

EXECUTIVE SUMMARY

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

SYSAPP-87/078

Contract No. A5-125-32

15 May 1987

Prepared for

California Air Resources Board
1800 15th Street
Sacramento, CA 95812

Prepared by

Lyle R. Chinkin
Bruce R. Weir
Douglas A. Latimer

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903

ACKNOWLEDGMENTS

We wish to thank several individuals who assisted the principal authors in the performance of this study and whose help and input was indispensable. We thank Professor David Brink of the Forestry Department of the University of California at Berkeley and Dr. William Dost, Head of the Wood Building Research Center, also associated with this university. Both individuals were extremely helpful at the outset of this project in pointing us in the right direction and providing background and valuable leads. We also thank Frank Palmer, David Meith, Albert Wellman, and Eric Gobler of the California State and Regional Water Quality Control Boards who provided helpful input. We thank Thomas Parker and Dale Shimp of the Stationary Source Control Division of the Air Resources Board for several valuable discussions in which they offered advice and feedback. We would like to give a special acknowledgment to the key technical staff members at Systems Applications who assisted the principal authors. They include Lenna Mahoney, Julie Fieber, Kara Dowdy, Barbara Austin, and Janet McDonald. Finally, we particularly want to thank Joseph Pantalone of ARB's Research Division, who provided the initial concept for the study and much helpful guidance, comment, contacts, and advice, all of which helped to keep us and the study on track. We appreciate his diligence and perseverance.

This report was submitted in fulfillment of California Air Resources Board Contract No. A5-125-32 entitled "Inventory of Chlorinated Use in the Forest Products Industry and Investigation Related Emissions of Chlorinated Dibenzodioxins and Dibenzofurans," by Systems Applications, Inc. under the sponsorship of the California Air Resources Board. Work was completed as of 7 May 1987.

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.

EXECUTIVE SUMMARY

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 the 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 sap-stain 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 that would be exposed to the elements.

There are two major homologs (series of chemicals having essentially the same structure) of chlorophenols used in the forest products industry. The most widely used homolog is pentachlorophenol (PCP). The other major chlorophenol homolog is tetrachlorophenol (TCP). 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. In addition to their presence as impurities in chlorophenol, PCDDs 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 is 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.

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 in California where chlorophenols are currently used. 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.

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 the locations of the industrial facilities in California

CONCLUSIONS

Potential emissions to the atmosphere of polychlorinated PCDDs and PCDFs, 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. PCDDs and PCDFs 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 PCDDs and PCDFs 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 PCDDs and PCDFs 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 PCDDs and PCDFs. 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 Resources 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 Resources 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 congener 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 PCDDs and PCDFs in air directly emitted from the chlorophenol wood treatment industry.

Emissions of chlorophenols and their toxic contaminants could be reduced by use of practical chemical substitutes for chlorophenols 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. 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.