SAIC-86/1105

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

FINAL REPORT

8 April 1988

Authors

Michael B. Rogozen
Harvey E. Rich
Michael A. Guttman

SCIENCE APPLICATIONS INTERNATIONAL CORPORATION
111 N. Sepulveda Blvd., Suite 370
Manhattan Beach, California 90266

and

Daniel Grosjean
Edwin L. Williams II

DANIEL GROSJEAN AND ASSOCIATES
4526 Telephone Road, Suite 205
Ventura, California 93003

Prepared For

State of California
AIR RESOURCES BOARD
Sacramento, California 95812

Contract No. A4-115-32
Joseph Pantalone, Project Officer

ACKNOWLEDGEMENTS

The following Science Applications International Corporation (SAIC) and Daniel Grosjean and Associates (DGA) staff, and other individuals, participated in this project:

LITERATURE REVIEW: Daniel Grosjean, Michael Guttman, Harvey Rich, Michael Rogozen

SURVEYS: Michelle H. Levine, Alan Miller, Harvey Rich

FIXED-SITE AMBIENT SAMPLING: Christopher Dhaliwal, Christopher Rowe

MARINE SAMPLING: Michael Guttman, Michael Rogozen

MOBILE AMBIENT SAMPLING: Christopher Dhaliwal, Michael Rogozen

WASTEWATER TREATMENT PLANT SAMPLING: Christopher Dhaliwal, Michael Guttman

SWIMMING POOL TESTING: Ricci Capirci, Douglas Cover, Michael Guttman, Michael Rogozen

LABORATORY TESTING: Daniel Grosjean, Edwin Williams

MODELING: Douglas Cover, Martin Jablonski, Hamid Nehoray, Michael Rogozen, Robert Soklow

GRAPHICS: Christopher Dhaliwal, Michael Rogozen

TECHNICAL TYPING: Robert Baca, Christopher Dhaliwal, Margaret Jones-Ryan, Mary Ann Levine, Linda McDermott

We would like to thank Joseph Pantalone, the Air Resources Board Research Contract Monitor, for his advice and encouragement throughout the project. Other ARB staff who participated actively in the study were Jack Paskind, Cliff Popejoy and Tom Parker. We would also like to thank Ed Yotter of the ARB for providing us with gridded population data, and Paul Allen for his comments on our modeling plans. Their cooperation is sincerely appreciated.

We would also like to thank Tom Gerlinger for piloting the Osprey in our search for chloroform off the coast of the South Coast Air Basin; the Cities of Los Angeles and Riverside for their assistance in our wastewater treatment plant sampling; and Leon Levan of EMSI for developing improved methods for analyzing carbon molecular sieve traps.

This report was submitted in fulfillment of ARB Contract No. A4-115-32, "Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin." Work was completed as of May 31, 1987.

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ABSTRACT

The objectives of this project were (1) to investigate both primary and secondary sources of chloroform ($CHCl_3$) in the South Coast Air Basin (SCAB) and (2) to identify and quantify the emission sources responsible for observed atmospheric concentrations. Of particular interest was the identification of possible chloroform precursors and atmospheric reactions which result in chloroform formation. The major elements of Phase I of the project were construction of a chloroform emission inventory for the SCAB, a literature review of atmospheric concentrations and reactions, a modeling exercise to compare measured ambient concentrations with those based upon emission estimates, and a review of chloroform sampling and analytical techniques. Phase II included ambient sampling, source testing at two wastewater treatment plants and a swimming pool, and laboratory studies of atmospheric chemistry.

Total emissions of chloroform in the SCAB are estimated to be 370 tons per year. The largest source appears to be drinking water chlorination, which accounts for about 51 percent of the annual total. Swimming pool chlorination accounts for another 39.5 percent. Pulp and paper manufacturing plants have a significant potential for chloroform generation, although their emissions occur at wastewater treatment plants. $CHCl_3$ produced by chlorination of final treated wastewater effluent is not likely to be significant unless ammonia has been removed during tertiary treatment; most of the chloroform emissions from wastewater treatment plants occur through release of influent chloroform during primary treatment. Emissions from domestic bleach use, industrial and utility cooling towers, laboratories, and pharmaceutical manufacturing total about 14.6 tons per year. Chloroform emissions from chlorinated rubber manufacturing, combustion of leaded gasoline, chlorodifluoromethane production, grain fumigation, contamination of chlorinated products, and marine organisms are negligible.

SAIC collected wastewater samples from the influent and effluent of the Hyperion Treatment Plant and the Riverside Water Quality Control Plant. Emissions from the two plants are estimated to be 15 lb and 0.5 lb/day, respectively; production of chloroform by postchlorination of tertiary-treated effluent at Riverside was taken into account. Ambient air sampling with a

portable gas chromatograph found $CHCl_3$ concentrations above treatment processes to be one to three orders of magnitude higher than in the rest of the basin. Concentrations increased through primary treatment.

Chloroform emissions from a residential swimming pool were measured with an emission isolation flux chamber. Significant emissions were found under all tested chlorine doses and water surface condition; fluxes increased greatly when the water surface was agitated. Chloroform levels in the pool were 5 to 9 times those in the municipal water, but flux rates did not appear to be related to chloroform concentration.

Our analysis of ARB data found that 24-hour average chloroform concentrations at four sites in the Basin were distributed lognormally for each receptor. Mean 24-hour concentrations between January 1983 and July 1984 (December 1984 for El Monte) were 45.1 ppt at Dominguez Hills, 47.8 ppt at El Monte, 60.5 ppt at Los Angeles, and 46.6 ppt at Riverside. The mean concentration at the Los Angeles site is significantly greater ($p < 0.05$) than those for the remaining sites. F-tests on the variances for all paired sites were not significant ($p > 0.05$), indicating that variation in the four samples is similar.

In the present study, SAIC collected air samples on carbon molecular sieve (CMS) traps at a 24-hour sampling site in Fullerton, a 6-hour sampling site in Hermosa Beach, and 1-hour samples at 12 sites off the coast of the SCAB and at 41 sites throughout the basin. Samples were analyzed by cryogenic preconcentration and gas chromatography with electron capture detection for chloroform, 1,1,1-trichloroethane (methyl chloroform), carbon tetrachloride, trichloroethylene (TCE), tetrachloroethylene (perchloroethylene), and ethylene dibromide (EDB). Since this was, to the best of our knowledge, the first large-scale use of CMS for ambient halocarbon sampling, considerable trial-and-error was necessary for developing suitable sampling and analytical methods.

Chloroform concentrations in the Fullerton samples were within the ranges measured at the ARB 24-hr sampling stations. Chloroform concentrations at Hermosa Beach ranged from 6 to 168 ppt and had an arithmetic mean and standard deviation of 58 and 40 ppt, respectively. No statistically significant difference among daily average or quarter-day average concentrations could be found.

Ranges of detectable concentrations in the ambient mobile sampling were: chloroform (12 - 480 ppt), 1,1,1-trichloroethane (13 - 3,500 ppt), carbon tetrachloride (10- 460 ppt), trichloroethylene (16 - 3,100 ppt), tetrachloroethylene (29 - 1,100), and ethylene dibromide (33 ppt). Most of the coastal samples had relatively high chloroform concentrations. The highest chloroform level of all of the mobile sampling (483 ppt) was measured directly downwind from the Los Angeles Hyperion Treatment Plant. It is possible, since the facility is on the coast, that chloroform present in marine air comprised a portion of the observed values. Some of the highest levels of $CHCl_3$ and the highest concentration of TCE were measured in Orange County in the afternoon and evening. One of these sites was near a hospital complex. Several locations in the basin had elevated levels of two or more halocarbons. However, correlations among concentrations of the different species were generally below 0.5. A hypothesis which we recommend for further testing is that inland sites in the late afternoon and early evening, and coastal sites whenever onshore breezes are blowing, are likely to have higher chloroform concentrations than other sites at the same times.

Chloroform concentrations offshore were generally higher than those observed during the mobile sampling on land; three of the values (309, 392 and 1,460 ppt) exceed 93 percent of the land-based concentrations and are similar to the 530 ppt measured by a previous researcher off San Pedro. Chloroform concentrations in our seawater samples ranged from below the detection limit of 5 ppt to 14 ppt; these are within the range reported in the literature for southern California waters, and do not indicate heavy contamination. The highest levels were found at the lowest depths from Marina del Rey to Resort Point, and near the surface from Los Angeles Harbor to Huntington Beach. From our findings, it may be tentatively concluded that marine waters off the South Coast Air Basin are not a chloroform source so much as a temporary chloroform reservoir. The finding of higher $CHCl_3$ concentrations in the deeper waters off the industrialized portion of the basin indicates an accumulation of anthropogenic inputs rather than production by marine organisms. The dissolved chloroform in the ocean probably diffuses slowly upward (aided by the observed concentration gradient) or rises more rapidly by advection during upwelling, and enters the atmosphere after a delay of unknown duration. Meanwhile, as part of the typical diurnal reversal of air flow in the basin, chloroform is carried to coastal waters by offshore breezes in the late night and early morning, and returns to the land with onshore breezes.

Consideration of potential reaction pathways and review of experimental data lead to the conclusion that formation of $CHCl_3$ by gas phase reactions involving the hydroxyl (OH) radical and chloroethenes is unlikely. In Phase II, mixtures of trichloroethylene and oxides of nitrogen (NO_x) in purified air were irradiated in a large Teflon film reactor. No chloroform could be detected for any of the TCE/NO_x ratios used; dichloroacetyl chloride was tentatively identified as a reaction product. An upper limit of 1.4×10^{-3} was calculated for the fractional yield of chloroform from TCE under the conditions studied; this yield, together with ambient concentration data for TCE, indicate that daily atmospheric formation of chloroform would be less than 1 percent of the chloroform emissions estimated in this study. Reactions of other atmospheric constituents, such as ozone, the nitrate radical, and chlorine atoms, with chlorinated hydrocarbons are not expected to yield chloroform. Aqueous phase reactions (e.g. in fogwater or raindrops) may be considered as a possible atmospheric pathway, although information concerning the abundance of reactive chlorine species in atmospheric droplets is lacking.

The major expected pathway for gas-phase removal of ambient $CHCl_3$ is reaction with OH. The present study therefore included other experiments, which were apparently conducted for the first time, involving sunlight irradiation of chloroform-NO_x mixtures. These confirmed that chloroform reacts only slowly, as expected from theoretical considerations. While phosgene is an expected major product of the OH-chloroform reaction, other chlorinated hydrocarbons are likely to be more important contributors to phosgene in ambient air. Because atmospheric concentrations of OH in urban air are negligible at night, removal of chloroform is also expected to vary diurnally. The average atmospheric half-life of chloroform, for typical OH concentrations, is about 80 days. Reactions with the nitrate radical are expected to be of negligible importance for atmospheric removal of $CHCl_3$. Reaction of chloroform with chlorine atoms would be significant if ambient atomic chlorine concentrations were similar to those of OH; ambient Cl concentrations are not known, but are assumed to be substantially below those of OH. Chloroform removal mechanisms which could occur in atmospheric droplets include photodecomposition in the presence of metal oxides and slow oxidation. Dry deposition velocities for chloroform have not been reported, but those for polar molecules may be as high as about 3 centimeters per second. Deposition velocities reported for a variety of atmospheric pollutants correspond to atmospheric residence times of 3 to 900 days.

In dispersion modeling exercises with the Industrial Source Complex Short Term model, modeled concentrations were within a factor of five of those measured by the ARB at the corresponding sampling site. The model predicts a significant contribution from some of the wastewater treatment plant point sources under certain meteorological conditions. This, along with our mobile sampling results, suggests that "hot spots" of chloroform concentrations may exist near point sources.

Techniques for collecting ambient air samples for chloroform analysis include Tenax GC adsorption, carbon molecular sieve adsorption, cryogenic trapping, activated carbon adsorption, and the use of passive monitors, whole air collection devices and portable gas chromatographs. After evaluating these methods against six criteria, we rated carbon molecular sieve adsorption highest. Methods for analyzing air samples for $CHCl_3$ include capillary column gas chromatography/mass spectrometry (GC/MS); gas chromatography with flame ionization detection (GC/FID), capillary column GC with electron capture detection (GC/ECD) and GC with the use of packed columns and a Hall electrolytic conductivity detector (GC/HECD). After evaluating these methods, we recommend use of GC/ECD with GC/MS for confirmation of compound identity.

The preferred method for collecting municipal and wastewater samples for $CHCl_3$ analysis is in glass vials equipped with Teflon-faced silicone septa and screw caps. Seawater samples are collected in Niskin bottles, which are lowered to pre-set depths and closed after deployment. The recommended method for water analysis is by GC, using packed columns and a Hall electrolytic conductivity detector.

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1.1 EMISSION SOURCES

1.1.1 Direct Production

(1) No chloroform is manufactured deliberately in the South Coast Air Basin.

(2) Published measurement and modeling data suggest that the tropical oceans are a major source of emissions of chloroform to the atmosphere, although the origin of this chloroform is unknown. However, the evidence that, outside of the tropics, there is a significant net transfer of chloroform from seawater to the atmosphere is very weak.

(3) Very little information on chloroform concentrations in seawater off California has been published; reported values for Southern California range from about 6 to 20 parts per trillion (ppt). Measurements conducted as part of this project found 5 to 14 ppt off the coast from Point Dume to Huntington Beach.

(4) One reviewed article concludes that an observed "gradient" of ambient chloroform concentrations from the northern California coast through two inland sites suggests a significant marine source for $CHCl_3$. However, the three concentrations were measured in different months, so that it cannot be stated with certainty that a gradient existed during any short-term interval.

(5) Virtually all of the observed biogenic production of halogenated organic compounds has been associated with macroalgae, such as seaweed.

(6) To date, chloroform has been detected in only one genus of seaweed, *Asparagopsis*, including a species from the Gulf of California, *A. taxiformis*.

(7) The haloforms in *Asparagopsis* are apparently produced by the classic haloform reaction. The chloroform produced by red algae is excreted by the living organism, rather than stored.

(8) No data on rates of biogenic chloroform production or release to seawater were found.

(9) Only one report of release of chloroform from terrestrial vegetation (northern white pine cedar and deciduous moss) was found; the data presented do not prove conclusively that this release occurs.

1.1.2 Indirect Production

Most of the chloroform emitted to the ambient air of the South Coast Air Basin (SCAB) is produced indirectly; i.e. through the reaction of chlorine with various organic precursors. Processes through which chloroform has been shown to be produced unintentionally and indirectly include chlorination of drinking water, wastewater, recirculating cooling tower water, and swimming pools; and bleaching of paper and pulp. Some chlorine may also be produced through use of chlorine-based bleach in laundry products. We reviewed and/or developed emission factors for various chloroform-emitting processes. These were then used with chlorine consumption data to estimate emissions.

1.1.2.1 Emission Factors for Chlorination Processes

Because several different chlorine-containing agents are used for disinfection, bleaching, and other industrial purposes, it was necessary to express quantities of these compounds on a common basis which is related to the potential for chloroform formation. We therefore defined "chlorine equivalent" as the mass of chlorine which would form the same amount of hypochlorous acid (HOCl) in aqueous solution as would one mass unit of the compound. Furthermore, we defined the "$CHCl_3/Cl_2$ molar ratio" (or "molar ratio" for short) as the ratio of moles of chloroform produced in a given process per mole of chlorine equivalent consumed. Using appropriate molecular weights and units conversion factors, it can be shown that emissions (in pounds) from a given process are equal to 1.68 RC, where R is the molar ratio and C is the chlorine equivalent (in pounds) of the precursor.

Drinking Water

(1) From reports of laboratory studies of chlorination of surface waters and solutions of humic and fulvic acids we calculated molar ratios of 0.0067 to 0.136.

(2) From literature data on studies of chlorinated municipal drinking water we estimated molar ratios of 0.011 to 0.013 at the plant outlet and 0.013 to 0.017 in the distribution system.

(3) For estimating chloroform emissions from drinking water chlorination, we chose a molar ratio of 0.015, which corresponds

to the midpoint of the distribution system calculation and is within the range calculated for the laboratory studies.

(4) Reported studies of chloroform in tap water found considerable hourly and daily variability in concentrations.

Freshwater Cooling

Chlorine compounds are added to most freshwater cooling systems to suppress the growth of algae, slime and other biota which would otherwise proliferate in the warm, nutrient-rich environment. Conditions conducive to the haloform reaction are frequently present. Although once-through cooling is not used to any significant extent in the SCAB, the literature on this subject contains information useful in assessing chloroform production in circulating cooling water systems.

(1) Using published data from laboratory chlorination of river water used for once-through cooling at a power plant, we estimated molar ratios of 0.002 to 0.02. These ratios take into account loss of free chlorine from the high-temperature water before it could participate in the haloform reaction.

(2) To the best of our knowledge, only two source tests of chloroform emissions from cooling towers have been conducted, including previous research by SAIC for the ARB. Results of these studies were reviewed in detail.

(3) To derive an emission factor for cooling tower chlorination, we first estimated a likely chlorine dose rate for the towers upon which source tests had been performed. Since these rates were not reported, we normalized dose rates reported in our industrial cooling tower surveys (see Section 1.1.2.2) to circulating water flow rate. These dose rates were then applied to the measured towers. Reported emissions were then divided by the chlorine equivalent dose rates to obtain emission factors. Resulting molar ratios were closer to 0.02 than to 0.002; hence the former value was used in later calculations.

Seawater Cooling

Chlorination of seawater was of interest to this study because seawater is used for once-through cooling at several electric power plants in the SCAB and because three large wastewater treatment plants in the Basin occasionally chlorinate untreated or partially treated effluents before discharging them to the ocean.

(1) Our literature review found that little or no chloroform formation may be expected from chlorination of seawater. Molar ratios calculated from reported experimental data range from 0 to 0.005.

(2) One reason why so little chloroform is produced is that when chlorine is added to seawater, which usually contains about 65 milligrams per liter of bromide ion, the bromide is rapidly oxidized to HOBr while the hypochlorous acid is reduced to chloride ion. Consumption of 99 percent of the HOCl may occur within 10 seconds; this rate is much faster than the haloform reaction.

(3) Our conclusion from this review is that chloroform production from seawater chlorination is likely to be negligible in comparison with that from drinking water chlorination and other sources.

Wastewater Treatment

Trihalomethanes are less likely to form in wastewater than in treated drinking water because the high ammonia content of the former results in the rapid formation of chloramines. The limited literature on chloroform production during wastewater treatment, as well as our field measurements in this project, suggest the following.

(1) Most of the chloroform entering the wastewater treatment system as a constituent of raw wastewater is probably transferred to the air during primary treatment.

(2) Chloroform which ends up in aerobic treatment processes (such as secondary treatment with activated sludge) is not degraded. Given the extensive contact with air during these processes, it is likely that most of chloroform is emitted to the atmosphere.

(3) Chloroform which is involved in anaerobic processes, such as sludge digestion, may be degraded, given a long enough time.

(4) The amount of chloroform produced by chlorination of final treated effluent is likely to be significant only if ammonia has been removed (such as by nitrification during tertiary treatment) before chlorination. If the effluent is discharged to the ocean, then chloroform emissions would be negligible.

Swimming Pool Chlorination

Given the large number of swimming pools in the SCAB and the widespread practice of treating them with chlorine, the literature was reviewed to ascertain whether chloroform formation in swimming pools had been observed.

(1) Most of the research reported to date has been on European pools; to the best of our knowledge, only one measurement program had been conducted in the United States prior to the present study.

(2) $CHCl_3/Cl_2$ molar ratios calculated from reports of tests on swimming pools are about 10 times those for drinking water chlorination.

(3) High concentrations of chloroform (up to 72,100 parts per trillion) have been observed in the air of indoor swimming pool facilities.

(4) Concentrations of chloroform in the air above indoor swimming pools decrease with height above the water surface.

(5) Concentrations of $CHCl_3$ in indoor swimming pool air increase with the number of pool users, probably as a result of the increased surface-air interface created by more pool activity.

(6) Several of the studies, including the one conducted in the U.S., have shown that the chloroform observed was formed in situ; i.e. it was not due to use of chlorinated municipal water.

(7) Emission isolation flux chamber tests conducted as part of this project (see Section 1.5.2) confirmed that chloroform is emitted from outdoor swimming pools.

Pulp and Paper Manufacturing

(1) Chlorine bleach is added to wood pulp during processing into paper, paperboard, rayon, cellophane and explosives.

(2) Chloroform emission factors for the types of processes likely to be found in the SCAB are 0.016 kilograms per metric ton (kg/MT) product for secondary tissue paper; 0.12 kg/MT for market bleached kraft; 0.23 kg/MT for bleached kraft paperboard, coarse papers, and tissue papers; and 0.36 kg/MT for secondary fiber mill fine papers.

1.1.2.2 Transfer of Chloroform From Water to Air

(1) Dissolved chloroform is transferred rapidly and thoroughly to the atmosphere.

(2) In laboratory experiments in which chloroform was allowed to evaporate into still air, its half life in solution was about 20 minutes.

(3) The flow of air across the water surface, as would occur under actual conditions, would increase the evaporation rate significantly (by about 17 percent in one experiment).

1.1.2.3 Emissions From Chlorination Processes

Drinking Water

In order to obtain an improved estimate of the use of chlorine and and chlorine-based disinfectants in the South Coast Air Basin, SAIC conducted a survey of all municipal water districts located in the Basin and serving 50,000 or more people. The results of this survey, and subsequent analyses by SAIC, were:

(1) The total estimated annual chlorine equivalent used for drinking water chlorination in the SCAB in 1985 was over 15 million lb.

(2) We estimate 190 tons/yr of chloroform emissions from drinking water chlorination.

Treated Wastewater

(1) Emission factors for $CHCl_3$ emissions from wastewater treatment processes are approximately an order of magnitude below those for drinking water chlorination.

(2) Because of this, the contribution of $CHCl_3$ to the Basin air by chlorination at sewage treatment plants is significantly smaller than the contribution due to the residual from the drinking water system.

(3) Additional chloroform is produced when nitrified tertiary-treated effluent is chlorinated prior to discharge; however, facilities at which these additional emissions occur represent only a small fraction of the wastewater treatment in the SCAB.

(4) Therefore, the independent contribution of wastewater treatment plants to ambient chloroform in the SCAB was not included in our emission inventory.

Industrial Cooling Towers

SAIC conducted a mail survey of potential industrial cooling tower users in the SCAB. The following findings emerged from this survey and subsequent analyses:

(1) Industries reporting the greatest number of towers were in Standard Industrial Classification codes 2086 (bottled and canned soft drinks) and 3069 (fabricated rubber products).

(2) Los Angeles County accounted for 76 percent of the reported tower using facilities and 73 percent of the reported towers.

(3) Some form of inorganic chlorine-based biocide was used in 55 of 176 towers reported (33 percent).

(4) Chlorine gas was used in 45 percent of reported towers, but represents 99.6 percent of total reported chlorine equivalent.

(5) Hypochlorite and "bleach" solutions were generally used on smaller towers.

(6) Chlorine is added continuously to all large towers (>7,000 gpm circulation), while smaller towers are chlorinated from once per week to once per month.

(7) $CHCl_3$ emissions from industrial cooling towers were estimated to be 2.3 tons/yr.

(8) At the 95-percent confidence level, the lower and upper bounds for chloroform emissions from industrial cooling towers are 0.70 and 5.17 tons/year, respectively.

Utility Cooling Towers

SAIC conducted a telephone survey of utilities having power plants with cooling towers in the SCAB to obtain data on chlorine or sodium hypochlorite used in tower chlorination. $CHCl_3$ emissions by utility power plant cooling towers in the SCAB are estimated to be 0.40 ton/yr.

Pulp and Paper Manufacturing

(1) Only 3 of the 14 potential pulp and paper manufacturing facilities located in the SCAB were confirmed as operating pulp and paper manufacturing plants. These three plants were contacted by telephone to obtain information on chlorine use.

(2) From reported chlorine use we estimated $CHCl_3$ emissions to the SCAB from this source to be about 21 tons/yr.

Chlorinated Rubber Manufacturing

Chlorination in synthetic rubber manufacturing occurs primarily in the manufacture of chloroprene rubber. No chloroprene or other chlorinated rubber manufacturers are located in California. Thus, chloroform emissions from this source are zero.

1.1.2.4 Emissions From Combustion of Leaded Gasoline

(1) The presence of halogenated compounds (e.g. ethylene dichloride) in leaded gasoline has led to only a modest amount of research into the potential for formation of halomethanes during combustion. An extensive literature review found only two reports of attempts to measure chloroform in automobile exhaust.

(2) In one study, the exhaust from a 1972 Rambler operated with leaded gasoline and lacking a catalytic converter contained 5.6 and 6.8 ppb of chloroform. Chloroform concentrations in the exhaust of a 1975 Pinto equipped with a catalytic converter and using unleaded gasoline yielded chloroform concentrations of 0.066 and 0.091 ppb, which bracketed the contemporaneous ambient air concentration of 0.088 ppb.

(3) In the other study, no chloroform was detected in the exhaust of a vehicle which burned leaded gasoline containing 1,2-dichlooethane. (The data detection limit was 9 ppb.)

(4) Recent federal regulations which reduce the lead content of gasoline from 1.50 to 0.10 grams per gallon should in effect eliminate motor vehicle fuel additives as a significant source of organochlorine emissions.

(5) Given the preceding evidence, and the lack of a plausible reaction pathway leading to formation of chloroform from 1,2-dichloroethane, we conclude that chloroform emissions from automobiles are likely to be negligible. They were therefore not considered further in developing the emission inventory for the SCAB.

1.1.2.5 Emissions From Swimming Pool Chlorination

(1) Through source tests on a residential swimming pool, we estimated emission flux rates of 12 $\mu g/m^2$-min for still conditions and 390 μg/m2-min for when the water surface is agitated.

(2) From information obtained from swimming pool industry representatives, and by making some assumptions about pool size, we estimate a total swimming pool surface area of 1.14×10^7 m^2 in the SCAB.

(3) After considering typical pool use patterns and schedules for chlorine addition, we calculated a weighted average flux rate of 22.3 $\mu g/m^2$-min.

(4) The resulting estimate of basin-wide choroform emissions is 147 tons/yr.

1.1.2.6 Other Indirect Sources

Tobacco Smoke

(1) Our literature review found only one attempt to determine whether chloroform was generated by cigarette smoking. No chloroform was found.

(2) Although the analytical method used in that study may have been too insensitive, the absence of any other evidence of chloroform generation from tobacco smoking led us to remove this potential source from further consideration.

Domestic Bleach Consumption

SAIC calculated the approximate quantity of bleach used weekly in the household wash by families in the SCAB. The following summarizes our findings:

(1) Emissions of chloroform to the ambient air from domestic bleach consumption are estimated to be 5.9 tons/yr.

(2) The calculated amount of chloroform released to the ambient air does not include commercial bleach consumption and thus may substantially underestimate actual emissions from liquid bleach.

1.1.3 Emissions From Consumptive Use

(1) Chloroform is used as a feedstock to produce chlorodifluoromethane by the Allied Corporation in El Segundo.

(2) Previous research by SAIC for the ARB determined that annual fugitive chloroform emissions from this plant were 0.089 to 0.163 tons per year.

1.1.4 Emissions From Nonconsumptive Use

1.1.4.1 Pharmaceutical Manufacturing

SAIC conducted a telephone survey of companies in SIC codes 2831 (biological products), 2833 (medicinals and botanicals), and 2834 (pharmaceuticals), and in postal ZIP codes for the SCAB. We found that:

(1) Six out of 25 companies contacted used some $CHCl_3$.

(2) After scaling up to the entire sample, and then to the Basin, we estimated that total $CHCl_3$ emitted annually by all pharmaceutical companies was 1.56 tons, with a 95-percent confidence interval of 0.4 - 3.5 tons.

1.1.4.2 Laboratory Use

We conducted a mail survey of 431 laboratory facilities in SIC codes 7391 (commercial research and development laboratories), 7397 (commercial testing laboratories), and 8071 (medical laboratories) to ascertain $CHCl_3$ use in laboratories in the SCAB. Our findings were that:

(1) About 8.5 percent of the responding laboratories reported using $CHCl_3$, with a mean use rate of 44 liters per laboratory reporting some use, and 4 liters per lab for all responding facilities.

(2) Total annual $CHCl_3$ use (and, therefore, emissions) for all laboratories in the SCAB were estimated to be 4.4 tons.

(3) Uncertainties in this estimate include: (a) possible inaccuracy of our list of laboratories in the chosen SIC codes, (b) the completeness of the SIC codes, and (c) statistical uncertainty.

(4) A 95-percent confidence interval for chloroform emissions from laboratories in the SCAB is 4.4 to 9.5 tons per year; the lower bound represents actual estimated emissions.

1.1.4.3 Grain Fumigation

SAIC has determined that $CHCl_3$ is not used as a fumigant in the SCAB, since other fumigants, such as aluminum phosphide and methyl bromide, have more desirable properties.

1.1.4.4 Contamination of Chlorinated Products

(1) Chloroform may be present as a minor contaminant in methyl chloride, methylene chloride, and carbon tetrachloride.

(2) Previous research by SAIC estimated that nationwide releases of $CHCl_3$ via product contamination were only about 7 tons per year. It is therefore unlikely that this mode would be important in the SCAB.

1.1.5 Emission Summary

Table 1.1-1 shows SAIC's estimates of chloroform emissions in the South Coast Air Basin in 1985. In reviewing these results it should be borne in mind that all estimates are based upon the use of emission factors having significant uncertainties.

(1) We estimate total emissions of chloroform in the SCAB to be 370 (340 MT) per year.

(2) The largest source of emissions appears to be drinking water chlorination, which accounts for about 51 percent of the annual total.

(3) Swimming pool and drinking water chlorination account for about 91 percent of the total emissions.

(4) Pulp and paper manufacturing plants are the only industrial facilities with a significant potential for chloroform generation, although their emissions occur at wastewater treatment plants.

1.2 ATMOSPHERIC CONCENTRATIONS AND REACTIONS

1.2.1 Ambient Concentrations in the South Coast Air Basin

The following discussion summarizes our review of ambient chloroform data collected prior to this study. The results of SAIC's ambient sampling studies are presented in Section 1.4.

(1) Relatively few chloroform measurements in the South Coast Air Basin have been reported, and measurements before this project had been limited to fewer than a dozen sites.

(2) Grab samples taken in various locations in the SCAB in 1974 contained 360 to 640 ppt of chloroform.

(3) An extensive program of grab sample measurement using gas chromatography with electron capture detection found mean concentrations of chloroform of 103 + 103 and 88 ± 40 ppt in Los Angeles in 1976 and 1979, respectively, and 703 ± 798 ppt in Riverside in 1980.

Table 1.1-1

SUMMARY OF SAIC ESTIMATES OF ATMOSPHERIC EMISSIONS OF CHLOROFORM IN THE SCAB

Source	Estimated Annual Emissions		
	MT	tons	Percent of Total
A. Indirect Production[a]			
Drinking water	172	190	51.0
Swimming pools	134	147	39.5
Pulp and paper manufacturing	19	21	5.6
Domestic bleach	5.3	5.9	1.6
Industrial cooling towers	2.1	2.3	0.6
Utility cooling towers	0.36	0.40	0.1
B. Non-Consumptive Use			
Laboratories	4.0	4.4	1.2
Pharmaceutical manufacturing	1.4	1.6	0.4
Totals	338	373	100.0

[a] No marine source estimated.

(4) Maximum 12-hour concentrations around the abandoned McColl waste disposal site in Fullerton were found to be 100 to 800 ppt at 7 of the 8 measurement points; at one off-site point, an 8,100-ppt concentration was measured.

(5) Although studies in other states have found a marked diurnal variation in ambient chloroform concentrations, no diurnal measurements in the SCAB have been reported in the literature.

(6) SAIC obtained and evaluated 24-hour average chloroform concentration data from four ARB halocarbon monitoring sites in the SCAB: Dominguez Hills (January 1983 - July 1984), El Monte (January 1983 - December 1984), Los Angeles (January 1983 - July 1984), and Riverside (January 1983 - July 1984).

(7) Concentration values above the limit of detection (20 ppt) were distributed lognormally for each receptor. Analyses were therefore performed on the logarithms of the reported concentration values.

(8) Mean 24-hour concentrations for the ARB sites were 45.1 ppt at Dominguez Hills, 47.8 ppt at El Monte, 60.5 ppt at Los Angeles, and 46.6 ppt at Riverside.

(9) The mean 24-hour concentration at the Los Angeles site is significantly higher ($p < 0.05$) than those for the remaining sites.

(10) Reported 24-hour average concentrations above 110 ppt at Los Angeles and above 130 ppt at El Monte are highly unlikely and may be considered outliers. The maximum values of 140 and 120 ppt at Dominguez Hills and Riverside, respectively, are not likely to be outliers.

1.2.2 In-Situ Formation Processes

The following is a summary of our literature review. The results of laboratory experiments conducted for this project are presented in Section 1.6.

1.2.2.1 Gas Phase Reactions

(1) Earlier studies and review articles suggest the possibility of chloroform production in the atmosphere by reactions involving trichloroethylene and tetrachloroethylene.

(2) Examination of rate constants indicates that, under tropospheric conditions, reaction with the hydroxyl (OH) radical is by far the major removal process for chlorinated ethylenes.

(3) From consideration of potential reaction pathways, we would not expect chloroform to form as a product of the reaction of OH with chlorinated ethylenes.

(4) In laboratory studies involving irradiated chloroethene-NO_x mixtures in air, reaction products included carbon monoxide, hydrochloric acid, phosgene, formyl chloride, formaldehyde, and chloroacetyl chlorides, but not chloroform.

(5) One study reported dichloroacetyl chloride as a major product of the reaction of ozone with chlorinated ethylenes. Dichloroacetyl chloride could photolyze in sunlight to yield chloroform. However, no chloroform was observed in the ozone experiments, and chloroacetyl chlorides are not likely to be formed by OH-initiated reactions.

(6) Formation of chloroform by gas phase reactions involving OH and trichloro- and tetrachloroethylene is unlikely but cannot be ruled out at this time; there is a need for additional studies of reaction products under SCAB atmospheric conditions.

(7) The reaction of the nitrate radical with chlorinated hydrocarbons is not expected to yield chloroform.

(8) The reaction of chlorine atoms with chlorinated hydrocarbons is not considered to be an important chloroform source, since ambient chlorine atom levels in California are presumably very small.

1.2.2.2 Aqueous Phase Reactions

(1) Chloroform has been identified in California rainwater. The presence of chloroform may be due to scavenging of gas phase chloroform or in-situ formation.

(2) The acidity of California fog, rainwater and cloud water includes the pH range (3-7) optimal for chlorine to be present as HOCl.

(3) Aliphatic organics which participate readily in the haloform reaction are ubiquitous and abundant in California hydrometeors.

(4) Aqueous phase production of chloroform may therefore be considered as a possible atmospheric pathway, although information concerning the abundance of reactive chlorine species in atmospheric droplets is lacking.

1.2.3 Removal Processes

1.2.3.1 Homogeneous Gas Phase Reactions

(1) Chloroform is thermally stable at ambient temperatures.

(2) Photolysis of chloroform is unlikely, since $CHCl_3$ absorbs radiation only well below the tropospheric cutoff of 290 nm.

(3) Reactions of chloroform with O, O_3 and HO_2 are of negligible atmospheric importance.

(4) Reaction with the hydroxyl radical is a major pathway for the removal of atmospheric chloroform. Surprisingly, no experimental study focusing on products of the OH-chloroform reaction could be found in the literature. From theoretical considerations, phosgene is the only expected product of the reaction, under SCAB atmospheric conditions.

(5) Because atmospheric concentrations of OH in urban air are negligible at night, removal of chloroform is also expected to exhibit substantial diurnal variation. Limited ambient sampling data support this expectation.

(6) Assuming 16 hours of daylight per day, the average atmospheric half-life of chloroform, for a typical average OH concentration of 10^6 molecules/cm^3, will be about 80 days.

(7) Reactions with the nitrate radical are expected to be of negligible importance for atmospheric removal of chloroform.

(8) Reaction of chloroform with chlorine atoms would be significant if ambient atomic chlorine concentrations were similar to those of the OH radical. Ambient chlorine concentrations are not known, but are assumed to be substantially below those of OH.

1.2.3.2 Liquid Phase Reactions

(1) Possible reactions of chloroform in hydrometeors include hydrolysis, photodecomposition, and reactions with free radicals (OH), atoms (Cl) and other oxidants (e.g. ozone and hydrogen peroxide). Hydrolysis and photolysis are negligible.

(2) Some photodecomposition of chloroform may take place in droplets containing metal oxides, which may act as oxidation catalysts.

(3) The reaction of chloroform with the hydroxyl radical in the aqueous phase has not been documented. However, using literature values of correlations between gas- and aqueous-phase reaction

rate constants for OH reactions, we estimate that any reaction with OH would be too slow to be significant in removing chloroform from hydrometeors.

(4) Removal by reaction with chlorine in hydrometeors is speculative at this time.

(5) Extrapolation of bulk liquid phase kinetic data suggests that slow oxidation of chloroform to phosgene and/or carbon dioxide and hydrochloric acid may take place in hydrometeors.

1.2.3.3 Dry Deposition

(1) Dry deposition velocities for chloroform have not been reported, but those for polar molecules may be as high as about 3 cm/s.

(2) Deposition velocities reported for a variety of atmospheric pollutants correspond to atmospheric residence times of about 3 to 900 days; these may be compared with the aforementioned estimated 80-day residence time for gas phase removal of chloroform through reaction with the OH radical.

1.3 REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES

1.3.1 Air Sampling Techniques

(1) Techniques for collecting ambient air samples for chloroform analysis include Tenax GC adsorption, carbon molecular sieve adsorption, cryogenic trapping, activated carbon adsorption, and the use of passive monitors, whole air collection devices and portable gas chromatographs.

(2) Use of Tenax GC adsorbent cartridges is perhaps the most widely used method of ambient air sampling for volatile organic compounds. The method is simple to use in the field, and is suitable for chloroform. However, the retention volume for chloroform on Tenax GC is relatively low, so that considerable care is necessary to prevent or minimize breakthrough.

(3) Carbon molecular sieves (CMS) can be used in place of Tenax GC in sampling cartridges. The retention volume for chloroform on these materials is reported to be higher than for Tenax GC, so that larger air samples can be collected without breakthrough. However, since compounds are more strongly adsorbed to the carbon molecular sieve, higher temperatures are needed to desorb them for analysis. Data on decomposition product or artifact formation when sampling in the presence of high humidity and reactive inorganic gases are not currently available.

(4) Cryogenic trapping has proven effective for collecting air samples to be analyzed for chloroform. The presence of high humidity, ozone and nitrogen dioxide does not, in limited tests, result in artifact peaks, deleterious column effects or decomposition of the compounds tested. The advantages of the method include avoidance of contaminants from adsorbents and consistency of recovery. A disadvantage is the need to transport the analytical system to the monitoring site.

(5) Activated charcoal adsorption is widely used in industrial hygiene, and is relatively inexpensive. Since thermal desorption of chloroform is not practical, solvent extraction must be used. This permits replicate analyses and injection of diluted samples into the analytical instrument. Sampling high-humidity air can reduce the adsorptive capacity of activated charcoal for some compounds.

(6) Although recently developed passive samplers using Tenax GC as the sorbent have shown promise, we believe that their use for ambient air characterization requires further study.

(7) Whole air samples can be collected using glass sampling bulbs, stainless steel canisters, polymeric sampling bags, and gas-tight syringes. Limitations of this collection method include adsorption or decomposition of compounds of interest through interaction with container walls, condensation of compounds at high concentrations, and sample leakage.

(8) The use of portable gas chromatographs (GCs) for field monitoring of ambient volatile organic compounds is feasible when concentrations of the compounds are sufficient to be detected and when some prior knowledge of the air composition is available.

(9) The detection limits of flame ionization detection (FID) GCs are generally too high to be suitable for chloroform sampling. GCs with photoionization detection (PID) are more selective and sensitive toward certain compounds, but their detection limits are also too high for monitoring ambient chloroform. The best portable GCs for monitoring chloroform and other halogenated hydrocarbons are equipped with electron capture detectors (ECD).

(10) After evaluating the aforementioned sampling methods against six evaluation criteria, we rated carbon molecular sieve adsorption highest for ambient sampling of chloroform.

1.3.2 Analytical Methods for Air

(1) Methods for analyzing air samples for chloroform include capillary column gas chromatography/mass spectrometry (GC/MS), GC/FID, GC/ECD, and GC with the use of packed columns and a Hall electrolytic conductivity detector (GC/HECD).

(2) Capillary columns provide better resolution of compounds than do packed columns. Packed columns, on the other hand, have greater

sample loading capacity, are easier to use, and are more suitable for analysis of highly volatile compounds. Wide-bore, thick-film, fused silica capillary columns combine the best features of the capillary and packed columns.

(3) GC/MS is a powerful tool for identifying organic compounds in ambient air samples. When used in the selected ion monitoring mode, it also allows accurate quantitation. GC/MS has been suggested by other reviewers as the method of choice for analyzing ambient air samples collected on Tenax GC or carbon molecular sieve.

(4) GC/ECD is preferred over GC/FID since it is specific toward halogenated hydrocarbons and has a sensitivity of about 1-10 picograms per compound. Two potential drawbacks to the electron capture detector is that, due to its high sensitivity, it is highly susceptible to contamination from the compounds of interest, and its response tends to drift during temperature programmed analyses.

(5) Both GC/FID and GC/ECD fall short of providing positive qualitative identification of compounds on a single analysis. This limitation can be overcome either by analyzing samples on a second column (of different retentive characteristics than the primary column) or by analyzing samples on a single column and passing the column effluent through two different detectors. Both methods have disadvantages. The first approach requires collection of duplicate samples, while the second reduces the sensitivity of the analysis.

(6) GC/HECD has an analytical sensitivity comparable to that of GC/FID, but is even more specific toward halogenated compounds than is GC/ECD. It is thus less susceptible to interferences from other types of compounds in the sample. The detector is also more stable during temperature-programmed analyses.

(7) After evaluating the aforementioned analytical techniques against six rating criteria, we ranked GC/MS the highest. For the best results, the GC should be used with an electron capture detector, while the MS should be used for confirmation of compound identity.

1.3.3 Water Sampling and Analysis

(1) Water sampling methods were selected to be compatible with the analytical techniques to be used.

(2) The preferred method for collecting municipal and industrial wastewater samples is in glass vials equipped with Teflon-faced silicone septa and screw caps. Air bubbles must be excluded from the sample during collection and storage.

(3) Seawater samples are collected in Niskin bottles, which are lowered to pre-set depths and closed after deployment.

(4) Water is analyzed for chloroform by bubbling an inert gas through an aliquot of the sample. Halocarbons are stripped from solution and trapped on an adsorbent, which in turn is thermally desorbed onto a GC column.

(5) The U.S. Environmental Protection Agency recommends using packed columns and the Hall electrolytic conductivity detector, but capillary columns can also be used. GC/MS can be used to provide more definitive qualitative information.

1.4 AMBIENT SAMPLING

1.4.1 Introduction

Three types of ambient sampling were conducted. In all cases, SAIC collected air samples on carbon molecular sieve (CMS) traps, which were then analyzed by Environmental Monitoring and Systems, Inc. (EMSI) by cryogenic preconcentration and gas chromatography with electron capture detection. Compounds measured included chloroform, 1,1,1-trichloroethane (methyl chloroform), carbon tetrachloride, trichloroethylene (TCE), tetrachloroethylene (perchloroethylene), and ethylene dibromide (EDB). Since this was, to the best of our knowledge, the first large-scale use of CMS for ambient halocarbon sampling, considerable trial-and-error was necessary for developing suitable sampling and analytical methods.

1.4.2 Fixed-Site Monitoring

The objectives of the fixed-site monitoring were to supplement the ARB halocarbon monitoring network by covering additional geographic areas and to measure diurnal variations in chloroform concentrations at one site.

(1) 24-hr samples were collected for 7 days in December 1986 on the roof of the Fullerton headquarters fire station.

(2) 6-hr samples were collected for 7 days in April 1987 on the roof of an office building in Hermosa Beach.

(3) Significant breakthrough of most of the compounds was detected in all of the two-trap samples collected at both sites; the safe sampling volume reported in the literature was seriously overestimated. Therefore the validity of the results from these sites is limited.

(4) Chloroform concentrations in the Fullerton samples were within the ranges measured at the ARB 24-hr sampling stations, but the valid results are too scanty to permit a discussion of variation within the week.

(5) Chloroform concentrations at Hermosa Beach ranged from 6 to 168 ppt and had an arithmetic mean and standard deviation of 58 and 40 ppt, respectively. No statistically significant difference among daily average or quarter-day average concentrations could be found.

1.4.3 Mobile Sampling

The main objective of this part of the study was to obtain short-term (1-hr) samples at a variety of sites in the South Coast Air Basin, at various times of the day and week. A secondary objective was to identify "hot spots," i.e. areas of elevated concentrations. To avoid the breakthrough problems experienced in the fixed-site monitoring, lower pump flow rates and volumes were used.

(1) Seven sets of ambient samples were collected at 41 sites between 13 and 22 May 1987. (See Figure 1.4-1.)

(2) Results of the ambient mobile sampling are summarized in Table 1.4-1. Ranges of detectable concentrations were: chloroform (12 - 480 ppt), 1,1,1-trichloroethane (13 - 3,500 ppt), carbon tetrachloride (10- 460 ppt), trichloroethylene (16 - 3,100 ppt), tetrachloroethylene (29 - 1,100), and ethylene dibromide (33 ppt). These values are consistent with those measured by the ARB monitoring network and others reported in the literature.

(3) On one day, chloroform concentrations rose from the coastal site in the morning to a maximum of 105 ppt at night in the northwest corner of the San Fernando Valley; as some of the highest concentrations of perchloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane also occurred at this site, it is possible that we sampled at least one day's accumulation of contributions of halocarbons from numerous upwind sources.

(4) Most of the coastal samples had relatively high chloroform concentrations.

(5) The highest chloroform level of all of the mobile sampling (483 ppt) was measured directly downwind from the Los Angeles Hyperion Treatment Plant. It is possible, since the facility is on the coast, that chloroform present in marine air comprised a portion of the observed values.

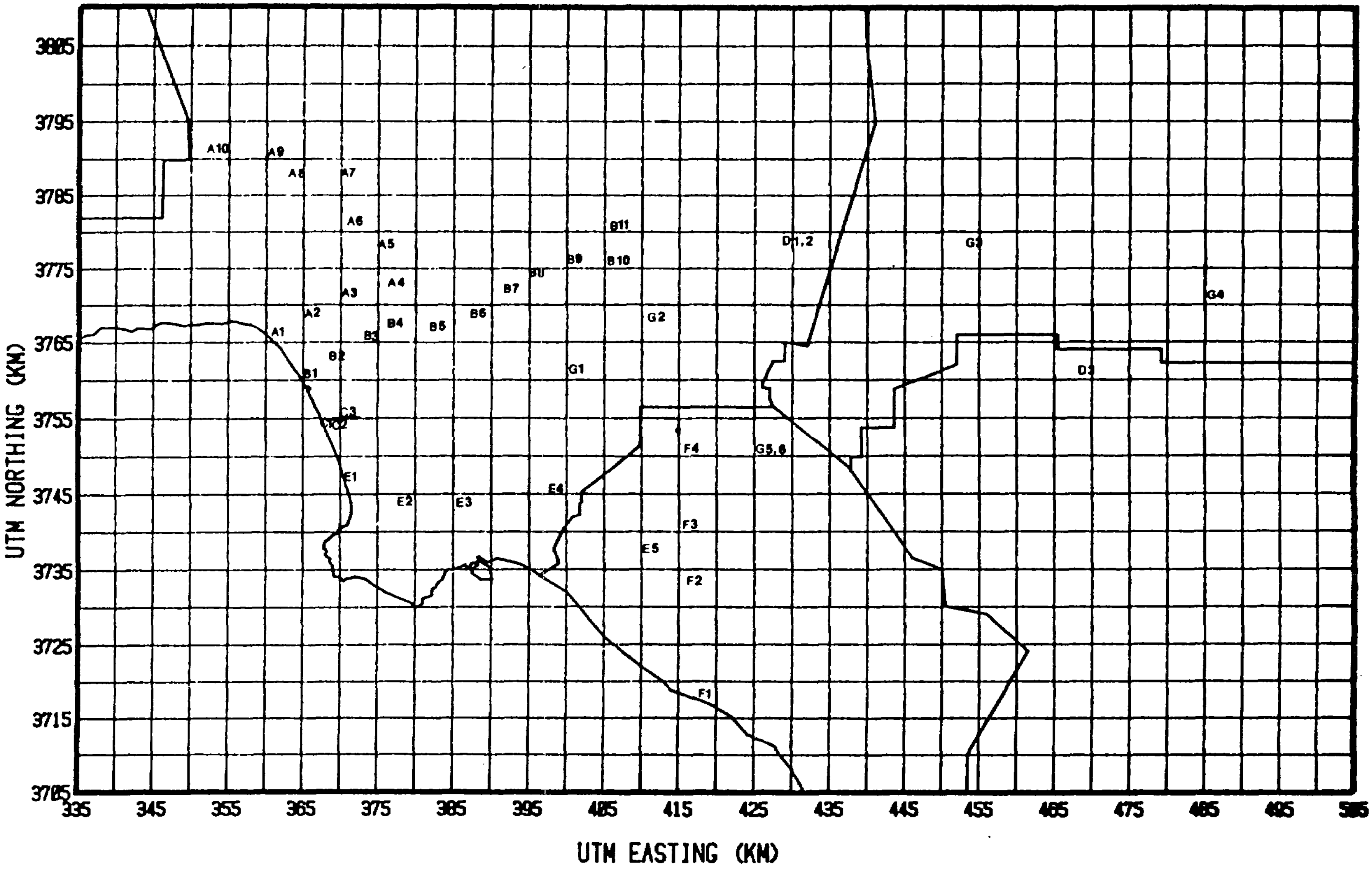


Figure 1.4-1. Locations of Mobile Sampling Sites.

Table 1.4-1

RESULTS OF MOBILE SAMPLING IN THE SOUTH COAST AIR BASIN

(Concentrations in ppt)

Sample	Date	Sampling Interval	Chloroform	1,1,1-Trichloro-ethane	Carbon Tetra-chloride	Trichloro-ethylene	Perchloro-ethylene	Ethylene Dibromide
A-1	5/18/87	0607-0705	55	255	ND	229	118	ND
A-2	5/18/87	0727-0824	53	319	ND	356	911	ND
A-3	5/18/87	0855-0950	ND[a]	50	ND	153	ND	ND
A-4	5/18/87	1017-1113	38	687	15	192	1,147	ND
A-5	5/18/87	1150-1246	ND	160	ND	18	ND	ND
A-6	5/18/87	1325-1423	54	178	42	197	741	ND
A-7	5/18/87	1508-1606	38	155	30	227	567	ND
A-8	5/18/87	1631-1728	37	213	ND	267	ND	ND
A-9	5/18/87	1824-1924	71	160	55	130	244	ND
A-10	5/18/87	2051-2151	104	1,741	297	174	775	ND
B-1	5/22/87	0715-0810	180	80	14	Sat	168	ND
B-2	5/22/87	0837-0933	121	16	27	426	175	ND
B-3	5/22/87	0959-1054	54	16	14	230	208	ND
B-4	5/22/87	1114-1214	63	28	12	57	Sat	ND
B-5	5/22/87	1241-1336	65	14	13	29	58	ND
B-6	5/22/87	1401-1456	93	17	43	34	241	ND
B-7	5/22/87	1522-1622	98	ND	38	30	82	ND
B-8	5/22/87	1649-1749	98	468	63	1,603	Sat	ND
B-9	5/22/87	1808-1903	19	17	44	35	ND	ND
B-10	5/22/87	1925-2020	34	ND	13	31	160	ND
B-11	5/22/87	2042-2136	36	ND	28	16	ND	ND
C-1	5/13/87	1736-1834	218	207	40	315	212	33
C-2	5/13/87	1850-1949	175	45	29	159	171	ND
C-3	5/13/87	2005-2100	483	281	ND	214	301	ND
D-1	5/22/87	1331-1428	114	38	17	175	215	ND
D-2	5/22/87	1443-1540	69	46	13	173	324	ND
D-3	5/22/87	1805-1901	112[b]	20[c]	35	ND[c]	86	ND
E-1	5/18/87	0606-0702	39	ND	10	47	419	ND
E-2	5/18/87	0727-0824	153	275	50	105	304	ND
E-3	5/18/87	0912-1012	12	123	ND	ND	63	ND
E-4	5/18/87	1053-1105	ND	3,490	ND	ND	ND	ND
E-5	5/18/87	1220-1318	40	274	10	ND	29	ND
F-1	5/18/87	1438-1538	296	109	135	285	163	ND
F-2	5/18/87	1620-1720	333	Sat[d]	82	3,076	Sat	ND
F-3	5/18/87	1758-1858	185	30	457	153	109	ND
F-4	5/18/87	2024-2124	201	75	39	228	132	ND
G-1	5/22/87	1019-1114	92	98	14	183	527	ND
G-2	5/22/87	1138-1233	80	18	139	109	416	ND
G-3	5/22/87	1615-1710	430	273	42	1,206	465	ND
G-4	5/22/87	1938-2034	115	73	13	179	248	ND
G-5	5/22/87	1837-1937	154	184	40	358	321	ND
G-6	5/22/87	1847-1937	111	66	14	757	40	ND
	Detection Limit		17	15	13	15	12	11

[a] Single trap below detection limit.

[b] Rear trap mass > front trap mass.

[c] Front trap below detection limit.

[d] Single trap saturated detector.

(6) Some of the highest levels of $CHCl_3$ and the highest concentration of TCE were measured in Orange County in the afternoon and evening. One site, where the chloroform concentration was 333 ppt, was near a hospital complex. The fact that the TCE concentration was 3,100 ppt and that methyl chloroform and perchloroethylene saturated the detector indicates that some industrial sources may have been upwind.

(7) Evaluation of the results of the mobile sampling showed no significant relationship between chloroform concentration and time of day. Furthermore, correlations among concentrations of different halocarbons were generally below 0.5.

(8) A hypothesis which we recommend for further testing is that inland sites in the late afternoon and early evening, and coastal sites whenever onshore breezes are blowing, are likely to have higher chloroform concentrations than other sites at the same times.

1.4.4 Marine Air and Water Sampling

Water samples were collected from a research boat at 14 points along the coast, from Point Dume to Huntington Beach. Water depths were generally around 50 ft. Air samples were collected at 13 locations for one hour on CMS traps from the bow of the boat. Seawater samples were collected simultaneously from six depths by deploying 5-liter Niskin bottles along a weighted line.

1.4.4.1 Marine Air Sampling Results

(1) Results of the air sampling are presented in Table 1.4-1. Values shown in boldface are those for which breakthrough was minimal.

(2) Ambient chloroform concentrations were generally higher than those observed during the mobile sampling on land; three of the values (309, 392 and 1,460 ppt) exceed 93 percent of the land-based concentrations and are similar to the 530 ppt measured by a previous researcher off San Pedro.

(3) The highest chloroform concentration (1,460 ppt) was observed around noon off Redondo Beach. The concentration of 1,1,1-trichloroethane was also high (1,700 ppt) there.

(4) For most of the sampling winds were onshore. Offshore air flow was apparent only at Resort Point, which had the highest perchloroethylene concentration of the sampling (513 ppt).

Table 1.4-2

CONCENTRATIONS OF HALOCARBONS IN MARINE AIR, SOUTH COAST AIR BASIN

(All concentrations in ppt)

Sample	Date	Sampling Interval	Chloroform	1,1,1-Trichloro-ethane	Carbon Tetra-chloride	Trichloro-ethylene	Perchloro-ethylene	Ethylene Dibromide
MA02	5/7/87	1847-1948	>245[a]	>155[a]	>11[a]	ND	ND	ND
MA04	5/7/87	2039-2139	392	ND[c]	43	ND	70	ND
MA06	5/7/87	2228-2329	>98[a]	ND	ND	>190[a]	ND	ND
MA07	5/7/87	2357-0059	>204[b]	ND	21	>1485[a]	216	ND
MA08	5/7/87	0808-0908	>268[b]	>53[a]	23	>95[a]	193	ND
MA09	5/7/87	0940-1053	>48[a]	ND	ND	ND	>35[a]	ND
MA10	5/7/87	1124-1226	1460	1679	69	501	43	ND
MA11	5/7/87	1252-1352	>282[b]	ND	12	>121[a]	513	ND
MA12	5/7/87	1417-1517	>251[b]	ND	11	ND	174	ND
MA13	4/29/87	1723-1827	>373[b]	ND	>94[b]	16	87	ND
MA15	4/29/87	1347-1448	309	ND	214	137	181	ND
MA16	4/29/87	1203-1304	>97[b]	ND	7	158	83	ND
MA17	4/29/87	1020-1120	>293[b]	>164[a]	>50[b]	>533[a]	>195[b]	ND
	Detection Limit		9	8	7	8	7	6

[a] Front trap below detection limit.

[b] Rear trap mass > front trap mass.

[c] Mass below the detection limit.

1.4.4.2 Marine Water Sampling Results

(1) Chloroform concentrations in our seawater samples ranged from below the detection limit of 5 ppt to 14 ppt; these are within the range reported in the literature for southern California waters, and do not indicate heavy contamination.

(2) As seen in Figure 1.4-2, there appear to be two zones of higher concentration: one at the lowest depths from Marina del Rey to Resort Point, and one nearer the surface from Los Angeles Harbor to Huntington Beach.

(3) Concentrations of $CHCl_3$ in the midst of kelp beds were generally lower than in other sampled areas, except for a value of 14 ppt at the bottom off Resort Point.

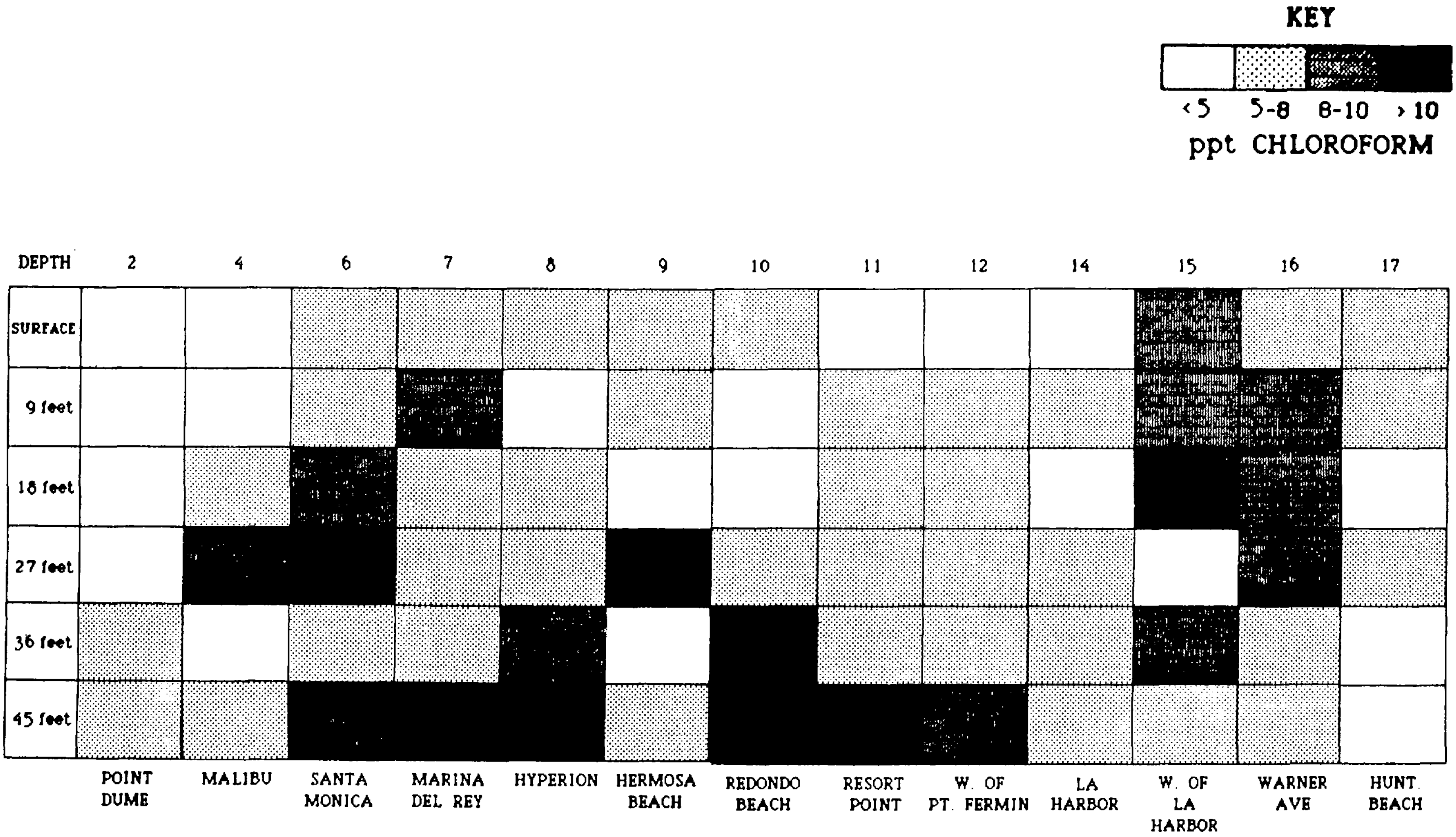
1.4.4.3 Discussion

From our findings, it may be tentatively concluded that marine waters off the South Coast Air Basin are not a chloroform source so much as a temporary chloroform reservoir. The finding of higher $CHCl_3$ concentrations in the deep waters off the industrialized portion of the basin, coupled with the fact that chloroform is about 1.45 times as dense as seawater, indicates an accumulation of anthropogenic inputs rather than production by marine organisms. The dissolved chloroform in the ocean probably diffuses slowly upward (aided by the observed concentration gradient) or rises more rapidly by advection during upwelling, and enters the atmosphere after a delay of unknown duration. Meanwhile, as part of the typical diurnal reversal of air flow in the basin, chloroform is carried to coastal waters by offshore breezes in the late night and early morning, and returns to the land with onshore breezes.

1.5 EMISSIONS TESTING

1.5.1 Wastewater Treatment Plants

The purpose of this portion of the field studies program was to verify that chloroform present in wastewater collection systems is released to the atmosphere at various points in sewage treatment plants, and to obtain a preliminary estimate of emissions. Sampling was conducted in November 1986 at the Los Angeles Hyperion Treatment Plant and the Riverside Water Quality Control Plant. Influent and effluent water samples were collected and



KEY

□	░	▒	█
<5	5-8	8-10	>10

ppt CHLOROFORM

DEPTH	2 POINT DUME	4 MALIBU	6 SANTA MONICA	7 MARINA DEL REY	8 HYPERION	9 HERMOSA BEACH	10 REDONDO BEACH	11 RESORT POINT	12 W. OF PT. FERMIN	14 LA HARBOR	15 W. OF LA HARBOR	16 WARNER AVE	17 HUNT. BEACH
SURFACE	□	□	░	░	░	░	░	□	□	□	▒	░	░
9 feet	□	□	░	▒	□	░	□	░	░	░	▒	▒	░
18 feet	□	░	▒	░	░	□	□	░	░	□	█	▒	□
27 feet	□	█	█	░	░	█	░	░	░	░	□	▒	░
36 feet	░	□	░	░	▒	□	█	░	░	░	▒	░	□
45 feet	░	░	█	█	█	░	█	█	▒	░	░	░	□

Figure 1.4-2. Distribution of Chloroform Concentrations With Depth, by Sampling Point.

analyzed for chloroform. In addition, grab samples above various wastewater treatment processes and conveyance systems were analyzed on-site with a portable GC/ECD.

1.5.1.1 Results for Hyperion Treatment Plant

(1) Influent chloroform concentrations ranged from 6.6 to 28 ppb, while those in the effluent to the five-mile outfall were 6.1 to 17.6 ppb. These results are very similar to those of previous researchers.

(2) No clear relationship between measured flow rates and chloroform concentrations can be discerned. In the East Headworks influent, flow and concentration had a high positive correlation ($r = 0.813$), while in the effluent, these variables were negatively correlated ($r = -0.886$). In the West Headworks, which accounts for most of the mass chloroform input to the HTP, the correlation between flow and concentration was weak ($r = 0.489$).

(3) Air concentrations ranged from 4 ppb (at the fast-flow inlet) to 3,660 ppb (above the primary effluent channel). All of the concentrations measured were at least an order of magnitude greater than those observed in the ambient air in the South Coast Air Basin.

(4) At a given sampling point, air concentrations varied little with sampling time, suggesting fairly constant emission rates at different points in the waste treatment process.

(5) Emissions appear to increase during each stage of primary treatment, reaching a maximum in the covered channel which conveys the highly turbulent primary effluent to the activated sludge aeration basins. Emissions from the aeration basin are lower than from the primary effluent, perhaps because a significant portion of the $CHCl_3$ has already volatilized during prior treatment stages.

(6) Emissions due to volatilization were estimated by subtracting effluent mass flows (water flow rate times concentration) from the influent mass flows that had occurred 11 hours earlier.

(7) For 36 of the 48 hours for which calculations were performed, mass flows into the plant exceeded those to the five-mile outfall; by our assumptions, then, chloroform was emitted during those hours. "Negative" emission results could be due to several factors, including variations in the residence time and uncertainties in flow measurement.

(8) Total transfer of chloroform from water to air during the 48 hours analyzed was about 14 kg, for a daily total of about 15 lb. Annual emissions would be about 2.8 tons. The maximum calculated

hourly emission rate was about 2.6 lb/hr. A clear diurnal pattern, with maxima in the late afternoon or early evening and minima in the early morning, is evident.

(9) Emission factors estimated for the Hyperion Treatment Plant varied from 0 to 1.7 grams $CHCl_3$ per mgd-hour, and averaged 0.668 g/mgd-hr, or 16.0 g/mgd-day. This emission factor is only applicable to plants in which no chlorination takes place.

(10) Another emission factor can be stated as the fraction of influent chloroform which ends up in the effluent. This "out/in" ratio, which varies with time of day, and averages 0.66 for the day, was used in the analysis of emissions from the Riverside facility.

1.5.1.2 Riverside Water Quality Control Plant

(1) Influent chloroform concentrations ranged from 0.9 to 3.2 ppb, while those in the effluent from tertiary treatment, chlorination and dechlorination were 1.9 to 28.0 ppb.

(2) Flow rates and concentrations were poorly correlated, with no r value exceeding 0.55.

(3) Concentrations ranged from 8 ppb (above the final effluent) to 359 ppb (above the primary-treated effluent). Although these concentrations were lower than those measured at Hyperion, they were nevertheless an order of magnitude greater than those encountered in the ambient air of the SCAB.

(4) Ambient chloroform concentrations appear to increase through primary treatment, reaching a maximum in the effluent from the primary clarifiers. They then decrease through secondary treatment. The fact that they again rise at the point of discharge from the plant is evidence that chlorination of the nitrified tertiary treatment effluent results in some chloroform generation.

(5) The mass flow of chloroform leaving the plant was greater than that entering the plant ten hours earlier; thus chloroform was being generated in the plant.

(6) To obtain an approximate estimate of total emissions from the plant, we assumed that (a) the fraction of the chloroform in the influent to the plant released through volatilization is the same as at the Hyperion Treatment Plant; (b) and the chloroform present in the plant effluent consists of the fraction of the influent chloroform which was not emitted, plus the chloroform generated by the haloform reaction during chlorination of tertiary treatment effluent.

(7) Emissions for a 24-hr period are estimated to be about 0.5 lb, while annual emissions from the facility would be about 190 lb.

1.5.2 Swimming Pool Emissions Tests

The objectives of this part of the field research were to confirm that chloroform is emitted from swimming pools and to estimate emission rates which could be generalized to pools in the SCAB. The pool used for the test was a 16,000-gallon residential pool which had not been chlorinated, and had been covered for almost three weeks. The emission flux, or emission per unit area, from the pool was measured with an emission isolation flux chamber. Water samples were collected periodically and analyzed for chlorine, chloroform, and total organic carbon (TOC). Emission fluxes were measured at four levels of chlorine addition and in two water surface conditions: still and agitated.

(1) Measurable emissions of chloroform occurred under all test conditions, including the baseline (no chlorine addition), and ranged from about 2 to 27 $\mu g/m^2$-min under still water conditions and about 180 to 460 $\mu g/m^2$-min when the water surface was agitated.

(2) For all four chlorine conditions, agitating the water under the flux chamber increased emissions by one to two orders of magnitude.

(3) Test results were highly repeatable, especially those corresponding to agitation of the water surface; the precision of these ranged from 3.1 to 13.9 percent.

(4) Chloroform concentrations in the pool during the baseline condition (55 - 74 ppb) were surprisingly high, considering that the pool had not been chlorinated in quite some time. Discussions with the pool owner's water supply agency confirmed that chloroform concentrations in water delivered to residential customers had averaged only 8.0 ppb during the three months before the emissions tests. Since the pool had been covered, it is possible that chloroform had been generated by the haloform reaction but had not had the opportunity to volatilize during that time.

(5) No chloroform appeared to be generated in the pool during the two days of measurement; indeed, the concentration decreased slightly. One key factor was probably the low level of organic material in the pool. TOC concentrations were all below the analytical detection limit of 2.8 ppm, and the pool cover had kept wind-blown soil from entering the pool.

(6) Experimental results were compared with the predictions of an empirical model based upon two-film resistance theory. Calculated flux rates for typical meteorological conditions and the measured pool parameters were higher than those measured for a still surface and lower than those measured for an agitated surface. We believe that our results are consistent with both theory and practical considerations.

1.6 LABORATORY STUDIES

Two types of studies were carried out in a large Teflon film reactor. The first series of experiments involved sunlight irradiation of mixtures of trichlorethylene and oxides of nitrogen (NO_x) in purified air, with focus on the detection of chloroform as a possible reaction product. The other experiments, which were apparently conducted for the first time, involved sunlight irradiation of chloroform-NO_x mixtures with focus on the rate of removal of chloroform under these conditions. Control experiements were also carried out to characterize the stability of TCE and chloroform in Teflon reactors.

(1) TCE and chloroform were quite stable at ppb to ppm concentrations in purified air in the dark, with and without added NO_x, in the Teflon reactor.

(2) TCE and chloroform did not interfere in the measurement of NO and NO_x using a commercial chemiluminescence analyzer equipped with a molybdenum converter.

(3) In sunlight irradiations of TCE-NO_x mixtures in pure air, no chloroform could be detected for any of the TCE/NO_x ratios used; dichloroacetyl chloride was tentatively identified as a reaction product.

(4) An upper limit of 1.4×10^{-3} was calculated for the fractional yield of chloroform from TCE under the conditions studied; this yield, together with ambient concentration data for TCE, indicate that daily atmospheric formation of chloroform would be less than 1 percent of the chloroform emissions estimated in this study.

(5) Sunlight irradiations of chloroform-NO_x mixtures in pure air confirmed that chloroform reacts only slowly, as expected from theoretical considerations.

(6) While phosgene is an expected major product of the OH-chloroform reaction, other chlorinated hydrocarbons are likely to be more important contributors to phosgene in ambient air.

1.7 MASS BALANCE COMPUTATIONS

The objective of the mass balance computation was to relate estimated emissions of chloroform from all major identified sources to historically observed ambient concentrations in the SCAB. Five 24-hour sampling intervals from each of the four ARB monitoring stations were chosen for modeling. Historical meteorological data corresponding to those intervals, along with emission estimates based upon SAIC's surveys and literature reviews, were input to the Industrial Source Complex Short Term model. The following were our findings and conclusions.

1.7.1 General Results

(1) Modeled hourly concentrations were well within the ranges reported in Section 1.2.1 and measured by SAIC as part of this project.

(2) For all but one of the runs, the model's predicted 24-hour average concentration was within a factor of five of the observed value.

(3) The correlation between all pairs of measured and modeled values was only 0.19.

(4) The highest correlation between modeled and measured values was 0.92, which was for the Riverside site. For the Dominguez Hills, Los Angeles, and El Monte sites, the absolute value of the correlation ranged from 0.34 to 0.65.

(5) About half of the model results exhibit a marked diurnal pattern, in which chloroform concentrations decrease rapidly from 9 a.m. until late morning, remain relatively low until midafternoon, increase steeply, then remain relatively high throughout the rest of the afternoon and evening, and begin to decrease at around 5 a.m. Meteorological conditions are probably responsible for the persistently high nighttime modeled concentrations.

1.7.2 Relationships Between Sources and Concentrations

(1) For 9 of 16 modeled hours examined for relationships between source strengths and hourly concentrations, swimming pool emissions were the largest source of chloroform concentrations.

(2) Drinking water area source emissions were the most important source for seven of the model hours examined.

(3) Cooling tower emissions, whether from point or area sources, never accounted for more than two percent of total model concentrations.

(4) The model predicts a significant contribution from some of the wastewater treatment plant point sources under certain meteorological conditions. The most striking example is the City of Riverside's plant's 12.2-percent contribution to total modeled chloroform concentration during an hour when the receptor was directly downwind of the treatment plant, the wind speed was low (0.4 m/s) and the atmosphere was extremely stable.

(5) The Los Angeles Hyperion Plant also made a significant contribution to the modeled chloroform concentration at the Los Angeles receptor in one run.

(6) Analysis of model inputs and outputs showed no clear relationship between hourly basinwide emissions and modeled hourly chloroform concentrations at the receptors of interest.

1.7.3 Assessment of Uncertainty

(1) Given the complex interplay of emissions, geographical location of sources and receptors, and meteorology, it is not easy to determine the effect of uncertainty in any one parameter on model results.

(2) The factor used to apportion drinking water chlorination emissions between residences and wastewater treatment plants is uncertain. By trial-and-error it was determined that an assumption of an 81-19 percent split between drinking water area sources and wastewater treatment plant point sources resulted in the lowest discrepancy between modeled and observed concentrations. However, the model results are fairly insensitive to the value of this factor.

1.7.4 Discussion

(1) The fact that predicted and observed 24-hour average chloroform concentrations were mostly within a factor of 5 indicates that our emission estimates are, on the whole, reasonably accurate; in other words, there is a balance between chloroform emissions and concentrations.

(2) The chief area of uncertainty is our estimate of emissions from swimming pool chlorination. It cannot be too much in error, however, inasmuch as deleting these emissions would seriously affect the aforementioned balance, and there is no other reasonable chloroform source of the same magnitude.

(3) The Riverside Water Quality Control Plant's influence on modeled concentrations suggests that "hot spots" of chloroform concentrations may exist near point sources; this is consistent with the findings of our mobile ambient sampling.

(4) One explanation why modeled concentrations sometimes exceed observed values is that chloroform is removed from the atmosphere by some of the mechanisms described in Section 1.2.3. However, the smog chamber research conducted for this study confirmed that the removal rate would be too low to influence concentrations on the time scale of the model runs.

2.0
RECOMMENDATIONS

2.1 RECOMMENDATIONS FOR FUTURE RESEARCH

On the basis of our findings in this study, we make the following recommendations for future research.

(1) Carbon molecular sieve (CMS) is an excellent medium for detecting concentrations of chloroform down to 10-15 ppt with a one-hour sample; however, to be able to measure higher, more common, concentrations in the SCAB, about 1.5 liters of air should be collected and the sampling flow rate should not exceed 18 ml/min.

(2) CMS does not appear to be useful for detecting low concentrations of ethylene dibromide. Its utility for other halogenated hydrocarbons needs further study.

(3) We recommend a test of our hypothesis that marine air and water constitute an important chloroform "reservoir." Hourly or two-hour samples should be collected for several weeks at a coastal site, and results should be compared with wind flow records to determine whether onshore flows produced significantly higher concentrations.

(4) Some of the "hot spots" identified in the mobile sampling should be investigated further to identify sources. If further short-term sampling in these areas confirms elevated concentrations of the halocarbons of interest, then long-term sampling should be conducted to determine human exposure.

(5) Our swimming pool tests confirmed that chloroform emissions do occur, and the modeling results indicate that they contribute significantly to observed exposures. Since there appears to be a time lag between chlorine dosage and chloroform generation, we recommend a long-term program of water testing at a statistically representative sample of swimming pools in the SCAB. The testing should include pools at various stages of chlorination, and should be repeated throughout the high-chlorination season.

(6) An improved estimate of emissions from wastewater treatment plants should be obtained by sampling at more frequent intervals, using tracer compounds to verify residence time.

2.2 OTHER RECOMMENDATIONS

We also recommend the following types of research, although they should have lower priority.

(1) Dry deposition of chloroform should be measured. Even order-of-magnitude estimates of the dry deposition velocity would allow determination of whether dry deposition is a major or negligible pathway for removal of atmospheric chloroform.

(2) A budget of chlorine emissions and urban concentrations should be developed, since the lack of chlorine data prevents us from testing two potential chloroform formation pathways and two potential removal pathways discussed in this report.

(3) Chloroform concentrations in California fogwater samples should be measured. This information would allow assessment of the relative importance of liquid- and gas-phase chloroform formation and removal processes and dry deposition.

(4) Reliable, sensitive personal samplers for chloroform should be developed, so that personal exposures could be measured directly.

(5) An indoor chloroform measurement program should be conducted, so that exposures from hot showers, use of chlorine bleach, and other domestic sources can be determined.

(6) More information is needed on the use of chlorine bleach in commercial laundries and of other chlorine-based products in the home.

3.0

INTRODUCTION AND BACKGROUND

3.1 PURPOSE AND OBJECTIVES

Chloroform ($CHCl_3$) has for several years been of concern as a potential carcinogen. Numerous studies have detected the compound in drinking water and in ambient urban air. In previous research performed for the California Air Resources Board (ARB), the compound was among the top 11 carcinogens recommended for source testing and ambient sampling (Margler et al., 1979a, 1979b). Although some source tests for chloroform were subsequently conducted (Ziskind et al., 1982), and estimates of emissions in the South Coast Air Basin (SCAB) have been made (Barcelona, 1979), very little is known about the relationships between emissions and ambient concentrations in the Basin. The objectives of this project were therefore:

- To investigate both primary and secondary sources of chloroform in the South Coast Air Basin and
- To identify and quantify the emission sources responsible for observed atmospheric concentrations in the SCAB.

Of particular interest was the identification of possible chloroform precursors and atmospheric reactions which result in chloroform formation.

3.2 OUTLINE OF THE RESEARCH

This assessment of chloroform sources and concentrations was conducted in two phases. Phase I, work for which was performed between August 1985 and May 1986, consisted of a literature review, a dispersion modeling exercise, and development of a field and laboratory research program. Phase II, which was conducted between June 1986 and May 1987, included ambient monitoring, emissions testing, smog chamber studies, additional dispersion modeling, and computer modeling of chloroform reaction kinetics. The major elements of the research were as follows.

3.2.1 Emission Inventory

Our first task in Phase I was to develop, through a literature review and surveys, a preliminary inventory of chloroform emissions from primary and secondary sources in the South Coast Air Basin (SCAB). This inventory was then revised in Phase II to incorporate findings from the field research. As seen in Chapter 4, four types of chloroform emission sources were investigated: direct production, indirect production, consumptive use, and nonconsumptive use.

Previous research had determined that there was no industrial production of chloroform in the SCAB. Our literature review therefore focused on the only other potential direct source, production by marine and terrestrial organisms. Several online data bases were searched for both indirect and direct evidence of biogenic production, particularly by marine biota. Researchers who have conducted recent field studies were also contacted.

From previous research, we expected that most of the chloroform emitted to the ambient air of the SCAB would be produced indirectly, i.e. through the reaction of chlorine with various organic precursors. We therefore concentrated our efforts on developing chloroform emission factors for various chlorination processes. Topics of our literature review included the haloform reaction (the mechanism by which trihalomethanes such as $CHCl_3$ and $CHBr_3$ form through the reaction of hypohalous acids, such as HOCl, with certain organic precursors); chlorination of drinking water, cooling water, and wastewater; swimming pool chlorination; use of chlorine in pulp and paper manufacturing; and use of household chlorine bleach. We also reviewed studies of the transfer of chloroform from water to air.

In order to estimate emissions from the aforementioned indirect sources, it was necessary to obtain information on the nature and rate of chlorine use in the Basin. We therefore conducted written and telephone surveys of municipal water supply districts, wastewater treatment plants, industrial and power plant cooling tower users, and pulp and paper manufacturers. We also contacted industry representatives to obtain information on the extent of chlorine use in swimming pools and household bleach in the

SCAB. Use rates determined from the surveys and industry contacts were combined with the aforementioned emission factors to estimate chloroform emissions from each indirect source category.

The only consumptive use of chloroform in the SCAB is in production of chlorodifluoromethane. As previous research had shown emissions from this source to be negligible, we did not investigate the matter further. Potentially important nonconsumptive uses of chloroform were determined to be pharmaceutical manufacturing, laboratory use, and grain fumigation. To obtain information on pharmaceutical manufacturing, we surveyed a random sample of facilities in the SCAB by telephone. To determine laboratory use, we sent written questionnaires to commercial research and development, commercial testing, and medical laboratories; and surveyed dental laboratories by telephone. Information on grain fumigation was obtained by contacting state and federal pesticide regulatory agencies. Information from these surveys was used to estimate chloroform emissions from nonconsumptive use.

3.2.2 Atmospheric Concentrations and Reactions

SAIC assembled all available information on ambient concentrations of chloroform in the SCAB. Measurement data reported in the literature were critically reviewed and summarized. In addition, SAIC obtained a computerized listing of 24-hour average concentration values at four of the ARB's ambient halocarbon monitoring sites in the SCAB. We then performed various statistical analyses of the data. Phase I findings were supplemented with data obtained through the Phase II ambient sampling program.

SAIC's subcontractor, Daniel Grosjean and Associates, Inc. (DGA), critically reviewed the literature on the potential for gas- and liquid-phase production of chloroform in the atmosphere. The review also covered removal processes, including thermal decomposition; photolysis; reactions with oxygen, ozone, hydroxyl radical, HO_2 and the nitrate radical; liquid-phase reactions, and dry deposition.

Reviews of previously reported ambient concentrations and atmospheric reactions of chloroform are presented in Chapter 5, while the results of our

Phase II ambient monitoring and smog chamber experiments are provided in Chapter 7 and 9, respectively.

3.2.3 Review of Sampling and Analytical Techniques

Methods for collecting and analyzing air and water samples for chloroform were critically reviewed and ranked for suitability in Phase II. Results of this review are presented in Chapter 6.

3.2.4 Ambient Sampling

In order to expand the data base on ambient concentrations of chloroform, SAIC conduct a three-part program of ambient sampling throughout the SCAB. Samples were collected by SAIC on carbon molecular sieve (CMS) traps and analyzed by our subcontractor, Environmental Monitoring Services, Inc. (EMSI) by cryogenic preconcentration and gas chromatography with electron capture detection (GC/ECD). At the ARB's request, samples were also analyzed for 1,1,1-trichloroethane, carbon tetrachloride, trichloroethene (trichloroethylene, or TCE), tetrachlorethene (perchloroethylene, or perc), and ethylene dibromide (EDB). Because this was the first attempt to use CMS for halocarbon sampling on a large scale, considerable research and development was necessary. The first part of the program consisted of collecting 24- and 6-hour samples for one week at Fullerton and Hermosa Beach, respectively. In the second part, termed "mobile sampling," SAIC collected 1-hour samples at 41 locations throughout the SCAB, including several downwind of suspected point sources. Finally, we sampled marine air from a boat at various points from Point Dume to Huntington Beach. The marine sampling included collection and analysis of seawater samples from six depths at each point. Methods and results of the ambient air and water sampling are presented in Chapter 7.

3.2.5 Emissions Tests

In order to confirm that chloroform is emitted from wastewater treatment plants, water samples were collected from the influent and effluent to the Los Angeles Hyperion Treatment Plant and the Riverside Water Quality Control Plant. A mass balance on chloroform was conducted to estimate emission rates. In addition, air samples were collected above various points in the treatment process at both plants, and analyzed on-site with a portable GC/ECD. To confirm and quantify emissions from chlorinated swimming pools, we used an emission isolation flux chamber to measure the chloroform flux rate from a typical residential pool. Source test methods and results are presented in Chapter 8.

3.2.6 Laboratory Experimentation

Possible in-situ formation of chloroform from trichloroethylene and the atmospheric persistence of chloroform in polluted air were studied by Daniel Grosjean and Associates (DGA). Experiments included sunlight irradiation of TCE-NO_x and chloroform-NO_x mixtures and real-time measurement of changes in reactant and product concentrations. The smog chamber studies are described in Chapter 9.

3.2.7 Analysis of Uncertainty

Uncertainty in the emissions estimates was evaluated in two ways. First, where possible, we calculated upper and lower confidence intervals about the reported results of the aforementioned industry surveys. In addition, we used the Industrial Source Complex Short Term model to estimate concentrations at the four ARB monitoring sites for which ambient chloroform data were available. Using reasonable assumptions, we distributed emission estimates spatially and temporally. Actual meteorological data for the 20 modeled days were also used in the modeling. We then compared resulting predictions of 24-hour concentrations with the values reported for the ARB monitoring sites. Next, discrepancies between actual and predicted values were evaluated. Finally, we tested the sensitivity of the model results to changes in certain key parameters. Uncertainty in our emission factors and survey results is discussed throughout Chapter 4, while the modeling exercise is presented in Chapter 10.

3.3 REFERENCES

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4.0
EMISSION SOURCES

4.1 DIRECT PRODUCTION

4.1.1 Industrial Sources

No chloroform is manufactured deliberately in the South Coast Air Basin.

4.1.2 Biogenic Production

4.1.2.1 Marine Sources

It has been suggested by several authors that the oceans may be a significant source of chloroform. Pollutants in surface waters are partitioned between aqueous and atmospheric phases. Thermodynamic equilibrium between the hydrosphere and the atmosphere is improbable; at any point there will be a state of disequilibrium causing a net transfer from one phase to the other (Pearson and McConnell, 1975). Our literature review therefore took two paths of inquiry. First, we sought indirect evidence of oceanic chloroform sources. In addition, we attempted to find plausible mechanisms by which any chloroform of marine origin would actually be produced.

Indirect Evidence for a Marine Source

An attempt to quantify the disequilibrium between seawater and oceanic atmospheric chloroform was recently made by Khalil et al. (1983), who also constructed a global mass balance model for that compound. Their analysis was based upon air measurement data from seven fixed sites at latitudes from 72^{o}N to 90^{o}S and seawater concentration data collected from sites at latitudes 54^{o}N to 15^{o}N. Average atmospheric and water concentrations were calculated for four latitudinal regions. An oceanic flux equation of the following form was then defined:

$$S_o = (K/H)\zeta\Delta C$$

where K is the ocean-air exchange velocity, H is the Henry's Law constant for $CHCl_3$ in seawater at the average temperature for the latitudinal region in question, and ζ is the surface area of the ocean in that region. The driving force for the flux, ΔC, is the difference between the atmospheric chloroform concentration and the atmospheric concentration which would result if the chloroform in seawater were in equilibrium between the aqueous and gaseous phases.

Using their measurement data and the flux model, Khalil et al. estimate worldwide oceanic emissions of 3.6×10^5 metric tons/yr (MT/yr) (4.0×10^5 tons/yr). Their emission estimate for the northern region (30^oN to 90^oN) is 20,000 MT (22,000 tons) per year. Khalil et al. conclude that the tropical oceans are a major source of $CHCl_3$ to the atmosphere but that "at higher latitudes, colder water and smaller supersaturations of $CHCl_3$ coupled with the uncertainties in determining the flux make it impossible to prove that regions of the ocean there also release $CHCl_3$ to the atmosphere."

Very little information on chloroform concentrations in seawater off California has been published. Su and Goldberg (1976) measured an average of 11.8 $\pm$ 5.8 ng/L in water from off the Scripps Institute of Oceanography pier in La Jolla, California from 28 January to 8 July 1975; if data from the rainy season are excluded, the average becomes 9.3 $\pm$ 3.6 ng/L. Su and Goldberg also report measurement of 14.8 $\pm$ 5.3 ng/L in the mixed layer of open ocean in the East Pacific, while Singh et al. (1977b) reported one measurement of 2854 ppt in "onshore water" at Point Reyes, California.

Singh et al. (1977a, 1977b) compared ambient chloroform concentrations at a coastal site in Northern California (Point Reyes) with a site about 25 km inland (Stanford Hills) and one about 280 km inland (Yosemite) and found a negative gradient. In order to minimize the effect of urban emissions on the analysis, Singh et al. considered only the lower 50 percent of the samples analyzed from the three sites. After analyzing their data, Singh et al. (1977a) stated that "one might conclude a significant marine source for $CHCl_3$," and that the source may be due to coastal water contamination. The validity of the gradient reported by Singh et al. may be questioned, however. The Point Reyes and Stanford Hills measurements were made in November and December 1975, respectively, while the Yosemite measurements were made in May 1976. It therefore cannot be stated with certainty that the gradient existed during any short-term interval.

Release of Volatile Halogenated Compounds From Marine Biota

According to Gschwend et al. (1985), whose work is discussed below, no researchers to date have ever observed the production of volatile halogenated organic compounds, other than methyl iodide, from diatom, dinoflagellate or blue-green algae cultures. Virtually all the observed biogenic halogenated organic production has been associated with macroalgae, such as seaweed.

Halogenated organic compounds have been found in four genera of the Bonnemaisoniaceae, a family of red seaweed (Moore, 1979). To date, however, chloroform has been detected in only one genus, Asparagopsis. Su and Goldberg (1976) reported finding chloroform in Asparagopsis armata; however, information on the amounts of chloroform present and the potential for atmospheric release were not discussed.

Analyses of A. armata from the Spanish Mediterranean coast were conducted by McConnell and Fenical (1977). To avoid loss of volatile components, fresh plants were placed in 95-percent ethanol immediately after collection. After extraction with pentane, halomethanes were analyzed by capillary column gas chromatography with electron capture detection. Halomethanes, including chloroform, were also detected in an Asparagopsis species from the Gulf of California, A. taxiformis (Fenical, 1982). Unfortunately, decomposition of the samples in storage prevented accurate determination of the relative amounts of the halomethanes detected, although total halomethane derivatives ($CHBr_3$, $CHBr_2I$, $CHBr_2Cl$, $CHCl_3$ and CCl_4) constituted about three to five percent of the dry mass (Fenical, 1982).

The haloforms in Asparagopsis are apparently formed by the classic haloform reaction. Enzymatic peroxidative halogenation and decarboxylation to 1,1,1-trihaloacetones has been postulated as the initial step (Moore, 1979). In the case of chloroform, 1,1,1-trihaloacetone could decompose (not necessarily enzymatically) to chloroform and acetic acid. The chloroform produced by this species of red algae is dynamically released to seawater; that is, it is synthesized and excreted by the living organism, rather than stored (Fenical, 1986).

Theiler et al. (1978) have suggested two means by which chloromethane compounds could form through biochemical mechanisms in seawater. An enzyme extracted from a marine red alga, Bonnemaisonia hamifera, can incorporate bromine into a number of organic substrates in the pH range 5 to 8. Theiler et al. demonstrated that this bromoperoxidase could add three bromine atoms to 3-oxooctanoic acid. Further studies showed that hydrolysis of the resulting 1,1,1-tribromoheptanone in basic solution gives rise to bromoform. Theiler et al. suggest that the reaction of bromomethanes in seawater could also give rise to chloromethanes. However, studies by Zafiriou (1975) show that the most likely species to be formed would be CH_3Cl. It is highly unlikely, given the stability of bromoform, that $CHBr_3$ would be converted to $CHCl_3$.

Chloromethanes could also be formed if there were a peroxidase capable of oxidizing chloride by a pathway similar to that of the aforementioned bromoperoxidase. Such an enzyme has been isolated from the red alga Cystoclonium purpurem (Pedersen, 1976). However, the only chlorinated species known to be produced through the activity of this peroxidase is a bromochlorophenol.

More recently, Gshwend et al. (1985) determined that intertidal macroalgae collected from Cape Cod released relatively large quantities of bromoform, dibromochloromethane and dibromomethane to seawater. They also found low releases of iodoalkanes and dihalomethanes. Monochloro compounds were not observed. According to Gschwend et al., "this apparent discrimination against chlorine in the production of [volatile halogenated organic compounds] must reflect enzyme specificities, since chloride is by far the most abundant halide in seawater." Dichloromethane and chloroform were observed in some samples, but suspected contamination of blanks by laboratory air precluded their verification (MacFarlane, 1985).

As will be discussed in Section 7.3, marine air and water sampling conducted as part of this project found relatively high concentrations of chloroform offshore from the South Coast Air Basin. Chloroform in the seawater tended to be concentrated at lower depths off areas of industrial discharges. We believe that these findings are consistent not with biological production of chloroform, but rather with the role of the ocean air and water as temporary chloroform reservoirs. Chloroform discharged from wastewater treatment plants and storm drains accumulates in the lower depths and slowly diffuses upward. Meanwhile, as part of the typical diurnal reversal of air flow in the basin, chloroform is carried to coastal waters by offshore breezes and returns to the land with onshore breezes.

4.1.2.2 Emissions From Terrestrial Vegetation

Isidorov et al. (1985) placed specimens of various plant species in a glass tube through which ambient, unfiltered air was passed. Chloroform was detected in the exhaust air from tubes containing northern white cedar and deciduous moss. Since the inlet air was not measured for chloroform, it cannot be said with certainty that chloroform was emitted from these plant species.

Our literature review found no other published data on chloroform emissions from terrestrial vegetation.

4.2 INDIRECT PRODUCTION

Most of the chloroform emitted to the ambient air of the South Coast Air Basin is produced indirectly, i.e. through the action of chlorine with various organic precursors and, perhaps, through combustion processes. Processes through which chloroform has been shown to be produced unintentionally and indirectly include chlorination of drinking water, wastewater, recirculating cooling tower water, and swimming pools; and bleaching of paper and pulp. Some chloroform may also be produced through use of chlorine-based bleach in household cleaning and laundry products. Other processes which could result in chloroform emissions, but are not likely to, include chlorination of seawater in coastal power plant cooling systems, chlorinated rubber manufacturing, combustion of leaded gasoline, and burning of tobacco.

In Section 4.2.1, emission factors for various chloroform-emitting processes are reviewed and/or developed. At the end of Section 4.2.1, mechanisms by which the indirectly generated chloroform is transferred to the atmosphere are reviewed. Indirect chloroform emissions in the SCAB are then estimated in Sections 4.2.2 through 4.2.9.

4.2.1 Emission Factors for Chlorination Processes

Before discussing the development of emission factors for chlorination processes, it is necessary to discuss the haloform reaction and to define "chlorine equivalent." Most chlorination processes use gaseous chlorine, aqueous sodium hypochlorite solutions, or powdered calcium hypochlorite.

At pH values typical of drinking water or wastewater, molecular chlorine (Cl_2) does not exist in aqueous solution; rather it reacts with water to form hypochlorous acid:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (4\text{-}1)$$

Likewise, salts of hypochlorous acid ionize as follows:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- \qquad (4\text{-}2)$$

Hypochlorous acid dissociates weakly:

$$HOCl \rightarrow H^+ + OCl^- \qquad (4\text{-}3)$$

The extent of dissociation depends upon the temperature and pH. For example, at pH 7.5 and 25°C, HOCl and OCl^- are essentially equimolar in concentration (Jolley and Carpenter, 1983). At a constant temperature, the relative concentrations of HOCl and OCl^- decrease and increase, respectively, as a solution becomes more basic. Other forms of chlorine, such as Cl_2O and Cl_2OH^+, exist in aqueous solution and may take part in chlorination reactions (Snider and Alley, 1979).

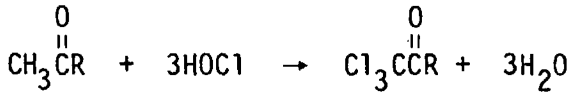
Chlorine in the form of HOCl and/or OCl^- is defined as "free chlorine," "free residual chlorine," or "free available chlorine" (Jolley and Carpenter, 1983). The amount of free chlorine in a solution may be significantly diminished by competing side reactions with inorganic reducing agents (H_2S, SO_3^{2-}, NO_2^-, Fe^{2+}, Mn^{2+}), ammonia and amines, various unsaturated organic compounds, and bacteria. The reducing agents convert the chlorine to chloride ion, which has no bactericidal ability. Reactions with ammonia and amines produce chloramines, in the following sequence (Metcalf and Eddy, 1972):

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \tag{4-4}$$

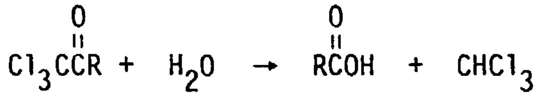
$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{4-5}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{4-6}$$

To assure that sufficient free available chlorine is present in solution, additional chlorine must be added. When this is done, most of the chloramine compounds are converted to nitrogen gas (which leaves the solution) and hydrochloric acid (which is neutralized by the alkalinity in the water). After a certain amount of chlorine is added, continued addition will result in a directly proportional increase in the free available chlorine; this is called the "breakpoint." The process of formation of trihalomethanes such as chloroform ($CHCl_3$) and bromoform ($CHBr_3$) from the hypohalous acids, such as HOCl, from certain organic precursors is known as the "haloform reaction." Organic precursors have the general formula CH_3CHOHR or CH_3COR, where R represents an organic functional group. The general sequence of reactions is:



$$CH_3\overset{\overset{O}{\|}}{C}R + 3HOCl \rightarrow Cl_3C\overset{\overset{O}{\|}}{C}R + 3H_2O \tag{4-7}$$



$$Cl_3C\overset{\overset{O}{\|}}{C}R + H_2O \rightarrow R\overset{\overset{O}{\|}}{C}OH + CHCl_3 \tag{4-8}$$

These reactions are discussed in more detail in Section 5.2.2.1. It is believed that the main precursors in raw waters and wastewaters are highly complex humic acids, which are defined as the fraction of soil organic material which is soluble in alkaline solutions and insoluble in acids and ethanol (NAS, 1979). The structures of these compounds are poorly characterized, but they are known to have functional groups which would permit their participation in the haloform reaction.

It would be convenient to be able to express quantities of chlorinating compounds on a common basis. Furthermore, the common basis should be related to the potential for chloroform formation. Since HOCl is considered the reactive chlorinated species in the haloform reaction, the chlorine equivalent of a compound is defined here as the mass of chlorine which would form the same amount of HOCl in aqueous solution as would one mass unit of the compound.

For chlorine gas (Cl_2), the chlorine equivalent is, by definition, 1. For sodium hypochlorite, we note that:

$$NaOCl \rightarrow Na^+ + OCl^- \qquad (4\text{-}9)$$

$$OCl^- + H^+ \rightleftarrows HOCl \qquad (4\text{-}10)$$

Thus one mole of NaOCl forms the same number of moles of HOCl as one mole of Cl_2, and one pound of NaOCl would form (1 lb)(453.6 g/lb)/(74.44217 g/mole) = 6.093 moles of HOCl. Now, since 1 mole of Cl_2 also forms 1 mole of HOCl, the 1 lb of NaOCl is equivalent to 6.093 moles of chlorine. This in turn is equivalent to (6.093 moles)(70.906 g/mole)/(453.6 g/lb) = 0.9525 lb. Therefore the chlorine equivalent of 1 lb of sodium hypochlorite is 0.9525 lb chlorine. A similar calculation shows that the chlorine equivalent of 1 lb of calcium hypochlorite is 0.9918 lb.

The theoretical yield of chloroform in the haloform reaction would be one-third mole $CHCl_3$ for every mole of chlorine entering into the reaction. However, most of the chlorine demand is accounted for by incorporation of chlorine into non-$CHCl_3$ reaction products (De Laat et al., 1982; Norwood et al., 1980). The distribution of chlorine among reaction products depends upon several factors, including pH, temperature and initial concentration of chlorine and THM precursors (Peters et al., 1980; Urano et al., 1983). In this report, we define the $CHCl_3/Cl_2$ ratio as the ratio of moles chloroform produced per mole of chlorine consumed.

For each of the chlorination processes in which chloroform is produced, we have developed an emission factor based upon the $CHCl_3/Cl_2$ molar ratio. In general, the emission factor EF (lb chloroform/lb chlorine equivalent) is calculated as follows:

$$\begin{aligned} EF &= R\left(\frac{\text{Molecular weight } CHCl_3}{\text{Molecular weight } Cl_2}\right) \\ &= 1.6836\ R \end{aligned} \tag{4-11}$$

where R is the molar ratio (moles $CHCl_3$/moles Cl_2). The emission factor is multiplied by the chlorine equivalent (lb) to obtain lb chloroform emissions. For example, suppose the molar ratio for a given chlorination process is R = 0.015, and 1000 lb of NaOCl are added. From the calculation shown above, the chlorine equivalent of the 1000 lb of NaOCl is (1000 lb)(0.9525) = 952.5 lb. Chloroform emissions would therefore be (952.5 lb)(1.6836)(0.015) = 24 lb.

4.2.1.1 Drinking Water

Laboratory Studies of Precursor Compounds

Table 4.2-1 presents ranges of $CHCl_3/Cl_2$ ratios calculated from published data on chlorination of drinking water.

Norwood et al. (1980) reacted HOCl with 10 compounds representing substituted aromatic degradation products of humic acids. The $CHCl_3/Cl_2$ ratios in Table 4.2-1 were calculated by dividing Norwood et al.'s reported values of moles $CHCl_3$/moles precursor by reported values of moles Cl_2/moles precursor. The highest $CHCl_3/Cl_2$ ratios occurred for orcinol (0.136), resorcinol (0.133) and 3,5-dihydroxybenzoic acid (0.0637); all other ratios were below 0.015.

Table 4.2-1

DRINKING-WATER CHLOROFORM/CHLORINE RATIOS CALCULATED FROM LITERATURE DATA

Medium	Range of Chloroform/Chlorine Ratio	References
Degradation products of humic acids	<0.015 - 0.136	Norwood et al., 1980
Humic acid solution	0.014	De Laat et al., 1982
French surface waters	0.012 - 0.018	De Laat et al., 1982
Humic and fulvic acids from Thames River	0.0067 - 0.010[a]	Peters et al., 1980
Water treatment plant		
- Effluent	0.011 - 0.013[b]	Otson et al., 1981
- Distribution system	0.013 - 0.017	Otson et al., 1981

[a] Varies with pH of experimental solution.

[b] Calculated from regression equation reported by Otson et al. (1981).

De Laat et al. (1982) reacted chlorine with various organic precursors in a sealed vessel at neutral pH. The highest chlorine demand was exerted by aromatic compounds having -OH and -NR_2 substituents (phenol and aniline derivatives); however, most of the reaction products were nonvolatile organochlorine compounds, rather than halomethanes. Aliphatic acids, aldehydes and alcohols were relatively unreactive. Amino acids and carboxylic acids yielded virtually no chloroform. The compounds giving the highest yields of $CHCl_3$ were metapolyhydroxybenzenes and metachlorophenols. The $CHCl_3/Cl_2$ molar ratios reported in Table 4.2-1 were calculated from De Laat et al.'s reported results of chlorination of waters from three French rivers and a humic acid mixture. The molar ratio for the latter was 0.014, while the ratios for the rivers were 0.012, 0.016 and 0.018.

Peters et al. (1980) reacted humic and fulvic acids isolated from the Thames River with NaOCl in a sealed vessel under several combinations of temperature and pH. They distinguish between "dissolved chloroform," which is chloroform produced by the haloform reaction in solution (and, presumably, during disinfection processes), and "residual chloroform," which is a product of the thermal decomposition of organochlorine intermediates when a sample is injected into a gas chromatograph. Whether these intermediates would eventually be transformed to chloroform at ambient temperatures is unknown. The residual chloroform was measured by first stripping the water sample of all dissolved chloroform and then injecting the remaining solution into the GC. The relative proportions of dissolved and residual chloroform varies with pH. For experiments with fulvic acid, the proportions were as follows:

	Percent of Total	
pH	Dissolved	Residual
6	51	49
7	62	38
8	71	29
9	80	20

Thus, experiments by others in which the same analytical method is used may overstate the amount of chloroform produced. On the other hand, Peters et al. also note that some $CHCl_3$ is lost through adhesion to the sample vessel walls and diffusion from the system; if these losses are appreciable, then the results of some other experiments may understate the chloroform production.

Peters et al. derived an equation relating chloroform produced to chlorine consumed at any point, t, in the reaction:

$$[CHCl_3]_t = 0.022\ ([Cl_2]_o - [Cl_2]_t), \tag{4-12}$$

where all concentrations are in mg/L. If we multiply $[CHCl_3]_t$ by the dissolved chloroform fractions shown above, then the $CHCl_3/Cl_2$ molar ratios would range from 0.0067 at pH 6 to 0.010 at pH 9; these values are shown in Table 4.2-1.

For estimating chloroform emissions from drinking water chlorination, we chose a molar ratio of 0.015. This value is at the midpoint of the distribution system data reported by Otson et al. (1981). The corresponding chloroform emission fraction is (0.015)(1.6386) = 0.025 lb $CHCl_3$ per lb chlorine equivalent.

Water Treatment Plant Studies

Several researchers have attempted to relate various operating characteristics of water treatment plants to concentrations of chloroform in the plant effluent and/or at various distribution points in the water system. A major motivating factor for this research has been to provide exposure data for epidemiological studies; since chloroform and other THMs were not routinely monitored in the past, perhaps the large body of operating data available at many plants can be used to estimate what the concentrations of these pollutants would have been (Reiches and Wilkins, 1983).

Otson et al. (1981) examined operating data and THM levels at various points in the treatment processes at three plants which obtain raw water from the Ottawa River. Water samples were also taken from a cold water tap 1.8 km from one of the plants. Overall, chlorine dosages and demand were the variables which showed the highest correlation with chloroform levels in water. However, Otson et al. caution the reader that "the interdependence of a large number of water quality parameters suggests that the use of correlation coefficients for identification of parameters which control THM production is limited." Nevertheless, multiple regression analyses resulted in models which were able to explain up to about 89 percent of the variation in the observed chloroform concentrations. For chloroform concentrations at the distribution point, the following equations were derived:

Plant A:

$$\begin{aligned}[\mathrm{CHCl_3}\ (\mu\mathrm{g/L})] = {} & 33.6\ [\text{prechlorination dosage (mg/L)}] \\ & + 33.5\ [\text{postchlorination dosage (mg/L)}] \\ & -\ 1.59\ [\text{raw water color (Pt-Co)}] \\ & -\ 0.098\ [\text{raw water temperature } (^{o}\mathrm{C})] \\ & -\ 10.6\ [\text{silicate (mg/L)}]\end{aligned} \tag{4-13}$$

Plant B:

$$\begin{aligned}[\mathrm{CHCl_3}] = {} & 97.9\ [\text{postchlorination dosage}] \\ & -\ 4.39\ [\text{alum (mg/L)}] \\ & + 23.8\ [\text{silicate}]\end{aligned} \tag{4-14}$$

Plant C:

$$\begin{aligned}[\mathrm{CHCl_3}] = {} & 33.5\ [\text{prechlorination dosage}] \\ & +\ 2.95\ [\text{raw water turbidity (NTU)}] \\ & +\ 5.92\ [\text{raw water alkalinity(mg/L)}] \\ & +\ 0.005\ [\text{raw water} + 4.65\ [\text{alum}] + 31.2\ [\text{silicate}]\end{aligned} \tag{4-15}$$

Using the average parameter values reported by Otson et al., we calculated the $\mathrm{CHCl_3}$ molar ratios for the three plants, for both the plant effluent and the distribution point. These were:

	Molar Ratio		
	A	B	C
Plant Effluent	0.011	0.013	0.011
Distribution Point	0.017	0.014	0.013

Reiches and Wilkins (1983) analyzed 21 months' operating data (170 days) for a 90-mgd water treatment plant in Columbus, Ohio. After defining 30 candidate predictor variables, they performed a stepwise linear regression, including a variable only if it added at least 0.001 to the value of r^2. The best predictors for chloroform were found to be raw water temperature, raw water color and the logarithm of the chlorine dose; these account for 94.0 percent of r^2. When all the predictor variables meeting the aforementioned criterion are included, r^2 for the regression is 0.618. The best regression equation was:

$$\begin{aligned}\log [\mathrm{CHCl_3}\ (\mu g/L)] = {} & 0.0083\ [\text{raw water temperature } (^{o}F)] \\ & + 0.0054\ [\text{raw water color (Pt-Co)}] \\ & + 0.4388\ \log [\text{chlorine dose (mg/L)}] \\ & - 0.0043\ [\text{mixed water phenolphthalein alkalinity (mg/L)}] \\ & + 0.0696\ [\text{finished water pH}] \\ & - 0.0007\ [\text{lime feed (mg/L)}] \\ & - 0.0007\ [\text{finished water total alkalinity (mg/L)}]\end{aligned} \tag{4-16}$$

It should be noted that non-volatile total organic carbon (TOC) was not included in the analysis because no monitoring data were available. Also, there may be some collinearity among the predictor variables. Despite these potential shortcomings, the chloroform concentration values predicted by this equation are within 18 μg/L of observed values. Residuals are normally distributed.

Variability in Chloroform Concentrations in Drinking Water

Smith et al. (1980) took samples of Houston tap water every 4 hours for 24 hours to study the variability of chloroform and other THMs at a relatively distant point in the distribution system. Various statistical analyses, including spectral analysis and harmonic regression, were performed on the data. Chloroform concentrations varied from 33 to 80 ppb. The weekend mean concentration was 56 ppb, while the weekday mean was 49 ppb. No consistent pattern was determined by the analysis. However, it is important to note the existence of considerable temporal variability.

4.2.1.2 Freshwater Cooling

Chlorine compounds are added to most freshwater cooling systems to suppress the growth of algae, slime and other biota which would otherwise proliferate in the warm, nutrient-rich environment. Conditions conducive to the haloform reaction are frequently present.

Once-Through Cooling

Although freshwater is not used to any significant extent for once-through cooling in the South Coast Air Basin, most of the literature on chlorination of cooling water pertains to these types of systems. We therefore reviewed the literature for information which could be useful in assessment of circulating cooling water systems, such as the chlorine-to-chloroform transformation rate at high temperatures.

Hollod and Wilde (1982) chlorinated samples of Savannah River water used for once-through cooling at the Savannah River nuclear power plant near Aiken, South Carolina, and measured formation of chloroform, other THMs and total THM after 5, 30, 90 and 300 minutes. Experiments were carried out at 25, 45, and 65°C, and the initial free chlorine concentration was 5.0 mg/L in all cases. Figure 4.2-1 shows the variation of total THM with time at the three experimental temperatures. At 45 and 65°C, THM compounds are lost through volatilization after reaching a peak. In addition, another experiment conducted by Hollod and Wilde showed that after 300 minutes at all three temperatures, about 28 percent of the initial free chlorine was also lost by volatilization. Therefore, in calculating the $CHCl_3/Cl_2$ molar ratio, the loss of chlorine must be taken into account.

Using Hollod and Wilde's reported data, we calculated the total amount of $CHCl_3$ generated at 25°C (after 300 minutes) and the peak amount generated at the other two temperatures. For 25°C, we assumed that 28 percent of the free chlorine volatilized before it could participate in the haloform reaction. For the other two temperatures, the $CHCl_3/Cl_2$ molar ratio was calculated with and without the 28-percent volatilization assumption. The resulting molar ratios were as follows:

Temperature (°C)	Molar Ratio Low	Molar Ratio High
25	0.019	0.019
45	0.0092	0.021
65	0.0023	0.013

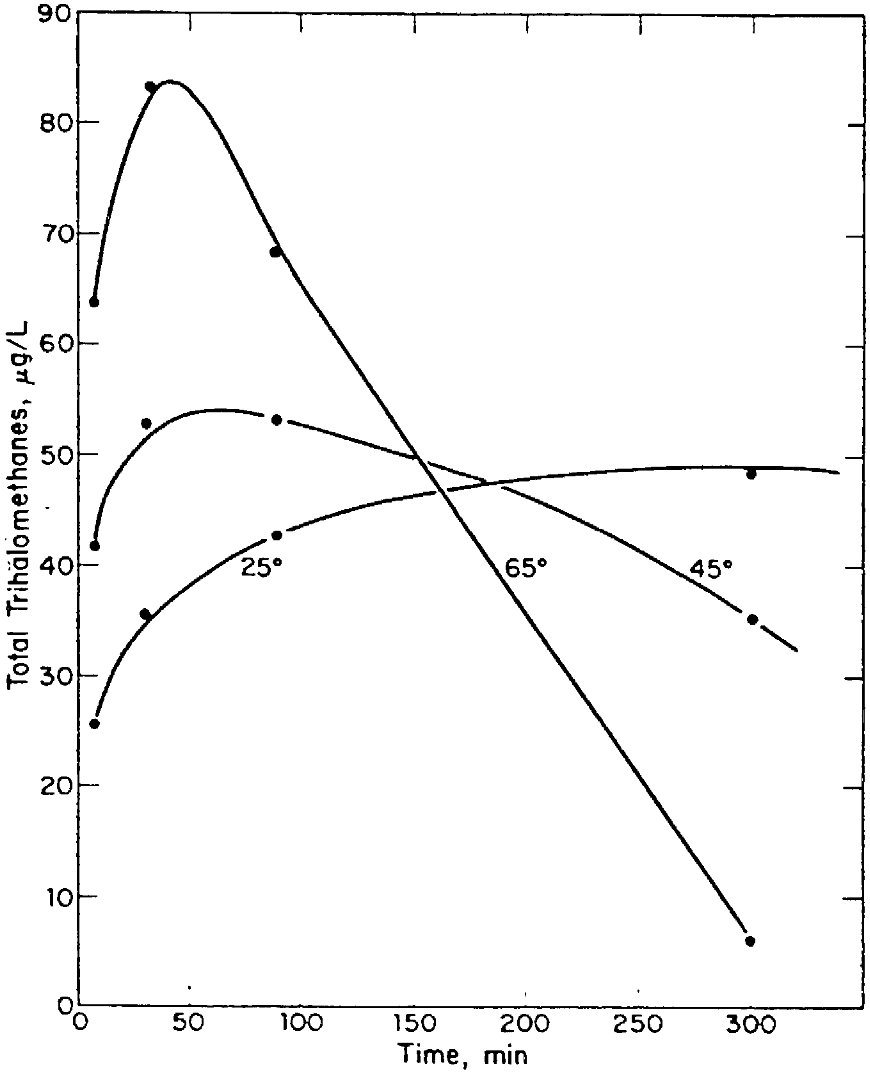


Figure 4.2-1. Formation and Loss of Total Trihalomethanes From Chlorinated River Water at Three Temperatures (Hollod and Wilde, 1982).

Cooling Towers

Research on chloroform production in, and emissions from, cooling towers is quite limited. Jolley et al. (1977a, 1977b) collected grab samples from towers serving the Oak Ridge Gaseous Diffusion Plant (ORGDP) and the High Flux Isotope Reactor (HFIR) in Oak Ridge, Tennessee. Municipal drinking water, initially chlorinated to 2 ppm chlorine residual, was the makeup source for the HFIR tower. The tower basin was chlorinated weekly to achieve a 2 ppm residual. The makeup water source for the ORGDP tower was softened Clinch River water chlorinated to a 1-ppm residual. Chlorine was added continuously to the tower basin to maintain a 0.5-ppm residual. Table 4.2-2 summarizes the results of analyses for THM's in the makeup water and the cold water basin. From these data (but not from direct emissions measurement) Jolley et al. (1977b) estimated emissions of 130 and 810 kg/year of chloroform from the ORGDP and HFIR towers, respectively.

In previous research for the ARB, SAIC investigated the formation and emissions of chloroform and other halogenated hydrocarbons from three cooling towers which use primary-treated municipal wastewater and one which uses recycled industrial wastewater (Rogozen et al., 1981). All four towers are in the South Coast Air Basin. Table 4.2-3 summarizes our measurements of chloroform in the makeup and circulating water of these towers. In general, chloroform concentrations in the hot and cold water basins were lower than in the makeup. No chloroform was detected in isokinetic samples of the exhaust from two of the municipal cooling towers or the industrial tower. (Emissions from the other municipal tower were not sampled.) The analytical technique used, gas chromatography with flame ionization detection, may have been too insensitive to the chloroform. It is possible that chloroform was generated in these towers but, given the enormous surface area of the circulating water and the high water temperature, all volatilized before we sampled. In any event, much of the chloroform present in the makeup water is evidently lost to the atmosphere. SAIC estimated emissions of about 110 lb/yr (49 kg/yr) from three of the towers.

Table 4.2-2

TRIHALOMETHANES IN OAK RIDGE NATIONAL LABORATORY COOLING TOWER WATER

(All concentrations in ppb)

	Sampling Location			
	ORGDP		HFIR	
Compound	Makeup	Basin	Makeup	Basin
Chloroform	86	12 - 31	120 - 137	1 - 38
Bromodichloromethane	7	0.5 - 0.7	15	ND
Dibromochloromethane	1	0.9	1	ND
Bromoform	0.2	0.7	0.4	ND

Source: Results reported by Jolley et al. (1977a).

Table 4.2-3

SUMMARY OF SAIC MEASUREMENTS OF CHLOROFORM IN COOLING TOWER WATER, 1979-1980

(All concentrations in ppb)

		Concentrations in		
Facility	Date	Makeup	Hot Water Basin	Cold Water Basin
City of Burbank/ Olive 1 Power Plant	11-27-79	22	14-20a	17-15
City of Glendale/ Grayson Power Plant	4-22-80	6	<1	<1
Industrial Plant[b]	8-5-80	16	2.3	2.3

Source: Rogozen et al., 1981.

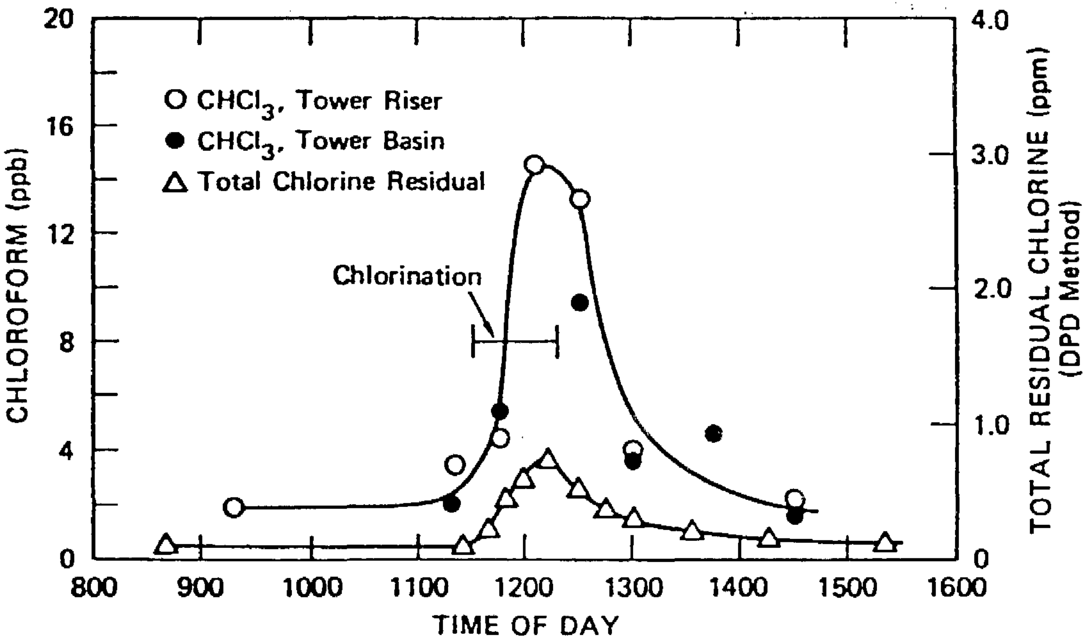
[a] Sample taken immediately after tower was chlorinated.

[b] Identity confidential.

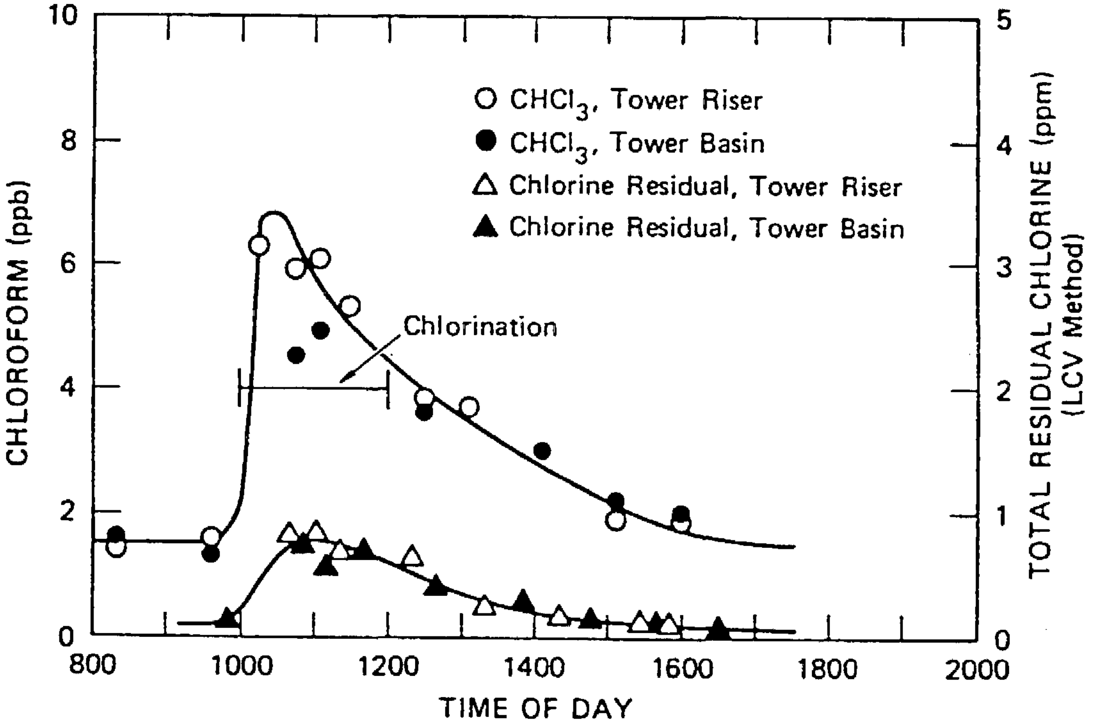
To the best of our knowledge, the only other study of chloroform emissions from cooling towers was conducted for the Electric Power Research Institute by Smith et al. (1983). Water and exhaust air samples were collected from one natural-draft cooling tower and two mechanical-draft towers. From water measurement data, these researchers concluded that 20 to 30 percent of the volatiles present in the system (whether contributed by the makeup or generated through the haloform reaction) are stripped on each pass through the tower. Figure 4.2-2 shows the chloroform and total chlorine residual measured during two of the tests. A rough estimate of emissions can be obtained by assuming that all chloroform generated during chlorination is released to the atmosphere. The circulating water flow rates for 3-cell and 5-cell tower are reported by Smith et al. to be 2.4 x 10^5 and 1.9 x 10^5 L/min, respectively. From Figure 4.2-2, we estimate the average concentration of chloroform above the prechlorination level to have been 5.75 and 4.7 μg/L, respectively. Emissions, assuming one chlorination per day and year-round operation, may be calculated as (concentration) x (flow rate) x (time of chlorination). Our rough estimates of emissions from the two towers are 200 and 280 lb/year (91 and 130 kg/yr).

Smith et al. used three different sampling trains to collect samples from the three towers' exhaust. Apparently, sampling was not isokinetic. Provisions were made to collect both drift droplets and organic vapors. Smith et al. found measurable concentrations of chloroform in the liquid phase (i.e. the drift droplets and steam condensate). More chloroform was collected on Tenax and activated charcoal adsorbent, but the large amount of condensation on sampling lines, contamination of the adsorbents with water, and apparent breakthrough in backup sampling traps led Smith et al. to the conclusion that the amount of chloroform detected was decidedly a lower bound on the actual value. From the test results reported by Smith et al., we estimate that the maximum emissions from any of the towers measured would be about 95 lb/yr (43 kg/yr).

To develop an emission factor for industrial cooling towers, we used a combination of the aforementioned measurement data and the results of the industrial cooling tower survey conducted for this project (see Section 4.2.4). According to our analysis of the laboratory test data mentioned above



Mechanical Draft, 3-Cell Tower



Mechanical Draft, 5-Cell Tower

Figure 4.2-2. Chloroform and Total Residual Chlorine Concentrations in Two Cooling Towers (Smith et al., 1983).

(Holloa and Wilde, 1982), reasonable values for the $CHCl_3/Cl_2$ molar ratio for cooling water would lie between about 0.002 and 0.02. The corresponding emission factor would be between about 0.0034 and 0.034 lb $CHCl_3$ per lb of chlorine equivalent. In order to see where along this order-of-magnitude range the actual emission factor might lie, the low and high extreme values were multiplied by the chlorine equivalent dosages reported by SAIC's cooling tower survey respondents. Since the size of the towers described by the respondents varied enormously, emissions were normalized to circulating water flow rate in 1000 gpm. In parallel with this calculation, the emissions from the towers measured by Rogozen et al. (1981) and Smith et al. (1983) were normalized to the corresponding circulating water flow rates; the normalized emission rates for these towers ranged from about 1 to 6 lb chloroform/1000 gpm. For the towers in the present survey, an emission factor of 0.0034 lb $CHCl_3$/lb Cl_2 equivalent would yield an average normalized emission rate of 1.4 lb chloroform/1000 gpm, with a range of < 0.1 to 7.7 lb/1000 gpm. If only the larger towers, i.e. those responsible for about 99 percent of the reported chlorine use, are considered, then the average normalized emission rate would be 4.1 lb chloroform/1000 gpm. Therefore, it appears reasonable to use a molar ratio of 0.002 and an emission factor of 0.0034 lb chloroform per lb chlorine equivalent.

4.2.1.3 Seawater Cooling

There are two reasons why chlorination of seawater is of interest to this study. First, seawater is used for once-through cooling at several electric power plants in the South Coast Air Basin. Since this cooling water is routinely chlorinated, there is at least a potential for the production of chloroform through the haloform reaction. The other reason is that the Hyperion, Terminal Island, and Joint Water Pollution Control wastewater treatment plants occasionally chlorinate untreated or partially treated effluents before discharging them to the ocean. There is thus a potential for chloroform production near the plant outfalls. Because most of the literature on seawater chlorination is concerned with cooling water, the general topic of haloform reactions in marine and estuarine environments is presented here.

Helz and Hsu (1978) added NaOCl to natural water samples having salinities from 0.00 to 31.54 g/kg. In the freshwater samples, chloroform was the major haloform reaction product. For salinities of 1.06 g/kg and above, however, brominated species predominated. Figure 4.2-3 shows the chloroform yield as a function of salinity for two chlorine dose rates. Chlorine consumption data (as distinguished from chlorine doses) were available only for the 14-μM dose rate. For the freshwater case, we calculated the $CHCl_3/Cl_2$ molar ratio to be 0.0079. For the saline water, the ratio ranged from 0 to 0.0049.

One reason why so little chloroform results from chlorination of seawater is that very little HOCl is available for the haloform reaction. When chlorine is added to seawater, which usually contains about 65 mg/L Br^-, the bromide is rapidly oxidized to HOBr by the following reaction:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (4\text{-}17)$$

Using literature values of ionization constant and rate constant data, Helz and Hsu (1978) show that under near-neutral conditions at sea salt concentrations above about 5 g/kg, consumption of HOCl by Br^- occurs within less than 1 minute; in many cases, 99 percent of the HOCl is consumed in less than 10 seconds. This rate is much faster than that for the haloform reaction. More recent modeling work by Haag and Lietzke (1980) predicts that when 0.8 mg/L of chlorine is added to seawater at pH 8.2 and a temperature of $25^\circ C$, the predominant species would be bromochloroamines. The molar ratio of HOBr to HOCl would increase from about 540 at 1 minute to about 10^8 after 10 minutes.

Very little information on chloroform generation in seawater used for once-through cooling is available in the literature. In a laboratory experiment in which 2.9 to 3.2 mg/L of chlorine was added to the seawater used for cooling at the San Onofre Generating Station, Bean et al. (1979) observed no chloroform formation after one hour. The limit of detection for $CHCl_3$ was 0.5 μg/L. Similar results were obtained from chlorination of a seawater sample from Cape Fear, North Carolina. Bean et al. (1980) also found no chloroform in chlorinated seawater used for once-through cooling at the Millstone Nuclear Power Station in Connecticut; the limit of detection of their analysis was not reported.

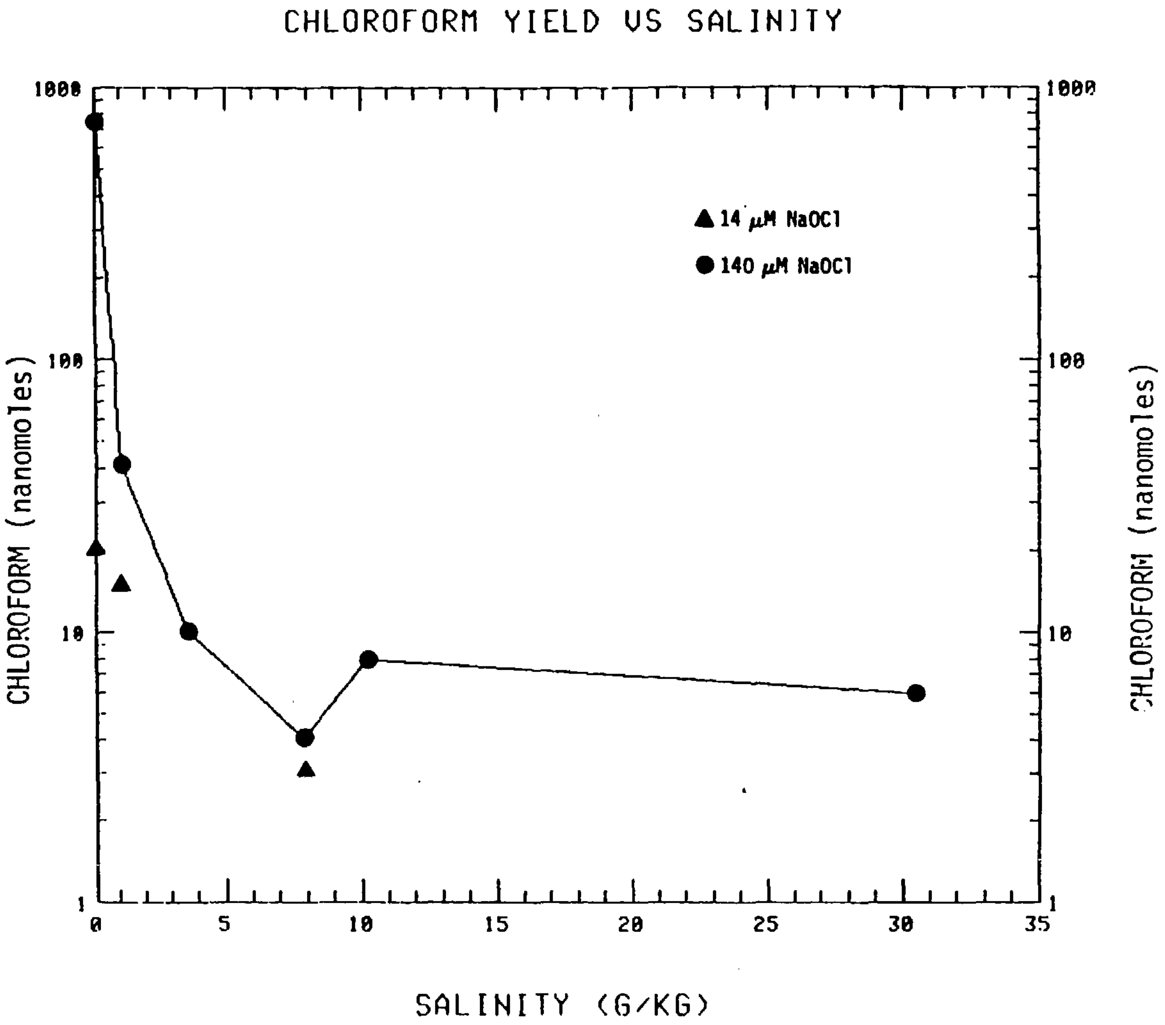


Figure 4.2-3. Chloroform Yield From Chlorination of Estuarine and Coastal Water Samples With Two Dose Rates of NaOCl (Plotted by SAIC from data presented by Helz and Hsu, 1978).

4.2.1.4 Wastewater Treatment

Trihalomethanes are less likely to form in wastewater than in treated drinking water because the high ammonia content of the former results in the rapid formation of chloramines. Relatively few studies of chloroform production during wastewater treatment conditions have been performed. As will be seen below, the limited information available suggests that:

- Relatively small amounts of chloroform are generated through chlorination of organic precursors;
- Chloroform production can occur when chlorination follows a nitrification step in tertiary treatment;
- Chloroform entering the wastewater treatment system as a constituent of raw wastewater is largely transferred to the air during primary treatment;
- The small amount of chloroform which ends up in aerobic treatment processes (such as secondary treatment with activated sludge) is not degraded; and
- Chloroform which is involved in anaerobic processes, such as sludge digestion, may be degraded, given a long enough time.

An idea of the effect of chlorination of raw wastewater upon chloroform formation may be obtained from laboratory tests conducted by Cooper et al. (1983). Wastewater samples from two treatment plants in Florida were chlorinated according to a breakpoint schedule. At each point in the breakpoint curve, the haloform reaction was allowed to continue for 24 hours. From Cooper et al.'s data, we have calculated $CHCl_3/Cl_2$ molar ratios of 0.0007 to 0.0017. The highest chloroform molar ratios were observed, as one might expect, at points where most or all of the chlorine was present as free chlorine. Note that these molar ratios are about an order of magnitude lower than those computed for drinking water chlorination.

Lurker et al. (1982) collected air and liquid samples from various points at the North Wastewater Treatment Plant in Memphis, Tennessee. At the time of their survey, none of the media in the plant were chlorinated. The concentration of chloroform in the wastewater declined from 19 to 5 ppb during primary treatment. At the same time, atmospheric concentrations of $CHCl_3$ were highest--about 3600 ppt--where the raw wastewater enters the plant. Only 1 to 4 ppb of chloroform are found in the secondary treatment portion of the plant. Lurker et al. see this as evidence that (1) most of the chloroform is transferred to the air near the beginning of the process and (2) chloroform does not adsorb onto suspended solids. If the latter is true, then it is unlikely that chloroform entering the system will "survive" long enough to be incorporated in the sludge. A rough estimate of emissions from the plant may be obtained by multiplying the flow of wastewater through the plant by the difference between the chloroform concentrations at the entry to the plant and in the final effluent: $(19 \times 10^{-6}$ g/L $- 4 \times 10^{-6}$ g/L$)(3.78 \times 10^{8}$ L/day) (lb/453.6 g)(ton/2000 lb)(365 days/yr) = 2.3 tons/yr. Note that the plant is in effect transferring chloroform from the raw wastewater to the air, not generating it.

To determine whether chloroform and other halogenated one- and two-carbon organic compounds are degraded by the bacteria in wastewater treatment processes, Bouwer et al. (1981) incubated the compounds aerobically in the presence of primary sewage bacterial cultures and anaerobically in the presence of mixed methanogenic bacterial cultures. Chloroform was not degraded aerobically, even after 25 weeks contact. The mixed methanogenic bacteria were able to remove about 81 percent of the chloroform after 2 weeks and about 99 percent after 16 weeks, when the initial chloroform concentration was about 10 ppb. For medium initial chloroform concentrations (~30 ppb), the anaerobic degradation rate was lower, and for high initial concentrations (~100 ppb), only about 25 percent of the chloroform was removed after 2 weeks. Bouwer et al. believe that the degradation of chloroform was primarily through biological mechanisms, although a small amount may have been removed through nucleophilic substitution of sulfhydryl for chlorine to produce a thiol:

$$CHCl_3 + HS^- \rightarrow CHCl_2SH + Cl^- \qquad (4\text{-}18)$$

Dixon and Bremen (1984) have reviewed several studies of volatilization of organic compounds from wastewater treatment processes. They cite pilot plant studies at the U.S. Environmental Protection Agency's Test and Evaluation Facility in Cincinnati, Ohio (Bishop, 1982; Petrasek et al., 1983) which showed that adsorption of volatile organics to primary sludge is not a significant removal mechanism and that, the more halogenated a compound is, the lower its biodegradability and the higher its volatility. Much, if not most, of the volatilization occurs during primary treatment, which may include bar screens, grit removal, roughing trickling filters, primary clarification and other processes. Bubble aeration in activated sludge treatment also strips VOCs from the wastewater. Studies summarized by Dixon et al. show that from 80.5 to 96.8 percent of the chloroform entering the process is removed by volatilization.

In Phase II of this study, SAIC measured chloroform concentrations in the influents and effluents of two wastewater treatment plants in the South Coast Air Basin. (See Section 8.1.) In performing a mass balance, the residence time in each system was taken into account, so that the outflows corresponded to the inflows a certain number of hours earlier. At the Los Angeles Hyperion Treatment plant, chloroform concentrations in the final effluent were lower than those in the influent; releases to the atmosphere were estimated to be about 15 lb/day, with a maximum rate of 2.6 lb/hr. An emission factor for the facility was calculated to be 16 ± 5 g per million gallons treated. In addition the fraction of incoming chloroform which was emitted to the atmosphere had a 95-percent confidence interval of 21 to 47 percent; the remaining $CHCl_3$ presumably ended up in the ocean.

At the Riverside Water Quality Control Plant, chloroform mass flows in the effluent were higher than those in the influent. The reason for this is that wastewater receives tertiary treatment to remove ammonia prior to chlorination of the final effluent. This removes competition for the haloform reaction. In recent research for the ARB, Chang et al. (1987) found increases of chloroform across wastewater treatment plants where nitrogen removal is practiced. We estimate that about 68 percent of the 0.5 lb/day of emissions from the Riverside plant was due to formation of chloroform during postchlorination.

4.2.1.5 Swimming Pool Chlorination

Given the large number of swimming pools in the South Coast Air Basin and the widespread practice of treating them with chlorine, the literature was reviewed to ascertain whether chloroform formation in swimming pools had been observed. Most of the research to date has been on European pools; to the best of our knowledge only one study has been conducted in the United States.

Extensive studies of THM formation and atmospheric release at eight covered swimming pools were conducted by Lahl et al. (1981); findings of the study and estimates of chloroform emission rates were presented by Batjer et al. (1980). Pool water chloroform concentrations ranged from 43 to 980 ppb; means for 7 to 11 monthly samples at individual pools ranged from 88 to 407 ppb. The water sources for the swimming pools contained relatively low chloroform concentrations (< 2 ppb). Therefore, THM compounds must have been generated through chlorination of the pools.

To ascertain the relationship between free chlorine dosages and THM concentrations, Lahl et al. chlorinated samples of water from three of the pools. Table 4.2-4 shows the results. We have converted the reported THM concentrations to those for chloroform by multiplying each THM value by the reported average fraction of THM represented by $CHCl_3$ at the three pools. The calculated $CHCl_3/Cl_2$ molar ratios are about 10 times those for drinking water chlorination (see Section 4.2.1.1).

Of particular interest to the present study were Lahl et al.'s measurements of chloroform concentrations in the air above the water surface. Ten monthly samples were taken at each facility. The average facility-specific $CHCl_3$ concentrations ranged from 36 to 241 $\mu g/m^3$ (6800 to 45,200 ppt), while the highest measured value was 384 $\mu g/m^3$ (72,100 ppt). By contrast, city air in Bremen at the time had a typical chloroform concentration of 19 ppt. As seen in Figure 4.2-4, the concentration in the poolhouse air depended strongly upon the distance above the water surface. In addition, Lahl et al. report that the concentration in air increased with the number of swimmers, presumably as a result of the increased surface-air interface created by more pool activity. Chloroform concentrations in the ventilation system exhaust air at an unreported number of pool facilities ranged from 10 to 50 $\mu g/m^3$ (Batjer et al., 1980). Using a typical air circulation rate of 40,000 m^3/hr, and assuming 12 hr/day operation, Batjer et al. estimate emissions of about 10 g/day per facility.

Table 4.2-4

CALCULATION OF MOLAR RATIOS FOR SWIMMING POOL CHLORINATION[a]

Free Chlorine mg/L	Pool A			Pool B			Pool C		
	THM μg/L	$CHCl_3$ μg/L	Molar Ratio	THM μg/L	$CHCl_3$ μg/L	Molar Ratio	THM μg/L	$CHCl_3$ μg/L	Molar Ratio
0.4	141	131	0.195	180	162	0.241	110	88	0.131
0.6	165	153	0.151	207	186	0.184	151	121	0.180
0.8	198	184	0.137	204	183	0.136	182	146	0.108
1.0	212	197	0.117	232	208	0.124	197	158	0.094
1.6	298	277	0.103	306	275	0.102	276	221	0.082

Source: Calculated by SAIC from data presented by Lahl et al. (1981).

[a] Percentages of THM represented by chloroform were 92.9 for Pool A, 89.8 for Pool B and 80.0 for Pool C.

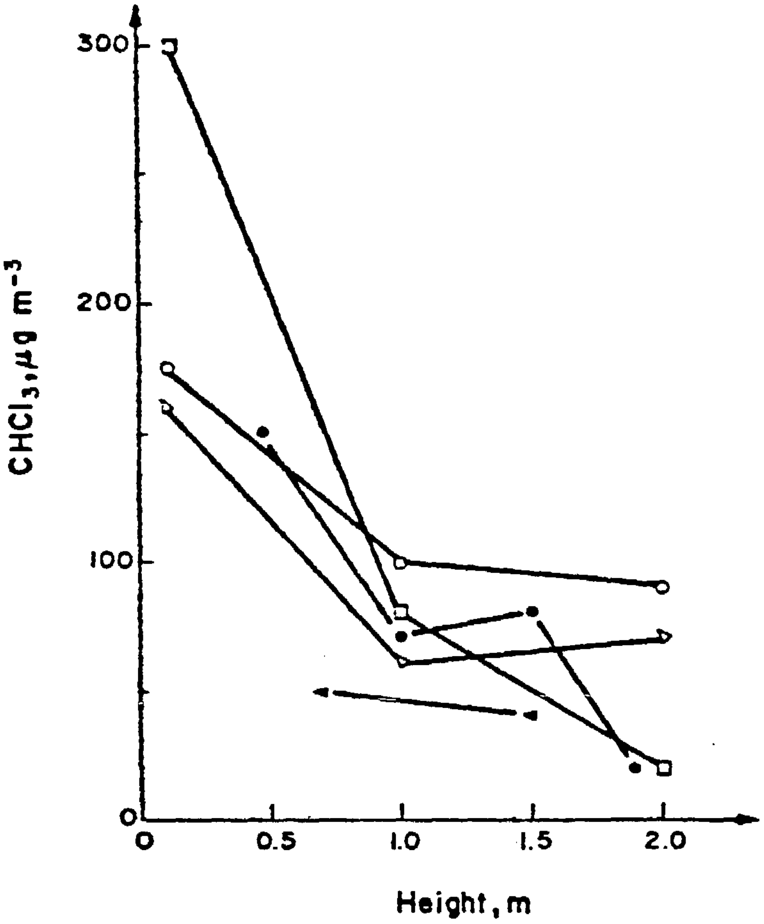


Figure 4.2-4. Chloroform Concentrations in the Air at Various Heights Above the Water Surface of Swimming Pools (Lahl et al., 1981).

Chambon et al. (1983) analyzed water from 24 chlorinated swimming pools in the Rhone-Alps region of France. Raw surface waters and finished drinking water in the area had mean chloroform concentrations of 7.5 and 1.1 ppb, respectively. "Total chlorine" (undefined in the paper) ranged from 0 to 1.5 mg/L, with a mean value of 0.28 mg/L. The swimming pools analyzed had the following chloroform concentrations (values in ppb):

	Treatment Method	
	Chlorine	NaOCl
Number of pools	10	14
Mean $CHCl_3$	301	163
Standard Deviation	176	126
Range	83-665	43-543

Because the water supply for these swimming pools had low quantities of organic matter, Chambon et al. postulated that the observed haloforms originated from "human biological products, such as sweat, traces of urine, and human grease" or from suntan oil and other grease-based cosmetics. Laboratory chlorination experiments confirmed that high doses of NaOCl (e.g. 200 mg/L) to urine at pH 6.6 could give rise to chloroform. Citric acid and 3,5-dihydroxybenzoic acid were identified as possible precursors in urine.

Several other researchers have reported finding chloroform in swimming pools in France (Laurent et al., 1983; Scotte, 1984), Italy (Aggazzotti et al., 1984), Japan (Ohashi et al., 1978, Ishikawa, 1982), Sweden (Norin and Renberg, 1980) and West Germany (Eichelsdoerfer et al., 1980; Weil et al., 1980; Kaminski and Von Loew, 1984). Reported results were consistent with those of Lahl et al. (1981). In most cases, chloroform concentrations were found to be related to the quality of the water supply and the concentrations of organic matter--much of it anthropogenic--in the water. In addition, Aggazzotti et al. (1984) confirm Lahl et al.'s finding of a direct correlation between the concentration of chloroform in the air of indoor swimming pools and the number of people in the pool at the same time.

The only U.S. swimming pool study found in the literature was conducted by Beech et al. (1980) in Miami. In contrast to many of the European cases cited above, Miami water had relatively high chloroform concentrations

(30 to 300 ppb). To determine the contribution of the municipal water to the chloroform content of the swimming pools, Beech et al. analyzed two unused, unchlorinated pools. As these contained only 1 and 4 ppb of chloroform, the authors postulate that the chloroform in the influent water evaporates rapidly; thus the observed chloroform had to have been formed in situ. No data on chlorination rates were presented. Chloroform levels in three groups of pools were as follows (concentrations in ppb):

Water Source for Pools

	Saline	Fresh (at beach)	Fresh (city)
Number of pools	18	20	81
Mean $CHCl_3$	6	106	103
Standard Deviation	6	79	82
High value	21	271	386

The finding of relatively low chloroform levels (and, incidentally, high bromoform levels) in the saline water swimming pools is consistent with the information on seawater chlorination presented in Section 4.2.1.3.

As seen in Table 4.2-4, molar ratios for swimming pool chlorination are about 0.1. Using Equation 4-11 yields an emission factor of 0.168 lb $CHCl_3$ per lb chlorine equivalent. This factor was used in Phase I to develop a preliminary estimate of chloroform emissions from swimming pool chlorination in the South Coast Air Basin.

As is described in Section 8.2, in Phase II we conducted emission tests on a typical residential swimming pool. These tests confirmed that emissions indeed occur, and that they increase by one to two orders of magnitude when the water surface is agitated. Our tests showed no appreciable formation of chloroform in the pool during the two-day period. However, concentrations in the pool water at the start of the tests were 7 to 9 times those in the municipal water with which the pool was originally filled. Our conclusion was that the haloform reaction had occurred some time before our tests, and that it was limited by a very low level of organic precursors (< 2.8 mg/L TOC) during the test period.

4.2.1.6 Pulp and Paper Manufacturing

Pulp and paper mills were considered likely sources of chloroform in the SCAB since a significant amount of chlorine bleach is added to wood pulp during processing into paper, paperboard, rayon, cellophane, and explosives. Major steps in processing include raw material preparation, pulping, bleaching, and papermaking (GCA, 1984). The two primary pulping processes are mechanical pulping and chemical pulping. In the former, wood chips are ground to produce pulp. Deinking, the removal of ink, fillers, coatings, and other noncellulosic materials, quite frequently takes place when secondary fibers are used as raw materials. Chemical pulping, on the other hand, uses alkaline materials to process the virgin product into useful pulp.

Following the pulping step, one or more bleaching agents are introduced. Hydrosulfites and peroxides are commonly used with mechanical pulp, while chlorine, calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are most likely used with chemical pulp. Inasmuch as chlorine compounds are added to an aqueous solution containing organic material, chloroform formation might be expected, during both the bleaching cycle and subsequent wastewater treatment.

Emission factors for chloroform released per weight of air dried pulp produced have been calculated and summarized by GCA Corporation (1984). Emission factors for the types of processes likely to be found in the South Coast Air Basin are:

Process	Emission Factor (kg $CHCl_3$/kkg product)
Secondary tissue paper	0.16
Market bleached kraft	0.12
Bleached kraft paperboard, coarse papers, and tissue papers	0.23
Secondary fiber mill-fine papers	0.36

4.2.1.7 Transfer of Chloroform From Water to Air

In the previous subsections we have demonstrated that chloroform is produced in several types of aqueous solutions found in the South Coast Air Basin. Our review of the literature has shown that this dissolved chloroform is transferred rapidly and thoroughly to the atmosphere.

A theoretical equation for the evaporation of low-solubility contaminants from water bodies such as lakes and rivers to the atmosphere was developed by Mackay and Wolkoff (1973). In their formulation, the half-life (in days) of species i in a perfectly mixed, homogeneous solution may be estimated from:

$$t = \frac{12.48\ G\ P_w\ C_{is}}{10^6\ EP_{is}\ M_i} \tag{4-19}$$

where G is the weight of water (g), P_w is the partial vapor pressure of water (mm), C_{is} is the solubility of the compound in water (mg/L), E is the mass evaporation rate of water (g/day), P_{is} is the vapor pressure of the pure compound, and M_i is the compound's molecular weight.

In laboratory experiments in which dilute solutions of various chlorinated compounds were allowed to evaporate from an uncovered, stirred beaker, Dilling et al. (1975) found evaporation half-lives to be one to two orders of magnitude higher than those predicted from Mackay and Wolkoff's equation. Part of the discrepancy was ascribed to the nonuniformity of concentrations in the beaker; after the solute near the air-water interface evaporates, there is a delay while additional solute travels to the surface. Nevertheless, under typical ambient environmental conditions, the half life of chloroform in a 1 ppm solution was 19 to 24 minutes.

In later experiments using the same methods, Dilling (1977) measured evaporation half-lives for chloroform of between 18.5 and 25.7 minutes at 25^oC and 34.5 minutes at 1 to 2^oC. Again, the measured values were much higher than those predicted by the Mackay and Wolkoff equation. An equation which predicted experimental results much more closely was one adopted from Liss and Slater (1974):

$$t = 0.6931\ d/K \tag{4-20}$$

where d is the average depth of the solution (cm) and K is the overall liquid exchange constant (cm/min). Here, K is estimated from the following equation:

$$K = \frac{221.1}{(1.042/H + 100.0)\ M_i^{1/2}} \tag{4-21}$$

and

$$H\ (\text{dimensionless}) = 16.04/P_{is}M_i/TC_{is} \tag{4-22}$$

where T is the temperature in ^{o}K and the other variables are defined as above.

Because the theoretical equations and the experimental findings presented thus far are based upon the assumption of still air above the water surface, they would tend to underestimate evaporation rates. The flow of air across the water surface would increase the evaporation rate significantly. Indeed, Dilling et al. (1975) report an increase of about 17 percent in solute evaporation at a wind speed of 2.2 ± 0.1 miles/hr (1.0 ± 0.04 m/s). An empirical model of chloroform evaporation from water surfaces which takes wind into account is presented in Section 8.2.2.2 and applied to the case of swimming pools.

4.2.2 Emissions From Chlorination of Drinking Water

4.2.2.1 Chlorination Survey

In order to obtain an improved estimate of the use of chlorine and chlorine-based disinfectants in the South Coast Air Basin, SAIC conducted a survey of all municipal water districts which (1) were located at least partially in the Basin and (2) served at least 50,000 people. Names and addresses of these districts were obtained from a computer printout furnished to SAIC by the California Department of Health Services (Balch, 1985). Figure 4.2-5 shows our questionnaire, which was sent to 59 districts in September and October 1985. Follow-up phone calls were made to nonrespondents and to obtain more detailed information from certain respondents. We received responses from 36 districts, for a response rate of 61 percent.

Table 4.2-5 shows the responding water supply districts, along with the reported amounts of disinfectant used and other pertinent data. Sodium hypochlorite use was converted to chlorine equivalent by the method described in Section 4.2.1. The total reported chlorine, 17,654,880 lb, overstates the amount of chlorine used for drinking water disinfection in the SCAB, since it includes chlorine applied to water used outside the Basin.

Scaling up from the survey data to the Basin as a whole was not a simple task, given the complexity of the water distribution network in Southern California. Most of the water in the area is obtained from the Colorado River and the State Water Project by the Metropolitan Water District of Southern California (MWD). The MWD treats the water at five plants and then distributes it to its member agencies, which include 13 wholesalers, such as the Chino Basin Municipal Water District, and 14 end users, such as the City of Beverly Hills. The wholesalers in turn sell the water to other wholesalers and/or final users. To make the system even more complex, several districts, such as the City of San Bernardino, are completely independent of the MWD system and may act as wholesalers. In addition, some end users, such as the Moulton-Niguel Water District, obtain their supply from two or more wholesalers. Finally, all of the MWD member districts and most of the end users obtain some of their water from non-MWD sources (generally ground water).

To be able to derive an estimate of chlorine use among these myriad agencies from limited survey data, we constructed a simplified conceptual model of water distribution and chlorination in the SCAB. First, we assumed a hierarchy of primary, secondary and tertiary suppliers. The primary suppliers are the MWD, the City of San Bernardino and five other districts (Davis, 1986a). The secondary suppliers are the 27 member agencies of the MWD. Finally, the tertiary suppliers are the cities and other local

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SURVEY OF CHLORINE AND CHLOROFORM IN MUNICIPAL WATER SYSTEMS

1. How much chlorine is added per year to the water supplied by your system (tons/year)?

2. What form of chlorine product is used?

_____ a. Chlorine (gas)
_____ b. Hypochlorite
_____ c. Chlorine dioxide
_____ d. Chloramines
_____ e. Other, please specify ______________________

3. What is the schedule of addition of chlorine (e.g. continuously or time of day added)?

4. Is there any seasonal variation in chlorine addition?
If so, how does the addition of chlorine vary by season?

5. Have you done any monitoring for chloroform or other trihalomethanes?

_____ a. Yes
_____ b. No

6. If yes, please list the results and places where measurements were taken, from 1982 to the present (e.g., at treatment plant, in the middle of the system, at the user end). Use a separate sheet of paper if necessary. Please attach any documents that you feel are helpful.

Thank you for taking the time to assist us in this survey. If you have any questions, please contact Dr. Michael Rogozen or Dr. Harvey Rich at (213) 318-2611.

Please return the completed questionnaire to:

Science Applications International Corporation
Attn: Dr. Michael Rogozen
2615 Pacific Coast Highway, Suite 300
Los Angeles, California 90254

Figure 4.2-5. Questionnaire Sent to Municipal Water Districts.

Table 4.2-5

CHLORINE USE REPORTED BY WATER DISTRICTS IN SAIC SURVEY

District ID No.	District Name	Chlorine (tons)	Sodium Hypochlorite (tons)	Chlorine Equivalent (lb)
19-001	Alhambra	3.8	0.2	7,981
19-008	Azusa Valley Water Co.	21	1	43,905
19-019	City of Cerritos	7.5	0	15,000
19-033	Dominguez Water Corp.	80	0	160,000
19-034	Downey Water District	0	0	0
19-036	East L.A. District	0.454	0	908
19-041	Three Valleys MWD	16	0	32,000
19-048	Castaic Lake Water Agency	41.4	0	82,800
19-065	Long Beach Water Dept.	300	0	600,000
19-067	Los Angeles DWP	1832.5	1832.5	7,155,904
19-087	MWD of So. Calif.	4400	0	8,800,000
19-092	City of Monterey Park	5	0	10,000
19-104	Palos Verdes	9	0	18,000
19-134	Hermosa Redondo District	1.5	0	3,000
19-146	Santa Monica	30	0	60,000
19-152	City of South Gate	0	0	0
19-155	So. Calif. Water Co.	11.2	4.8	31,544
19-156	City of Beverly Hills	0	0	0
19-179	City of Burbank	6	0	12,000
19-199	Whittier	7.3	0	14,600
19-213	Torrance MWD	31	0	62,000
19-234	Walnut Valley Water District	0	0	0
30-001	City of Anaheim	36	0	72,000
30-003	City of Buena Park	0	0	0
30-004	Mesa Consolidated WD	5.3	0	10,600
30-007	Orange County MWD	0	0	0
30-023	City of Newport Beach	50	0	100,000
30-027	City of Orange Water Dept.	0	0	0
30-038	City of Santa Ana	0	0	0
30-062	City of Garden	0	2.78	5,296
30-073	Moulton-Niguel WD	56	0	112,000
33-001	Coachella Valley WD	1	0	2,000
33-011	Eastern MWD	57.98	3.94	123,466
33-031	City of Riverside	15.05	0	30,100
33-037	Corona Water District	10.95	0	21,900
36-039	City of San Bernardino	2.7	0.3	5,971
36-050	Upland City	9	1	19,905
36-094	Chino Basin MWD	21	0	42,000
Totals		7068.634	1846.52	17,654,880

districts who receive their water from the secondary suppliers. Note that some secondary suppliers, such as the City of Santa Monica, have no tertiary-level districts below them. The following additional simplifying assumptions were made:

- Chlorine added by the MWD is distributed to each secondary supplier in proportion to that supplier's fraction of the MWD's total supply;
- Chlorine added by secondary suppliers is associated with water not furnished by the MWD; that is, chlorination by the secondary suppliers is in addition to that performed by the MWD;
- If the amount of chlorine added by a secondary supplier is known, then the chlorine added by the tertiary suppliers subordinate to it may be ignored;
- Any group of tertiary suppliers associated with a given secondary supplier (e.g. the 35 communities which receive water from the Central Basin MWD), uses the same amount of chlorine per unit of water supplied.

The last assumption was necessary because of the limited number of tertiary suppliers surveyed. This set of assumptions may lead to errors of omission in some cases and of double counting in others. However, the amount of chlorine added by most secondary districts and all secondary districts is at least an order of magnitude lower than that added by the MWD and by the Los Angeles Department of Water and Power. Therefore errors resulting from the assumptions will not significantly affect our estimate of basin-wide chlorine use. As will be seen below, they could have a small effect on our estimates of per-capita chlorination dosages by county.

The following sample calculation shows how non-MWD chlorine use was estimated for a group of tertiary suppliers, in this case the ones associated with the Central Basin MWD:

Community	Chlorine Use (lb)	Water Supply (acre-feet)
Cerritos	15,000	9,929
East L.A.	908	27,616
South Gate	0	13,157
Total	15,908	50,702

The average chlorine dosage for these tertiary suppliers is 0.31375 lb/acre-ft. Since the Central Basin MWD supplies 169,822 acre-ft of non-MWD water (see Table 4.2-6), the scaled-up value for chlorination is (0.31375 lb/acre-ft)(169,822 acre-ft) = 53,282 lb chlorine.

4.2.2.2 Estimation of Emissions

Table 4.2-6 summarizes the scale-up calculations. From our survey results, we estimate a total chlorine use of 15,157,302 lb for drinking water chlorination in the SCAB in 1985. Using the emission factor reported in Section 4.2.1.1 (0.025 lb $CHCl_3$/lb chlorine equivalent) yields an emissions estimate of 190 tons/year (170 MT/year) from drinking water chlorination.

4.2.3 Emissions From Chlorination of Treated Wastewater

The names of all large wastewater treatment facilities within those portions of Los Angeles, San Bernardino, Orange, Riverside, and San Diego counties which lie within the South Coast Air Basin were obtained in order to conduct a telephone survey of chlorine usage and chloroform monitoring. Treatment district names were obtained from the California Department of Health Services and Regional Water Quality Control Districts 4, 6, 8, and 9.

Approximately 20 wastewater treatment districts or municipalities were contacted. In this manner information was obtained on 100 percent of the large sewage treatment plants in the Basin. The information we obtained included amount and type of chlorine product added, schedule of additions, monitoring data for chloroform or total trihalomethanes, and locations of plants and discharge points.

Due to the large amount of ammonia present in the water in wastewater treatment plants which do not have a nitrification step, emission factors for chloroform at these plants are approximately one order of magnitude lower than those for drinking water (see Section 4.2.1.4). Where nitrified effluent is chlorinated prior to discharge, chloroform is indeed generated. However, facilities having this combination of nitrification and

Table 4.2-6

SCALE-UP OF DRINKING WATER CHLORINATION SURVEY RESULTS

Secondary Supplier	MWD Supply[a] (AF/yr)	Non-MWD Supply[a] (AF/yr)	Non-MWD Chlorine (lb/yr)	MWD Chlorine (lb/yr)	Total Chlorine (lb/yr)	People Served[b]
MWD Member Agencies						
Anaheim	35,943	29,887	72,000	221,694	293,694	230,000
Beverly Hills	14,654	0	0	90,385	90,385	38,467
Burbank	23,304	299	12,000	143,738	155,738	84,600
Central Basin	90,422	169,822	53,300	557,718	611,018	1,280,000
Chino Basin	26,362	149,407	42,000	162,599	204,599	386,000
Coastal	40,364	443	110,600	248,963	359,563	180,000
Compton	3,824	5,906	ND	23,586	23,586	83,000
Eastern	28,657	95,901	123,466	176,755	300,221	150,000
Foothill	9,733	6,252	0	60,033	60,033	80,000
Fullerton	24,870	8,406	ND[c]	153,397	153,397	106,000
Glendale	24,450	4,688	ND	150,806	150,806	145,624
Las Virgenes	12,666	0	0	78,123	78,123	38,000
Long Beach	52,319	22,382	600,000	322,701	922,701	368,500
Los Angeles	29,102	622,193	7,155,904	179,499	7,335,403	3,062,000
Orange County	201,686	179,199	364,000	1,243,988	1,607,988	1,650,000
Pasadena	15,861	21,999	ND	97,830	97,830	140,237
San Fernando	0	3,737	ND	0	0	18,600
San Marino	18	5,033	ND	111	111	13,250
Santa Ana	15,762	31,070	0	97,219	97,219	222,950
Santa Monica	10,801	7,800	60,000	66,620	126,620	88,500
Three Valleys	51,688	56,444	32,000	318,809	350,809	385,000
Torrance	19,162	10,506	62,000	118,190	180,190	131,000
Upper San Gabriel	23,105	153,832	ND	142,510	142,510	900,000
West Basin	182,833	4,795	181,000	1,127,703	1,308,703	740,000
Western MWD-Riverside	40,524	163,620	52,000	249,950	301,950	365,000
Independent Agencies						
City of San Bernardino	0	ND	5,971	0	5,971	131,030
Azusa Valley	0	ND	43,905	0	43,905	50,000
Monterey Park	0	10,092	10,000	0	10,000	54,100
Alhambra	0	ND	7,981	0	7,981	69,189
Castaic Lake	0	ND	82,800	0	82,800	80,000
So. Calif. Water Co.	0	0	31,544	0	31,544	152,733
Coachella Valley	0	ND	2,000	0	2,000	65,354
Upland	0	ND	19,905	0	19,905	51,988
Totals	978,110	1,763,713	9,124,376	6,032,926	15,157,302	11,541,122

[a] Data from Metropolitan Water District of Southern California (MWD, 1984).

[b] Data from computerized listing provided by California Department of Health Services (Balch, 1985).

[c] ND = no data.

post-chlorination account for a small percentage of the wastewater treated in the SCAB. Furthermore, the City of Los Angeles' Hyperion Treatment Plant, Los Angeles County's Joint Water Pollution Control Plant, and the Orange County Sanitation Districts' Plants 1 and 2, which treat 72 percent of the basin's wastewater, all discharge their final effluent through submerged pipes to the ocean (Pamson, 1985; Sizemore, 1985). This effluent is not nitrified prior to chlorination, and competition by bromide ion (see Section 4.2.1.3) would severely limit the chloroform generation after discharge.

Considering all these facts, we chose not to compute the very small contribution of chloroform to the basin air by chlorination at sewage treatment plants. However, the contribution of chloroform, generated by the water supply and released at the treatment plants, was accounted for in our calculation of emissions due to drinking water chlorination (Section 4.2.2) and in the air modeling exercise (Section 10.4.1.2).

4.2.4 Emissions From Cooling Tower Chlorination

4.2.4.1 Industrial Cooling Towers

Survey Methods

In order to obtain an estimate of chloroform emissions from industrial cooling towers, SAIC conducted a mailed survey of potential industrial cooling tower users in the South Coast Air Basin. The names and addresses of the potential cooling tower user facilities were obtained from National Business Lists, Inc. (NBL), which conducted a search of their data base using combinations of standard industrial classification (SIC) codes and postal ZIP codes specified by SAIC. SIC codes of industries likely to use cooling towers were identified from the results of a previous SAIC survey of industrial cooling towers in California (Rogozen et al., 1981). ZIP codes for the appropriate geographical areas were identified from the 1981 National Zip Code and Post Office Directory (NIDC, 1981).

Figure 4.2-6 shows the questionnaire which was sent to the potential cooling tower users. A copy of the entire survey package is provided in Appendix A. The main objective of the questionnaire was to determine the

ID No. 199

SCIENCE APPLICATIONS INTERNATIONAL CORPORATION/CALIFORNIA
AIR RESOURCES BOARD

SURVEY OF CHLOROFORM AND CHROMIUM IN COOLING TOWERS

Background Questions on Cooling Towers

1. Does your firm use cooling towers in the South Coast Air Basin (Los Angeles County, Orange County, western portion of Riverside County, and southwestern portion of San Bernardino County)?

2. a. If yes, please report the number of towers, their locations, and the combined circulation rate of the towers in each location.

   b. If no, please check here and return the form in the self addressed return envelope provided. ✓

	Number of Towers	City	Combined Circulation Rate (gals/min)
1.			
2.			
3.			
4.			

3. Please list the total make-up water rate, type of water used (municipal surface or ground, municipal or industrial wastewater, natural brackish, saline, or other recycled), and rate of use of recycled or wastewater make-up (if different from total make-up rate).

	Make-up Water Rate (gals/min)	Type of Water	Recycled Waste Water Make-up Rate (gals/min)
1.			
2.			
3.			
4.			

Figure 4.2-6. Questionnaire Used in Industrial Cooling Tower Survey.

Chlorine Use in Cooling Towers

4. Which of the following chlorine products are used in your cooling towers?
    _____ a. No chlorine additives
    _____ b. Chlorine (gas)
    _____ c. Hypochlorite
    _____ d. Chlorine dioxide
    _____ e. Other, please specify ______________________________

5. Where is this product added?
    _____ a. Make-up water
    _____ b. Blow-down water
    _____ c. Circulating water

6. How often do you add the chlorine product?
    _____ a. Number of times per day. At what time(s) of day? ______________
    _____ b. Number of days per week
    _____ c. Continuously

7. Is there a seasonal variation in use of this chemical?
    _____ a. Yes
    _____ b. No

8. If yes, what is the rate of application in each of the four seasons?
    _____ a. Winter
    _____ b. Spring
    _____ c. Summer
    _____ d. Autumn

    If no, just note the rate of application once.

9. What is the total amount of chlorine product added per year?

10. Do you have any plans to change the amount or method of chlorination in the future? If so, how?

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Figure 4.2-6. Questionnaire Used In Industrial Cooling Tower Survey (Continued).

Chromium Use in Cooling Towers

11. Do you use a chromate or chromate-containing compound as a corrosion inhibitor in your cooling towers?
    _____ a. Yes
    _____ b. No

12. If yes, what levels of chromate do you maintain in the tower's circulating water [in parts per million (ppm) or milligrams per liter (mg/L)]?

13. What is the total amount of chromate used per year?

Once again, thank you for taking the time to assist us in this survey. If you have any questions, please contact Dr. Michael Rogozen or Dr. Harvey Rich at (213) 318-2611.

Please return the completed questionnaire to:

Science Applications International Corporation
Attn: Dr. Michael Rogozen
2615 Pacific Coast Highway, Suite 300
Los Angeles, California 90254

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Figure 4.2-6. Questionnaire Used in Industrial Cooling Tower Survey (Continued).

nature, amount and scheduling of chlorine products added to the circulating water systems of the towers. At the request of the ARB, additional questions on chromium use were included in the survey.

The NBL search identified 1,116 firms in 36 SIC codes. A 50-percent sample was drawn, for an initial sample size of 558. Survey packages were mailed between late September and early October, 1985, and follow-up calls were made to most of the non-respondents. In 74 cases, either mailed questionnaires were returned by the U.S. Postal Service with no forwarding address or the telephone numbers provided by NBL had been disconnected. These companies were assumed to have gone out of business or moved from the SCAB. Thus, after subtracting the 74 non-existent companies from the initial mailing of 558 we arrived at an effective sample size of 484. There were 317 responses by both return mail and telephone call-back for an effective response rate of 65.5 percent.

Table 4.2-7 lists the SIC codes selected, the number of questionnaires mailed to firms in each code, the number of companies unavailable due to moving or going out of business, and the number of questionnaires returned.

Analysis of Survey Data

General Results. Of the 317 firms which responded to our survey, 78 (24.6 percent) reported using industrial cooling towers. These firms reported having a total of 176 towers. Slightly fewer than half of the tower users reported having only one tower. The firms having the greatest number of towers per facility were a chemical plant (12 towers) and an oil refinery (10 towers). The SIC codes reporting the greatest number of towers were 2086 (bottled and canned soft drinks) and 3069 (fabricated rubber products, not elsewhere classified). Los Angeles County accounts for 76 percent of the reported tower-using facilities and 73 percent of the reported towers. Only one Riverside County firm reported using a cooling tower.

Some form of inorganic chlorine-based biocide was used in 58 (33.0 percent) of the 176 towers reported. Table 4.2-8 shows the distribution of use of the four major chlorinating agents (chlorine gas, sodium hypochlorite,

Table 4.2-7

COOLING TOWERS QUESTIONNAIRE RESPONSES BY SIC CODE

SIC Code	Industry	Questionnaires Mailed	Unavailable	Questionnaires Returned Number	Questionnaires Returned Percent[a]
2022	Cheese, natural and processed	4	0	3	75.0
2023	Condensed and evaporated milk	3	0	3	100.0
2024	Ice cream and frozen desserts	11	1	7	70.0
2026	Fluid milk	5	0	5	100.0
2033	Canned fruits and vegetables	13	3	9	90.0
2066	Chocolate and cocoa products	1	0	1	100.0
2076	Vegetable oil mills, nec[b]	1	0	1	100.0
2079	Shortening and cooking oils	5	0	5	100.0
2082	Malt beverages	1	0	0	0.0
2083	Malt	1	0	1	100.0
2084	Wines, brandy, and brandy spirits	19	7	9	75.0
2085	Distilled liquor, except brandy	2	2	0	0.0
2086	Bottled and canned soft drinks	45	2	24	55.8
2095	Roasted coffee	3	1	1	50.0
2813	Industrial gases	5	0	5	100.0
2816	Inorganic pigments	4	0	3	75.0
2819	Industrial inorganic chemicals, nec	32	4	21	75.0
2821	Plastics materials and resins	31	3	19	67.9
2822	Synthetic rubber	9	2	6	85.7
2824	Organic fibers, noncellulosic	2	1	1	100.0
2831	Biological products	6	1	3	60.0
2833	Medicinals and botanicals	17	3	7	50.0
2834	Pharmaceutical preparations	26	5	11	52.4
2851	Paints and allied products	111	15	48	50.0
2865	Cyclic crudes and intermediates	5	0	3	60.0
2879	Agricultural chemicals, nec	8	1	6	85.7
2899	Chemical preparations, nec	38	6	24	75.0

Table 4.2-7

COOLING TOWERS QUESTIONNAIRE RESPONSES BY SIC CODE

SIC Code	Industry	Questionnaires Mailed	Unavailable	Questionnaires Returned Number	Percent[a]
2911	Petroleum refining	12	2	7	70.0
3011	Tires and inner tubes	5	1	2	50.0
3069	Fabricated rubber products, nec	63	5	40	69.0
3321	Gray iron foundries	16	1	10	66.7
3339	Primary nonferrous metals, nec	7	2	3	60.0
3341	Secondary nonferrous metals	21	4	14	82.4
3361	Aluminum foundries	2	0	2	100.0
3362	Brass, bronze, and copper foundries	18	1	9	52.9
3463	Nonferrous forgings	6	1	4	80.0
Totals		558	74	317	65.5

[a] Effective return rate [replies/(questionnaires mailed - unavailable)].

[b] nec = not elsewhere classified.

Table 4.2-8

REPORTED USE OF CHLORINATING AGENTS IN INDUSTRIAL COOLING TOWERS IN THE SOUTH COAST AIR BASIN

Agent	No. of Facilities	No. of Towers	Chlorine Equivalent[a] lb	lb Chlorine Equivalent per Tower
Chlorine gas	7	26	409,870	15,764
Sodium hypochlorite	9	15	1,376	92
Calcium hypochlorite	5	14	266	19
"Bleach"	2	3	15	5
Totals	23	58	411,527	7,095

[a] See Section 4.2.1 for definition of chlorine equivalent.

Table 4.2-9

REPORTED AND ESTIMATED CHLORINE USE[a] IN INDUSTRIAL COOLING TOWERS

SIC Code	Survey	Responses	Reported Use (lb)	SIC Total (lb)	Basin-wide (lb)	Total (tons)
2022	4	3	0.3	0.4	1	0.0
2033	13	9	8,900.0	12,855.6	25,711	12.9
2079	5	5	53.6	53.6	107	0.1
2086	45	24	82.9	155.4	311	0.2
2813	5	5	7,899.9	7,899.9	15,800	7.9
2819	32	21	6.0	9.1	18	0.0
2821	31	19	115.0	187.6	375	0.2
2822	9	6	96,000.0	144,000.0	288,000	144.0
2851	111	48	33.8	78.2	156	0.1
2865	5	3	11.6	19.3	39	0.0
2911	12	7	298,400.0	511,542.9	1,023,086	511.5
3069	63	40	23.9	37.6	75	0.0
Totals			411,527.0	676,839.6	1,353,679	676.8

[a] Use is in chlorine equivalent (see text).

calcium hypochlorite, and "bleach") by number of firms and number of towers. Masses of the hypochlorite and bleach solutions were converted to Cl_2 equivalent by the methods shown in Section 4.2.1. Although chlorine gas is used in only about 45 percent of the reported towers, it represents about 99.6 percent of the total reported chlorine equivalent. Hypochlorite and "bleach" solutions are generally used on the smaller towers. On all of the larger towers (>7,000 gpm circulation) chlorine is added continuously. Smaller towers are generally chlorinated from once per month to once per week. Users of all of the larger towers and many of the smaller ones reported seasonal variation in chlorination, with slightly more chlorine added in summer.

Emission Calculations. For each SIC code, chlorine use reported by the survey respondents was scaled up by dividing by the fraction of responding firms in that SIC code. For example, we sent questionnaires to 13 firms in SIC code 2033, and 9 firms responded; the fraction of responding firms was therefore 0.692. Reported chlorine use in the responding firms' cooling towers was 8,900 lb/yr. Thus the chlorine use by all the surveyed firms (respondents and nonrespondents) in SIC code 2055 is estimated to be 8,900/0.692 = 12,860 lb/yr. Because the sample size was 50 percent, the total amount of chlorine equivalent used in the South Coast Air Basin would be twice that quantity obtained after scaling up from the percent of questonnaires returned. Therefore the basin-wide use of chlorine in cooling towers in SIC 2033 would be 25,700 lb/yr. Table 4.2-9 shows the results of the scale-up calculations for the 12 SIC codes in which cooling towers were reported. Total basin-wide use of chlorine in industrial cooling towers is about 680 tons per year.

The following equation was used to estimate total chloroform emissions from cooling towers in tne basin.

$$E_{CT} = 2\,F \sum_{i=1}^{36} (1/P_i)U_i \qquad (4\text{-}23)$$

where

E_{CT} = basinwide chloroform emissions from cooling towers
P_i = proportion of questionnaires returned by firms in SIC code i
U_i = chlorine equivalent use by reporting firms in SIC code i
F = emission factor for cooling towers (0.0034 lb chloroform/lb chlorine equivalent)

Applying this formula to the data in Table 4.2-9 results in an estimate of 2.3 tons (2.1 MT) per year of chloroform from industrial cooling towers in the South Coast Air Basin.

Uncertainties in the Emission Estimate

The emission estimates presented in this section are subject to three types of uncertainty. The first pertains to the accuracy of NBL's reported total number of firms in each of the SIC codes surveyed; inaccuracies in these values would lead to errors in the scale-up procedure described above. Our survey found that 74 companies had moved or changed addresses, while an unknown number had moved into the SCAB in the same time period. We assumed that the original sample was a reasonable estimate of the number of companies presently in the chosen SIC codes. Possible errors in this interpretation could result from (1) a favorable business climate, in which a greater number of companies moved in than moved out; (2) unfavorable business conditions, in which fewer companies moved in than out; and (3) improper classification of firms by SIC code in the NBL data base.

A second type of uncertainty concerns the exhaustiveness of our selection of SIC codes in which cooling tower users were expected to be found. The magnitude of this error cannot be estimated. However, insofar as this study used a recent report on California cooling towers as the primary source of high-probability SIC codes, this error is likely to be small.

The third source of error is statistical uncertainty. In order to obtain a measure of the statistical uncertainty in our estimate of $CHCl_3$, we calculated the upper bound of $CHCl_3$ emissions using confidence intervals about the mean sample value, at the 95 percent level of confidence. The sample of respondent $CHCl_3$ values is positively skewed. A law of large numbers (Blalock, 1960) states that the sampling distribution of repeated samples drawn from any population will approach normality with a mean equal to the population mean and standard error equal to the sample standard deviation divided by the square root of one less than the sample size, as the sample size becomes large. Thus, regardless of the shape of the population distribution, the sampling distribution from which confidence limits are calculated approaches normality. This law allows us to compute the upper bound for estimated $CHCl_3$ emissions from cooling towers. These results are reported below. We used z-scores and a sample size of 558 to estimate the upper bound emission. The lower bound emission was taken to be the actual emissions calculated from the respondents' reported chlorine use.

Amounts of chlorine gas, commercial strength sodium hypochlorite, bleach, and calcium hypochlorite were converted to chlorine equivalent, as outlined previously. To obtain an appropriate upper-bound estimate, the same weighting factors (proportionate response by SIC code) used in the basin-wide analysis described above had to be used. However, in order to calculate the sample mean and standard deviation, the weighting factors were applied to each individual respondent's $CHCl_3$ emission score. The following equation describes the transformation from user chlorine equivalent to weighted respondent chloroform emission:

$$\text{Individual Respondent } CHCl_3 \text{ Emissions} = 2(F)(U_i)(P_i)$$

Where F, U_i, and P_i are as defined in Equation 4-23.

This product represents the individual user-emitted $CHCl_3$ and is therefore not summed over all SIC codes.

Applying this equation to each respondent results in a mean estimated $CHCl_3$ emission of 4.10 lb/respondent, a sample standard deviation of 62.20, and a standard error of 2.63. At the 95-percent confidence level the upper bound estimate for the mean emission per repondent is 9.26 lb. This limit was multiplied by the sample size (558) and then by 2 to scale up to the entire basin.

We therefore conclude that at the 95-percent confidence level, the upper bound for annual $CHCl_3$ emission to the SCAB by industrial cooling towers is 5.17 tons. Using this method the estimated lower bound $CHCl_3$ emissions would be 0 but, of course, the actual lower bound emissions would be that value we found to be emitted by our respondents. From reported chlorine use by the respondents we estimated emissions of 0.70 tons $CHCl_3$, which represents the least possible amount of $CHCl_3$ emitted annually in the SCAB.

4.2.4.2 Utility Cooling Towers

Five utilities (Southern California Edison, the Los Angeles Department of Water and Power, the City of Glendale, the City of Pasadena, and the City of Burbank) operate electric power plants with cooling towers in the South Coast Air Basin. SAIC conducted a telephone survey of these utilities to obtain data on the total amount of chlorine or sodium hypochlorite used in tower chlorination.

Table 4.2-10 shows the power plants operated by each of those entities, the amount of chlorine or sodium hypochlorite added, and the calculated chloroform emissions from each plant. The total chlorine equivalent used annually by the nine power plants is about 118 tons.

Chlorine use estimates for each tower were multiplied by an emission factor of 0.0034 lb chloroform/lb chlorine equivalent (see Section 4.2.1.2). The total chloroform emitted by utility power plant cooling towers in the South Coast Air Basin is estimated to be 0.40 tons (0.36 MT) per year.

4.2.5 Emissions From Pulp and Paper Manufacturing

4.2.5.1 Assumptions

Several assumptions were made in computing chloroform emissions from the pulp and paper industry in the South Coast Air Basin. The first assumption was that the amount of chloroform released during the bleaching cycle was small in comparison with that released during treatment of effluent at publicly owned wastewater treatment plants. Undoubtedly some chloroform evaporates from process water during bleaching. No information is available on such emissions, however.

Table 4.2-10

CHLORINE USE AND CHLOROFORM GENERATED BY ELECTRIC POWER PLANT COOLING TOWERS IN THE SOUTH COAST AIR BASIN

Power Plant	Chlorine Gas (lb/yr)	Sodium[a] Hypochlorite (lb/yr)	Chlorine Equivalent[b]	Chloroform[c] (lb/yr)
Southern Calif. Edison[d]				
Coolwater	8,000	1,250	9,191	31
Etiwanda		81,250	77,390	263
San Bernardino	8,000	0	8,000	27
Los Angeles Department of Water and Power[e]				
Valley	26,250	0	26,250	89
City of Glendale[f]				
Grayson	43,800	0	43,800	149
City of Pasadena[g]				
Glenarm	16,000	0	16,000	54
Broadway	17,333	0	17,333	59
City of Burbank[h]				
Magnolia	6,000	0	6,000	20
Olive	32,850	0	32,850	112
Totals	158,233	82,500	236,814	804

[a] Weight of NaOCl = (gal) x (10 lb/gal NaOCl solution) x (0.125 lb NaOCl/lb solution).

[b] See text for definition of chlorine equivalent.

[c] Based upon emission factor of 0.0034 lb chloroform/lb chlorine equivalent.

[d] Alcaino (1985)

[e] Damron (1985), Burt (1985)

[f] McElhiney (1985)

[g] Dubie (1985)

[h] Westbury (1985)

Emission factors have been reported for the chloroform remaining in pulp and paper plant effluent after on-site treatment, i.e. in the wastewater discharged to the public sewer system (GCA, 1984). These emission factors are generally one or two orders of magnitude lower than those associated with bleaching processes. However, the pulp and paper plants we contacted informed us that they do not treat their effluents on site. Therefore, the on-site treatment emission factors were not used.

Although one company adds sodium sulfite to excess to "kill" the remaining active bleach as the effluent leaves the facility on its way to the sewage treatment plant, our third assumption was that most chloroform had already been formed prior to this addition.

Our final assumption is a consequence of the previous three: because effluent from each of the pulp and paper plants in the South Coast Air Basin is treated at a public sewage treatment plant, all chloroform produced at the manufacturing facilities is carried through the municipal sewage system to the wastewater treatment plant, where it is released during primary treatment.

4.2.5.2 Method

Pulp and paper manufacturing facilities in the South Coast Air Basin were identified through a review of Locating and Estimating Air Emissions from Sources of Chloroform (GCA, 1984), and discussions with the Technical Association of Pulp and Paper and the Pulp and Paper Division of the American Paper Institute (Slatin, 1985).

The 14 potential pulp and paper manufacturing facilities which were identified by these sources were reduced to three by a telephone survey. The remainder had gone out of business, relocated, or were distributors or warehouses. The three operating plants were owned by Kimberly-Clark, B.J. Fibres, and Simpson Paper. The plant operated by Kimberly-Clark, which is located in Fullerton, manufactures tissue paper from secondary fibers as well as virgin fiber product using market bleached pulp. Simpson Paper's plant in Pomona is a secondary fiber mill which manufactures fine paper, while B.J.

Fibres in Santa Ana uses the bleached Kraft process to manufacture paperboard, coarse paper, and tissue paper. All three facilities were contacted by telephone to obtain information on bleaching processes and amounts of air-dried pulp produced per year.

4.2.5.3 Results

Emission factors reported in Section 4.2.1.6 were multiplied by the air-dried pulp throughput for each process to obtain chloroform emissions from pulp and paper plants in the South Coast Air Basin. Table 4.2-11 shows these calculations and their results. We estimate chloroform emissions from pulp and paper manufacturing in the SCAB to be about 21 tons (19 MT) per year.

4.2.6 Emissions From Chlorinated Rubber Manufacturing

According to the International Institute of Synthetic Rubber Producers, there are no member rubber firms in California (Davis, 1985b). The chlorination process in synthetic rubber manufacturing is primarily used in the manufacturing of chloroprene rubber. No chloroprene or other chlorinated rubber manufacturers are located in California (Andrews, 1985; Systems Applications, Inc., 1980). Thus, chloroform emissions in the SCAB from this source are zero.

4.2.7 Emissions From Combustion of Leaded Gasoline

Ethylene dichloride (EDC) is added to leaded gasoline as a scavenger; the reaction of lead with ethylene dichloride produces lead chloride salts, which prevent the buildup of abrasive lead oxides on moving engine parts. Lead chloride salts tend to volatilize and be emitted with the exhaust rather than to remain in the engine.

The presence of halogenated compounds in leaded gasoline has led to only a modest amount of research into the potential for formation of halomethanes during combustion. Harsch et al. (1977) collected automobile exhaust samples in stainless steel canisters and analyzed them for chloroform

Table 4.2-11

EMISSIONS OF CHLOROFORM BY PULP AND PAPER MILLS IN THE SOUTH COAST AIR BASIN

Paper Mill	Type of Process	Amount of Air Dried Pulp (kkg)	Emission Factor[a]	Chloroform Emissions (kg/yr)
Kimberly-Clark[b]	Secondary tissue paper	29,419	0.16	4,707
Kimberly-Clark[b]	Market bleached kraft	29,419	0.12	3,530
B.J. Fibres[c]	Bleached kraft paperboard, coarse papers, and tissue papers	17,433	0.23	4,010
Simpson Paper[d]	Secondary fiber mill-fine papers	19,477	0.36	7,012
Totals		95,748		19,259

[a] In kg chloroform/kkg product (GCA Corporation, 1984).

[b] Neil (1985).

[c] Grana (1985).

[d] Shua (1985).

by gas chromatography with electron capture detection (GC/ECD); the presence of chloroform in the samples was confirmed by gas chromatography/mass spectrometric analysis. In two runs, the exhaust from a 1972 Rambler operated with leaded gasoline and lacking a catalytic converter contained 5.6 and 6.8 ppb of chloroform. Two tests of the exhaust of a 1975 Pinto equipped with a catalytic converter and using unleaded gasoline yielded chloroform concentrations of 0.066 and 0.091 ppb. No analysis of the incoming combustion air was reported, although ambient air measured on the same day as the second Pinto emissions test contained 0.088 ppb.

An extensive review of the literature has found only one other attempt to measure chloroform in automobile exhaust. Hasanen et al. (1979) collected exhaust samples in aluminized plastic bags from an automobile at the Laboratory of Automobile Engineering of Helsinki University of Technology. Scavengers in the leaded gasoline combusted included 1,2-dibromoethane and 1,2-dichloroethane. The gas samples were analyzed by FID-GC for various halogenated compounds, including chloroform, for which the limit of detection was 0.05 mg/m^3 (9 ppb). No chloroform at or above this level was present. It should be noted that the analytical method used by Harsch et al. was considerably more sensitive, in that they were able to report chloroform concentrations as low as 0.091 ppb. Thus it is possible that chloroform was present in the automobile exhaust analyzed by the Finnish researchers, but was not detected.

A telephone survey of several refinery industry representatives by SAIC determined that ethylene dichloride is the only chlorine-based compound used in association with lead in gasoline. The two primary reasons for this are (Dickison, 1985; Goss, 1985; Oliver, 1985; Zimmerman, 1985):

- Chlorine compounds are likely to form weak solutions of hydrochloric acid, which is corrosive to engine and exhaust train parts; and
- Chlorine products tend to be more difficult to dispose.

EPA issued new regulations on March 7, 1985 which required manufacturers to reduce the lead content of gasoline from 1.50 to 0.10 g/gal, effective January 1, 1986 (50 FR 9386-9397). This was a substantial reduction in lead content and should virtually eliminate motor vehicle fuel additives as a significant source of organochlorine emissions.

The lack of a plausible reaction pathway leading to formation of chloroform from 1,2-dichloroethane, the absence of a repetition of Harsch et al.'s findings, and the rapid decrease in the use of EDC as a scavenger in gasoline, lead to the conclusion that chloroform emissions from automobiles are likely to be negligible. They were therefore not considered in the emissions inventory for the South Coast Air Basin.

4.2.8 Emissions From Swimming Pool Chlorination

In Phase I, we applied the chlorine-based emission factor developed in Section 4.2.1.2 to amount of chlorine equivalent used for swimming pool disinfection to obtain an estimate of swimming pool-related chloroform emissions. Dispersion modeling in Phase I predicted ambient concentrations about an order of magnitude higher than those observed under the same meteorological conditions as used in the model. Since swimming pool emissions accounted for about 85 - 95 percent of the modeled concentrations, source testing was conducted in Phase II to improve our estimate. As described in Section 8.2, emission flux rates for a typical pool were measured. For Phase II, we decided to base emission estimates and modeling inputs on these results, rather than the chlorine-based emission factors.

The first step in estimating pool emissions was to determine the number of pools in the South Coast Air Basin. Information for the following analysis was obtained through conversations with representatives from the National Spa and Pool Association, the Chlorine Institute, the California Independent Pool Servicemen's Association, and Swimming Pool Age.

There are three categories of "swimming pools" in the state. The first category is "in-ground swimming pools." The National Spa and Pool Association keeps fairly detailed records of total sales of such pools and their geographic distribution in the United States. A large majority of the domestic swimming pools installed in California is of this type. The second category is "above ground swimming pools," which comprises prefabricated pools which are placed in or on the ground. Seventy-five percent of such pools are sold in the Northeast, North Central, Great Lakes, and North Atlantic states. In contrast, individually constructed "in-ground pools" predominate in the warmer regions of the country, as do sales of the third category, "spas and hot tubs." California has 20 percent of the estimated 939,000 spas and hot tubs in the country; southern California has 65 percent of the state's share (Simmons, 1985).

Data on the number of pools were available either at the national level or for California. For our emissions analysis, it was necessary to apportion these numbers to the SCAB. According to California Department of Finance projections, the total population for southern California (defined here as Imperial, Kern, Los Angeles, Orange, Riverside, San Bernardino, San Diego, San Luis Obispo, Santa Barbara and Ventura counties) on July 1, 1985 was 15,729,750 (CDF, 1983). We have estimated the population within the South Coast Air Basin by summing the populations of Los Angeles and Orange counties and 80 percent of the populations of Riverside and San Bernardino counties, for a total of 11,530,566 people. Therefore, the ratio between the populations of the SCAB and southern California is 0.73.

4.2.8.1 In-Ground Swimming Pools

The National Spa and Pool Association estimates that there are 570,000 in-ground swimming pools in California and that 60 to 65 percent of them are located in southern California (Schmidt, 1985). We decided to conservatively estimate the number of pools in the SCAB by multiplying the state total by 60 percent to obtain the number in southern California (342,000) and then by 0.73 to obtain the number in the SCAB. We thus calculated a total of 249,660 swimming pools in the SCAB.

We obtained a second estimate of the number of pools in southern California from Baker Advertising. Using county permit information, Baker Advertising estimated the number of pools in southern California to be 325,382 (Caspellanos, 1985). This figure is slightly lower than our estimate of 342,000. However, Baker Advertising pointed out that their list is not exhaustive, since it is compiled solely as a sales aid, and suggested that we use the aforementioned National Spa and Pool Association estimate. The latter estimate includes public swimming pools, which are not likely to be on a list compiled for residential suppliers (Schmidt, 1985).

Most pool users add chlorine in the form of NaOCl, which is sold as 10 and 12.5 percent by weight solutions; the majority of sales is in the latter category. A reasonable estimate of the typical NaOCl solution used would be an average of 12 percent by weight of the total solution (Marlow, 1985). Table 4.2-12 shows a typical chlorine addition schedule for swimming pools located in the SCAB (Marlow, 1985), along with our estimates of NaOCl use in four seasons. From this information we estimate that 57 gallons of NaOCl are added per year to a typical residential swimming pool.

4.2.8.2 Above-Ground Swimming Pools

According to the editor of Swimming Pool Age there are approximately 1,900,000 above-ground swimming pools in the United States. As mentioned previously, 75 percent of these pools are located in the Northeast, North Atlantic, North Central, and Great Lakes regions. Thus, 25 percent would be found in the South, Southwest, and Northwest, which we assume to comprise 21 states, including California. Using U.S. Census Bureau projections for July 1, 1983, (USDOC, 1985), we estimated that California accounts for 24.5 percent of the regions' total population. Since 25 percent of the existing above-ground pools are presumed to be located in these regions, California's share of this would be 25 percent of 24.5 percent, or 6.1 percent of the national total. Thus,

Pools in California = (1,900,000)(0.061) = 115,900
Pools in the SCAB = (115,900)(0.6)(0.73) = 50,764

Sales in 1984 of above-ground pools in various size categories are shown in Table 4.2-13. Given that most swimming pools in southern California are constructed in the ground, many large above-ground pools are not likely to be sold in the state. Thus, we combined the medium and large categories, leaving 52.4 percent of pool sales in the small category and 47.6 percent in

Table 4.2-12

TYPICAL SODIUM HYPOCHLORITE ADDITION SCHEDULE FOR SWIMMING POOLS IN SOUTHERN CALIFORNIA

Time of Year	Duration	NaOCl Use Rate	NaOCl Added (gal)
March 1 - May 15	10 weeks	1 gal/week	10
May 15 - September 15	17 weeks	2 gal/week	34
September 15 - November 1	9 weeks	1 gal/week	9
November 1 - March 1	4 months	1 gal/month	4

Source: California Independent Pool Servicemens Association (Marlow, 1985).

Table 4.2-13

1984 NATIONAL SALES OF ABOVE-GROUND SWIMMING POOLS

Size	Assumed Diameter	Sales	Percent Sales
Small	<12 feet	165,000	52.4
Medium	15-24 feet	130,000	41.3
Large	>24 feet	20,000	6.3
Total		315,000	100.0

Source: Simmons (1985)

the medium category. Inasmuch as further data on the average pool size in each category were unavailable, we reasonably assumed that the average diameters of the small and medium pools were 10 and 20 feet, respectively, and that both types were 3.5 feet high. The nominal capacities of these pools would thus be about 2,060 and 8,230 gallons, respectively.

4.2.8.3 Spas and Hot Tubs

The National Spa and Pool Institute 1984 Industry Survey reports nationwide sales of 939,000 spas and hot tubs between 1977 and 1984. No data on sales prior to 1977 are available. However, it is reasonable to assume that the number of such sales is quite small, given the explosion of sales since then (Simmons, 1985). Furthermore, a small percentage of spas sold are probably not actually in use or have been disposed. We therefore used 939,000 as the approximate total number of spas and hot tubs in use.

Twenty percent of national sales occur in California and approximately 65 percent of these are to southern California customers (Simmons, 1985). Thus, 122,070 spas and hot tubs are estimated to be located in southern California, and (0.73)(122,070) = 89,111 are estimated to be in the SCAB. A typical hot tub contains approximately 1000 gallons of water (Schmidt, 1985).

4.2.8.4 Emissions Estimate

The swimming pool emissions test described in Section 8.2 resulted in two estimates of the emission flux rate, i.e., the emissions per unit of pool surface area per unit time. For "still" conditions, when the water surface is undisturbed by activity in the pool, the average flux was 12 $\mu g/m^2$-min. When the surface was agitated, the average flux was 320 $\mu g/m^2$-min. We may obtain a rough estimate of basin-wide swimming pool emissions by multiplying the total pool water surface area by each flux rate and the time for which each of the two conditions exist.

Data on in-ground pool areas are unavailable. The area of the pool at which the flux tests were conducted was approximately 40 m^2. Our qualitative judgement is that this size was typical for the SCAB, and that the actual average size would not be different by more than a factor of 1.5. The total area for in-ground pools was thus estimated to be (40 m^2)(249,660 pools) = 9.99×10^6 m^2. As mentioned above, the typical diameters for small and medium above-ground pools are 5 ft and 10 ft, respectively; their corresponding surface areas are thus 7.3 and 29.2 m^2. The basin-wide surface areas of these pools would be:

$$\text{Above-ground pool area} = (50{,}764 \text{ pools})[(0.524)(7.3 \text{ m}^2) + (0.476)(29.2 \text{ m}^2)]$$
$$= 9.00 \times 10^5 \text{ m}^2$$

Hot tubs and spas come in a variety of sizes and shapes. As noted above, a typical spa contains 1,000 gal of water. Assuming a circular shape and a water depth of of 2 ft results in an area estimate of 6.2 m^2. The total area accounted for by spas and hot tubs would therefore be (6.2 m^2)(89,111 units) = 5.52×10^5 m^2. The total area for all three types of pools would then be 1.14×10^7 m^2.

$$\text{Average FLUX} = \sum_{j=1}^{12} d_j \, (F_1 \, T_{1,j} \div F_2 \, T_{2,j})/(8760)$$

where F_1 and F_2 are the two flux rates, d_j is the number of days in month j, and $t_{1,j}$ and $t_{2,j}$ are the hours per day spent in each condition. Using the above assumptions and flux rates, we calculated a weighted average flux rate of 22.3 $\mu g/m^2$-min. Annual emissions were then estimated as follows:

$$\text{Annual emissions} = (22.3 \ \mu\text{g/m}^2\text{-min})(1.14 \times 10^7 \text{ m}^2) \ \frac{8670 \text{ hr}}{\text{yr}} \ \frac{60 \text{ min}}{\text{hr}}$$
$$= 1.34 \times 10^{14} \ \mu\text{g/yr} = 147 \text{ tons/yr}$$

4.2.9 Other Chloroform Sources

4.2.9.1 Tobacco Smoke

Barcelona (1979) inferred from his review of the literature that chloroform and other halocarbons are present in cigarette smoke. To the best of our knowledge, the only attempt to measure chloroform in tobacco smoke was conducted by Holzer et al. (1976). Air in a closed room was sampled before and after cigarettes were smoked, and no chloroform was detected in any sample. It is possible that the analytical method, gas chromatography with flame ionization detection, was not sufficiently sensitive. However, in the absence of any hard evidence for chloroform production from tobacco smoking, this source was not considered further.

4.2.9.2 Domestic Consumption of Bleach

Bleaching agents are widely used around the home for a variety of purposes, including laundry brightening, toilet cleaning, and sink cleaning. The largest category for domestic consumption of bleach is likely to be household laundry use. No data on national use of chlorine compounds in household bleach are available (Doyle, 1985). To find the quantity of bleach used by Amerrican households, we consulted the Simmons 1984 Study of Media and Markets (SMRB, 1984). The Simmons Market Research Bureau conducts annual surveys on a variety of consumer products, using a sample of 19,110 adults, and is "projectable to the population age 18 years and over living in the conterminous 48 states of the United States."

The 1984 Simmons report itemizes the quantity of bleach used weekly in the househould wash, whether liquid or powder is used, and brand types; and provides a detailed breakdown of product use by demographic variable such as sex and age of respondent. Our analysis used the information on number of washloads using liquid and dry bleach that were done by households during the week of the Simmons survey. Table 4.2-14 shows the projected frequency distribution of washes per week per household. This distribution is the same as that for cups of bleach used per week since household wash consumes one cup of bleach per load, assuming that instructions on bleach bottles are followed.

Table 4.2-14 also estimates the total number of cups used annually in the U.S. An examination of brand name powdered bleaches at local supermarkets revealed that chlorine is not a constituent; therefore, only chlorine-based liquid bleach was of interest to this study. According to the Simmons (1984) survey, 23.6 percent of households use powdered bleach while 76.4 percent use liquid, although a given household may use both liquid and dry bleach at different times. Labels on typical household bleach containers indicate that NaOCl is present at 5.25 percent by weight. The density of bleach solution is 9.11 lb/gal. The mass of NaOCl used nationally in liquid bleach is therefore (6,516,250,000 cups)(0.0625 gal/cup) (9.11 lb/gal) (0.764)(0.0525) = 1.488×10^8 lb. The chlorine equivalent is (1.488×10^8 lb) (0.952) = 1.417×10^8 lb .

Table 4.2-14

DOMESTIC BLEACH USE

Washes or Cups/wk	No. Households	Cups/yr
8.5[a]	1,935,000	855,270,000
6.5[b]	1,959,000	662,142,000
4.5[c]	5,353,000	1,252,602,000
3.0	7,890,000	1,230,840,000
2.0	14,343,000	1,491,672,000
1.0	19,687,000	1,023,724,000
Total		6,516,250,000

[a] Reported as "eight or more."
[b] Reported as "six or more."
[c] Reported as "five or more."

Emissions of chloroform in the SCAB were estimated by assuming a molar ratio of 0.001, or half that of the cooling towers. (This lower molar ratio was used because of the shorter reaction time available during household bleach use.) The corresponding emission factor is 0.00168 lb $CHCl_3$ per lb chlorine equivalent. From U.S. Census data, we estimate that the population of the SCAB is 4.93 percent of the U.S. population. Therefore emissions in the SCAB are estimated to be $(1.417 \times 10^8$ lb Cl_2 equivalent)(0.00168 lb $CHCl_3$/lb Cl_2 equivalent)(0.0493) = 1.174×10^4 lb/yr. Bleach emissions are thus 5.9 tons/yr (5.3 MT).

Liquid bleach may be used for domestic and commercial purposes other than household laundry. However, discussions with the Chlorine Institute (Doyle, 1985) have convinced us that data on these uses are not readily available.

4.3 EMISSIONS FROM CONSUMPTIVE USE

Chloroform is used as a feedstock in the production of the chlorinated fluorocarbon chlorodifluoromethane ($CHClF_2$), whose trade names include Freon-22 (when manufactured by duPont) and Genetron-22 (when manufactured by Allied Corporation). The only chlorodifluoromethane producer in the SCAB is the Allied Corporation plant in El Segundo, which alternates between chloroform and carbon tetrachloride as feedstock. As part of a previous research program for the ARB, SAIC determined that fugitive leaks were the most important chloroform emission sources at the plant (Ziskind et al., 1982). After conducting field tests, Ziskind et al. estimated that annual fugitive emissions were between 178 and 325 lb (0.089 and 0.163 tons) per year. From a discussion with an Allied representative, it appears that chloroform is still used as a feedstock (Bao, 1985). Given the relatively low emission rate and our previous investigation, extensive further research is not necessary. Also, SAIC has estimated the release of chloroform contaminants in chlorodifluoromethane to be negligible (Hall et al., 1981).

4.4 EMISSIONS FROM NONCONSUMPTIVE USE

4.4.1 Pharmaceutical Manufacturing

Because the Food and Drug Administration (FDA) banned chloroform as an ingredient in drugs and toiletries in 1976, the compound is used primarily as an extraction solvent in pharmaceutical manufacturing. To obtain data on the use of chloroform in pharmaceutical manufacturing in the SCAB, SAIC conducted a telephone survey of companies listed in standard industrial classification (SIC) codes 2831 (biological products), 2833 (medicinals and botanicals), and 2834 (pharmaceuticals), and in the postal ZIP codes for the SCAB. Companies located in the SCAB were identified by searching the Electronic Yellow Pages, an on-line data base available through Dialog Information Systems, Inc.

During September 1985, 25 companies out of a total population of 104 were randomly contacted by telephone. Four out of the 25 companies (16 percent) had moved or gone out of business. Scaling this percent up, we calculated that 17 companies would be unreachable in the entire population of 104 companies, leaving 87 estimated pharmaceutical companies in the basin. We then selected four additional companies to restore the sample to 25. The response rate was thus 25/87 (28.7 percent).

Six companies reported using some chloroform; the amount ranged from 5 ml/yr to 52 gal/yr (Table 4.4-1). The mean amount of chloroform used by the 25 respondents was 2.89 gal/yr. Given the density of chloroform (12.38 lb/gal) and assuming that all $CHCl_3$ used in pharmacutical processing is emitted, we estimate the total chloroform emitted annually by all pharmaceutical companies in the SCAB to be 1.56 tons (1.40 MT).

Let N be the number of pharmaceutical companies in the SCAB and n be the number of facilities contacted by SAIC. The sample mean (i.e. the mean emissions per facility in the sample) and sample variance are denoted by $\bar{x}$ and s, respectively. Then the expected value of the total emissions from the sampling frame. $\hat{T}$, may be calculated as $N\bar{x}$. The half-width of a 95-percent confidence interval about the total emissions is (McClave and Benson, 1982):

$$CI = 2 \sqrt{N^2\left(\frac{s^2}{n}\right)\left(\frac{N - n}{N}\right)}$$

The confidence interval about the total emissions in the sampling frame is then calculated as $N\bar{x} \pm CI$. Using this equation and substituting reported emissions for the lower bound (which would otherwise be negative), we estimate a 95-percent confidence interval of 0.4 to 3.5 tons (0.4 to 3.1 MT).

Table 4.4-1

CHLOROFORM USE IN PHARMACEUTICAL COMPANIES IN THE SOUTH COAST AIR BASIN

Company	Chloroform Use (gals/yr)
Allergan	52.0
Anthony Products	6.0
Biochemical Labs	12.0
General Research Labs	0.0013
Newport Pharmaceuticals International	0.25
Vitaminerals	2.0
Total	72.25

4.4.2 Laboratory Use

4.4.2.1 Survey Methods

Because chloroform has traditionally been used in a variety of hospital, industrial, and research laboratories, these sources were chosen for detailed examination.

In order to ascertain the amount of chloroform actually used by laboratories in the South Coast Air Basin, SAIC conducted a mail survey of facilities in SIC codes 7391 (commercial research and development laboratories), 7397 (commercial testing laboratories), and 8071 (medical laboratories). Electronic research and development and x-ray laboratories were not included in the survey because their potential uses for chloroform were small. Calls to approximately 15 randomly chosen dental laboratories determined that choroform was highly unlikely to be used in such settings.

A computer search by National Business Lists, Inc. for SAIC found 861 laboratories in the three selected SIC codes in the SCAB. We sent questionnaires to 431 of these facilities. The initial mailing and telephone follow-ups were conducted during three weeks in late September and early October, 1985. Fifty eight laboratories had gone out of business or moved with no forwarding address. Thus, the effective survey size was 373. Mailed questionnaires or responses by telephone follow-ups were obtained from 270 laboratories. Therefore, the effective response rate for this survey was 72.4 percent.

4.4.2.2 Survey Results

About 8.5 percent (23) of the responding laboratories reported using chloroform. These laboratories used 1,010 liters of chloroform per year for a mean use rate of 43.9 liters per laboratory reporting some use, or 3.7 liters per laboratory for all responding facilities.

Table 4.4-2 shows the number of laboratories in each SIC code, the average chloroform use per sample respondent, the total chloroform use reported for each SIC code, and the estimated total use scaled up to all laboratories in the SCAB. Chloroform emissions from our sample were estimated as follows:

$CHCl_3$ emitted = (2,695 L)(gal/3.785 L)(12.38 lb/gal)

by labs

= 8,817 lb

= 4.41 tons = 4.00 MT

4.4.2.3 Uncertainties in the Estimate

Uncertainty can enter these estimations at several points. The first pertains to the accuracy of the NBL lists of laboratories within the chosen SIC codes. As the following paragraph indicates, the estimate may be either positively or negatively in error. The second involves the completeness of the examined categories. The third refers to statistical uncertainty. This will be estimated below using standard equations for confidence interval estimation.

An upper bound on the uncertainty in the number of laboratories that should actually be listed in the chosen SIC codes is 13.5 percent (58/431). This represents the percent of labs that moved or were not locatable. If we assume that the total number of labs included in the SIC codes of interest is accurate, then the number that have moved or relocated (58) is a reasonable estimate of the number of new laboratories that may have moved into the four counties in this study and replaced them. It is possible that the number of existing laboratories has actually increased beyond that originally present in the SIC codes. Then again, it is possible that the number has decreased, due to the business climate or a variety of other factors. Having no data that indicate a finding to the contrary, we assume that these two factors have counterbalanced each other and, therefore, that the actual number of laboratories in the SCAB is 861.

The second source of uncertainty pertains to the exhaustiveness of the selection of SIC codes. It is possible that hospital laboratories may have been overlooked using the laboratory-specific SIC codes. Most hospitals have their own laboratories but are classified under a non-laboratory-specific SIC code. In order to determine whether any bias exists in our results, we randomly telephoned eight hospitals to obtain information on chloroform use. Laboratory staff at all but one of the contacted hospitals indicated that chloroform is no longer used in the hospital setting. One laboratory administrator (Repique, 1986) indicated that hospitals had switched primarily to immunoassay as a replacement for extraction of drugs in medical labs, but that chloroform was still occasionally used in very small quantities for chromatography in toxicology laboratories.

Table 4.4-2

LABORATORY CHLOROFORM USE IN THE SOUTH COAST AIR BASIN, BY SIC CODE

SIC Code	Use per Respondent (liters)	Number in SIC Code	Used by Respondents (liters)	Use in SCAB (liters)
7391	1.31	198	86.6	259
7397	11.08	197	897.6	2,183
8071	0.54	466	67.3	253
Totals		861	1,051.5	2,695

Statistical uncertainity was estimated by treating the survey sample as a stratified sample, with each SIC code comprising a stratum. Let N_i, n_i and s_i be the total facilities, number of respondents, and sample variance for the ith SIC code, respectively. Total chloroform use is estimated by (McClave and Benson, 1982):

$$\hat{T} = N_1\bar{x}_1 + N_2\bar{x}_2 + N_3\bar{x}_3$$

and the half-width of a 95-percent confidence interval about T is:

$$CI = 2\sqrt{\sum_{i=1}^{3} N_i^2 \left(\frac{N_i - n_i}{N_i}\right)\left(\frac{S_i^2}{n_i}\right)}$$

Using these formulas, we calculated an upper bound of 9.54 tons (8.7 MT) of chloroform emissions from laboratory use. The lower bound would be the actual reported emissions, or 4.41 tons (4.0 MT).

4.4.3 Grain Fumigation

Chloroform has useful anaesthetic and toxic properties which make it an effective fumigant or component in a mixture of fumigants. In fact, chloroform has been registered with the U.S. Environmental Protection Agency as a commodity fumigant for the protection of harvested crops and food products in storage and prevention of insect, rodent, and other vermin infestation in mills, warehouses, grain elevators, railcars, shipholds, and other storage areas. However, SAIC has determined that chloroform is not used as a fumigant in the SCAB, since other fumigants, such as aluminum phosphide and methyl bromide, have more desirable properties (Heleniki, 1985). For example, aluminum phosphide may be applied in pelletized form and is thus considerably easier to use than gas. It also disperses more quickly after application, allowing storage areas to rapidly air out.

4.4.4 Contamination of Chlorinated Products

Chloroform is produced concurrently with methyl chloride, methylene chloride, and carbon tetrachloride in the methane chlorination process; and with methylene chloride and carbon tetrachloride by the further chlorination of methyl chloride. These products are later separated by distillation, but remain contaminated with low concentrations of chloroform. A previous study by SAIC (Hall et al., 1981) estimated that nationwide releases of chloroform via product contamination were only about 7 tons (6.4 MT) per year. It is therefore unlikely that this mode would be important in the SCAB.

4.5 EMISSION SUMMARY

Table 4.5-1 shows SAIC's estimates of chloroform emissions in the SCAB. In reviewing these results it should be borne in mind that all estimates are based upon the use of emission factors having significant uncertainty.

The largest source of chloroform emissions by far appears to be chlorination of drinking water, with 190 tons/yr (172 MT/yr) emitted in the basin, for 51.0 percent of estimated emissions. Swimming pool chlorination results in about 147 tons/yr (134 MT/yr), 39.5 percent of the total. Thus, swimming pools and drinking water supply systems together account for 90.5 percent of all chloroform emitted to the atmosphere in the SCAB. Emissions from all other sources, including domestic bleach use, paper and pulp manufacturing, industrial and utility cooling towers, pharmaceutical manufacturing, and laboratory use, account for only 9.5 percent of the total.

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Table 4.5-1

SUMMARY OF SAIC ESTIMATES OF ATMOSPHERIC EMISSIONS OF CHLOROFORM IN THE SCAB

Source	Estimated Annual Emissions		
	MT	tons	Percent of Total
A. Indirect Production[a]			
Drinking water	172	190	51.0
Swimming pools	134	147	39.5
Pulp and paper manufacturing	19	21	5.6
Domestic bleach	5.3	5.9	1.6
Industrial cooling towers	2.1	2.3	0.6
Utility cooling towers	0.36	0.40	0.1
B. Non-Consumptive Use			
Laboratories	4.0	4.4	1.2
Pharmaceutical manufacturing	1.4	1.6	0.4
Totals	338	373	100.0

[a] No marine source estimated.

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5.0

ATMOSPHERIC CONCENTRATIONS AND REACTIONS

5.1 AMBIENT CONCENTRATIONS IN THE SOUTH COAST AIR BASIN

Relatively few chloroform measurements in the South Coast Air Basin have been reported. Table 5.1-1 summarizes the data available prior to this study.

5.1.1 Results of Previous Monitoring

In April 1974, Su and Goldberg (1976) made spot measurements of ambient chloroform concentrations in the Chinatown area of Los Angeles, in a residential area of Santa Monica and in an unspecified location in Orange County. Their sampling and analytical procedures were not reported. Chloroform concentrations ranged from 360 to 620 ppt. These values are high compared with the others reported in Table 5.1-1. Su and Goldberg also report a measurement of 530 ppt $CHCl_3$ in marine air off San Pedro.

Singh et al. (1977, 1981, 1982) used a gas chromatograph with electron capture detection to measure $CHCl_3$ in Los Angeles in April and May 1976 and in April 1979, and in Riverside in July 1980. In all three cases, sampling was conducted "around the clock" from a mobile laboratory. The actual sampling locations were not reported in the references cited, nor were the number of samples collected in 1979 and 1980.

Although Singh et al. (1981, 1982) presumably measured diurnal variations in chloroform concentrations at the Los Angeles and Riverside sites, the cited references do not report these data. However, a marked variation was reported for two other cities in the measurement program, Phoenix and Staten Island. Over several days in each city, the highest chloroform concentrations were observed at night (3 - 6 a.m. and 9 - 11 p.m. in Phoenix).

In October 1980, the ARB and the South Coast Air Quality Management District measured chloroform in the ambient air at eight points in and around the abandoned McColl waste disposal site in Fullerton (ARB/SCAQMD, 1980).

Table 5.1-1

REPORTED CHLOROFORM CONCENTRATIONS IN THE SOUTH COAST AIR BASIN, 1974-1984
(All concentrations in ppt)

Date	Location	Sampling Frequency	Concentrations Reported[a]	Reference
6 April 1974	Los Angeles Chinatown	Grab Samples[b]	360	Su and Goldberg, 1976
6 April 1974	Santa Monica (residential)	Grab samples[b]	640	Su and Goldberg, 1976
16 April 1974	Orange County	Grab samples[b]		Su and Goldberg, 1976
0830			360	
1200			450	
1700			620	
9 May 1974	Marine air-San Pedro Basin	Grab samples[b]	530	Su and Goldberg, 1976
29 April - 4 May 1976	Los Angeles	113 Grab samples	R 23.1-877.8 M 103.1 SD 103.4	Singh et al., 1977
9-21 April 1979	Los Angeles	Grab samples[b]	R 24.3-223.5 M 88.2 SD 39.9	Singh et al., 1981
2-12 July 1980	Riverside	Grab samples[b]	R 109-4747 M 703 SD 798	Singh et al., 1982
3 January 1983- 30 August 1984	Los Angeles (downtown)	76 24-hr samples	R 20[c]-210[d] M 60.5 SD 24.7	McNerny, 1985
4 January 1983- 6 August 1984	Dominquez Hills (Cal State U.)	77 24-hr samples	R 20[c]-140 M 45.1 SD 30.0	McNerny, 1985
13 January 1983- 24 September 1984	El Monte	311 24-hr samples	R 20[c]-640[e] M 47.8 SD 25.1	McNerny, 1985
15 February 1983- 9 August 1984	Riverside (Magnolia)	77 24-hr samples	R 20[c]-120 M 46.6 SD 29.3	McNerny, 1985

[a] R = Range, M = Mean, SD = Standard Deviation

[b] Number unknown.

[c] Limit of detection was 20 ppt.

[d] Value of 3000 ppt believed to be an outlier.

[e] Value of 1100 ppt believed to be an outlier.

Samples were collected in bags and analyzed by cryogenic concentration followed by gas chromatography. The type of detection used was not specified, but from the reported limit of detection (0.1 and 100 ppb with and without cryogenic preconcentration, respectively), it was probably flame ionization. The range of $CHCl_3$ maximum concentrations in 12-hr samples was 100 to 800 ppt at 7 of the sites; at one off-site point, an 8,100-ppt concentration was measured. No "distinctive differences" between daytime and nighttime (12-hr) concentrations were found. The report compares the McColl values with a 28,300-ppt 12-hr concentration at the ARB monitoring station in El Monte. In view of other concentrations reported in this section, this value appears to be anomalous.

5.1.2 Ongoing Monitoring

In November 1982 the ARB began an ambient halogenated hydrocarbon monitoring program in the South Coast Air Basin (Shikiya et al., 1984). Figure 5.1-1 shows the four sites chosen for monitoring, while the operating dates for each site are listed in Table 5.1-1. According to Shikiya et al., all four sites "can be characterized spatially as neighborhood scale;" that is, concentrations measured at each site are characteristic of areas having uniform land use within an 0.5- to 4.0-km radius. The downtown Los Angeles (DOLA) site is in a homogeneous mobile source area and is within 0.8 to 1.6 km of three freeways. The Dominguez site, which is located on the campus of California State University, Dominguez Hills, is downwind of a heavily industrialized area and about 4.5 to 8 km of refineries and chemical plants. The El Monte site is a downwind receptor in an urban area with some light industry nearby. Finally, the Riverside site is a downwind receptor in an urban area.

Samples are collected by pumping ambient air into Tedlar bags continuously for 24 hours. From 1 to about 20 samples are collected each month from each station. After the bags are collected, a measured volume of sample is concentrated in a cryogenic trap and then analyzed by gas chromatography with electron capture detection. (Descriptions of this and other analytical methods are presented in Chapter 7.) For chloroform the lower limit of quantitation is 20 ppt by volume.

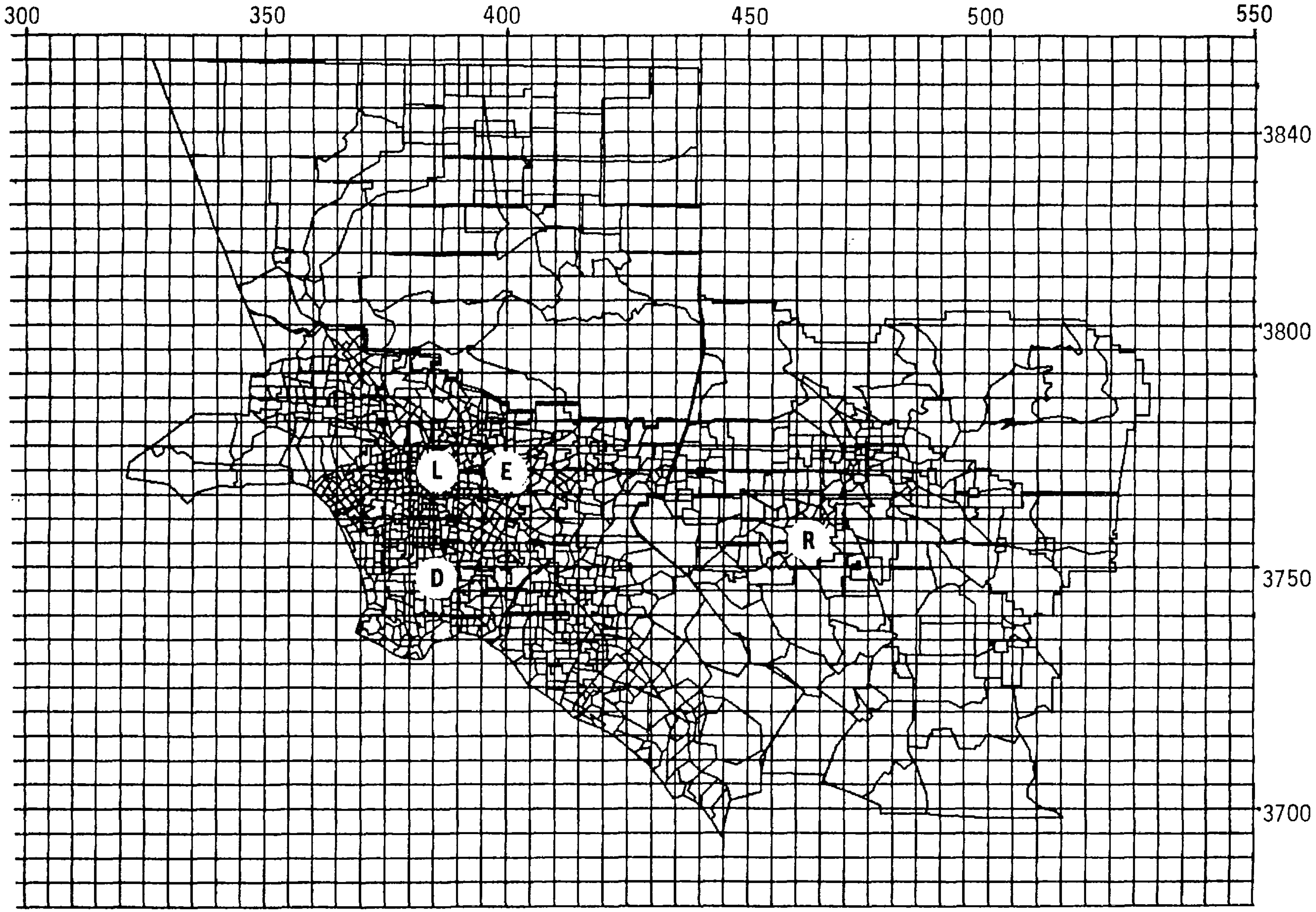

Figure 5.1-1. Locations of the ARB Ambient Halogenated Hydrocarbon Monitoring Stations at Dominguez Hills (D), El Monte (E), Los Angeles (L) and Riverside (R). Grid is based on Zone 11 Universal Transverse Mercator Coordinates.

For this study, SAIC obtained a computerized listing of chloroform concentration data for January 1983 through December 1984 for El Monte and through July 1984 for the remaining sites (McNerny, 1985). Note that we did not obtain the results for November and December, 1982, when only the El Monte site was operational. The following discussion summarizes SAIC's analysis of the data provided.

A preliminary graphical analysis showed that the concentration values above the limit of detection were distributed lognormally for each receptor, and that the probability of occurrence of certain of the high values was very low*. Therefore, subsequent analyses were performed on the logarithms of a subset of the concentration values rather than on all of the original values. An analysis of variance of the concentrations at all four sites produced a significant F-ratio ($F = 14.85$; $p < 0.01$) indicating that the differences among the mean chloroform values are likely to be due to more than random variation. Pairwise t-tests of differences in mean concentrations were performed for all combinations of sites. The mean concentration at the Los Angeles site (60.5 ppt) is significantly different from that of each of the other sites ($p < 0.05$). Other pairwise tests showed no significant differences in mean chloroform concentrations. F-tests on the variances for all paired sites were not significant ($p > 0.05$), indicating that variation in the four samples is similar. Figure 5.1-2 presents the means, 50- and 95-percent confidence limits, and extreme values of the four data sets. For convenience in interpretation, logarithmic values have been converted back to concentrations in ppt. It is for this reason that the confidence limits about the means do not appear to be symmetrical.

Using the calculated means and standard deviations for the subsets examined, it may be shown that chloroform concentrations above 110 ppt at the Los Angeles site are highly unlikely ($p < 0.001$) and may be considered outliers. The same conclusion is valid for concentrations above 130 ppt at the El Monte station ($p < 0.0026$). None of the high values measured at the Dominguez Hills and Riverside sites are likely to be outliers.

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* See Appendix D for a discussion of the lognormality of the concentration distribution.

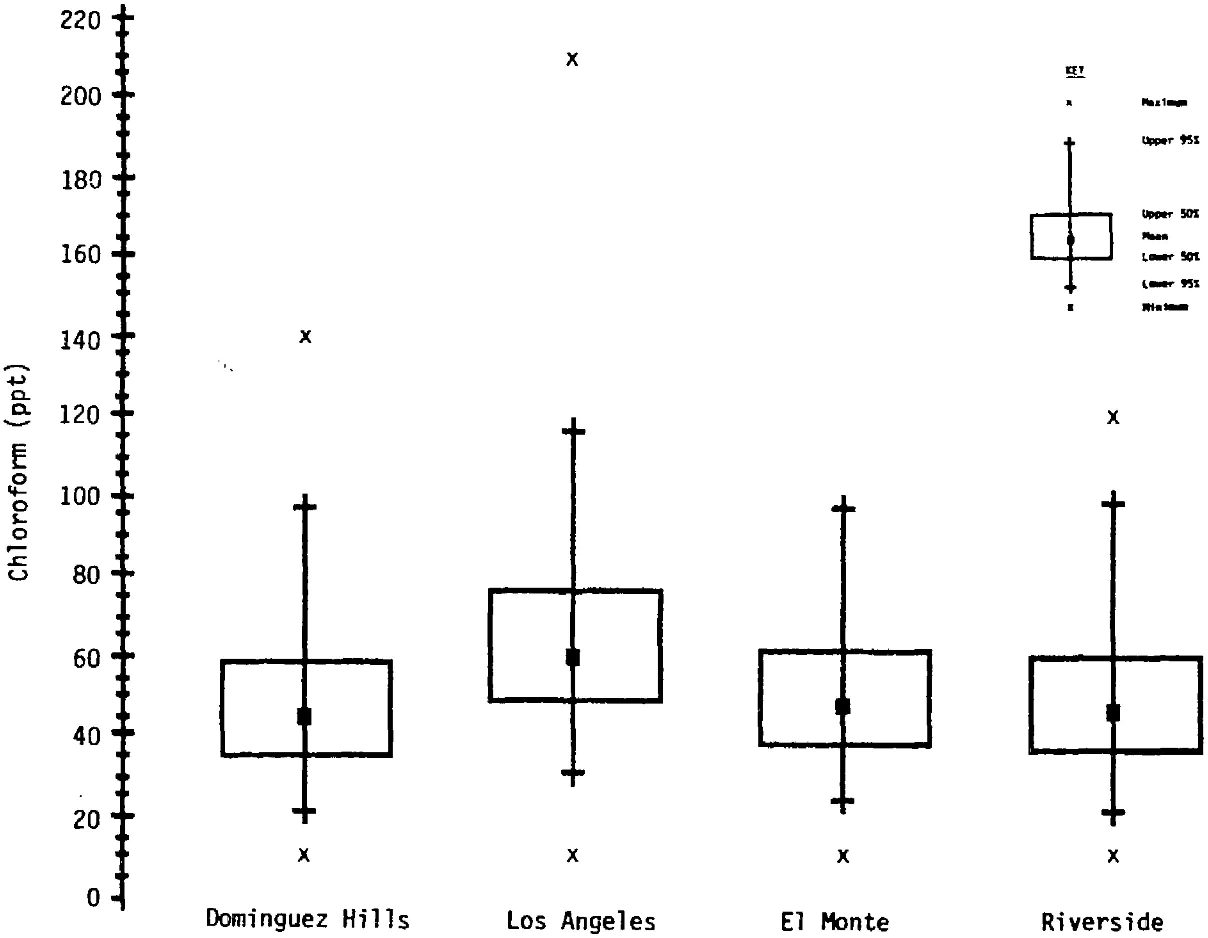


Figure 5.1-2. Distributions of Ambient Chloroform Concentrations at ARB Halogenated Hydrocarbon Monitoring Stations (Calculated by SAIC from Data Provided by McNerny, 1985). Maximum Value at El Monte Was 640 ppt.

5.2 IN-SITU FORMATION PROCESSES

5.2.1 Gas Phase Reactions

The peer-reviewed literature contains conflicting information regarding the production of chloroform in the atmosphere by gas phase reactions. On the one hand, the latest comprehensive review of atmospheric chemistry published by the National Academy of Sciences (1984) states that there are no known reactions leading to the production of chloroform in the atmosphere. On the other hand, several earlier studies and review articles suggest the possibility of chloroform production in the atmosphere by reactions involving the chlorinated olefins trichloroethylene and tetrachloroethylene.

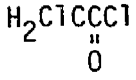
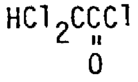
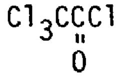
In the discussion presented below, available literature data are reviewed with focus on trichloro- and tetrachloroethylene as possible atmospheric precursors of chloroform. We will first review the "expected" atmospheric chemistry of these compounds, namely that initiated by their reaction with the hydroxyl radical (OH) followed by well-documented free radical reaction pathways. We will then compare the "expected" results to those of actual experimental studies carried out under laboratory conditions, point out agreement and discrepancies, and discuss the relevance of the laboratory studies to atmospheric situations. Finally, reaction pathways other than those initiated by reaction with OH will be discussed with respect to their possible role in atmospheric production of chloroform. A list of the organic compounds discussed in this section is given in Table 5.2-1.

5.2.1.1 Atmospheric Reactions of Chlorinated Ethylenes

Chlorinated ethylenes may be removed from the atmosphere by photolysis (in sunlight) or by reaction with ozone, atomic oxygen, OH, with HO_2, nitrate radicals, or chlorine atoms. Loss by photolysis is negligible under tropospheric conditions. Reactions with NO_3 and with chlorine atoms are

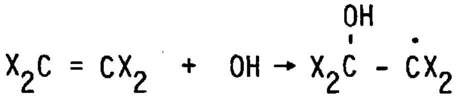
Table 5.2-1

ORGANIC COMPOUNDS DISCUSSED IN SECTION 5.2

Haloalkanes	
Chloroform	$CHCl_3$
Carbon Tetrachloride	CCl_4
Chlorinated Ethylenes	
Vinyl chloride	$H_2C = CHCl$
Vinylidene chloride (1,1-dichloroethylene)	$H_2C = CCl_2$
1,2-dichloroethylene	$HClC = CHCl$
Trichloroethylene	$HClC = CCl_2$
Tetrachloroethylene (perchloroethylene)	$Cl_2C = CCl_2$
Carbonyls	
Phosgene	$Cl_2C = O$
Formyl chloride	$ClHC = O$
Chloroacetyl chloride	 $H_2ClC\underset{\overset{\parallel}{O}}{C}Cl$
Dichloroacetyl chloride	 $HCl_2C\underset{\overset{\parallel}{O}}{C}Cl$
Trichloroacetyl chloride	 $Cl_3C\underset{\overset{\parallel}{O}}{C}Cl$

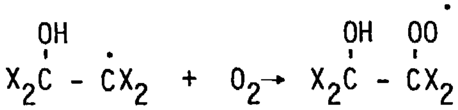
discussed later in this chapter, and their contribution to the atmospheric removal of chlorinated ethylenes is speculative at this time. Available reaction rate constants for ozone, atomic oxygen, and OH are listed in Table 5.2-2. Examination of these rate constants indicates that, under tropospheric conditions, reaction with OH is by far the major removal process for chlorinated ethylenes. The mechanism of this reaction and the corresponding reaction products are as follows.

The initial OH-chlorinated ethylene reaction step involves OH addition to the unsaturated carbon-carbon bond (X = H or Cl):



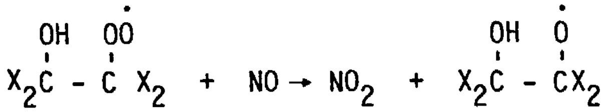
$$X_2C = CX_2 + OH \rightarrow X_2\overset{OH}{C} - \dot{C}X_2 \qquad (5\text{-}1)$$

The alkyl radical thus formed reacts with oxygen to form a peroxy radical:



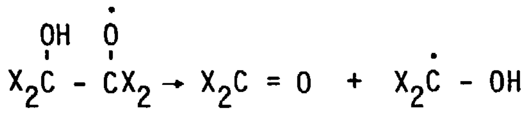
$$X_2\overset{OH}{C} - \dot{C}X_2 + O_2 \rightarrow X_2\overset{OH}{C} - \overset{O\dot{O}}{C}X_2 \qquad (5\text{-}2)$$

In the remote troposphere, where levels of oxides of nitrogen are very low, the peroxy radical is expected to react mainly with HO_2 to form peroxy-type products (Hanst and Gay 1983). This "low-NO_x" chemistry regime is not discussed here since it has little relevance to California air. In urban and rural air, concentrations of oxides of nitrogen are nearly always sufficiently high for the peroxy radical formed in Reaction 5-2 to react mainly (if not exclusively) with nitric oxide:



$$X_2\overset{OH}{C} - \overset{O\dot{O}}{C}X_2 + NO \rightarrow NO_2 + X_2\overset{OH}{C} - \overset{\dot{O}}{C}X_2 \qquad (5\text{-}3)$$

followed by unimolecular decomposition of the alkoxy radical:



$$X_2\overset{OH}{C} - \overset{\dot{O}}{C}X_2 \rightarrow X_2C = O + X_2\dot{C} - OH \qquad (5\text{-}4)$$

Table 5.2-2

RATE CONSTANTS FOR THE REACTION OF CHLORINATED ETHYLENES WITH ATOMIC OXYGEN, OZONE, THE HYDROXYL RADICAL, AND CHLORINE ATOM

(Units: cm^3 $molecule^{-1} sec^{-1}$)

Compound	k_O	k_{O_3}	k_{OH}	k_{Cl}
Ethylene	0.76×10^{-12} (a)	1.4×10^{-18} (b)	7.3×10^{-12} (f)	1.06×10^{-10}(k)
Vinyl Chloride	0.60×10^{-12} (a)	0.14×10^{-18} (c)	6.6×10^{-12} (f)	
1,1-dichloroethylene	-	0.37×10^{-20} (d)	4.0×10^{-12} (g)	
1,2-dichloroethylene	-	-	4.0×10^{-12} (g)	
Trichloroethylene	-	$<3.0 \times 10^{-20}$ (b)	2.2×10^{-12} (h)	5.8×10^{-11} (j)
Tetrachloroethylene	0.80×10^{-13} (j)	$<2.0 \times 10^{-23}$ (e)	0.17×10^{-12} (h)	5.3×10^{-12} (j)
Chloroform (for comparison)	-	-	1.06×10^{-13} (i,k)	1.23×10^{-13} (k)

(a) Gaffney and Levine (1979)
(b) Atkinson et al. (1982)
(c) Gay et al. (1976)
(d) Hull et al. (1973)
(e) Mathias et al. (1974)
(f) Atkinson et al. (1979)
(g) Singh et al. (1981)
(h) Baulch et al. (1982)
(i) Jet Propulsion Laboratory (1981)
(j) Dimitriades et al. (1983) and references therein.
(k) Watson (1977)

and rapid reaction of the -hydroxy alkyl radical with oxygen:

$$X_2\dot{C} - OH \ + \ O_2 \rightarrow HO_2 \ + \ X_2C = O \qquad (5\text{-}5)$$

The above reaction sequence (5-1 through 5-5) can be summarized as follows:

$$X_2\dot{C} = CX_2 \ + \ OH \xrightarrow[\downarrow NO_2]{O_2,NO,O_2} HO_2 \ + \ 2\ X_2C = O \qquad (5\text{-}6)$$

The expected carbonyl products are listed in Table 5.2-3 for each of the chloroethenes. All three carbonyls in turn may react in the atmosphere: formaldehyde by photolysis and by reaction with OH, phosgene by slow photolysis, and formyl chloride due to rapid thermal decomposition to CO + HCl. Note that from the above discussion, no chloroform is expected to form as a product of the OH-chlorinated ethylene reaction.

5.2.1.2 Review of Experimental Studies

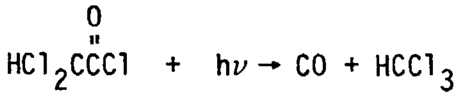
There has been no comprehensive study of the reaction products of chlorinated ethylenes under conditions resembling closely those of rural and urban atmospheres. Singh and Lillian (1975) irradiated tetrachloroethylene in purified air (with no oxides of nitrogen added) and reported phosgene (70-85 percent yield) as a major product along with carbon tetrachloride (~8 percent yield), trace amounts of chloroform, trichloracetyl chloride (no quantitative measurements) and tentatively dichloroacetyl chloride. Reaction mechanisms were not discussed, and the authors stated that "the overall reaction is probably initiated by photolysis of C_2Cl_4 followed by a chlorine-sensitized photooxidation." The experimental conditions employed have limited relevance to ambient air (photolysis only, no NO_x therefore no OH chemistry, unknown and possibly reaction vessel-mediated heterogeneous production and reaction of chlorine atoms). However, the results of Singh and Lillian have been included in discussions of the global atmospheric budgets of carbon tetrachloride (e.g., Singh et al. 1976; National Academy of Sciences, 1978). In the same way, Yung et al. (1975) have speculated on the in-situ production of chloroform from tetrachloroethylene, by assuming that the dichloroacetyl chloride

Table 5.2-3

EXPECTED PRODUCTS OF THE OH-INITIATED ATMOSPHERIC OXIDATION OF CHLORINATED ETHYLENES

	Carbonyl Products		
Compound	Formaldehyde $H_2C=O$	Formyl Chloride $HClC=O$	Phosgene $Cl_2C=O$
Ethylene	X		
Vinyl chloride	X	X	
1,1-dichloroethylene	X		X
1,2-dichloroethylene		X	
Trichloroethylene		X	X
Tetrachloroethylene			X

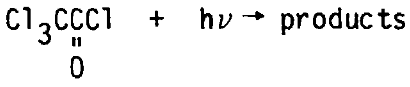
tentatively observed in the experiments of Singh and Lilian (1975) would, in turn, photolyze to yield chloroform and carbon monoxide:



$$HCl_2C\overset{O}{\overset{\|}{C}}Cl + h\nu \rightarrow CO + HCCl_3 \qquad (5\text{-}7)$$

While Reaction 7 is quite plausible, the formation of dichloroacetyl chloride remains to be explained, both in the experiments of Singh and Lillian, which did not involve OH chemistry, and in the OH-initiated reactions (5-1 through 5-6) discussed above.

Unfortunately, few detailed product studies have been carried out under conditions where OH chemistry should be predominant. These studies are summarized in Table 5.2-4. Joshi and Bufalini (1978) reported $Cl_2C = CCl_2$, O_3 and NO_x concentration-time profiles in only one experiment, and did not report on reaction products and mechanisms. Lillian et al. (1975) identified phosgene as the major reaction product (60 percent yield on a chlorine basis). Neither chloroform nor dichloroacetaldehyde were reported as reaction products. Dimitriades et al. (1983) also found no production of chloroform from perchloroethylene. They also studied the photolysis of trichloroacetyl chloride:



$$Cl_3C\underset{O}{\underset{\|}{C}}Cl + h\nu \rightarrow \text{products}$$

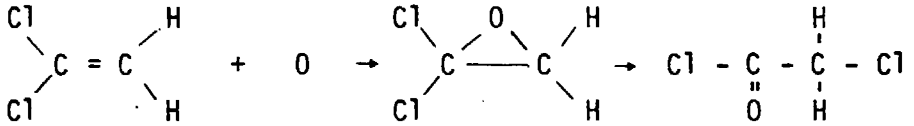
and found carbon monoxide as the only product. Phosgene was formed, as expected, upon addition of chlorine. Gay et al. (1976) studied all five chlorinated ethylenes and reported a number of carbonyls, chloroacetyl chlorides, and related reaction products. Trichloroethylene yielded dichloroacetyl chloride as a major product. However, chloroform, postulated by Yung et al. (1975) to form upon photolysis of dichloroacetyl chloride (Reaction 5-7), was not observed. Gay et al. interpreted their results in terms of reactions involving atomic oxygen and ozone, but not OH. In particular, they postulated a bridged intermediate (epoxide) to explain the observed 1,2-chlorine atom transfer, as is shown here for vinylidene chloride:

Table 5.2-4

SUMMARY OF LABORATORY STUDIES RELEVANT TO IN-SITU PRODUCTION OF CHLOROFORM: IRRADIATED ORGANIC-NO_x MIXTURES IN PURE AIR

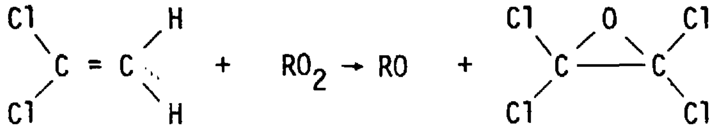
Reference	Precursors	Initial Concentrations Precursor (ppm)	NO_x (ppm)	Products	Chloroform Observed
Joshi and Bufalini (1978)	Tetrachloroethylene	4	0.2	None reported	No
Lillian et al. (1975)	Tetrachloroethylene	0.8	0.5	$COCl_2$	No
Dimitriades et al. (1983)	Tetrachloroethylene	2 - 9.2	0.5	CO, $COCl_2$[a]	No
	Trichloroethylene	2 - 2.5	0.5	None reported	No
Gay et al. (1976)	Vinyl chloride	4.6	1.5	CO, HCl, HCHO, formyl chloride	No[b]
	1,1-dichloroethylene	4.8	2.2	CO, HCl, HCHO, $COCl_2$, chloroacetyl chloride	No[b]
	1,2-dichloroethylene	5.0	1.7	CO, HCl, formyl chloride	No[b]
	Trichloroethylene	3.4	1.3	$COCl_2$, formyl chloride, dichloroacetyl chloride	No
	Tetrachloroethylene	5.0	1.8	CO, HCl, $COCl_2$, trichloroacetyl chloride	No

[a] In experiments with added trichloroacetyl chloride.
[b] No chloroform can be produced from vinyl chloride and dichloroethylenes.



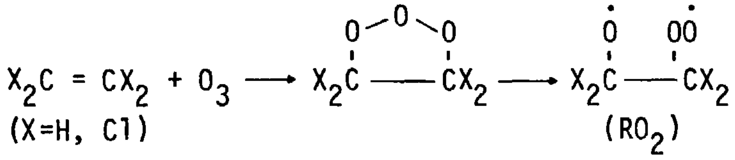
(5-8)

Gay, et al. also identified chloroacetyl chloride as a product of the reaction of ozone with vinyl chloride in the dark. They therefore postulated, in agreement with an earlier suggestion of Hull et al. (1973), that Reaction 5-8 may also be involved in the ozone-chloroethene reaction, e.g.:



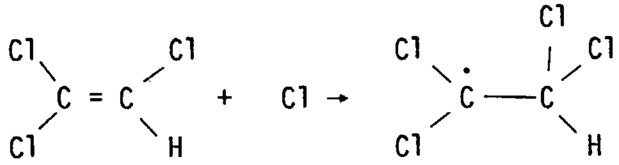
(5-8a)

where RO_2 are peroxy radicals including the Criegee biradicals formed following addition of ozone to the unsaturated carbon-carbon bond:

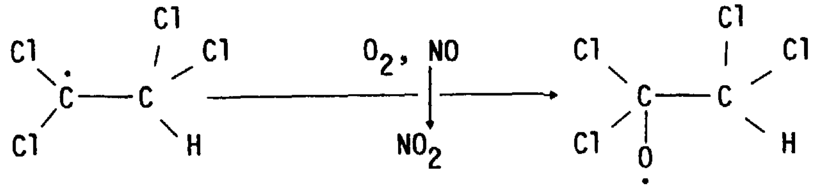


(5-9)

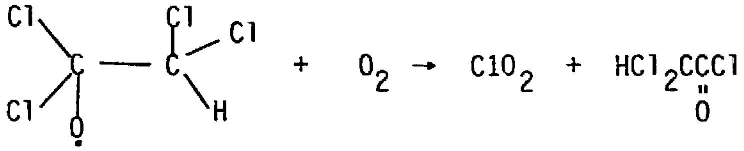
It should be noted that, even though Gay et al. did not discuss OH as a major reacting species in their system, their carbonyl products are entirely consistent with the "expected" OH chemistry discussed earlier, i.e., Reactions 5-1 through 5-6. Furthermore, the acetyl chloride products they observed can also be explained by chlorine atom chemistry, e.g.:



(5-10)



(5-11)



(5-12)

The above sequence, initiated by the rapid addition of Cl atoms, yields dichloroacetylchloride from trichloroethylene and may represent a valid alternative to the epoxide/1,2-chlorine atom transfer sequence of Gay et al. (Reactions 5-8 and/or 5-8a and 5-9).

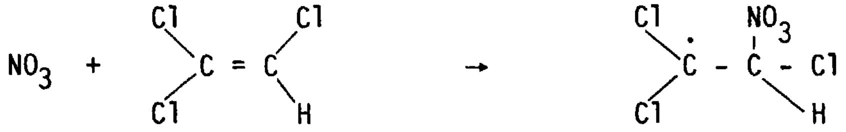
The literature data described in the preceding paragraph can be summarized as follows:

- Chloroform was not reported as a reaction product in any of the studies involving irradiated chloroethene - NO_x mixtures in air.
- Phosgene, the "expected" OH chemistry reaction product, was indeed observed as a major product in all studies.
- Dichloroacetyl chloride, which could photolyze in sunlight to yield chloroform, was reported as a major product from trichloroethylene in the study of Gay, et al.
- Chloroacetyl chlorides are not expected to form in the OH-initiated reaction sequence. Either the "normal" olefin-OH chemistry does not entirely apply to chloroethenes, or artifact reactions (chlorine atom chemistry, heterogeneous wall effects, etc.) masked the OH chemistry in some of the studies cited.
- Formation of chloroform by gas phase reactions involving OH and trichloro and tetrachloroethylene is unlikely but cannot be ruled out at this time; there is a need for additional studies of reaction products (including chloroform) from chlorinated ethylenes under conditions of OH-initiated chemistry relevant to the atmosphere.

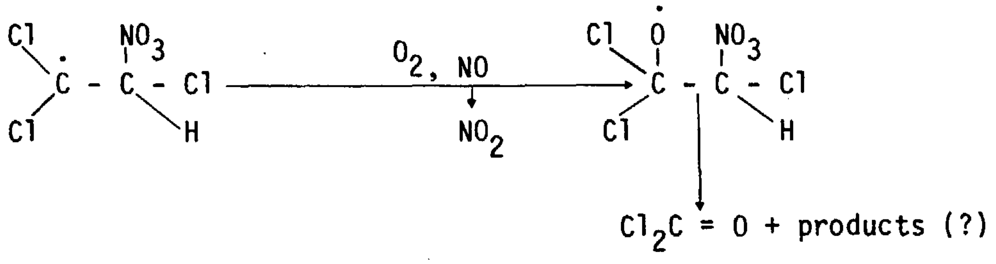
5.2.1.3 Other Gas Phase Reactions

The reaction of chlorine atoms with chloroethylenes has not been studied in detail, but most likely involves pathways such as Reactions 5-10 through 5-12 mentioned above. While there is, to our knowledge, no detailed budget for chlorine in California air, and while many sources and reactions may be involved in the production of atmospheric chlorine, chlorine atoms are not expected to compete with OH radicals under most atmospheric conditions. An important exception, documented in previous studies (Grosjean, 1985; Hov, 1985) concerns industrial areas with significant chlorine emissions. In this case, chlorine has been shown to accelerate substantially the process of smog formation, including conversion of NO to NO_2 and formation of ozone and of peroxyacetyl nitrate (PAN). In the absence of reliable information, we will assume that chlorine atom chemistry is of negligible importance in California air.

Reaction with the nitrate radical (NO_3) may also constitute a removal process for chlorinated ethylenes at night (NO_3 photolyzes rapidly in sunlight). No rate constants are available for the NO_3-chloroethenes reactions, and reaction mechanisms are unknown. A probable sequence may be initiated by addition of NO_3 to the unsaturated carbon-carbon bond, e.g.:


(5-13)

followed by:


(5-14)

Thus, nighttime formation and accumulation of phosgene could be expected from such a speculative reaction sequences. No chloroform is expected to be produced in the NO_3-chloroethenes reactions.

Another sequence of reactions possibly leading to chloroform production would involve the reaction of methane with chlorine atoms:

$$CH_4 + Cl \rightarrow CH_3Cl \xrightarrow{Cl} CH_2Cl_2 \xrightarrow{Cl} CHCl_3 \xrightarrow{Cl} CCl_4 \qquad (5\text{-}15)$$

Lovelock (1974) mentioned "preliminary laboratory experiments in glass vessels in which the reaction between CH_4 and Cl_2 in air, each at a concentration of 10^{-4} (100 ppm), results in the production of small, but significant, quantities of CCl_4". Production of chloroform was not mentioned. The experiments of Lovelock most likely involved reaction vessel-promoted (heterogeneous) reactions, since the gas phase chlorination of methane (reaction sequence 5-15) is kinetically unfavorable (NAS, 1978). In fact, the reaction of chlorine atoms with alkanes, including methane, proceeds exclusively by hydrogen atom abstraction, e.g.:

$$CH_4 + Cl \rightarrow \dot{C}H_3 + HCl \qquad (5\text{-}16)$$

followed by reactions of the methyl radical.

5.2.2 Aqueous Phase Reactions

Chloroform has been identified in California rainwater (Su and Goldberg, 1976) at concentrations of 17 ± 13 μg/L. The presence of chloroform in hydrometeors may be due to scavenging of gas phase chloroform or to in-situ formation. In this section, we consider the possibility of chloroform production by reactions taking place in the aqueous phase, which includes aquated aerosols, cloudwater, fog and rain. We will first describe chloroform formation in the bulk aqueous phase, with emphasis on trihalomethane production during water chlorination. We will then examine the possibility that similar reactions may produce choloroform in hydrometeors and/or aerosol droplets.

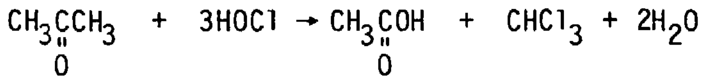
5.2.2.1 Halomethane Production in Water Chlorination

It is well established that the oxidation of many organic contaminants during water chlorination yields trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) as reaction products. Considering the high volatility and low aqueous solubility of chloroform, water chlorination is considered to be a major source of chloroform release in the atmosphere (this issue is discussed in detail in Section 4.2.1).

While the chemical pathways for chloroform production are complex and are not fully understood at the present time, studies conducted with "model" compounds as well as with complex mixtures of organics, including humic acid and sediments, have shown that many classes of organic compounds may yield chloroform upon water chlorination (e.g., Amy et al. 1984; Lin and Carlson, 1984; Lin et al. 1984; Uhler and Means, 1985, de Leer et al., 1985). At pH 3-7, aqueous chlorine consists essentially of HOCl (Aoki and Munemori 1983):

$$\mathrm{Cl_2 + H_2O \rightarrow HOCl + HCl} \qquad (5\text{-}17)$$

which is a strong oxidant. Aliphatic organic molecules may simply react with HOCl by chlorine atom substitution, as is shown below for a simple carbonyl, acetone (Jolley, 1982):



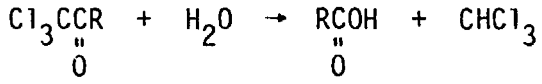
$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}CH_3 + 3HOCl \rightarrow CH_3\underset{\underset{O}{\|}}{C}OH + CHCl_3 + 2H_2O}$$

(5-18)

or, more generally for carbonyl - containing aliphatic organics (Yung et al., 1975):

$$\mathrm{CH_3\underset{\underset{O}{\|}}{C}R + 3HOCl \rightarrow Cl_3\underset{\underset{O}{\|}}{C}CR + 3H_2O}$$

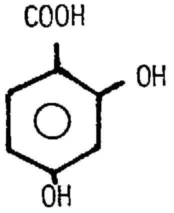
(5-19a)

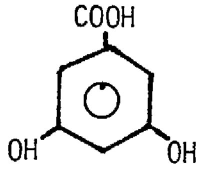


$$\mathrm{Cl_3\underset{\underset{O}{\|}}{C}CR + H_2O \rightarrow R\underset{\underset{O}{\|}}{C}OH + CHCl_3}$$

(5-19b)

For aromatic molecules, such as the hydroxybenzoic acids often used as models for studies of humic acid, production of chloroform first requires opening of the aromatic ring. This is generally achieved through oxidation sequences initiated by reaction with HOCl and/or chlorine atoms, followed by hydrolysis of the aliphatic products to yield chloroform and the corresponding carboxylic acids (see reactions 5-18 and 5-19). Lin et al. (1984) and de Leer et al. (1985) have carried out comprehensive studies of chloroform production from 2,4-dihydroxy and 3,5-dihydroxy benzoic acid, respectively:





and their articles should be consulted for details of the reaction pathways. The study of de Leer et al. (1985) also involved chlorination of humic acid, and included the identification of about 200 reaction products, of which at least 12 compounds (all chlorinated carboxylic acids) were precursors of chloroform.

The reaction mechanisms briefly summarized above include chlorine addition, substitution, oxidation and hydrolysis pathways. In addition, HOCl photolyzes readily in the gas phase (Spence et al., 1980) as well as in water (Oliver and Carey, 1977) to yield OH radicals and chlorine atoms:

$$HOCl + h\nu \rightarrow \overset{\bullet}{OH} + \overset{\bullet}{Cl} \qquad (5\text{-}20)$$

Thus, as demonstrated by Oliver and Carey (1977) for several organic compounds, chlorinated organics, including chloroform, can be produced photochemically by sunlight in water being disinfected with chlorine.

5.2.2.2 Application to Hydrometeors

For the following reasons, it is tempting to speculate that chloroform may be formed in fog, cloud, rainwater and/or aerosol droplets by reactions identical to those discussed above for water chlorination processes.

- The acidity of California fog, rainwater and cloudwater (as has been mentioned by Munger et al., 1983) includes the range pH 3-7, which is optimal for chlorine to be present as HOCl.
- Aliphatic organics, including carbonyls which react readily with HOCl to yield chloroform (Reactions 5-18, 5-19), are ubiquitous and abundant in California hydrometeors (see, for example Grosjean and Wright, 1983).

- Many other organics, including potential chloroform precursors such as polar aromatic compounds, have also been identified in aerosols and hydrometeors, both in California (e.g., Schuetzle et al., 1975; Kawamura and Kaplan, 1983) and elsewhere (e.g., Nojima et al., 1976; Ligocki et al., 1985).
- Exposure to sunlight will obviously favor photochlorination processes in hydrometeors and aerosol droplets.

From the above considerations, aqueous phase production of chloroform could be considered as a possible atmospheric pathway, provided of course that enough chlorine is available. Unfortunately, there is no information concerning the presence and abundance of reactive chlorine species (Cl_2, $\dot{Cl}$, ClO_2, etc.) in atmospheric droplets. As for the corresponding gas phase reactions involving chlorine-initiated pathways, liquid phase chlorine reactions, including chloroform production, must remain untested hypotheses until atmospheric chlorine data become available.

5.3 REMOVAL PROCESSES

5.3.1 Homogeneous Gas Phase Reactions

5.3.1 Thermal Decomposition

Chloroform is thermally stable at ambient temperatures (NAS, 1978). The high temperature (300-800^{o}C) thermal decomposition of chloroform has recently been studied by Hall et al. (1985). Pentachloroethane (C_2HCl_5) and tetrachloroethylene ($Cl_2C=CCl_2$) are the major decomposition products, and are probably formed via reactions of a dichlorocarbene intermediate ($:CCl_2$):

$$CHCl_3 \rightarrow HCl + :CCl_2 \quad (5\text{-}21)$$

$$:CCl_2 + CHCl_3 \rightarrow C_2HCl_5 \quad (5\text{-}22)$$

$$2\ :CCl_2 \rightarrow C_2Cl_4 \quad (5\text{-}23)$$

These reactions are relevant to the incineration of hazardous wastes and to the regeneration of activated carbon used for filtration of drinking water and industrial wastewater. Large quantities of chloroform are expected to be converted to C_2HCl_5 and C_2Cl_4 in these operations. If released into the atmosphere, both C_2Cl_4 and C_2HCl_5 will react with OH to produce phosgene.

5.3.1.2 Photolysis

Chloroform absorbs radiation only well below the tropospheric cut-off of 290 nm (Lillian et al., 1975).

5.3.1.3 Reactions With O, O_3, OH and HO_2

Reactions of chloroform with O, O_3 and HO_2 are of negligible atmospheric importance (Singh et al., 1981). Reaction with the hydroxyl radical:

$$OH + CHCl_3 \rightarrow H_2O + \dot{C}Cl_3 \qquad (5\text{-}24)$$

is a major pathway for removal of atmospheric chloroform. The recommended value for the reaction rate constant at 298°K is $k = 1.06 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} (Watson, 1977; Jet Propulsion Laboratory, 1981). Because OH concentrations in urban air are expected to exhibit strong diurnal variations (OH radical concentrations drop to negligible levels at night, and vary during daytime with sunlight intensity and with photochemical activity), removal of chloroform is also expected to exhibit substantial diurnal variations (including no loss at night). The absence of OH-based chloroform removal mechanisms at night is consistent with the findings of Singh et al. (1981, 1982) that daily chloroform peaks occur at night. (See Section 5.1.) Assuming 16 hours of daylight per day, the average atmospheric half-life of chloroform will be ~80 days for a typical average OH concentration of 10^6 molecules cm^{-3}.

5.3.1.4 Reaction With the Nitrate Radical

The nitrate radical (NO_3) has been shown to react at appreciable rates with aldehydes, olefins and phenols, thus providing a possible nighttime pathway for the atmospheric removal of these hydrocarbons (e.g. Atkinson et al., 1984). No rate constants are available for the reaction of NO_3 with alkanes or haloalkanes including chloroform, but these reactions are expected to be very slow (i.e., $k << 10^{-17}$ cm^3 $molecule^{-1}$ sec^{-1}) and of negligible atmospheric importance for chloroform removal.

5.3.1.5 Reaction With Chlorine Atoms

This reaction, like Reaction 5-24 of OH with chloroform, involves hydrogen atom abstraction:

$$Cl + CHCl_3 \rightarrow HCl + \dot{C}Cl_3 \qquad (5\text{-}25)$$

The recommended rate constant for this reaction at 298°K is $k = (1.23 \pm 0.34) \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} (Watson, 1977), where the large uncertainty reflects the spread of individual literature values. With k_{Cl}/k_{OH} ~1.0 - 1.5, removal of chloroform by reaction with chlorine will compete with removal by reaction with OH only if ambient levels of chlorine are comparable to ambient levels of OH, e.g., 10^6 atoms/cm^3 (~0.1 ppt). As pointed out in Section 5.2, ambient levels of chlorine are not known, but are assumed to be substantially lower than the corresponding OH levels. Thus, removal of chloroform by reaction with chlorine is deemed negligible, but a definitive conclusion must await the availability of ambient chlorine data.

5.3.1.6 Products of the OH-Chloroform Reaction

Perhaps surprisingly, no experimental study focusing on products of the OH-chloroform reaction could be found in the literature. Joshi and Bufalini (1978) reported concentration-time profiles for chloroform, NO, NO_2 and ozone in one smog chamber experiment involving irradiation of 4 ppm chloroform, 0.17 ppm NO and 0.02 ppm NO_2 in air. Products (other than ozone) and mechanisms were not discussed. Cox et al. (1976) irradiated mixtures of HONO (as a source of OH) and halocarbons, including chloroform, in air but reported only on kinetic data with no attempt to identify reaction products. Spence et al. (1976) irradiated mixtures of chlorine (2-5 ppm) and chloroform (4-20 ppm) in air, with no oxides of nitrogen added. They observed phosgene as the dominant reaction product, accounting for 90 percent of the reacted chloroform. The study of Spence et al., while providing valuable information concerning the chlorine-chloroform reaction, is not entirely relevant to the atmosphere since NO_x were not included in these experiments.

5.3.1.7 Mechanism of the OH-Chloroform Reaction

The initial step, common to the OH-initiated (Reaction 5-24) and chlorine-initiated (Reaction 5-25) sequences, involves hydrogen atom abstraction:

$$OH + CHCl_3 \rightarrow H_2O + \dot{C}Cl_3 \qquad (5\text{-}24)$$

followed by reaction of the trichloromethyl radical with oxygen:

$$Cl_3\dot{C} + O_2 \rightarrow Cl_3C\dot{O}_2 \qquad (5\text{-}26)$$

and by reaction of the peroxy radical Cl_3CO_2 with nitric oxide:

$$Cl_3C\dot{O}_2 + NO \rightarrow Cl_3C\dot{O} + NO_2 \qquad (5\text{-}27)$$

The fate of the alkoxy radical $Cl_3\dot{C}O$ is not certain at this time. By analogy with well-documented reactions of other alkoxy radicals, it is expected to yield phosgene and chlorine atoms or phosgene and ClO_2, the two pathways being essentially equivalent:

$$\begin{tikzcd}[column sep=small] Cl_3\dot{C}O \arrow[r] & Cl_2C{=}O & + & \dot{C}l \arrow[d, "O_2"] & (5\text{-}28a) \\ Cl_3\dot{C}O \arrow[r, "O_2"] & Cl_2C{=}O & + & Cl\dot{O}_2 & (5\text{-}28b) \end{tikzcd}$$

Thus, phosgene is the only expected product of the OH-chloroform reaction under atmospheric conditions. Phosgene is a highly toxic compound; it is stable in the atmosphere, and is only removed slowly by photolysis (Singh, 1976), presumably to form carbon monoxide and chlorine atoms. As discussed in Section 5.2.1, phosgene is also expected to form in urban air from several chlorinated compounds besides chloroform. Phosgene has been monitored at several locations in California with typical values of ~50 ppt (Singh, 1976; Singh et al., 1981).

5.3.2 Liquid Phase Reactions

As noted earlier, chloroform has been measured in California rainwater at concentrations of 17 $\pm$ 13 μg/L (Su and Goldberg 1976). There appears to be no data on chloroform concentrations in fog or in cloudwater. Many organics, such as carbonyls are present in urban fog at concentrations substantially higher than those in rainwater (Grosjean and Wright, 1983), and this may by the case for chloroform as well. Examination of recent data on Henry's law constants for chloroform and other trihalomethanes (e.g., McKay and Shiu, 1981; Nicholson et al., 1984) indicates that hydrometeor scavenging of chloroform is not solubility-limited.

Possible reactions of chloroform in hydrometeors include hydrolysis, photodecomposition, and reactions with free radicals (OH), atoms (Cl) and other oxidants (e.g. ozone and hydrogen peroxide). Of these, hydrolysis (e.g., Radding et al., 1977) and photolysis (Ollis, 1985) are negligible. However, rapid photodecomposition of chloroform has been achieved by irradiation of aqueous solutions of chloroform (120 ppm) in the presence of TiO_2 as oxidation catalyst (Ollis, 1985). The "mineralization" of chloroform was complete under the conditions studied and had the following overall stoichiometry:

$$CHCl_3 + H_2O + 1/2O_2 \rightarrow CO_2 + 3HCl \qquad (5\text{-}29)$$

Thus, some photodecomposition of chloroform may take place in droplets containing metal oxides (e.g., scavenged particles) which may act as oxidation catalysts.

The reaction of chloroform with the hydroxyl radical in the aqueous phase has not been documented. Gusten et al. (1981) have shown that gas phase and aqueous phase OH reaction rate constants are well correlated for a number of organic compounds. Using the known value of 1.0 x 10^{-13} cm^3 molecule^{-1}sec^{-1} for the gas phase reaction and the correlation of Gusten et al. (1981), we estimate a rate constant of ~0.8 x 10^8 liter mol^{-1}sec^{-1} for the reaction of OH with chloroform in water. From this low value, it appears that reaction with OH will not be of importance in removing chloroform from hydrometeors.

Removal by reaction with chlorine is speculative at this time. As discussed earlier, photochlorination of organics (Oliver and Carey, 1977) may be relevant to hydrometeor concentrations of reactive chlorine species (Cl_2, HOCl, etc.).

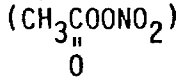
Reactions with oxidants including ozone and hydrogen peroxide, may also be relevant to the hydrometeor chemistry of chloroform. The presence of hydrogen peroxide in California fogwater and rainwater is well documented (e.g., Munger et al., 1983). Extrapolation of bulk liquid phase kinetic data suggests that slow oxidation of chloroform to $COCl_2$ and/or CO_2 + HCl may take place in hydrometeors.

5.3.3 Dry Deposition of Chloroform

In a recent comprehensive study of organic pollutants in the atmosphere of the Netherlands, Guicherit and Schulting (1985) attempted to estimate dry decomposition fluxes for many organics, including chloroform. While dry deposition flux calculations are straightforward, considerable uncertainties are associated with the selection of appropriate dry deposition velocities for volatile organics. Guicherit and Schulting (1985) used an arbitrary value of 0.1 cm/sec for volatile organic compounds including chloroform. They also pointed out that much lower values had been used by Cupitt (1980) in earlier estimates of deposition velocities for halocarbons. However, deposition velocities are now available for a number of atmospheric pollutants and some values for polar molecules are as high as ~3 cm/sec. (See compilation in Table 5.3-1). Values in the range 0.01 to 3.0 cm/sec correspond to atmospheric residence times of ~3 to 900 days, as compared to ~100 days for gas phase removal of chloroform initiated by reaction with OH.

Table 5.3-1

DRY DEPOSITION VELOCITIES FOR SELECTED ATMOSPHERIC POLLUTANTS

Compound	Deposition Velocity (cm/sec)	Substrate (when specified)	Reference
Formaldehyde (HCHO)	0.4 - 1.0	=	Lowe and Schmidt 1983; Zafiriou et al., 1980
Acetone (CH_3COCH_3)	up to 3.1[a]	clay soil	Judeikis, 1982
Methyl sulfide (CH_3SCH_3)	0.6 - 0.28[a]	clay and sand	Judeikis and Wren, 1977
Hydrogen sulfide (H_2S)	0.015	clay and sand	Judeikis and Wren, 1977
Sulfur dioxide (SO_2)	0.52 ± 0.16	nylon	Japar et al., 1985[b]
Nitric acid ($HONO_2$)	2.5 ± 1.5 2.5 ± 0.9	nylon grass	Japar et al., 1985[b] Huebert and Robert, 1985
Ozone (O_3)	0.4 to 1.6	grass and soil	Garland and Penkett, 1976
Peroxyacetyl nitrate  $(CH_3\overset{}{\underset{\overset{\parallel}{O}}{C}}OONO_2)$	0.25	grass and soil	Garland and Penkett, 1976
Methyl iodide	10^{-2} to 10^{-4}	-	Cupitt, 1980
Carbon tetrachloride	$\leq 10^{-4}$ (estimated)	-	Cupitt, 1980

[a] Decreased with increased humidity.

[b] We thank Dr. Robert A. Gorse, Jr. for a preprint of this work prior to publication.

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