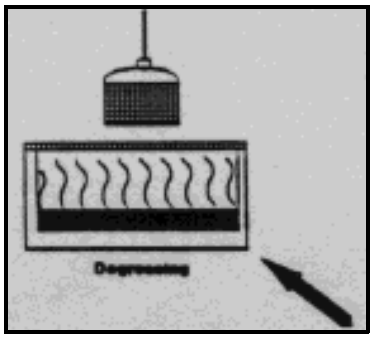
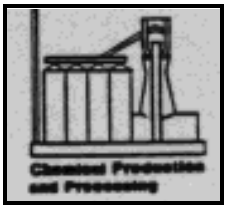
STAFF REPORT

PROPOSED IDENTIFICATION OF METHYLENE CHLORIDE AS A TOXIC AIR CONTAMINANT



CH_2C1_2



State California
Air Resources Board
Stationary Source Division

May 1989

Proposed Identification of Methylene Chloride as a Toxic Air Contaminant

Prepared by the Staffs of
the Air Resources Board and
the Department of Health Services

Stationary Source Division
Air Resources Board
May 1989

Proposed Identification of Methylene Chloride as a Toxic Air Contaminant

Date and Address of Board Hearing:

July 13 and 14, 1989

Lincoln Plaza
Auditorium, First Floor
400 P Street
Sacramento, California 95814

Address of the Air Resources Board:

Air Resources Board
Stationary Source Division
1102 'Q' Street
Sacramento, California 95814

(This report has been reviewed by the staffs of the California Air Resources Board and the California Department of Health Services and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board or the Department of Health Services, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.)

INTRODUCTION AND RECOMMENDATION

Definition of a Toxic Air Contaminant. Health and Safety Coda section 39655 defines a toxic air contaminant as an air pollutant which the Air Resources Board or the Department of Food and Agriculture finds "may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."

Evaluation and Recommendation. The staffs of the Air Resources Board (ARB) and the Department of Health Services (DHS) have reviewed the available scientific evidence on the presence of methylene chloride in the atmosphere of California and its potential adverse effect on public health. Based on the finding of carcinogenicity and the results of the risk assessment, the DHS staff finds that methylene chloride meets the definition of a toxic air contaminant.

Findings of the Scientific Review Panel. The Scientific Review Panel (SRP), which is established pursuant to Health and Safety Code section 39670, reviewed the report in accordance with Health and Safety Code section 39661, and found the report to be without serious deficiency. The findings of the SRP are attached at the end of this Report.

Recommendation. The staff of the Air Resources Board recommends that the Board identify methylene chloride as a toxic air contaminant. In making this recommendation, the ARB and DHS staffs found that there is not sufficient available scientific evidence at this time to support the identification of an exposure level below which carcinogenic effects would not have some probability of occurring. Therefore, we recommend that methylene chloride be treated as having no identified threshold.

Reasons for Recommendation. Methylene chloride was chosen for evaluation because: the International Agency for Research on Cancer (IARC) and the U.S. Environmental Protection Agency (U.S. EPA) have concluded that there is ample evidence that methylene chloride is

carcinogenic in animals. (The IARC considers methylene chloride a possible human carcinogen and the U.S. EPA considers methylene chloride to be a probable human carcinogen.) Methylene Chloride is emitted from a variety of sources in the State, and it does not break down at a rate that would significantly reduce public exposure.

About these Documents. In addition to making a recommendation, this report summarizes the information in the accompanied technical support document. The technical support document includes four parts which are the “Overview and Recommendation,” the Part A report, the Part B report, and the Part C report. The “Overview and Recommendation" summarizes and integrates the information in Parts A and B; Part A was prepared by the ARB staff and reviews the public exposure to, environmental fate of, and sources of atmospheric methylene chloride in California; Part B was prepared by the DHS and reviews the health effects and risks associated with exposure to methylene chloride; and Part C contains the public comments that were received during the public comment periods and the ARB and the DHS staffs' responses to those comments.

I.

SOURCES OF METHYLENE CHLORIDE

Methylene chloride is a popular chemical, primarily because of its excellent solvent characteristics, low flammability, and low boiling point. Although methylene chloride is not produced in California, it is widely used in the state with estimated emissions of approximately 20,000 tons per year.

Methylene chloride is a constituent in products used by industry as well as by the general population. The major use categories, representing about 90 percent of the estimated annual emissions of methylene chloride, in decreasing order are paint removers, aerosols, degreasers, and polyurethane foam manufacturing. In addition to these, several other source categories use hundreds of tons of methylene chloride each year. These categories include pharmaceuticals, electronics, chemical production and processing, and pesticide manufacturing. For some source categories such as aerosols and decreasing, the consumption of methylene chloride has or is expected to decline. This decrease has resulted from concern over health effects as well as proposed restrictions on the use of methylene chloride.

Because emissions from many of the uses for methylene chloride are not controlled, a high percentage (about 80 percent) of the methylene chloride used in California is emitted to the atmosphere. For some categories, such as paint removers and aerosols, emissions from evaporation equal the amount used.

II.

EXPOSURE. HEALTH EFFECTS. AND RISK

A. EXPOSURE TO METHYLENE CHLORIDE

Persistence in the atmosphere. In the atmosphere, methylene chloride is a relatively stable pollutant. Methylene chloride's lifetime in the atmosphere is estimated to range from 80 to 250 days. Thus, methylene chloride is sufficiently persistent that it will be transported throughout an air basin and beyond before it is degraded.

Ambient concentrations. Since ARB's air toxics monitoring network was instituted in January of 1985, methylene chloride has been detected at eacthehe 20 monitoring stations in California. The mean concentrations have been determined for each of the monitoring stations during the 27 month period covering January 1985 through March 1987. Mean concentrations range from 0.4 ppb at the Merced station to 2.5 ppb at the El Monte station. Peak 24-hour average concentrations range from 2.0 ppb at the Concord, Richmond, and Stockton stations to 21 ppb at the Santa Barbara station.

Exposure based on monitoring data. General population exposure to atmospheric methylene chloride was estimated for several areas in California by using ambient monitoring data from January 1985 through March 1987. The staff estimates that 20.3 million people (approximately 80 percent of the state's population) are exposed to a population-weighted mean methylene chloride concentration of 1.1 to 2.4 ppb. For the South Coast Air Basin (SCAB), where the highest mean concentrations occurred, approximately 10.9 million people are exposed to a population-weighted mean concentration of 1.5 to 3.1 ppb.

Exposure based on modeling. In addition to estimating general population exposure, dispersion modeling was used to estimate population exposure for people living near methylene chloride emission sources in the SCAB. Dispersion modeling of emissions from three large sources (annual emissions greater than 45 tons) indicates that many people may be exposed to concentrations significantly above the mean concentration for the SCAB. The three sources are a mobile home manufacturer, an automobile assembler, and a polyurethane foam manufacturer. Based on the emissions from the polyurethane foam manufacturer, the exposure results show that approximately 1,300 people are exposed to a maximum annual average concentration of 10.7 ppb. For the motor home manufacturer the results show that approximately 1000 people are exposed to a maximum annual average concentration of 5.7 ppb, while the results for the automobile assembler show that approximately 2,000 people are exposed to a maximum annual average concentration of 1.0 ppb. Because these exposure estimates consider emissions from the modeled sources only, and because of the extensive use and emissions of methylene chloride by industry as well as consumers throughout the SCAB, the actual population exposure near these sources may be under-represented.

Indoor exposure. Because only limited data are available, an estimate of exposure to methylene chloride through indoor air is not presented in this report. However, because methylene chloride is a constituent in many consumer products, short-term indoor concentrations may be several orders of magnitude higher than ambient concentrations. Inhalation of methylene chloride from the indoor environment is expected to vary depending on the degree and manner of use of products containing methylene chloride.

A limited indoor monitoring study, conducted in Italy, monitored the indoor air of 15 structures for several organic compounds including methylene chloride. The mean indoor concentration of methylene chloride over a period of four to seven days was 193 ppb with the concentration for one of the structures reported as 1,450 ppb.

As part of a study conducted in Los Angeles County, the indoor and outdoor air of eight homes during the summer season was sampled and subsequently analyzed for several compounds including methylene chloride. For these homes, draft results show overnight indoor concentrations to range from 0.3 to 3.6 ppb with daytime indoor concentrations ranging from 0.3 to 3.9 ppb. Overnight outdoor concentrations range from 0.1 to 1.3 ppb while daytime outdoor concentrations range from 0.2 to 3.9 ppb. The results for the this study indicate that indoor concentrations of methylene chloride in some homes may not be substantially higher than outdoor concentrations. In addition, the contrasting results reported by the Italian and Los Angeles study illustrate the need for a comprehensive indoor monitoring study where methylene chloride is sampled and analyzed throughout California.

Other studies have evaluated personal breathing zone concentrations resulting from the use of consumer products containing methylene chloride. Results from a chamber study where a paint stripper was being used resulted in breathing zone exposures up to 2,000 ppm averaged over an hour with peak breathing zone concentrations of up to 3,300 ppm.

Breathing zone concentrations of the magnitude reported above are generally found during the time period the product is being applied and declines rapidly, depending on ventilation rate, once application is finished.

Other routes of exposure. In addition to inhalation, exposure to methylene chloride may occur when drinking water and food products which contain methylene chloride are ingested. The ARB staff reviewed the results of studies that analyzed food-products and drinking water for the presence of methylene chloride. The data indicate that concentrations of methylene chloride in drinking water are typically below detection levels of approximately 0.5 micrograms per liter. The study results also indicate that, for most people, the ingestion of food is not a substantial route of exposure to methylene chloride. Therefore, the ARB staff believes that inhalation is the most important route of exposure for the majority of California's population.

B. HEALTH EFFECTS OF METHYLENE CHLORIDE

The health effects of methylene chloride have been reviewed and evaluated to determine whether methylene chloride meets the definition of a toxic air contaminant. What follows is a summary of the DHS's findings regarding the health effects of methylene chloride.

Non-carcinogenic health effects. Methylene chloride has a relatively low acute toxicity. The median LC50 values for rats and mice exposed for six hours to methylene chloride vapors are approximately 17,000 ppm and 14,100 ppm, respectively. Environmental concentrations of methylene chloride estimated in California (24-hour average concentrations up to 21 ppb) are well below any levels that may cause adverse acute and noncarcinogenic chronic health effects.

The EPA concluded that methylene chloride is capable of inducing mutations in exposed human cells; the IARC reviewed short-term tests of DNA damage for methylene chloride and concluded that there was sufficient evidence to classify methylene chloride as genetically active. IARC also concluded that methylene chloride causes cell transformation in mammalian cells cultured in vitro.

The staff of the DHS concurs with the IARC's and the EPA's evaluations but stresses that the high concentrations of methylene chloride necessary to induce mutagenic and cellular transformations demonstrate that methylene chloride should be considered weakly genotoxic.

Carcinogenic health effects. Several long-term rodent studies have shown that methylene chloride increases tumor rates in some organs, primarily the mouse liver and lung and the rat mammary gland at concentrations ranging from 1,000 ppm to 4,000 ppm.

Both the EPA and the IARC have concluded that methylene chloride is carcinogenic in animals with inadequate evidence for carcinogenicity in humans. Overall, the EPA assigned methylene chloride to category B2, which means that methylene chloride should be considered a "probable" human carcinogen. IARC assigned methylene chloride a rating of 2B and considers methylene chloride a “possible” human carcinogen.

The DHS staff agrees with the EPA and the IARC that methylene chloride is carcinogenic in animals with inadequate evidence for carcinogenicity in humans. The DHS staff have concluded that methylene chloride is a potential human carcinogen. The DHS staff recommends that methylene chloride be considered as not having a threshold for carcinogenicity because:

1) The DHS staff found no evidence for a carcinogenic threshold level; and

2) because there are several short-term tests suggesting that methylene chloride is mutagenic.

C. RISK DUE TO METHYLENE CHLORIDE

The DHS staff recommends that the range of risks for ambient exposures to methylene chloride be based on the 95 percent upper confidence limit predicted from fitting two different mathematical models to the animal data. The DHS report (Part B) also includes the range of risks based on EPA's application of a physiologically based pharmacokinetic (PBPK) model to estimate exposure. The DHS staff estimate that the unit risk from a lifetime continuous exposure to 0.29 ppb (1 $g/\mu m^3$) of methyleng chloride ranges from 0.3×10^{-6} to 3×10^{-6} (1×10^{-6}/ppb to 10×10^{-6}/ppb). The SRP estimates that the range of lifetime excess cancer risk from exposure to 1 ppb of atmospheric methylene chloride based on the upper 95% confidence limit is from 9×10^{-8}/ppb (PBPK model without surface area correction) to

10 x 10^{-6}/ppb (applied dose). The DHS staff and the SRP conclude that the most plausible estimate of the unit risk based on application Of the PBPK model high-to-low dose adjustment, is 1 x 10^{-6} per 1 $\mu g/m^3$, which is equivalent to 4 x 10^{-6}/ppb.

Exposure to the range of mean ambient concentrations (weighted by population) of 1.1 to 2.4 ppb, as estimated by the Air Resources Board staff for a population of 20.3 million people, could result in up to 20 to 500 excess lifetime cancers, based on the upper-bound of the 95% confidence interval of the models used by the DHS. Applying the range of risk estimated by the SRP (9 x 10^{-8}/ppb to 10 x 10^{-6}/ppb) to the mean range of ambient exposure (weighted by population) for a population of 20.3 million people, could result in up to 2 to 500 excess lifetime cancers. Applying the most plausible estimate of upper limit risk (4 x 10^{-6}/ppb) to the mean range of ambient exposure (weighted by population) for a population of 20.3 million people, could result in up to 90 to 200 excess lifetime cancers. These calculations which are summarized in Table 1 are for the upper range of plausible excess cancer risks, the actual risk which cannot be calculated may approach zero.

Table 1

Estimate of Statewide Excess Lifetime Cancer Cases
from Exposure to Methylene Chloride

Group	**Estimate of Risk**	**Lifetime Cancer Cases[a]**
DHS/SRP	4 x 10^{-6}/ppb (most plausible)[b]	90 to 200
DHS	1 x 10-6/ppb to 10 x 10^{-6}/ppb	20 to 500
SRP	9 x 10^{-8}/ppb to 10 x 10^{-6}/ppb	2 to 500

[a] - Based on exposure to mean ambient concentrations (weighted by population) ranging from 1.1 to 2.4 ppb for a population of 20.3 million people.

[b] - The most plausible estimate of risk according to the DHS and the SRP.

Individuals exposed to the maximum annual mean concentration, estimated for people living near a ethylene chloride emission source, of 10.7 ppb for a lifetime would have a risk of

developing cancer equal to 40 cases per million exposed. (This estimate of cancer cases is obtained by applying the most plausible estimate of upper limit risk of 4×10^{-6}/ppb to the lifetime exposure estimate.) These calculations are for the upper range of plausible excess cancer risks, the actual risk, which cannot be calculated, may approach zero.

Based on the finding of methylene chloride-induced carcinogenicity and the results of the risk assessment, the DHS staff finds that at ambient concentrations, methylene chloride is an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health.

III.

ALTERNATIVES AND ENVIRONMENTAL IMPACTS

A. ALTERNATIVES

Government Code Section 11346.14 requires agencies to describe alternatives to the regulation considered by the agency and the agency's reasons for rejecting those alternatives. The only alternative to identifying methylene chloride as a toxic air contaminant is to not identify it. The ARB staff is not recommending this alternative because the ARB staff believes that methylene chloride meets the statutory definition of a toxic air contaminant.

There are no alternatives considered by the ARB staff which would be more effective in carrying out the purpose for which the amendment is proposed or would be as effective and less burdensome to affected private persons than the proposed amendment.

B. ENVIRONMENTAL IMPACTS

The identification of methylene chloride as a toxic air contaminant is not in itself expected to result in any environmental effects. The identification of methylene chloride as a toxic air contaminant by the Board may result in the Board and air pollution control districts adopting control measures in accordance with the provisions of state law (Health and Safety Code sections 39665 and 39666). Any such toxic control measures would result in reduced emissions of methylene chloride to the atmosphere, resulting in reduced ambient concentrations, thereby reducing the health risk due to methylene chloride exposure. Therefore, the identification of methylene chloride as a toxic air contaminant may ultimately result in environmental benefits. Environmental impacts identified with respect to specific control measures will be included in the consideration of such control measures pursuant to Health and Safety Code sections 39665 and 39666.

Also considered was methylene chloride's importance in contributing to global warming as well as depletion of the stratospheric ozone layer. After consulting with the U.S. EPA and other scientists in the field it was determined that methylene chloride is not a significant contributor to either of these phenomenon. Thus, any reduction in emissions of methylene chloride would not be expected to significantly reduce global warming or stratospheric ozone depletion.

STATE OF CALIFORNIA ATTACHMENT George Deukmejian

AIR RESOURCES BOARD
1102 Q STREET P.O. BOX 2815
SACRAMENTO. CA 95812

May 15, 1989

Mr. William C. Lockett, Chief
Office of External Affairs
California Air Resources Board
1102 Q Street
Sacramento, California 95814

Dear Bill:

The Scientific Review Panel on Toxic Air Contaminants has reviewed the Report on Methylene Chloride, which includes Tables 8-5 and 8-7 from Part B of the report by the Department of Health Services, and has formulated its findings regarding the report. I am formally submitting the Scientific Review Panel's findings to the Air Resources Board.

Sincerely,

//s//
Dr. James N. Pitts
Acting Chairman, SRP

Enclosure

cc: Scientific Review Panel

Findings of the Scientific Review Panel on
THE REPORT ON METHYLENE CHLORIDE
As Adopted at the Panel's April 18, 1989 Meeting

In accordance with the provisions of Health and Safety Code section 39661, the Scientific Review Panel (SRP) has reviewed the reports of the staffs of the ARB and DHS on the public exposure and biologic and health effects of methylene chloride, and the public comments on these reports. Based on this review, the SRP finds that the reports are without serious deficiencies ant further finds that:

1. Methylene chloride has been identified as an animal carcinogen and should be regarded as a potential human carcinogen.

2. Methylene chloride is emitted into the air by a variety of stationary sources in California.

3. Based on its gas-phase reactivity with hydroxyl radicals, methylene chloride has an atmospheric lifetime estimated to range from 80 to 250 days.

4. Approximately 20.3 million people in California are estimated to be exposed to a population-weighted mean methylene chloride concentration of 1.1 to 2.4 parts per billion.

5. Adverse health effects other than cancer are not known to occur at predicted concentrations of methylene chloride in ambient outdoor air.

6. Based on available scientific information, a methylene chloride exposure level below which carcinogenic effects are not expected to occur cannot be identified.

7. Based on an interpretation of available scientific evidence, DHS staff estimated risks using both the applied dose and a physiologically based pharmacokinetic model (PBPK) (see attached table). The range of lifetime excess cancer risk from exposure to 1 ppb (3.5 $\mu g/m^3$) of atmospheric methylene chloride based on the upper 95% confidence limit is from 9×10^{-8}/ppb (PBPK model without surface area correction)[(a)] to 10×10^{-6}/ppb (applied dose). This includes EPA's application of the PBPK model which would estimate a risk of 1×10^{-6}/ppb with a surface area correction). DHS uses a PBPK model with a high to low dose adjustment which generates a risk of 4×10^{-6}/ ppb. Based on available data it is the most plausible estimate of the upper limit of risk. These upper bound excess lifetime risks are health protective estimates; the actual risk may be below these values.

8. Exposure to the range of mean ambient concentrations (weighted by population) of 1.1 to 2.4 ppb for a population of 20.3 million people, could result in up to 2 to 500 excess lifetime cancers, based on the upper-bound of the 95% confidence interval of the models.

For these reasons, we agree with the ARB staff recommendation to its Board that methylene chloride be listed by the ARB as a toxic air contaminant.

(a) **NOTE**: The DHS staff chose only to report a range using a surface area correction.

I certify that the above is a true and correct copy of the findings adopted by the Scientific Review Panel on April 18, 1989

//s//

Dr. James N. Pitts
Acting Chairman, SRP

Attachments

CONDENSATION OF DHS TABLES 8-5 AND 8-7

COMPARISON OF HUMAN CANCER RISK ESTIMATES FROM A CH_2Cl_2 EXPOSURE, BASED ON LUNG TUMORS IN FEMALE MICE, USING VARIOUS MODELS AND ASSUMPTIONS [a]

Approach	Mathematical Model	Lifetime Risk	
Applied Dose	Linearized Multistage	ppb^{-1}	$(\mu g/m^3)^{-1}$
Applied Dose	Time-Dependent Multistage	9×10^{-6}	3×10^{-6}
High-to-Low Dose[b]	Linearized Multistage	10×10^{-6}	3×10^{-6}
High to Low Dose	Time Dependent Multistage	4×10^{-6}	1×10^{-6}
Total PBPK[c]	Linearized Multistage	5×10^{-6}	1×10^{-6}
Total PBPK[d]	Linearized Multistage	1×10^{-6}	3×10^{-7}

[a] All values were adjusted for continuous exposure. That is, the mouse exposure in ppm was multiplied by (6 hours/day)/(24 hours/day) x (5 days/week)/(7 days/week). The concentrations are calculated from the female mouse lung tumor data (NTP 1986). The extrapolation was also corrected for surface area (a factor of 12.7) unless indicated otherwise. The risks are based on the linearized multistage model. Surface area conversion for rodent to human risks, and risk estimates are reported at 95% upper bound values.

[b] High-to-low adjustment for saturation of MFO pathway based on the HRAC report (EPA 1987a).

[c] High-to-low adjustment for saturation of MFO pathway and the species to-species adjustment based on the HRAC report which includes a 12.7 surface area correction (EPA 1987a).

[d] High-to-low adjustment for saturation of MFO pathway and the species adjustment based on the HRAC report (EPA 1987a), except without use of a surface area correction.