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

EXECUTIVE SUMMARY

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DISCLAIMER

1.0

INTRODUCTION AND BACKGROUND

1.1 PURPOSE AND OBJECTIVES OF THE STUDY

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 placed among the top 11 carcinogens recommended for source testing and ambient sampling. Although some source tests for chloroform were subsequently conducted, and estimates of emissions in the South Coast Air Basin (SCAB) have been made, very little was 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.

1.2 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.

1.2.1 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. Chloroform emission sources investigated were: 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.

1.2.2 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.

1.2.3 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.

1.2.4 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.

1.2.5 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.

1.2.6 Laboratory Experimentation

Possible in-situ formation of chloroform from trichloroethylene and the atmospheric persistence of chloroform in polluted air were studied by DGA. Experiments included sunlight irradiation of TCE-NO_x and chloroform-NO_x mixtures in a Teflon reaction chamber and real-time measurement of changes in reactant and product concentrations.

1.2.7 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.

2.0

FINDINGS AND CONCLUSIONS

2.1 EMISSION SOURCES

2.1.1 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) To date, chloroform has been detected in only one genus of seaweed, Asparagopsis, including a species from the Gulf of California, A. taxiformis. 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. No data on rates of biogenic chloroform production or release to seawater were found.

(5) 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.

2.1.2 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.

2.1.2.1 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 derive an emission factor for cooling tower chlorination, we first estimated a likely chlorine dose rate for 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 2.1.2.2) 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 2.5.2) 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.

2.1.2.2 Transfer of Chloroform From Water to Air

Dissolved chloroform is transferred rapidly and thoroughly to the atmosphere. In laboratory experiments in which chloroform was allowed to evaporate into still air, its half life in solution was about 20 minutes. The flow of air across the water surface, as would occur under actual conditions, would increase the evaporation rate significantly.

2.1.2.3 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 survey findings were:

(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

Only three facilities in the SCAB were confirmed as operating pulp and paper manufacturing plants. From their 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. Since chloroprene or other chlorinated rubber manufacturers are not located in California, chloroform emissions from this source are zero.

2.1.2.4 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 detection limit was 9 ppb.)

(4) Recent federal regulations which reduced 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.

2.1.2.5 Emissions From Swimming Pool Chlorination

(1) Through source tests on a residential swimming pool, we estimated emission flux rates of 12 μg/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 x 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 μg/m^2-min.

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

2.1.2.6 Other Indirect Sources

Tobacco Smoke

Our literature review found only one attempt to determine whether chloroform was generated by cigarette smoking. No chloroform was found. 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, therefore, may substantially underestimate actual emissions from liquid bleach.

2.1.3 Emissions From Consumptive Use

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

2.1.4 Emissions From Nonconsumptive Use

2.1.4.1 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.

2.1.4.2 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 lab reporting some use, and 4 liters per laboratory 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) At the 95-percent confidence level, an upper bound for emissions from this source is 9.5 tons/yr.

2.1.4.3 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.

2.1.4.4 Contamination of Chlorinated Products

Chloroform may be present as a minor contaminant in methyl chloride, methylene chloride, and carbon tetrachloride. Because nationwide releases of $CHCl_3$ via product contamination were only about 7 tons per year, it is unlikely that this mode would be important in the SCAB.

2.1.5 Emission Summary

Table 2.1-1 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 tons (340 metric tons) per year.

Table 2.1-1

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.

(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.

2.2 ATMOSPHERIC CONCENTRATIONS AND REACTIONS

2.2.1 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 2.4.

(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.

(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. (Tests of normality are discussed in Appendix D of the main report.)

(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.

2.2.2 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 2.6.

2.2.2.1 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.

2.2.2.2 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.

2.2.3 Removal Processes

2.2.3.1 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.

2.2.3.2 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.

2.2.3.3 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.

2.3 REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES

2.3.1 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.

2.3.2 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.

2.3.3 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.

2.4 AMBIENT SAMPLING

2.4.1 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.

2.4.2 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.

2.4.3 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 2.4-1.)

(2) Results of the ambient mobile sampling are summarized in Table 2.4-1. 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.

(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.

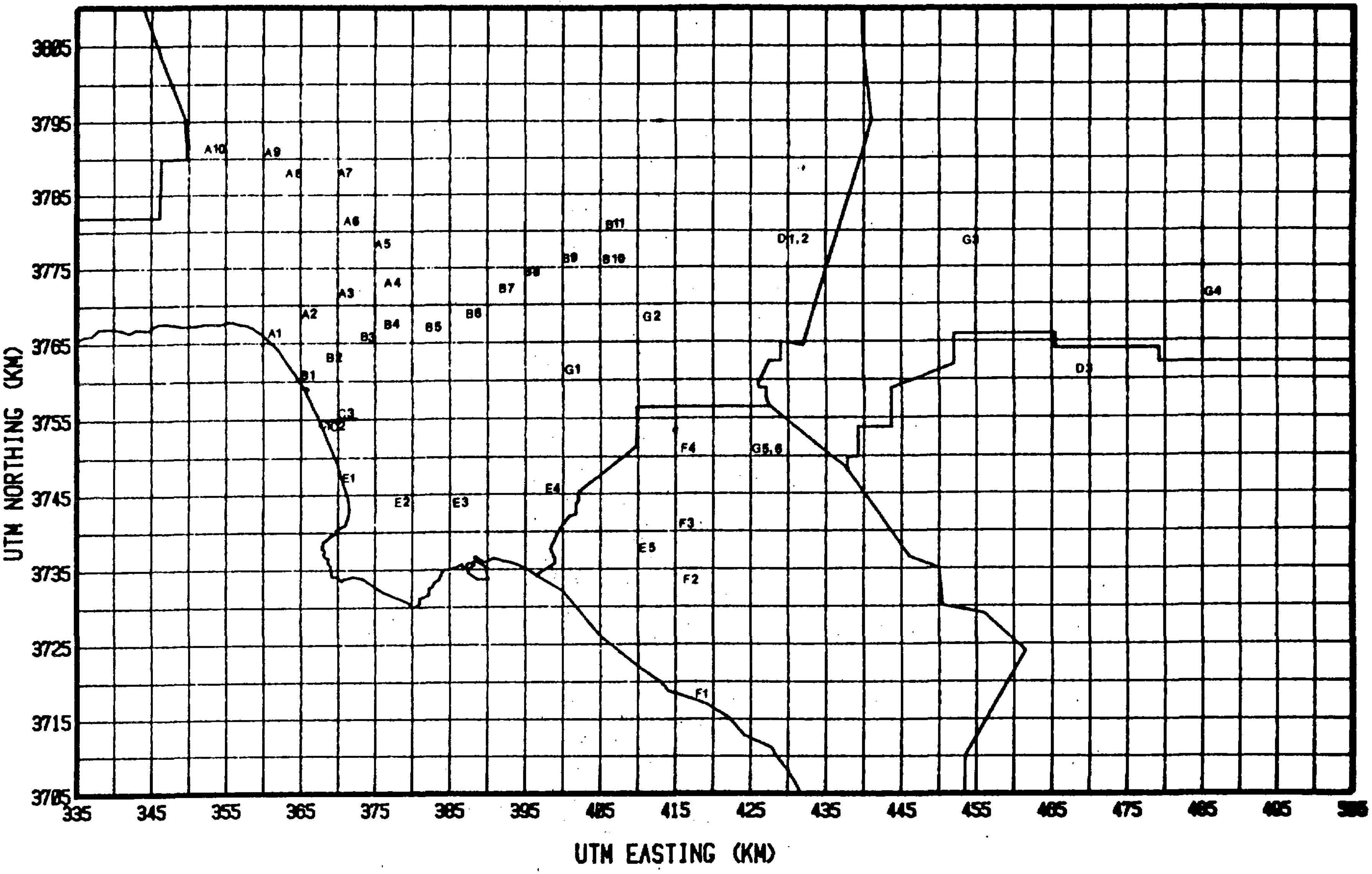


Figure 2.4-1. Locations of Mobile Sampling Sites.

Table 2.4-1

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]	32	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.

2.4.4 Marine Air and Water Sampling

Air and 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.

2.4.4.1 Marine Air Sampling Results

(1) Results of the air sampling are presented in Table 2.4-1. 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).

2.4.4.2 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 2.4-2, 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.

Table 2.4-2

CONCENTRATIONS OF HALOCARBONS IN MARINE AIR, SOUTH COAST AIR BASIN

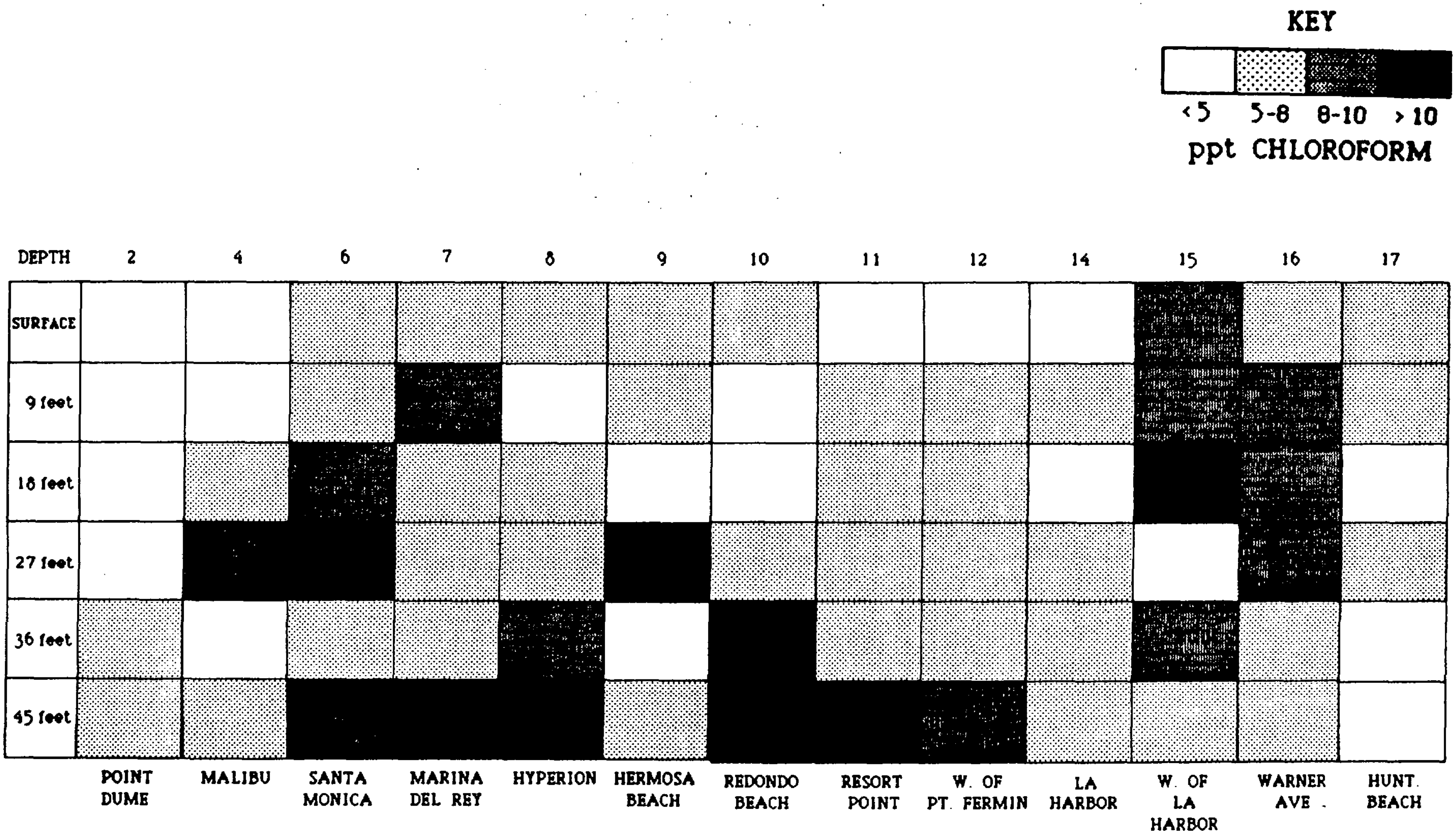
(All concentrations in ppt)

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



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 2.4-2. Distribution of Chloroform Concentrations With Depth, by Sampling Point.

2.4.4.3 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.

2.5 EMISSIONS TESTING

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

2.5.1.1 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.

2.5.1.2 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.

2.5.2 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.

2.6 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 experiments 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 (i.e. moles $CHCl_3$ per mole 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.

2.7 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.

2.7.1 General Results

(1) The modeled area included the entire South Coast Air Basin. Receptor points were the locations of the ARB monitoring stations at Dominguez Hills, El Monte, Los Angeles and Riverside.

(2) Modeled hourly concentrations at the four receptors were well within the ranges reported in Section 2.2.1 and measured by SAIC as part of this project.

(3) 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.

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

(5) 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.

(6) 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.

2.7.2 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.

2.7.3 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.

2.7.4 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 2.2.3. 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.

3.0

RECOMMENDATIONS

3.1 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.

3.2 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.