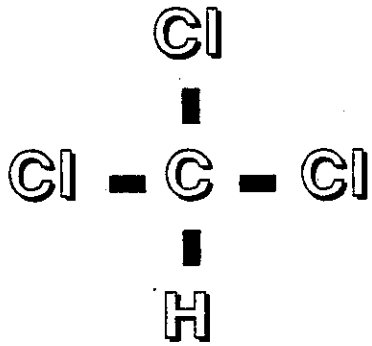
California Air Resources Board

Proposed Identification of CHLOROFORM



As a Toxic Air Contaminant

Part C
Public Comments and ARB/DHS Staff Responses

State of California
Air Resources Board
Stationary Source Division

SEPTEMBER 1990

PART C - PUBLIC COMMENTS AND RESPONSES TO THE PRELIMINARY DRAFT PART A AND B CHLOROFORM

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

July 1990

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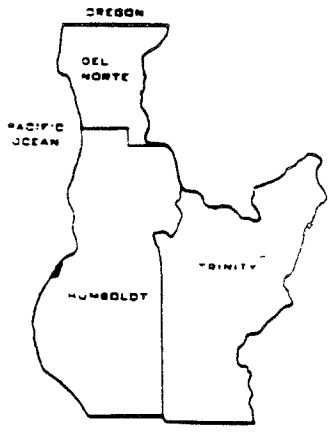
I.

Comment Letters and ARB Staff Responses to Comments on the Preliminary Draft Version of Chloroform Part A

NORTH COAST UNIFIED AIR QUALITY MANAGEMENT DISTRICT

5630 SOUTH BROADWAY EUREKA, CALIFORNIA 95501

PHONE (707) 443-3093



January 3, 1990

Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

ATTEN: Chloroform

Dear Ms. Denton:

We have reviewed the Draft Technical Support Document "Report to the Air Resources Board on Chloroform" and have some corrections noted as follows:

Page A-9:

1. The pulp & paper mill noted in Eureka as Crown Simpson & Fairbanks should be deleted, since it is represented by the Simpson Paper Co. mill at Fairhaven. The Crown Simpson mill changed names several years ago.

2. The Louisiana-Pacific mill at Sonoma should be corrected to read at Somoa.

3. The fibreboard Corp. plant in Antioch was previously owned by Louisiana-Pacific Corp. There is only one kraft mill at this location. Delete LP and make Fibreboard type kraft.

4. We do not know of any kraft pulp mill in Fullerton? (There are only four kraft pulp mills in California)

5. There is no pulp or paper mill in Ukiah owned by Masonite Corp. This is a manufacturer of hardboard - no chloroform is produced.

If there are any questions, please give us a call.

Sincerely,

Robert Clark

Robert Clark
Air Pollution Engineer

o North Coast Unified Air Quality Management District, January 3, 1990

Comment:

1. The pulp & paper mill noted in Eureka as Crown Simpson & Fairbanks should be deleted, since it is represented by the Simpson Paper Co. mill at Fairhaven.

2. The Louisiana-Pacific mill at Sonoma should be corrected to read at Somoa.

3. The fibreboard (sic) Corp. plant in Antioch was previously owned by Louisiana-Pacific Corp. There is only one kraft mill at this location. Delete Louisiana-Pacific and make Fibreboard type kraft.

4. We do not know of any kraft pulp mill in Fullerton? (There are only four kraft pulp mills in California.)

5. There is no pulp or paper mill in Ukiah owned by Masonite Corp. This is a manufacturer of hardboard - no chloroform is produced.

Response: The corrections have been made.

WASTEWATER RECLAMATION
SOLID WASTE MANAGEMENT

COUNTY SANITATION DISTRICTS OF LOS ANGELES COUNTY

1955 Workman Mill Road / Whittier, California
Mailing Address: / P. O. Box 4998, Whittier, California 90607-4998
Telephone: (213) 699-7411 / From Los Angeles (213) 685-5217

CHARLES W. CARRY
Chief Engineer and General Manager

January 8, 1990

File No.: 70-00.00-00

Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Denton:

Submittal of Comments on Draft Report: "Public Exposure To, and Emissions of Chloroform In California," December 1989

We wish to comment on one issue addressed in the subject report: the estimated emissions of chloroform from Publicly Owned Treatment Works (POTWs) in California. The report estimates that these emissions total 50 tons per year or roughly 4 percent of the total estimated emissions of 1,200 tons per year from all sources within California.

We believe the estimate of 50 tons per year is high and that a better estimate is a number less than 10 tons per year.

We note from the discussion on Page 11 of the draft report that the 50 tons per year estimate was obtained from a University of California, Davis study conducted in 1987. Our review of that study indicates that the authors computed estimated VOC emissions from POTWs by using a "...worst-case, uncontrolled..." emission model. (see page 46 of "Final Report. Emissions of Volatile and Potentially Toxic Organic Compounds From Sewage Treatment Plants and Collection Systems" by D.P.Y. Chang, E.D. Schroeder, R.L. Corsi, Department of Civil Engineering, University of California, Davis, July 1987).

The U.C. Davis report estimates that chloroform emissions from the Los Angeles County Sanitation Districts' (LACSD) Joint Water Pollution Control Plant (JWPCP) total 2.63 tons per year (see Table 17b, page 84 of report). However, subsequent to 1987

the LACSD has conducted source testing of VOC emissions from this facility. Our data, however, suggest that chloroform emissions total only 0.4 tons per year, or roughly 15 percent of that estimated in the U.C. Davis report.

In addition to source testing conducted at the JWPCP, the LACSD, subsequent to publication of the 1987 U.C. Davis report, also conducted source testing at two of it's other facilities: a residential POTW and a domestic POTW. All three of these source test studies inventoried total chloroform emissions, including emissions of chloroform which entered the POTW in the raw sewage and emissions of chloroform which were produced by in-plant chlorination processes. Our data supports the hypothesis that water supplies are the principal source of chloroform in wastewater. Chloroform emissions from these POTWs, expressed as an emission mass per liter of water treated at the facility, ranged from 0.7 to 2.5 μg/L. From our understanding of the sources of water used in the tributary areas of these facilities, there appears to be a relationship between the amount of surface water used in the drinking water supply and the emissions of chloroform from the POTW serving that tributary area. Utilizing this information an estimate of chloroform emissions from POTWs in California can be made. The U.C. Davis report states that all POTWs in California have a total daily treated flow of 2,800 MGD (see Table 11, page 50 of report). From these data it is easily calculated that the estimated maximum emissions of chloroform from all of California's POTWs are approximately 11 tons per year. Actual emissions are undoubtedly less and probably range somewhere between 5 and 10 tons per year.

Thank you for this opportunity for allowing us to provide you with this information. If you have any questions, please do not hesitate to contact me at (213) 775-2351.

Very truly yours,

Charles W. Carry

Ross C Caballero

Ross C. Caballero
Supervising Research Engineer
Joint Water Pollution Control Plant

RC:dm

o County Sanitation Districts of Los Angeles County (LACSD), January 8, 1990

1. **Comment:** The Los Angeles County Sanitation District (LASCD) believes that the 50 tons per year estimate to be high. The 50 tons per year estimate was obtained from a University of California, Davis study conducted in 1987. Our review of that study indicates that the author computed estimated VOC emissions from POTWs by using a '..worst-case, uncontrolled..' emission model.

Response: Regarding the use of the worst-case, uncontrolled model to estimate VOC emissions from POTWs, the UCD study clarifies that "While the worst-case assumption was conservative with respect to emission estimates, it was partially offset by not accounting for volatile emissions of the chlorination that were generated as a result of chlorination..." (UCD, 1987 - pg. 47). Therefore, we believe that the method developed by UCD to estimate chloroform emissions from POTWs is valid.

2. **Comment:** The U.C. Davis report estimates that chloroform emissions from the LASCD Joint Water Pollution Control Plant (JWPCP) total 2.63 tons per year. Our data, however, suggest that chloroform emissions total only 0.4 tons per year.

Response: Regarding the difference in chloroform emissions estimated by the UCD and the County Sanitation District of Los Angelos County (CSDLAC), there is no direct comparison between the two methods. However, the UCD report has pointed out several factors which could account for the discrepancies between the emission estimates, such as the periods during which the samples were drawn, the efficiencies of the scrubbers and the activated carbon beds, the emissions from digester tanks and during composting, and biodegradation (UCD, 1987 - pp. 86-87). These variables may result in differences among chloroform emission estimates from POTWs.

3. **Comment:** The LASCD also conducted source testing at two of it's other facilities: a residential POTW and a domestic POTW. Chloroform emissions from POTWs, expressed as an emission mass per liter of water treated at the facility, ranged from 0.7 to 2.5 ug/L. The LASCD believe the actual emissions probably range from 5 to 10 tons per year.

Response: Regarding the chloroform emission factors developed by LASCD, we have used these numbers to estimate a lower bound for the range of chloroform emissions from POTWs. Because the emission estimate from POTWs does not include chloroform emissions from the collection system of the POTWs nor from other types of facilities that treat their own wastewater, there is some uncertainty in the chloroform emission estimate from POTWs. Therefore, we have revised our draft report to include an emission estimate based on LASCD suggestions and have considered this number as a lower limit of the estimated range of emissions.

CBE Comment #90630

1/19/90

Mimi Jones
California Air Resources Board
1219 K St.
Esquire Theatre Bld.
PO Box 2815
Sacramento, CA 95812
916/327-5627

CITIZENS FOR A BETTER ENVIRONMENT

Re: Comments on Draft Report on Chloroform

Dear Ms. Jones,

Here are a few comments on Draft Report on Chloroform, Part A, December 1989, of which you and I briefly spoke by telephone last week. I also spoke with Fred Medina regarding cooling towers. You indicated that comments could be submitted by 1/22/90.

Cooling Towers emissions may be underestimated

It appears from page 11 of part A that the calculation of emissions of chloroform from cooling towers only includes that portion caused by the addition of chlorine (or chlorine compounds) at the cooling tower facility, and neglects chloroform already present in the water due to the addition of chlorine (or chlorine compounds) by public water treatment facilities. Since millions of gallons of water per day go through some cooling towers, even a small percentage of additional chloroform per gallon may add up to significant emissions.

Since the ARB document does not give details on how the original calculation was done, it is difficult at this time for me to properly compare emissions. Fred Medina is sending me some information from the SAIC report cited, but I will be receiving it after the comment period has ended. Therefore these comments are preliminary, but do indicate that this issue should be investigated by you further.

Your document does give 45.2 ug/liter as the average concentration of chloroform in drinking water in California (see page A-7). If all of the chloroform per liter were to end up in the air (an assumption supported by your document, again p.A-7) and a facility had a throughput of a million gallons per day, this facility would emit about 138 pounds per year (45.2 ug/liter x 1 liter/.2642 gal. x 10E6 gal/day x 365 days/yr x 10E-9 kg/ug x 2.205 lbs/kg). This amount by itself may be relatively small, but the total water throughput for all cooling towers using drinking water in the state could multiply this number by a large factor.

The ARB document Proposed Hexavalent Chromium Control Measure for Cooling Towers, January 20, 1989, does give some data on numbers of cooling towers in the state (pages 251-253). Page 252 gives

CITIZENS FOR A BETTER ENVIRONMENT

several methods of estimating numbers of cooling towers. One estimate gave 3,536 cooling towers in the South Coast Air Basin, which covered industrial process cooling towers, and some, but not all comfort cooling towers. If the South Coast represents around half of the state's total (this is a rough estimate based on our experience that for other pollution sources, the South Coast can represent between 40-60% of state emissions), then there may be around 7,000 cooling towers in the state.

Page 253 says that 1,980,000 gpm of cooling water is circulated by 588 chromate-using towers. If this number is representative of all cooling towers, then 7,000 cooling towers in the state could circulate about 12 times this amount. Doing the same kind of calculation as above for chloroform emitted over a year from all cooling towers, this gives 2337 tons/year! (7,000/588 x 1.98E6 gpm x 60m/hour x 24 hours/day x 365 days/year x 45.2 ug/liter x 1 liter/.2642 gal x 10E-9kg/ug x 2.205 lbs/kg x 1 ton/2000 lbs). This would be almost twice that from all the other sources identified.

Realistically, there may be factors which could reduce this estimate given a more detailed analysis, for instance the gallons per minute figure in the ARB document may be from large facilities, and not representative as an average figure for all cooling towers. In addition, perhaps not all these facilities use municipal water supplies treated with chlorine-based disinfectants. I believe PG&E in Pittsburg uses San Francisco Bay water which should not already be a source of chloroform. However, the numbers are potentially high enough that they should definitely be looked into further.

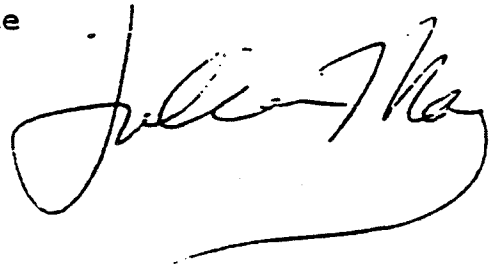
Please notify me directly of your investigation of this issue. This would be very helpful.

We may have more extensive comments on the final document. Thanks for your time.

Sincerely,

Julia May
Research Associate

cc. Fred Medina



o Citizens for a Better Environment, January 19, 1990

Comment: Citizens for a Better Environment (CBE) commented that they believe the ARB has under-estimated cooling tower emissions. CBE makes the following statements in support of their assertion:

1. **Comment:** ARB has included in their calculations only that portion caused by the addition of chlorine (or chlorine compounds) at the cooling tower facility neglecting chloroform already present in the water due to the addition of chlorine (or chlorine compounds) by the public water treatment facility.

Response: ARB used information on cooling towers from the SAIC study to calculate the emissions. It is questionable to predict the amount of chloroform that remains in the water system after treatment by a public water treatment facility. Even if chloroform existed in water before entering the cooling system, the levels of chloroform emissions will still yield similar results as the SAIC study. Furthermore, the SAIC survey does consider whether the baseline water usage was municipal surface or ground, municipal or industrial wastewater, natural brackish, saline, or otherwise recycled.

2. **Comment:** The draft chloroform document gives 45.2 ug/l as the average concentration of chloroform in drinking water. If one hundred percent of the chloroform concentration present in drinking water were emitted into the air, and a cooling tower facility had a throughput of a million gallons per day, then a facility would emit approximately 138 pounds per year.

Response: There are many variables in estimating cooling tower emissions such as: cooling tower type (open or closed), type of water used, how much used, and the type of biocide present. Further studies will be needed to examine all of these variables in the control phase.

3. **Comment:** CBE uses data from an ARB document Proposed Hexavalent Chromium Control Measure for Cooling Towers, January 20, 1989, to estimate the number of cooling towers in California, and the gallons per minute circulated by a chromate-using cooling tower. CBE estimates 7,000 cooling towers statewide, circulating 1,980,000 gallons per minute. Using the same method as above, CBE estimates that 2,337 tons per year of chloroform are emitted.

Response: The ARB document showed that 1,980,000 gallons per minute of cooling water is circulated by 588 chromate-using cooling towers. In addition, chlorine concentrations in the circulating water vary widely for all tower types. The staff at ARB recognizes that there is a probable under-estimate of chloroform emissions from cooling towers, but limited data keeps us from estimating statewide emissions. Further studies will be needed in the control phase.

MWD
METROPOLITAN WATER DISTRICT OF SOUTHERN CALIFORNIA

January 12, 1990

FEDERAL EXPRESS

Ms. Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
Post Office Box 2815
Sacramento, California 95812

Dear Ms. Denton:

Testimony Regarding Draft Report on Chloroform

The Metropolitan Water District of Southern California (Metropolitan) appreciates the opportunity to provide comments on the California Air Resources Board (ARB) December 1989 draft report on chloroform as a toxic air contaminant.

Metropolitan is a public, municipal corporation created by the State of California that wholesales supplemental water through 27 member agencies (cities and water districts). Metropolitan serves 14.7 million people in an area along the coastal plain of Southern California that covers approximately 5,200 square miles. Water deliveries are currently averaging over 2.0 million acre-feet per year.

Metropolitan's supplies come from two different sources. One source is Colorado River water obtained through a contract with the Federal Government and delivered to Southern California through 242 miles of aqueduct. The other source is Northern California water obtained through a contract with the State and delivered to Southern California through the 444-mile-long State Water Project. Metropolitan uses conventional treatment and provides disinfection through a combination of chlorine and ammonia. Current total trihalomethane (THM) levels in Metropolitan's distribution system average between 50 and 60 parts per billion. Total THMs are comprised of chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

The U.S. Environmental Protection Agency (USEPA) has begun the process of revising the current drinking water standard for THMs. Chloroform is one of the four THM disinfection by-products (DBPs) in drinking water that are

currently regulated by the USEPA and the California Department of Health Services (DHS). As you know, THMs are formed in water when chlorine comes into contact with naturally occurring organics, such as humic and fulvic acids. The current standard is set at 100 μg/L. The USEPA has indicated that the future standard (to be promulgated in 1991/92) will be 50 μg/L or 25 μg/L.

In anticipation of the revision of the THM standard, Metropolitan, in 1986, undertook an extensive program to research and evaluate alternate ways of controlling THMs. As a result of our efforts to date, Metropolitan is anticipating spending upwards of $200 - 300 million to install ozone or PEROXONE, a combination of ozone and hydrogen peroxide, at our treatment plants, by 1996, in order to comply with the future THM standard. In light of the extensive activities we have undertaken up to now, Metropolitan is concerned about possible regulatory actions by the Air Resources Board that could impact our efforts (and the efforts of utilities throughout the state) to comply with any future USEPA drinking water standards.

Metropolitan is concerned about the limited data presented in the ARB's technical support document. The December 1989 technical support document states that there is no recent data on levels of chloroform in California drinking water. Metropolitan would like to provide the following as data to supplement the support document. In 1987, the American Water Works Association developed a national THM survey database. Of the 1,255 utilities serving more than 10,000 people, which were sent a survey form, 145, or 12 percent, were California water utilities. A total of 79 California utilities returned a valid survey form with usable THM data. The California THM data are shown on Figure 1. (We are also enclosing a copy of the January 1988 article in the Journal of American Water Works Association that discusses the results of the nationwide survey.)

In early 1988, DHS entered into a cooperative agreement with the California Public Health Foundation (CPHF) to fund a study of the occurrence and control of DBPs in California drinking waters. After submitting a grant proposal to the CPHF, Metropolitan was contracted to perform the study. The principal objective of the study was to collect data from 10 representative water utilities in the State on the occurrence and control of DBPs in drinking water, including chloroform. Four quarters of data were collected at each utility, beginning in March 1988 and ending February 1989. As you can see on Figure 2 there are other DBPs besides THMs. Figure 3 reveals that THMs represent the largest percentage of DBPs and of the DBPs, chloroform represents

the largest percentage of THMs (Figures 4 and 5). Table 1 gives the median values of the DBPs for all four quarters of data in the ten utility systems. (In addition to the above-mentioned tables, we are submitting a copy of the entire report entitled Disinfection By-Products in California Drinking Water.) This data should be reviewed by the Air Resources Board.

Regarding the second document we received, Health Effects of Chloroform (California Department of Health Services, March 1989), Metropolitan is concerned that data from the NCI (1976) study were used in the risk estimation. Over the last several years, serious questions have arisen regarding the validity of data generated in studies where chloroform was administered in corn oil. Volume 7 of Drinking Water and Health, Disinfectants and Disinfectant By-Products (Safe Drinking Water Committee, National Research Council) presents an excellent review of these studies. We believe the concerns raised in Volume 7 must be addressed in DHS' Health Effects of Chloroform. In particular, we would draw your attention to page 127, of Volume 7, where the Committee states:

> "Thus chloroform in corn oil caused more marked hepatotoxic effects in mice than did chloroform in Emulphor or, in comparison with other investigations (Jorgerson et al., 1985), than did chloroform in water. This seems to suggest that the discrepancy between the incidences of liver tumors in the investigations of NCI (1976) and of Jorgerson et al (1985) can be accounted for by the vehicle of administration, chloroform in corn oil causing more marked hepatic effects than chloroform in other vehicles."

The USEPA's Office of Drinking Water (ODW) has determined that the risk estimates based on animal studies with chloroform in corn oil are not appropriate for inclusion in future THM regulations. Metropolitan would be concerned if by incorporating these studies (i.e., NCI, 1976) in the ARB process, chloroform would be identified as a toxic air contaminant with an incorrect risk level.

We are also sending a copy of a draft paper submitted to "Toxicology and Applied Pharmacology" ("Estimating the Risk of Liver Cancer Associated with Human Exposures to Chloroform [Draft Manuscript]") for your consideration. The physiologically based pharmacokinetic model laid out in the manuscript allows for a more realistic evaluation of exposure and risk assessment.

We hired a toxicologist, Dr. Richard Bull, of Washington State University, to review the DHS health effects document of chloroform. The attached report presents his review and critique of the health effects document.

Very truly yours,

Michael J. McGuire Ph.D.
Director of Water Quality

JSS:DJA:ra

Enclosure

- Metropolitan Water District of Southern California (MWD), January 12, 1990

1. **Comment:** MWD anticipates spending $200 - 300 million to install equipment and processes in order to comply with the future trihalomethane (THM) standard of the U.S. EPA. The MWD is concerned that possible regulatory actions by ARB will impact MWD efforts to comply with future U.S. EPA standards.

Response: The regulatory actions will be addressed in the control phase if chloroform is identified as a toxic air contaminant.

2. **Comment:** MWD is concerned with the limited data in the draft chloroform document on the levels of chloroform in California drinking water.

Response: MWD provided results of several surveys on chloroform concentrations in drinking water. The surveys provided by MWD contain estimates of levels of chloroform found in drinking water. These surveys estimate that trihalomethane (THM) concentrations in water are 5 to 80 ppb.: of which chloroform represents the greatest percentage. Our chloroform emission estimate of 45.2 ppb. is well within this range. In addition, this reflects a population-weighted emission factor which provides a better estimate of California emissions.

MBR ENVIRONMENTAL CORPORATION
5839 Green Valley Circle, Suite 201
Culver City, CA 90230
(213) 338-8717

L-MBR-90-007

January 18, 1990

Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn.: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Subject: Comments on Draft Technical Support Document, Proposed Identification of Chloroform as a Toxic Air Contaminant. Part A. Public Exposure to, And Emissions of Chloroform in California

Dear Ms. Denton:

Thank you for the opportunity to review the subject report. As the Principal Investigator for a study which is frequently cited in the document, I was especially interested in the Air Resources Board's findings. I am limiting my review to Part A. In general, I found the report to be quite thorough, informative, and readable. I do, however, have several comments, which I have divided into two parts. The first part lists substantive issues, while the second addresses typographical errors and other minor matters.

1.0 SUBSTANTIVE COMMENTS

(1) General Comment. It is not clear what the ARB's conclusions are regarding exposure to chloroform; there is no summary showing what values were provided to the Department of Health Services (DHS) for its analysis. Indeed, it appears from a quick look at the March, 1989 report "Health Effects of Chloroform," that the DHS did not use information from the Part A report.

(2) Pharmaceutical Manufacturing Emissions. The ARB's estimate of 190 tons of chloroform emissions from this source is two orders of magnitude higher than what we at Science Applications International Corporation (SAIC) estimated for the South Coast Air Basin (Rogozen et al., 1988). Were the respondents to the

Pharmaceutical Manufacturers Association (PMA) survey representative of the industry? I do not know whose estimate is more "correct;" however, the ARB should take a close look at the PMA data.

(3) Fluorocarbon 22 Production. Chloroform is used as a feedstock in the production of some chlorofluorocarbons, but not all, as the report implies. For example, carbon tetrachloride, not chloroform, is the feedstock for Freon-12 (Pool, 1988). Who prepared the report on which the emission estimate for the Allied Corporation plant is based? Science Applications, Inc. conducted fugitive leak tests there in the early 1980s and determined that annual chloroform emissions were between 0.089 and 0.163 ton per year (Ziskind et al., 1982). This is quite at odds with your estimate.

(4) Cooling Towers. The South Coast Air Quality Management District did not estimate that 2.3 tons per year of chloroform were emitted from industrial cooling towers; we at SAIC did (Rogozen et al., 1988).

(5) Combustion of Leaded Gasoline. Entirely too much weight is placed on Harsch et al.'s reported results. In our study for the ARB (Rogozen et al., 1988), we could find only one other published analysis of chloroform in automotive exhaust, and it was inconclusive. Furthermore, there is no plausible reaction pathway leading to formation of chloroform from 1,2-dichloroethane.

(6) Section III-D-3 (Vaporization from Water Sources), Page 17. Emission flux rates for indoor and outdoor pools are not likely to be similar. First, the flux is driven primarily by a concentration gradient equal to the difference between the actual chloroform concentration in the water and the aqueous chloroform concentration which would occur if the $CHCl_3$ in the overlying air and in the water were in equilibrium. In the case of an outdoor pool, the overlying air's chloroform content would likely not be much above ambient concentrations. In the case of an indoor pool, as demonstrated by the findings of Lahl et al. (1981), chloroform concentrations in the overlying air are much higher. Therefore the concentration gradient would be lower for the indoor case. Second, the flux rate also depends upon the mass transfer coefficient, which, in the case of chloroform, is dominated by the liquid phase mass transfer coefficient, which increases nonlinearly with increasing wind speed. Outdoor pools

are likely to have significantly higher surface wind speeds than indoor pools. For both reasons cited, emission flux rates from outdoor pools are likely to be higher than those from indoor pools.

(7) Section IV-A (Ambient Monitoring for Chloroform). Why did you not use, or even mention, the data collected through the ARB's ambient halogenated hydrocarbon monitoring program in the South Coast Air Basin (Shikiya et al., 1984)? That program provided measurement data over several years, while the data used in the present document cover only 12 months in Northern California and 6 months in Southern California. Because many researchers are aware of the larger data set, your report should state the reasons why it was not used. If you do use the Shikiya data, it would be interesting to compare the results for different years. For example, our analysis of measurement data for 1983-1984 found slightly higher 24-hour average concentrations. Could the reason for this be the Los Angeles Department of Water and Power's switch from chlorine to chloramines in treatment of drinking water?

Table IV-2 does not give the results based upon the Gleit method, so its title should say "USING THREE METHODS..."

(8) Section V-G (Ambient Concentrations). Given the detailed analyses in Section IV, is this section relevant?

(9) Appendix A-5. When applied to SAIC's data on actual chlorinated water use in the South Coast Air Basin (3.38×10^{12} liters in 1985), the method of Appendix A-5 yields a chloroform emission estimate of 119 tons. Our estimate, based upon amounts of chlorine applied, was 190 tons. This discrepancy should be addressed.

2.0 MINOR COMMENTS

(1) Page 1, Line 3: Change "$CHCL_3$" to "$CHCl_3$".

(2) Page 1, Line 4: Add a comma after "synonyms."

(3) Page 1, ¶ 2, Line 1: Delete the semicolon.

(4) Page 2, ¶ 1, Line 10: Change density of chloroform to pounds per gallon or grams per liter; don't mix units. Also, the value for the density appears to be wrong.

(5) Table II-1: The L's in the structural formula should be lower case.

(6) Page 6, ¶ 6, Line 1: Remove "The."

(7) Page 6, ¶ 6, Line 8: Add comma after 373.

(8) Page 6, ¶ 6, Line 10: Change "was" to "were."

(9) Page 10, ¶ 4, Line 7: Add comma after "which."

(10) Page 12, Line 1: Delete "to water." (Steam is water.)

(11) Page 24, ¶ 2, Line 4: Change "is statistically different then..." to "are statistically different from those of..."

(12) Page 26, ¶ 1, Line 3: Change "between the data reported for each site" to "among the data reported for different sites."

(13) Page 26, ¶ 1, Line 7: Delete "however."

(14) Table IV-6, Footnote 3: Change "Coefficient of Variations" to "Coefficients of Variation."

(15) Page 34, ¶ 4, Line 2: Change "absorbent" to "adsorbent."

(14) Page 26, ¶ 2, Line 11: Change "less" to "other."

(15) Page 55 - 57, throughout: Change "CL" to "Cl." Also, denote radicals by placing a dot over the atom which has the abstracted hydrogen, e.g. the C in $\dot{C}Cl_3$.

(16) Page 55, ¶ 2, Line 2: Change "$CHCl_3$" to $\dot{C}Cl_3$.

(17) Page 57, 2nd Equation: In the subscript for τ, change "photyolysis" to "photolysis."

(18) Page 58, Line 4: If you keep this section, then change "AR" to "AZ."

(19) Appendix A-6: Change "CHC13" to "$CHCl_3$" throughout. Also, what is the Lockwood Directory? It is never introduced or identified.

(20) Appendix A-7: Change "CL" to "Cl" throughout and put subscripts on molecular formulas where appropriate.

(21) References, Page 2: One of the halocarbon formulas in the Davis et al. title appears to be wrong, and the "CL" should be changed to "Cl."

(22) References, Page 3: In the Dognon et al. reference, change "daus" to "dans."

(23) References, Page 5: In the Robbins reference, change "Internationsl" to "International."

(24) References, Page 5: Delete the Rogozen et al. reference, since it's listed right afterwards.

(25) References, Page 6: In the Rogozen et al. reference, change "Manhatten" to "Manhattan" and remove the period from after "CA."

(26) References, Page 6: In the SMRB reference, change "Simmars" to "Simmons."

3.0 REFERENCES

Pool, R. 1988. "The Elusive Replacements for CFCs," Science 242:666-668.

Rogozen, M.B., H.E. Rich, M.A. Guttman, D. Grosjean, and E.L. Williams II. 1988. Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin. Prepared by Science Applications International Corporation and Daniel Grosjean and Associates for the California Air Resources Board, Contract No. A4-115-32.

Shikiya, J., G. Tsou, J. Kowalski and F. Leh. 1984. "Ambient Monitoring of Selected Halogenated Hydrocarbons and Benzene in the California South Coast Air Basin." Paper No. 84-1.1, presented at the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, CA.

Ziskind, R.A., M.B. Rogozen, D.M. Baxter, M.A. Guttman, N.W. Flynn, R.F. Shokes, S.E. Salot and R.J. Gordon. 1982. Inventory of Carcinogenic Substances Released into the Ambient Air of California. Phase II. Prepared by Science Applications, Inc. for the California Air Resources Board, Report No. ARB-R-82/178.

Thank you again for the opportunity to review the document. If you or your staff would like to discuss my comments with me, I can be reached at (213) 338-8717.

Sincerely,

MBR Environmental Corporation

Michael B. Rogozen, D.Env.
President

o MBR Environmental Corporation, January 18, 1990

1. **Comment:** It is not clear what ARB's conclusions are regarding exposure to chloroform; there is no summary showing what values were provided to the Department of Health Services (DHS) for its analysis. Indeed, it appears from a quick look at the March, 1989 report "Health Effects of Chloroform," that the DHS did not use information from the Part A report.

Response: The Executive Summary included in this version of the report provides a summary of our conclusions. In Part B the DHS used data from Part A to calculate the health risk from exposure to chloroform.

2. **Comment:** The ARB's estimate of 190 tons of chloroform emissions from Pharmaceutical Manufacturing industries are two orders of magnitude higher than what Science International Corporation (SAIC) estimated for the South Coast Air Basin (Rogozen et al., 1988). Were the respondents to the Pharmaceutical Manufacturing Association (PMA) survey representative of the industry? Commenter urges ARB to take a close look at the PMA data.

Response: The response rate to the PMA survey was near 50%, while the response rate to the SAIC survey was 28.7%. The PMA surveyed the entire nation, while the SAIC surveyed only the South Coast. We believe the estimate using the PMA survey data gives a better estimate for chloroform emissions of Pharmaceutical Manufacturing companies in California.

3. **Comment:** Chloroform is used as a feedstock in the production of some chlorofluorocarbons, but not all. Who prepared the report on which the emission estimate for the Allied Corporation plant is based? Science Applications, Inc. conducted fugitive leak tests there in the early 1980s and determined that annual chloroform emissions were between 0.089 and 0.163 ton per year (Ziskind et al., 1982). This is different than ARBs estimate.

Response: The report did not intend to imply that chloroform is used as a feedstock in the production of all chlorofluorocarbons. Your comment is noted and the text was changed to read "Chloroform is used as a feedstock in the production of some chlorofluorocarbons." The report on the emission estimate for the Allied Corporation plant is based upon the Technical Report: Chlorofluorocarbon Production (TRCP, 1986). ARBs policy is to use the most recent data for estimating emissions so the Ziskind et al., 1982 reference was not used.

4. **Comment:** The South Coast Air Quality Management District did not estimate that 2.3 tons per year of chloroform were emitted from industrial cooling towers; SAIC did (Rogozen et al., 1988).

Response: The correction has been made.

5. **Comment:** Combustion of Leaded Gasoline. Entirely too much weight is placed on Harsch et al.'s reported results. In our study for the ARB (Rogozen et al., 1988), we could find only one other published analysis of chloroform in automotive exhaust, and it was inconclusive. Furthermore, there is no plausible reaction pathway leading to formation of chloroform from 1,2-dichloroethane.

Response: Changes in the document have been made to reflect your comment by inserting this paragraph on pg 13:

" According to SAIC, only only one other report was found to have attempted to measure chloroform from automobile exhaust. The results of this report entitled " On the Occurrence of Aliphatic Chlorine and Bromine compounds in Automobile Exhaust " by E. Hasanen, et al was inconclusive of the presence of chloroform. "

6. **Comment:** Emission flux rates for indoor and outdoor pools are not likely to be similar. First, the concentration gradient would be lower for an indoor pool. Second, emission flux rates from outdoor pools are likely to be higher than those from indoor pools.

Response: Changes in the document have been made to reflect your comment. On pg 21,22; the last sentence on of the third paragraph has been revised to read, "Emission flux rates for indoor and outdoor pools are not likely to be similar. This is due to different concentration gradients between the actual chloroform concentration in the water and the aqueous chloroform concentration which would occur if the chloroform in the overlying air and in the water were in equilibrium. In the case of an outdoor pool, the overlying air's chloroform content would not be much higher than ambient concentrations. Whereas, in the case of an indoor pool (Lahl et al. 1981), chloroform concentrations in the overlying air are much higher. Therefore, the concentration gradient would be lower for the indoor pool. Second, the flux rate also depends upon the mass transfer coefficient, which, in the case of chloroform, is dominated by the liquid phase mass transfer coefficient, which increases non-linearly with increasing wind speed. For both reasons cited, emission flux rates from outdoor pools are likely to be higher than those from indoor pools."

7. **Comment:** Section IV-A (Ambient Monitoring for Chloroform). Why did you not use, or even mention, the data collected through the ARB's

ambient halogenated hydrocarbon monitoring program in the South Coast Air Basin (Shikiya et al., 1984)?

Response: We did not use the Shikiya data because it is our policy at ARB to use the most recent 12 months of data and there were only 4 sites in the South Coast at which data were collected. The reasons for not using these sites are: 1) the sites were discontinued after 2 years and 2) the data are of low quality.

7a. **Comment:** Table IV-2 does not give the results based upon the Gleit method, so its title should say "USING THREE METHODS...."

Response: The correction has been made.

8. **Comment:** Given the detailed analysis in Section IV, is section V-G relevant?

Response: Section IV provides California ambient concentrations; section V-G provides national ambient data and a global tropospheric average for chloroform.

9. **Comment:** When applied to SAIC's data on actual chlorinated water use in the South Coast Air Basin (3.38×10^{12} liters in 1985), the method of Appendix A-5 yields a chloroform emission estimate of 119 tons. Our estimate, based upon amounts of chlorine applied, was 190 tons. This discrepancy should be addressed.

Response: Our estimate of emissions is also 190 tons as shown in Table III-1 and Appendix A-1. Using the method of Appendix A-5 for the South Coast:

$$2{,}741{,}823 \ \frac{\text{Acre-Feet}}{\text{Year}} = 3.38 \times 10^{12} \text{ L/yr.} - \text{conversion factor}$$

$$(3.38 \times 10^{12} \text{L/yr})\ (45.2 \text{ ug/L}) = 152{,}849 \ \frac{\text{kg } CHCl3}{\text{Year}} = 168.5 \text{ Tons/yr}$$

168.5 tons per year is within 13% of the estimate of 190 Tons/yr, so we've determined that the estimate of 190 tons will remain in the report.

10. **Comment:** Numerous (26) typographical errors.

Response: All minor changes have been made.

DAVID L. GOODMAN
Vice President
Public Affairs and
Marketing Services

May 21, 1990

Ms. Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Denton:

The Clorox Company, headquartered in Oakland, California, manufactures and markets a wide variety of consumer household products, food products, charcoal briquets and bottled water. The company owns and operates 35 facilities in 19 states and employs approximately 5,000 people nationwide. The following represents the company's position regarding the technical support document, Part A, Public Exposure To, and Emissions of Chloroform in California, dated December, 1989. These comments are based on the company's extensive experience in formulating, packaging and marketing consumer products and on our commitment to the safe manufacture, distribution, use and disposal of these products.

The Clorox Company strongly objects to the use of cooling tower chloroform emission data in estimating chloroform emissions from household bleach used for laundry. CARB estimates the use of liquid bleach in domestic laundering produces an esimtated 13.5 tons of chloroform air emissions in California. The estimate is extrapolated from calculations by Rogozen et al. (1988). The referenced document states that emissions of chloroform in the South Coast Air Basin were estimated by assuming a molar ratio of 0.001, or half that of the cooling towers. The company firmly believes that such estimates are inappropriate as a calculation of chloroform emissions from household bleach and should not be used, particularly as a basis for regulation. There are significant differences in pH, soil level, bleach concentration, contact time, soil type and temperature, all of which are known to affect reaction products.

The company recommends modeling of household laundry practices and direct measurements as the most appropriate form of data generation. We will be happy to provide you with the parameters and technical data necessary to develop a meaningful model.

The Company appreciates the efforts taken by CARB staff to involve industry in the rulemaking activities and staff's consideration of The Clorox Company's concerns regarding this document.

Sincerely,

DLG:rmg

The Clorox Company
1221 Broadway
Oakland, California
94612-1888
P.O. Box 24305
Oakland, California
94623-1305
(415) 271-7207

o The Clorox Company, May 21, 1990

Comment: The Clorox Company objects to the use of cooling tower chloroform emission data in estimating chloroform emissions from household bleach. CARB estimates the use of liquid bleach in domestic laundering processes to be 13.5 tons of chloroform air emissions in California, an estimate extrapolated from calculations by Rogozen et al. (1988).

Response: The estimate of 13.5 tons per year of chloroform probably underestimates emissions since it does not include commercial bleach consumption. The emission estimate for household bleach was based on an available published methodology and data from SAIC. The report by SAIC assumed a molar ratio of 0.001, or half that of cooling towers. We believe this is a reasonable assumption. When compared to the table of molar ratio ranges of drinking water as shown on page 4-10 pf SAIC report, the molar ratio of 0.001 is lower. Based on this and the assumption that household bleach used for laundry would contain more chlorine and thus form more chloroform, it appears that a molar ratio of 0.001 is a reasonable assumption for domestic bleach consumption. We are aware that chloroform formation is dependent on many variables including the ones mentioned in the Clorox letter; however in the absence of more specific data, the estimate of 13.5 tons per year of chloroform is the best estimate available at this time.

Olin

4363 NORTH OCOEE STREET. CLEVELAND. TN 37312

(615) 336-4006 Fax: (615) 336-4060

May 9, 1990

Joan E. Denton, Manager
Substance Evaluation Section
Stationery Source Division
Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Dear Ms. Denton:

Over the past few weeks I have tried unsuccessfully to reach you or members of your staff to discuss a technical support document regarding chloroform emissions.

In this technical support document prepared for California's Air Resources Board, swimming pools are identified as the major source of chloroform emissions to California air amounting to 29% of the total emissions, and pegged at 340 tons/year. While we did not receive this document in time to respond to the January 15, 1990 deadline, it is my understanding that Part C of the document, which compiles the public comment and the responses to them, has been published. I would like to request a copy of this from you.

My calls to your office, however, were to discuss how the chloroform emissions were calculated. The information provided shows that in estimating the emission flux, the determinate was over only one (1) swimming pool which had been covered for a substantial period prior to the test. With respect to the magnitude of the calculated emissions from swimming pools, a rough check of the sensitivity shows that the

most crucial determination is the emission flux, and an error of 1 ug/m^3-min can result in a change of more than fifteen (15) tons/year in the estimate. Therefore, one must question whether or not adequate, scientific data was used.

In addition, we would like this concern presented either with any additional public comment, or supplied to your Scientific Review Board. We would also be willing to provide public testimony or supply data on our own calculations if necessary.

I would very much appreciate hearing from you.

Sincerely,

John J. Chiaramonte, Jr.
Manager, State Affairs

jjc/L043

cc: Carvin DeGiovanni
National Spa and Pool Institute

Mike Neal
Dow

Olin
RESEARCH CENTER
350 KNOTTER DRIVE, P.O. BOX 586
CHESHIRE, CT 06410-0586
(203) 271-4000

June 25, 1990

Mr. Robert Krieger
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Krieger:

John Chiaramonte of our state legislative affairs department has reported that you are still accepting comments on the draft Technical Support Document to the "Proposed Identification of Chloroform as a Toxic Air Contaminant". I understand that the initial comments have not as yet been published and that our response will be forwarded with the initial comments to the Science Review Panel for their consideration.

The attached comments deal with our concern about emissions of chloroform from swimming pools. We were very surprised to read that they were believed to be such a significant portion of the total statewide emissions. Particularly when compared with the estimated emissions for drinking water treatment and publicly owned treatment works, where the volume of treated water is so large, the portion seems high. Further reading of the study upon which the calculation was based showed that emission flux was calculated on the basis of measurements at one pool over one 26 hour period. Because there is tremendous variability in the way that people maintain and use their swimming pools both from person to person and from season to season in the year, I do not believe that a representative picture can be made on the basis of such limited information. And, while the experiment done to measure the emissions seems direct, I have to question the use of such high flow rates and temperatures inside the dome. Both of these factors would seem to perturb the equilibrium distribution of chloroform between air and water and both would seem to overestimate the flux.

I have heard from NSPI that we will be meeting to discuss some of the issues raised by the ARB's report. I look forward to this meeting as a chance to discuss the issues, implications and possibilities for further study on the very complex problem of chloroform emissions from swimming pools.

Sincerely,

Bonnie B. Sandel

Bonnie B. Sandel, Ph.D.
Senior Research Associate
Water Products and Services

cc: Joan Denton, Ph.D.
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Bonnie B. Sandel, Ph.D.
Senior Research Associate
Olin Corporation

Comments on Chloroform Emissions from Swimming Pools

This is a response to the request for comments on the Draft Report on Chloroform issued in December of 1989. As manufacturers of swimming pool disinfectant products, our interest and comments relate to the report's finding that emissions from swimming pools and spas amounted to 29% of the total emissions of chloroform and represented the largest source of chloroform in California's air. We believe that additional data gathering is necessary to test this contention.

We have reviewed Part A of the Technical Support Document and the contract research (R[illegible]gozen, et al., Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin, April, 1988) upon which the calculation was based. As set forth in these documents the swimming pool emissions were based on measurements made over one pool during one 26 hour period in mid-May. The measurements allowed the contractor to estimate a flux value for still conditions, 12 ug/m^2-min, and for agitated conditions, 320 ug/m^2-min. Next the contractor estimated the average amount of time spent in each condition on a month-to-month basis for the South Coast Air Basin and came up with a weighted flux value of 22.3 ug/m^2-min. This same weighted flux value was later multiplied by the estimated surface area of the pools and spas of California and the number of minutes in the year to yield the calculated emissions of 340 tons/yr, statewide.

Our major issues with this work fall into two areas: the appropriateness of this one pool on this one day as a model for all pools all year; and the technical difficulties of the measurement techniques utilized. The first area of concern was recognized by the contractors who stated, "The chief area of uncertainty is our estimate of emissions from swimming pool chlorination," and recommend that further study including "a long-term program of water testing at a statistically representative sample of swimming pools" be carried out. We would include air sampling in the recommended testing and suggest that year-round data are needed to reflect the high use, high temperature, high chlorination periods and the low to no use, lower temperature, low or no chlorination periods throughout the state. As a model for this great variability, data from one pool on one day will be inadequate for several reasons, some of which are summarized below.

Bonnie B. Sandel, Ph.D.
Senior Research Associate
Olin Corporation

(1) The pool in question had been covered for at least 3 weeks prior to the test and only uncovered 24 hours prior to the onset of measurement. Because most chloroform emission will be blocked by the cover, levels in the water are generally higher than they would be had normal equilibration with air occurred, and emissions are likely to be elevated by the contribution of three weeks' formation of chloroform. That the steady state has not been reached is demonstrated by the downward trend in the aqueous measurements during the 24 hours of sampling despite the addition of chlorine (Figure 8.2-3).

(2) The levels of chloroform in the water of the one sampled pool were 53 ppb. How typical is this for residential pools in California? In European studies there is substantial variability in measured levels of aqueous chloroform for outdoor and indoor pools depending on treatment methods, local vegetation, temperature and batherload.

(3) The equation used to calculate the weighted flux (4.63) deals explicitly with only variation in swimming activity levels from month to month. These levels were derived for local conditions in the South Coast Air Basin. While they may have been considered on some level, variations in temperature and chlorination rates were not included in the calculation. Because periods of the year exist when most pools, especially in northern California, are covered and not used or chlorinated at all, use of the South Coast Air Basin flux for all the pools is inappropriate and tends to exaggerate the emissions.

(4) Cyanuric acid levels for the pool are not determined, but may have a profound effect on the proportion of added chlorine that reacts to form chloroform. We agree with the contractors that a steady level of measured chlorine would indicate that this pool was stabilized (loss of chlorine in sunlight would be rapid otherwise). For comparison, consideration of emissions from unstabilized pools should be made.

With respect to the flux measurement itself, we appreciate the difficulty of such a determination, but must raise several points concerning the measured values:

Bonnie B. Sandel, Ph.D.
Senior Research Associate
Olin Corporation

(1) The use of dry "zero air" will yield a substantial flux of chloroform "pulled along" with the evaporating water.

(2) The flow rate utilized in the study (10.7 L/min) is substantially higher than the flows recommended by Dupont (<1 L/min) in the reference cited by the contractors. Dupont states that flows less than 1 L/min were required in a similar emissions flux chamber in order to avoid pressure build-up. The high flow rate of air across the surface could substantially change the liquid-side mass transfer coefficient. Also, in view of the position of the sampling port, can the possibility that droplets were sampled be ruled out?

(3) The temperature inside the chamber was elevated (95-120°F), during the sampling. A potential source of error is the resulting evaporation as water is splashed onto the heated surface. Such splashing would unavoidably occur during the plugging of the exit hole (a step made just before sampling).

(4) During the agitation "by hand" that the contractors describe, the effective surface area becomes ill-defined, and flux from draining films splashed onto the sides of the chamber may well be the dominant contribution to the high measured values.

A statistical analysis of the experimental results described in the contractors' Table 8.2-2 shows that the standard deviations for the "still" and "agitated" conditions are 6.28 and 34.7 ug/m^2-min, respectively. The calculated mean flux has a standard deviation of 6.18. Even if this represented the only source of error in the calculated emissions from swimming pools the value would be reported as 340±94 tons of chloroform/year. For the reasons stated above we believe that the calculated values may be substantially higher than the true emissions and that further study is merited.

PPG Industries, Inc. One PPG Place Pittsburgh, Pennsylvania 15272 (412) 434-2350

W. B. Graybill
Director
Environmental Affairs
Chemicals Group

June 28, 1990

Mr. Robert Kriger
Assistant Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attention Chloroform
P. O. Box 2815
Sacramento, CA 95812

Dear Mr. Kriger:

The purpose of this letter is to provide comment resulting from our review of the test protocol reported in:

SAIC-86/1105 [*SCIENCE APPLICATIONS INTERNATIONAL CORPORATION*]

"SOURCES AND CONCENTRATIONS OF CHLOROFORM EMISSIONS IN THE SOUTH COAST AIR BASIN"

FINAL REPORT

8 April 1988

The particular protocol in question relates to the Swimming Pool Emissions Tests described in Section 8, pages 29 to 47 [8-29 to 8-47].

(1) This part of Section 8 is attached.

The results of this protocol were used in a later report.

DRAFT FOR PUBLIC REVIEW AND COMMENT

PROPOSED IDENTIFICATION OF CHLOROFORM AS A TOXIC AIR CONTAMINANT

TECHNICAL SUPPORT DOCUMENT

REPORT TO THE AIR RESOURCES BOARD ON CHLOROFORM

PART A

PUBLIC EXPOSURE TO AND EMISSIONS OF CHLOROFORM IN CALIFORNIA

Project Coordinator: Mimi Jones

(2) Page 9 and Appendix A-4 are attached.

The stated objectives of the field research on Swimming Pool Emissions were "(1) **to confirm that chloroform is emitted from swimming pools and (2) to estimate emission rates which could be generalized to pools in the South Coast Air Basin**".

Our review finds that objective (1) was satisfied in the one pool tested, but the protocol was inadequate to satisfy objective (2).

The protocol was, in our opinion, inadequate for the following reasons.

1. **The population of pools tested was only one.**

This assumes that this pool emits chloroform at the mean level for all pools in the region of concern. It should be expected that there would be a normal distribution of emission flux levels for a large population of pools. There is no basis to know where in that distribution this particular pool falls.

There is a basis to say that the chloroform concentrations present in this pool were higher than a typical pool would exhibit. The experimenters stated, "**The concentrations during the baseline conditions (55 - 74ppb) were surprisingly high, considering that the pool had not been chlorinated in quite some time.**"

No data were presented for other pools of the levels of chloroform in the water to provide a comparison basis. What if the typical or mean pool has an order of magnitude lower level of chloroform and the resulting flux rat is proportionally lower? Any estimate of chloroform contribution to the air would be reduced considerably. A similar statement could be made for the potential for higher levels but the experimenters comment was that "**—the concentrations during the baseline conditions were surprisingly high,—**"

2. **The test pool was not a normal operating and maintained pool.**

The pool had been covered for 2.5 weeks prior to the testing with no additions of chlorine or fresh water (does this mean there was no rainfall during this period?).

The operation and use history of the pool prior to the 2.5 week period to establish the "baseline" condition was not defined.

It is likely that the 2.5 week covered period would cause higher chloroform levels due to accumulation as a result of the cover essentially eliminating any water-air interface for transport of chloroform from the water.

3. **The four protocol conditions: baseline, transition, normal and high with respect to free chlorine levels, did not produce data to demonstrate that any chloroform was generated during the measurement period (Attachment 1).**

These observations were made by the experimenters and should have been the basis to disqualify the test for not having answered the question being asked.

4. **Operation of the emission isolation flux chamber at elevated temperature conditions would contribute to higher than normal chloroform emission rates.**

These elevated chamber temperatures create a condition within the chamber similar to "steam stripping", particularly during the agitated water testing periods. The significance of this elevated thermal condition is that the emission rate of volatiles from the water body would be artificially high.

The above 4 comments are offered as primary reasons that the subject protocol and testing did not answer the questions that were being asked.

These data were nevertheless utilized to develop the emission estimates given in a subsequent report (Attachment 2).

It is recommended that this study be reexamined in view of the comments and concerns pointed out in this correspondence. It is in the best interest of all concerned that the quality of the data being used to make important environmental regulatory recommendations should be technically and statistically valid.

Sincerely,

W. B. Graybill

WBG/yra

Attachments

NATIONAL
SPA AND POOL
INSTITUTE

2111 EISENHOWER AVENUE
ALEXANDRIA, VA 22314-4698
(703) 838-0083

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June 19, 1990

Joan E. Denton, Manager
Substance Evaluation Section
Stationery Source Division
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Re: California Study of Chloroform Emissions on Swimming Pools

Dear Ms. Denton:

Founded in 1956, the National Spa and Pool Institute (NSPI) is an industry-supported association of over 4,300 firms involved in the pool, spa and hot tub industry. NSPI members share a commitment to public health and safety in the installation, maintenance and operation of pools, spas and hot tubs. They also share a commitment to establish voluntary uniform design and construction standards. (Copies enclosed).

NSPI conducts numerous consumer education and member training programs on local, state and national levels, and keeps members apprised of the latest scientific and technological developments through seminars, workshops, publications and an annual convention and exposition.

The Technical Council of NSPI is responsible for all of the technical affairs of the association, including the development of policy recommendations to the Board of Directors and the implementation of such policies. The Council develops and revises product-related consensus standards, conducts appropriate scientific research and carries out such other technical activities as may be required by the association and its committees.

The Chemical Treatment and Process Subcommittee of the Technical Council is made up of industry experts in the technical and chemical operational areas of swimming pools and spas. These two bodies have realized the growing concern and attention being given to overall water and environmental quality in general and safety, in particular.

One area of immediate interest is that of Air Quality and trihalomethane. Obviously, this concern includes chloroform. We are in receipt of your notices for comment from the California Air Resources Board and while we clearly both understand and appreciate the concern over chloroform emissions, we question the accuracy or sensitivity of the data cited in the report.

Swimming pools and spas are not necessarily simplistic to operate; a great many factors, including physical, chemical and biological, are involved. Each of these areas must be properly managed. Each can have an impact on overall water quality and thus, indirectly, chloroform emissions.

The intent of our work is to provide operational parameters which result in optimal water quality. This in turn, would logically lead to reductions of the by-products of concern. Again, it is a priority of our organization to address the entire THM issue. We share the concern of the Air Resources Board, however, we feel it imperative to have an accurate assessment of the potential problem and would welcome an opportunity to work with the Board in an evaluation of its current information, as well as a proper and defined study.

However, at this point in time we have serious questions concerning the methodology of the emission calculations. We request an immediate opportunity for our company representatives to sit down with your researchers to review the methodology used.

Action based on the very limited information now available could not only be misleading, but also a disservice to the public. This office requests to be apprised of future developments/progress of this activity.

Sincerely,

William W. Sadd

William W. Sadd
Executive Vice President

WWS:ns

Monsanto

Monsanto Chemical Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167
Phone: (314) 694-1000

Monsanto Water Treatment

June 22, 1990

Ms. Joan E. Denton, Manager
Substances Evaluation Section
Stationary Source Division
Air Resources Board
Attention: Chloroform
P. O. Box 2815
Sacramento, CA 95812

Dear Ms. Denton:

Monsanto has just learned about the "Report To The Air Resources Board on Chloroform, Part A - Public Exposure To Environmental Fate of, and Sources of Atmospheric Chloroform In California." Since the report indicates that swimming pools treated with chlorine sanitizers are a major source of chloroform emissions in California and Monsanto is a major chlorine sanitizer producer, we would like to learn more about your staff's research work and future plans. Therefore, we hope that it is not too late to participate in this evaluation program and comment on some of the research data.

Although I have not had the opportunity to study the report in great detail, I did find the results to be rather surprising. I had expected that other applications; e.g., chloroform users, chlorine sanitization of drinking water, etc. would be greater sources of chloroform emissions. For this reason, I reviewed the report "Sources and Concentrations of Chloroform Emissions In the South Coast Air Basin," Final Report, April 8, 1988 by M. B. Rogogen, et al. It is a well-written report and appears to be thorough. However, even though the experimental technique used in the swimming pool research work was elegant, I had a difficult time accepting the results of the calculations. The basis for my concern is that the data from a few experiments over a couple of days on one pool in May were used to estimate the chloroform emissions for all swimming pools in California. As a scientist, I know my peers would make me run many more experiments on several pools at different times of the year, different water temperatures, and various organic contamination levels, chlorine concentrations and pH before they would even consider that the

calculations were statistically significant. Thus, we would like to have the opportunity to review this important research work in greater detail so that we can gain a better assessment of the scientific validity of the results.

In closing, please let us know when we can get together and discuss the issues. After all, Monsanto wants to clearly understand the implications and potential impact of this important work.

Thanks in advance.

Sincerely,

Lawrence F. Rakestraw

Lawrence F. Rakestraw, Ph.D.
Marketing Technical Service Manager

/bd

® Registered Trademark of Monsanto

Dr. Bonnie Sandel, Olin Research, 350 Knotter Dr., Cheshire, CT 06410
Dr. J. Charamonte, Olin Corp., 4363 Ocole, Cleveland,TN 37312

- Olin Corporation, National Spa and Pool Institute, Monsanto, PPG Industries, June-July, 1990

Comment: Swimming pool industry representatives from Olin Corporation, National Spa and Pool Institute, Monsanto, and PPG Industries all commented that they are concerned over the limited emission data used in the technical support document of chloroform. They are concerned that the emission estimate used by ARB of one swimming pool on one day to model all pools all year is not representative of average pool emissions. They also question whether test measurements and methodologies used are reliable.

Response: There is a wide range of chloroform emission estimates from swimming pools due to such variabilities as photodegradation of chloroform and its precursors, complexity of chemical reactions, differing chlorination practices, uncertain test protocal, limited test data, varying loading factors, and uncertain number of pools. The staff therefore adjusts the swimming pool emissions to be approximately 3 tons to 340 tons of chloroform per year (See Appendix A-4). These emission estimates do not include commercial pools such as health clubs. The upper limit was estimated using the method developed by Science Applications International Corporation (SAIC) while the lower limit was estimated by adjusting the upper estimate based on preliminary data from an on-going study by the University of California at Davis (D. Chang, 1990).

II.

Comment Letters and DHS Staff Responses to Comments on the Preliminary Draft Version of Chloroform Part B

MWD
METROPOLITAN WATER DISTRICT OF SOUTHERN CALIFORNIA

January 12, 1990

FEDERAL EXPRESS

Ms. Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
Post Office Box 2815
Sacramento, California 95812

Dear Ms. Denton:

Testimony Regarding Draft Report on Chloroform

The Metropolitan Water District of Southern California (Metropolitan) appreciates the opportunity to provide comments on the California Air Resources Board (ARB) December 1989 draft report on chloroform as a toxic air contaminant.

Metropolitan is a public, municipal corporation created by the State of California that wholesales supplemental water through 27 member agencies (cities and water districts). Metropolitan serves 14.7 million people in an area along the coastal plain of Southern California that covers approximately 5,200 square miles. Water deliveries are currently averaging over 2.0 million acre-feet per year.

Metropolitan's supplies come from two different sources. One source is Colorado River water obtained through a contract with the Federal Government and delivered to Southern California through 242 miles of aqueduct. The other source is Northern California water obtained through a contract with the State and delivered to Southern California through the 444-mile-long State Water Project. Metropolitan uses conventional treatment and provides disinfection through a combination of chlorine and ammonia. Current total trihalomethane (THM) levels in Metropolitan's distribution system average between 50 and 60 parts per billion. Total THMs are comprised of chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

The U.S. Environmental Protection Agency (USEPA) has begun the process of revising the current drinking water standard for THMs. Chloroform is one of the four THM disinfection by-products (DBPs) in drinking water that are

currently regulated by the USEPA and the California Department of Health Services (DHS). As you know, THMs are formed in water when chlorine comes into contact with naturally occurring organics, such as humic and fulvic acids. The current standard is set at 100 µg/L. The USEPA has indicated that the future standard (to be promulgated in 1991/92) will be 50 µg/L or 25 µg/L.

In anticipation of the revision of the THM standard, Metropolitan, in 1986, undertook an extensive program to research and evaluate alternate ways of controlling THMs. As a result of our efforts to date, Metropolitan is anticipating spending upwards of $200 - 300 million to install ozone or PEROXONE, a combination of ozone and hydrogen peroxide, at our treatment plants, by 1996, in order to comply with the future THM standard. In light of the extensive activities we have undertaken up to now, Metropolitan is concerned about possible regulatory actions by the Air Resources Board that could impact our efforts (and the efforts of utilities throughout the state) to comply with any future USEPA drinking water standards.

Metropolitan is concerned about the limited data presented in the ARB's technical support document. The December 1989 technical support document states that there is no recent data on levels of chloroform in California drinking water. Metropolitan would like to provide the following as data to supplement the support document. In 1987, the American Water Works Association developed a national THM survey database. Of the 1,255 utilities serving more than 10,000 people, which were sent a survey form, 145, or 12 percent, were California water utilities. A total of 79 California utilities returned a valid survey form with usable THM data. The California THM data are shown on Figure 1. (We are also enclosing a copy of the January 1988 article in the Journal of American Water Works Association that discusses the results of the nationwide survey.)

In early 1988, DHS entered into a cooperative agreement with the California Public Health Foundation (CPHF) to fund a study of the occurrence and control of DBPs in California drinking waters. After submitting a grant proposal to the CPHF, Metropolitan was contracted to perform the study. The principal objective of the study was to collect data from 10 representative water utilities in the State on the occurrence and control of DBPs in drinking water, including chloroform. Four quarters of data were collected at each utility, beginning in March 1988 and ending February 1989. As you can see on Figure 2 there are other DBPs besides THMs. Figure 3 reveals that THMs represent the largest percentage of DBPs and of the DBPs, chloroform represents

the largest percentage of THMs (Figures 4 and 5). Table 1 gives the median values of the DBPs for all four quarters of data in the ten utility systems. (In addition to the above-mentioned tables, we are submitting a copy of the entire report entitled Disinfection By-Products in California Drinking Water.) This data should be reviewed by the Air Resources Board.

Regarding the second document we received, Health Effects of Chloroform (California Department of Health Services, March 1989), Metropolitan is concerned that data from the NCI (1976) study were used in the risk estimation. Over the last several years, serious questions have arisen regarding the validity of data generated in studies where chloroform was administered in corn oil. Volume 7 of Drinking Water and Health, Disinfectants and Disinfectant By-Products (Safe Drinking Water Committee, National Research Council) presents an excellent review of these studies. We believe the concerns raised in Volume 7 must be addressed in DHS' Health Effects of Chloroform. In particular, we would draw your attention to page 127, of Volume 7, where the Committee states:

> "Thus chloroform in corn oil caused more marked hepatotoxic effects in mice than did chloroform in Emulphor or, in comparison with other investigations (Jorgerson et al., 1985), than did chloroform in water. This seems to suggest that the discrepancy between the incidences of liver tumors in the investigations of NCI (1976) and of Jorgerson et al (1985) can be accounted for by the vehicle of administration, chloroform in corn oil causing more marked hepatic effects than chloroform in other vehicles."

The USEPA's Office of Drinking Water (ODW) has determined that the risk estimates based on animal studies with chloroform in corn oil are not appropriate for inclusion in future THM regulations. Metropolitan would be concerned if by incorporating these studies (i.e., NCI, 1976) in the ARB process, chloroform would be identified as a toxic air contaminant with an incorrect risk level.

We are also sending a copy of a draft paper submitted to "Toxicology and Applied Pharmacology" ("Estimating the Risk of Liver Cancer Associated with Human Exposures to Chloroform [Draft Manuscript]") for your consideration. The physiologically based pharmacokinetic model laid out in the manuscript allows for a more realistic evaluation of exposure and risk assessment.

We hired a toxicologist, Dr. Richard Bull, of Washington State University, to review the DHS health effects document of chloroform. The attached report presents his review and critique of the health effects document.

Very truly yours,

Michael J. McGuire Ph.D.
Director of Water Quality

JSS:DJA:ra

Enclosure

THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN 48674

January 11, 1990

Joan E. Denton, Manager
Substance Evaluation Section
Stationary Source Division
Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

DRAFT REPORT: HEALTH EFFECTS OF CHLOROFORM

The California Department of Health Services document, "Health Effects of Chloroform," March, 1989, has been reviewed by Dow scientists. Several changes should be made to better reflect appropriate interpretation of the data available on chloroform, and to make the interpretation clear to readers of the document.

1. The executive summary should state that epidemiological evidence for human carcinogenicity is inadequate to conclude the compound is a human carcinogen.

2. Page 1-3 states IARC has classified chloroform as a probable human carcinogen. This statement is not true. Chloroform is in IARC category 2B: "The agent is possibly carcinogenic to humans." (IARC Monographs, Supplement 7, 1987).

3. The executive summary indicates metabolism is essential to the hepatotoxicity and nephrotoxicity of chloroform. The metabolites responsible for toxicity are likely to be responsible for carcinogenicity. Under conditions where metabolism is a precursor to the toxic effect, the use of surface area as a dose scaling factor is inappropriate (see the enclosed article by Reitz, et al., Fd. Cosmet. Toxicol. 16, 511-514, 1978).

4. The most appropriate procedure for extrapolation of dose across species and exposure levels takes into account metabolic and pharmacokinetic factors to compare doses of active metabolites (or parent compound) at the target tissue. A physiologically-based pharmacokinetic model has been developed by Reitz and Corley (with co-workers) for chloroform to provide an appropriate mathematical basis for such extrapolations. Copies

of the preprints by Corley, et al., and Reitz, et al., are enclosed. Both have been submitted for publication. Estimates of the upperbound to risk should be changed based on application of the PB-PK model.

5. The executive summary includes the statement: "Concentrations of chloroform in air producing adverse effects other than cancer in experimental animals are about five orders of magnitude greater than ambient air concentrations of chloroform (<0.4 ppb) in California." Cancer is not an exception to this statement. As it stands there is the implication that cancer has been observed in experimental animals at levels below those showing other toxic effects. Actually, the reverse is true. Cancer has only been observed at doses greater than or in the range of doses producing other toxic effects.

   The reference to 0.4 ppb as the ambient air concentration of chloroform in California is misleading. Later in the executive summary the more appropriate median value of 0.06 ppb is given.

Sincerely,

Robert J. Moolenaar/kaj

Robert J. Moolenaar
Health & Environmental Issues
1803 Building
517/636-0655

kaj

Enclosures

Responses to Comments on the Chloroform document:

I. Response to points made in the letter from the Metropolitan Water District of Southern California (MWDSC) to Joan Denton of the ARB dated January 12, 1990.

Comment 1:. The MWDSC states that the NCI (1976) data should not be used in the risk asssment because the chloroform was given in corn oil.

Response:

DHS staff consider all the available data when evaluating chemicals and associated risks for the toxic air contaminant program. Staff evaluated 11 data sets from 4 carcinogenicity bioassays to develop a range of 95% upper bounds on cancer risk. Included among these studies were NCI (1976), Jorgenson et al. (1985), Roe et al. (1979), and Tumasonis et al. (1985). We included all studies which showed a statistically elevated tumor incidence in treated animals compared to controls. The NCI study showed that chloroform treatment induced tumors in both rats and mice at more than one anatomical location. In the report, we discussed data showing that chloroform in corn oil results in greater hepatotoxicity in mice relative to chloroform given in an aqueous vehicle (2% Emulphor) (Bull et al. 1986). Other investigators reported that corn oil or fatty diets may increase tumorigenicity of other carcinogens (Newberne et al. 1979, Rogers and Newberne, 1975). While this is a source of uncertainty in the risk assessment of chloroform, DHS staff do not believe that this is reason enough to completely ignore the study. We are aware that the U.S. EPA Office of Drinking Water decided to exclude the NCI study in their assessment of risk from drinking water containing trihalomethanes. However, renal tumors in male rats are induced by chloroform without regard to the carrier. In addition, in Tumasonis et al. (1985), cholangiocarcinomas and hepatic neoplastic nodules were induced in rats given chloroform in water. The human diet does contain a significant amount of fat. The mechanism of potentiation of hepatotoxicity is not known. It is not clear if the administration of corn oil has to be simultaneous or if corn oil or fats in the diet will also potentiate the induction of hepatic tumors induced by chloroform in water or air. Given the above reasoning, DHS staff have included potencies derived from data on hepatocellular carcinoma in male and female mice and renal tumors in male rats reported in the NCI (1976) study in the reported range of risks. However, the best estimate of unit risk excludes the hepatocellular carcinoma data in B6C3F1 mice, but includes data on renal tumors in rats reported by NCI. The hepatocellular tumors are excluded from the best estimate of risk because of the potentiation of hepatotoxicity by the corn oil vehicle, possible exacerbation of the carcinogenic response by the corn oil vehicle, and lack of liver tumors in B6C3F1 mice in the Jorgenson et al. (1985) drinking water study.

Comment 2: The MWDSC sent a copy of a draft paper by Corley et al. entitled "Estimating the risk of liver cancer associated with human exposures to chloroform" for our review, and stated that they believe "the physiologically

based pharmacokinetic model laid out in the manuscript allows for a more realistic evaluation of exposure and risk assessment".

Response: DHS staff reviewed PBPK models used by Corley et al. (1990) and by Bogen et al. (1989) and the application of these models to the risk assessment of chloroform. Staff have incorporated the Bogen et al, (1989) model into the risk assessment of chloroform. DHS staff did not incorporate the analysis of Corley et al. because it focuses on hepatocellular carcinomas which have been excluded from the best estimate calculation, and for other reasons discussed in the response to comment number 4 submitted by Dow Chemical Company.

Comment 3: The MWDSC sent a review of the health effects document by R.J. Bull. Staff has responded below to the main points of this critique:

a. The reviewer, R.J. Bull, believes that chloroform acts solely as a promoter, at least in the liver, and that there is no evidence that chloroform is an initiator.

Response: Dr. Bull cites 4 papers to support his contention that chloroform given in corn oil is a promoter and not an initiator. While a few of these papers could not find evidence for initiation, 3 of 4 of the studies could not find evidence for promotion either. The fourth paper (Deml and Oesterle, 1987) did report some evidence of promotion of chloroform given in corn oil using ATPase deficient and GGTase positive foci in the liver as the endpoint. One of the authors (who wrote 2 of the negative studies) stated that further study of the promoting ability of chloroform is needed. In addition, the study by Tumasonis et al. (1985) showed that chloroform given in drinking water induced cholangiocarcinomas and hepatic neoplastic nodules in rats. It is not clear how the reviewer construes these studies as evidence that "it is abundantly clear that chloroform in combination with corn oil is a hepatocarcinogen acting primarily, if not entirely, as a tumor promoter".

Chloroform is metabolized to phosgene, a very reactive electrophile. There is evidence of binding of radiolabel to cellular lipids and proteins of kidney and liver in vivo and in vitro. Diaz Gomez and Castro (1980) found no evidence of binding to DNA or RNA after ip administration of ^{14}C-chloroform. Reitz et al. (1982) observed weak binding of radiolabel to rat and mouse liver and kidney DNA following oral administration of ^{14}C-chloroform. Di Renzo et al. (1982) found binding to calf thymus DNA in an in vitro incubation with microsomal preparation. The reviewer, Dr. Bull, does not believe the in vitro evidence should challenge the in vivo data. DHS staff do not think that, in this case, one study overrides another. Rather, we believe that it is health-protective to consider the in vitro data of DiRenzo et al. and the weak in vivo binding data of Reitz et al. as evidence of potential initiating ability of chloroform. As stated in the document (p. 8-3), current evidence and current understanding of the carcinogenic process are insufficient to classify chloroform as either a genotoxic or epigenetic carcinogen, and it is possible that both types of mechanisms are involved.

c. Dr. Bull believes that exacerbation of hepatotoxicity by corn oil, and some evidence that chloroform is a promoter when given in corn oil is enough to ignore the NCI study in our assessment of carcinogenic potency. However, for reasons discussed above, DHS staff believe the evidence is not strong enough to completely ignore the NCI (1976) study in our assessment of carcinogenic potency, although use of corn oil is a limitation in the applicability of the study to risk assessment. As noted in the response to comment 1, we have included the potencies estimated from NCI data on mouse hepatocellular carcinomas in the range of risks, but have used only the renal tumor data in rats reported by NCI in the derivation of the best estimate of unit risk.

d. In Dr.Bull's specific recommendations, he suggests using a nonthreshold model with the data from Jorgenson et al. (1985), because the mechanism of tumor induction in the kidney has not been defined. DHS staff do not believe that the mechanism of tumor induction in mouse liver has been defined either. We have used a nonthreshold model for all data sets including the renal tubular tumors seen in NCI (1976) and Jorgenson et al. (1985). DHS staff recognize that the female mouse hepatocellular carcinomas induced by administration of chloroform in corn oil, were not seen in the Jorgenson study where chloroform was administered in drinking water. We also realize that data are reported in the literature indicating that corn oil may be involved in potentiating cancers caused by chloroform and other carcinogens. DHS staff believe it is reasonable to include the potency derived from the female mouse hepatocellular carcinomas in the NCI study in our reported range of risks. It is also reasonable to choose a best estimate from the available data sets. The potency estimated from the renal tumor data reported in Jorgenson et al. (1985) is the lowest estimate. The estimate derived from the female mouse hepatocellular data in NCI (1976) was the highest potency estimate. The best estimate may lie in between. Estimates of potency based on Roe et al. (1979) where chloroform was given either in a toothpaste base or arachis oil were an order of magnitude larger than the potency derived from Jorgenson et al. Potency estimates derived from the Tumasonis et al. (1985) data fall in the range of those from Roe et al. (1979). DHS staff have derived a best estimate of unit risk as described in the current draft of the health effects document. This best estimate does not incorporate potencies derived using hepatocellular carcinoma data in B6C3F1 mice from the NCI study. However, the best estimate does weight the rat renal tumor data in Jorgenson et al. (1985) equally with the rat renal tumor data in NCI (1976). In addition other potencies from data sets in Roe et al. (1979) describing mouse renal tumors, and from data sets in Tumasonis et al. (1985) describing cholangiocarcinoma (hepatic adenofibrosis) in male and female rats are incorporated into the best estimate of unit risk.

II. DHS staff responses to the comments from Dow Chemical Company expressed in a letter to Joan Denton of ARB dated January 11, 1990.

Comment 1: The executive summary should state that epidemiological evidence for human carcinogenicity is inadequate to conclude that chloroform is a human carcinogen.

Response: The executive summary does state this in several places (on pages 1-3, 1-6 and 1-7).

Comment 2: Page 1-3 states that IARC has classified chloroform as a probable human carcinogen, when in fact the agency classified chloroform as a possible human carcinogen.

Response: The executive summary of the document has been changed as suggested.

Comment 3: The executive summary indicates metabolism is essential to hepatotoxicity and nephrotoxicity of chloroform. The metabolites responsible for toxicity are likely to be responsible for carcinogenicity. Under conditions where metabolism is a precursor to toxic effects, the use of a surface area as a dose scaling is inappropriate (see the enclosed article by Reitz et al).

Response: DHS staff use surface area scaling to account for a number of species differences. Application of an adjustment for metabolism of the parent compound to the ultimate carcinogen does not replace use of the surface area correction. Using either applied or metabolized doses as input to an analysis of potency does not account for a number of unquantified species differences. Such differences include sensitivity of target tissues to the carcinogenic effects of metabolites or parent compound, differences in distribution, detoxification and clearance of the parent compound and metabolites, differences in number of target cells in exposed tissue, DNA repair, and cell proliferation rates. Part of the reasoning to use a surface area correction factor is that the locus of action of any drug is on some surface area. It is not known which extrapolation is correct, either the surface area scaling or extrapolating on a mg/kg dosage scale. DHS staff prefer to use surface area scaling as it affords some protection from differences which could increase human sensitivity relative to the rodents used in the bioassays.

Comment 4: The most appropriate procedure for extrapolation of dose across species and exposure levels takes into account metabolic and pharmacokinetic factors to compare doses of active metabolites (or parent compound) at the target tissue. A physiologically-based pharmacokinetic model has been developed by Reitz et al. for chloroform to provide an appropriate mathematical basis for such extrapolations. Copies of preprints by Corley et al. and Reitz et al. were enclosed. Dow believes that estimates of the upper bound to risk should be changed based on application of the PB-PK model they submitted.

Response: DHS staff reviewed PBPK models by Bogen et al. (1989, draft) as well as those submitted by Dow (Corley et al. 1990; Reitz et al. 1989 draft). The study by Bogen et al. was conducted under contract with the California Department of Health Services to assess risk from exposure to chloroform in drinking water. The PBPK model by Bogen et al. derived estimates of

metabolized dose. A linearized multistage model was then applied to these metabolized doses to estimate cancer potency. DHS staff have incorporated these estimates of risk into our latest draft of the health effects document. The cancer potencies derived by Bogen et al. (1989, draft) were slightly higher than those derived by DHS staff using administered dose. In the risk assessment by Reitz et al. (1989, draft) a linearized multistage model is applied to values representing macromolecular binding or cytotoxicity as surrogate doses. In the first case, macromolecular binding is presented as a surrogate for dose delivered to the target organ. The target organ used in these studies was the liver. In the second case, the average percentage of cells killed by chloroform is used as the dose surrogate for chloroform toxicity. Both measures of surrogate dose were used with data on liver tumors in male and female mice from the NCI study (significant excess), data on liver tumors from Roe et al. (1979) (no excess) and from Jorgenson et al. (1985) (no excess of liver tumors). It is not clear how either of these dose surrogates is related to carcinogenicity induced by chloroform in the bioassays. In addition, the treatment of tumor incidence data is questionable. It appears that tumor incidence data from NCI (1976) was mixed with data from Roe et al. (1979), but it is difficult to tell from the draft document (Reitz et al. 1989, draft) what tumor incidence data was actually used as input to the linearized multistage model. The Reitz et al. (1989, draft) paper also presents a risk assessment based on use of uncertainty factors. The rationale presented for this is that chloroform may act in the liver solely as a promoter. However, DHS staff do not agree that this statement can be made with enough confidence to apply an uncertainty factor approach.

Comment 5: The executive summary includes the statement:"Concentrations of chloroform in air producing adverse effects other than cancer in experimental animals are about five orders of magnitude greater than ambient air concentrations of chloroform (<0.4 ppb) in California." Cancer is not an exception to that statement. As it stands there is the implication that cancer has been observed in experimental animals at levels below those showing other toxic effects. Actually, the reverse is true. Cancer has been observed at doses greater than or in the range of doses producing other toxic effects.

Response: The statement in the executive summary was meant to convey that noncancer health effects from current ambient air concentrations of chloroform in California air are not expected to occur because there is an enormous difference between concentrations in ambient air and those concentrations observed to induce toxicity in laboratory animals. This statement is made under the assumption that a threshold approach to evaluating noncancer health effects is appropriate. It is true that cancer has been observed in animals at doses in the range of those producing other toxic effects. Cancer bioassays use high doses in order to detect effects, given the low statistical power of carcinogenicity bioassays. The power of a bioassay to detect cancer drops off sharply at lower doses, due to the logistic impediments to a large sample size. However, unlike the case of noncancer toxic effects, DHS staff treat cancer as a nonthreshold phenomenon. DHS considers that there is some risk, significant or not, associated with any dose of carcinogen. Therefore, cancer is excluded from the quoted statement.

Comment 5 (second part): The reference to 0.4 ppb as the ambient air concentration of chloroform in California is misleading. Later in the executive summary the more appropriate median value of 0.06 ppb is given.

Response: The ambient air concentrations of chloroform are measured at several places throughout the state. Average measurements from the various monitoring stations ranged up to 0.36 ppb. Consequently, staff referred to the concentrations of chloroform in ambient air as <0.4 ppb. Since we are trying to compare concentrations which induce observable noncancer toxic effects in animals to concentrations to which persons in California are exposed, DHS staff do not agree that this statement is misleading. DHS staff present the median, and the population-weighted average concentrations in the appropriate places in the executive summary.

PART C ADDENDUM

PUBLIC COMMENTS AND RESPONSES TO THE DRAFT CHLOROFORM REPORT

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

SEPTEMBER 1990

Part C Addendum contains the letters received from the public after July 30, 1990 and before the SRP meeting on August 14, 1990. The responses of the Air Resources Board and the Department of Health Services to those comments are also contained in this Addendum.

Contents of the Addendum to Part C

III.

Comment Letters and ARB Staff Responses to Comments on the Draft Version of Chloroform Executive Summary and Part A

Olin
RESEARCH CENTER
350 KNOTTER DRIVE. P.O. BOX 586
CHESHIRE. CT 06410-0586
(203) 271-4000

August 2, 1990

Ms. Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch
California Air Resources Board
Attn: Chloroform
1102 Q Street
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Shiroma:

Thank you for this second opportunity to review and comment on the draft document entitled Proposed Identification of Chloroform as a Toxic Air Contaminant. We understand that these comments on the executive summary and the revisions to parts A and B are to be forwarded to the Science Review Panel to aid in their August 14th meeting.

First, with respect to the revised swimming pool emissions, I believe the range of 3 to 340 tons/yr is likely to encompass the true value and goes far to address the problem posed by the lack of data and by the disagreement in what results exist. Clearly, further study is needed before a clear picture of the emissions and the risk they pose can emerge. Somewhat misleading, however, is the statement (in footnote 3 of Table III-1 of Part A) that commercial pools are not considered. The calculation of total emissions leading to the range maximum (340 tons/yr) utilized an emission flux estimated from measurement at a residential pool and a surface area for inground pools typical of a residential pool, but the number of pools and spas considered was developed by the National Spa and Pool Institute (NSPI) and includes commercial pools and spas. NSPI calls them "semipublic".

With respect to the new Executive Summary, there is a misstatement on page 4. IARC classifies chloroform as a class 2b chemical, a possible human carcinogen rather than a probable human carcinogen. This is stated correctly in Part B of your document.

On page 6, under environmental impact, the statement that "implementation of these control measures will benefit the public health" makes many assumptions which should be considered and discussed rather than passed over. Since much of the airborne chloroform comes from indirect sources, especially chlorination of water, any attempt to control these sources will involve consideration of reductions in the use of chlorination for water treatment. But chlorination is the most efficient and economical

way to disinfect water for most uses. What if attempts to reduce chloroform lead to an increase in the probability of waterborne infection? Many waterborne diseases are debilitating and difficult to treat, and just as not all cancers are incurable, neither are all waterborne infections curable -- in fact some are fatal. What are the risks to the public health associated with this identification? Has an attempt to consider them been made? The statement that lowering chloroform levels below the existing levels in air will result in an increase in public health requires many qualifiers, none of which appear in the summary or the support document.

Finally, Dr. Steven J. Barbee, Manager of Environmental Hygiene and Toxicology has provided comments on the carcinogenicity and exposures set forth in the summary. They are attached.

Again thank you for the opportunity to respond to this document and for your consideration of the information we have provided. Developing regulations to benefit the public health is an important and very difficult task. We at Olin would be happy to provide what further assistance we can as these discussions and studies continue.

Sincerely,

Bonnie B. Sandel

Bonnie B. Sandel, Ph.D.
Senior Research Associate
Water Products and Services

o Olin Corporation, August 2, 1990

1. **Comment:** Olin commented that the National Spa and Pool Institute survey used by ARB does include commercial swimming pools and are considered "semi-public" in the survey. This comment refers to footnote 3 of Table III-1 in Part A.

Response: Table III-1, footnote 3 is changed to read:

"A range is reported to reflect the uncertainty in emission estimates due to minimal test results and wide variability among test data. Although the number of commercial pools statewide was taken into consideration, emissions may be underestimated for commercial pools because commercial pools generally have a larger surface area, more activity, and require more chlorination than residential pools."

2. **Comment:** Olin comments that the Executive Summary page 4 should read IARC classifies chloroform as a class 2b chemical, a possible human carcinogen rather than a probable human carcinogen.

Response: The correction has been made.

3. **Comment:** Olin comments that the environmental impacts were not addressed sufficiently in the Executive Summary.

Response: Changes in the Executive Summary were modified to address your comment by replacing the 3rd sentence in the second paragraph on page 6 with:

"In considering the adoption of control measures the ARB will consider all potential impacts of these measured on human health as well as the potential benefits to public health by reducing chloroform emissions."

SCIENCE REGULATORY SERVICES
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August 6, 1990

Ms. Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch
California Air Resources Board
Attention: Chloroform
1219 K Street
Sacramento, CA 95812

Subject: Technical Support Document to Proposed Identification of Chloroform as a Toxic Air Contaminant, Part A, Exposure Assessment July, 1990

Dear Ms. Shiroma:

On behalf of Nissan Chemical America Corporation ("Nissan"), we wish to comment on the above referenced report.

We understand that:

1) You and your staff discussed the chloroform emission data for swimming pools with the various representatives from the pool sanitizer industry.

2) Your personnel listened objectively and modified the final report to take into account Olin's research data and the industry's opinions.

3) Nissan and its pool industry associates want to support your staff's efforts to develop sufficient pool test data to have a statistically valid representation on the emission rate of chloroform from swimming pools in California.

To this end, the members of CMA's Chlorinated Pool Chemicals CHEMSTAR Panel - the 10 major producers of CAL HYPO (calcium hypochlorite) and ISOS (trichloro- and dichloro-isocyanuric acid) worldwide - have agreed to fund a test program cooperatively with your staff to achieve this important objective.

In closing, Nissan and its associates are looking forward to working with your staff on this important issue. Perhaps we will have an opportunity to discuss a co-funded pool test program shortly after the Scientific Review Panel meeting on August 14.

Sincerely,

N. Bhushan Mandava

N. Bhushan Mandava, Ph.D., FAIC, DABT
Agent for Nissan Chemical
America Corporation

cc: Mr. T. Kometani

Monsanto

Monsanto Chemical Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167
Phone: (314) 694-1000

Monsanto Water Treatment

August 6, 1990

Ms. Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch
California Air Resources Board
Attention: Chloroform
1219 K Street
Sacramento, CA 95812

Subject: Technical Support Document to Proposed Identification of Chloroform as a Toxic Air Contaminant, Part A, Exposure Assessment July, 1990

Dear Ms. Shiroma:

Monsanto wishes to comment on the above referenced report that we received last week. First, we want to thank you, Joan Denton and her staff for taking the time on July 3, 1990 to discuss the chloroform emission data for swimming pools with the various representatives from the pool sanitizer industry. Second, we appreciate the fact that your personnel listened objectively and modified the final report to take into account Olin's research data and the industry's opinions. Third, Monsanto and its pool industry associates want to support your staff's efforts to develop sufficient pool test data to have a statistically valid representation on the emission rate of chloroform from swimming pools in California. To this end, the members of CMA's Chlorinated Pool Chemicals CHEMSTAR Panel - the 10 major producers of calcium hypochlorite and chlorinated isocyanurates worldwide - have agreed to fund a test program cooperatively with your staff to achieve this important objective.

In closing, Monsanto and its associates are looking forward to working with your staff on this important issue. Perhaps we will have an opportunity to discuss a co-funded pool test program shortly after the Scientific Review Panel meeting on August 14.

Sincerely,

Lawrence D. Rakestraw/bd

Lawrence F. Rakestraw, Ph.D.
Marketing Technical Service Manager

/bd

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o Science Regulatory International and Monsanto, August 6, 1990

1. **Comment:** Science Regulatory International and Monsanto thanked ARB for changing the swimming pool emissions number in our report. They are also willing to work cooperatively with ARB to develop a test program on emission factors for swimming pools.

Response: ARB has agreed to do so.

THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN 48674

1803 BUILDING
August 3, 1990

Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch
California Air Resources Board
Attn: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Shiroma:

The Final Draft Report to the Scientific Review Panel on Chloroform (July, 1990) states (p. 4): "The International Agency for Research on Cancer and the U.S. EPA both classify chloroform as a probable human carcinogen based on adequate evidence for cancer in animals." This statement is incorrect. IARC classified chloroform as a possible human carcinogen. (IRAC Monographs, Supplement 7, 1987).

The response to public comment in the Final Draft (p. II-10) indicates the executive summary has been changed to accurately reflect IARC's classification of chloroform as a possible, not probable, human carcinogen. Somehow this change must have been inadvertently omitted from the Final Draft. Please advise the Review Panel of the correct IARC classification prior to their deliberations and make the necessary changes in the draft.

Very truly yours,

Robert J. Moolenaar

Robert J. Moolenaar
Health and Environmental Sciences

t m

o Dow Chemical Company, August 3, 1990

Comment: Dow comments that the Executive Summary page 4 should read IARC classifies chloroform as a possible human carcinogen rather than a probable human carcinogen.

Response: The correction has been made.

PPG Industries, Inc. One PPG Place Pittsburgh, Pennsylvania 15272 (412) 434-2350

W. B. Graybill
Director
Environmental Affairs
Chemicals Group

August 1, 1990

Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch
California Air Resources Board
Attention: Chloroform
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Shiroma,

This is to acknowledge receipt of the California Air Resources Board (ARB) Document "Proposed Identification of Chloroform As a Toxic Air Contaminant", Parts A, B, C, and Executive Summary, July 1990, and to take the opportunity offered to review and comment on those portions of the report that have been revised with the understanding that comments received before August 7, 1990 will be reviewed by the Scientific Review Panel (SRP) and responded to by the ARB and Department of Health Services (DHS) during the SRP meeting on August 14, 1990.

Comment 1: (Part A - pg. 11)

It is deemed of particular significance to see that the chloroform emission estimate from swimming pools has been modified to consider the preliminary measurements coming from the UCD study which are lower by a factor of 100 from the SAIC study. This revision reflects the responsiveness of the ARB to our initial comments on the limited data base being used.

Comment 2: (Executive Summary - pg. 6)

The answer to the question, What would be the environmental impact of the identification of chloroform as a toxic air contaminant?, does not consider the impact of control measures that could prevent the use of chlorine products for water treatment applications for which there are no viable alternatives. For example, not using chlorine for swimming pool water treatment can be expected to result

in inadequate sanitization and an increase in the potential hazard for bathers to be exposed to infection with various pathogenic organisms, thus adversely affecting the public health. The same situation exists for the sanitization of drinking water. It is recommended that this answer be modified to reflect this point.

Comment 3: (Executive Summary - pg. 2-5)

Two issues concerning the chlorination of drinking water are raised in the report. The report states that "the major indirect source of chloroform emissions is the chlorination of water (pg. 2)" and that "chloroform in drinking water and inhalation from indoor sources may contribute more to the overall risk from chloroform than chloroform in ambient air (pg. 5)". It is important to state for the record that the International Agency for Research on Cancer (IARC) Working Group on the Evaluation of Carcinogenic Risks to Man has recently completed a review of the published scientific evidence concerning the cancer risk to man posed by the chlorination of drinking water. (A table summarizing the final classification decisions of IARC is attached.) The final decision of IARC was to classify chlorination of drinking water as category 3, i.e., not classified as to carcinogenicity. This classification means that IARC decided that the scientific evidence did not support a conclusion that chlorination of water presents a cancer risk to man. Therefore, it is inappropriate to include ingestion of drinking water in the risk calculations on pg. 5, where the risk is stated to be "The risk from inhalation + risk from ingestion = 3.6×10^{-4}". When the risk from ingestion is removed from calculation, the incremental risk from inhalation is reduced to 16 cases per 20.3 million persons exposed (pg. 5), or less than 1×10^{-6}, a level that is normally not of regulatory concern.

The opportunity to participate in the review and comment phases of this environmental project is appreciated. Please continue to involve PPG Industries, Inc. by keeping us on your distribution list. Future communications should continue to be sent to:

Robert B. Simmons, Ph.D.
PPG Industries, Inc.
Technical Center
440 College Park Drive
Monroeville, PA 15146

Sincerely,

W. B. Graybill

jabmar21/wbg

o PPG Industries, August 1, 1990

1. **Comment:** PPG industries commented that they are pleased to see that the swimming pool emission estimate was modified. They also commented that the ARB did not address the environmental impacts sufficiently in the Executive Summary.

Response: Changes in the Executive Summary were modified to address your comment by replacing the 3rd sentence in the second paragragh on page 6 with:

"In considering the adoption of control measures the ARB will consider all potential impacts of these measured on human health as well as the potential benefits to public health by reducing chloroform emissions."