and must include components specified in the regulations (40 CFR 268.6).
- (3) An extension has been granted (up to 2 years after November 8, 1988) for disposal in landfills or surface impoundments. Extensions may be granted only upon a showing that there is insufficient capacity for treatment, and that the applicant has made a good faith effort to locate alternative treatment, recovery, and disposal services. (Such disposal services must meet the requirement stated in item (2) above.)

Between November 8, 1986 and November 8, 1988, the wastes may be disposed of in a landfill or surface impoundment if the facility meets the requirements specified in the regulations.

TABLE A-1. Dioxin-Containing Wastes

Industry and EPA Hazardous Waste No.	Hazardous Waste
F020	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri-, or tetrachlorophenol, or of intermediates used to produce their pesticide derivatives. (This listing does not include waste from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol).
F021	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol, or of intermediates used to produce its derivatives.
F026	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.
F027	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component).
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027.

Source: 40 CFR 261.31

TABLE A-2. Concentration of constituent in waste extract, below which land disposal not prohibited.

F020-F023 and F026-F028 Dioxins Containing Wastes	Concentration
HxCDD - All hexachlorodibenzo-p-dioxins	< 1 ppb
HxCDF - All hexachlorodibenzofurans	< 1 ppb
PeCDD - All pentachlorodibenzo-p-dioxins	< 1 ppb
PeCDF - All pentachlorodibenzofurans	< 1 ppb
TCDD - All tetrachlorodibenzo-p-dioxins	< 1 ppb
TCDF - All tetrachlorodibenzofurans	< 1 ppb
2,4,5 trichlorophenol	< 0.05 ppm
2,4,6 trichlorophenol	< 0.05 ppm
2,3,4,6 tetrachlorophenol	< 0.10 ppm
Pentachlorophenol	< 0.01 ppm

Source: 40 CFR 268.41

Appendix B

FEDERAL STANDARD INDUSTRIAL CLASSIFICATION
FOR LUMBER AND WOOD PRODUCTS, EXCEPT FURNITURE

Major Group 24.—LUMBER AND WOOD PRODUCTS, EXCEPT FURNITURE

The Major Group as a Whole

This major group includes logging camps engaged in cutting timber and pulpwood; merchant sawmills, lath mills, shingle mills, cooperage stock mills, planing mills, and plywood mills and veneer mills engaged in producing lumber and wood basic materials; and establishments engaged in manufacturing finished articles made entirely or mainly of wood or wood substitutes. Certain types of establishments producing wood products are classified elsewhere. For example, furniture and office and store fixtures are classified in Major Group 25; musical instruments, toys, and playground equipment, and caskets in Major Group 39. Woodworking in connection with construction, in the nature of reconditioning and repair, or performed to individual order, is classified in non-manufacturing industries.

Group Industry
No. No.

241 LOGGING CAMPS AND LOGGING CONTRACTORS

2411 Logging Camps and Logging Contractors

Logging camps and logging contractors primarily engaged in cutting timber and in producing rough, round, hewn, or riven primary forest or wood raw materials. Independent contractors engaged in estimating or trucking timber, but who perform no cutting operations, are classified in nonmanufacturing industries. Logging and woods operations conducted in combination with sawmills, pulp mills, or other converting establishments, and not separately reported, are classified in their respective industry groups; namely, with sawmills in Group 242, veneer and plywood mills in Group 243, pulp mills in Major Group 26, and charcoal and wood distillation plants in Group 286. Establishments primarily engaged in the collection of bark, sap, gum, and other forest byproducts are classified in Major Group 08.

Bolts, wood: handle, heading, shingle, stave, etc.
Booming timber
Burls, wood
Croches, wood
Driving timber
Excelsior stock, hewn
Last blocks, wood: hewn or riven
Logging camps and logging contractors, not operating sawmills
Legs
Mine timbers, hewn
Peeler logs
Pickets and paling: round or split
Piling, wood: untreated
Pole cutting contractors

Poles, wood: untreated
Posts, wood: hewn, round or split
Pulpwood camps
Pulpwood contractors engaged in cutting, not operating pulp mills
Rails, fence: round or split
Saw logs
Skidding logs
"Stumping" for turpentine or powder manufacturing
Stumps
Ties, railroad: hewn
Timber (product of logging camps)
Veneer logs
Wheelstock, hewn

242 SAWMILLS AND PLANING MILLS

2421 Sawmills and Planing Mills, General

Establishments primarily engaged in sawing rough lumber and timber from logs and bolts, or resawing cants and fitches into lumber, including box lumber and softwood cut stock; planing mills combined with sawmills; and separately operated planing mills which are engaged primarily in producing surfaced lumber and standard workings or patterns of lumber. This industry includes establishments primarily engaged in sawing lath and railroad ties, and in producing tobacco hogshead stock, wood chips, and snow fence lath. Establishments primarily engaged in manufacturing box shoo or boxes are classified in Group 244; sash, doors, wood molding, window and door frames, and other fabricated millwork in Group 243; and hardwood dimension and flooring in Industry 2426. Logging camps combined with sawmills, when not separately reported, are included in this industry.

Group Industry
No. No.

242 SAWMILLS AND PLANING MILLS—Continued

2421 Sawmills and Planing Mills, General—Continued

<p>Cants, resawed (lumber) Ceiling lumber, dressed Chipper mills Custom sawmills Cut stock, softwood Flitches (veneer stock), made in sawmills Flooring (dressed lumber), softwood Fuelwood, from mill waste Kiln drying of lumber Lath, made in sawmills and lathmills Logging camps combined with sawmills Lumber, kiln drying of Lumber: rough, sawed, or planed Lumber stacking or sticking</p>	<p>Planing mills, independent: except millwork Planing mills, operated in conjunction with sawmills Resawing lumber into smaller dimensions Sawdust and shavings Sawmills, except special product mills Siding (dressed lumber) Silo stock, wood: sawed Snow fence lath Ties, railroad: sawed Tobacco hogshead stock Wood chips manufacturing</p>
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2426 Hardwood Dimension and Flooring Mills

Establishments primarily engaged in manufacturing hardwood dimension lumber and workings therefrom; and other hardwood dimension, semifabricated or ready for assembly; hardwood flooring; and wood frames for household furniture. Establishments primarily engaged in manufacturing stairwork, molding, and trim are classified in Industry 2431; and those manufacturing textile machinery bobbins, picker sticks, and shuttles in Industry 3552.

<p>Blanks, wood: for bowling pins, handles, and textile mach. accessories Blocks, wood: for bowling pins, handles, and textile mach. accessories Bobbin blocks and blanks, wood Brush blocks, wood: turned and shaped Carvings, furniture: wood Chair frames for upholstered furniture, wood Chair seats, hardwood Dimension, hardwood Flooring, hardwood Frames for upholstered furniture, wood Furniture dimension stock, hardwood</p>	<p>Furniture squares, hardwood Furniture turnings and carvings, wood Gun stocks, wood Handle blanks, wood Handle stock, sawed or planed Lumber, hardwood dimension Parquet flooring, hardwood Picker stick blanks Rounds or rungs, ladder and furniture: hardwood Shuttle blocks: hardwood Spool blocks and blanks, wood Stock, chair: hardwood—turned, shaped, or carved Table slides, for extension tables: wood Turnings, furniture: wood Vehicle stock, hardwood</p>
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2429 Special Product Sawmills, Not Elsewhere Classified

Mills primarily engaged in manufacturing excelsior, wood shingles, and cooperage stock; and in sawing special products, not elsewhere classified.

<p>Barrel heading and staves, sawed or split Cooperage stock mills Cooperage stock: staves, heading, and hoops—sawed or split Excelsior, including pads and wrappers: wood Hoops, wood: for tight or slack cooperage—sawed or split</p>	<p>Sawmills, special product: except lumber and veneer mills Shakes (hand split shingles) Shingle mills Shingles, wood: sawed or hand split Wood wool (excelsior) Wrappers, excelsior</p>
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243 MILLWORK, VENEER, PLYWOOD, AND STRUCTURAL WOOD MEMBERS

2431 Millwork

Establishments primarily engaged in manufacturing fabricated millwork. Planing mills primarily engaged in producing millwork are included in this industry, but planing mills primarily producing standard workings or patterns of lumber are classified in Industry 2421. Establishments primarily manufacturing wood kitchen cabinets and bathroom vanities are classified in Industry 2434.

Group Industry
No. No.

243 MILLWORK, VENEER, PLYWOOD, AND STRUCTURAL WOOD MEMBERS—Con.

2431 Millwork—Continued

<p>Awnings, wood Blinds (shutters), wood Brackets, wood Door shutters, wood Door trim, wood Doors, combination screen-storm: wood Dormers, wood Floor baseboards, wood Garage doors, overhead: wood Jalousies, glass: wood frame Louver windows and doors, glass with wood frame Millwork products Moldings, wood: unfinished and pre-finished Newel posts, wood Ornamental woodwork: cornices, mantels, etc. Panel work, wood Planing mills, millwork</p>	<p>Porch work, wood Railings, stair: wood Sash, door and window: wood Screens, door and window: wood Shutters, door and window: wood Silo staves, wood Stair railings, wood Staircases and stairs, wood Trellises, wood Trim, wood Venetian blind slats, wood Wainscots, wood Weather strip, wood Window frames and sash, wood Window screens, wood Window trim, wood Woodwork, interior and ornamental: windows, doors, sash, mantels, etc.</p>
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2434 Wood Kitchen Cabinets

Establishments primarily engaged in manufacturing wood kitchen cabinets and wood bathroom vanities.

<p>Cabinets, to be built-in: wood Kitchen cabinets, wood: factory made</p>	<p>Vanities, bathroom and other</p>
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2435 Hardwood Veneer and Plywood

Establishments primarily engaged in producing commercial hardwood veneer, either face or technical, and those primarily engaged in manufacturing commercial plywood, or prefinished hardwood plywood. This includes nonwood backed or faced veneer and nonwood faced plywood, from veneer produced in the same establishment or from purchased veneer. Establishments primarily engaged in the production of veneer which is used in the same establishment for the manufacture of end products such as fruit and vegetable baskets and wood boxes are classified in Industries 2441 and 2449.

<p>Panels, hardwood plywood Plywood, hardwood or hardwood faced Prefinished hardwood plywood</p>	<p>Veneer mills, hardwood Veneer stock, hardwood</p>
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2436 Softwood Veneer and Plywood

Establishments primarily engaged in producing commercial softwood veneer and plywood, from veneer produced in the same establishment or from purchased veneer. Establishments primarily engaged in producing commercial hardwood veneer and plywood are classified in Industry 2435. Establishments primarily engaged in the production of veneer which is used in the same establishment for the manufacture of end products such as fruit and vegetable baskets and wood boxes are classified in Industries 2441 and 2449.

<p>Panels, softwood plywood Plywood, softwood</p>	<p>Veneer mills, softwood Veneer stock, softwood</p>
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2439 Structural Wood Members, Not Elsewhere Classified

Establishments primarily engaged in producing laminated or fabricated trusses, arches, and other structural members of lumber. Establishments primarily engaged in fabrication on the site of construction are classified in Division C, Construction. Establishments primarily engaged in producing prefabricated wooden buildings, sections, and panels are classified in Industry 2452.

Structural members, laminated wood:
arches, trusses, timbers, etc.

Group Industry
No. No.
244

WOOD CONTAINERS

2441 Nailed and Lock Corner Wood Boxes and Shook

Establishments primarily engaged in manufacturing nailed and lock corner wood boxes (lumber or plywood), and which also may produce shook for nailed and lock corner boxes.

Ammunition boxes, wood
Box cleats, wood
Boxes, wood: plain or fabric covered,
nailed or lock corner
Carrier trays, wood
Cheats for tools, etc.: wood
Cigar boxes, wood and part wood
Egg cases, wood

Flats, wood: greenhouse
Packing cases, wood: nailed or lock
corner
Shipping cases, wood: nailed or lock
corner
Shook, box
Trunk slats, wood

2448 Wood Pallets and Skids

Establishments primarily engaged in manufacturing wood and wood-metal combination pallets and skids.

Cargo container and pallet combination,
wood or wood and metal combination
Pallet containers, wood or wood and
metal combination

Pallets and skids, wood or wood and
metal combination
Skids and pallets, wood or wood and
metal combination

2449 Wood Containers, Not Elsewhere Classified

Establishments primarily engaged in manufacturing wood containers, not elsewhere classified, such as cooperage, wirebound boxes and crates, and other veneer and plywood containers. Establishments primarily engaged in manufacturing tobacco hogshead stock are classified in Industry 2421, and those manufacturing cooperage stock in Industry 2429.

Barrels, wood: coopered
Baskets, fruit and vegetable: till, berry,
climax, round stave, etc.
Berry cups, veneer and splint
Boxes, wood: wirebound
Buckets, wood: coopered
Casks, wood: coopered
Chicken coops (crates), wood: wire-
bound for shipping poultry
Climax baskets
Containers except boxes, veneer and
plywood
Containers made of staves
Cooperage
Crates: berry, butter, fruit, and vege-
table—wood, wirebound
Drums, plywood
Drums, shipping: wood—wirebound
Firkins and kits, wood: coopered

Fruit baskets, veneer and splint
Hampers, fruit and vegetable: veneer
and splint
Hogsheads, wood: coopered
Kegs, wood: coopered
Kits, wood: coopered
Market baskets, fruit and vegetable:
veneer and splint
Pails, plywood
Pails, wood: coopered
Splint baskets, for fruits and vege-
tables
Tanks, wood: coopered
Tierces (cooperage)
Till baskets, veneer and splint
Tobacco hogsheads
Tubs, wood: coopered
Vats, wood: coopered
Vegetable baskets, veneer and splint

245 WOOD BUILDINGS AND MOBILE HOMES

2451 Mobile Homes

Establishments primarily engaged in manufacturing mobile homes. These mobile homes are generally over 35 feet long, at least 8 feet wide, do not have facilities for storage of water or waste, and are equipped with wheels. These products may also have nonresidential uses, such as classrooms or offices. Trailers that are generally 35 feet long or less, 8 feet wide or less and with self-contained facilities are classified in Industry 3792. Portable buildings not equipped with wheels are classified in Industry 2452.

Mobile buildings for commercial use
(offices, banks, etc.)
Mobile classrooms

Mobile dwellings
Mobile homes, except recreational

Group Industry
No. No.

245 **WOOD BUILDINGS AND MOBILE HOMES—Continued**

2452 **Prefabricated Wood Buildings and Components**

Establishments primarily engaged in manufacturing prefabricated wood buildings, sections, and panels. Establishments primarily engaged in fabricating buildings on the site of construction are classified in Division C, Construction.

Buildings, prefabricated and portable:
wood
Chicken coops, prefabricated: for housing poultry
Corn cribs, prefabricated: wood
Farm buildings, prefabricated or portable: wood

Houses, portable: prefabricated wood
Marinas, prefabricated: wood
Panels for prefabricated wood buildings
Sauna rooms, prefabricated: wood
Sections for prefabricated wood buildings

249

MISCELLANEOUS WOOD PRODUCTS

2491 **Wood Preserving**

Establishments primarily engaged in treating wood, sawed or planed in other establishments, with creosote or other preservatives to prevent decay and to protect against fire and insects. This industry also includes the cutting, treating, and selling of poles, posts, and piling, but establishments primarily engaged in manufacturing other wood products, which they may also treat with preservatives, are not included.

Bridges and trestles, wood: treated
Creosoting of wood
Cross-ties, treated
Flooring, wood block: treated
Millwork, treated
Mine props, treated
Piles, foundation and marine construction: treated
Piling, wood: treated

Poles and pole crossarms, treated
Poles, cutting and preserving
Posts, wood: treated
Preserving of wood (creosoting)
Railroad cross bridge and switch ties, treated
Structural lumber and timber, treated
Vehicle lumber, treated
Wood products, creosoted

2492 **Particleboard**

Establishments primarily engaged in manufacturing wood panel products from small wood particles. This includes preparation of small particles of wood, drying, mixing with a synthetic resin binder, and compressing. Pressing may take place in hydraulic presses with heated platens or by extrusion.

Particleboard

2499 **Wood Products, Not Elsewhere Classified**

Establishments primarily engaged in turning and shaping wood, and manufacturing miscellaneous wood products, not elsewhere classified, from rattan, reed, splint, straw, veneer, veneer strips, wicker, and willow. This industry also includes establishments manufacturing lasts and related products, cork products, hardboard, and wood or metal mirror and picture frames. Establishments primarily engaged in manufacturing particleboard are classified in Industry 2492, and those manufacturing pallets and skids in Industry 2448.

Applicators, wood
Bakers' equipment, wood
Baskets, except fruit, vegetable, fish and bait: rattan, reed, straw, etc.
Battery separators, wood
Bearings, wood
Beekeeping supplies, wood
Bentwood (steam bent) products, except furniture
Blocks, tackle: wood
Blocks, tailors' pressing: wood
Boards, bagasse
Boards, bulletin: wood and cork
Boards, clip, ironing, meat, and pastry—wood
Boot and shoe lasts, regardless of material
Bowls, wood: turned and shaped
Briquettes, sawdust or bagasse: non-petroleum binder

Bungs, wood
Buoys, cork
Bushings, wood
Cane, chair: woven of reed or rattan
Carpets, cork
Cloth winding reels, wood
Clothes driers (clothes horses), wood
Clothes drying frames, wood
Clothespins, wood
Clubs, policemen's: wood
Cooling towers, wood or wood and sheet metal combination
Cork products
Corks, bottle
Covers, bottle and demijohn: willow, rattan, and reed
Curtain stretchers, wood
Dishes, wood
Display forms for boots and shoes, regardless of material

Group Industry
No. No.

249 MISCELLANEOUS WOOD PRODUCTS—Continued

2499 Wood Products, Not Elsewhere Classified—Continued

<p>Dowels, wood Extension planks, wood Faucets, wood Fellies, wood Fencing, wood except rough pickets, poles and rails Flour, wood Frames: medallion, mirror, photo- graph, and picture—wood or metal Framing pictures and mirrors for the trade Furniture inlays (veneers) Garment hangers, wood Gavels, wood Grain measures, wood: turned and shaped Hammers, meat: wood Hampers, laundry: rattan, reed, splint, veneer, and willow Handles, wood: turned and shaped Hardboard, tempered or untempered Hubs, wood Insulating materials, cork Jacks, ladder: wood Knobs, wood Ladders, wood Last sole patterns, regardless of ma- terial Letters, wood Life preservers, cork Mallets, wood Marbleboard (stone-face hard board) Market baskets, except fruit and vege- table: veneer and splint Marquetry, wood Mashers, potato: wood Masts, wood Mauls, wood Moldings, picture frame: finished Mulch, wood and bark Novelties, wood fiber Oars, wood Pads, table: rattan, reed, and willow Paint sticks, wood Pencil slats Plugs, wood Poles: clothesline, tent, flag, etc.</p>	<p>Pressed logs of sawdust and other wood particles, nonpetroleum binder Pulleys, wood Racks, for drying clothes: wood Rattan ware, except furniture Reed ware, except furniture Reels, cloth winding: wood Reels, for drying clothes: wood Reels, plywood Rollers, wood Rolling pins, wood Rules and rulers, wood Saddle trees, wood Sawdust, reground Scaffolds, wood Scoops, wood Seat covers, rattan Seats, toilet: regardless of material Shoe stretchers, regardless of material Shoe trees, regardless of material Signboards, wood Skewers, wood Snow fence Spars, wood Spigots, wood Spokes, wood Spools except for textile machinery, wood Stakes, surveyors': wood Stepladders, wood Stoppers, cork Tile, cork Tool handles, wood: turned and shaped Toothpicks, wood Trays: wood, wicker, and bagasse Trophy bases, wood Vats, wood: except coopered Washboards, wood and part wood Webbing: cane, reed, and rattan Willow ware, except furniture Wood, except furniture: turned and carved Wood flour Woodenware, kitchen and household Yard sticks, wood</p>
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Appendix C

ARB 1983 FOREST PRODUCT FACILITIES DATA

TABLE C-1. Sawmills, planing & dimensioning mills in California ARB 1983 Emission Data System.
SIC's: 2420 - 2429

COLLINS PINE CO CHESTER COUNTY CODE: 32 FACILITY ID: 15	TAYMAC INDUSTRIES SACRAMENTO COUNTY CODE: 34 FACILITY ID: 30	KELBRO CORP SACRAMENTO COUNTY CODE: 34 FACILITY ID: 83	SF DEBRIS, INC SAN FRANCISCO COUNTY CODE: 38 FACILITY ID: 1215
AMERICAN FOREST PRODUCTS STOCKTON COUNTY CODE: 39 FACILITY ID: 48	LOUISIANA PACIFIC INC BURNLEY COUNTY CODE: 45 FACILITY ID: 6	ROSEBURG LUMBER CO. ANDERSON COUNTY CODE: 45 FACILITY ID: 13	PAUL BUNYAN ANDERSON COUNTY CODE: 45 FACILITY ID: 15
SIERRA PACIFIC INDUSTRIES BURNLEY COUNTY CODE: 45 FACILITY ID: 18	HYAMPOM LUMBER CO REDDING COUNTY CODE: 45 FACILITY ID: 22	SIERRA PACIFIC CENTRAL VALLEY COUNTY CODE: 45 FACILITY ID: 39	HUDSON LMBR CO. ANDERSON COUNTY CODE: 45 FACILITY ID: 40
GIRVAN LMBR CO. ANDERSON COUNTY CODE: 45 FACILITY ID: 41	SIERRA PACIFIC INDUST LOYALTON COUNTY CODE: 46 FACILITY ID: 1	SOUTHWEST FOREST IND HAPPY CAMP COUNTY CODE: 47 FACILITY ID: 27	ANNAPOLIS MILLING, ANNAPOLIS ANNAPOLIS COUNTY CODE: 49 FACILITY ID: 5001
LOUISIANA-PAC CORP CLOVERDALE COUNTY CODE: 49 FACILITY ID: 5012	MASONITE WESTERN LUMBER DIV. CLOVERDALE COUNTY CODE: 49 FACILITY ID: 5015	SNIDER LUMBER PRODUCTS TURLOCK COUNTY CODE: 50 FACILITY ID: 49	LOUISIANA PACIFIC CORP RED BLUFF COUNTY CODE: 52 FACILITY ID: 2
CRANE MILLS PASKENTA COUNTY CODE: 52 FACILITY ID: 3	DIAMOND INTERNATL CORP RED BLUFF COUNTY CODE: 52 FACILITY ID: 4	DIAMOND INTERNATL CORP RED BLUFF COUNTY CODE: 52 FACILITY ID: 13	PACKAGING CO. OF CALIFORNIA RED BLUFF COUNTY CODE: 52 FACILITY ID: 14
LOUISIANA PACIFIC CORP RED BLUFF COUNTY CODE: 52 FACILITY ID: 15	LOUISIANA PACIFIC CORP RED BLUFF COUNTY CODE: 52 FACILITY ID: 16	HARRIS-CRESTLINE CORNING COUNTY CODE: 52 FACILITY ID: 17	TRINITY RIVER LUMBER COMPANY WEAVERVILLE COUNTY CODE: 53 FACILITY ID: 7
SIERRA PACIFIC, IND. HAYFORK COUNTY CODE: 53 FACILITY ID: 8	WICKES FOREST IND COUNTY CODE: 54 FACILITY ID: 2	PICKERING LUMBER COUNTY CODE: 55 FACILITY ID: 1	L S JONES TIMER SOULSBYVILLE COUNTY CODE: 55 FACILITY ID: 3
PICKERING LUMBER CORP LAGRANGE COUNTY CODE: 55 FACILITY ID: 7	DIAMOND INTERNATIONAL CORP LINDA COUNTY CODE: 58 FACILITY ID: 3	ERICKSON LUMBER CO. MARYSVILLE COUNTY CODE: 58 FACILITY ID: 4	SIERRA MOUNTAIN MILLS NORTH SAN JUAN COUNTY CODE: 58 FACILITY ID: 5
SIERRA MOUNTAIN MILLS CELESTIAL VALLEY COUNTY CODE: 58 FACILITY ID: 9	+++++	+++++	+++++

TABLE C-2. Millwork, plywood & structural plants in California ARB 1983 Emission Data System.
SIC's: 2430 - 2439

PACIFIC FINISHING COMPANY PARAMOUNT COUNTY CODE: 19 FACILITY ID: 105	UNIVERSAL EXHIBITS SOUTH EL MONTE COUNTY CODE: 19 FACILITY ID: 181	WHAM-O MFG COMPANY SAN GABRIEL COUNTY CODE: 19 FACILITY ID: 801	SCHRY WAY CASE PASADENA COUNTY CODE: 19 FACILITY ID: 1043
CATALINA FURNITURE LOS ANGELES COUNTY CODE: 19 FACILITY ID: 1169	WESTERN STATES PLYWOOD CORP SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 1284	S & S CASKET SOUTH GATE COUNTY CODE: 19 FACILITY ID: 2006	ARTMASTER STUDIOS, MERCH SAN FERNANDO COUNTY CODE: 19 FACILITY ID: 2972
BAILLY SHOWCASE/FIXTURE LOS ANGELES COUNTY CODE: 19 FACILITY ID: 3060	BALBOA PROD. LOS ANGELES COUNTY CODE: 19 FACILITY ID: 3160	PACIFIC PANEL SYSTEMS SOUTH EL MONTE COUNTY CODE: 19 FACILITY ID: 3193	TEXTONE LA MIRADA COUNTY CODE: 19 FACILITY ID: 3506
LA BANCA CABINET & FORMICA SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 3540	SPECIALTY TOOLS INDUSTRY COUNTY CODE: 19 FACILITY ID: 3743	SINICROPE & SONS ALHAMBRA COUNTY CODE: 19 FACILITY ID: 4793	BASILE CABINETS VAN NUYS COUNTY CODE: 19 FACILITY ID: 5382
AMERICAN SHEDS AZUSA COUNTY CODE: 19 FACILITY ID: 5824	OHLINE CORPORATION GARDENA COUNTY CODE: 19 FACILITY ID: 6163	ACTIVE SUPPLY LOS ANGELES COUNTY CODE: 19 FACILITY ID: 6408	ITAL TECHN NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 6822
PALDINO & SONS GARDENA COUNTY CODE: 19 FACILITY ID: 7909	IVARS CABINET SHOP SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 7943	L & N FIXTURES SOUTH EL MONTE COUNTY CODE: 19 FACILITY ID: 8065	STD CABINET WKS LOS ANGELES COUNTY CODE: 19 FACILITY ID: 8093
DUSCHAKS INTL HELICOPTERS TORRANCE COUNTY CODE: 19 FACILITY ID: 8219	LA BRASS PROD. LOS ANGELES COUNTY CODE: 19 FACILITY ID: 8325	GOLDEN ST CASKET LOS ANGELES COUNTY CODE: 19 FACILITY ID: 8811	THE WOODMART VAN NUYS COUNTY CODE: 19 FACILITY ID: 8912
MCCONNELL CABINETS EL MONTE COUNTY CODE: 19 FACILITY ID: 8918	WST COAST PLYWOOD, TEMPO AZUSA COUNTY CODE: 19 FACILITY ID: 9246	MELLIES CONST NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 9674	T. A. DAVIS NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 10151
THE WOODSHOP SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 11116	GEN VENEER MFG SOUTH GATE COUNTY CODE: 19 FACILITY ID: 12528	ARTCRAFTERS CABINETS NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 12627	COMMODORE PROD., G. J. IND DBA CHAYSWORTH COUNTY CODE: 19 FACILITY ID: 13421
ARTMASTER STUDIOS, MERCH SAN FERNANDO COUNTY CODE: 19 FACILITY ID: 13494	CRAWFORD & SCHROEER MFG INGLEWOOD COUNTY CODE: 19 FACILITY ID: 14094	T & V IND GARDENA COUNTY CODE: 19 FACILITY ID: 14467	PACIFIC GAME NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 15486

TABLE C-2. Millwork, plywood & structural plants in California ARB 1983 Emission Data System.
SIC's: 2430 - 2439

BONDED PROD. SOUTH EL MONTE COUNTY CODE: 19 FACILITY ID: 15989	STONER AMBULANCE MFRS SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 17009	HOWARD E. SHIRLEY CONST CANOGA PARK COUNTY CODE: 19 FACILITY ID: 17613	ZEPHYR SYSTEMS EL MONTE COUNTY CODE: 19 FACILITY ID: 17974
G & H CABINET VAN NUYS COUNTY CODE: 19 FACILITY ID: 18317	EARLS OF BRENTWOOD LOS ANGELES COUNTY CODE: 19 FACILITY ID: 20183	WOOD CITY LOS ANGELES COUNTY CODE: 19 FACILITY ID: 21316	VALLEY PLANING MILL OF VAN NUY VAN NUYS COUNTY CODE: 19 FACILITY ID: 21737
COMPTON UNI SCH DIST, MAINT COMPTON COUNTY CODE: 19 FACILITY ID: 22222	FRED K. ANDERSON & SONS LOS ANGELES COUNTY CODE: 19 FACILITY ID: 22235	GALAXIE DISPLAYS SANTA FE SPRINGS COUNTY CODE: 19 FACILITY ID: 22466	H & L MARINE WOODWORK COMPTON COUNTY CODE: 19 FACILITY ID: 22584
WOLSEY SOUTH EL MONTE COUNTY CODE: 19 FACILITY ID: 23354	SEATING PROD. IND, WOODWORK LOS ANGELES COUNTY CODE: 19 FACILITY ID: 25251	CURTIS & SWEET WHITTIER COUNTY CODE: 19 FACILITY ID: 25397	CANNON CRAFT WESTERN LOS ANGELES COUNTY CODE: 19 FACILITY ID: 25564
SAN FERNANDO CASKET SOUTH GATE COUNTY CODE: 19 FACILITY ID: 35206	ROYLES , SEMCO DBA GARDENA COUNTY CODE: 19 FACILITY ID: 35363	RIEHL HOME IMPROVEMENT NORTH HOLLYWOOD COUNTY CODE: 19 FACILITY ID: 38702	F.F. OLEA EXHIBITS DOWNEY COUNTY CODE: 19 FACILITY ID: 39572
PERMA-BILT IND, VANITY DIV LOS ANGELES COUNTY CODE: 19 FACILITY ID: 800102	HI-JAY LAMINATES, JERRY FULLERTON COUNTY CODE: 30 FACILITY ID: 1364	WYATT WOODWORKS ANAHEIM COUNTY CODE: 30 FACILITY ID: 2331	PLASTIC TOPS LA HABRA COUNTY CODE: 30 FACILITY ID: 10958
WALTER & CLINE SANTA ANA COUNTY CODE: 30 FACILITY ID: 14503	SHUTTER KIT ORPORATED ORANGE COUNTY CODE: 30 FACILITY ID: 18964	HEIRWOOD, J. B. COLBY ETC COSTA MESA COUNTY CODE: 30 FACILITY ID: 19023	MARK DRAPERY HARDWARE SANTA ANA COUNTY CODE: 30 FACILITY ID: 19643
C & R CABINETS & FIXTURES ORANGE COUNTY CODE: 30 FACILITY ID: 19724	STYLES ORPORATED COSTA MESA COUNTY CODE: 30 FACILITY ID: 19941	THE CABINETMAKER'S TREASURY LAGUNA HILLS COUNTY CODE: 30 FACILITY ID: 20072	SOUTHLAND CABINETS BUENA PARK COUNTY CODE: 30 FACILITY ID: 20603

TABLE C-2. Millwork, plywood & structural plants in California ARB 1983 Emission Data System.
SIC's: 2430 - 2439

MISSION CUSTOM SHUTTERS	DELGLEIZE WOODWORKING	WOODWORKS UNLIMITED	SACRAMENTO VALLEY MOULD
SANTA ANA	HUNTINGTON BEACH	IRVINE	TWAIN
COUNTY CODE: 30	COUNTY CODE: 30	COUNTY CODE: 30	COUNTY CODE: 32
FACILITY ID: 21146	FACILITY ID: 21336	FACILITY ID: 39660	FACILITY ID: 14
SACRAMENTO VALLEY MOULDING	JACK STANFIELD	PHIL LEHMAN IND	CREST FLOORS AND PLASTICS
TWAIN	BANNING	HEMET	CORONA
COUNTY CODE: 32	COUNTY CODE: 33	COUNTY CODE: 33	COUNTY CODE: 33
FACILITY ID: 21	FACILITY ID: 6953	FACILITY ID: 8347	FACILITY ID: 10365
ROY E. WHITEHEAD	SETZER FOREST PROD	MCKUEN MOULDING	DORRIS LMBR MOULDING
RIVERSIDE	SACRAMENTO	SACRAMENTO	SACRAMENTO
COUNTY CODE: 33	COUNTY CODE: 34	COUNTY CODE: 34	COUNTY CODE: 34
FACILITY ID: 19272	FACILITY ID: 25	FACILITY ID: 59	FACILITY ID: 63
RED RIVER LUMBER	THUNDERBIRD MLDG	LIFETIME DOORS	SEMANS MOULDING
SACRAMENTO	SACRAMENTO	SACRAMENTO	SACRAMENTO
COUNTY CODE: 34	COUNTY CODE: 34	COUNTY CODE: 34	COUNTY CODE: 34
FACILITY ID: 80	FACILITY ID: 84	FACILITY ID: 86	FACILITY ID: 87
LAURELWOOD PRODS	TAYLOR CABINETS	LASCA DOOR	HALEY BROS
RANCHO CORDOVA	SACRAMENTO	CHINO	SAN BERNARDINO
COUNTY CODE: 34	COUNTY CODE: 34	COUNTY CODE: 36	COUNTY CODE: 36
FACILITY ID: 98	FACILITY ID: 102	FACILITY ID: 6448	FACILITY ID: 13003
GEN MARBLE	BESTILE MFG	LOWPENSKY MOULDING	TRIANGLE PACIFIC CORP
CUCAMONGA	ONTARIO	SAN FRANCISCO	LODI
COUNTY CODE: 36	COUNTY CODE: 36	COUNTY CODE: 38	COUNTY CODE: 39
FACILITY ID: 14414	FACILITY ID: 23199	FACILITY ID: 1173	FACILITY ID: 179
SEQUOIA MILL	QUALITY CRAFTSMAN CABINETS	FORMS AND SURFACES, SB	MINTON COMPANY
REDWOOD CITY	REDWOOD CITY	CARPINTERIA	SANTA CLARA
COUNTY CODE: 41	COUNTY CODE: 41	COUNTY CODE: 42	COUNTY CODE: 43
FACILITY ID: 655	FACILITY ID: 1293	FACILITY ID: 6436	FACILITY ID: 637
SOUTHWEST FOREST IND	ROSEBURG LUMBER	CAL-WOOD DOOR	WINDSOR MILL
HAPPY CAMP	WEED	ROHNERT PARK	WINDSOR
COUNTY CODE: 47	COUNTY CODE: 47	COUNTY CODE: 49	COUNTY CODE: 49
FACILITY ID: 28	FACILITY ID: 29	FACILITY ID: 507	FACILITY ID: 1514

Appendix D
WOOD TREATMENT QUESTIONNAIRE

AIR RESOURCES BOARD

1202 Q STREET
P.O. BOX 2815
SACRAMENTO, CA 95812



Dear Sir or Madam:

Systems Applications, Inc. (SAI) is under contract to the California Air Resources Board (ARB) to obtain information related to the quantities of chlorophenolic chemicals used in California in 1985 and the location where they are used. Since the major users of these substances are wood-treatment plants and related facilities, we are making a survey of such facilities as part of our inventory effort.

Included with this letter is a questionnaire. This questionnaire should be completed by an individual who is knowledgeable as to your facility operations and use of chlorophenolic chemicals.

The attached forms A, B, and C request information on the type of equipment and waste disposal at the treatment plant, and the consumption of chlorophenolic chemicals at your facility. If the form does not allow for a complete or accurate description of the process or consumption, please feel free to append additional information. In regions where we cannot obtain detailed survey information, we will have to use the "fall-back" methods of prorating chlorophenol usage by county from state totals and make assumptions regarding treatment and disposal techniques that will tend to produce emissions estimates. This approach could lead to overestimates of chlorophenol consumption and emissions in many counties. Therefore, we are making every effort to obtain comprehensive information for all areas of the state.

This request for data is a formal one, made pursuant to Sections 39607, 39701, and 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code, which authorize the ARB, or its duly appointed representative, to require the submission of air pollution-related information from owners and operators of air pollution emission sources.

Systems Applications, Inc. plans to issue a report as a result of this study. The report will be available to all participants. The only information in the report regarding use of chlorophenolic chemicals at wood-treatment facilities will be gross aggregates by county of consumption and possible emissions. Air Resources Board regulations require me to notify you that the information which you provide may be released (1) to the public upon request, except trade secrets which are not emissions data or other information which is exempt from disclosure, or the disclosure of which is prohibited by law, and (2) to the federal Environmental Protection Agency, which protects trade secrets as provided in Section 114(c) of the Clean Air Act and amendments thereto (42 U.S.C. 7401 et seq.) and in federal regulations.

If you wish to claim that any of the information you submit is trade secret or otherwise exempt from disclosure under applicable law, you must identify in writing the portion of the submittal claimed to be confidential and provide the name, address, and telephone number of the individual to be consulted if the ARB receives a request for disclosure or seeks to disclose the data claimed to be confidential. Emissions data shall not be identified as confidential. Data identified as confidential will not be disclosed unless the ARB determines in accordance with Title 17, California Administrative Code, Sections 91000 et seq., and the California Public Records Act (Government Code Sections 6250 et seq.) that the data do not in fact qualify for a legal exemption from disclosure. The regulations establish substantial safeguards before any such disclosure. Please note that Systems Applications, Inc. has formally agreed with the ARB to protect against the disclosure of trade secrets to the public.

Information on ARB policy may be obtained from the ARB research contract monitor, Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. The ARB contract number for this research project is A5-125-32. Questions regarding the legal aspects of this request may be directed to the ARB's Office of Legal Affairs (916) 322-2884.

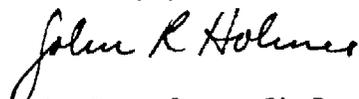
Please complete and return the questionnaire forms with thirty (30) days to:

Mr. Lyle R. Chinkin
Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903

We believe that an accurate estimate of the usage of chlorophenolic chemicals will benefit all concerned parties, including members of the wood-treatment industry as well as the ARB. Your assistance is needed and will be greatly appreciated.

Thank you very much for your cooperation and assistance.

Sincerely yours,



John R. Holmes, Ph.D.
Chief, Research Division

Attachment

WOOD TREATMENT QUESTIONNAIRE

Part A. Sawmill/Treating Plant Information for 1985

NOTE: This survey concerns the treatment of wood products with chlorophenolic chemicals by pressure, vacuum, or hot and cold bath open tank methods (dip, brush, and spray treatments included). If you do not treat wood with these chemicals, please check here [] and return the form in the enclosed envelope. If you do not operate any wood-treatment facilities, please check here [] and return the form in the enclosed envelope.

1. Name and phone number of individual completing this form:

2. Company headquarters: [] same as this plant or []:

3. Did this plant treat wood in 1985? [] Yes [] No

If plant was idle in 1985, do you intend to resume operations?

[] No [] Yes, on (date): _____

Does facility include a sawmill? [] Yes [] No

4. Treating equipment at this plant: [] Pressure [] Nonpressure

Number of pressure cylinders _____ Number of nonpressure tanks _____

Sizes of
pressure
cylinders:

Diameter (Inches)	Length (Feet)	Diameter (Inches)	Length (Feet)	Diameter (Inches)	Length (Feet)	Diameter (Inches)	Length (Feet)
_____	_____	_____	_____	_____	_____	_____	_____

Sizes of nonpressure tanks: List dimensions in feet or capacity in gallons for each tank on the first line, and temperature of treatment in degrees Fahrenheit on the second line (open tanks only):

5. Does this plant have equipment for accelerated drying of material before and/or after treatment? (e.g., forced-air dryer, conventional dry kiln, high-temperature kiln) [] Yes [] No

<u>Type of Equipment</u>	<u>Capacity per Charge (FBM, cu ft)</u>
_____	_____
_____	_____
_____	_____

6. Does this plant have equipment for dip, brush or spray treatments?

[] Brush [] Spray [] Dip [] None of these

If so, please list the equipment type, its capacity, and any control measures used (such as asphalt area coatings, sumps, enclosures, etc.):

<u>Type of Equipment</u>	<u>Capacity per Charge (FBM, cu ft)</u>	<u>Control Measures</u>
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Please continue to Part B (Disposal Methods Information)

Part B. Disposal Methods Information for 1985

If it is necessary to specify different forms of waste disposal for different chlorophenolic chemicals used at your facility, please fill out one copy of this form for each chemical, marking the chemical in the boxes below. If your plant was idle in 1985 but still contained chlorophenolic wastes from previous years, please complete the form for those wastes that are onsite.

- Pentachlorophenol Tetrachlorophenate Tetrachlorophenol
 Pentachlorophenate Trichlorophenate Pentachlorophenoxide
 Other _____

Contaminated media to be disposed of (if detailed records are not available, please give best estimates):

1. Soil contaminated by dripping or spills: _____ tons
Approximate chlorophenolic concentration: _____ wt %
Please indicate the form(s) of disposition, amount disposed of, and disposal location:

Unencapsulated landfill: _____ tons Storage in drums _____ tons
Location _____ Location _____

Encapsulated landfill: _____ tons Other (type, amount, location)?
Location _____

2. Treated wood waste: _____ cu ft
Approximate chlorophenolic concentration: _____ wt %
Please indicate the form(s) of disposition, amount disposed of, and disposal location:

Combustion: _____ cu ft Pulp mill: _____ cu ft
Location _____ Location _____

Other (type, amount, location)? _____

3. Wastewater sludge: _____ tons
Approximate chlorophenolic concentration: _____ wt %
Capacities of holding ponds, if applicable (dimensions in feet or volume in gallons):

Vapor vented (if any) from wastewater treatment system: _____ ACF
Approximate chlorophenolic concentration: _____ wt %

Please indicate the form(s) of sludge disposition, amount disposed of, and disposal location:

Incineration: _____ tons Encapsulated landfill: _____ tons
Location: _____ Location: _____

Unencapsulated landfill: _____ tons Storage in drums: _____ tons
Location: _____ Location: _____

Other (type, amount, location)? _____

NOTE: If this plant was idle in 1985, stop here and return the completed forms in the enclosed envelope.

Part C. Usage of Chlorophenolic Chemicals

Please fill out one copy of this form for each chlorophenolic chemical used at your facility, and mark the chemical in the boxes below.

Pentachlorophenol Trichlorophenolate Pentachlorophenolate Tetrachlorophenol
 Tetrachlorophenolate Pentachlorophenoxide Other _____

1. Amount of chlorophenolic chemical and solvent used in 1985.

Chlorophenol _____ pounds dry chemical Solvent type _____ Quantity _____ gallons

2. Materials treated with chlorophenolic chemical in 1985. Please show, for each product, the amount in usual units and/or cubic feet, the wood species used, the approximate treated concentration of chlorophenol (weight percent), and the reasons(s) for the treatment (i.e., sapstain control in-state, export requirements, etc.). If detailed records are not available, please give best estimates.

Product	Amount Treated in 1985	No. of Pieces	cu ft	Species	Concentration	Reasons
Crossties						
Switch & Bridge Ties		Board feet	cu ft			
Poles		No. of pieces	cu ft			
Pilings		Linear feet	cu ft			
Fence posts		No. of pieces	cu ft			
Lumber ¹		Board feet	cu ft			
Timbers ²		Board feet	cu ft			
Plywood ³		Sq ft 3/8"	cu ft			
Other ³		(Specify)				
			cu ft			
			cu ft			
			cu ft			
			cu ft			
			cu ft			
			cu ft			
			cu ft			

¹ Lumber = Sawn products whose least dimension is less than 5 inches (e.g., 2 x 10, 3 x 8, 4 x 6).
² Timbers = Sawn products whose least dimension is 5 inches or more (e.g., 5 x 7, 6 x 8).
³ List products such as block flooring, crossarms, crossing planks, sign and highway posts, mine ties and timbers, or any other products not listed above. Write in usual units for each and amount treated in usual units and/or cubic feet.

Appendix E

CHEMICAL PROPERTIES FOR PENTACHLOROPHENOL
AND TETRACHLOROPHENOL

Pentachlorophenol Vapor Pressure Data
(Perry & Chilton, 1973)

Vapor Pressure (mm Hg)	Temperature (C)	1 ----- Temperature (1/K)	Log(VP)
20	192.2	0.0021496	1.30103
40	211.2	0.0020653	1.60206
60	223.4	0.0020145	1.77815
100	239.6	0.0019508	2.00000
200	261.8	0.0018699	2.30103
400	285.0	0.0017921	2.60206
760	309.3	0.0017173	2.88081

Regression of Log(VP) vs 1/T for Pentachlorophenol

The regression equation is
 $\log VP = 9.15 - 3657 / T(K)$

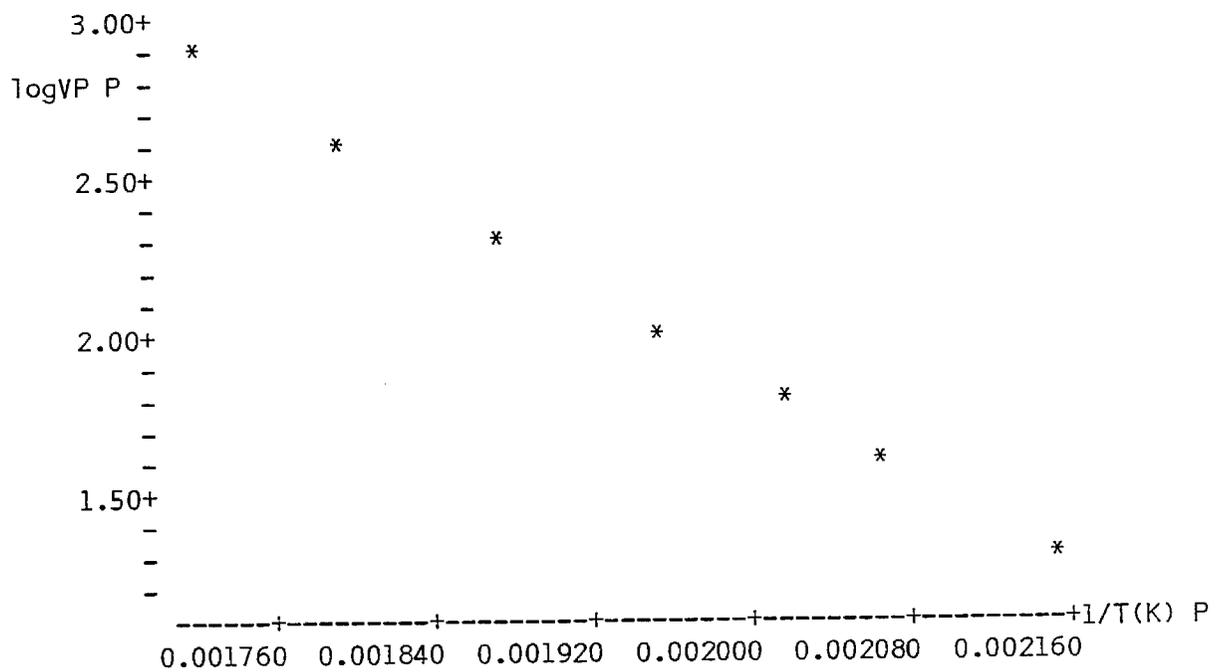
Predictor	Coef	Stdev	t-ratio
Constant	9.14958	0.06182	148.01
1/T(K)	-3656.61	31.83	-114.89

s = 0.01198 R-sq = 100.0% R-sq(adj) = 100.0%

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	1.8934	1.8934
Error	5	0.0007	0.0001
Total	6	1.8942	

Plot of Log (VP) vs 1/T for Pentachlorophenol



Tetrachlorophenol Vapor Pressure Data
(Perry & Chilton, 1973)

Vapor Pressure (mm Hg)	Temperature (C)	1 ----- Temperature (1/K)	Log(VP)
1	100.0	0.0026810	0.00000
10	145.3	0.0023906	1.00000
40	179.1	0.0022119	1.60206
100	205.2	0.0020912	2.00000
400	250.4	0.0019106	2.60206
760	275.0	0.0018248	2.88081

Regression of Log(VP) vs 1/T for Tetrachlorophenol

The regression equation is
 $\log VP = 9.03 - 3362 \cdot 1/T(K)$

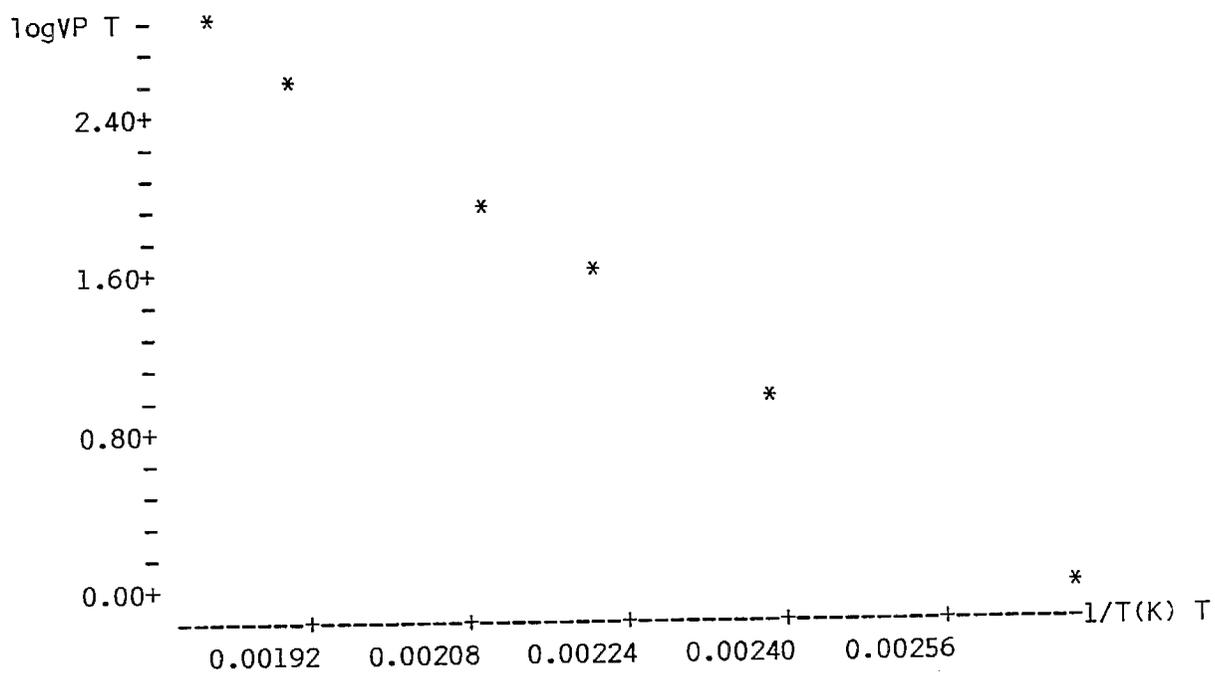
Predictor	Coef	Stdev	t-ratio
Constant	9.02773	0.03682	245.18
1/T(K)	-3362.41	16.71	-201.28

s = 0.01185 R-sq = 100.0% R-sq(adj) = 100.0%

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	5.6849	5.6849
Error	4	0.0006	0.0001
Total	5	5.6854	

Plot of Log (VP) vs 1/T for Tetrachloropheno



Calculation of Vapor Pressures Using
the Equations Derived Above

Tetrachlorophenol

The equation is: $\text{Log}(\text{VP}) = 9.03 - 3362 (1/T)$

for a temperature of 20 C (293 K), $1/T = 3.41\text{E-}3$

then, $\text{Log}(\text{VP}) = 9.03 - 3362 \times (3.41\text{E-}3)$

$$\text{Log}(\text{VP}) = -2.44$$

and,

$$\text{VP} = 3.59\text{E-}3 \text{ mm Hg or torr @ 20 C}$$

and,

$$\text{VP} = 4.72\text{E-}6 \text{ atm @ 20 C}$$

Pentachlorophenol

The equation is: $\text{Log}(\text{VP}) = 9.15 - 3657 (1/T)$

for a temperature of 20 C (293 K), $1/T = 3.41\text{E-}3$

then, $\text{Log}(\text{VP}) = 9.15 - 3657 \times (3.41\text{E-}3)$

$$\text{Log}(\text{VP}) = -3.32$$

and,

$$\text{VP} = 4.78\text{E-}4 \text{ mm Hg or torr @ 20 C}$$

and,

$$\text{VP} = 6.29\text{E-}7 \text{ atm @ 20 C}$$

Appendix F
ESTIMATING ATMOSPHERIC DIFFUSION COEFFICIENTS

Appendix F

ESTIMATING ATMOSPHERIC DIFFUSION COEFFICIENTS

Estimation of the physical properties of chemicals has long been a goal of environmental chemists. Since the modern-day environmental chemist must deal with literally thousands of chemicals, an understanding of their physical and chemical properties is essential. Because measurements of esoteric physical parameters of large numbers of chemicals are not available, various estimation methods have been developed. An excellent compilation of estimation methods is found in Lyman, et al. (1982); this appendix is based on this work.

The definition of molecular diffusion in any medium is that it is a result of intermolecular collisions and not bulk transport such as turbulence. The rate of diffusion is a function of the properties of both the solvent and the solute, as well as the pressure and temperature of the mixture. The diffusion coefficient, or diffusivity, is then defined as:

$$D_{BA} = \frac{J_B}{\nabla X_B}$$

where

D_{BA} = diffusion coefficient of compound B in compound A

J_B = net molal flux of B across a hypothetical plane

∇X_B = concentration gradient of B at the hypothetical plane

The estimation method of Fuller, Schettler and Giddings (FSG) (1966) was chosen for prediction of the diffusion coefficients of the chemicals in this study. The FSG method is the method recommended by Lyman et al. (1982) for this prediction. The FSG method is based on the following correlation:

$$D_{BA} = \frac{10^{-3} \cdot T^{1.75} \cdot (M_r)^{0.5}}{P [(V_A)^{0.33} + (V_B)^{0.33}]^2}$$

where

T = temperature (K)

M_r = molecular weight factor

P = pressure (atm)

V_A = molar volume for air

V_B = molar volume for the solute

The molecular weight factor, M_r , is defined by:

$$M_r = \frac{(M_A + M_B)}{M_A \cdot M_B}$$

The molar volume of air is 20.1 cm³/mol, and its gram molecular weight is 28.97.

The molar volume of the particular solutes is estimated by summing the molar volume of its constituent elements. The molar volumes for the common elements are:

Element	Molar Volume (ΔV_B)
C	16.5
H	1.98
O	5.48
N	5.69
Cl	19.5
S	17.0
Aromatic & Heterocyclic rings	-20.2

The methodology employed in this technique is simple to use and the results of the calculations are shown in the tables in Section 4. A note of caution regarding the application of this method is in order. The calculations involved may look simple; however, proper attention to the units

is required. The reader is strongly advised to examine the detailed discussion in Lyman et al. (1982) before attempting to apply this method to other molecules.

Appendix G

DISCUSSION OF AN AIR EMISSION RELEASE RATE (AERR) MODEL

Appendix G

DISCUSSION OF AN AIR EMISSION RELEASE RATE (AERR) MODEL

The concentration of a material in the gas phase is dependent upon a number of factors, principally on the vapor pressure of that substance. Normal simplifying assumptions include equilibrium conditions and ideal gas behavior. The determination of the vapor (gas) phase concentration of an organic material in a dilute aqueous solution is governed by Henry's Law; i.e.,

$$P_B = k x_B$$

where

P_B = The partial pressure of component B (solute)

k = The Henry's law constant

x_B = The mole fraction of component B in the solution

For an ideal vapor, the partial pressures of the components sum up to be the total pressure, shown as

$$P_T = P_A + P_B + P_C + \dots$$

where

P_T = The total pressure

P_A = The partial pressure of component A (the solvent)

P_B = The partial pressure of component B, etc.

The mole fraction is a measure of the concentration of the component in the solution, and can be determined through use of the partial pressures of the constituents. This is known as Raoult's Law and is shown as

$$P_A = x_A P_A^0$$

$$P_B = x_B P_B^0$$

where

x_A, x_B = The mole fractions of components A and B

P_A^0 = The vapor pressure of the pure substance, A

P_B^0 = The vapor pressure of the pure substance, B

One difficulty with this discussion is that it assumes ideal solution and vapor behavior, which is reasonable in the case of non-polar materials such as the PCDD's, but tenuous in the case of polar materials such as water and chlorinated phenols. Nonetheless, a detailed discussion of the nonideality corrections and possible ramifications is beyond the scope of this work. The reader is referred to the excellent works of Thibodeaux (1979) and Ehrenfeld et al. (1986) for further discussion.

An additional, and more immediate, problem concerning these theoretical equations is that they apply to the equilibrium state of a vapor/liquid interface and do not address the rate of vaporization of a substance from a solution, especially in a "real world" situation (i.e., in a tank of tetrachlorophenol that is evaporating). Fortunately, this problem has been addressed for a number of different scenarios, such as aerated and nonaerated lagoons, and for complex mixtures of varying vapor pressures and concentrations.

There are a number of air emission release rate (AERR) models for estimating emissions from a large variety of confined and open areas. A complete cataloging is beyond the scope of this work and the state-of-the-art is rapidly changing. A discussion of a number of AERR models for a variety of hazardous waste treatment, storage and disposal facilities is given in Ehrenfeld et al. (1986); more recent models are currently being used for some facilities by EPA (D. Layland, personal communication); however, documentation is not yet available. The choice of an appropriate model for estimating these emissions is bounded by a number of factors: the availability of the needed parameters (or the means to estimate them), and the appropriateness of the model to the particular physical site and to the characteristics of the compound being modeled.

Since different chemicals have different volatilities, diffusivities in air and water (a measure of the movement through air or water), and attraction to the solvent (both air and water) and to themselves, the particular model used must correctly treat these factors. The principal

rate-limiting factors for a substance volatilizing from an aqueous solution appear to be its diffusivity through air, or its diffusivity through the solvent (water). These rate-limiting steps have obviously not been confirmed for all types of solutions and all conditions. Rather, this is a "rule of thumb," given the available physical data for a variety of situations and solutions.

A model must also be appropriate to the physical site that one is trying to model; that is, models appropriate to aerated spray ponds would not be appropriate to a quiescent tank, etc. Additionally, the atmospheric conditions (temperature, wind speed, relative humidity) affect the rate, and different models account for these conditions differently.

The final criteria for the choice of a model is perhaps the most relevant, though least "esthetically" pleasing. That is, in theory one would not like to be limited by the availability of different parameters and should choose a model based only on the two previous points; however, all parameters are not known for all substances. This is especially true for the more esoteric parameters demanded by some of the AERR models, for which laboratory determinations are required. Since the scope of this project precludes such effort, other means were used to determine the requisite parameters for the model chosen. Especially for the PCDDs and PCDFs for which very little physical data has been measured (due to their toxicity and difficulty in obtaining standards), estimation methods are the only means of obtaining any parameters. Lyman, Reehl and Rosenblatt (1982) have collected numerous physical parameter estimation methods and their work was used to derive the diffusivity parameters discussed here.

Given these criteria for choice of a model, the work of McCord (1981) was chosen as the best model for the evaporation of tetrachlorophenol from the dip tanks used in the sawmills in California. Other models might work equally well, such as those discussed in Ehrenfeld et al. (1986) and DaRos (1982); however the availability of the parameters required, the physical state of the chemical, and the physical layout of the dip tanks led to the choice of the McCord steady-state predictive model for nonaerated surface impoundments.

McCord's model has been adapted for this work because it was designed for a constantly filling lagoon; however, the adaptation does not change the basic calculation, merely the subsequent calculations that his model requires. Instead of a constantly filled lagoon, we use a tank that is sporadically filled with a TCP solution to achieve an average concentration of one percent. The adaptation assumes that the replenishment is performed in small steps so that the depletion of the tetrachlorophenol (and contaminants) from the tank does not reduce or raise the concentration below or above the one percent level. This is not a bad assumption,

given that the replenishment rate is unknown, and that the evaporation rate is small and directly related (see below) to the concentration of the chemical in the mixture. Since the average concentration is one percent, an evaporation calculation for an entire year is adequate.

The adapted model of McCord (1981) is as follows:

$$E = 0.53425 A_m (D/L)^{0.22} (\%) (VP) (W)^{0.78}$$

where

E = Evaporation rate of a compound at steady state (lb/hr)

A_m = Surface Area of the tank (m^2)

D = Diffusivity coefficient of the compound in air (m^2/hr)

L = The shortest tank dimension (m)

% = The weight percent of the compound in the tank solution

VP = The vapor pressure of the pure compound (atm)

W = The average wind velocity (m/sec)

All of these parameters were readily available for the TCP solutions, with the exception of the vapor pressure for the PCDDs and PCDFs, and the atmospheric diffusivity of all of the compounds. The vapor pressure for TCP and PCP was estimated as described in the previous appendixes. The vapor pressure for 4CDD (Firestone, 1977) was estimated from gas chromatography and was used for the other PCDDs and PCDFs as the best available data.

The atmospheric diffusivity of a compound is a measure of how fast it will transport itself through air, given still wind conditions and uncontaminated air (obviously, air saturated with a vapor would have a different diffusivity). Since the McCord model assumes that this is a rate-limiting step, this is a critical parameter. It was estimated for all of the PCDDs, PCDFs, PCP and TCP using the method of Fuller et al. (1966). This method is considered accurate for aromatics (Lyman et al., 1982) and involves the calculation of several intermediate parameters. A more complete discussion is given in the previous appendix.

For each site, the following factors were assumed:

Wind velocity = 2.5 m/sec

An even distribution of the contaminants in the tank (that is, the diffusivity through the water of all of the contaminants and the chlorophenols is not rate-limiting)

The concentration of the chlorophenols and contaminants is the same as the average of the SWRCB data (Tables 4-4 and 4-5)

The following example calculation is for 4CDD (TCDD) stored in a tank with 18.97 m² surface area.

TCDD concentrations of dip tank liquids (from Table 4-5) is from <0.002 to <0.34 ppb. Assuming (most conservatively) that the level is right below the detection limit, the average concentration is then:

$$(0.002 + 0.34)/2 = 0.171 \text{ ppb}$$

Expressed as a percentage the concentration is then:

$$0.171 \text{ ppb} \times 10^{-7} (\%) / \text{ppb} = 1.71 \times 10^{-8} (\%)$$

$$E = 0.53425 A_m (D/L)^{0.22} (\%) (VP) (W)^{0.78}$$

$$E = 0.53425 (18.97) (1.77 \times 10^{-2} / 19.66)^{(0.22)} (1.7 \times 10^{-8}) (2.24 \times 10^{-9}) (2.5)^{0.78}$$

which gives

$$E = 1.68 \times 10^{-16} \text{ lbs/hr, and}$$

$$E = 1.47 \times 10^{-12} \text{ lbs/yr}$$

The preceding calculations were performed for all the PCDDs and PCDFs for all the processes described in Section 4. This model was also applied to the evaporation of the PCDDs, PCDFs, TCP and PCP from the treated wood, since the rate-limiting step is assumed to be the diffusion through the air and not the solution (which would be wood). This assumption for the wood is extremely conservative and most likely overpredicts the amounts evaporating from the wood, but was used as the best available means of estimating the evaporation from all the various media. The results of the application of this model to treated wood are given in Section 4.

Appendix H

ADDITIONAL STATE WATER RESOURCES
CONTROL BOARD DATA

Appendix H

REVISED STATE WATER RESOURCES CONTROL BOARD DATA

Subsequent to the completion of the draft report, Dr. F. Palmer supplied Systems Applications with revised data regarding the contamination of commercial chlorophenol products. Table 4-4 presents the original data received, Table H-1 shows the new data. Since the data in Table 4-4 were used in estimating certain emissions (Tables 4-8 and 4-11), these data may be misleading. Given the importance of the risk estimates used in Table 5-7, the new data shown in Table H-1 were used there.



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TABLE H-1. Concentrations (ppb) of TCP, PCP, PCDD, and PCDF levels in commercial chlorophenol products.*

	Tetrachlorophenolate (Sodium)	Pentachlorophenolate (Sodium)	Pentachlorophenolate (Sodium)	Pentachlorophenol
TCP	140,000,000	140,000,000	77,000,000	§
PCP	31,000,000	170,000,000	150,000,000	
PCDDs				
Tetra	<1.0	<0.5	16	<0.46
Penta	238	11	1,400	220
Hexa	1,100	4,800	14,000	260
Hepta	614	88,000	64,000	5,000
Octa	700	216,000	69,000	170,000
PCDFs				
Tetra	1,060	190	2,800	980
Penta	22,100	380	3,400	2,300
Hexa	17,600	1,900	18,000	5,100
Hepta	3,000	4,100	18,000	4,600
Octa	62	2,900	840	180

* State Water Resources Control Board unpublished data

§ Not analyzed