6.0

REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES

As will be discussed in the next two chapters, an extensive program of ambient sampling and emissions testing was conducted in Phase II of this project. In order to develop efficient plans for this field research, we reviewed techniques for sampling and analyzing air and water for chloroform and other halogenated hydrocarbons. Methods for ambient air sampling and analysis are described and evaluated in Sections 6.1 and 6.2, respectively. We have also reviewed techniques for collecting and analyzing samples of municipal drinking water, seawater, and wastewater; the results of our review are presented in Section 6.3. The emissions tests conducted in Phase II involved the same types of sampling and analytical techniques as were used for the ambient sampling. They are therefore not discussed in this chapter.

6.1 AIR SAMPLING

A variety of sampling and analytical techniques have been used in the last 20 years to characterize the ambient atmosphere for its volatile organic compound content. Generally these methods have involved collecting and concentrating the compounds of interest using an appropriate trapping medium, then using an analytical method to identify and quantify these compounds at the concentrations present. The most common trapping and collection media have included solid adsorbent cartridges, passive monitors, glass bulbs, stainless steel cylinders, and polymeric sampling bags. The most common analytical methods have included gas chromatography-mass spectrometry (GC/MS), gas chromatography-flame ionization detection (GC/FID), and gas chromatography-electron capture detection (GC/ECD). This review will focus on the sampling and analytical methods most appropriate for chloroform. Particular emphasis will be placed on methods recommended by the U.S. Environmental Protection Agency's Environmental Monitoring Systems Laboratory (EPA/EMSL), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Riggin, 1984).

The collection techniques recommended for chloroform in the EPA/EMSL Methods Compendium include Tenax GC adsorption, carbon molecular sieve adsorption, and cryogenic trapping. In addition to these methods, activated charcoal adsorption and the use of passive monitors, whole air collection devices, and portable gas chromatographs will be investigated.

6.1.1 Evaluation Criteria

Attributes to be compared among the various sampling methods include:

- Sampling efficiency: the sampling device must retain chloroform and other halogenated hydrocarbons such that breakthrough, decomposition, and sample loss are negligible;
- Sampling specificity: the sampling device must be capable of trapping halocarbons with negligible interferences due to temperature, humidity, or other pollutants;
- Ease of sampling operations: the sampling equipment should be easy to handle and ship as well as durable for field use; the sampling protocol should be easy to implement in the field and not require lengthy, specialized training of the field testing staff;
- Flexibility of sampling operations: the sampling protocol should be easily modified such that sampling times and rates can be adjusted for unusual sampling situations; and
- Cost-effectiveness: the sampling method should be inexpensive enough to permit collection of a large number of samples.

Each of the sampling methods will be rated for the above listed attributes and assigned an overall rating.

6.1.2 Description of Methods

6.1.2.1 Tenax GC Adsorption

Perhaps the most widely used method of ambient air sampling for volatile organic compounds involves the use of Tenax GC adsorbent cartridges (Pellizzari, 1978; Pellizzari and Bunch, 1979; Krost et al., 1982; Van Langenhove et al., 1982; Pellizzari, 1982; Walling et al., 1982; Pellizzari et al., 1984; Ligocki and Pankow, 1985). One of the advantages of this sampling approach is that a wide variety of volatile organics are retained and concentrated on the Tenax from relatively large volumes of sampled air with little or no interference. In addition, Tenax GC is hydrophobic, thermally stable up to 400°C, and easily elutes even high molecular weight compounds upon thermal desorption.

The basic approach used in this sampling technique involves pulling air through a glass or stainless steel cartridge containing Tenax GC using a vacuum pump and some kind of flow measuring device such as a rotameter. Following collection, samples are usually analyzed using thermal desorption of the Tenax cartridges coupled with capillary column GC or GC/MS methods.

The Tenax sampling method is relatively easy to use in the field, and the cartridges are durable when made from stainless steel. Care must be taken, however, in preparing the cartridges prior to their use in sampling, as the Tenax requires extensive cleaning to eliminate interferences (Krost et al., 1982; Riggin, 1984). Sampling times and rates can be readily adjusted to reflect detection limit requirements or suspected compound levels in the ambient air. However, each compound has a characteristic retention volume on Tenax GC (liters of air/gram of adsorbent) which should not be exceeded during sampling to avoid breakthrough. Some considerations and guidance in the selection of sampling times, rates, sample volumes, and size of the Tenax GC sampling cartridge are provided in recent reports (Walling et al., 1982; Riggin, 1984). The retention volume for chloroform on Tenax GC is relatively low (Riggin, 1984), therefore limiting the volume of air which could be sampled before breakthrough would be expected to occur. Another disadvantage of the Tenax adsorption sampling method is the potential for decomposition product or artifact formation which might occur during sampling in the presence of high humidity and reactive inorganic gases such as ozone, nitrogen oxides, and molecular halogens (Pellizzari and Bunch, 1979; Pellizzari et al., 1984; Ligocki and Pankow, 1985). However, none of the artifacts or decomposition products encountered in the three reports suggested any interferences which would affect sampling for chloroform.

The use of Tenax GC as an ambient air sampling adsorbent is suggested for organics having boiling points in the range of approximately 80 to 200°C (Riggin, 1984). The following is a summary of the quality assurance measures suggested by the EPA/EMSL Methods Compendium for the use of Tenax GC:

(1) Each user should generate Standard Operating Procedures (SOPs) which describe the assembly, calibration, and operation of the sampling system, as well as the preparation, handling, and storage of the Tenax cartridges. The SOPs should also describe all aspects of data recording and processing in the field.

(2) For each batch of Tenax cartridges prepared, one cartridge should be analyzed immediately after preparation as a check for contamination.

(3) For each sampling event one Tenax cartridge should serve as a field blank by accompanying the samples to and from the field but without being used for sampling.

(4) During each sampling event a minimum of one set of replicate samples should be collected as an indication of sampling precision.

(5) Backup Tenax cartridges (two cartridges in series) should be collected whenever the potential for compound breakthrough exists.

(6) Spiked Tenax cartridges should be generated in the laboratory prior to the sampling event and accompany the samples to and from the field as an indication of sample stability (Riggin, 1983).

6.1.2.2 Carbon Molecular Sieve Adsorption

The use of carbon molecular sieves for sampling of ambient air for volatile organics is similar in many regards to the Tenax method, except that carbon molecular sieves are used in place of Tenax GC in the sampling cartridges. The carbon molecular sieve sampling approach, according to Riggin (1984), reduces the potential for compound breakthrough which can occur with Tenax GC for the lower boiling hydrocarbons. However, since the compounds are more strongly adsorbed to the carbon molecular sieve, higher temperatures are generally required for thermal desorption. This could lead to compound degradation or, in the case of less volatile compounds, incomplete desorption (Riggin, 1983). In the case of chloroform, though, thermal degradation and incomplete desorption do not appear to be problematic.

Two recent studies (Averill and Purcell, 1978; Brooks and West, 1980) have demonstrated the use of a carbon molecular sieve as a backup to Tenax GC contained in a single trap. The composite trap not only extends the range of volatility of compounds which could be sampled, but also allows for increased volumes of air to be sampled before breakthrough would be expected to occur. However, no data were presented in either study as to the use of these traps in the field.

Since the carbon molecular sieve adsorption approach has been used only to a limited extent, more work is required to document its applicability to various compound types under varying ambient conditions. The technique has been documented to some extent for chloroform (Riggin, 1984), however, and appears to be relatively easy to use in the field. As with the Tenax method, the sampling cartridges are field durable when made from stainless steel. Care must also be taken in the preparation of the sampling cartridges to avoid contamination. Since the retention volume for chloroform is relatively high (Thomason et al., 1986) with carbon molecular sieve, one has greater flexibility in adjusting sampling times, rates, and sample volumes to meet specific needs in the field.

Data on decomposition product or artifact formation using carbon molecular sieves in the sampling of air in the presence of high humidity and reactive inorganic gases are currently not available. This unknown is a potential disadvantage to the carbon molecular sieve adsorption sampling approach.

The use of carbon molecular sieve as an ambient air sampling medium is suggested for nonpolar and nonreactive organics having boiling points in the range of -15 to +120^{0}C (Riggin, 1984). The quality assurance measures suggested in the EPA/EMSL Methods Compendium for the use of carbon molecular sieve are identical to those already described for Tenax GC adsorption.

6.1.2.3 Cryogenic Trapping

The collection of volatile organics from ambient air by condensation in a cryogenic trap offers the following advantages (Riggin, 1983): (1) a wide range of organic compounds can be collected, (2) contamination problems with adsorbents are avoided, and (3) consistent recoveries are generally obtained. However, two important limitations of the technique are: (1) condensation of large quantities of moisture and, to a lesser degree, of certain reactive gases, and (2) the requirement that the analytical system be transported to the monitoring site.

Nafion tube driers have been successfully used to remove interfering moisture from ambient air samples while leaving most of the volatile organics intact (Foulger and Simmonds, 1979; Cox and Earp, 1982; McClenny et al., 1984), and the use of these driers is suggested in the EPA/EMSL Methods Compendium (Riggin, 1984). Collection of whole air samples (discussed later) in cylinders or polymeric bags with subsequent laboratory analysis can be used to overcome the second limitation.

The basic approach used in the cryogenic method of sampling involves passing a given volume of air through a suitable trap (usually a nickel or stainless steel tube packed with glass beads) held at reduced temperature in a liquid cryogen to efficiently collect the trace organics. If necessary, a Nafion tube drier held at ambient temperature is placed upstream of the collection trap. Following sample collection the cryogen is removed, and the trap is heated followed by GC or GC/MS analysis of the eluting components.

Cryogenic sampling has been shown to be an effective way to sample ambient air for chloroform analysis (Singh et al., 1982; Riggin, 1984). Initial studies on interferences from humidity and the presence of ozone and nitrogen dioxide, although not exhaustive, showed no artifact peaks, deleterious column effects, or decomposition of the compounds tested (one of which was chloroform) during or subsequent to the tests (McClenny et al., 1984).

As stated previously, the use of cryogenic collection methods requires the presence of a GC in the field. A recent study (Singh et al., 1982) reported the use of an instrumented mobile environmental laboratory for measuring volatile organics using cryogenic trapping. Their system was demonstrated to be field durable, and they conducted on-site field data collection in seven U.S. cities for 18 halogenated hydrocarbons. However, without a well equipped mobile laboratory, collection of whole air samples becomes necessary. The cryogenic trapping method for ambient air sampling is suggested for volatile organics having boiling points in the range of -10 to +200°C (Riggin, 1984). With this sampling technique the EPA/EMSL Methods Compendium suggests the use of user generated SOPs which describe in detail the assembly, calibration, and operation of the sampling system and also all aspects of data recording in the field.

6.1.2.4 Activated Charcoal Adsorption

The activated charcoal adsorption method for sampling ambient air has seen its greatest use in industrial hygiene. Since compounds are difficult to recover by thermal desorption from activated charcoal, solvent extraction is usually used. Solvent extraction dilutes the sample, in contrast to thermal desorption, where the entire sample is introduced into the analytical instrument at once. Solvent extraction can be advantageous in this regard since the analyte concentration introduced into the analytical instrument can be adjusted (i.e., diluted), and also replicate analyses can be performed, a feature not available when using thermal desorption. Since only a small fraction of the extract is introduced into the analytical instrument, this method of sampling is mainly useful when relatively high concentrations of compounds are expected.

The use of activated charcoal adsorption sampling for chloroform has been well documented by NIOSH (1984) and ASTM (1984), both of whom have published methods which are easy to use in the field. The tubes used in sampling are commercially available and, although glass, are durable. Sampling high humidity air can reduce the adsorptive capacity of activated charcoal for some compounds, and condensed water droplets in the sampling tube can reduce recovery of some compounds from the charcoal (ASTM, 1984). Information on the formation of artifacts or decomposition products when sampling atmospheres containing reactive inorganic gases is unavailable. There is, however, nothing to suggest that this sampling method is free from the types of potential artifact or decomposition product formation encountered with the Tenax GC sampling method.

6.1.2.5 Passive Air Monitors

As with activated charcoal adsorption, passive air monitors have been primarily used in the field of industrial hygiene to determine personal exposure in the workplace. As such, passive monitors have been tested mainly for monitoring areas having relatively high volatile organic compound levels. A recent study (Coutant and Scott, 1982) examined the applicability of these devices to ambient air monitoring for a group of toxic and chlorinated hydrocarbons. The devices tested were commercially available and used activated carbon as the collecting agent. Therefore they required solvent extraction to desorb the compounds for analysis. Because of inconsistent blank levels and inadequate detection limits, the passive monitors were judged to be of only limited use in performing ambient air monitoring.

More recently a passive sampling device which uses Tenax GC as the sorbent was developed and tested (Coutant et al., 1985; Lewis et al., 1985). The device was designed to be thermally desorbed, thus making it reusable, and was tested for short-term, low-level air monitoring applications. A major advantage of this device over the charcoal based monitors is the greatly enhanced sensitivity achievable by thermal desorption. A potential disadvantage with the thermally desorbable device is that it may be restricted to short sampling times for the more volatile compounds. The use of different sorbents is currently being studied by the authors of those papers to try to overcome the sampling time limitation. Although passive air monitors are extremely easy to use in the field, it is felt that their use for ambient air characterization requires further study.

6.1.2.6 Whole Air Collection

Whole air samples can be collected using glass sampling bulbs, stainless steel cylinders or canisters, polymeric sampling bags, and gas-tight syringes. This method of sampling is also easy to implement in the field, but has several potential limitations including (Riggin, 1983): (1) adsorption or decomposition of compounds of interest through interaction with the container walls, (2) condensation of compounds at high concentrations, and (3) sample leakage from the collection device. In addition, recent studies have shown the potential for hydrocarbons to be released from Teflon air sampling bags if great care is not taken to prevent this (Lonneman et al., 1981; Kelley, 1982; Kelley et al., 1985). Blanks should be frequently analyzed for each bag to determine if the bag has been contaminated or is releasing hydrocarbons under the sampling conditions.

The Air Resources Board (ARB) has used Tedlar bag sampling in its study of selected halogenated hydrocarbons and benzene in the South Coast Air Basin (Shikiya et al., 1984). The quality control measures used by the ARB sampling team addressed potential contamination from the sampling bags and the sampling system prior to their initial use. In addition, the bags were tested for leaks after they were made and before use. However, no tests were performed to define sample stability over the range of concentrations measured or the lengths of storage times before analysis. All samples were analyzed on the same day they were collected, so sample losses would be expected to be minimized. One additional potential shortcoming is that bag blanks were not analyzed between uses to check for contamination.

6.1.2.7 Portable Gas Chromatographs

The use of portable gas chromatographs (GCs) for field monitoring of volatile organics in ambient air is an attractive alternative when concentrations of the compounds of interest are sufficient to be detected and when some prior knowledge of the composition of the air to be sampled is available. Commercially available portable GCs can be obtained with a variety of commonly used detectors, including flame ionization detection (FID), photoionization detection (PID), and electron capture detection (ECD).

Portable FID devices, which are relatively non-specific organic compound detectors, are usually used as "total hydrocarbon" analyzers, but when used in the gas chromatographic mode can provide qualitative and quantitative information. The portable GC/FID's detection limit, which is approximately 0.5 ppmv (volume parts per million), is in most cases inadequate for ambient air monitoring. For the most accurate quantitative information, the GC/FID should be calibrated with the compounds of interest.

An advantage of portable PID instruments is that they can be more selective and sensitive toward certain organic compound types (e.g., aromatic hydrocarbons) without detecting other compound types (e.g., aliphatic hydrocarbons) in their presence. This can be accomplished through selecting a lamp with the appropriate radiation energy. As with the portable GC/FIDs, portable PIDs can be used in the gas chromatographic mode to provide qualitative and quantitative data. In general, detection limits are better with the PID than with the FID devices, and can range from 0.1 to 100 ppbv depending on the compounds detected and the manufacturer. Since response varies according to compound, the PID must be calibrated with specific analytes in order to produce accurate quantitative data.

Portable ECD devices are both extremely sensitive and selective and are generally used to detect halogenated hydrocarbons. These instruments are best used in the gas chromatographic mode, and as such have detection limits equal to or better than the portable PID systems. The ECD must also be calibrated with specific analytes to obtain accurate quantitative data.

In summary, portable GCs are probably best used as screening devices for ambient air monitoring where a quick analysis might yield information to determine sampling times and volumes. Response is compound specific in many cases, and the potential for coeluting compounds is high for ambient air samples when using a portable GC which is limited to an isothermal analysis. As such, these devices would require a substantial effort to standardize and calibrate for the purpose of obtaining both qualitative and quantitative results. However, a portable GC would be useful when looking for a few designated compounds occurring at high concentrations relative to background concentrations of other compounds where calibration could be accomplished more easily.

6.1.3 Rating of Sampling Methods

The sampling methods described in the preceding section were rated against each of the six evaluation criteria. For each criterion, we assigned a score of 1 (lowest) to 5 (highest). The overall score for each alternative was defined as the sum of the scores for the six criteria. Since all criteria were weighted equally, the maximum total score was 30. Table 6.1-1 shows the results of the rating exercise.

Each of the reviewed methods has been used successfully to sample ambient air for chloroform, and each has strengths and limitations. Associated with carbon molecular sieve adsorption, which was rated highest overall, is the potential for compound decomposition at the high temperatures required for desorption and analysis. However, for the compounds of interest, this is probably not a problem, and the sampling ease, efficiency and flexibility of carbon molecular sieve adsorption outweigh its shortcomings.

Activated charcoal, which was rated second overall, was also rated high in sampling ease, efficiency, and flexibility, but it is subject to interferences from water vapor. In addition, it is necessary to handle toxic solvents (i.e. carbon disulfide) during desorption.

Next in the overall ranking were Tenax GC adsorption and cryogenic trapping, which received the same rating. The major limitation of using Tenax for chloroform sampling is the potential for breakthrough, which affects the flexibility of the method. However, Tenax sampling is easy to use in the field and has probably been the most thoroughly tested of the methods reviewed here. The major limitation of cryogenic trapping is the need to have a complete analytical system in the field during sampling; handling a liquid cryogen could in certain situations be problematic. Moisture condensation, another potential problem for cryogenic trapping, appears to be of little concern for sampling of most volatile organic compounds when Nafion tubes are incorporated into the sampling system. Cryogenic trapping can be efficient and flexible when a gas chromatograph is located on-site for analyses. Cryogenic preconcentration can also be used in analyzing samples collected by other methods, as it provides better analyte focusing and thus better peak shape.

The methods rated lowest were passive monitors and whole air collection. Passive monitors are the easiest to use in the field and are more cost-effective than most of the other methods. However the sampling efficiency and flexibility of current devices are limited. Whole air

Table 6.1-1

NUMERICAL RATINGS OF VARIOUS AIR SAMPLING METHODS
FOR CHLOROFORM AND OTHER HALOGENATED HYDROCARBONS.

Method	Sampling Efficiency	Sampling Specificity	East of Sampling	Flexibility of Sampling	Cost Effectiveness	Analytical Factors[a]	Overall Rating
Tenax GC Adsorption	3	4	4	3	3	4	21
Carbon Molecular Sieve Adsorption	5	4	4	4	3	3	23
Cryogenic Trapping	5	3	2	4	4	3	21
Activated Charcoal Adsorption	5	2	4	4	5	2	22
Passive Monitors	2	3	5	1	5	3	19
Whole Air Collection	2	3	4	4	3	3	19

[a] Analytical factors include ease of analysis and sensitivity.

collection is also relatively easy to use, but is subject to sample losses through adsorption, condensation and leakage.

6.2 ANALYTICAL METHODS FOR AIR

6.2.1 Evaluation Criteria

The analytical techniques suggested in the EPA/EMSL Methods Compendium for ambient air samples include capillary column GC/MS, GC/FID, and GC/ECD. These are by far the most commonly employed techniques in the studies reviewed for this report. Our review also included the use of packed columns and the Hall electrolytic conductivity detector (HECD), another device which is specific towards halogenated hydrocarbons. Attributes to be evaluated include:

- Analytical efficiency: the method must be able to analyze simultaneously and efficiently for chloroform and other halogenated hydrocarbons of interest, including carbon tetrachloride, ethylene dichloride, perchloroethylene, 1,1,1-trichloroethane, and ethylene dibromide;
- Analytical sensitivity: analytical detection limits should be in the nanogram range for quantitation of chloroform in ambient air, both indoors and outdoors;
- Flexibility of analytical method: operating conditions should be amenable to rapid modifications in order to address analytical difficulties specific to a given source type (e.g., unknown compound coeluting with chloroform);
- Analytical dynamic range: the method should be applicable over several orders of magnitude in halogenated hydrocarbon concentrations;
- Comprehensive documentation of methods: analytical protocols should be well documented, including quality assurance and quality control aspects of the measurement method; and
- Cost-effectiveness: the analytical procedures should be inexpensive enough to permit analysis of a large number of samples, including those analyzed for quality assurance.

Each of the analytical methods will be rated for the above listed attributes and assigned an overall rating. Before discussing the applicability of various GC detectors as used in ambient air monitoring, a brief discussion of packed and capillary columns and a summary of the various modes of sample injection into a GC will be presented.

6.2.2 Description of Methods

6.2.2.1 General Considerations

GC Columns

The EPA/EMSL Methods Compendium recommends the use of capillary columns, in view of the potentially complex mixture of trace organics present in an ambient air sample. Capillary columns are more inert and provide better resolution than packed columns. In addition a single capillary column is generally applicable towards a broader range of compound types than would be a single packed column.

Packed columns, on the other hand, are usually easier to use and are generally superior for analysis of highly volatile compounds. Sample loading capacity is greater with packed columns than with capillary columns. A fairly recent innovation which combines the inertness, superior resolution, and broad applicability of the capillary column with the ease of use and sample loading capacity of the packed column is the wide bore, thick film, fused silica capillary column. These columns should see increasing use where packed columns have been most appropriate in the past.

Sample Injection Modes

Depending on how the ambient air is sampled, a sample can be introduced into the GC in various ways. For Tenax GC or carbon molecular sieve adsorption, the sample is thermally desorbed into a stream of inert gas passing through the cartridge. The desorbed analytes released into the inert gas stream can be either passed directly onto a GC column, or cryogenically trapped and then desorbed quickly onto the head of a GC column. The latter technique permits better focusing of the analytes at the head of the column, thus affording better peak shape (i.e., less peak broadening). Air samples collected on activated charcoal (sorbent tubes or passive monitors) are desorbed with solvent and then injected into the GC using standard liquid injection techniques. Whole air samples can be directly injected into a GC using a gas-tight syringe or an appropriately configured gas loop connected to a GC column. Alternatively, whole air samples can be cryogenically concentrated prior to injection into a GC.

6.2.2.2 Gas Chromatography/Mass Spectrometry

GC/MS is a powerful tool for identifying and quantifying organic compounds in ambient air samples. Although more expensive than conventional GC detection methods, the GC/MS system gives the analyst more flexibility than any of the other analytical techniques. When used in conjunction with capillary column GC techniques, the MS is capable of positively identifying over 100 compounds in a single analysis.

The GC/MS is generally used in one of two operating modes when analyzing ambient air samples. In the full scan mode the MS acquires mass spectral data over the range of about 40-400 atomic mass units (amu) at the rate of about one scan per second during the GC run. This generalized mode of operation gives the most information about the identities of compounds present. The GC/MS can be calibrated in the full scan mode for compounds of interest; this is the most commonly used mode of operation for the GC/MS and can achieve detection limits of about 1-5 nanograms per compound.

The second mode of operation of the GC/MS is called selected ion monitoring (SIM). In this mode, only a few selected ions of interest are scanned during the GC run. This operating mode is generally used only when looking for a few specific compounds. The GC/MS is not only more specific in the SIM mode of operation, but it also allows more accurate quantitation and is approximately one order of magnitude more sensitive than one the full scan approach.

GC/MS is suggested as the analytical method of choice when performing ambient air sampling with Tenax GC or carbon molecular sieve (Riggin, 1984). The analytical protocols contained in the EPA/EMSL Methods Compendium include well-documented GC/MS performance criteria and quality assurance measures. In addition, information is provided for suggested instrument set-up and calibration.

6.2.2.3 Gas Chromatography/Flame Ionization Detection and Electron Capture Detection

The use of GC/FID and GC/ECD as analytical tools in ambient air monitoring has already been discussed in Section 6.1.2.7. In brief, the GC/FID is a relatively non-specific detector for organic compounds and has sensitivity of approximately 1-5 nanograms per compound. Conversely, GC/ECD is specific towards halogenated hydrocarbons and has sensitivity of about 1-10 picograms per compound. The GC/FID, however, has a greater linear working range than the GC/ECD (about 106 vs. about 104 for FID and ECD, respectively). Both analytical methods are suitable for analyzing simultaneously and efficiently for a variety of halogenated hydrocarbons. Since the ECD is more specific towards halogenated hydrocarbons, it could potentially be subject to fewer interferences from other compound types present in the sample than the FID would be. Two potential drawbacks to the ECD are that, due to its great sensitivity, it is highly susceptible to contamination from the compounds of interest, and the response of the detector drifts during temperature programmed analyses.

An additional consideration is that both GC/FID and GC/ECD fall short of providing positive qualitative identification of compounds on a single analysis of a sample. To overcome this limitation one can either analyze samples on a second column (generally of different polarity and therefore of different retentive characteristics than the primary analytical column), or one can analyze samples on a single column and pass the column effluent through two different detectors, either in series or in parallel. The obvious limitation of the former approach is that it requires two separate analyses, which in the case of adsorbent cartridge sampling would necessitate collecting samples in duplicate. For the latter approach to work in the series mode requires the initial detector to be nondestructive towards the sample components. For the two-detector approach to work in the parallel mode requires a tee connected to the column exit which would reproducibly split the sample components to both detectors. In the parallel mode, sensitivity would decrease since only about half of the sample would be going to either detector. In either case when using the two-detector approach, the response ratio from the two detectors can be used to help confirm a compound's identity.

GC/FID and GC/ECD are suggested in the EPA/EMSL Methods Compendium (Riggin, 1984) for analyzing ambient air for volatile organics using cryogenic preconcentration techniques. Included in the method are suggested calibration procedures, method performance criteria, and quality assurance measures.

6.2.2.4 Gas Chromatography/Hall Electrolytic Conductivity Detection

GC/HECD is another analytical tool which, when operated in the halogen specific mode, can be useful in analyzing ambient air samples for halogenated hydrocarbons. The analytical sensitivity of this device is comparable to or slightly better than that of the GC/FID. Like the GC/ECD, however, GC/HECD is highly specific towards halogenated compounds and thus is potentially less susceptible to interferences from other compound types present in the sample. The HECD offers the additional advantage of detector stability during temperature programmed analyses.

The HECD is limited to the same extent at providing positive qualitative identification of sample components as are the FID and ECD. In this regard, the comments addressing this issue in the previous section (GC/FID and GC/EDC) are applicable.

6.2.3 Rating of Analytical Methods

Table 6.2-1 presents our ratings of the analytical methods described in the previous section. Each of the methods is capable of analyzing samples for chloroform and other halogenated hydrocarbons, and each has strengths and limitations. GC/MS, which was rated the highest, along with GC/FID, is probably the most flexible, efficient, and well documented of all the methods described here. The major limitation of GC/MS is its cost. GC/FID is relatively inexpensive to use, but is limited by its relatively poor sensitivity and its inability to provide positive qualitative information in a single analysis.

Table 6.2-1

NUMERICAL RATINGS OF VARIOUS ANALYTICAL METHODS FOR CHLOROFORM AND OTHER HALOGENATED HYDROCARBONS

Analytical Method	Analytical Efficiency	Analytical Sensitivity	Analytical Flexibility	Analytical Range	Documentation	Cost Effectiveness	Overall Rating
GC/MS	5	3	5	3	5	2	23
GC/FID	4	2	3	5	4	5	23
GC/ECD	4	5	2	3	4	4	22
GC/HECD	4	3	3	3	3	4	20

6.3 WATER SAMPLING AND ANALYSIS

6.3.1 Sampling Methods

The water sampling methods reviewed for this project are those compatible with the analytical method to be used, which is described in the next section. Freshwater and wastewater samples are collected in glass vials equipped with Teflon-faced silicone septa and screw caps. Because the analytical method involves stripping the volatile organic carbons from solution, it is important to exclude air bubbles from the samples during sample collection and storage.

Seawater samples are collected in 5-liter vessels called Niskin bottles. The bottles are attached to a cord at pre-set intervals, so that nearly simultaneous samples may be collected at different depths. When lowered, the bottles are all open. A messenger weight is then lowered on the cord to trip each bottle's closing mechanism. Samples are later transferred from the Niskin bottles to the aforementioned glass vials.

6.3.2 Analytical Methods

The purge-and-trap method of analysis for volatile halocarbons (including chloroform) in water is widely used. U.S. Environmental Protection Agency Method 601 is the standard method for analyzing municipal and industrial discharges for halocarbons (Longbottom and Lichtenberg, 1982), and was the method used in Phase II of this project. Samples are analyzed by bubbling an inert gas through an aliquot of the sample. The halocarbons, which are efficiently transferred to the vapor phase, are swept onto a sorbent tube, on which they are trapped. After purging is complete, the sorbent tube is quickly heated and backflushed with carrier gas to desorb the halocarbons onto the head of a GC column. A temperature program is then used in the GC to separate the halocarbons before detection. EPA Method 601 recommends using packed columns and the Hall electrolytic conductivity detector, but capillary columns can also be used (Kirschen, 1984). In addition, GC/MS can be used to provide more definitive qualitative information about sample components.

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7.0

AMBIENT SAMPLING

A major portion of the Phase II field effort was devoted to collecting and analyzing ambient air samples. Although the focus of the project was to be upon chloroform, the ARB desired to obtain data on other halogenated hydrocarbons as well. SAIC's laboratory subcontractor, Environmental Monitoring and Services, Inc. (EMSI) was directed to analyze ambient samples for methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethene (tetrachloroethylene), tetrachloroethene (perchloroethylene), and ethylene dibromide.

At the end of Phase I, we recommended that carbon molecular sieve (CMS) traps be used for the ambient chloroform sampling. It was believed that use of CMS would enable us to detect relatively low levels of chloroform with relatively short sampling times. In the end this belief proved to be warranted, in that we were able to "see" as little as 9 ppt of chloroform in a 1-hour air sample. However, as no large-scale experience with CMS sampling for halocarbons had been reported in the literature, considerable developmental effort, on the part of both SAIC and EMSI, was necessary. A literature report of a breakthrough volume of 1,100 liters per gram of CMS (Thomason et al., 1986) proved to be seriously underestimated; as a result, breakthrough was observed in all of the double traps exposed in the fixed-site sampling. Furthermore, the detector used in the analyses was saturated. Lower sampling flow rates and volumes were used for the marine sampling, which came next. The amount of breakthrough decreased, but was still significant. In the mobile sampling, which was the final portion of the ambient sampling effort, flow rates were decreased even further, and our confidence in the results was greatly increased. The "research and development" aspect of this study should be borne in mind when reviewing the following sections.

7.1 FIXED SITE MONITORING

7.1.1 Selection of Sites

The objectives of the fixed-site ambient monitoring were:

- To supplement the ARB halocarbon monitoring network by covering different geographical areas; and
- To measure diurnal variations in chloroform concentrations at one site.

To satisfy the first objective, we decided to conduct 24-hour sampling in Fullerton. Except for an unstated number of grab samples taken by Su and Goldberg (1976) in "Orange County" in April 1974, no chloroform measurements in the southeastern portion of the SCAB had been reported in the literature. (See Section 5.1.)

To satisfy the second objective, we sought a site where marked diurnal variations in ambient chloroform concentrations were likely. The Industrial Source Complex-Short Term (ISC-ST) model, which is described in detail in Chapter 10, was used in Phase I to predict hourly average chloroform concentrations on a grid thoughout the SCAB, for 24 modeled hours. Inputs to the model included point and area source emission estimates developed in Phase I, as well as actual meteorological data for 8 August 1983. (The August date was chosen since fixed-site monitoring was originally planned for that month.) Hourly average modeled concentrations at each grid point were then grouped into four six-hour averages. The measure of diurnal variation was defined as the ratio of the standard deviation to the mean of the quarter-day averages. For the 100 grid points for which concentrations were modeled, this ratio varied from 0.24 to 1.69. The point having the highest ratio was on the coast near the Los Angeles Hyperion Wastewater Treatment Plant. For convenience, we conducted the diurnal sampling in nearby Hermosa Beach.

Twenty-four hour sampling was conducted on the roof of the Fullerton headquarters fire station at 312 E. Commonwealth Avenue (Figure 7.1-1). The

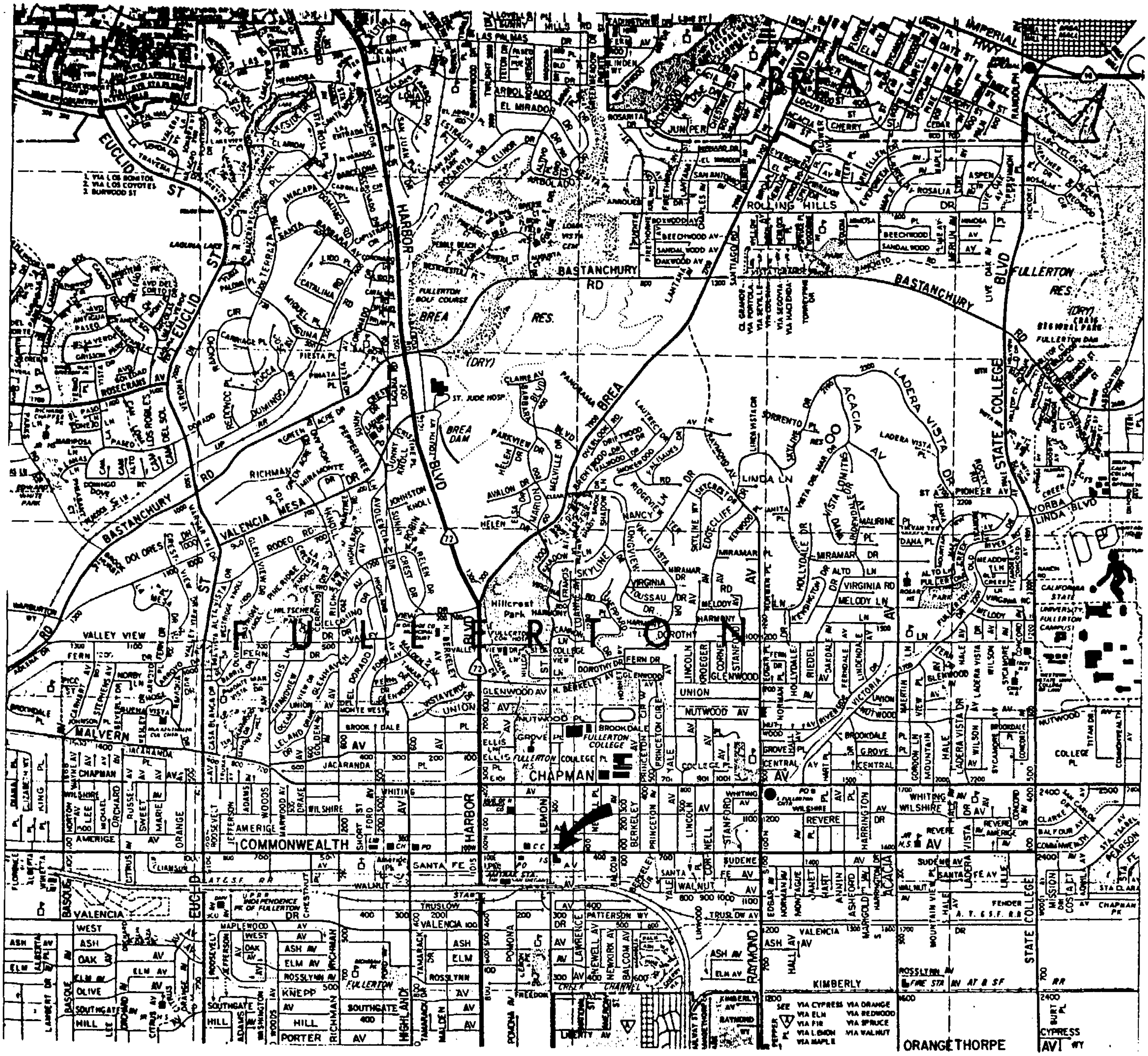

Figure 7.1-1. Location of 24-Hour Fixed-Site Sampling Site (Fullerton, CA).

diurnal sampling site was on the roof of SAIC's office building at 2615 Pacific Coast Highway in Hermosa Beach (Figure 7.1-2).

Both sites were chosen for their 24-hour access, distance from potential point sources of $CHCl_3$ or other organic compounds which might interfere with data analysis, and for security from theft or tampering. During the sampling period, however, an office building across from the Fullerton site was re-roofed. Therefore, on three days, there was a potential for contamination of the CMS traps with high-molecular weight hydrocarbons, including particulate matter. The analytical laboratory was advised of this.

7.1.2 Methods

7.1.2.1 Air Sampling

Air samples were collected on carbon molecular sieve (CMS) traps which were custom-prepared by Supelco, Inc. (Bellefonte, PA) for this project. Each trap consists of an 0.25 in i.d., 3-inch long stainless steel tube containing 400 mg of CMS material. A glass wool plug was placed at each end of the trap to contain the CMS material and reduce particulate contamination. CMS traps were chosen for this project because of their reported low potential for breakthrough and their ability to adsorb not only chloroform but also other low-molecular halocarbons of interest to the ARB. (See Sections 6.1.2.1 and 6.1.2.2.) It should be noted that, to the best of our knowledge, this was the first attempt to use CMS for a large-scale halocarbon field sampling program, and, as will be discussed below, several major problems were encountered.

An a.c.-powered Gast Model MOA-101-JH diaphragm vacuum pump was used for the sampling. Our original plan was to monitor air flow with a pre-calibrated rotameter. We found it to be more accurate, however, to measure flow directly before and after each sample with a soap film flowmeter. To account for the pressure drop through the CMS traps, one or two "dummy" traps were used for the flow measurement. At least three flow measurement were made for each run, and the average flow rate was calculated.

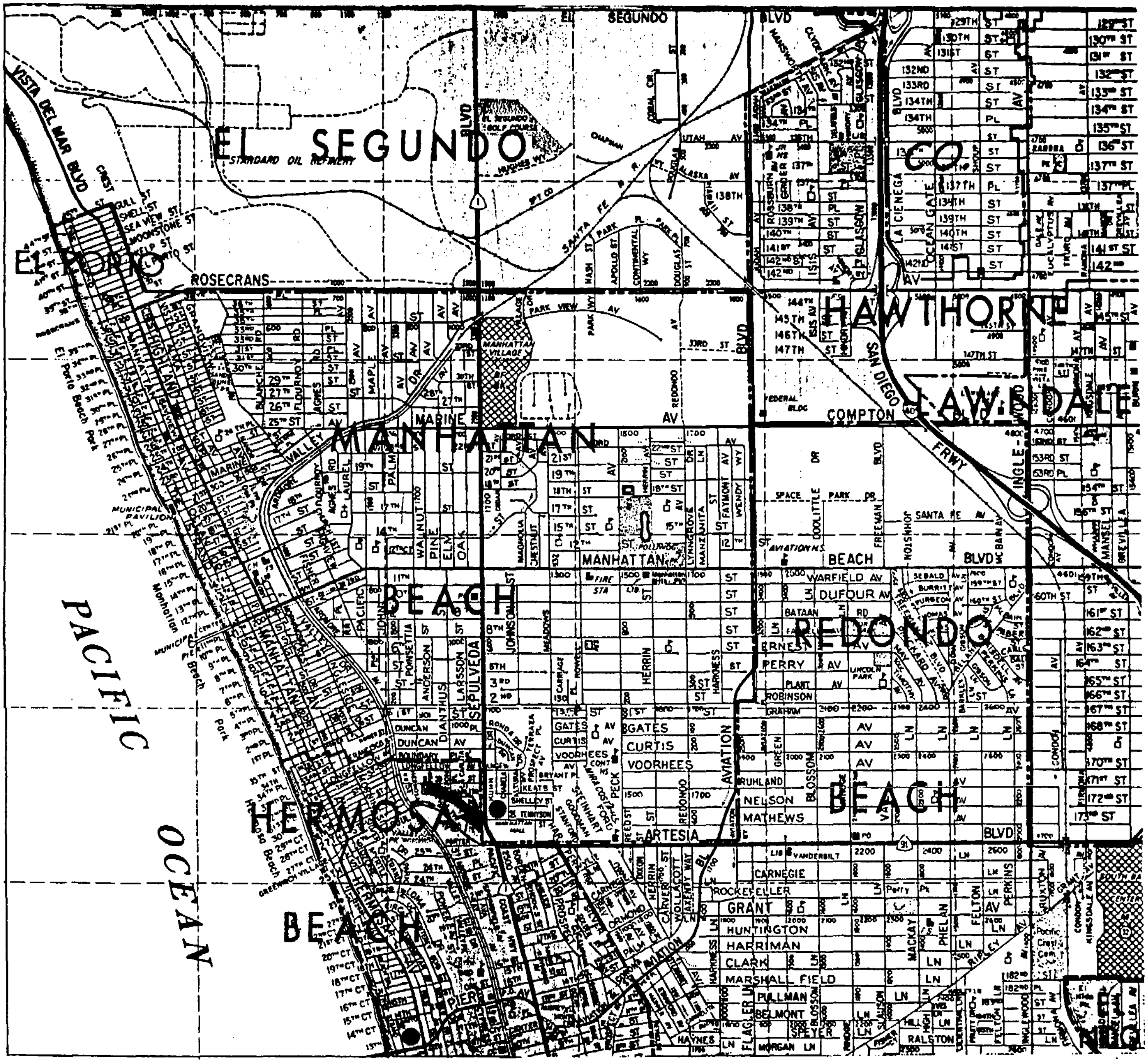

Figure 7.1-2. Location of 6-Hour Fixed-Site Sampling Site (Hermosa Beach, CA).

On the basis of our literature review, we believed a safe sampling volume to be about 293 L. Flow rates for the Fullerton sampling were just over 200 ml/min, except for the duplicate sampling (see below), for which the rate through each pair was about 100 ml/min. Sample volumes ranged from 89 to 291 L. At Hermosa Beach, sample volumes ranged from 95 to 188 L. Sampling flow rates were about 500 ml/min. We now know that this rate was too high.

Teflon tubing was used throughout the system. CMS traps were connected to the Teflon line with brass Swagelok fittings and ferrules. Stainless steel Swagelok fittings with Teflon ferrules were used when connecting traps in series. After each Fullerton sample was collected, tubes were sealed with plastic caps and placed in Ziplok^{TM} bags. For the Hermosa Beach sampling (and all other sampling described in this chapter), the CMS tubes were sealed with aluminum foil and placed in cleaned and conditioned glass vials.

To determine whether breakthrough occurred, approximately half the samples were taken with both front and back traps. We intended to sample in triplicate at least once at each site to check the precision of the sampling technique. We were able to do this at the 6-hour site but, because of technical difficulties, only a duplicate sample was obtained at the 24-hour site. For duplicate or triplicate sampling, four or six traps were connected via a manifold. The front and back traps remained in series, as before, while each pair of traps was connected in parallel with the other pair or pairs. Air flow was measured separately at each pair of traps.

Figures 7.1-3 and 7.1-4 show the sampling schedules for the 24- and 6-hour fixed site sampling, respectively, including field blanks used. Traps were randomly numbered to avoid bias in laboratory analysis.

7.1.2.2 Analysis of CMS Traps

CMS traps were analyzed by Environmental Monitoring Systems, Inc. (EMSI) of Camarillo, CA, using a modified version of the U.S. Environmental Protection Agency's recommended Method T03 for the determination of volatile organic compounds in ambient air using cryogenic preconcentration (Riggin,

Tu	W	Th	F	Sat	Sun	M
■▨	■▨ □	■	■▨ ■▨ ■▨	■ □	■	■

Front = ■

Back = ▨

Field blank = □

Figure 7.1-3. Schedule for 24-Hour Fixed-Site Sampling at Fullerton, CA.

Day Time	F	Sat	Sun	M	Tu	W	Th
6 AM	█▨	█▨	█▨	█	█▨ █▨ █▨	█	█
12 PM	█▨	█▨	█▨ ▯	█	█	█	█
6 PM	█▨	█▨	█▨	█ ░	█	█	█
12AM	█▨	█▨	█▨	█	█	█ ░	█

Front = █

Back = ▨

Field blank = ▯

Spiked blank = ░

Figure 7.1-4. Schedule for 6-Hour Fixed-Site Sampling at Hermosa Beach, CA.

1984). Samples were prepurged with helium for 8 minutes at 25°C to remove water, and then desorbed at 420°C for 12 minutes in a Tekmar Model 5010 solid desorber, onto two cryogenic traps (-100°C and -110°C) in series. After problems with excessive water vapor in some of the early analyses, a Permapure Nafion membrane dryer was placed between the desorber and the cryogenic traps. The samples were then flash evaporated for 3 minutes at 250°C, split, and transferred onto a Megabore DB 624 capillary column for quantitation and a Megabore DB 5 capillary column for confirmation. Each column was 30 m x 0.53 mm i.d. with 1 μm film thickness. The temperature program for the columns included heating from 55°C to 75°C at 4°C/min, from 75°C to 111°C at 6°C/min, and from 111°C to 230°C at 35°C per minute. The instrument used for the quantitation was an IBM 9630 gas chromatograph with dual electron capture detectors. (See Appendix C for a complete discussion of methods.)

7.1.3 Results

Results for the Fullerton and Hermosa Beach fixed-site sampling are presented in Tables 7.1-1 and 7.1-2, respectively. The Fullerton samples were analyzed before the dryer was incorporated in the system. Interferences from water vapor resulted in unreliable measurements of the compounds other than chloroform. For the Hermosa Beach samples, and all other ambient samples, EMSI was successful in quantifying 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, perchloroethylene and ethylene dibromide, but not methylene chloride.

It is clear from the results of the fixed-site monitoring that the sampling flow rate and/or volume was too high. Breakthrough of most of the compounds was observed in all of the front-back pairs. To estimate the total likely concentration when front and backup CMS traps collected detectable amounts of VOC compounds, we used the method of Smith (1979). Let Y be the ratio of the front trap mass (minus the field blank mass) to the sum of the masses detected by the two traps. The overall efficiency of the two-trap system is estimated by:

$$e = 2/Y - 1/Y^2$$

Table 7.1-1

RESULTS OF 24-HOUR SAMPLING AT FULLERTON

(Concentrations in ppt)

Sample	Date	Sampling Interval	Chloroform
1	12-2-86	1246-1245	208[a]
2	12-3-86	1305-1217	11
3	12-4-86	1252-1241	1
4	12-5-86	1306-1247	41
5	12-6-86	1301-1242	Lost[b]
6	12-7-86	1306-1244	Sat[c]
7A	12-8-86	1317-1305	Water[d]
7B	12-8-86	1317-1305	267

[a] Rear trap mass > front trap mass.

[b] Sample lost during analysis, due to power failure.

[c] Front trap mass saturated the detector.

[d] Water interference with detector.

Table 7.1-2

RESULTS OF 6-HOUR SAMPLING AT HERMOSA BEACH
(All concentrations in ppt)

Sample	Date	Sampling Interval	Chloroform	1,1,1-Trichloroethane	Carbon Tetrachloride	Trichloroethylene	Perchloroethylene	Ethylene Dibromide
1-2	4-10-87	0613-1205	111[a]	2[a]	Sat	>16[c]	>0[c]	1
1-3	4-10-87	1214-1809	80	Sat	Sat	207	Sat	ND
1-4	4-10-87	1833-0009	63	Sat	Sat	Sat	Sat	>6[e]
2-1	4-11-87	0020-0638	Sat[b]	Sat	Sat	Sat	Sat	Sat
2-2	4-11-87	0647-1213	18	6	>4[e]	28[a]	25	>1[e]
2-3	4-11-87	1220-1804	Sat	Sat	Sat	Sat	Sat	Sat
2-4	4-11-87	1812-0005	>59[c]	Sat	Sat	Sat	Sat	7
3-1	4-12-87	0011-1615	106[a]	Sat	Sat	>278[c]	Sat	Sat[g]
3-2	4-12-87	0622-1201	39	35	Sat	169	Sat	1
3-3	4-12-87	1207-1801	102[a]	Sat	Sat	132[a]	Sat	19[a]
3-4	4-12-87	1807-0002	>49[c]	54[a]	Sat	Sat	Sat	90[a]
4-1	4-13-87	0008-0616	128	Sat	Sat	Sat	Sat	10
4-2	4-13-87	0626-1156	13	15	Sat	14	4	3
4-3	4-13-87	1211-1758	57	Sat	Sat	Sat	Sat	1
4-4	4-13-87	1815-0008	6	15	7	4	4	ND
5-1	4-14-87	0013-0616	Sat	Sat	Sat	Sat	Sat	ND
5-2	4-14-87	0633-1228	125	39	26	Sat	Sat	14
5-2	4-14-87	0633-1228	168	Sat	Sat	Sat	Sat	Sat[g]
5-2	4-14-87	0633-1228	Sat	Sat	Sat	Sat	Sat	Sat[g]
5-3	4-14-87	1248-1802	9	2	7	7	4	3
5-4	4-14-87	1806-0011	24	Sat	Sat	Sat	Sat	0
6-1	4-15-87	0020-0626	161	Sat	ND[f]	Sat	Sat	ND
6-2	4-15-87	0629-1222	Sat	Sat	Sat	Sat	Sat	Sat
6-3	4-15-87	1227-1819	Lost[d]	Lost	Lost	Lost	Lost	Lost
6-4	4-15-87	1824-0016	68	Sat	Sat	Sat	Sat	29
7-1	4-16-87	0020-0620	17	Sat	Sat	Sat	Sat	ND
7-2	4-16-87	0625-1230	77	Sat	Sat	Sat	Sat	ND
7-3	4-16-87	1242-1834	39	Sat	Sat	Sat	Sat	8
7-4	4-16-87	1840-0030	Sat	Sat	Sat	Sat	Sat	ND

[a] Rear trap mass > front trap mass.

[b] Front trap mass saturated the detector.

[c] Rear trap mass saturated the detector.

[d] Sample lost during analysis, due to power failure.

[e] Front trap below detection limit.

[f] Mass below detection limit.

[g] Front trap below detection limit, rear trap saturated detector.

The total likely mass is then calculated by dividing the sum of the front and back trap concentrations by e. Where the rear trap mass exceeded the front trap mass, this method could not be used; instead we merely summed the mass on the two traps. For six of the chloroform analyses of the Hermosa Beach samples and most of the analyses of the other halocarbons, the amount of material collected saturated the electron capture detector, so that no value could be reported. In Tables 7.1-1 and 7.1-2, we have printed in boldface those results which can be reported without additional reservations. The remaining results should be used, if at all, with caution.

The Fullerton samples were within the normal range for the South Coast Air Basin (see Section 5.1). The results are too scanty to permit a discussion of variation within the week. A limited amount of analysis can be performed with the Hermosa Beach data, if one accepts all Table 7.1-2 values not reported as "greater than," "Sat" or "Lost." These values ranged from 6 to 168 ppt and had an arithmetic mean and standard deviation of 58 and 40 ppt, respectively. Clearly, chloroform concentrations at this site are highly variable, at least on a six-hour basis. No statistically significant difference among daily average or quarter-day average chloroform concentrations could be found.

7.2 MOBILE SAMPLING

The main objective of this part of the study was to obtain short-term (one-hour) samples at a variety of sites in the South Coast Air Basin, at various times of the day and week. Special attention was to be paid to sites not covered by the existing ARB toxic air pollutant monitoring network or by the fixed-site monitoring described in Section 7.1. A secondary objective was to determine whether elevated $CHCl_3$ concentrations would be found downwind of suspected point or area sources.

7.2.1 Program Design

Seven sets of ambient samples were collected and analyzed. Sites within each of these sets are shown in Figure 7.2-1 and described in Table

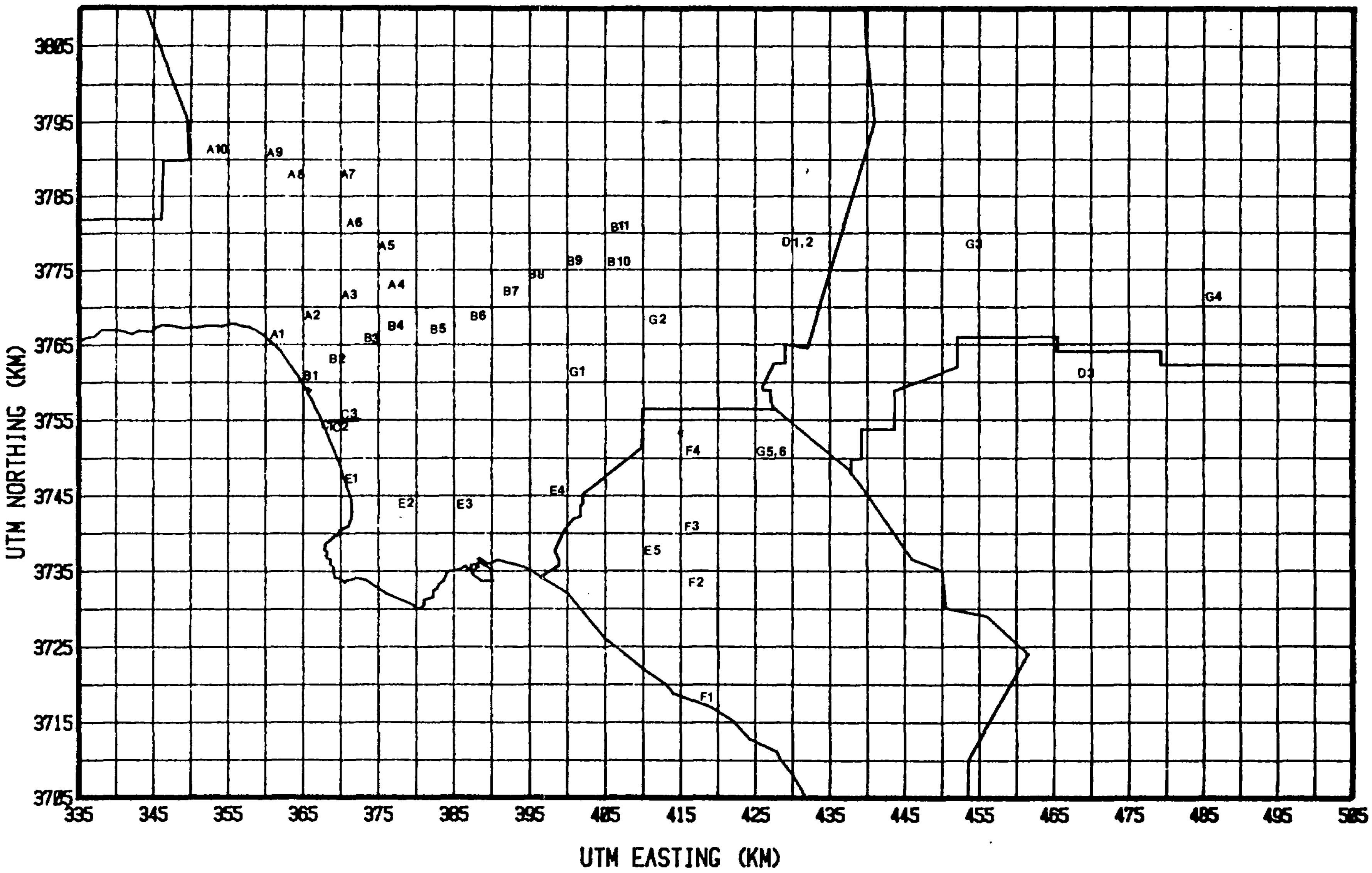

Figure 7.2-1. Locations of Mobile Sampling Sites.

7.2-1. The sets were defined as follows:

Set	Definition
A	Route of onshore air flow through west Los Angeles and the San Fernando Valley
B	Route of onshore air flow through central Los Angeles and Pasadena area
C	Downwind of Los Angeles Hyperion wastewater treatment plant
D	Downwind of Metropolitan Water District (MWD) water chlorination facilities
E	Industrial belt in South Bay area
F	Orange County
G	San Gabriel Valley, Orange County, San Bernardino County

The routes used for Sets A and B follow air flow patterns described by Keith (1980) for July at 1200 PST. Locations of the MWD facilities were obtained from the District (MWD, Undated). Except for Sets C and D, the general areas of the sampling sites were selected in advance to be roughly equally spaced along the travel route. The actual sites were chosen in the field. In general, they were located in quiet residential neighborhoods, away from heavy automobile or pedestrian traffic.

7.2.2 Methods

Samples were collected for about one hour on carbon molecular sieve (CMS) traps, using Gillian Instrument Corporation personal sampling pumps. The trap inlet was 95 cm above the ground in most cases. Pump flow rates were measured before each run with a Hewlett-Packard Model 0101-0113 soap film flowmeter. Most sampling was at about 18 ml/min, and sample volumes varied from 0.89 to 1.6 L. Air temperatures before and after each run were measured with a mercury laboratory thermometer. CMS traps were analyzed by EMSI, using the same methods as described in Section 7.1.3.

Table 7.2-1

MOBILE CHLOROFORM SAMPLING SITES

Site No.	Location	City	Description of Area	Date	Times	Mean Temp. (°C)
A-1	Ocean Ave., N. of Santa Monica Blvd.	Santa Monica	Park above S.M. Bay	5-14-87	0607-0705	18.9
A-2	Camden Ave., S. of Santa Monica Blvd.	W. Los Angeles	Residential	5-14-87	0727-0824	21.0
A-3	Maple Dr., N. of Santa Monica Blvd.	Beverly Hills	Beverly Gardens Park	5-14-87	0855-0950	22.5
A-4	Cahuenga Blvd., N. of Santa Monica Blvd.	Hollywood	Residential	5-14-87	1017-1113	28.0
A-5	Barham Blvd., near Los Angeles R.	Los Angeles[a]	Open area	5-14-87	1150-1246	30.0
A-6	Tiara St. and Tujunga Ave.	N. Hollywood	Residential	5-14-87	1325-1423	27.8
A-7	Sharp Ave and Peoria St.	Los Angeles[b]	Near high school	5-14-87	1508-1606	29.8
A-8	Orion Ave., N. of Roscoe Blvd.	Sepulveda	Residential	5-14-87	1631-1728	27.0
A-9	Tuba St. and Genesta	Granada Hills	Residential	5-14-87	1824-1924	23.8
A-10	Devonshire St., W. of Valley Circle Blvd.	Chatsworth	Residential near pool	5-14-87	2051-2151	20.6
B-1	Venice Blvd. between Dell Ave. and Grand Canal	Venice	Residential/Commercial[c]	5-16-87	0715-0810	20.5
B-2	Bledsoe Ave., S. of Venice Blvd.	W. Los Angeles[d]	Residential	5-16-87	0837-0933	24.5
B-3	Burchard Ave., S. of Venice Blvd.	W. Los Angeles	Residential[e]	5-16-87	0959-1054	24.3
B-4	Arlington Ave. between Venice Blvd. and Pico Blvd.	Los Angeles	Next to high school	5-16-87	1114-1214	20.4
B-5	14th Place and Main St.	Los Angeles	Commercial/Industrial	5-16-87	1241-1336	20.3
B-6	Mission Road	Los Angeles	Commercial	5-16-87	1401-1456	23.2
B-7	Castalia Ave., N. of Navarro St.	El Sereno	Residential[c]	5-16-87	1522-1622	22.4
B-8	State St. and Garfield Ave.	Alhambra	Mall parking lot	5-16-87	1649-1749	24.6
B-9	Oak Ave. between Las Tunas Dr. and Workman Ave.	Temple City	Residential	5-16-87	1808-1903	23.9
B-10	Halsey Ave., S. of Live Oak	Irwindale	Residential	5-16-87	1925-2020	20.5
B-11	Myrtle Ave. and Oaks Ave.	Monrovia	Residential	5-16-87	2042-2146	19.2
C-1	W. end of Acacia Ave.	El Segundo	Residential[f]	5-12-87	1736-1834	18.0
C-2	Main St. and Mariposa Ave.	El Segundo	Park in business district	5-12-87	1850-1949	17.9
C-3	Douglas St. and Imperial Hwy.	El Segundo	Commercial	5-12-87	2005-2106	17.8
D-1	Pelota Park	La Verne	Residential[g]	5-17-87	1331-1428	24.8
D-2	Loma Ave. near Logan Ave.	La Verne	Residential[g]	5-17-87	1443-1540	24.9
D-3	Allessandro Blvd. between Cole Ave. and Barton St.	Riverside	Open area[h]	5-17-87	1805-1901	17.1
E-1	Veterans Park	Redondo Beach	Parking lot 45 m from beach	5-13-87	0606-0702	17.3
E-2	259th St., E. of Western Ave.	Los Angeles	Residential/Commercial[c]	5-13-87	0727-0824	19.0
E-3	San Francisco St., E. of Los Angeles River	Long Beach	Residential/Industrial[c]	5-13-87	0912-1012	20.3
E-4	Woodruff Ave., W. of Palo Verde Ave.	Long Beach	Commercial	5-13-87	1053-1205	21.0
E-5	Katella Ave. and Knott Ave.	Stanton	Residential[i]	5-13-87	1220-1318	21.5
F-1	Nutwood Ave. and State College Blvd.	Fullerton	University[j]	5-13-87	1438-1538	24.0
F-2	Manchester Pl., N. of Compton Ave.	Orange	Residential/Commercial	5-13-87	1620-1720	23.0

Table 7.2-1 (Continued)
MOBILE CHLOROFORM SAMPLING SITES

Site No.	Location	City	Description of Area	Date	Times	Mean Temp. (°C)
F-3	Warner Ave. and Bristol St.	Santa Ana	Shopping center	5-13-87	1758-1858	20.2
F-4	Corona del Mar State Park	Newport Beach	Parking lot at beach	5-13-87	2024-2124	18.5
G-1	San Gabriel River Parkway	Pico Rivera	Industrial park	5-17-87	1019-1114	26.2
G-2	Hacienda Blvd. near Francisquito Ave.	La Puente	Shopping center	5-17-87	1138-1233	30.2
G-3	Miller at Sierra Highway	Fontana	Open area	5-17-87	1615-1710	23.5
G-4	Redlands Blvd. and Alabama St.	Redlands	Commercial	5-17-87	1938-2034	15.8
G-5[k]	Carbon Canyon Regional Park	Olinda	Agricultural/Oilfields	5-18-87	1836-1937	18.0
G-6[k]	Carbon Canyon Regional Park	Olinda	Agricultural/Oilfields	5-18-87	1847-1937	18.0

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[a] Near intersection of boundaries of Toluca Lake, Universal City, and Burbank.

[b] Sun Valley area.

[c] In a parking lot.

[d] Just outside Culver City.

[e] Near a major hospital.

[f] 150 m directly downwind of Los Angeles Hyperion Treatment Plant.

[g] Downwind of Metropolitan Water District's Weymouth Softening and Filtration Plant.

[h] Downwind of Metropolitan Water District's Mill Filtration Plant.

[i] In a condominium complex.

[j] Parking lot directly west of California State University at Fullerton.

[k] Tandem sample.

7.2.3 Results

Table 7.2-3 shows the results of the mobile ambient sampling. Except for ethylene dibromide, the compounds of interest were generally well above their limits of detection, and only a few of the traps had such a heavy mass loading that the electron capture detector was saturated. Only one chloroform sample was below the limit of detection of 12 ppt. Ranges of detectable concentrations were as follows:

Compound	Concentrations (ppt)
Chloroform	12 - 480
1,1,1-trichloroethane	13 - 3,500
Carbon tetrachloride	10 - 460
Trichloroethylene	16 - 3,100
Perchloroethylene	29 - 1,100
Ethylene dibromide	33

These values are consistent with those reported for the South Coast Air Basin by Shikiya et al. (1984) and Singh et al. (1982), although, as will be discussed below, elevated concentrations were found at a few sites. Findings for each set were as follows.

Set A. Chloroform concentrations generally rose from the coastal site in the morning to a maximum of 104 ppt at night in the northwest corner of the San Fernando Valley. It is possible that the chloroform at Site A-10 was influenced by a nearby swimming pool, but it is more likely that the level represents at least one day's accumulation of VOC contributions from numerous upwind sources. It is interesting that the highest concentration of perchloroethylene (1,100 ppt), the second highest concentration of carbon tetrachloride (297 ppt) and the third highest level of 1,1,1-trichloroethane (775 ppt) of all the mobile sampling were also measured at this site.

Set B. The highest chloroform concentrations on this route occurred at the two sites nearest the coast (B-1 and B-2) in the morning. As will be discussed in Section 7.3, this may result from a nighttime accumulation of chloroform over marine waters. Site B-8 in Alhambra had high levels of 1,1,1-trichloroethane (470 ppt), trichloroethylene (1,600 ppt) and perchlorethylene (saturated detector). In fact, the TCE level is well above

Table 7.2-3

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.

the monthly means reported by Shikiya et al. (1984) for May in the SCAB (200 - 600 ppt). The air sample was collected in the parking lot of a shopping mall in a residential area. The coincidence of high 1,1,1-trichloroethane and TCE levels suggests a degreasing emission source nearby, although we did not explore the area.

Set C. The highest chloroform concentration of all of the mobile sampling (483 ppt) was measured directly downwind from the Los Angeles Hyperion wastewater treatment plant. As will be discussed in Section 8.1.1, the plant is definitely a source of chloroform emissions. The other two downwind concentrations (218 and 175 ppt) were also relatively high, but not unusual for the SCAB. It is possible, since the treatment plant is on the coast, that chloroform present in marine air comprised a portion of the observed values.

Set D. The three sites downwind of the MWD water treatment plants did not have particularly high $CHCl_3$ levels. The value for Site D-3 (112 ppt) may be an underestimate, since significant breakthrough occurred.

Set E. This route was notable for having the highest 1,1,1-trichloroethane concentration of all of the sampling. No likely source was observed in the vicinity.

Set F. This set of samples, which was collected in the afternoon and evening, had some of the highest levels of $CHCl_3$ and the highest level of trichloroethylene. Site F-1 was next to a university and may have been influenced by emissions from laboratories. Likewise, Site F-2, which had 333 ppt of chloroform, was about 600 m from the University of California at Irvine Medical Center in Orange. The hospital and its associated laboratories could have been a source. The fact that the TCE concentration was so high (3,100 ppt) and that the 1,1,1-trichloroethane and perchloroethylene mass on the trap saturated the electron capture detector, indicate that some industrial sources may have been upwind.

Set G. The second-highest chloroform concentration of the mobile sampling (430 ppt) was found at Site G-3, which was in a semi-rural area near

Fontana. The TCE concentration (1,200 ppt) was also high at this location. Potential sources of these concentrations are unknown.

7.2.4 Discussion

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. Location, on the other hand, appears to be a likely determinant of hourly average concentrations. 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. Other areas of elevated concentration, such as Sites B-8, F-2 and G-3, and the sites downwind of the Hyperion Treatment Plant, should be investigated further as "hot spots," and specific point sources should be identified.

7.3 MARINE AIR AND WATER SAMPLING

The objectives of this part of the field work were (1) to assess the potential for an oceanic source of chloroform emissions in the South Coast Air Basin and (2) to measure chloroform concentrations upwind of the basin during times of onshore flow and integrated Basin-wide concentrations during times of offshore flow. To these ends, air and water samples were collected offshore from Point Dume to Huntington Beach, aboard the research boat Osprey.

7.3.1 Methods

7.3.1.1 Sampling Plan

Our original plan was to collect air and water samples at 18 points during 36 consecutive hours at sea. Inclement weather, however, forced us to terminate the cruise after only five sets of samples had been collected. A second cruise, eight days later, obtained nine more sets of samples, until heavy seas again forced a return to port.

Figure 7.3-1 shows the locations of the sampling points, while Table 7.3-1 summarizes sampling conditions and defines the sample sets. Note that the latitudes and longitudes of Sites 7, 8, and 13 through 17 were determined by LORAN triangulation at the time of anchoring. Due to the failure of the LORAN equipment, the remaining latitudes and longitudes were estimated by sighting landmarks, observing the depth, and referring to charts. At all sites, an attempt was made to anchor near the 50-ft depth contour. This depth was chosen because it defines the habitat of most of the local macroalgae, which were identified in Chapter 5 as potential biotic sources of chloroform. Indeed, several sites were deliberately located in kelp beds.

7.3.1.2 Air Sampling and Analysis

Air samples were collected for one hour on carbon molecular sieve (CMS) traps, using the same methods as in the mobile ambient sampling (see Section 7.2.2). During the first round of sampling (Points 13-17), the sampling flow rate varied from 36 to 70 ml/min. After preliminary analyses of these samples revealed some breakthrough, we reduced the flow rate to about 23 ml/min and the sample volume to 1.4 L. CMS traps and a thermometer were mounted on a wire basket which was lashed to a rail along the port bow. In all cases, front and backup traps were deployed in series, and two field blanks were submitted for analysis. Samples were analyzed by EMSI using the procedures described in Section 7.1.2.2.

7.3.1.3 Water Sampling and Analysis

Seawater samples were collected nearly simultaneously at the surface and at five other points to a depth of 50 ft by deploying 5-liter Niskin bottles at regularly-spaced intervals along a weighted line. When the Niskin bottle is deployed, the lids at each end are kept open by springs which are attached to a plunger. A "messenger" weight is dropped along the line; when it strikes the plunger, the springs holding the lids open are released and the bottle closes. Another messenger weight, which is also released by the plunger, then drops to close the next bottle, and so on. Bottles were raised

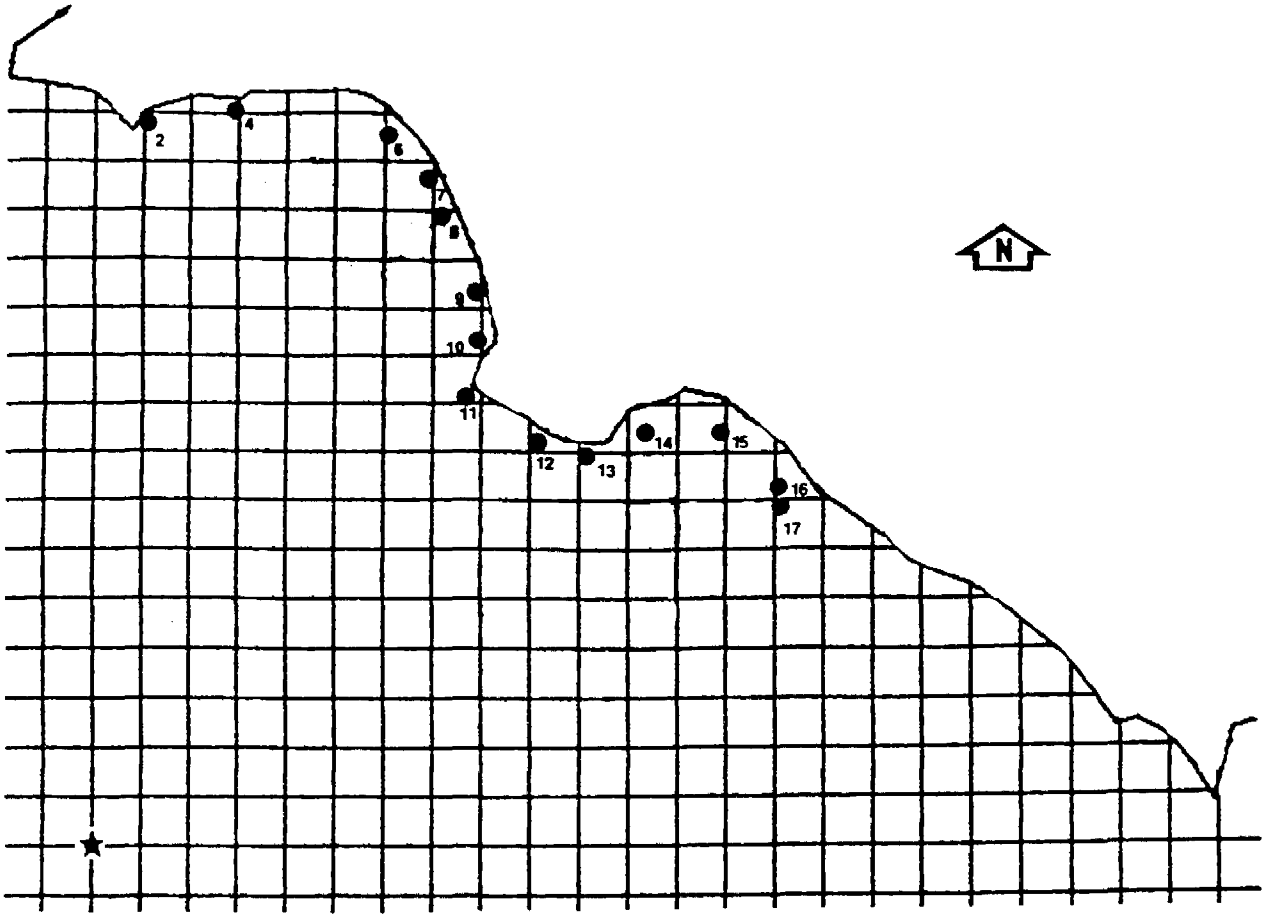

Figure 7.3-1. Locations of Marine Air and Water Sampling Points. The UTM Coordinates of the Star are 3690 N, 335 E. Points are Described in Table 7.3-1.

Table 7.3-1

MARINE AIR AND WATER SAMPLING SITES

Site No.	Date	Air Sample Interval	Latitude	Longitude	Depth (ft)	Shore Description
2	5-7-87	1847-1948	34°00'49"	118°46'52"	56	Between Point Dume and Paradise Cove
4	5-7-87	2039-2139	34°01'29"	118°40'48"	54	Malibu Point
6	5-7-87	2228-2329	33°59'52"	118°30'50"	57	Santa Monica Pier
7	5-7-87 5-8-87	2357-0059	33°57'19"	118°27'45"	53	Marina Del Rey Breakwater
8[a]	5-7-87	0808-0908	33°55'15"	118°26'44"	49	Hyperion Treatment Plant
9[a]	5-7-87	0940-1053	33°51'33"	118°24'40"	50	Hermosa Beach
10	5-7-87	1124-1226	33°48'40"	118°24'20"	53	South end of beach, Redondo Beach
11	5-7-87	1252-1352	33°45'20"	118°25'10"	60	Near Resort Point (kelp bed)
12	5-7-87	1417-1517	33°43'00"	118°20'05"	60	West of Point Fermin
13[a]	4-29-87	1723-1827	33°42'02"	118°17'22"	20	Point Fermin (kelp bed)
14[a]	4-29-87	1532- b	33°43'37"	118°13'20"	53	L.A. Harbor Breakwater, south of entrance
15[a]	4-29-87	1347-1448	33°43'13"	118°08'40"	52	500 m West of Breakwater
16[a]	4-29-87	1203-1304	33°40'44"	118°04'22"	50	End of Warner Avenue
17[a]	4-29-87	1020-1120	33°39'15"	118°04'41"	52	Huntington Beach, near Platform Emmy

[a] Latitudes and Longitudes for these points were determined by LORAN triangulation; other latitudes and longitudes estimated by map measurement.

[b] Pump failed at undetermined time.

one at a time by means of a winch and davit, and emptied into 40-ml glass volatile organic analysis (VOA) vials. Bottles found to contain gas bubbles were emptied and refilled. Samples were analyzed by the method described in Section 8.1.1.3. (See Appendix C for more details.)

7.3.2 Results

7.3.2.1 Air Sampling

Results of the analyses of the marine air samples are presented in Table 7.3-2. The sample volumes were high enough to permit fairly low detection limits, such as 9 ppt for chloroform. On the other hand, breakthrough was observed in almost all CMS trap pairs. As in the case of the fixed-site sampling, those concentrations in which we feel most confident are shown in boldface in the table.

One result which is immediately striking is that ambient chloroform concentrations were generally higher than those observed during the mobile sampling on land. The three "sure" values (309, 392 and 1,460 ppt) exceed 93 percent of the land-based concentrations, and are similar to the 530 ppt observed by Su and Goldberg (1976) in marine air off San Pedro. The highest chloroform value was observed around noon off Redondo Beach. The concentration of 1,1,1-trichloroethane was also high (1,700 ppt) there.

For most of the sampling, winds were onshore. Offshore flow was readily apparent only at Site 11 (Resort Point). This site had the highest perchloroethylene concentration of the marine sampling (513 ppt), but 1,1,1-trichloroethane was below the detection limit of 8 ppt.

7.3.2.2 Water Sampling

Table 7.3-3 shows the chloroform concentrations measured at various depths at each of the sampling points. They range from below the detection limit of 5 ppt to 14 ppt. By comparison, Su and Goldberg (1976) measured 11.8 ± 5.8 ppt in waters off La Jolla. In the following discussion, therefore, the terms "high" and "low" are used only in the context of the

Table 7.3-2

CONCENTRATIONS OF HALOCARBONS IN MARINE AIR, SOUTH COAST AIR BASIN

(All concentrations in ppt)

Sample	Date	Sampling Interval	Chloroform	1,1,1-Trichloroethane	Carbon Tetrachloride	Trichloroethylene	Perchloroethylene	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.

Table 7.3-3

CHLOROFORM CONCENTRATIONS IN SEAWATER OFF THE COAST OF THE SCAB
(Concentrations in ppt)

Depth[a]		Sampling Point														Mean[e,f] for Depth
ft	m	2	4	6[c]	7	8	9	10	11	12	13[d]	14	15	16	17	
0	0	<5[b]	<5	7.3	6	5	6	5	<5	<5	9	<5	9	6	6	5.1 ± 2.4
9	2.7	<5	<5	6.3	10	<5	5	<5	5	5	5	7	9	8	5	5.4 ± 2.6
18	5.5	<5	6	10	5	5	<5	<5	6	6	<5	<5	13	10	<5	5.7 ± 3.4
27	8.2	<5	9	14	7	6	12	6	7	6	<5	6	<5	9	5	7.6 ± 3.5
36	11.0	7	<5	7.5	7	10	<5	11	7	5		6	9	5	<5	6.3 ± 2.8
45	13.7	7	7	8	12	12	5	12	14	10		7	6	5	<5	8.3 ±3.4
Mean[e]		4.0	4.9	8.9	7.8	6.8	5.5	6.5	6.9	5.8	4.8	5.2	8.1	7.2	3.9	6.6
Std. Dev.		2.3	2.8	2.8	2.6	3.5	3.5	4.1	3.9	2.4	3.1	2.1	3.5	4.6	1.6	6.9

[a] Distance from surface to center of vertically-deployed Niskin bottle.

[b] Detection limit = 5 ng/L = 5 ppt.

[c] Mean of duplicate samples, samples below detection limit were assumed to be 2.5 ppt.

[d] Depths for samples at Point 5 were 0 ft, 5 ft (1.5 m), 10 ft (3.0 m), and 15 ft (4.6 m).

[e] In calculating means, samples below detection limit were assumed to be 2.5 ppt.

[f] Point 13 is not included in means for depths below the surface.

measurements reported here: the waters off the SCAB are not heavily polluted with chloroform. The distribution of concentration with depth and along the coast is shown graphically in Figure 7.3-2. There appear to be two zones of higher concentration. One is at the lowest depths from Marina del Rey to Resort Point, while another is nearer the surface from Los Angeles Harbor to Huntington Beach. Concentrations in the vicinity of the kelp beds were fairly low, except for values of 9 ppt at the surface at Point 13 and 14 ppt at the bottom at Point 11.

7.3.2.3 Discussion

From the findings reported in this chapter, 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, 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.

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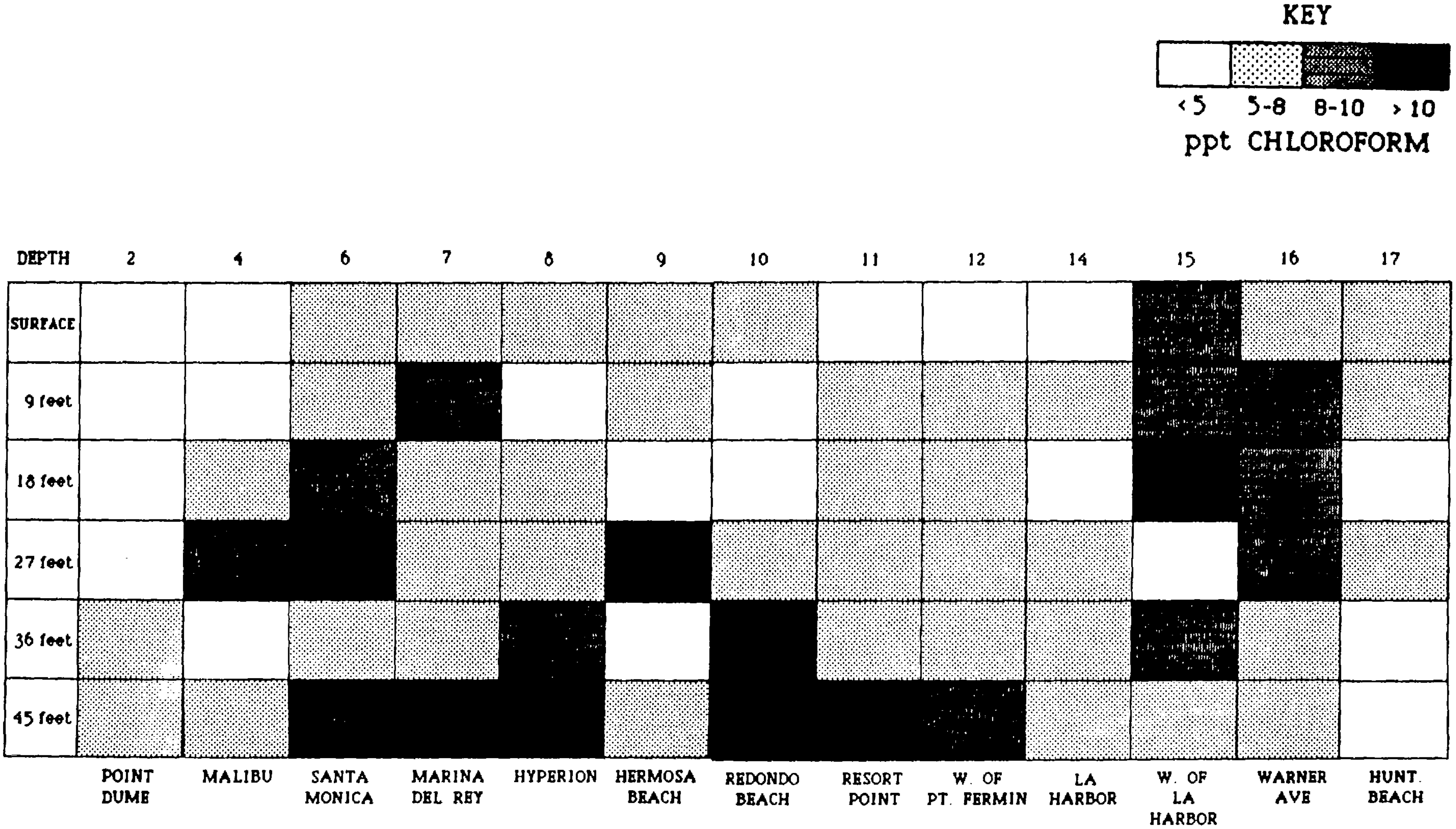

Figure 7.3-2. Distribution of Chloroform Concentrations With Depth, by Sampling Point.

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8.0
EMISSIONS TESTING

8.1 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. As a comprehensive, rigorous testing program would have required resources beyond those available for this project, only a preliminary estimate of emissions was attempted. Two wastewater treatment plants were selected for sampling: the Hyperion Treatment Plant (HTP), which is operated by the City of Los Angeles, and the City of Riverside's Water Quality Control Plant. The former was chosen because it is the largest in the SCAB and receives a wide variety of wastes. In addition, volatile organic compound concentrations in the wastewater had been measured recently by the ARB (Simeroth et al., 1985) and the HTP staff (Mohamed, 1986); the ARB had also measured air pollutant concentrations at various points. The Riverside plant was chosen because the modeling performed in Phase I showed that it could have a significant local influence on chloroform concentrations, and because nitrified final effluent is chlorinated.

8.1.1 Hyperion Treatment Plant

8.1.1.1 Description of Plant

The Hyperion Treatment Plant is located in Playa del Rey, immediately southwest of Los Angeles International Airport. It collects residential and industrial waste from approximately 6,000 miles of mainline sewers in the City of Los Angeles' wastewater collection system. It also treats wastewater from other municipalities in the area and services almost 4 million people across nearly 600 square miles.

The plant has a design capacity of 420 million gallons per day (mgd) of primary treatment, although it frequently processes approximately 520 mgd.

Excess sewage is treated with coagulants and processed to approximately 80 percent of the quality of the remaining primary sewage. Hyperion also has a secondary treatment system, which currently operates at approximately 100 mgd. Secondary effluent is blended with primary effluent and disposed to the ocean at a submarine outfall five miles offshore.

Raw wastewater first enters the plant at the East and West Headworks facilities, in which bar screens remove coarse debris, detritors reduce the size of the debris, and sand and heavier inorganic material settle out in grit chambers. Organic solids remain in suspension during these processes. Detention times at the East and West Headworks average about one and ten minutes, respectively (CLA, undated). Air emissions are likely to occur in the headworks because of the turbulent mixing that takes place when the wastewater from the various influent pipes converges. The mechanical agitating action of the bar screens creates additional turbulence and may enhance stripping of volatile compounds from the water.

From the East and West Headworks facilities, wastewater enters primary sedimentation tanks, in which most of the organic solid material (sludge) settles to the bottom. The sludge is then conveyed to anaerobic digesters for further processing. Wastewater remains in these tanks for approximately 1.3 hours (CLA, undated). Approximately 76 percent of the primary-treated wastewater is conveyed to the effluent pumping station for final ocean disposal; the remaining 24 percent undergoes secondary treatment.

Primary-treated effluent destined for secondary treatment travels through covered-channels and into aeration tanks containing biologically active material known as activated sludge. The combination of activated sludge and vigorous bubbling of injected compressed air (which supplies the oxygen necessary to sustain the viability of the activated sludge) promotes the degradation of biologically oxidizable organic materials in the wastewater. When the aeration cycle is completed, the effluent is conveyed to clarifying tanks where the activated sludge is collected for later use in the next cycle. The aeration tanks possess significant air emission potential because of the tremendous increase in the air-liquid interface created by the bubbling action. The channels feeding the aeration tanks also present an emission potential because of the agitation occurring during conveyance. Secondary treated wastewater is then pumped to the effluent pumping plant before its final disposal to the submarine outfall offshore.

8.1.1.2 Description of Sampling Points

Air samples were taken at all sites in the plant where wastewater is exposed to the atmosphere and/or agitated; water samples were taken at the influent and effluent pipes. Sampling took place from 1:00 p.m. on Thursday, 6 November through 11:30 p.m. on Friday, 7 November 1986. Figure 8.1-1 is a map of the HTP. Sampling locations are labeled to correspond to the following sites.

Fast Flow Influent Pipe (Sites W1-FF and A2-FF). Influent to the East Headworks flows very rapidly through a buried pipe. During the sampling, the water surface was approximately 10 to 12 feet below the ground. Access to the pipe was obtained via a covered manhole. The influent pipe was one-half to two-thirds filled during most of the sampling; the water level was slightly lower between 1 a.m. and 6 a.m. The manhole diameter was about three feet. The water was slightly warm to the touch, and, although temperatures were not measured, the headspace air appeared to be warmer than the ambient air. Water and air samples were collected through a small hole in the manhole cover. (See Section 8.1.1.3.) Air samples were drawn with a 1-ml syringe placed about four to five inches below the manhole cover.

Slow Flow Influent Pipe (Sites W1-SF and A2-SF). Influent to the West Headworks flows slowly through a buried pipe. Water and air samples were taken from a manhole about 10 ft southwest of the fast flow influent manhole.

Foul Air Duct (Site A3). The foul air duct conveys air from the headspaces of the influent pipes to a compressor, the outflow from which is injected into the secondary aeration tanks. Air samples were taken from a 3-inch diameter hole in a manhole cover east of the West Headworks building. Air flowed through this hole under slight positive pressure. Samples were taken about two to three inches below the cover, using a 0.1-ml syringe. The

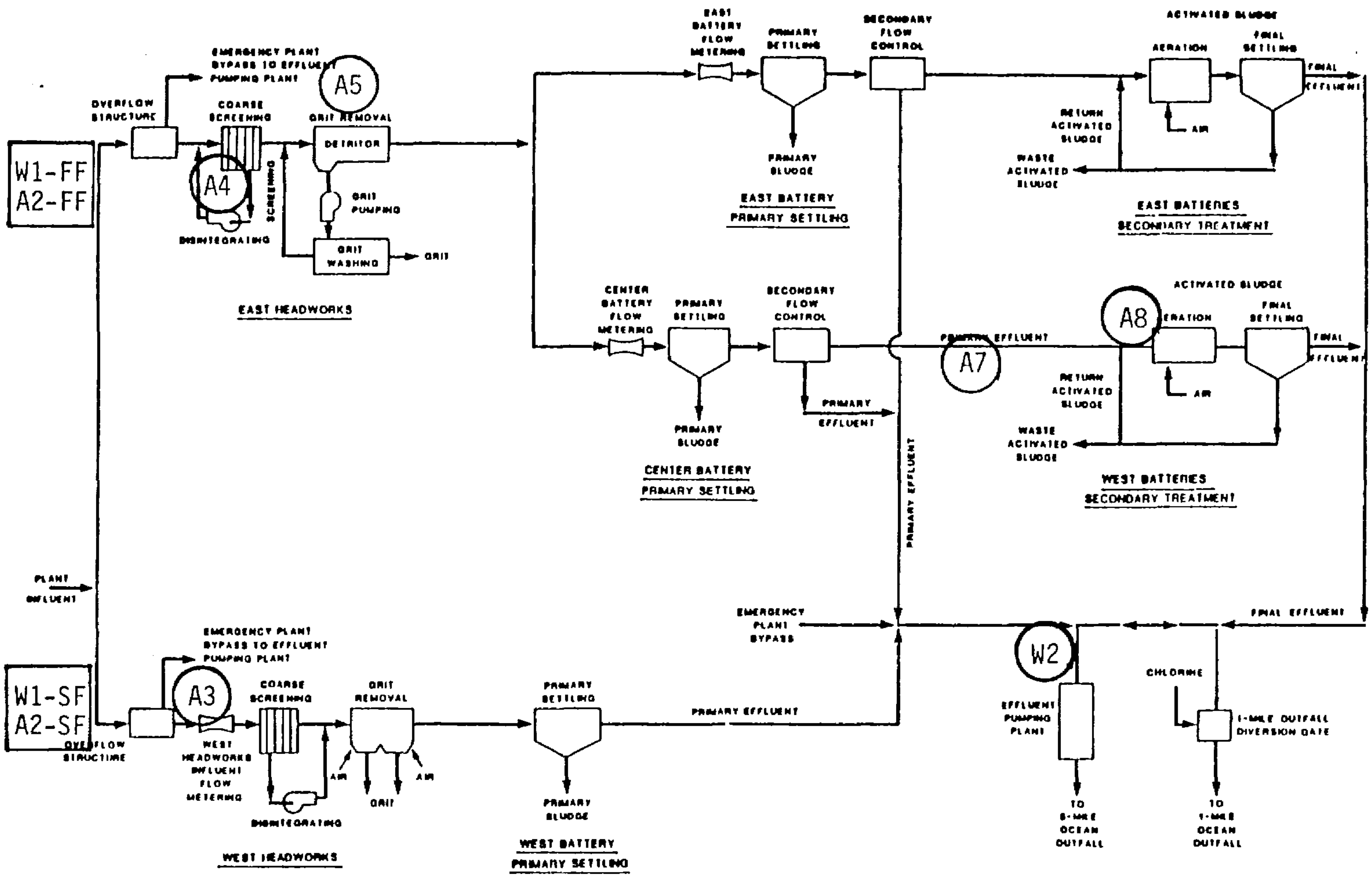


Figure 8.1-1. Air and Water Sampling Points at The Hyperion Treatment Plant.

air flowing out was somewhat warmer than the ambient air.

East Headworks Bar Screens (Site A4). Bar screens are located in the East Headworks building, whose doors are usually open. Air samples were taken from the bar screen closest to the west door placing a 1-ml syringe about two to three feet above the water surface. The bar screen agitated the water at one- or two-minute intervals; otherwise, the water surface was calm.

Hydraulic Grit Chambers (Site A5). The grit chambers are also located in the East Headworks building, although in a different room from the bar screening operation. Water is slowly agitated in circular tanks, while vapors are collected by negative pressure hoods and conveyed to roof vents. Because of the difficulty of approaching the water surface, we taped the GC sampling syringe to a 6-ft pole, and affixed a string to the plunger. The syringe was then lowered into one of the tanks to a height about 1 ft above the water surface and a distance of 4 to 5 feet from the tank wall.

Primary Effluent Channel to Aeration Basins (Site A7). The primary effluent channels convey primary-treated effluent to the activated sludge aeration basins. The channels are covered with steel plates. However, several plates are missing, and the gaps between plates permit emissions of volatile compounds. Air samples were taken from a 4-inch by 5-ft opening between two steel plates. Water in the channel moved rapidly and was slightly agitated by a small amount of bubbling from within. The air rising from the channel was warmer and moister than the ambient air. The samples were taken at the northwest corner of the opening, 4 to 5 inches below the plates and about 1 ft above the water surface.

Activated Sludge Aeration Basins (Site A8). Secondary treatment is conducted in a battery of 32 rectangular aeration basins separated by walkways. Air samples were taken at the eastern end of these basins, near the intake side. The water was highly agitated from turbulence and bubbling. The syringe was placed about 1 to 1.5 ft from the water surface and 8 to 12 inches below the walkway, and 1 ft horizontally out from the basin wall.

Five-Mile Outfall Pumping Station (Site W9). Effluent samples were obtained directly from a spigot at the five mile outfall pumping station. Water obtained from this point consists of a mixture of primary and secondary effluent.

8.1.1.3 Sampling and Analytical Methods

Water Samples

Because the influent wastewater was not accessible directly, water samples from Sites W1-FF and W1-SF were first obtained by lowering a plastic bucket through holes in the manhole covers. A 40-ml glass VOA sampling vial was then filled by slow immersion into the bucket; when filled, the vial was topped and sealed with a Teflon-faced septum and a screw cap. Vials were topped to insure an absence of air bubbles. Effluent samples were taken from a continuously running spigot, except from 4 a.m. to 10 a.m., when they were taken from a manhole, as described previously. After filling, the vials were put into Ziplok^{TM} plastic bags and placed in an ice chest.

Water samples were analyzed by Environmental Monitoring and Services, Inc. (EMSI) of Camarillo, California, using EPA Method 601 (Longbottom and Lichtenberg, 1982), which is the standard method for analyzing municipal and industrial discharges for halocarbons. Samples are analyzed by bubbling an inert gas through an aliquot. The halocarbons, which are efficiently transferred to the vapor phase, are swept onto a sorbent. After purging is complete, the sorbent is quickly heated and backflushed with carrier gas to desorb the halocarbons onto the head of a GC column. EMSI used a 30 m x 0.53 mm ID DB-624 megabore column for quantitation and a 60 m x 0.75 mm ID VOCOL capillary column for confirmation. Prior to the analysis of each sample batch, three concentrations of a chloroform standard were analyzed, the detection limit was checked, and a method blank was analyzed to ensure the performance of the analytical system. A standard check was also analyzed after every ten samples, and the analysis sequence was always completed with a standard. To prevent carryover contamination, the purging chamber was rinsed twice with 12 ml of organic-free water between every standard and sample analysis. The retention time for $CHCl_3$ was calculated daily using the aforementioned standards to determine location in the sample chromatograms. All positive identifications of $CHCl_3$ were confirmed with the second column. The detection limit of the analysis was 50 ng/l (ppt).

Air Samples

Before each sample was collected, the sampling syringe was cleaned by filling it with nitrogen and heating it after 10 to 15 seconds with an Hejet Model HJ-700 heat gun (Pamran Company, Inc.). It was then allowed to cool to the ambient temperature and evacuated. At the sampling site, the syringe was filled and evacuated two to three times before the actual sample was taken. After sampling, the syringe was closed and returned to the portable GC for injection and analysis.

The instrument used for analysis was an Analytical Instrument Development Corporation Model 210 portable gas chromatograph with an electron capture detector and a 1.82-m x 3.2 mm ID column packed with 10 percent SP-1000 Supelcoport. The oven temperature was maintained at 79°C and the N_2 carrier gas flow rate was 23.4 ml/min. For a 1-ml injection of air sample, the chloroform detection limit was about 6 ppb. N_2 blanks and chloroform standards were injected periodically throughout the sampling.

8.1.1.4 Results

Water Sampling

Combined East and West Headworks flow rates for the sampling interval were obtained from a continuous recorder chart provided by the plant operator. On the basis of historical records, we apportioned 73 percent of the influent flow to the West Headworks and 27 percent to the East Headworks. Effluent flow rates are not monitored. According to the plant operator (Turhollow, 1987), the average residence time in the facility is about 11 hours. The effluent flow rate at a given time was therefore assumed equal to the combined influent flows 11 hours earlier.

To estimate chloroform emissions from the plant, we wished to examine a 48-hour period running from midnight to midnight. However, flow data were unavailable for the first 8 hours of 6 November (before our sampling). In addition, influent data for the last 11 hours of 5 November were needed to project the effluent flows for the first 11 hours of 6 November. To overcome these problems, we created the following "synthetic data" sets:

Data Set Synthesized	Origin of Synthetic Data
Inflow, 6 November, 0000 - 0730 hrs	Inflow, 8 November, 0000 - 0730 hrs
Outflow, 6 November 0000 - 1030 hrs	Inflow, 7 November, 1300 - 2330 hrs

Figures 8.1-2 through 8.1-4 show the West Headworks, East Headworks, and effluent flows, respectively, along with the results of the wastewater analyses. Flows have a marked diurnal pattern, with maxima at around 1 p.m. and minima at about 8 a.m. This pattern is consistent with the one used in this project for dispersion modeling.

Measured wastewater chloroform concentrations are reported in Table 8.1-1, along with corresponding flow rates, which were estimated by interpolating between measured values. Influent concentrations ranged from 6.6 to 28.0 ppb, while those in the five-mile effluent varied from 6.1 to 17.6 ppb. These results are quite similar to those obtained in previous studies by the ARB (Simeroth et al., 1985) and the Hyperion Treatment Plant staff (Mohamed, 1986). The ARB found 9.7 and 8.4 ppb of $CHCl_3$ in two grab samples collected from the West Headworks influent at about 1100 hrs on 20 June 1985, while the mean and standard deviation of 5 grab samples collected at the same point by the HTP staff between 10 February and 1 April 1986 were 21.4 and 3.4 ppb, respectively. The HTP staff also found 12.7 ± 7.4 ppb of chloroform in 5 grab samples of the 5-mile outfall effluent collected between 24 January and 1 April 1986; our corresponding values were 11.4 ± 4.9 ppb.

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 are negatively correlated ($r = -0.886$). In the

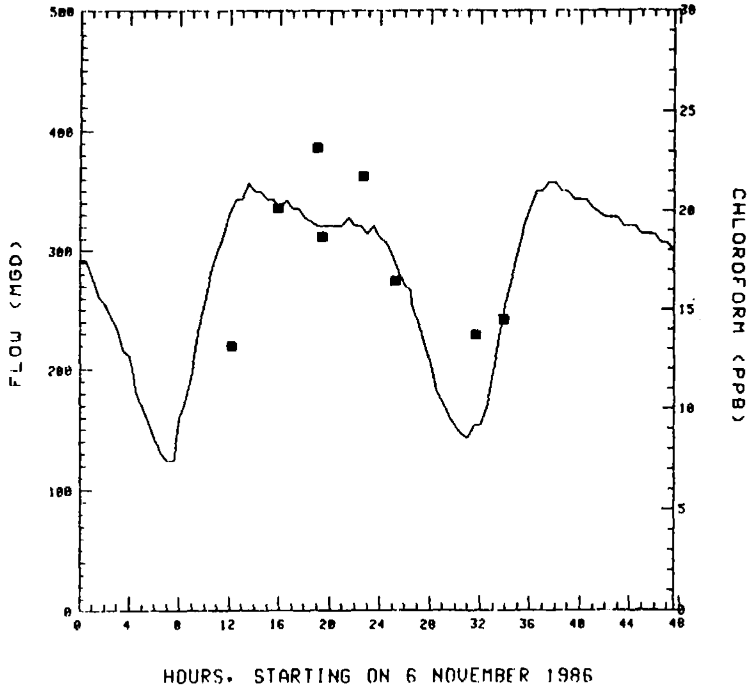


Figure 8.1-2. Influent Flow Rates and Chloroform Concentrations During SAIC Sampling at Hyperion Treatment Plant ("Fast Flow").

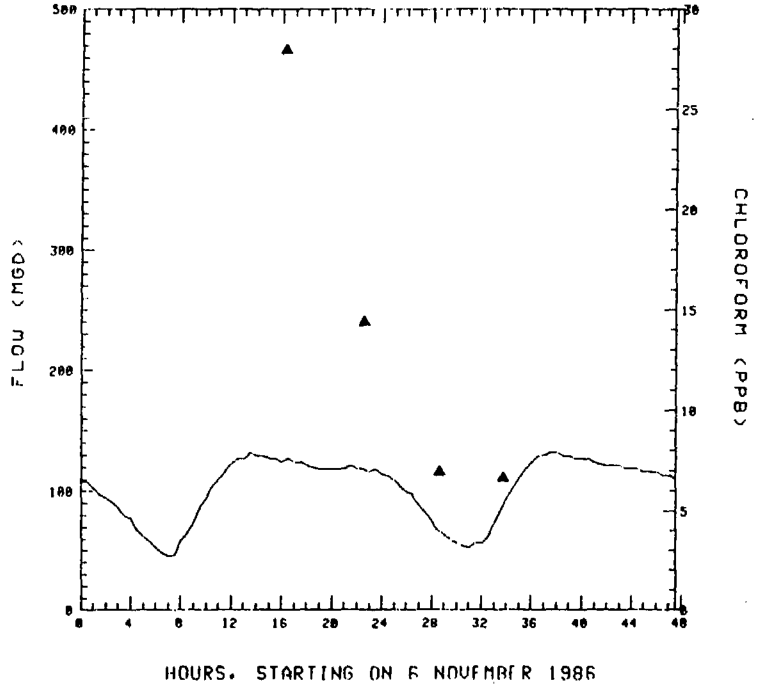


Figure 8.1-3. Influent Flow Rates and Chloroform Concentrations During SAIC Sampling at Hyperion Treatment Plant ("Slow Flow").

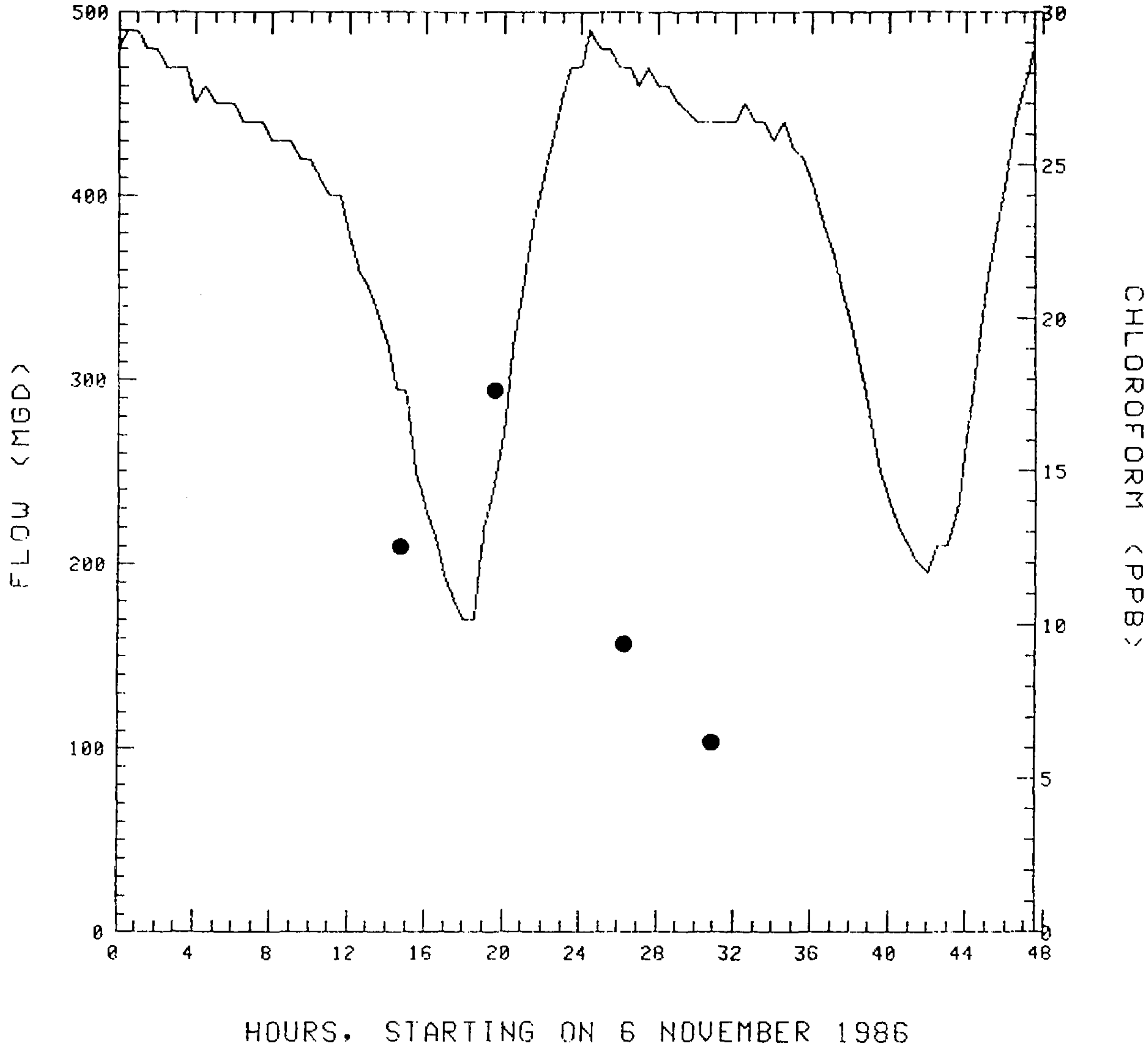


Figure 8.1-4. Effluent Flow Rates and Chloroform Concentrations During SAIC Sampling at Hyperion Treatment Plant.

Table 8.1-1

SUMMARY OF CHLOROFORM MEASUREMENTS IN WASTEWATER AT HYPERION TREATMENT PLANT, 6-7 NOVEMBER 1986

		Influent Measurements				Effluent Measurements	
Date	Time	East Headworks Flow (mgd)	Conc (ppb)	West Headworks Flow (mgd)	Conc (ppb)	Flow[a] (mgd)	Conc (ppb)
11/6/86	1315			350.4	13.0		
11/6/86	1455					294.2	12.6
11/6/86	1600			335.8	20.0		
11/6/86	1603	124.5	28.0				
11/6/86	1911			321.2	23.2		
11/6/86	1921			321.2	18.6		
11/6/86	1937					247.0	17.6
11/6/86	2239	118.0	14.2				
11/6/86	2242			318.3	21.7		
11/7/86	0114			289.1	16.2		
11/7/86	0226					470.0	9.3
11/7/86	0441	66.2	6.9				
11/7/86	0648			143.8	13.6		
11/7/86	0700					434.3	6.1
11/7/86	0947			242.8	14.2		
11/7/86	0950	90.9	6.6				

[a] Estimated by lagging total influent flow by 11 hours.

West Headworks, which accounts for most of the mass chloroform input to the HTP, the correlation between flow and concentration is weak (r = 0.489).

Air Sampling

Table 8.1-2 shows the ambient chloroform concentrations measured at each of the sampling points described in Section 8.1.1.2. 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. At a given sampling point, concentrations varied little with sampling time, suggesting fairly constant emission rates at different points in the waste treatment process.

In Figure 8.1-5 the sampling points are displayed on the x-axis in order of wastewater treatment stage. Plus signs represent chloroform measurements, while dots represent the geometric mean for each sampling point. High concentrations near the start of the process (in the slow-flow inlet and in the foul air duct) reflect volatilization of chloroform from the wastewater as it flows through the collection system. 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.

8.1.1.5 Emissions Analysis

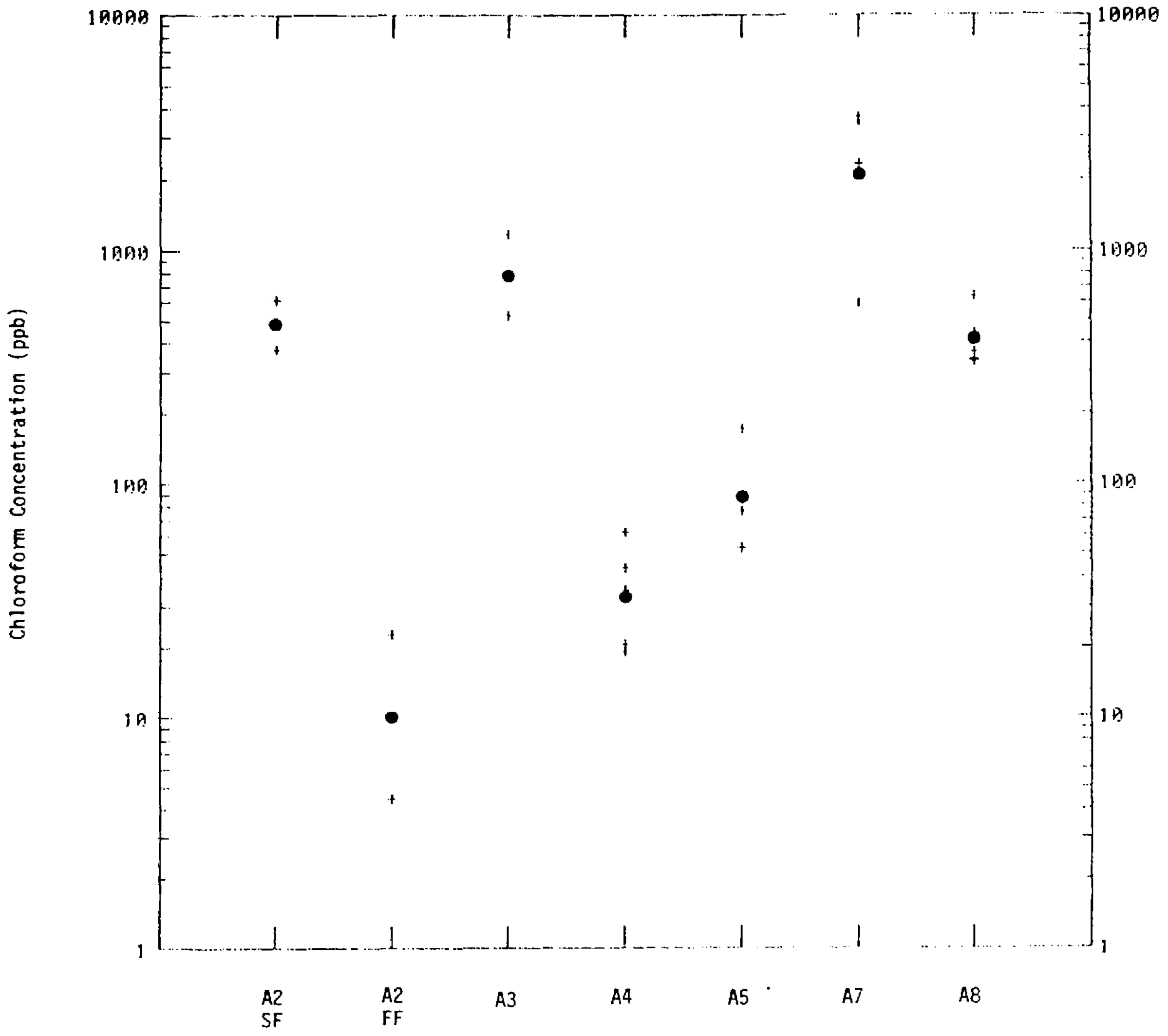
An analysis of emissions from the HTP must take into account two emission sources: transfer of VOCs from water to air at various stages of the treatment process and release of headspace air from the influent pipes; the latter source represents volatilization that has occurred during collection and transport of wastewater to the plant.

Table 8.1-2

AMBIENT CHLOROFORM CONCENTRATIONS ABOVE VARIOUS POINTS AT THE HYPERION TREATMENT PLANT

(Concentrations in ppb)

Time	Inlet (Slow)	Inlet (Fast)	Foul Air Duct	Bar Screens	Grit Chamber	Primary Effluent	Activated Sludge
6 November 1986							
1344			1,180				
1419				62			
1440				21			
1538						600	
1621						3,520	
1657					76		
1755							330
1831	380						
1924		4					
2005			770				
2036				19			
2215					170		
2311						3,660	
2336							340
7 November 1986							
0039							370
0128		23					
0147			790				
0200				35			
0511					53		
0538						2,320	
0559							440
0726			530				
0745				43			
0817	620						
0928					86		
1006						2,140	
1041							640
Geometric Mean	484	10	786	33	88	2,073	410



KEY

A2 SF = Slow flow influent pipe
A2 FF = Fast flow influent pipe
A3 = Foul air duct
A4 = East Headworks bar screen
A5 = Hydraulic grit chambers
A7 = Primary effluent channel
A8 = Activated sludge aeration basins

Figure 8.1-5. Chloroform Concentrations Measured Above Various Processes in the Hyperion Treatment Plant.

Volatilization of Chloroform at the HTP

It was beyond the scope of this study to estimate chloroform emissions from individual processes. Instead, we attempted a mass balance over the entire plant. Our assumptions were:

- No significant chloroform sources are present in the HTP; and
- A negligible fraction of the chloroform entering the plant is partitioned to the solid phase (i.e. sludge).

In order to calculate an accurate mass balance, it is necessary to take the residence time in the plant into account. At the HTP, the effluent discharged to the five-mile outfall entered the plant an average of 11 hours earlier. Therefore, the mass balance equation is:

$$M_o(t) + E(t) = M_i(t-11) \tag{8-1}$$

where $M_o(t)$ is the mass flow to the five-mile outfall at time t, $M_i(t-11)$ is the mass flow into the plant at t - 11, and E is emissions at time t. Mass flow, in turn, is equal to chloroform concentration times volumetric flow rate. If C_o and C_i are the concentrations in the effluent and influent, respectively, and Qo and Q_i are the corresponding volumetric flow rates, then emissions are calculated from:

$$E(t) = C_i(t-11)Q_i(t-11) - C_o(t)Q_o(t) \tag{8-2}$$

By interpolating between measured values, we first calculated flow rates and concentrations for every half hour and every measurement time between 0000 hrs on 6 November and 2330 hrs on 7 November. Time-weighted averages of mass flows were then calculated for each hour. Finally, hourly emissions were calculated with Equation 8-2.

For 36 of the 48 hours for which calculations were performed, mass flows into the plant exceed 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. In the following discussion, we treat these "negative" emissions as zero.

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. Figure 8.1-6 shows the estimated emission rate during each of the 48 hours analyzed. A clear diurnal pattern, with maxima in the late afternoon or early evening and minima in the early morning, is evident.

Emissions Via the Foul Air Duct

As reported in Section 8.1.1.4, chloroform concentrations in the foul air duct ranged from 532 to 1179 ppb. The mean and standard deviation were 818 and 268 ppb, respectively. Assuming an ambient temperature of 25°C and pressure of 1 atmosphere, the mean concentration is equivalent to 3968 $\mu g/m^3$. According to the HTP staff (Turnollow, 1986), the flow through the foul air duct varies from 30 to 160 cfm. If we assume this flow to be proportional to the combined East and West Headworks wastewater flow, then we may scale it to the wastewater flows observed on 6-7 November 1986. The minimum, mean and maximum combined influent flows were 170, 378.9, and 490 mgd, respectively. The scaled mean foul air duct flow rate would therefore be:

$$\text{Foul air flow} = 30 + \left(\frac{378.9 - 170}{490 - 170}\right)(160 - 30) = 114.9 \text{ cfm}$$

$$= 3.25 \text{ m}^3/\text{min}$$

Average emissions would therefore be:

$$\left(\frac{3.25 \text{ m}^3}{\text{min}}\right)\left(\frac{60 \text{ min}}{\text{hr}}\right)\left(\frac{24 \text{ hr}}{\text{day}}\right)\left(\frac{3968\ \mu g}{\text{m}^3}\right)\left(\frac{2.205 \times 10^{-9} \text{ lb}}{\mu g}\right)$$

$$= 0.041 \text{ lb/day}$$

Since this value is significantly lower than the emissions from volatilization, it may be ignored. Total annual chloroform emissions from

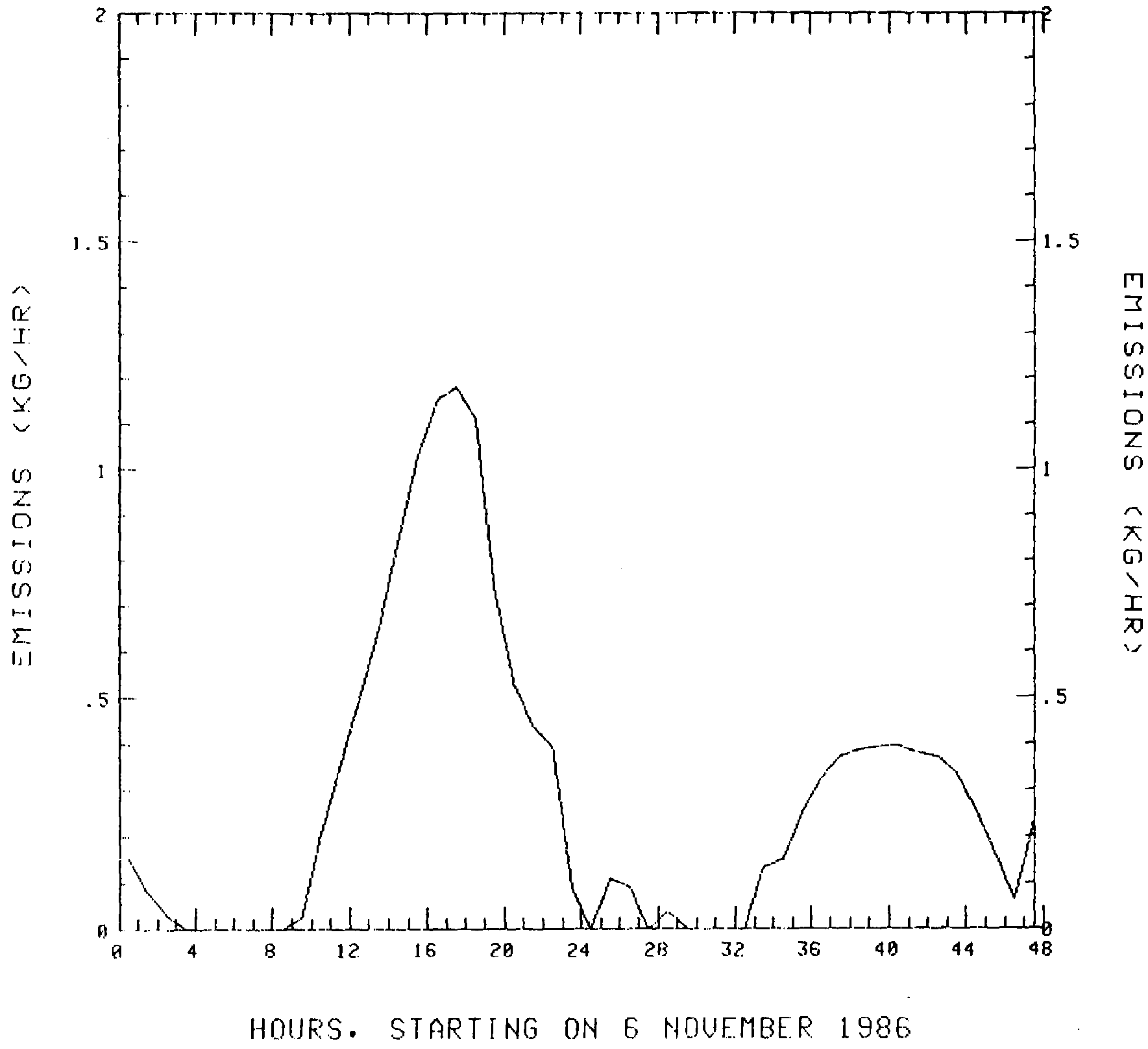


Figure 8.1-6. Estimated Hourly Chloroform Emissions at the Hyperion Treatment Plant.

the HTP are therefore estimated to be about 2.8 tons.

Emission Factors

Two types of emission factors were estimated for the Hyperion Treatment Plant. The first one is based upon the total wastewater treated per hour. This emission factor varied from 0 to 1.7 grams $CHCl_3$ per mgd-hr, and had a 95-percent confidence interval of 0.67 ± 0.21 g/mgd-hr, or 16 ± 5 g/mgd-day. This emission factor is only applicable to plants in which no chlorination takes place.

Another emission factor can be used to estimate the fraction of influent chloroform which ends up in the effluent. This "out/in" ratio varies with time of day, and has a 95-percent confidence interval of 0.66 ± 0.13 for the day. This ratio was used in the analysis of emissions from the Riverside facility.

8.1.2 Riverside Water Quality Control Plant

8.1.2.1 Description of the Plant

The Riverside Water Quality Control Plant is located near the intersection of Jurupa Avenue and Van Buren Boulevard, just south of the Santa Ana River. It provides primary, secondary and tertiary treatment to about 26 mgd of wastewater. Primary and secondary treatment are carried out in two parallel facilities. "Plant 1," which receives wastewater from Rubidoux, Jurupa and a portion of the City of Riverside, uses trickling filters for secondary treatment. "Plant 2," which handles effluent from Riverside, uses activated sludge. The residence time in the plant is 10 hours. Effluent from tertiary treatment is chlorinated for about two hours in a contact basin and then dechlorinated for one minute with sulfur dioxide (Seccombe, 1987). Final effluent is discharged into the Santa Ana River.

8.1.2.2 Sampling Points

Air samples were taken at all points in the plant where wastewater was exposed to the atmosphere and was agitated. Water samples were taken at the influent and effluent pipes. Sampling took place from 1 p.m. on Thursday, 13 November through 1 p.m. on Friday, 14 November 1986. Figure 8.1-7 is a schematic of the Riverside plant. Sampling points are labelled to correspond to the following sites.

Combined Raw Influent, Plant 1 (Sites RW1 and A2). Water was withdrawn from a basin which received both raw sewage and overflow from another area of the plant. As water from the latter source was green and appeared different from the raw sewage, the water sample (RW1) was taken from the corner of the basin next to the raw sewage influent, before the two flows mixed. Flow was slow with no turbulence. The air sample (A2) was taken at the same location as the water sample, a few inches from the water surface. Vapor rose from the liquid at the site.

Influent from Rubidoux and Jurupa, Plant 1 (Site A1). This site was about 100 ft upstream from site RW1. The water was turbulent since it flowed over a weir into a small basin. The air sample was taken at the basin approximately 8 ft from the water surface. Some vapor could be seen rising from this site.

Bar Screens, Plant 1 (Site A3). The water was turbulent after flowing over a 3-ft weir into a 4-ft wide canal. The air sample was drawn past the weir, about 2.5 ft from the water surface; vapor could be seen rising from this site.

Low Rate Trickling Filter, Plant 1 (Site A4). The water was sprayed onto activated carbon "rocks" by a 100-ft rotating irrigation arm. The water fell about 1 ft from the arm onto the rocks. The air sample was taken a few inches from the rock surface, just after the arm passed. Vapor appeared to be rising from the rocks.

Downstream of Trickling Filters, Plant 1 (Site A5). This site was a trapezoidal basin (roughly 15 ft x 20 ft), downstream of a 3-ft weir and the outlet of a 1.5-ft diameter pipe. The water in the basin was turbulent. The air sample was drawn about 2.5 ft from the water surface and about 3 ft from

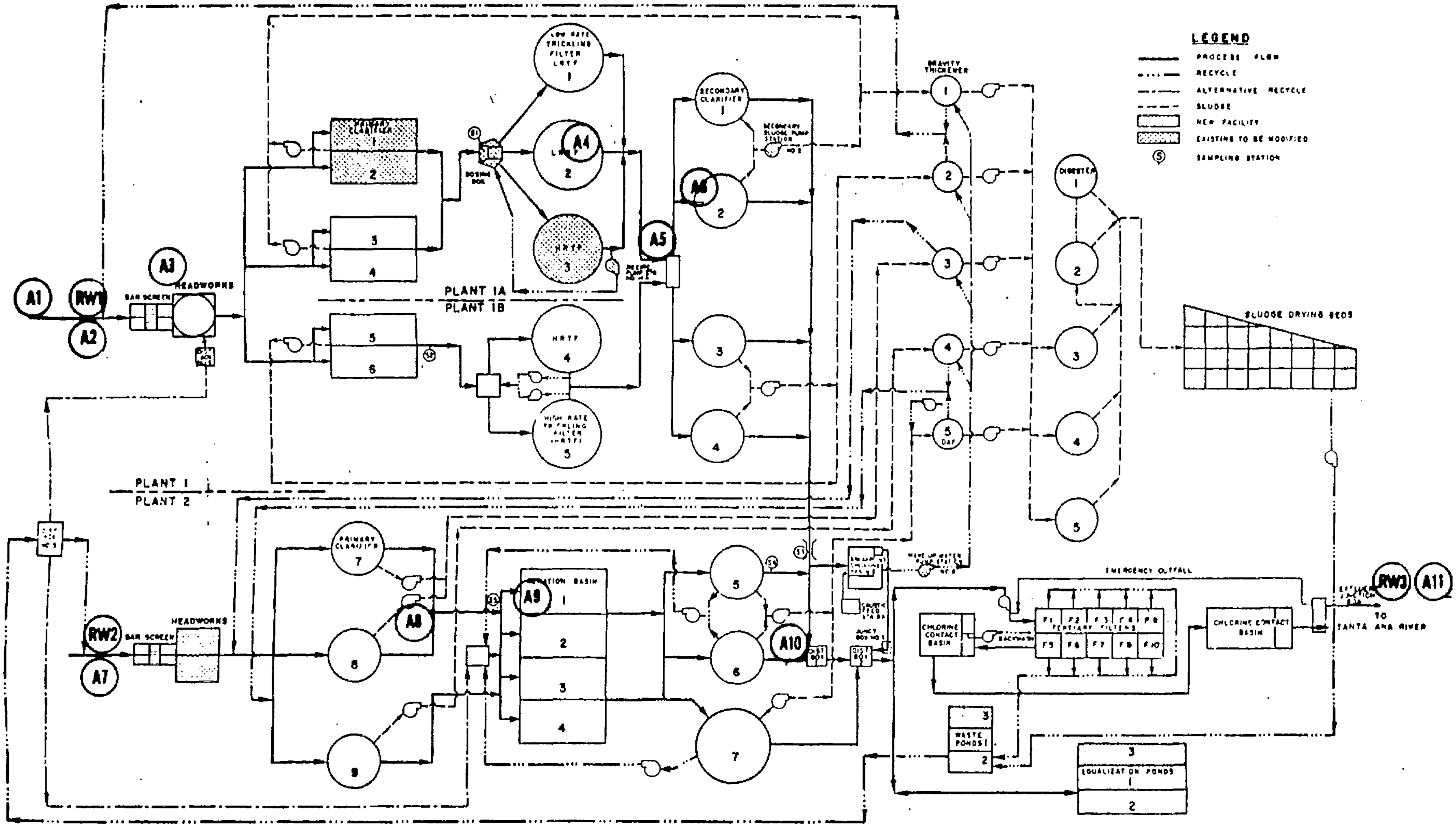


Figure 8.1-7. Air and Water Sampling Points at Riverside Water Quality Control Plant.

teh weir. Little or no vapor could be seen at this site.

Influent to Secondary Clarifiers, Plant 1 (Site A6). Water flowed at a moderate rate with little turbulence through a 6-ft wide open air canal, with 3 to 4 ft of freeboard. The air sample was taken about 2 - 2.5 ft from the water surface.

Raw Influent, Plant 2 (Sites RW2 and A7). Flow was very turbulent due to a 2-ft drop over a weir. The water sample was taken approximately 5 ft downstream from the weir where flow merged into a 4-ft wide canal. The air sample was taken about 2 ft from the water surface, above this point.

Downstream from Primary Clarifier, Plant 2 (Site A8). The site consisted of a 5-ft x 5-ft concrete mixing basin. The air sample was taken 2 - 4 inches from the turbulent water surface. Some vapor was present over the basin.

Secondary Treatment Aeration Basin, Plant 2 (Site A9). The water in this 4-ft wide canal was somewhat turbulent. The air sample was taken about 2 ft from the surface. Vapor was present at the site.

Effluent from Secondary Treatment, Plant 2 (Site A10). The sample was taken through a 4-ft x 6-ft steel grating. The water was slightly turbulent. The air sample was drawn about 3 - 4 ft from the surface.

Combined Effluent Flow (Sites RW3 and A11). The water flowed rapidly over a 4-ft weir and was turbulent. The water sample was taken just above the weir. The air sample was drawn about 10 ft from the water surface, just downstream from the weir. Considerable vapor was rising from the effluent.

8.1.2.3 Sampling and Analytical Methods

Procedures for collecting and analyzing air and water samples were the same as described in Section 8.1.1.3, except that metal buckets were used to obtain water samples.

8.1.2.4 Results

Thursday, 13 November, was warm, clear and sunny; increased cloudiness appeared during Friday morning. Thursday night was cool and the sky was clear. Little or no wind was present during monitoring activities.

Water Sampling

Plant 1 and 2 influent flow data were obtained from the plant operator (Seccombe, 1987). The effluent flow rate was assumed equal to the combined influent flow rate ten hours earlier. As in the case of the Hyperion Treatment Plant (see Section 8.1.1.4), it was necessary to construct a synthetic data set to cover hours for which actual flow data were unavailable.

Figures 8.1-8 through 8.1-10 show the Plant 1, Plant 2, and effluent flows, respectively, along with the results of the wastewater analyses. As at the Hyperion Treatment Plant, influent flows have a diurnal pattern. Times of the extreme flows at the two facilities are different, however; at Riverside, the maxima are at about 10 a.m. and 10 p.m., while the minimum flow is at around 5 p.m.

Measured chloroform concentrations are reported in Table 8.1-3, along with corresponding flow rates, which were estimated by interpolating between measured values. Influent concentrations ranged from 0.87 to 3.17 ppb, while those in the combined effluent from tertiary treatment, chlorination and dechlorination ranged from 1.85 to 2.80 ppb. Flow rates and concentrations were poorly correlated, with no r value exceeding 0.55.

Air Sampling

Ambient chloroform concentrations measured above various processes at the Riverside Water Quality Control Plant are reported in Table 8.1-4. Concentrations ranged from 8 ppb (above the final effluent) to 359 ppb (above the primary-treated effluent from Plant 2). Although these levels were generally lower than those measured at the HTP, they were nevertheless at

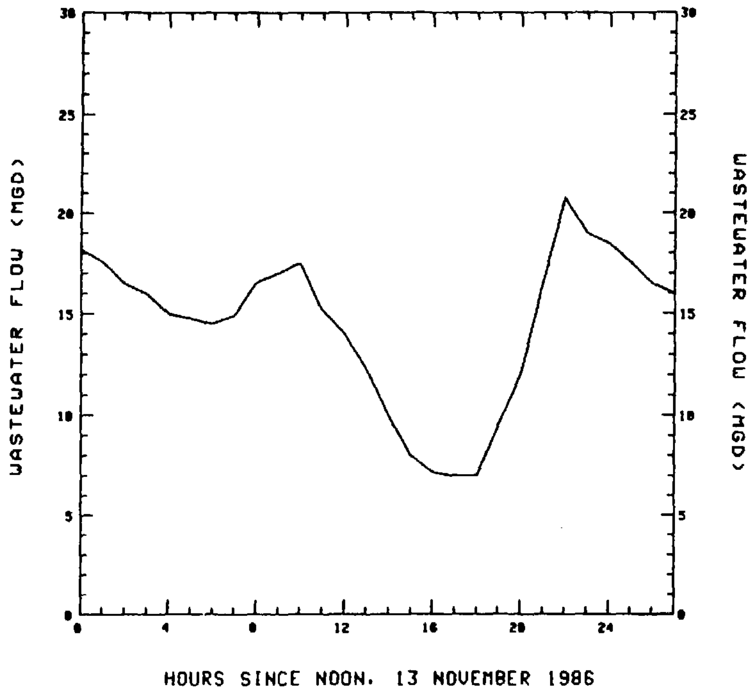


Figure 8.1-8. Influent Flow Rates During SAIC Sampling at Riverside Water Quality Control Plant (Plant 1).

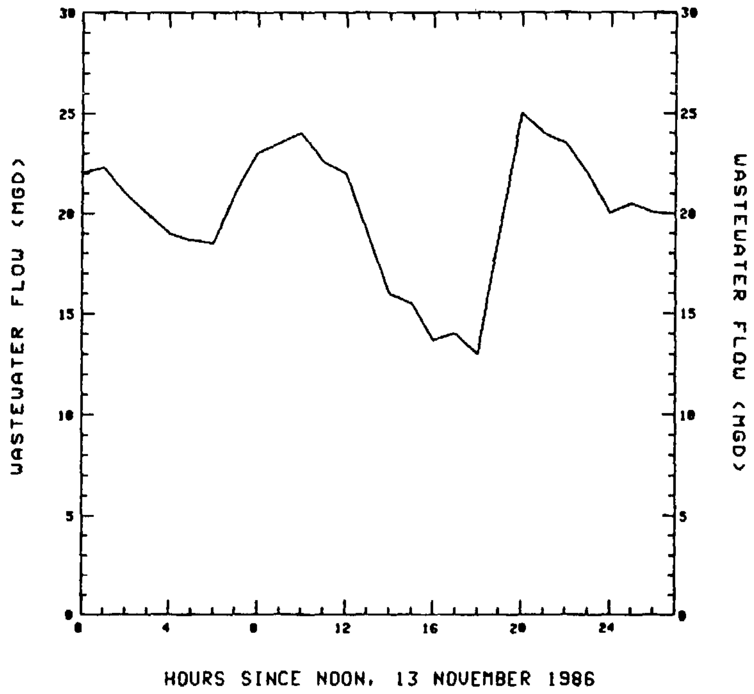


Figure 8.1-9. Influent Flow Rates During SAIC Sampling at Riverside Water Quality Control Plant (Plant 2).

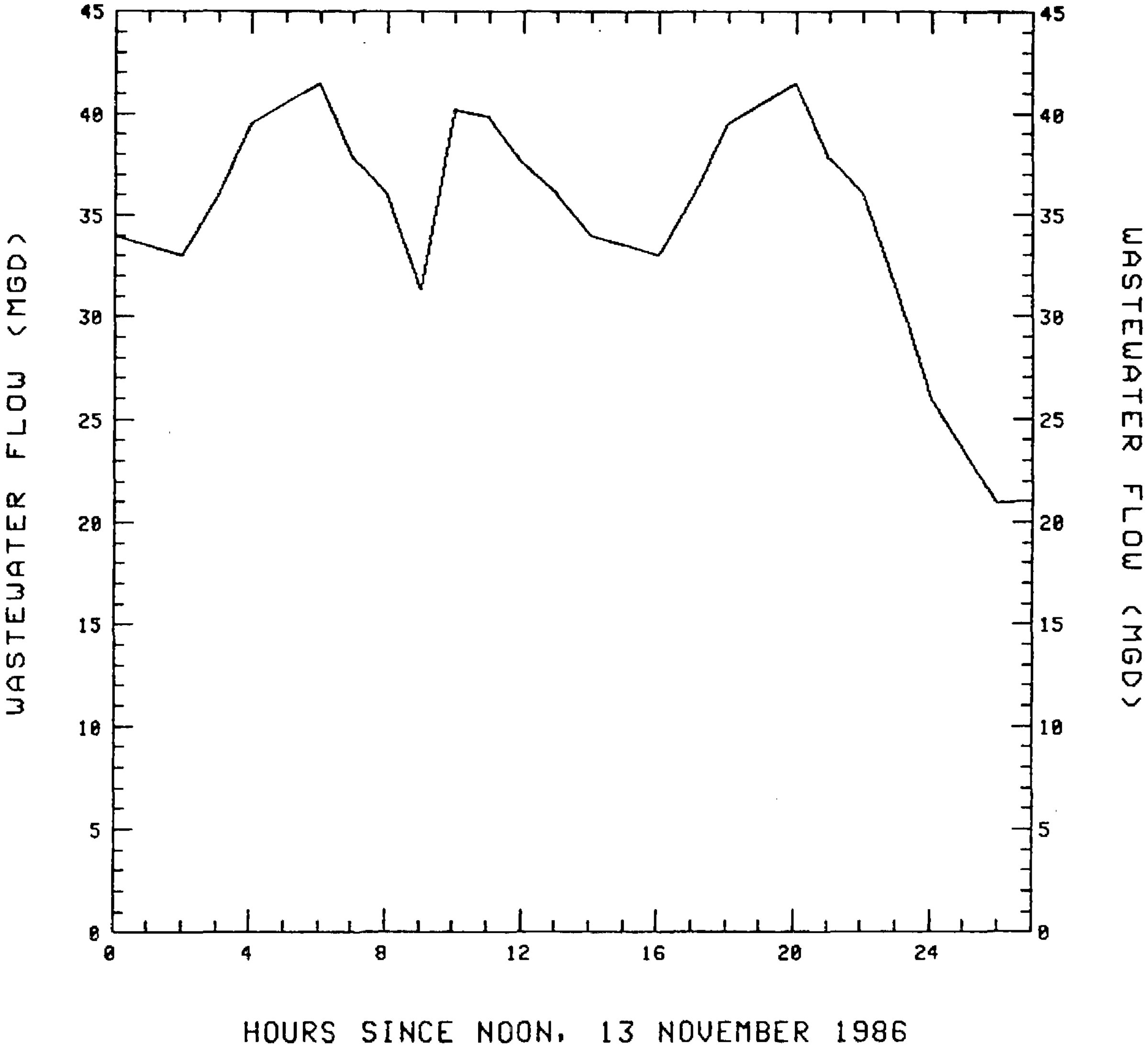


Figure 8.1-10. Effluent Flow Rates During SAIC Sampling at Riverside Water Quality Control Plant.

Table 8.1-3

SUMMARY OF CHLOROFORM MEASUREMENTS IN WASTEWATER AT RIVERSIDE WATER QUALITY CONTROL PLANT, 13-14 NOVEMBER 1986

Date	Time	Influent Measurements				Effluent Measurements	
		Plant 1 Flow(mgd)	Conc. (ppb)	Plant 2 Flow (mgd)	Conc. (ppb)	Flow[a] (mgd)	Conc. (ppb)
11/13/86	1407	16.4	3.06				
11/13/86	1500			20.0	1.58		
11/13/86	1643	14.9	2.29				
11/13/86	1722					40.9	1.85
11/13/86	1949	17.8	2.30				
11/13/86	2048			23.2	1.59		
11/13/86	2318	14.8	3.17				
11/14/86	0020					34.4	2.80
11/14/86	0216	9.5	1.29				
11/14/86	0442			13.9	1.17		
11/14/86	0622	7.9	0.87				
11/14/86	0642					26.0	2.19
11/14/86	0819	13.4	1.06				
11/14/86	0845			24.2	1.01		
11/14/86	1058	19.1	1.98				
11/14/86	1141					39.3	2.07

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[a] Estimated by lagging total influent flow by 10 hours.

Table 8.1-4

AMBIENT CHLOROFORM CONCENTRATIONS ABOVE VARIOUS POINTS AT THE RIVERSIDE WATER QUALITY CONTROL PLANT

(Concentrations in ppb)

Time	Rubidoux and Jurupa Influent	Riverside Influent	Combined Influent	Bar Screens	Plant 2 Primary Effluent	Plant 1 Trickling Filter	Plant 2 Aeration Basin	Plant 1 Trickling Filter Effluent	Plant 1 Secondary Clarifier Influent	Plant 2 Secondary Effluent	Final Effluent
13 November 1987											
1410	25										
1437			17								
1513				49							
1538						28					
1608								51			
1631									18		
1659		28									
1735					359						
1829							77				
1856										19	
1920											38
2003	11										
2033			38								
2109				111							
2138						24					
2208								62			
2304									13		
2345		28									
14 November 1986											
0024											63
0052					73						
0129										16	
0203							63				
0234											45
0306	18										
0337			24								
0425					106						
0446				44							
0519						28					
0546								25			
0622									15		
0645											59
0709		25									
0736					98						
0806							25				
0832										17	
0857	20										
0913			100								
0934				37							
1012								100			
1109									27		
1128		12									
1143											8
1230							54				
Geometric Mean	18	22	35	55	128	27	51	53	18	17	35

least an order of magnitude greater than those encountered in the ambient air of the South Coast Air Basin. At each sampling point, the chloroform concentration did not vary appreciably with sampling time.

In Figure 8.1-11, the sampling points are displayed on the x-axis in order of wastewater treatment stage. Chloroform concentrations appear to increase through primary treatment. The highest values were measured at the effluent from the primary clarifiers in Plant 1. Concentrations 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.

8.1.2.5 Emissions Analysis

To estimate emissions from the Riverside facility we first attempted to use the mass balance approach described in Section 8.1.1.5. It was discovered, however, that 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. Given the fact that chlorination followed nitrification of the secondary-treated wastewater, the haloform reaction was probably occurring.

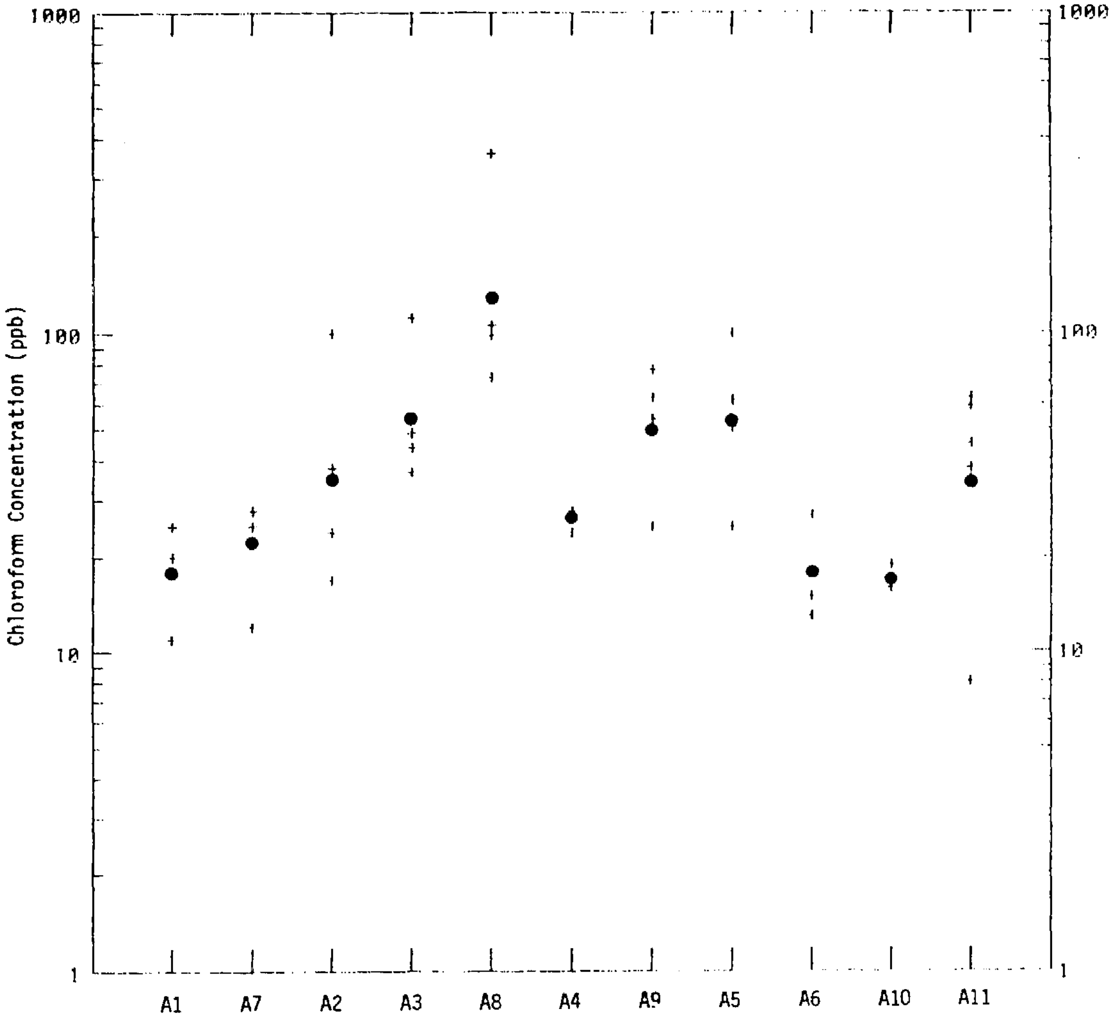
In order to obtain an approximate estimate of total emissions from the plant, we envisioned the following "model" of how emissions occur:

(1) A significant fraction of the chloroform in the influent to the plant is released through volatilization; the fraction released is the same as at the Hyperion Treatment Plant.

(2) 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.

(3) Emissions due to chlorination occur near the plant, i.e. during discharge to the Santa Ana River, and therefore can be counted as emissions from the plant.

In Section 8.1.1.5, we estimated that the average fraction of the influent chloroform which ends up in the effluent at Hyperion was 0.66. The



KEY

A1 = Influent, Plant 1
A2 = Combined raw influent, Plant 1
A3 = Bar screens, Plant 1
A4 = Low rate trickling filters, Plant 1
A5 = Downstream of trickling filters, Plant 1
A6 = Influent to secondary clarifiers, Plant 1
A7 = Raw influent, Plant 2
A8 = Downstream from primary clarifier, Plant 2
A9 = Secondary treatment aeration basin, Plant 2
A10 = Effluent from secondary treatment, Plant 2
A11 = Combined effluent flow

Figure 8.1-11. Chloroform Concentrations Measured Above Various Processes in the Riverside Water Quality Control Plant.

fraction emitted is therefore 0.34. Let this value be called EF_p. Let E_p be wastewater process emissions. Then

$$E_p(t) = EF_p\ M_i(t-10) \tag{8-3}$$

If there were no chlorination step, the the amount of chloroform which would be present in the effluent would be $M_i(t-10) - E_p(t)$, or $(1-EF_p)\ M_i(t-10)$. Let E_c be chloroform emissions due to chlorination. Then, by mass balance,

$$E_c(t) = M_o(t) - (1-EF_p)\ M_i(t-10) \tag{8-4}$$

Total emissions would then be the sum of $E_p(t) + E_c(t)$:

$$E_{tot}(t) = M_i(t-10)\ (2EF_p - 1) + M_o(t) \tag{8-5}$$

Figure 8.1-12 shows emissions (g/hr), as estimated by Equation 8-5. Total emissions for the first 24-hour period are 232 g, or about 0.5 lb. Annual emissions from the facility would be about 190 lb.

8.2 SWIMMING POOL EMISSIONS TESTS

The objectives of this part of the field research were (1) to confirm that chloroform is emitted from swimming pools and (2) to estimate emission rates which could be generalized to pools in the South Coast Air Basin. The pool used for the test was a 15,880-gallon kidney-shaped, in-ground, gunnite, plaster-lined pool in the back yard of a private home. The maximum length and width were 36 and 16 feet, respectively. The pool depth was about 4.5 ft at the end at which emissions were measured, 3.5 ft at the opposite end, and 6 ft in the middle.

8.2.1 Methods

8.2.1.1 Flux Measurement

The emission flux, or emissions per unit area, from the swimming pool was measured directly with an emission isolation flux chamber. As seen

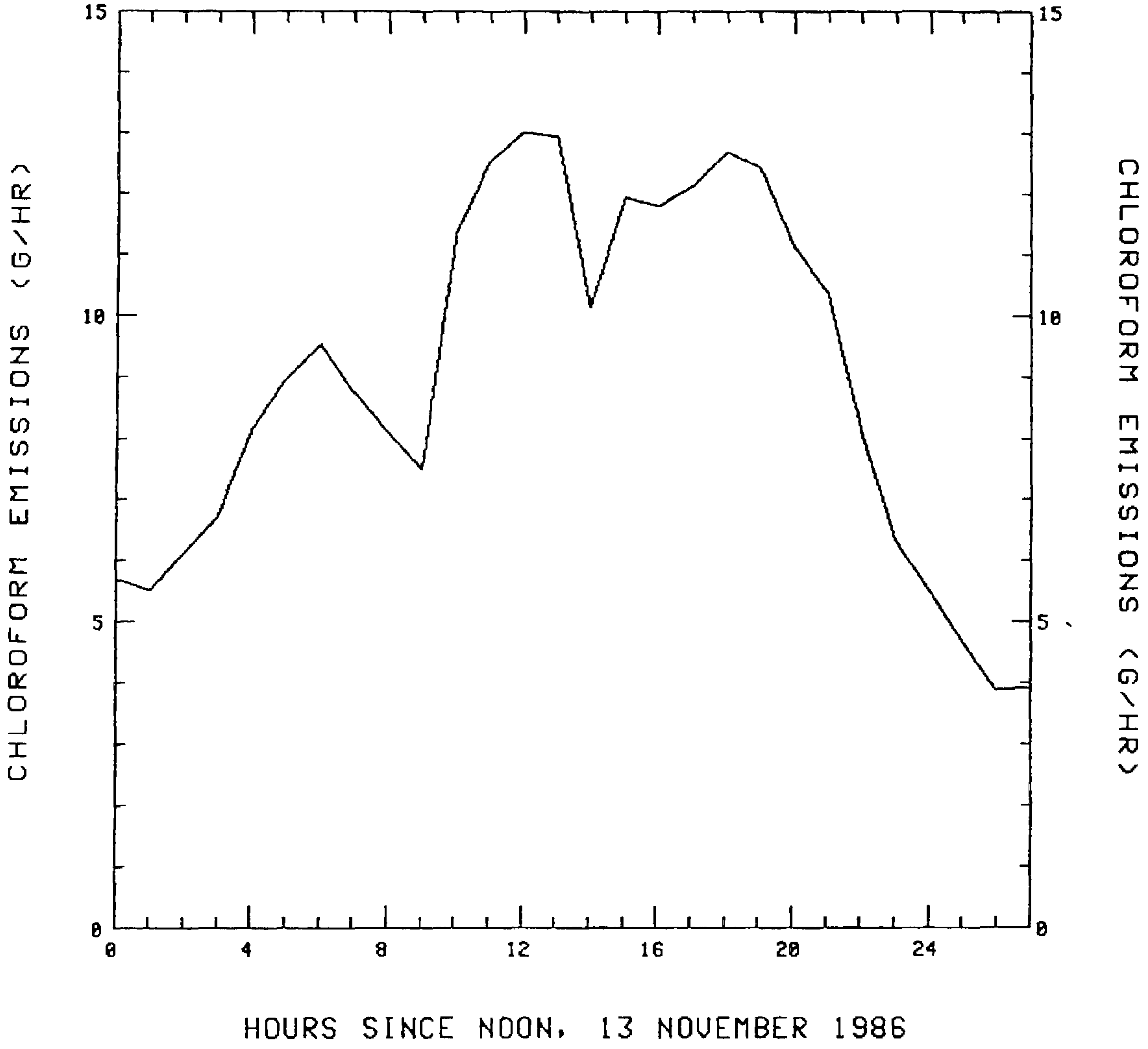


Figure 8.1-12. Estimated Hourly Chloroform Emissions at the Riverside Water Quality Control Plant.

in Figure 8.2-1, a flux chamber is half of a spherical acrylic shell, which is placed over a soil or water surface. Purified "zero air" is introduced into the chamber, where it is mixed with pollutants entering the chamber from the surface being investigated. Air exits the chamber through a Teflon sampling line and through a hole in the top of the dome. After sufficient time, an equilibrium concentration is established in the chamber, and the flux rate can be calculated from the following equation (Balfour and Schmidt, 1984):

$$E = \frac{Q_s C}{A} \tag{8-6}$$

where

E = Emission flux ($\mu g/m^2$-min)
Q_s = Sweep air flow rate (m^3/min)
C = Pollutant concentration in the chamber ($\mu g/m^3$)
A = Flux area (m^2)

For this investigation, we used a flux chamber originally constructed for measuring soil gas emissions from the Stringfellow Hazardous Waste Site (SAIC, 1987). Following recently published U.S. Environmental Protection Agency guidelines (Kienbusch, 1986; Radian Corporation, 1986), we modified the chamber by (1) removing a mixing fan, (2) adding a 7-inch stainless steel skirt and mounting flange, (3) adding a manifold to enable uniform introduction of zero air radially from the entire base of the chamber, (4) providing for monitoring of interior pressure with a U-tube manometer, and (8) adding a polystyrene foam collar to enable to the chamber to float.

Calibration and validation of flux chambers have been discussed in the literature by Schmidt and Balfour (1983), Dupont (1987), and others, while the design, calibration, and performance of SAIC's flux chamber have been described in detail in the <u>Stringfellow Remedial Investigation Draft Report</u> (SAIC, 1987). Calibration with an inert tracer gas established that

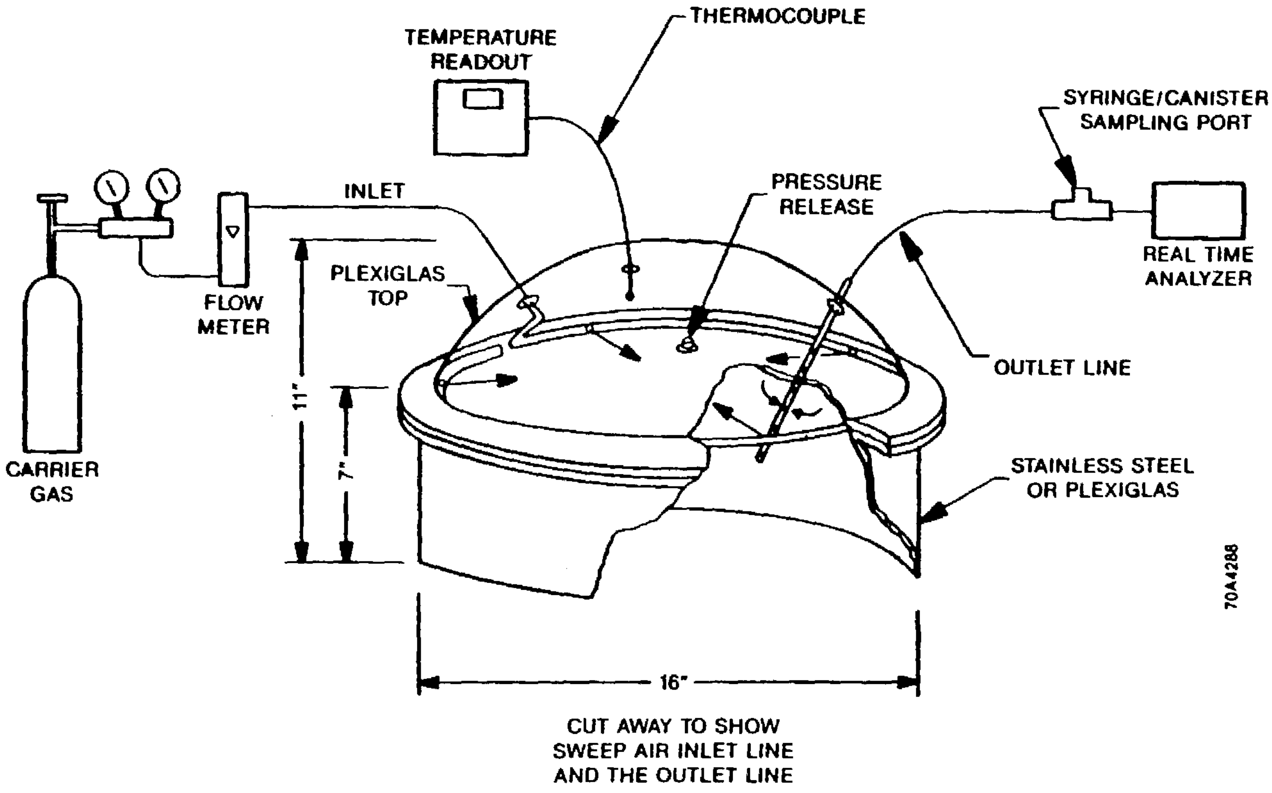


Figure 8.2-1. A Cutaway Diagram of the Emission Isolation Flux Chamber and Support Equipment (Kienbusch, 1986).

equilibrium concentrations were reached in the chamber after about 3.5 residence times, where a residence time is defined as the time for one chamber volume of air to pass through; i.e. the volume divided by the sweep air flow rate. The volume enclosed by SAIC's chamber, including the freeboard on the stainless steel skirt, is about 70.4 liters. The sweep air flow rate for all of the flux chamber runs in the present investigation was 10.71 L/min. The residence time was therefore 6.6 minutes and the required time to equilibrium was 23 minutes. A minimum of 23 minutes was therefore allowed to elapse after each change of pool conditions.

Air samples for GC analysis were obtained by placing a syringe into a tee connection on the Teflon chamber exhaust line. During sampling, the bleed hole on the top of the dome was sealed to assure ample flow through the exhaust line. Equipment and methods were the same as for the GC analysis performed during the wastewater treatment plant sampling. (See Section 8.1.1.3.)

8.2.1.2 Water Sampling and Analysis

Samples for analysis of free and total chlorine, pH, and total alkalinity (as $CaCO_3$) were obtained by immersing an Aquality Mark IV test kit in the water at about 18 inches depth. Parameters were measured by colorimetry. Samples for TOC analysis were collected by immersing 40-ml volatile organic analysis (VOA) vials at about 18 inches depth and sealing them under water. This technique was not suitable for the samples to be analyzed for chloroform, since approximately 5 mg of Na_2SO_3 preservative had been added to each VOA vial in advance. Therefore a plastic cup was immersed in the water, tapped against the pool side to release any bubbles, and then brought slowly to the surface. The water was then decanted into VOA vials in such a way as to preclude bubble formation. All TOC and $CHCl_3$ samples were collected in duplicate.

TOC concentrations in the water samples were measured by SAIC's Trace Environmental Chemistry Laboratory in La Jolla, using an OI Corporation (College Station, TX) Model 700 TOC analyzer. The chloroform samples were analyzed by EMSI using the same methods described in Section 8.1.1.3.

8.2.1.3 Sampling Schedule

In order to determine whether chlorine addition resulted in the haloform reaction and consequent chloroform emissions, we defined four test conditions. To establish the "baseline" condition, no chlorine or fresh water was added to the pool for approximately 2.5 weeks before the tests. A pool cover, which had been in place during those 2.5 weeks, was removed 24 hours before the testing began. Pool water was circulated for 5 out of every 24 hours, both before and during the tests. Cyanuric acid powder, which prevents photodecomposition of HOCl, had been added six months before. Although its concentration was not measured as part of this investigation, it appeared to be effective, in that chlorine levels did not decrease in the presence of intense sunlight. As seen in Table 8.2-1, free and total residual chlorine levels were < 0.02 ppm during the baseline testing on 4 May 1987.

After the baseline tests were completed, HCl was added to the pool to reduce the pH from 8.0 to 7.7. Approximately 0.25 gal of 10-percent NaOCl solution was then added to increase the free chlorine level to a "transition" condition of 0.3 ppm. After the second round of testing, another 0.25 gal of NaOCl solution was added to bring the level up to the "normal" condition of 1.0 ppm. Sampling was then discontinued for 16 hours, in order for the new condition to become fully established. On 5 May 1987, the "normal" condition tests were conducted. Then 0.75 gal of NaOCl was added to establish the "high" dosage condition of 3.0 ppm chlorine.

Under each chlorine condition, flux chamber tests were conducted under two conditions. In the first, the water surface under the chamber was undisturbed. In the second, the surface under the chamber was agitated vigorously by hand for approximately 15 minutes before and during collection of the gas sample with the syringe.

Table 8.2-1

SAMPLING CONDITIONS DURING SWIMMING POOL EMISSIONS TESTS

Chlorine Condition	Sampling Time	Chlorine Residual (mg/L)	pH	Total Alkalinity (mg/L)	Temp. (°C)	Flux Chamber Runs
	4 May 1987					
Baseline	1238	<0.2	8.0	140	26	1-4
Transition	1549	0.3	7.7[a]	140	27	5-6
Transition	1641	0.3	7.7	170	27	7
Transition	1710	0.3	7.7	160	27	8-9
	5 May 1987					
Normal	0935	1.0	7.8	140	25	10-11
Normal	1049	1.0	7.7	140	25	12-13
High	1238	3	7.8	140	26	14-15
High	1350	3	7.8	150	26	16-17

[a] HCl at 31.4 percent added at 1414 hrs.

8.2.2 Results

8.2.2.1 Estimation of Emission Flux Rates

Before, during and after the flux chamber testing, six sample blanks were obtained by filling the GC syringe with either zero air or purified nitrogen. The first of these produced a peak at the retention time of chloroform. This sample blank value was subtracted from the next six measured peak heights. Peak heights for subsequent samples were not adjusted, since no other nonzero blanks were encountered. Peak heights for all injected standards and samples were normalized to an injection volume of 1 ml and an attenuation of 4. For example, the chloroform peak for flux chamber Run 12 had a height of 43.5 mm, for an 0.2-ml injection and an attenuation of 8. The adjusted height was:

$$\text{Adjusted height} = \left(\frac{1}{0.2}\right)\left(\frac{8}{4}\right)(43.5) = 435 \text{ mm}$$

Standards were prepared by diluting the 1100-ppb $CHCl_3$ calibration gas with purified nitrogen by means of a Dasibi 1009 mass flow controller. Their corresponding normalized peak heights were as follows:

Standard (ppb)	Normalized Peak Height (mm)
0	0
25.1	13
82.9	20
161.9	35.25
241.2	56
1100	172

Note that the peak height for the 161.9-ppb standard is the mean of two values (35.0 and 35.5 mm). Concentrations with peak heights below 172 mm were obtained by interpolation. For peak heights above 172 mm, concentrations were estimated by:

$$\text{Concentration} = \left(\frac{\text{Measured peak}}{172}\right)(1100\ \text{ppb}) \qquad (8\text{-}7)$$

For all of the runs, the sweep air flow rate was 10.71 L/min, as determined with a pre-calibrated rotameter. The flux area was 0.292 m^2. Substituting these values into Equation 8-1, we find that the flux rate is equal to 0.3664 C. The chloroform concentration in the chamber was converted from ppb to $\mu g/m^3$ by the following equation:

$$C\ (\mu g/m^3) = \frac{1000\ C\ (\text{ppb})\ P\ MW}{RT} \qquad (8\text{-}8)$$

where

P = Atmospheric pressure (atm)
MW = Molecular weight of chloroform (119.3779 g/mole)
R = 82.05 ml-atm/mole^{o}K
T = Flux chamber air temperature (^{o}K)

Pressure inside the chamber was monitored continually during the testing and, for the purpose of these calculations, may be assumed to be 1 atm. Substituting known values into Equation 8-3 yields:

$$C\ (\mu g/m^3) = \frac{1354.9\ C\ (\text{ppb})}{T} \qquad (8\text{-}9)$$

Substituting C into Equation 8-6 yields, finally:

$$E\ (\mu g/m^2\text{-min}) = \frac{53.309\ C\ (\text{ppb})}{T} \qquad (8\text{-}10)$$

Flux chamber emission test results are shown in Table 8.2-2 and Figure 8.2-2. Several of the findings are quite interesting. First, measurable emissions of chloroform occurred under all test conditions,

Table 8.2-2

FLUX CHAMBER AND WATER SAMPLING RESULTS

Flux Chamber Run	Chlorine Condition	Water Surface Condition	$CHCl_3$ (ppb)[a]	TOC[a,b] (ppm)	Chamber Temp (°C)	$CHCl_3$ in Chamber (ppb)	Flux ($\mu g/m^2$-min)
1	Baseline	Still	55	<2.8	48.9	162	26.8
2	Baseline	Still	55	<2.8	48.9	71.6	11.9
3	Baseline	Agitated	74	<2.8	48.9	1080	179
4	Baseline	Agitated	73	<2.8	48.9	1430	237
5	Transition	Still	73	<2.8	37.8	9.7	1.7
6	Transition	Still	52	<2.8	37.8	19.3	3.3
7	Transition	Agitated	59	<2.8	35.0	1370	237
8	Transition	Agitated	48.5	<2.8	35.0	1460	253
9	Transition	Still	48.5	<2.8	35.0	74.7	12.9
10	Normal	Still	43.5	<2.8	46.7	95.9	16.0
11	Normal	Still	43.5	<2.8	46.7	106	17.7
12	Normal	Agitated	43.5	<2.8	47.2	2780	463
13	Normal	Agitated	52	<2.8	47.2	2560	426
14	High	Still	58	<2.8	48.3	78.8	13.1
15	High	Still	57.5	<2.8	48.3	22.2	3.7
16	High	Agitated	54	<2.8	42.2	2400	406
17	High	Agitated	52	<2.8	42.2	2000	338

[a] Mean of 2 samples.

[b] Detection limit = 3σ of 5 spiked samples.

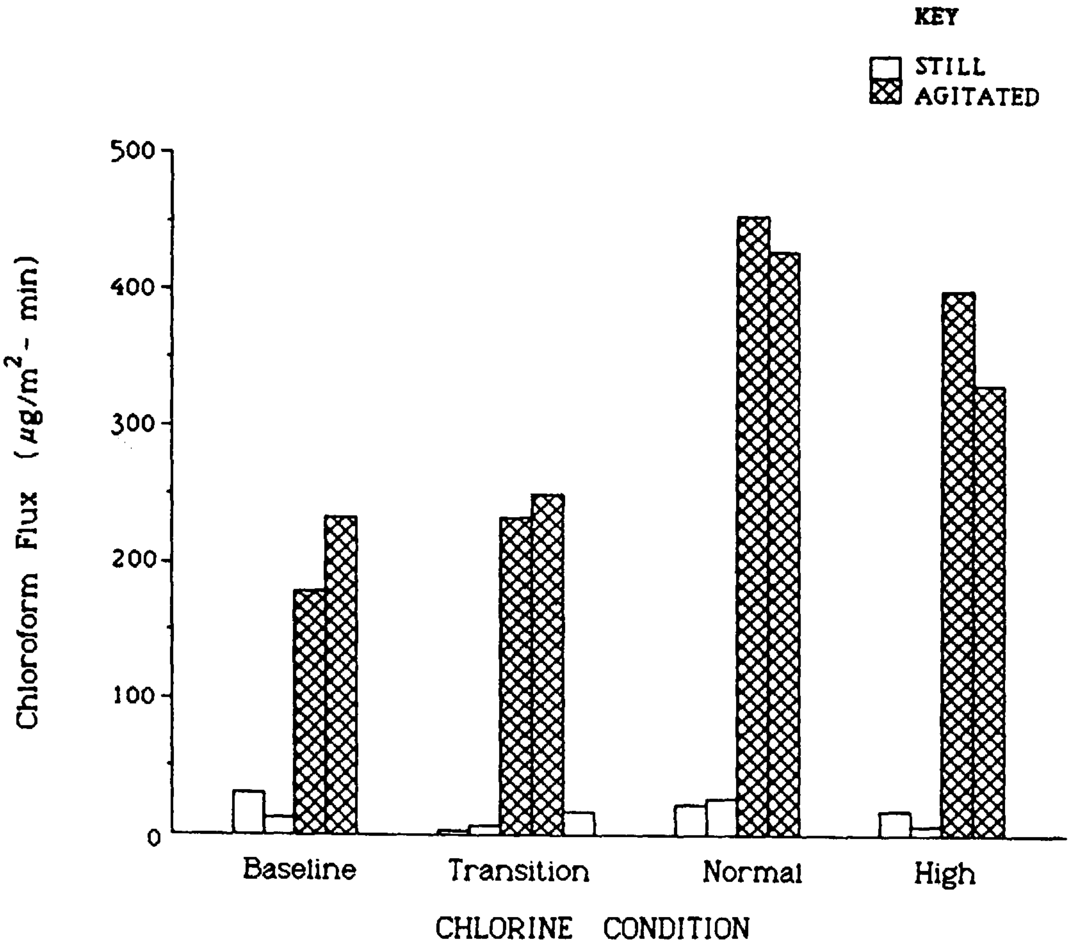


Figure 8.2-2. Emission Flux From Swimming Pool for Different Chlorine and Water Surface Conditions.

including the baseline, 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. Second, for all four chlorine conditions, agitating the water under the flux chamber increased emissions by one to two orders of magnitude. Third, 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.

8.2.2.2 Relation to Water Quality Parameters

Figure 8.2-3 shows the variation of chloroform in the swimming pool water during the emissions tests. The concentrations 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 for 2.5 weeks, it is possible that chloroform had been generated by the haloform reaction but had not had the opportunity to volatilize during that time. It appears, in contrast, that no chloroform was generated in the pool during the two days of measurement. As seen in Figure 8.2-3, $CHCl_3$ levels decreased slightly; the slope of a time-series regression line for these data is -0.51 ppb/hr and is significant at the $p < 0.05$ level. 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.

As seen in Figure 8.2-4, the measured flux rate for agitated surfaces and the pool chloroform concentration are negatively correlated ($r = 0.750$). Only limited weight should be given to this finding, however, since other factors may have influenced the flux rate. The most important of these may have been the energy input to agitation of the water surface. The "amount" of agitation was not quantified, and probably varied from run to run.

How reasonable are our estimates of emission flux? One way to

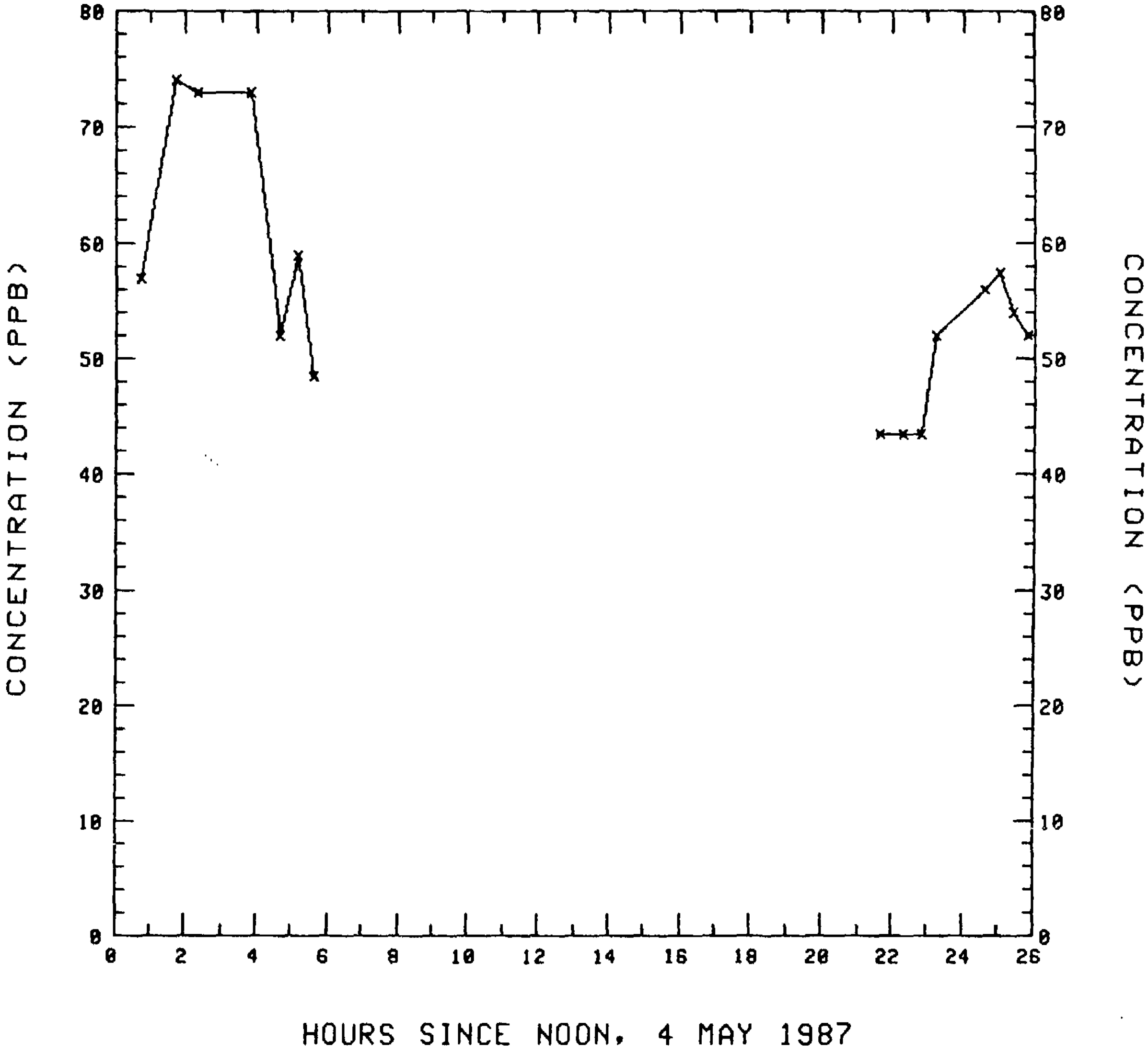


Figure 8.2-3. Chloroform Concentrations in the Swimming Pool During Flux Chamber Tests.

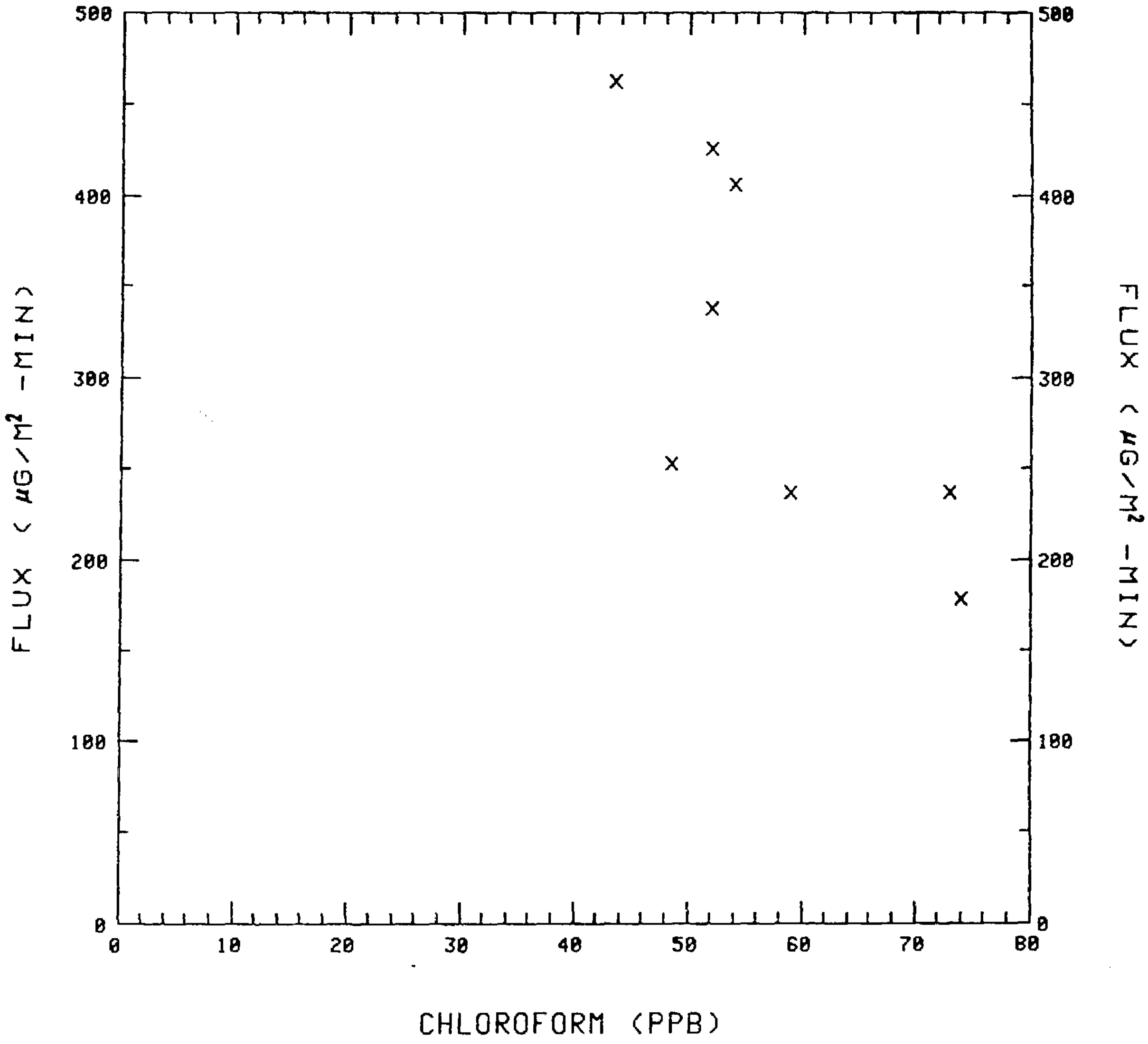


Figure 8.2-4. Measured Flux Rate for Agitated Water Surface vs Chloroform Concentration in Pool.

answer this is to compare our experimental results with values predicted by an empirical model developed by Thibodeaux et al. (1981) and recommended by Breton et al. (1984) for use in estimating emissions from surface impoundments. The "Thibodeaux-Parker-Heck" model is based upon two-film resistance theory. Mass transfer of chloroform from water to air requires it to pass through four stages, starting with the bulk liquid, to a laminar liquid layer at the liquid surface, through a similar laminar air layer, and finally into the atmosphere (Breton et al., 1984). The rate of transfer through all four media determines the release rate to the atmosphere. Generally, transfer rates in one or two of the layers may be so slow that these layers will control the overall flux rate. As we shall see, this is the case for chloroform.

The basic equation for the emission rate is:

$$Q = K_{oa} A (x - x^*) MW \tag{8-11}$$

where

Q = Emission rate (lb/hr)
K_{oa} = Overall mass transfer coefficient (lb-mol/ft^2-hr)
A = Area of surface (ft^2)
x = Mole fraction of chloroform in the water
x^* = Equilibrium concentration of gas and liquid phases (as a mole fraction)
= (mole fraction in air/K)

$$K = \frac{H \rho_w}{P_T (18)} \tag{8-12}$$

and

H = Henry's law constant (atm-ft^3/lb-mol)
ρ_w = Density of water (lb/ft^3)
P_T = Atmospheric pressure (atm)

The expression for the overall mass transfer coefficient is:

$$\frac{1}{k_{oa}} = \frac{1}{k_L} + \frac{1}{k_G K} \tag{8-13}$$

where

k_L = Liquid phase mass transfer coefficient (lb-mol/ft^2-hr)
k_G = Gas phase mass transfer coefficient (lb-mol/ft^2/hr)

Consider a typical swimming pool with water temperature of 80^{o}F (26.7^{o}C). According to Nicholson et al. (1984), the Henry's law constant for chloroform may be estimated by:

$$H\ (\text{atm-m}^3/\text{g-mol}) = e^{[10.3 - (4720/T)]} \tag{8-14}$$

For this example, H = 4.33 x 10^{-3} atm-m^3/g-mol = 69.35 atm-ft^3/lb-mol, and the density of water is 62.2 lb/ft^3. At one atmosphere pressure, then, K = 239.7.

Now suppose that the swimming pool chloroform concentration is 50 ppb (50 x 10^{-9} mole fraction) and the concentration in the ambient air is 100 ppt (100 x 10^{-12} mole fraction). Then $x^* = (100 \times 10^{-12})/239.7 = 4.2 \times 10^{-13}$. Since $x^* << x$, as it will be for all practical cases, we can ignore it in applying Equation 8-11. Furthermore, though it will not be shown here, the product $k_G K$ will be two to three orders of magnitude higher than k_L, so that the gas phase transfer coefficient can be ignored. Combining Equations 8-11 and 8-13 and simplifying, we obtain:

$$Q/A = k_L \times MW \tag{8-15}$$

The liquid phase mass transfer coefficient may be estimated from the following empirical equation:

$$k_L = 3.12(1.024)^{\theta - 20} U_o^{0.67} H_o^{-0.85} (32/MW)^{0.5} \qquad (8\text{-}16)$$

where

θ = Water temperature (^oC)
U_o = Surface wind velocity (ft/s) = 0.035 x speed at 10 m
H_o = Pool depth (ft)

The average depth of the pool at which the flux tests were conducted is about 4.7 ft. For a typical wind velocity of 2 m/s (6.6 ft/s), U_o = 0.231 ft/s, and k_L = 0.19 lb-mol/ft^2-hr. The emission flux is then:

$$Q/A = \left(\frac{0.190 \text{ lb-mol}}{\text{ft}^2\text{-hr}}\right)(50 \times 10^{-9})\left(\frac{119.4 \text{ lb}}{\text{lb-mol}}\right)$$

$$= 1.13 \times 10^{-6} \text{ lb/ft}^2\text{-hr}$$

$$= 91.9 \ \mu\text{g/m}^2\text{-min}$$

This flux rate is higher than those measured under still conditions, but lower than those measured under agitated conditions. Fluxes into the chamber during still conditions are likely to be lower than those from a free water surface. First, the chamber shields the surface from winds of the velocities likely to be encountered in the South Coast Air Basin. Also, the high concentration in the chamber results in a non-trivial value for x^*, thus lowering the concentration gradient which drives the emission flux. We therefore believe that our results are consistent with both theory and practical considerations.

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9.0

LABORATORY STUDIES OF CHLOROFORM ATMOSPHERIC FORMATION AND REMOVAL PROCESSES

9.1 INTRODUCTION AND RATIONALE

Following a critical examination of literature data (see Section 5.2), two issues relevant to the atmospheric formation and removal of chloroform were recommended for additional laboratory studies. The first issue involves the possible in-situ formation of chloroform as a product of the reaction of trichloroethylene (TCE) with the hydroxyl radical. While currently accepted major reaction pathways for the OH-olefin reaction do not predict chloroform formation from TCE, it has been speculated that chloroform may form in secondary pathways involving the photolysis of dichloroacetaldehyde, which in turn may be produced by reaction of TCE with chlorine atoms. The second issue involves the experimental verification of the atmospheric persistence of chloroform derived form literature data. Accordingly, two types of experiments were carried out using a large Teflon film reactor. The first series of experiments involved sunlight irradiations of mixtures of trichloroethylene and oxides of nitrogen (NO_x) in purified air, with focus on the detection of chloroform as a possible reaction product. The second series of experiments involved sunlight irradiations of chloroform-NO_x mixtures in purified air with focus on the rate of removal of chloroform under these simulated atmospheric conditions. Control experiments were also carried out, with emphasis on a comprehensive characterization of the stability of TCE and chloroform in Teflon reactors. The next section of this chapter describes our measurement and calibration methods. Sections describing the TCE-NO_x and chloroform-NO_x irradiations, respectively, then follow. Findings and their interpretation are described next, followed by a summary of conclusions and recommendations.

9.2 METHODS

9.2.1 Teflon Reaction Chamber

The reactor employed in this study is constructed of panels of FEP Teflon type 200A film heat-sealed together. Seams are reinforced externally with 2-inch wide mylar tape. The large volume of the chamber (initial volume 3.45 m^3, surface-to-volume ratio = 3.93 m^{-1}) minimizes loss of reactants and products by diffusion to the chamber walls. Teflon film is transparent to sunlight, exhibits minimum susceptibility to contamination, and is chemically inert towards most organics, including TCE and chloroform. An all-Teflon port and Teflon tubing connect the Teflon chamber to a pyrex glass sampling manifold to which all instruments are connected via Teflon lines.

In a typical experiment the Teflon chamber is first covered with black plastic film and then inflated with purified air (see Section 9.2.2); the pollutants are injected into the chamber using a 200-cm^3 glass bulb filled with the pollutant of interest diluted in pure air or nitrogen. After a few minutes for mixing, as indicated by stable instrument readings of pollutant concentrations, the black cover is removed, thus exposing the chamber contents to sunlight. Control experiments and stability studies are carried out in the same manner but without removing the black cover.

No dilution or "make-up" air is needed since the flexible, pillow-shaped chamber collapses slowly as air is withdrawn to the measurement manifold.

9.2.2 Air Purification System

The DGA pure air generator consists of four sorbent cartridges and a particulate filter through which compressed (10-20 psi) ambient air is passed to remove ozone, oxides of nitrogen, hydrocarbons and a number of polar organic contaminants. The four cartridges, each made of 18-inch i.d. plastic pipe, contain, in order, silica gel (grade 03, 3-8 mesh, Aldrich Chemical Co.), Purafil (alumina impregnated with 4% potassium permanganate, HP Associates), molecular sieves 13X (Union Carbide 1/8 pellets, VB Anderson) and activated carbon (BPL carbon, 6-16 mesh, Calgon Corp.). Silica gel removes water, hydrocarbons, and polar organic compounds; Purafil removes NO, NO_2, ozone, sulfur-containing contaminants such as H_2S, amines, chlorinated hydrocarbons, and a number of low molecular weight organics. Molecular sieves retain several classes of aliphatic and aromatic hydrocarbons. Activated carbon removes aliphatic, aromatic and chlorinated hydrocarbons, along with polar organics including alcohols, esters, ethers and ketones. Finally, the particulate matter filter retains particles, both initially present in ambient air and entrained from the sorbent cartridges. The pure air generator can be operated at flow rates of 1-60 L/min.

The filtration efficiency of the pure air generator is monitored frequently. Silica gel and molecular sieves are regenerated and Purafil and activated carbon are replaced as needed. Tests carried out involve the measurement, upstream and downstream of the pure air generator, of NO and NO_2 (Teco 14 BE chemiluminescent analyzer), ozone (Dasibi 1008 PC ultraviolet photometer), peroxyacetylnitrate (electron capture gas chromatograph with Teflon column packed with 10% Carbowax 400 on chromosorb P), and for this project, trichloroethylene and chloroform (electron capture gas chromatograph with Teflon column packed with 0.1% AT-1000 on Graphpac GC). "Upstream" air included both ambient Ventura, CA, air and mixtures of pollutants at ppm concentrations in air in Teflon chambers. Removal of these pollutants was achieved in all cases, with purified air concentrations lower than our detection limits of 2 ppb (NO and NO_2), 1 ppb (chloroform and trichloroethylene), 1-2 ppb (ozone) and 0.5-1 ppb (PAN).

9.2.3 Analytical Methods

NO and NO_2 were measured using a Thermoelectron 14 BE chemiluminescence analyzer. Ozone was monitored using a Dasibi 1008 PC ultraviolet photometer. Trichloroethylene and chloroform were measured by gas chromatography with electron capture detection using a Shimadzu Instruments Mini-2 gas chromatograph equipped with an automated 5-cm^3 Valco sampling valve, a ^{63}Ni 10 millicuries electron capture detector, and a Teflon column, 8 x 1/8 inch, packed with 0.1% AT-1000 (a nonpolar phase) on Graphpac GC 80/100 mesh (Alltech Associates, Inc.). Operating conditions were column temperature 75°C, injector and detector temperatures 120°C, nitrogen carrier gas flow rate 29 ± 1 ml/minute. Two oxy-trap cartridges (Alltech Associates), one of large capacity and the other including a colored indicator of oxygen breakthrough, were used to remove traces of oxygen from the nitrogen carrier gas. (Oxygen-free carrier gas is critical to the performance of the electron capture detector). Dichloroacetylchloride was measured by electron capture gas chromatography after trapping in a methanol impinger.

Using the gas chromatographic conditions described above, calibration curves (Figures 9.2-1 and 9.2-2) were constructed for TCE and chloroform by dynamic dilution in purified air. For TCE, calibration curves were constructed over one range of concentrations, i.e. 0-5 ppm. For chloroform, calibrations were required over two ranges of concentration, "high" (0-5 ppm) for chloroform-NO_x experiments and "low" (0-60 ppb) for precise detection of chloroform as a trace product, if any, in TCE-NO_x experiments.

9.2.4 Interference Studies

Joshi and Bufalini (1978) reported large positive interferences from chloroform, trichloroacetaldehyde, and other chlorine-containing compounds when measuring NO_2 with commercial chemiluminescent analyzers. The interference was most severe for a NO_x analyzer equipped with a carbon converter operated at high temperature (the converter reduces NO_2 to NO prior to chemiluminescence detection), and was much lower with an $FeSO_4$ converter operated at lower temperature. The chemiluminescent analyzer we use has a molybdenum converter operated at 310°C and was not tested by Joshi and Bufalini. Thus, we carried out a number of tests with both NO_x and ozone analyzers for potential interferences of TCE and chloroform. These tests included (a) chloroform, up to 4.7 ppm in pure air; (b) TCE, up to 3.6 ppm in pure air; (c) mixtures of TCE and chloroform in pure air and (d) addition of chloroform and/or TCE to pure air containing NO (up to 300 ppb), NO_2 (up to 220 ppb) and ozone (up to 290 ppb). Under these conditions, there was no evidence for positive or negative interferences due to TCE or chloroform in either NO_x or ozone measurements.

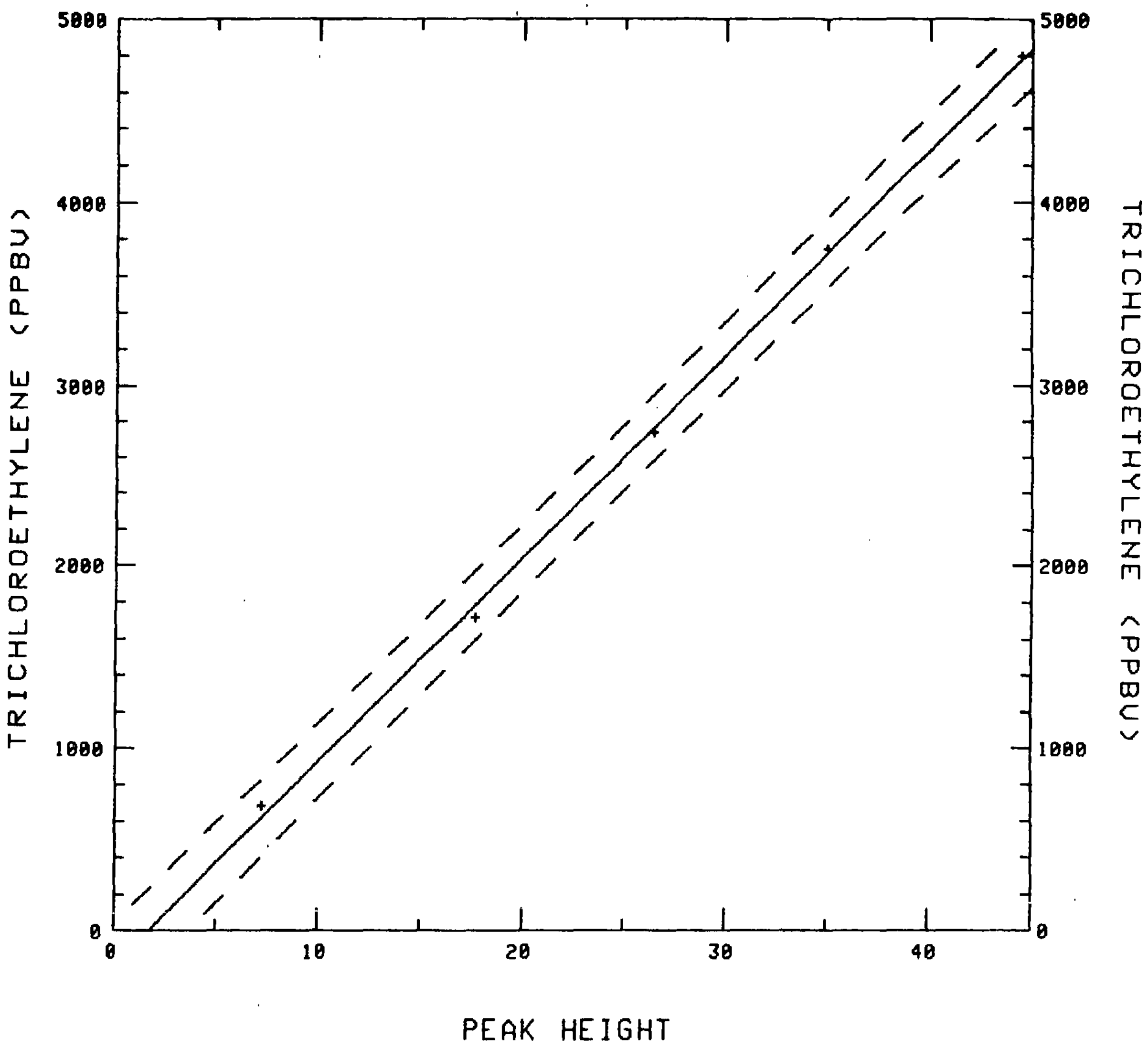


Figure 9.2-1. Calibration Curves for GC/ECD Analysis of Trichloroethylene in Pure Air for Direct Injection of 3 cm^3. (See Text for Conditions.)

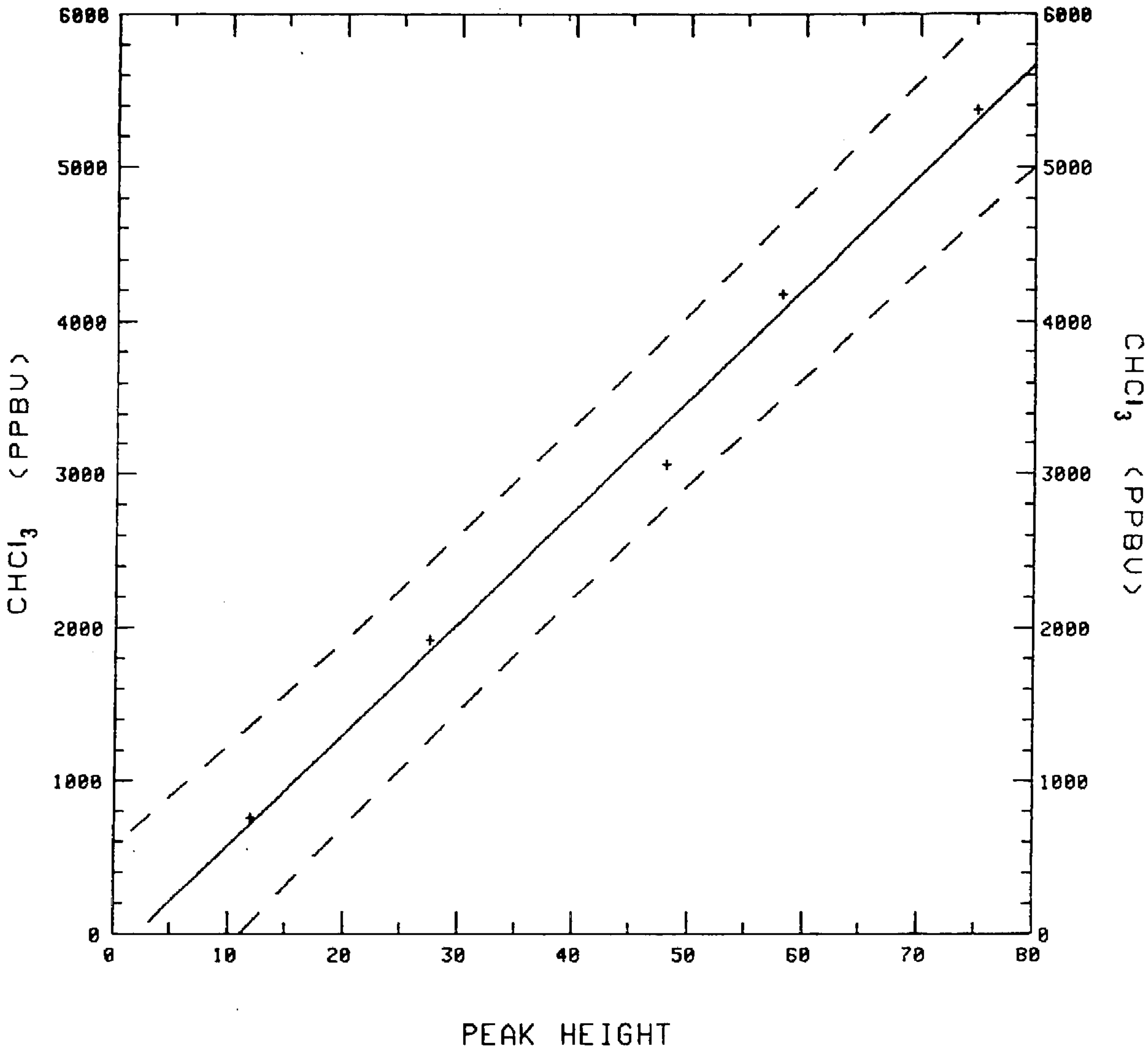


Figure 9.2-2. Calibration Curves for GC/ECD Analysis of Chloroform in Pure Air for Direct Injection of 3 cm^3. (See Text for Conditions.)

9.3 RESULTS

9.3.1 Stability Studies (Control Experiments)

A number of control experiments were carried out to determine the stability of the trace pollutants of interest in the Teflon reactor. Loss rates of NO, NO_2, ozone and organic pollutants (but not TCE and chloroform) have been reported by Grosjean (1985). Loss rates of NO, NO_2 and ozone measured in this chamber were consistent with (and generally lower than) those reported by Grosjean for similar FEP Teflon reactors.

Loss rates of TCE and $CHCl_3$ were studied in some detail in experiments carried out with TCE and/or chloroform in purified air in the dark (Table 9.3-1). In these stability runs, TCE and $CHCl_3$ concentrations were monitored every 15-20 minutes over periods of 3 to 114 hours. All TCE and chloroform concentration-time profiles exhibited small positive slopes corresponding to small concentration increase rates of $0.19 - 2.0 \times 10^{-2}$ hr^{-1}. To investigate a possible systematic effect, pollutants such as NO and NO_2, whose loss rates are well characterized and which do not react with TCE or chloroform in the dark, were added in some runs. As can be seen from Table 9.3-1, loss of NO_x was indeed observed during these runs, and the corresponding apparent increase rates for TCE and chloroform were similar to those measured in the absence of NO_x. A possible explanation for these observations may involve a slow increase in the response of the electron capture detector by some self-cleaning process taking place upon repeated "exposure" to TCE and chloroform. This was not investigated further, but a small correction factor was applied to all concentration-time profiles described below.

9.3.2 Photolysis Experiment

While TCE and chloroform are not expected to photolyze in sunlight, one control experiment was carried out with 1.02 ppm TCE in purified air (NO < 5 ppb, no detectable amounts of NO_2 and ozone) and exposed to sunlight for ~70 minutes. No loss of TCE could be detected.

Table 9.3-1

SUMMARY OF STABILITY STUDIES

Run Duration (hours)[a]	Initial Concentrations (ppb)					Loss Rate (10^{-2} hr^{-1})				
	TCE	$CHCl_3$	NO	NO_2	O_3	TCE	$CHCl_3$	NO	NO_2	O_3
4.5	900	1,000	0	0	0	-1.6[b]	-2.1	-	-	-
19.1	900	1,000	0	0	0	-1.0	-1.3	-	-	-
4.0	1,140	1,280	0	0	0	-1.9	-2.0	-	-	-
16.1	1,140	1,280	0	0	0	-1.8	-1.9	-	-	-
17.0	650	0	85	110	0	-0.9	-	0.7	0.3	-
16.4	4,770	0	130	280	0	-2.0	-	0.4	0.1	-
18.1	0	3,570	215	155	0	-	-0.8	1.3	0.2	-
15.5	0	0	0	30	290	-	-	-	0.2	0.45
15.8	940	0	300	0	0	-0.48	-	0.8	-	-
26.1	850	0	230	130	0	-0.40	-	0.8	-	-
19.5	3,000	3,400	0	0	0	-0.19	ND	-	-	-
23.3	3,000	3,400	0	0	0	-0.19	-0.25	-	-	-
3.0	300	3,400	0	0	0	-0.19	ND	-	-	-

[a] All runs carried out in 3.5-m^3 Teflon reactor, with purified air in the dark.

[b] Minus signs denote an increase in concentration; see text.

9.3.3 Nighttime Chemistry Regime Experiment

As for photolysis, the reaction of TCE with NO_3 (and/or N_2O_5) at night is expected to be of negligible importance, and only one experiment was performed to verify this. Mixtures of TCE (1.4 ppm), NO_2 (200 ppb) and ozone (74 ppb) in purified air were allowed to react in the dark for nearly 5 days (114 hours). The observed TCE loss rate, while measurable, was only 0.47 x 10^{-2} hr^{-1}. After correction using the average value of the stability runs reported in Table 9.3-1, the TCE loss rate was 1.44 x $10^{-2}hr^{-1}$.

9.3.4 TCE-NO_x Sunlight Irradiation Experiments

Only five TCE-NO_x runs could be completed. The experiments were carried out in October to December 1986; a number of runs had to be aborted due to high winds, heavy smoke from nearby brushfires, increasing cloud cover, or rain. Initial conditions (Table 9.3-2) included TCE concentrations of 0.5-6.2 ppm, NO_x concentrations of 0.19-0.41 ppm, TCE/NO_x ratios of 2.8-15.2, and NO/NO_x ratios of 0.28 to 1.00. Sunlight irradiation times ranged from 2.4 to 4.8 hours. Concentration-time profiles (Figures 9.3-1 through 9.3-4) are consistent with those expected for a hydrocarbon of somewhat low reactivity towards OH. At high initial TCE, TCE/NO_x and NO/NO_2 values (e.g. Run 1), TCE consumption and conversion of NO to NO_2 proceeded slowly. As the initial NO_2/NO and TCE/NO_x ratios increase and decrease, respectively, the overall reactivity of the system increases: the NO-NO_2 crossover is reached late in Run 2 and earlier in Run 3, and the NO_2 maximum is reached late in Runs 2 and 3 and earlier in run 4, in which ozone reached its maximum value near the end of the run.

As a check of consistency of the overall reactivity of the TCE-NO_x system, average concentrations of the hydroxyl radical were calculated for each run according to:

$$\ln(TCE/TCE_o) = -k_{OH}(OH)_{av}t$$

where TCE and TCE_o are the final and initial TCE concentrations, k_{OH} is the OH-TCE reaction rate constant, 2.4 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1}, and t is the

Table 9.3-2

SUMMARY OF INITIAL CONDITIONS FOR TCE-NO_x AND $CHCl_3$-NO_x SUNLIGHT IRRADIATION EXPERIMENTS

	Initial Concentration (ppb)					Time in Sunlight	Initial Concentration Ratios	
Run[a]	TCE	$CHCl_3$	NO	NO_2	O_3	(hours)	NO/NO_x	HC/NO_x
1	1,420	0	260	10	0	2.4	0.96	5.30
2a	740	0	155	40	0	4.4	0.79	3.75
2b	570	0	95	105	6	3.0	0.47	2.85
3	6,250	0	410	0	0	4.8	1.00	15.2
4	2,280	0	75	190	7	4.6	0.28	8.70
5	0	3,870	230	145	0	4.1	0.61	10.2
6	0	2,600[b]	125	115	0	3.6	0.52	10.8, 15.6[b]

[a] Same run code as in Figures 9.3-1 to 9.3-6.

[b] With 1.16 ppm of 2-methyl-2-butene added as "booster."

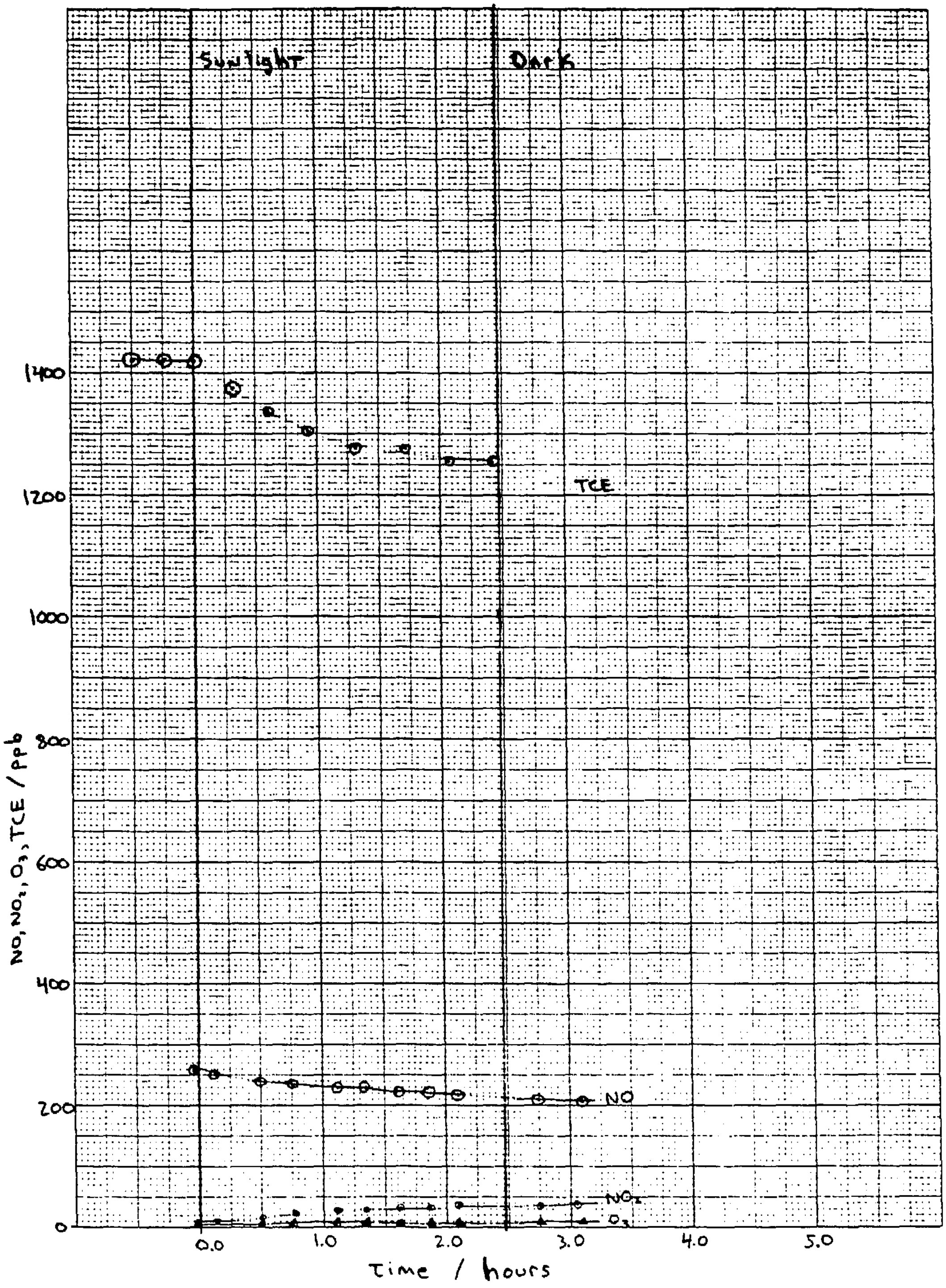


Figure 9.3-1. Concentration-Time Profiles for TCE, NO, NO_2 and O_3 in TCE-NO_x Irradiation Run 1. (See Table 9.3-2 for Initial Conditions.)

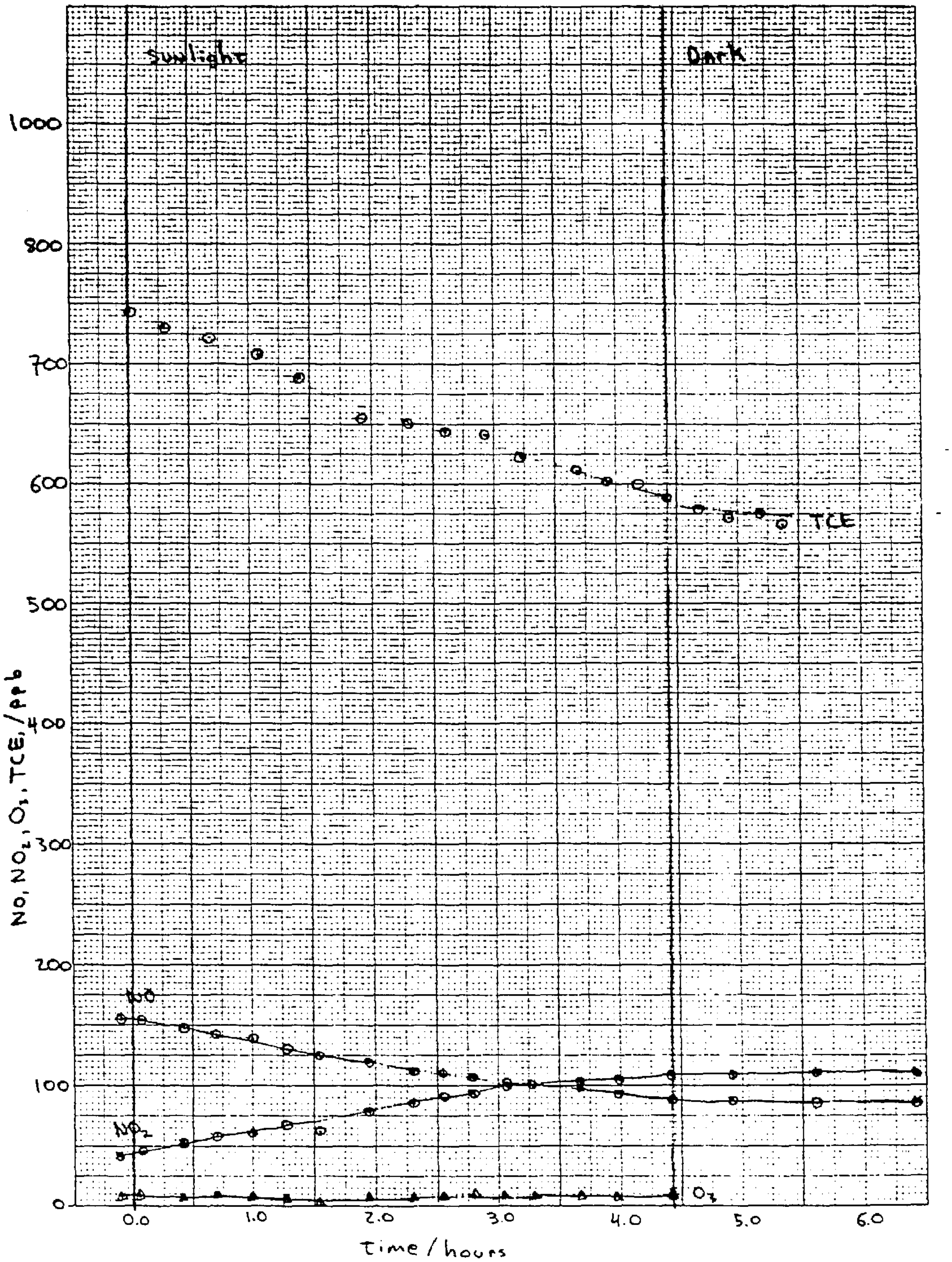


Figure 9.3-2. Concentration-Time Profiles for TCE, NO, NO_2 and O_3 in TCE-NO_x Irradiation Run 2a. (See Table 9.3-2 for Initial Conditions.)

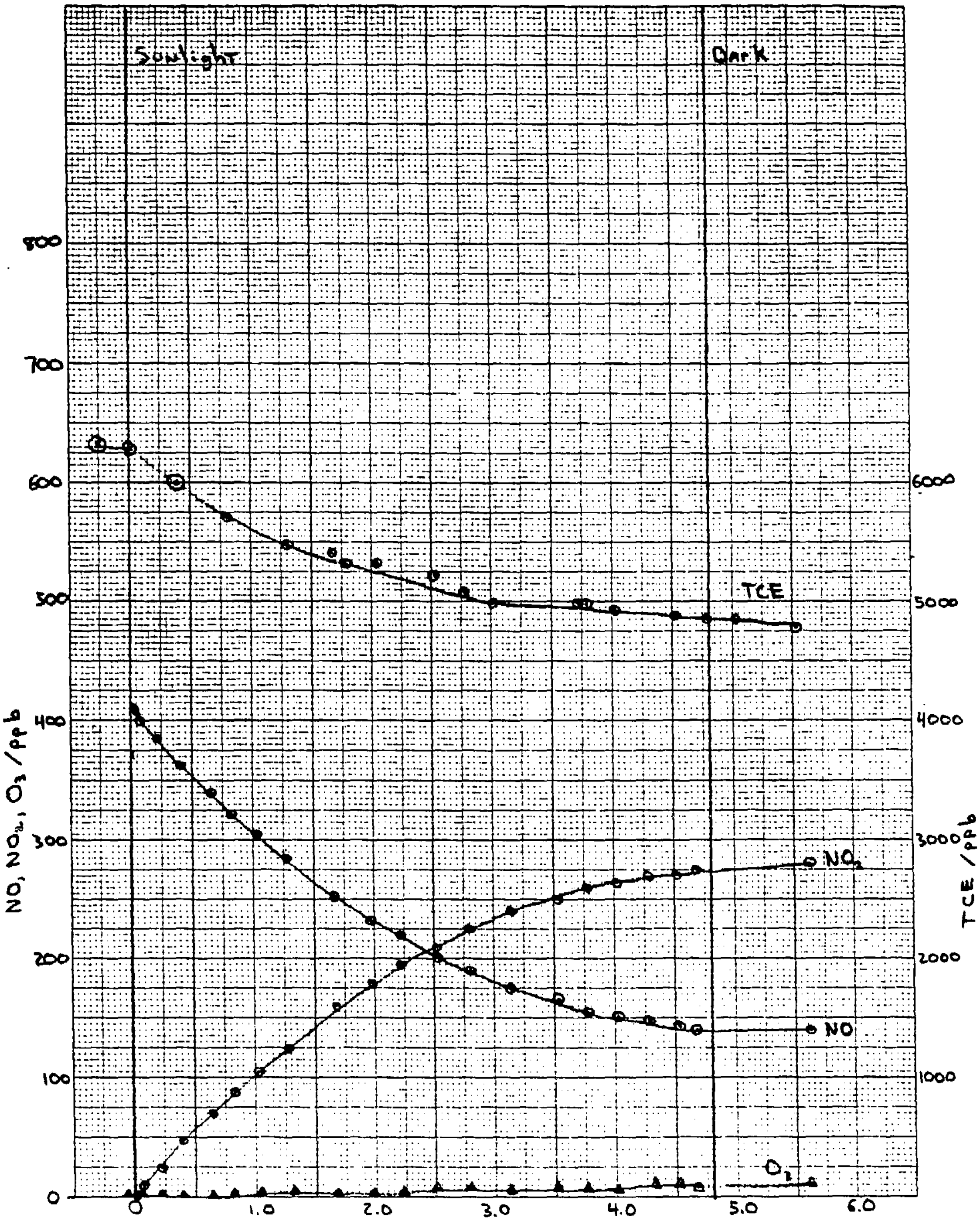


Figure 9.3-3. Concentration-Time Profiles for TCE, NO, NO_2 and O_3 in TCE-NO_x Irradiation Run 3. (See Table 9.3-2 for Initial Conditions.)

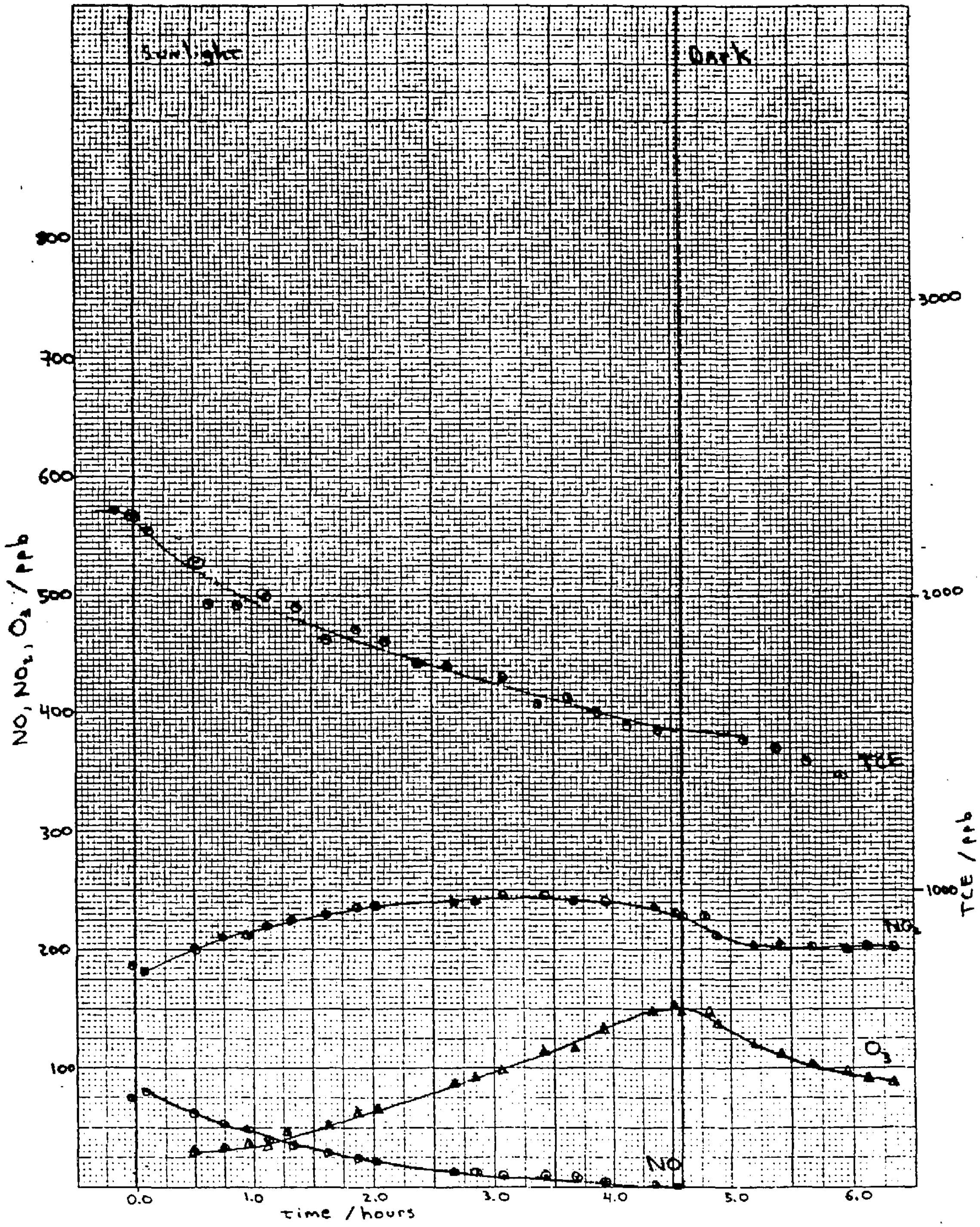


Figure 9.3-4. Concentration-Time Profiles for TCE, NO, NO$_2$ and O$_3$ in TCE-NO$_x$ Irradiation Run 4. (See Table 9.3-2 for Initial Conditions.)

time of exposure to sunlight. Average OH values were 5.8×10^6, 5.9×10^6, 6.1×10^6, and 9.9×10^6 molecules cm^{-3} for Runs 1, 2a, 3 and 4, respectively, and were entirely consistent with the overall reactivity experimentally observed for each run (and also expected from the initial TCE-NO_x and NO/NO_x ratios). For comparison, an average OH value of 1.8×10^8 molecules cm^{-3} was calculated for the chloroform-NO_x Run 6, in which the highly reactive olefin 2-methyl-2-butene was added as a booster.

No chloroform could be detected in any of the TCE-NO_x irradiation experiments (Table 9.3-3). Control experiments indicated that no detectable amounts of chloroform were present in the purified air or as an impurity in TCE. With an analytical detection limit of 25-50 picograms and a sampling loop volume of 5 cm^3, 1-2 ppb of chloroform would have been detected in the TCE-NO_x irradiation experiments. Using the data for Runs 3 and 4 as upper limits, we estimate that chloroform yields in our NO_x photooxidations of TCE are, respectively, $\leq 2.8 \times 10^{-3}$ and $\leq 1.4 \times 10^{-3}$ molecules of chloroform produced per molecule of reacted TCE.

9.3.5 Chloroform-NO_x Irradiation Experiments

Of the several experiments involving sunlight irradiation of chloroform-NO_x mixtures, only two could be completed (again due to adverse weather conditions). Initial conditions are listed in Table 9.3-2, and concentration-time profiles are shown in Figures 9.3-5 and 9.3-6. With chloroform as the only hydrocarbon present in the Teflon reactor, the conversion of NO to NO_2 proceeded very slowly, little chloroform was consumed (< 7 percent in 4 hr) and no ozone was formed. With 2-methyl-2-butene [$(CH_3)_2C=CHCH_3$, a very reactive olefin] added as a "booster," conversion of NO to NO_2 and ozone formation took place within minutes, and the more rapid consumption of chloroform (~20 percent in 4 hr) reflects the higher levels of OH radicals produced in the NO_x-2-methyl-2-butene system.

Table 9.3-3

CHLOROFORM YIELDS FROM TCE IN SUNLIGHT-IRRADIATED TCE-NO_x MIXTURES IN AIR

Run[a]	Matrix	TCE (ppb)	Exposure to sunlight (hours)	Measured $CHCl_3$ (ppbv)[b]
Control	Pure air only	0	dark	0
1	TCE in pure air	1,420	dark	0
	TCE-NO_x	1,330	0.6	0
	TCE-NO_x	1,250	2.4	0
2a	TCE-NO_x	740	dark	0
	TCE-NO_x	590	4.4	0
2b	TCE-NO_x	570	dark	0
	TCE-NO_x	380	3.0	0
Control	Pure air only	0	dark	0
3	TCE in pure air	6,250	dark	0
	TCE-NO_x	6,000	0.1	0
	TCE-NO_x	5,720	0.8	0
	TCE-NO_x	4,850	4.8	0
4	TCE-NO_x	2,280	dark	0
	TCE-NO_x	1,580	4.6	0

[a] Same run code as in Table 9.3-2.

[b] With analytical detection limit of $\leq$ 2 ppb.

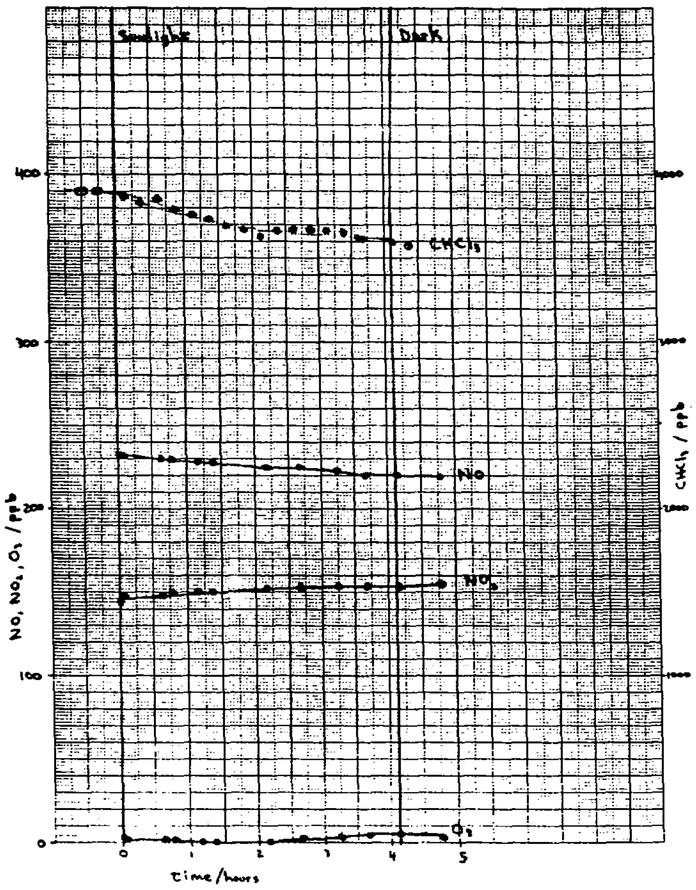


Figure 9.3-5. Concentration-Time Profiles for TCE, NO, NO_2 and Ozone in Chloroform-NO_x Irradiation Run 5.

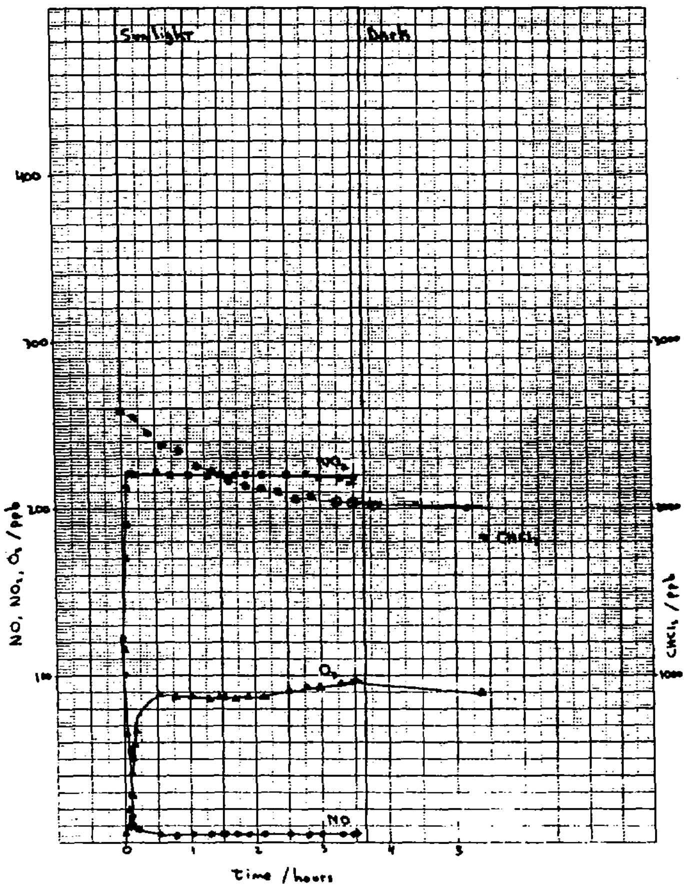


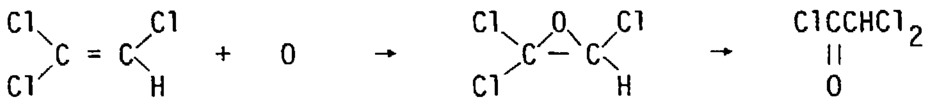
Figure 9.3-6. Concentration-Time Profiles for TCE, NO, NO_2 and Ozone in Chloroform-NO_x Irradiation Run 6.

9.4 DISCUSSION

9.4.1 Chloroform Formation From TCE

For chloroform to be produced from TCE would require (a) production of dichloroacetyl chloride in the TCE-OH reaction, and (b) photolysis of dichloroacetyl chloride to yield products including chloroform. We examine below the TCE-OH reaction mechanism with focus on these two pathways.

The reaction of OH with TCE involves addition as the major pathway (Figure 9.4-1). The β-hydroxy alkyl radicals thus formed are assumed to react exclusively with O_2. The corresponding β-hydroxyperoxy radicals are expected to react with NO to form β-hydroxyalkoxy radicals. A minor pathway of the NO-peroxy radical reaction may involve the elimination of chlorine atoms, as suggested by Howard (1976) for tetrachloroethylene. The alkoxy radicals may undergo unimolecular decomposition, leading to phosgene and formyl chloride as the major products. Another pathway may involve reaction of the β-hydroxyalkoxy radicals with O_2 to yield hydroxyacetyl chlorides. None of these pathways, and none of the subsequent reactions of the "first-generation" products, produce dichloroacetyl chloride or chloroform. However, dichloroacetyl chloride has been observed experimentally among products of the TCE-OH (or TCE-NO_x) reaction (Gay et al., 1976; Goodman et al., 1986). Our own results for TCE-NO_x Run 3 indicate a yield of 8 ± 4 percent. Gay et al. have proposed a 1,2 chlorine atom shift involving an epoxide formed by reaction with oxygen atoms or RO_2 radicals (where RO_2 includes Criegee intermediates of the ozone-chloroethene reaction):



A more likely possibility for dichloroacetyl chloride formation under atmospheric conditions (where concentrations of O atoms and RO_2 radicals are too low for the above reaction to be important) involves the reaction of TCE with chlorine atoms as shown in Figure 9.4-2. This tentative mechanism is analogous to that given in Figure 9.4-1 for the OH-TCE reaction, and predicts formyl chloride and phosgene as major reaction products, along with chloral,

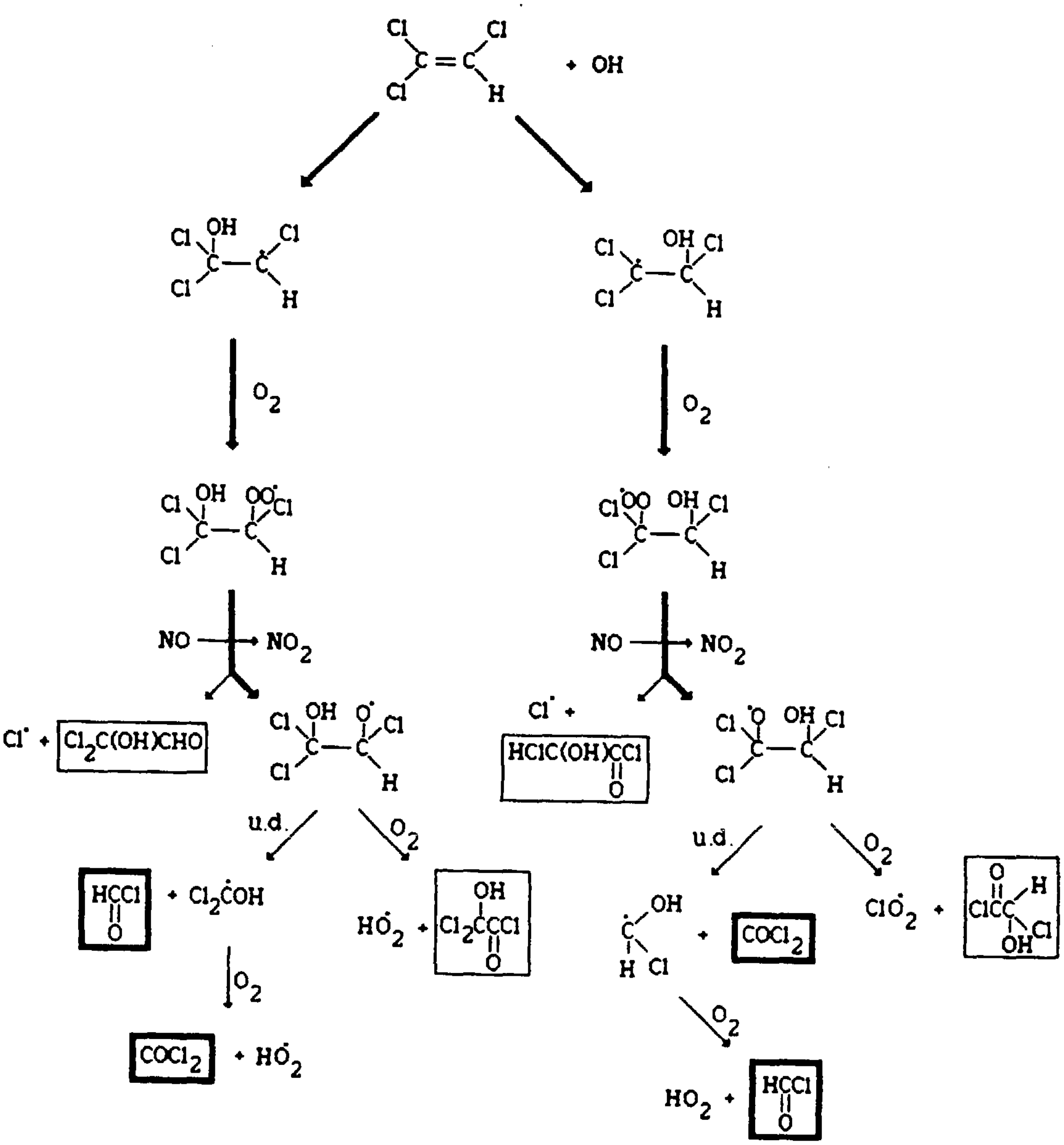


Figure 9.4-1. Hydroxyl Radical-Trichloroethylene Reaction Mechanism. Bold Arrows and Squares Indicate Major Pathways and Products.

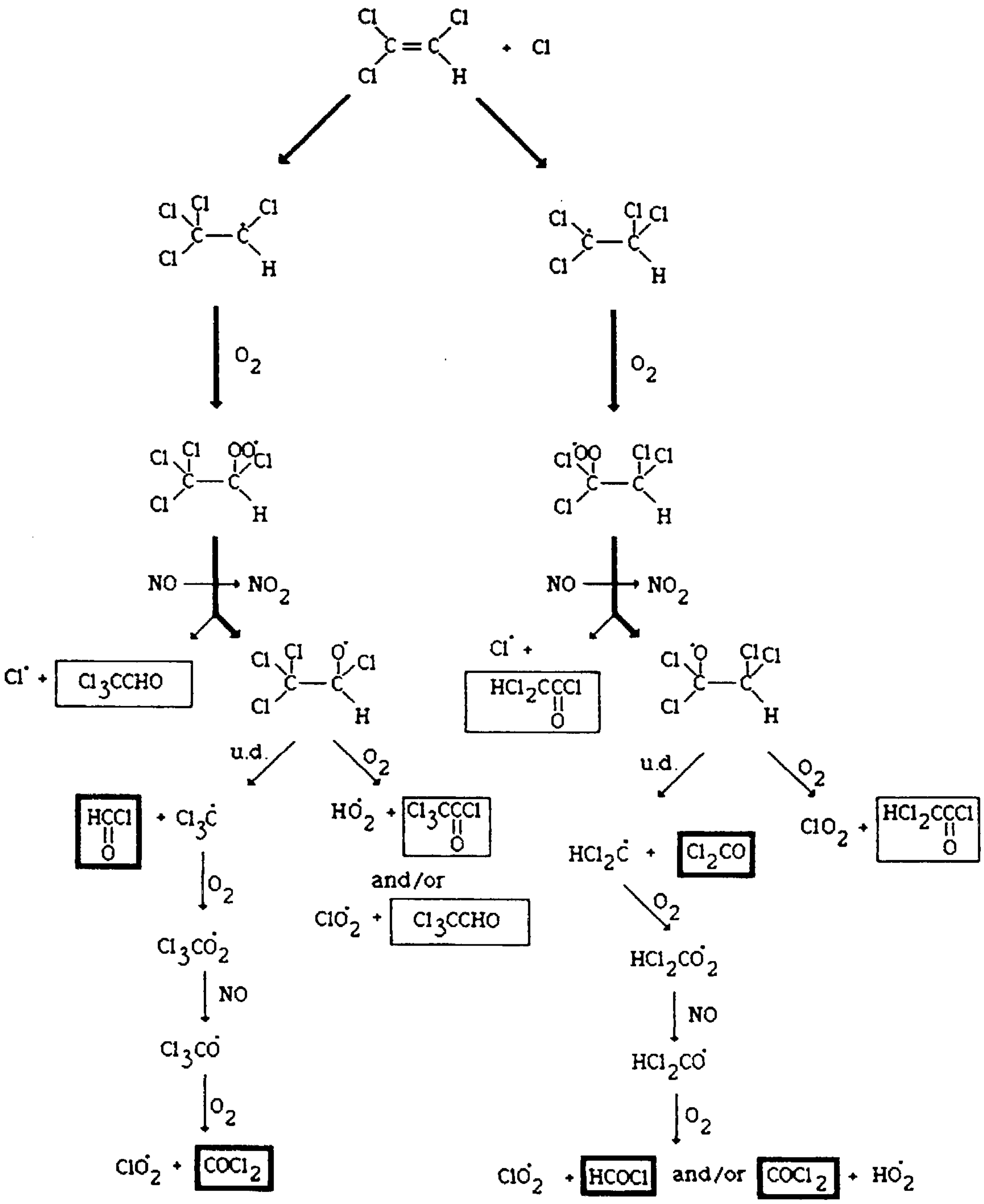


Figure 9.4-2. Chlorine Atom-Trichloroethylene Reaction Mechanism. Bold Arrows and Squares Indicate Major Pathways and Products.

dichloroacetyl chloride, and trichloroacetyl chloride.

The TCE-chlorine atom reaction, while of possible importance in systems containing TCE as the only hydrocarbon, is probably negligible in ambient air. In our laboratory study of TCE-NO_x, chlorine atoms formed in the OH-TCE reaction (see Figure 9.4-1) are expected to react with TCE as shown in Figure 9.4-2. Since the Cl-TCE reaction is about 25 times faster than the OH-TCE reaction (e.g. Jet Propulsion Laboratory, 1981), even a small amount of Cl formed in a minor pathway of the OH-TCE reaction may contribute to the observed TCE removal. In polluted air, however, many hydrocarbons will effectively compete with TCE for any available chlorine atoms:

$$-d\,[Cl]/dt = k_{TCE}[Cl][TCE] + k_1[Cl][HC_1] + k_2[Cl][HC_2] + \ldots$$

Since for many hydrocarbons $[HC_i] >> [TCE]$ <u>and</u> $k_i > k_{TCE}$ (see Table 9.4-1), the reaction of TCE with chlorine atoms is <u>not</u> an important removal process for TCE in urban air.

The photolysis of dichloroacetyl chloride has not been studied experimentally. In experiments with irradiated tetrachloroethylene in pure air (no OH chemistry), Singh and Lillian (1975) reported on several reaction products including <u>trace amounts</u> of chloroform and, <u>tentatively</u>, dichloroacetyl chloride. Yung et al. (1975) have further speculated that photolysis of the dichloroacetyl chloride tentatively reported by Singh and Lillian would in turn explain the trace amounts of chloroform observed in the same experiments:

$$Cl_2HCCOCl + h\nu \rightarrow CHCl_3 + CO$$

While this reaction is plausible, other pathways may also be involved, e.g. $Cl_2HCCOCl + h\nu \rightarrow CO + Cl^{\cdot} + Cl_2HC^{\cdot}$, which would lead to phosgene and/or formyl chloride but not chloroform. Furthermore, dichloroacetyl chloride may

Table 9.4-1

AMBIENT CONCENTRATIONS (LOS ANGELES) AND CHLORINE ATOM REACTION RATE CONSTANTS FOR CHLOROFORM AND SELECTED HYDROCARBONS

Hydrocarbon	A= Ambient Concentrations[a] (ppb)	B= k_{Cl} (cm^3 molecule^{-1} sec^{-1})[b]
Olefins:		
Trichloroethylene	0.5 - 1.0[c]	5.8×10^{-11}
Tetrachloroethylene	1.4 - 2.8[c]	$< 5 \times 10^{-11}$
Ethylene	30 - 90	1.06×10^{-10}
Propene	7 - 32	2.44×10^{-10}
Alkanes:		
Ethane	32 - 220	6.4×10^{-11}
Propane	10 - 100	1.34×10^{-10}
n-Butane	21 - 70	1.97×10^{-10}
Haloalkanes:		
Methylene chloride	0.6 - 5[c]	5.2×10^{-13}
Chloroform	0.05 - 0.2[c]	1.23×10^{-13}
Aromatics:		
Benzene	12 - 29	1.5×10^{-11}
Toluene	20 - 68	5.9×10^{-11}
Aldehydes:		
Formaldehyde	4 - 80	7.3×10^{-11}
Acetaldehyde	2 - 40	7.6×10^{-11}

---

[a] Grosjean and Fung (1984), unless otherwise indicated.

[b] Baulch et al., (1982), Watson (1977), Jet Propulsion Laboratory (1981).

[c] See Table 9.4-2.

also react with OH to form products other than chloroform, e.g.:

$$\mathrm{Cl_2HCCOCl + OH \rightarrow Cl_2\dot{C}COCl + H_2O}$$

$$\mathrm{\rightarrow ClH\dot{C}COCL + HOCl}$$

Our results for Run 3 (reacted TCE = 1400 ppb, $CHCl_3$ < 2 ppb, dichloroacetyl chloride = 116 ± 60 ppb) suggest that photolysis of dichloroacetyl chloride is not a major pathway for the formation of chloroform from TCE. Our observations are consistent with one or more of the following hypotheses for removal of dichloroacetyl chloride: (a) reaction with OH, to form products other than $CHCl_3$, predominates over photolysis, (b) photolysis is important but proceeds by one or more channels not leading to $CHCl_3$ and (c) photolysis leads to $CHCl_3$ as a major product but proceeds at a very slow rate, i.e. less than 1 percent per hour.

While the reactions of dichloroacetyl chloride and other pathways leading to $CHCl_3$ should warrant further investigations, our results indicate that in-situ formation of chloroform by atmospheric reactions of trichloroethylene is of negligible importance. Recent South Coast Air Quality Management District (SCAQMD) estimates for emissions of trichloroethylene in the South Coast Air Basin are 4,121 kg/day. This estimate, together with our upper limit of 1.4×10^{-3} for $CHCl_3$ yield from TCE and a TCE atmospheric residence time of ~ 4 days, would give an upper limit of 1.4 kg/day for in-situ formation of chloroform from TCE in the atmosphere. This estimated upper limit is negligible when compared to SAIC's estimate of 926 kg/day (see Table 4.5-1) for direct emissions of chloroform in the South Coast Air Basin.

9.4.2 Chloroform Removal Processes

The only important chemical removal process for chloroform in the atmosphere is by reaction with the hydroxyl radical. The reaction is slow, $k = 1.03 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} (Jet Propulsion Laboratory, 1981; Watson, 1977). For a "typical" OH concentration of 10^6 molecules cm^{-3}, the atmospheric half-life of chloroform is about 80 days.

The pathways initiated by reaction of OH with chloroform are summarized in Figure 9.4-3. Hydrogen atom abstraction is expected to yield phosgene; chlorine atom abstraction is expected to yield phosgene and HCOCl, formyl chloride. Both pathways are possible since C-H and C-Cl have comparable bond strengths. Formyl chloride may decompose to HCl + CO. Spence et al. (1976) observed rapid thermal decomposition of formyl chloride, with a half-life of 10 minutes at room temperature. In contrast, Goodman et al., (1986) found formyl chloride to be stable; its higher homologue, acetyl chloride, CH_3COCl, has also been described to be a stable product (Basco and Parmar, 1985).

The HOCl formed in the C-Cl abstraction pathway may photolyze (Spence et al., 1980) to yield OH and chlorine atoms. Since Cl reacts with chloroform somewhat faster than OH does ($k = 1.23 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}; Jet Propulsion Laboratory, 1981), the Cl-chloroform reaction should also be considered as is shown in Figure 9.4-3. The expected end products are identical to those of the OH-chloroform reaction, i.e. phosgene and formyl chloride or the latter's decomposition products CO and HCl. Products of the OH-chloroform reaction have apparently not been studied. Products of the Cl-chloroform reaction have been reported to be phosgene (90-percent), CO and HCl (Spence et al., 1976), in agreement with the reaction scheme shown in Figure 9.4-3. As discussed above for TCE, the reaction of chlorine atoms with chloroform, while possibly important under laboratory conditions where chloroform is the only hydrocarbon present, is deemed negligible in polluted ambient air (see Table 9.4-1).

Reaction of the "first generation" products, phosgene and formyl chloride, have received limited attention. Besides its thermal decompostion to CO + HCl, formyl chloride may photolyze (presumably to CO and HCl) and may react with OH to yield carbon monoxide:

$$HCOCl + OH \rightarrow H_2O + \dot{C}OCl \xrightarrow{O_2} CO + Cl\dot{O}_2$$

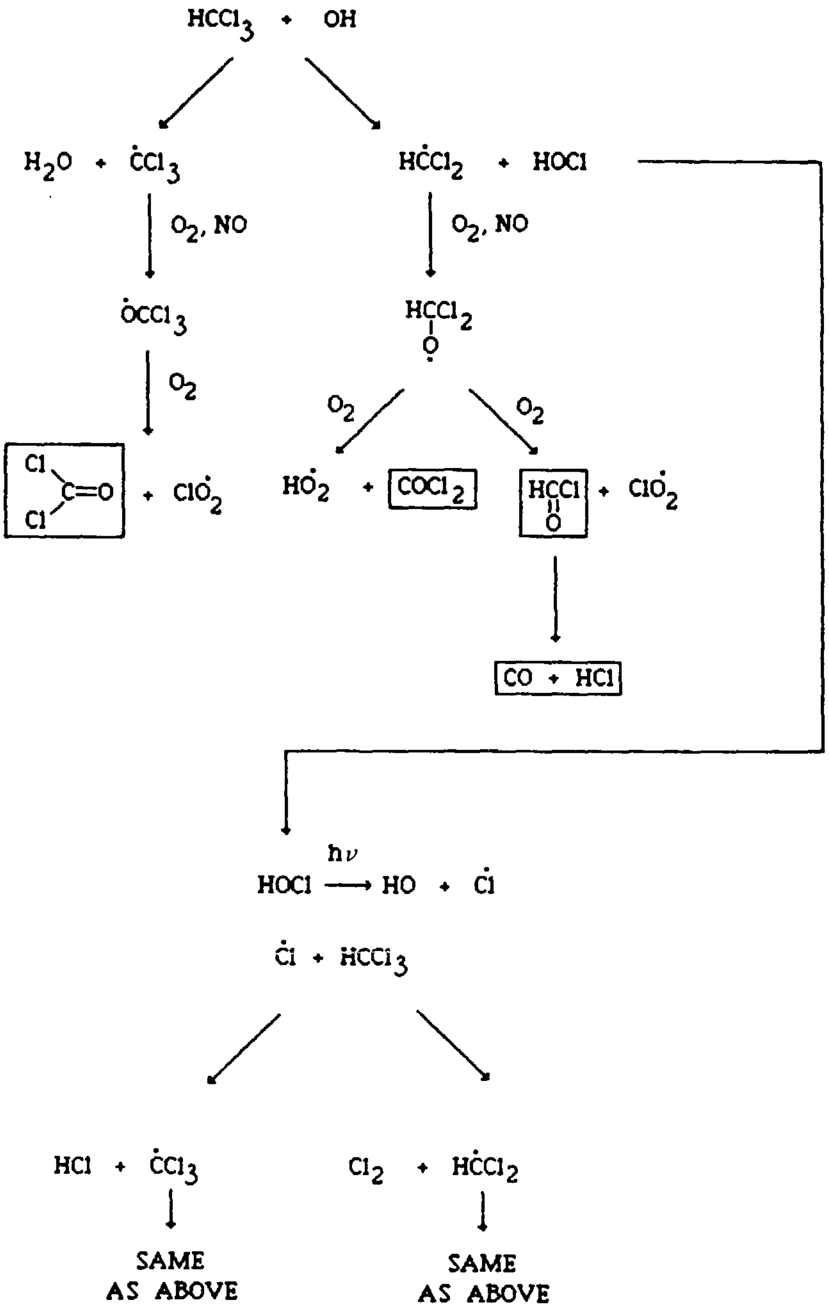


Figure 9.4-3. Hydroxyl Radical-Chloroform Reaction Pathways.

$$HCOCl + OH \rightarrow HOCl + H\dot{C}O \xrightarrow{O_2} CO + HCl$$

A rough estimate of $k = 5 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} is proposed for the OH-formyl chloride reaction rate constant. Thus, formyl chloride is not expected to accumulate in polluted air. In contrast, phosgene is expected to be quite stable in the atmosphere, since its photolysis, reaction with OH, and hydrolysis are negligible (Singh, 1976).

Because of phosgene's toxicity and its predicted long persistence in the atmosphere, it is of interest to compare chloroform to other hydrocarbons that may yield phosgene by in-situ reactions. Phosgene is a documented or expected product of the reaction of (a) OH with the chloroethenes: vinylidene chloride, TCE and tetrachloroethylene; (b) ozone with the same three chloroethenes; (c) chlorine atoms with chloroethenes; (d) OH with chloroalkanes containing at least one CCl_2 group, e.g. methylene chloride, chloroform; and (e) chlorine atoms with chloroalkanes. Assuming in first approximation that only OH reactions are of importance, a ranking of the phosgene precursors can be obtained by simply multiplying the ambient concentration of the precursor (or its emission rate) by its OH reaction rate constant. The results are shown in Table 9.4-2. They indicate that chloroform is only a minor contributor to ambient phosgene in urban air.

9.5 CONCLUSIONS AND RECOMMENDATIONS

Following a critical review of available literature data, laboratory studies were carried out to investigate (a) possible in-situ formation of chloroform from trichloroethylene (TCE) and (b) the atmospheric persistence of chloroform in polluted ambient air. These studies were carried out using a large Teflon reactor and include a number of interference and pollutant stability studies. Major conclusions are as follows.

- TCE and chloroform were quite stable at ppb to ppm concentrations in purified air in the dark, with and without added oxides of nitrogen in a Teflon reactor.
- TCE and chloroform did not interfere in the measurements of NO and NO_x using a commercial chemiluminescence analyzer equipped

Table 9.4-2

RANKING OF PHOSGENE PRECURSORS

Precursor	A = OH Reaction Rate Constant (10^{-12} cm^3 $molecule^{-1}$ sec^{-1})	B = Ambient Concentration (ppt)	Product A x B	Ranking
Chloroethenes:				
Vinylidene chloride	6.5	5 - 10	32 - 65	4
Trichloroethylene	2.4	500 - 1,000	1,200 - 2,400	1
Tetrachloroethylene	0.17	1,400 - 2,800	238 - 476	3
Hexachloro-1,3-butadiene	0.17	4	0.7	10
Halocarbons:				
Methylene chloride	0.14	600 - 5,000	84 - 700	2
Chloroform	0.10	50 - 200	5 - 20	6
Carbon tetrachloride	<0.001	215	<0.21	-
1,1-dichloroethane	0.26	66	17	5
1,1,1-trichloroethane	0.01	1,030	10.3	7
1,1,2-trichloroethane	0.33	9	2.9	8
1,1,1,2-tetrachloroethane	<0.01	4	<0.04	-
1,1,2,2-tetrachloroethane	<0.01	12	<0.12	-
Hexachloroethane	<0.001	no data	small	-
Bromodichloromethane	0.1	10	1.0	9
Fluorotrichloromethane	<0.001	470	<0.47	-
CF_3CCl_3	<0.001	300	<0.30	-

with a molybdenum converter, in contrast to earlier findings with similar chemiluminescence analyzers equipped with carbon and $FeSO_4$ converters.

- Sunlight irradiations of chloroform-NO_x mixtures in pure air, apparently studied experimentally for the first time, confirmed that chloroform reacts only slowly, as expected from theoretical considerations. While phosgene is an expected major product of the OH-chloroform reaction, a comparison of phosgene yields from chloroform and other chlorinated hydrocarbons indicates that chloroform is a minor contributor to phosgene in urban air.

- In experiments involving sunlight irradiations of TCE-NO_x mixtures in pure air, no chloroform could be detected for any of the TCE/NO_x and NO/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 yield of chloroform from TCE under the conditions employed. This yield, together with emission rate and ambient concentration data for TCE, indicate that in-situ formation of chloroform from TCE is negligible.

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10.0

MASS BALANCE COMPUTATIONS

10.1 METHODS

The objective of the mass balance computation was to relate estimated emissions of chloroform from all major identified sources to historically observed concentrations in the South Coast Air Basin. To accomplish this, we selected, for each of the four halocarbon monitoring stations in the ARB's network (see Section 5.1.2), five 24-hour sampling intervals to model. Historical meteorological data corresponding to those intervals, along with chloroform emissions based upon the surveys and literature reviews conducted in Phase I and the source tests conducted in Phase II, were input to the Industrial Source Complex Short-Term model. Resulting predictions of ambient concentrations were then compared with the measured values.

10.1.1 Modeling Approach

The Industrial Source Complex Short-Term (ISCST) model was used at the ARB's suggestion (Allen, 1985). The ISCST is a steady-state Gaussian plume model which can calculate ground-level concentrations of pollutants from stack, area, or volume sources, given hourly meteorological data, including mixing height (Bowers et al., 1979). The program can calculate 1-, 2-, 3-, 4-, 6-, 8-, 12-, and/or 24-hour average concentrations, or an average over the number of hours of meteorological data input. Source locations can be placed anywhere in a Cartesian coordinate system, while receptor locations can be referenced to either Cartesian or polar coordinates. Concentrations can be computed for all sources or for any combination of sources. Output options can include tables of highest and second highest concentrations at each receptor and tables of the 50 maximum values for each selected averaging period. ISCST is a non-guideline model, and is identified as File Number 18 on Version 5 of the User's Network for Applied Modeling of Air Pollution (UNAMAP) magnetic tape. For our modeling exercise, both sources and receptor locations of interest were located on a grid corresponding to Zone 11 of the Universal Transverse Mercator (UTM) grid system.

10.1.2 Selection of Scenarios

Five 24-hour periods of chloroform emissions were simulated for each of the four ARB receptor stations. Each modeled period corresponded to a measurement period running from 9 a.m. on one day to 9 a.m. on the next day. Table 10.1-1 lists the receptor station, its UTM coordinates, and the date for each run. Dates were chosen to provide a representative range of observed chloroform concentrations, including extreme high and low values. The runs are divided almost equally between months of relatively low and high potential for photochemical activity. No attempt was made to incorporate photochemical processes in the model; this provided an opportunity to observe the relationship between modeled and measured concentrations in the absence of these processes.

10.1.3 Meteorological Data Input

Meteorological data for the four sites during the time periods to be modeled were obtained from several sources, including the ARB, the South Coast Air Quality Management District (SCAQMD), the U.S. Department of Commerce, and literature to be cited below. The following discussion presents the methodology by which these data were used to derive wind speed, wind direction and stability class inputs to the model.

Table 10.1-2 presents 24-hour average wind speed, wind direction, and temperature data for the four sites on each of the days to be modeled. Each data set begins at 9 a.m. on the day reported in the table, and ends at 9 a.m. on the next day. Thus "model hour 1" corresponds to 9 - 10 a.m. on the first day and "model hour 24" corresponds to 8 - 9 a.m. on the next day. Wind speed and direction data for the Los Angeles and Riverside monitoring sites were obtained from SCAQMD wind observation summaries (Foon, 1985). For the El Monte site, wind data were available from the ARB's Haagen-Smit Laboratory (ARB, 1983) for all modeled days except 8-9 August 1983. For this date, we used wind data from the nearest SCAQMD monitoring station, which is at Pico

Table 10.1-1
DEFINITION OF RUNS FOR PHASE I MODELING

Run	Receptor	UTM Coordinates (km)[a] East	UTM Coordinates (km)[a] North	Modeled Dates[b]
1	Dominguez Hills	384.5	3747.4	1-20-83
2	Dominguez Hills	384.5	3747.4	5-16-83
3	Dominguez Hills	384.5	3747.4	7-11-83
4	Dominguez Hills	384.5	3747.4	3-19-84
5	Dominguez Hills	384.5	3747.4	5-24-84
6	Los Angeles	386.9	3770.1	1-11-83
7	Los Angeles	386.9	3770.1	1-16-83
8	Los Angeles	386.9	3770.1	4-10-83
9	Los Angeles	386.9	3770.1	5-24-83
10	Los Angeles	386.9	3770.1	7-29-84
11	El Monte	401.8	3770.4	6-26-83
12	El Monte	401.8	3770.4	8-8-83
13	El Monte	401.8	3770.4	9-15-83
14	El Monte	401.8	3770.4	11-30-83
15	El Monte	401.8	3770.4	12-8-83
16	Riverside	463.0	3756.0	5-9-83
17	Riverside	463.0	3756.0	6-6-83
18	Riverside	463.0	3756.0	11-24-83
19	Riverside	463.0	3756.0	12-13-83
20	Riverside	463.0	3756.0	3-18-84

[a] Refer to Figure 5.1-1 for the coordinate system.
[b] Modeled 24-hr period begins at 9 a.m. on date reported.

Table 10.1-2

METEOROLOGICAL CONDITIONS FOR MODELED DAYS

Run	Mean Wind Speed (m/s)	Mean Wind Direction (degrees)	Mean Temperature (°K)
1	1.5	6 (N)	284.0
2	1.8	328 (NNW)	291.7
3	1.5	260 (W)	299.2
4	1.6	274 (W)	292.2
5	1.5	174 (S)	292.9
6	1.8	36 (NE)	292.4
7	1.6	340 (NNW)	287.9
8	1.8	278 (W)	285.7
9	1.7	231 (SW)	289.7
10	2.0	228 (SW)	295.7
11	2.1	178 (S)	291.8
12	2.5	232 (SW)	301.8
13	1.7	175 (S)	297.7
14	2.2	41 (NE)	285.3
15	0.9	359 (N)	286.1
16	1.5	349 (N)	289.8
17	1.6	341 (NNW)	292.9
18	4.4	22 (NNE)	296.8
19	0.8	38 (NE)	290.5
20	3.9	39 (NE)	282.6

Rivera (Foon, 1985). As no meteorological measurements were made at the Dominguez Hills site during the ARB halocarbon sampling program during the dates of interest, we used data from the SCAQMD monitoring station in Long Beach (Foon, 1985). Hourly data used for the modeling are presented in Appendix B.

As hourly ground-level temperatures for the four chloroform monitoring stations were unknown, surrogate values were obtained from surface weather observations at Los Angeles International Airport (Los Angeles site), Ontario Airport (El Monte and Riverside sites), and Long Beach Airport (Dominguez Hills site).

Pasquill stability classes for each modeled hour were derived from hourly wind speed data and observations of surface temperature, sky cover and ceiling at the aforementioned airports. These stability classifications depend primarily on net radiation and wind speed. Net radiation during the day is a function of solar altitude, which in turn is a function of time of day and day of year, and ranges from 4 (the highest positive incoming net radiation) to -2 (highest negative outgoing net radiation). When clouds are present, both net incoming and outgoing radiation are reduced. Instability occurs with high positive radiation and light winds. Stability occurs with high negative net radiation and light winds. Neutral conditions correspond to cloudy skies and high wind speeds.

To compute the net radiation index value for each sampling hour, an appropriate insolation class number was first determined from a chart (Berdahl et al., 1978) which relates solar altitude to time of day, time of year, and position of the sun in the sky. This insolation number was then modified for existing conditions of total cloud cover and ceiling height by following a procedure described by Turner (1964). According to this procedure, solar radiation is not a factor at night; hence, nighttime estimates of net outgoing radiation were made by considering only cloud cover. Finally, a table which relates stability class to net radiation and wind speed was used to assign one of the following stability classes to each hour:

1 - Extremely unstable
2 - Unstable
3 - Slightly unstable
4 - Neutral
5 - Slightly stable
6 - Stable
7 - Extremely stable

The final type of meteorological data required for the modeling is the mixing height at each station during each modeled hour. Monitoring data for deriving mixing heights were insufficient or nonexistent for the four stations. Therefore, we used mean seasonal morning and afternoon mixing heights tabulated by the National Climatic Center (Holzworth, 1972). The tabulated values are based upon historical data from Santa Monica Airport.

10.1.4 Emission Data Input

10.1.4.1 Area Sources

Drinking Water Chlorination

For the modeling, it was assumed that chloroform emissions resulting from drinking water chlorination would be divided between area and point sources. The area sources consisted of the places of water use, i.e. residential areas. The point sources, which are discussed in Section 10.1.4.2, were assumed to be individual wastewater treatment plants. Since the spatial distribution of water use was unknown, population was used as a surrogate measure. Population data corresponding to 5 x 5 km grid squares in the South Coast Air Basin in 1979 were provided by the ARB (Yotter, 1985). The origin of the population grid system was UTM 320 E, UTM 3600 N. Thus each grid square could be unambiguously located by specifying the length of its side and the UTM coordinates of its southwest corner. The modeling grid, along with the locations of the four receptor sites, was presented in Chapter 5 as Figure 5.1-1.

The basic equation for emissions from drinking water use in a given cell during a given hour is, in FORTRAN notation:

```
AEDW(RUN,CELL,HOUR) = POP(CELL) * GF(RUN, COUNTY (CELL)) *
                      CR(COUNTY(CELL)) * HF(RUN, HOUR) * HUF * EF
```

Each of these terms will now be explained. POP(CELL) is the population in the grid square of interest. In several cases, four of the original ARB 5 km x 5 km grid squares were combined into single 10 km x 10 km cells. This was done only when (1) the populations of the original four cells were roughly equal and (2) the composite grid cell was at least 25 km from any receptor site. ARB grid cells which were partly over the ocean were divided into cells 1-, 2-, or 2.5-km square, so that the emissions per unit area would not be underestimated.

COUNTY (CELL) is an index denoting the county in which the grid square is located (1 = Los Angeles, 2 = Orange, 3 = Riverside, 4 = San Bernardino). Because the ARB grid system is superimposed on county boundaries, 26 of the cells contain portions of two counties. To simplify the calculations, area source emissions from these cells were input as two separate sources.

GF(RUN, COUNTY(CELL)) is a growth factor used to adjust the 1979 population values to the years for which the model was to be run, 1983 and 1984. Unfortunately, 1983 and 1984 population data were not available from the same sources as were the 1979 data provided by the ARB. It was therefore necessary to use another, internally consistent, data set containing values for all three years of interest. An appropriate data set was obtained from the California Department of Finance (Gage and Schlosser, 1983). Table 10.1-3 shows population estimates for 1979, 1983, and 1984 for all four counties of interest, along with ratios of 1983 and 1984 county populations to those of the base year, 1979.

The next factor in the equation, CR(COUNTY(CELL)), is the per-capita chlorine equivalent dose rate. Using data from Table 4.2-6, different per-capita dose rates were calculated for each of the basin's four counties. Those used in the model were:

County	CR(COUNTY(CELL)) (lb Cl_2/person-year)
Los Angeles	1.470276
Orange	1.027428
Riverside	1.041038
San Bernardino	0.405040

The factors mentioned up to now, when multiplied by an emission factor (to be discussed below) would yield an annual chloroform emission rate for a given cell on a given run. Because drinking water chlorination rates vary from month to month and drinking water use varies both monthly and hourly, it was necessary to convert these annual emissions to hourly average values. Monthly, daily, and hourly chlorination rates were assumed to follow the same pattern as monthly, daily, and hourly water use. The fraction of annual water use occurring in each month was obtained by dividing that month's MWD deliveries by the MWD's total deliveries in the 1983-1984 water year. The fraction of annual use occurring in each day of a given month was then calculated by dividing the month's share of annual use by the number of days in each month. Table 10.1-4 summarizes the calculations.

Finally, the daily water use fractions had to be apportioned to each hour of the day. In the absence of SCAB-specific data, we used the hourly water use pattern presented by Linsley and Franzini (1964) for Palo Alto, CA. Figure 10.1-1 shows the fractional water use for each hour of the day. For the modeling, the factor HF(RUN, HOUR) was calculated by multiplying the daily use factor for the month corresponding to each run by the hourly fraction for each hour. Units of HF(RUN, HOUR) are lb/hr per lb/year.

Table 10.1-3

POPULATIONS AND RATIOS USED FOR SCALING UP GRIDDED POPULATION VALUES

County	July 1, 1979 Population	July 1, 1983 Population	Ratio 1983/1979	July 1, 1984 Population	Ratio 1984/1979
Los Angeles	7,387,626	7,767,684	1.0514	7,829,886	1.0599
Orange	1,896,388	2,057,439	1.0849	2,093,781	1.1041
Riverside	638,988	747,760	1.1702	776,057	1.2145
San Bernardino	853,307	1,007,212	1.1804	1,044,382	1.2239

Source: California Department of Finance (Gage and Schlosser, 1983).

Table 10.1-4

CALCULATION OF DAILY WATER USE FRACTIONS

Month	MWD Deliveries[a] (acre-ft)	Pct	Days	Daily Factor
1	77657.2	5.4	31	0.0017543
2	95166.1	6.7	28	0.0023802
3	123870.7	8.7	31	0.0027983
4	126720.3	8.9	30	0.0029581
5	155149.3	10.9	31	0.0035049
6	151117.4	10.6	30	0.0035276
7	153592.2	10.8	31	0.0034697
8	143944.9	10.1	31	0.0032518
9	142780.1	10.0	30	0.0033330
10	103917.1	7.3	31	0.0023475
11	81588.2	5.7	30	0.0019046
12	72438.5	5.1	31	0.0016364
Totals	1427942.0	100.0	365	

[a] MWD deliveries for 1983-1984 water year (MWD, 1984).

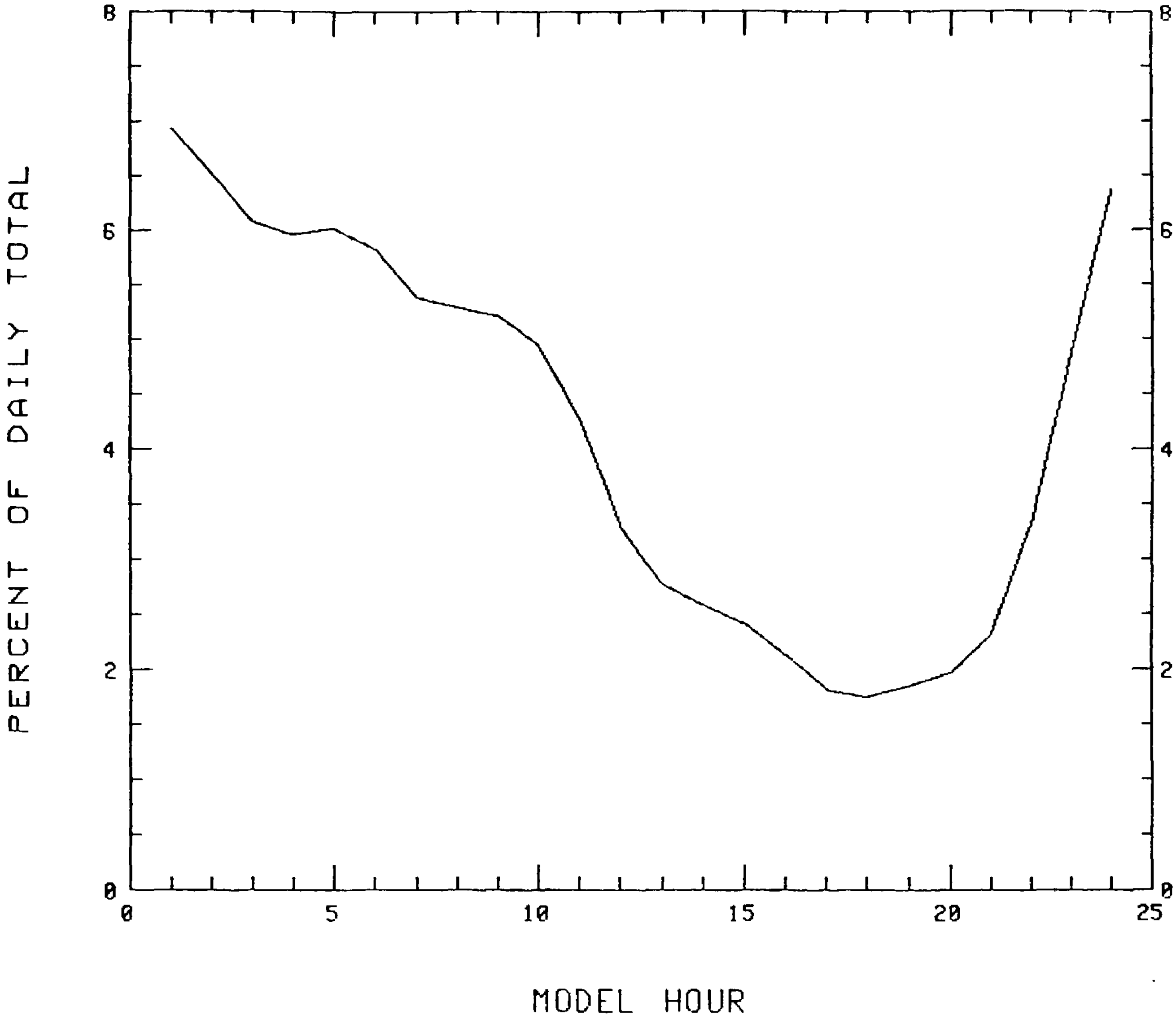

Figure 10.1-1. Percent of Daily Drinking Water Use Assigned to Each Model Hour (Data From Linsley and Franzini, 1964).

The factor HUF is the fraction of the drinking water-related chloroform which is emitted at residences. The value of HUF is highly uncertain. A considerable portion of the chloroform present in drinking water may be emitted through watering of lawns and plants and use of hot water in showers. For other household water uses, however, the time of contact with the air is so brief that the potential for chloroform emissions is low. In Phase I, we chose 0.4 as an initial value for HUF. On the basis of our emissions test at wastewater treatment plants, however, we felt that a higher fraction of the emissions should be associated with residences. Various values of HUF were tried until the mean square difference between modeled and actual values was minimized; the optimum value was 0.81.

The final factor in the drinking water area source equation is the emission factor, EF. Each lb of chlorine equivalent applied to the drinking water represents (1 lb)(453.6 g/lb)/(70.906 g/mole) = 6.3972 moles of Cl_2. As is discussed in Section 4.2.1.1, our literature review-based estimate for the molar transformation ratio of chlorine to chloroform is 0.015. Thus (0.15) (6.3972 moles) = 0.095958 moles of $CHCl_3$ are assumed to form from every lb of chlorine added. Since the molecular weight of chloroform is 119.3779 g/mole, the emission factor becomes (0.095958 mole)(119.3779 g/mole) = 11.455 g $CHCl_3$/lb Cl_2. Finally, to convert the hourly chlorination rate discussed above, we divide by 3,600 seconds/hour to obtain EF = 3.182×10^{-3} (g/s $CHCl_3$)/(lb/hr Cl_2).

The ISCST model requires the user to specify a final plume rise value for each area source. The rise of emissions from drinking water use most likely varies widely from source to source. We used the simplifying, but reasonable assumption that the plume rise would average about 2 meters.

Swimming Pool Chlorination

Because determining the distribution of swimming pools in the South Coast Air Basin was beyond the scope of this project, we assumed that swimming pool use per unit area is proportional to population density. The implications of this assumption will be discussed in Section 10.3.1. The ARB population grid was used as the basis for the emission calculations.

The equation for emissions from swimming pool chlorination in a given cell during a given hour is, in FORTRAN notation:

```
AESP(RUN,CELL,HOUR) =  POP(CELL) * PW(RUN, COUNTY (CELL))
                       * PEM(RUN, HOUR)
```

POP(CELL) and COUNTY(CELL) are as defined for the drinking water emission calculations. The elements of the matrix PEM(RUN, HOUR) are basin-wide hourly swimming pool emissions (g/s) for each hour of each run. Three daily patterns of emissions were assumed. In the first, which corresponds to runs for January, February, November and December, only the "still" water emission rate applies, and emissions are the same for each hour. The second pattern, which applies to runs in March through May and October, assumes that the pool is agitated for 7.2 minutes out of each hour from 10 a.m. to 8 p.m. (model hours 2 through 11). The third pattern represents months of heavier pool use: 12 minutes out of every hour from 10 a.m. to 8 p.m. Still- and agitated-water flux rates were applied to each hour of each pattern to obtain an hourly basin-wide emission rate. PEM(RUN, HOUR) was then set up by selecting the appropriate diurnal pattern for each run.

The factor PW(RUN, COUNTY(CELL)) apportions basin-wide emissions to individual cells. Since the POP(CELL) values correspond to 1979, it was necessary to adjust them to 1983 or 1984, taking into account the different growth rates in different counties. We therefore defined the population weighting factor as:

$$\text{PW(RUN, COUNTY(CELL))} = \frac{\text{GF(RUN, COUNTY(CELL))}}{\text{GP(COUNTY(CELL)) * GF(RUN, COUNTY(CELL))}}$$

where GP(COUNTY(CELL)) is the total gridded 1979 population of the county in which the cell of interest is located. For example POP(CELL) for cell 240 in Orange County was 6,664 in 1979. From data presented in table 10.3-1, we calculated, for Run 7, $PW(7,2) = 9.369 \times 10^{-8}$. The cell's share of basin-wide swimming pool emissions is therefore $(9.369 \times 10^{-8})(6664) = 6.244 \times 10^{-4}$.

Cooling Tower Chlorination

Although our survey of industrial cooling towers yielded information on individual towers, information is lacking on the large number of towers associated with facilities which did not respond to the survey. Therefore, industrial cooling towers were modeled as an area source. A review of land use maps to define an "industrial area" was beyond the scope of the research. We therefore defined an "industrial area" as the set of of 10-km x 10-km UTM coordinate grid squares containing the known towers (i.e. those reported by survey respondents). These squares were identified by locating each responding facility on the U.S. Geological Survey's "Los Angeles," "San Bernardino," "Long Beach," and "Santa Ana" quadrangles (scale 1:250,000). Where portions of 10-km x 10-km squares were over water, the squares were subdivided into 2.5-km and 5-km squares. Figure 10.1-2 shows the "industrial area" defined by this process. Its aggregate area is 1,325 km^2. The density of estimated emissions from all towers in the Basin was assumed to be uniform within the total industrial area.

The final emission height (physical stack height plus plume rise) for the cooling tower area sources was calculated using formulas presented in the ISCST documentation (Bowers et al., 1979) and typical stack characteristics, as determined in a previous study for the ARB (Rogozen et al., 1981). Stack parameters and other variables in the plume rise calculation are summarized in Table 10.1-5. To simplify the calculation, average values for ambient temperature and other meteorological values were used. The final plume rise used in the model was 33 m. Emissions were assumed not to vary by season or hour of day.

10.1.4.2 Point Sources

Power Plant Cooling Towers

Nine cooling towers associated with electric power plants were modeled as point sources, since they are all relatively large chlorine users. Because chloroform emissions from cooling towers were estimated to be

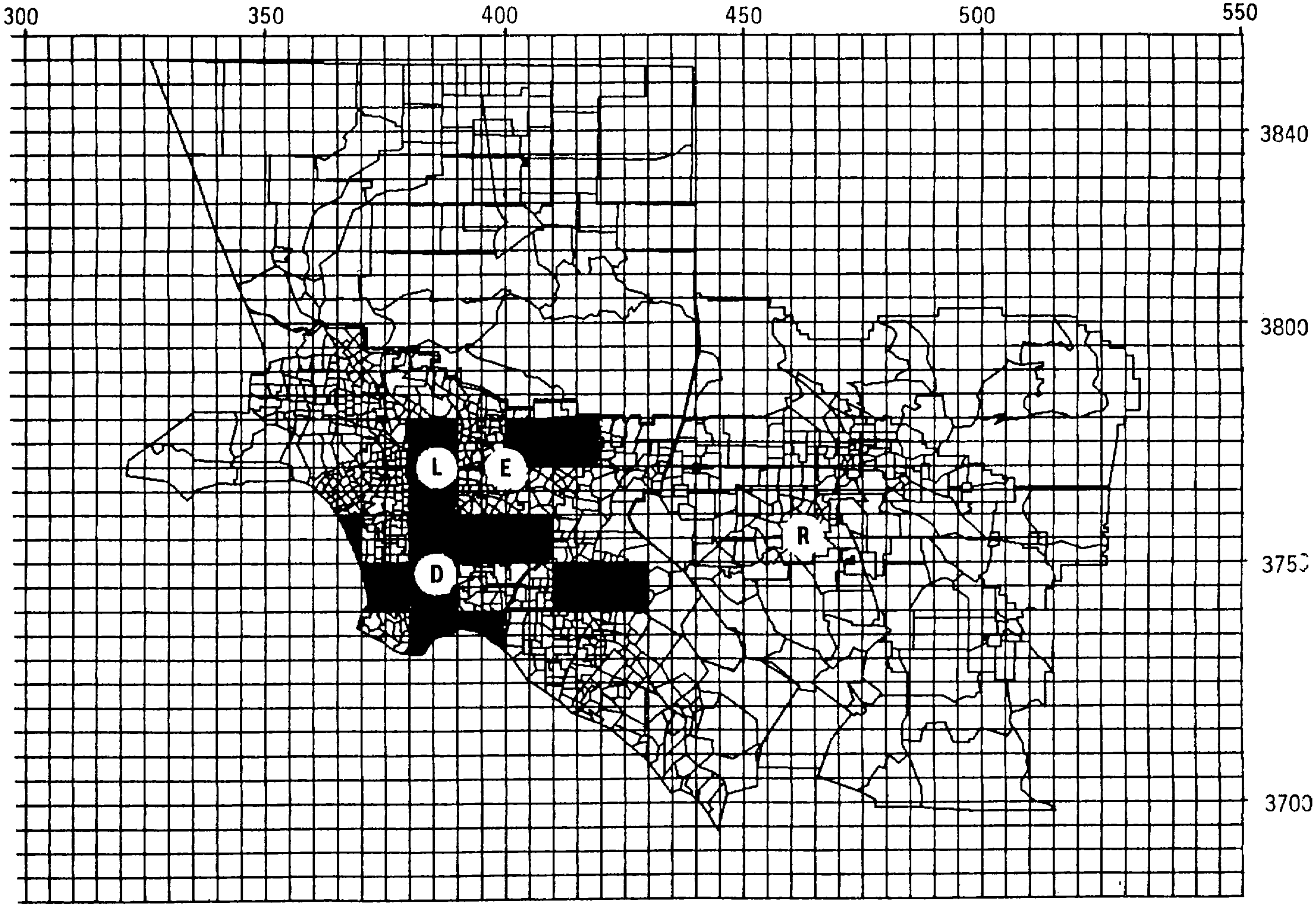

Figure 10.1-2. Industrial Area Assumed for Area Source Modeling of Cooling Tower Emissions.

Table 10.1-5

PARAMETERS USED IN COOLING TOWER PLUME RISE CALCULATION

Parameter	Units	Value Used
Physical stack height	m	11
Stability class	-	6-7
Wind speed at 10 m	m/s	2.33[a]
Vertical potential temperature gradient ($\partial\Theta/\partial z$)	$^{o}K/m$	0.0275[b]
Ambient temperature	^{o}K	291.3[c]
Stack diameter	m	7.6
Stack temperature	^{o}K	300
Exhaust velocity	m/s	11
Adiabatic entrainment coefficient (β_1)	-	0.6
Stable entrainment coefficient (β_2)	-	0.6

Source: Cooling tower physical parameters from Rogozen et al. (1982). Others are from Bowers et al. (1979), unless otherwise noted.

[a] Mean value for modeled hours for which stability class $\geq$ 5.

[b] Mean of values for stability classes 6 and 7 (Bowers et al., 1979).

[c] Mean of temperatures for all modeled hours.

relatively small, however, the same physical stack parameters were used for all towers, and emissions were assumed not to vary by season or hour of day. Stack parameter were those used for modeling the industrial cooling towers (Table 10.1-5), except that meteorological variables were those assigned to each combination of run and model hour.

Wastewater Treatment Plants

As was noted in Section 10.1.4.1, chloroform emissions resulting from drinking water chlorination were assumed to be distributed among area sources and wastewater treatment plants. In addition, it was assumed that all of the chloroform emissions resulting from household use of bleach and from industrial pulp and paper operations occur at the wastewater treatment plants. The equation for emissions for a given run, plant, and hour is:

$$\mathrm{WWTE(RUN,PLANT,HOUR)} = (\mathrm{BLCHFM} + \mathrm{PPCHFM(PLANT)} + \mathrm{BCR(RUN)} * (1-\mathrm{HUF}) * \mathrm{WWEF}) * \mathrm{WWF(PLANT,\ RUN)} * \mathrm{WWHF(HOUR)}$$

In this equation, BLCHFM represents the annual basinwide rate of chloroform emissions from household use. As discussed in Section 4.2.9.2, annual bleach-related emissions are estimated to be 11,700 lb. The method of apportioning these emissions to individual WWT plants is discussed below.

PPCHFM(PLANT) represents annual chloroform emissions from pulp and paper processing, as received at each WWT plant. Through discussions with pulp and paper plant operators and city water departments, we determined that all or most of the effluent from the known pulp and paper processing facilities is likely to be treated at the Pomona and Orange County No. 1 WWT plants. Annual pulp and paper-related chloroform emissions at these two plants are estimated to be 15,461 and 27,005 lb/yr, respectively.

The next variable in the equation, BCR(RUN), is the total amount of chlorine equivalent used in drinking water chlorination in the SCAB during the year corresponding to a given run. For example, in Run 6, the day to be modeled was in 1983. Multiplying the county-specific population growth factors presented in Table 10.1-3 by the per-capita chlorination rates listed in Section 10.1.4.1 and the 1979 county population totals on the ARB grid, we obtain an estimate of 13,956,396 lb of chlorine equivalent for Run 6.

The household use factor, HUF, was defined in Section 10.1.4.1. The wastewater emission factor, WWEF, is the same as the drinking water emission factor, EF, except that it is in different units. The value used in the modeling was 0.0253 lb $CHCl_3$/lb Cl_2.

The next step in calculating emissions from wastewater treatment plants is to determine the fraction of total basinwide effluent treated by each plant during each run, WWF(PLANT, RUN). To calculate this variable, we first determined each WWT plant's fraction of total wastewater flows in each county. For example, the Hyperion WWT plant treats 41.8 percent of Los Angeles County's wastewater. Then we calculated each county's fraction of basinwide population in the year corresponding to the run in question. This value is the same as PW(RUN, COUNTY(CELL)), as defined above, where the code for the county in which the plant is located is substituted for COUNTY(CELL).

It was necessary to convert daily emissions to hourly values. It was assumed that chloroform emissions at the wastewater treatment plants would be proportional to influent flow rates. The hourly variation in these rates is generally different from the variation in drinking water use. Since basin-specific data were unavailable, we used an hourly flow pattern presented in a textbook on wastewater engineering (Metcalf and Eddy, Inc., 1972). Figure 10.1-3 shows the percentage of influent flow rates--and chloroform emissions--assigned to each model hour. This pattern, it turns out, is quite similar to what we observed at the Hyperion Treatment Plant. (See Section 8.1.1). The hourly apportionment factor, WWHF(HOUR), was the same for all runs. Finally, it was necessary to convert various intermediate values to the proper units. The conversion factor, CWWT, was 3.4521×10^{-4} g-hr-yr/lb-day-s.

10.2 MODELING RESULTS

10.2.1 General Results

Table 10.2-1 compares the observed 24-hour average chloroform concentrations on the 20 modeled days with those calculated by the ISCST model, for the optimal value of HUF (0.81). For all of the 20 runs, the model's prediction was within one order of magnitude of the observed value,

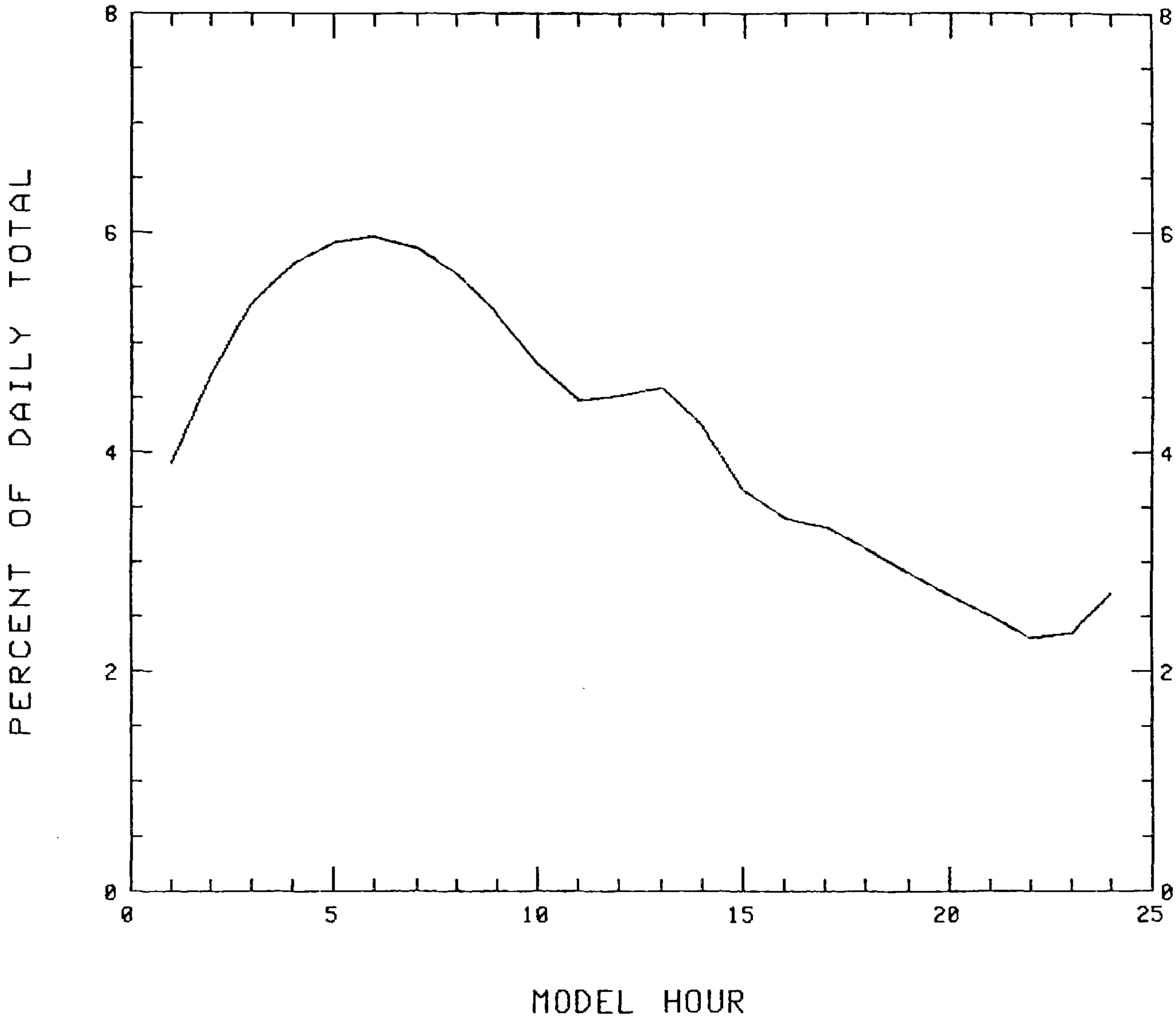

Figure 10.1-3. Percent of Daily Wastewater Treatment Plant Influent Assigned to Each Model Hour (Data from Metcalf and Eddy, Inc., 1972).

Table 10.2-1

MODELED VS OBSERVED 24-HR AVERAGE CHLOROFORM CONCENTRATIONS

(All concentrations in ppt)

Run	Receptor[a]	Modeled Value[b]	Observed Value	Model/ Observed
1	Dominguez Hills	65	20	3.3
2	Dominguez Hills	84	140	0.60
3	Dominguez Hills	19	57	0.33
4	Dominguez Hills	115	94	1.2
5	Dominguez Hills	67	22	3.0
6	Los Angeles	43	200	0.22
7	Los Angeles	51	40	1.3
8	Los Angeles	91	22	4.1
9	Los Angeles	80	210	0.38
10	Los Angeles	161	33	4.9
11	El Monte	77	24	3.2
12	El Monte	98	110	0.85
13	El Monte	110	65	1.7
14	El Monte	8	27	0.30
15	El Monte	113	86	1.3
16	Riverside	13	51	0.25
17	Riverside	40	100	0.40
18	Riverside	3	<20	<0.15
19	Riverside	39	57	0.68
20	Riverside	4	<20	<0.25

---

[a] See Figure 10.1-2 for modeling grid and locations of Dominguez Hills (D), Los Angeles (L), El Monte (E) and Riverside (R) receptors.

[b] At optimal value of HUF (0.81).

and in all but one case the modeled concentrations were within a factor of 5 of the actual value. Figure 10.2-1 is a scatter plot of modeled versus measured concentrations. The correlation between the two sets of data is quite low (r = 0.019). For all of the individual sites except Riverside, the correlations were also low:

Receptor Site	Correlation
Dominguez Hills	0.34
Los Angeles	-0.46
El Monte	0.65
Riverside	0.92

10.2.2 Diurnal Variations

Figures 10.2-2 through 10.2-5 are typical examples of the variation of hourly average chloroform concentrations over 24-hour periods simulated by the model. Note that the first modeled hour corresponds to 9 - 10 a.m.; modeled hour 4 is noon and modeled hour 16 is midnight. Because modeled hourly average concentrations varied over one or two orders of magnitude on many runs, the concentration values are plotted on a logarithmic scale. The solid horizontal line in each graph represents the 24-hour average concentration calculated by the model, while the line with tick marks represents the observed chloroform concentration for the same 24-hour period.

About half of the runs exhibit a similar diurnal pattern, in which chloroform concentrations decrease rapidly from 9 a.m. until late morning, remain at relatively low levels until about 2 or 3 p.m., increase steeply, and remain at relatively high levels throughout the afternoon and evening, and then begin to decrease at around 5 a.m. As will be discussed in Section 10.3, meteorological conditions are probably responsible for the persistently high nighttime concentrations. For the remaining runs, no common pattern of hourly variation was exhibited. The hour of maximum modeled chloroform concentration is distributed fairly evenly between 5 p.m. and 9 a.m.; no maxima occur between 10 a.m. and 5 p.m. Almost half of the minimum modeled concentrations occur between 6 and 9 a.m.

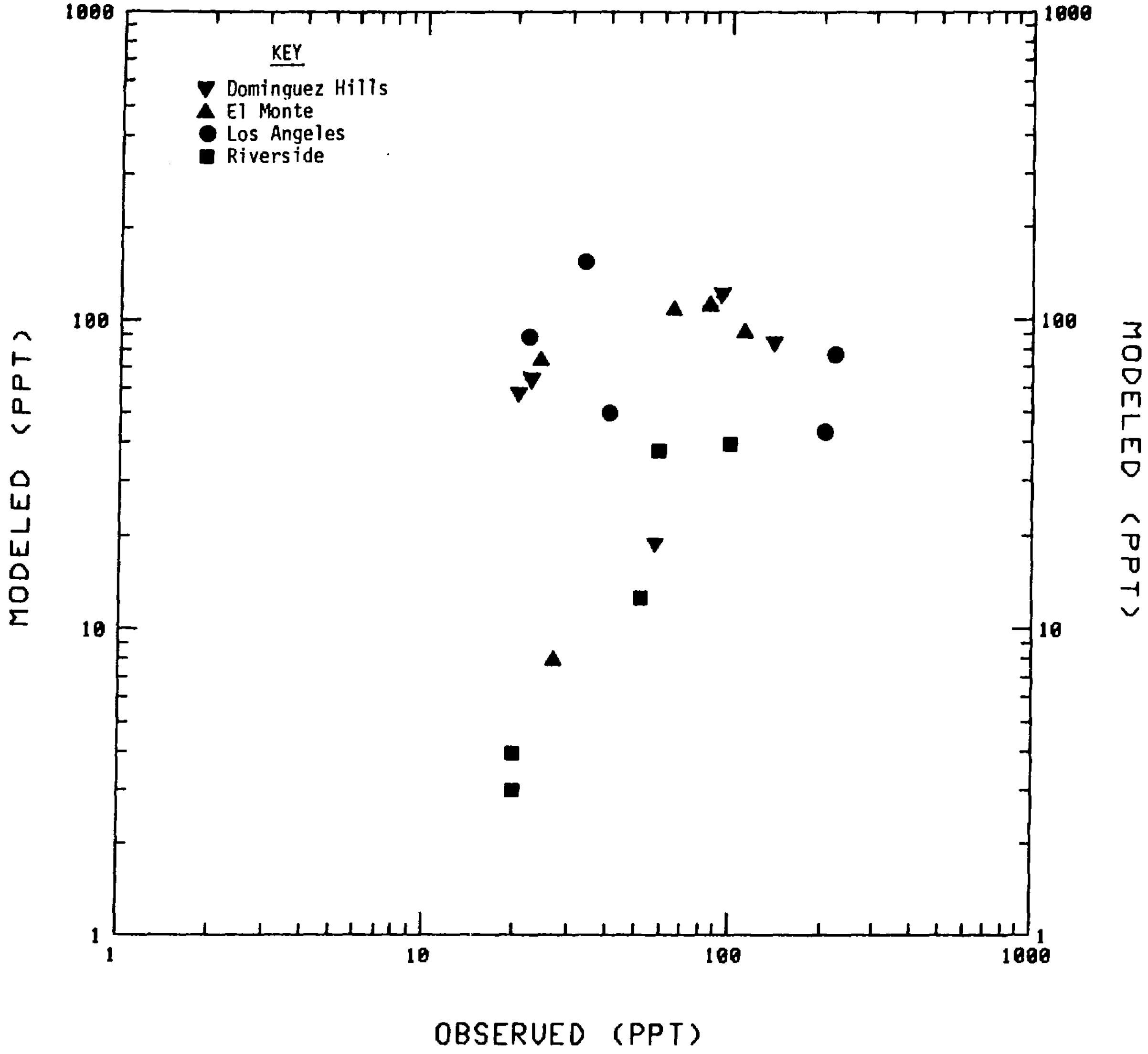

Figure 10.2-1. Modeled Chloroform Concentrations vs. Values Observed at ARB Monitoring Stations.

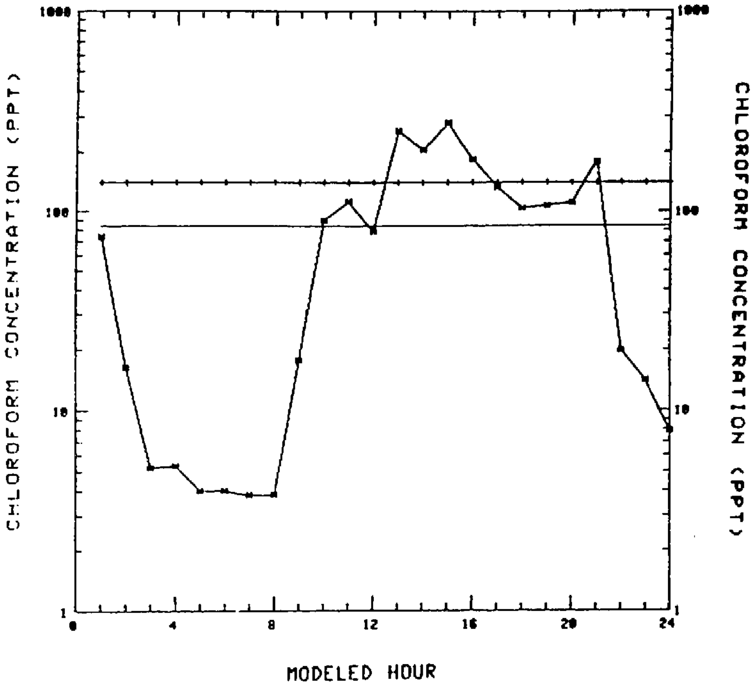

Figure 10.2-2. Modeled Concentrations vs Modeled Hour, 24-Hour Average Modeled Concentration (Solid Line), and Observed 24-Hour Average Concentration (Tick Marks) for Run 2.

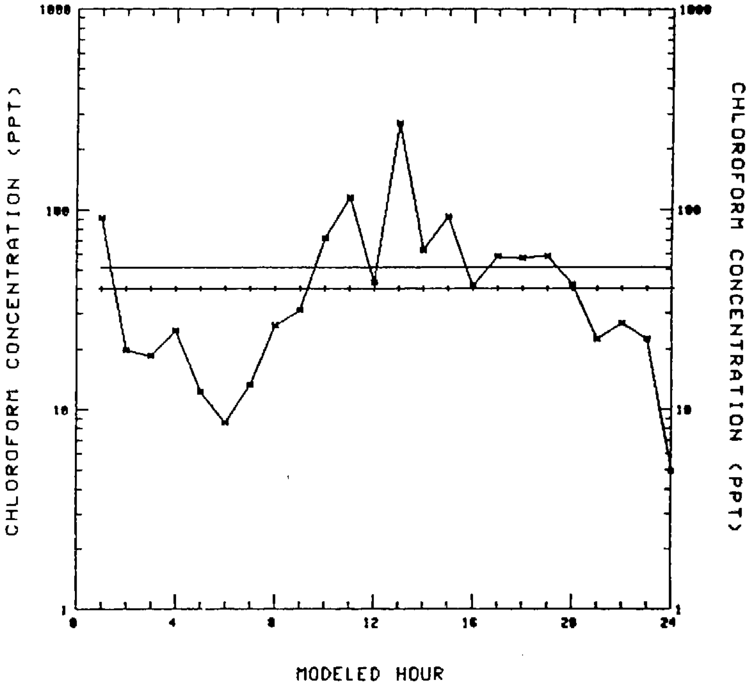

Figure 10.2-3. Modeled Concentrations vs Modeled Hour, 24- Hour Average Modeled Concentration (Solid Line), and Observed 24-Hour Average Concentration (Tick Marks) for Run 7.

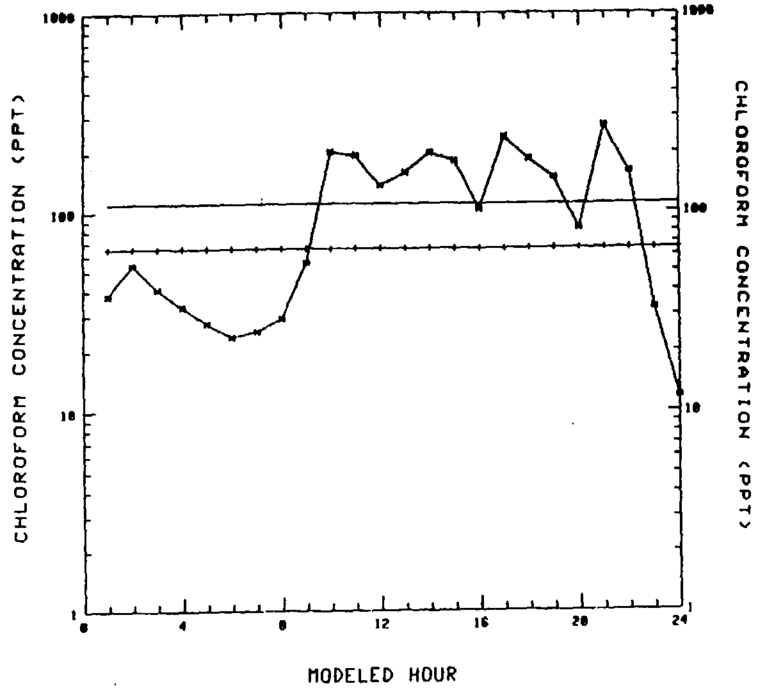

Figure 10.2-4. Modeled Concentrations vs Modeled Hour, 24-Hour Average Modeled Concentration (Solid Line), and Observed 24-Hour Average Concentration (Tick Marks) for Run 13.

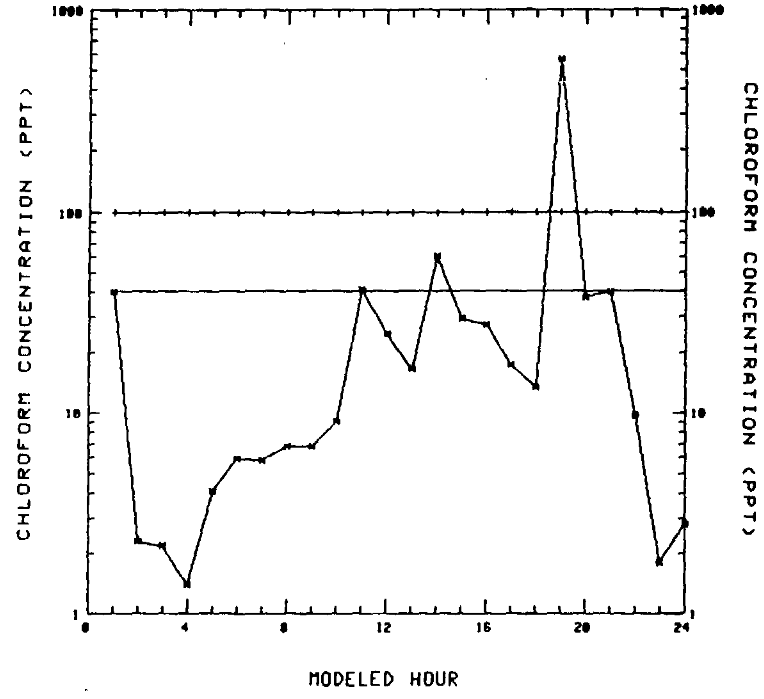

Figure 10.2-5. Modeled Concentrations vs Modeled Hour, 24-Hour Average Modeled Concentration (Solid Line), and Observed 24-hour Average Concentration (Tick Marks) for Run 17

Maximum modeled hourly average concentrations ranged from 4 to 758 ppt. In general, modeled hourly concentrations were within the ranges reported in Section 5.1 and measured by SAIC as part of this project. It is interesting to note that on the two modeled days when the observed 24-hr average concentration was below the detection limit of 20 ppt (Runs 18 and 20), the model also predicted very low concentrations (4 and 6 ppt).

10.2.3 Examination of Sources

Four runs were selected for more detailed analysis, in order to determine the relative roles of emission sources and meteorological conditions, and to quantify the contributions of different source classes. Run 1 (Dominguez Hills receptor) was chosen as a typical winter case, in which contributions from drinking water and swimming pool sources would be relatively low and photochemical removal mechanisms would be relatively unimportant. Run 10 (Los Angeles receptor) had the second-highest modeled 24-hour average chloroform concentration, as well as one of the lowest measured concentrations, and thus was of interest. Run 12 (El Monte receptor) was chosen as a typical summer case. Finally, Run 17 (Riverside-Magnolia receptor) had one of the lowest ratios of modeled to measured 24-hour average concentrations.

For each of the four runs, the hours corresponding to the minimum and maximum one-hour concentrations were chosen for further analysis. We also chose a "typical daytime" and a "typical nighttime" hour, for which modeled concentrations were comparable, to see whether certain sources were more influential during either portion of the day.

Table 10.2-2 shows, for each modeled hour analyzed, the contribution of each source or group of sources to the modeled concentration at the relevant receptor site. For all of the 16 hours examined, the drinking water and swimming pool area source contributed to the modeled concentration. Cooling tower area sources were responsible for at least 0.1 percent of the concentrations during 10 of the 16 hours. Cooling tower point sources (which were examined in the aggregate) were influential in only two of the hours examined. Finally, only six wastewater treatment plants contributed more than 0.01 percent of the modeled concentrations during any of the 16 hours.

In Table 10.2-2, it may be seen that swimming pool emissions were the largest source of chloroform concentrations during nine of the examined model hours. Drinking water area source emissions were the most important source for all the other six model hours examined. For Run 1, which corresponds to a day in January, the influence of drinking water emissions was higher than for most of the other runs, which correspond to summer days. Cooling tower emissions, whether from point or area sources, never accounted for more than 1.7 percent of total modeled concentrations. For some of the runs, cooling tower emissions are slightly more influential during nighttime hours; this is probably because we assumed no diurnal variation in their emission rates.

It is interesting to note that 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 the total modeled chloroform concentration at the Riverside receptor in Run 17 at model hour 19. Examination of model inputs reveals that during that hour the receptor was directly downwind of the treatment plant, the wind speed was very low (0.4 m/s) and the atmosphere was extremely stable. Since the ARB monitoring station is only 5.7 km from the treatment plant, these conditions combined to produce a high reading. Examination of another hour of the same run (not shown in Table 10.2-2) shows a much lower contribution (and absolute concentration) due to the plant when the wind direction was the same but the wind speed was twice as great and the atmosphere was unstable. During model hour 19, the Pomona and Ontario-Upland wastewater treatment plants, which were also directly upwind of the Riverside receptor, also contributed to the concentration at Riverside; however, being about 21 and 39 km distant, respectively, their influence was much lower.

The Los Angeles Hyperion Plant also made a significant contribution to the modeled chloroform concentration at the Los Angeles receptor in Run 10. In model hours 6 and 9, the receptors were almost directly downwind of Hyperion, the atmosphere was slightly unstable and the wind speed was relatively high (4.9 m/s).

Table 10.2-2

SOURCE CONTRIBUTIONS TO MODELED CONCENTRATIONS FOR SELECTED RUNS
(Values shown as percentages of total concentration)[a]

	Run 1 (Dominguez Hills) 20-21 January 1983				Run 10 (Los Angeles) 29-30 July 1984				Run 12 (El Monte) 8-9 August 1983				Run 17 (Riverside) 6-7 June 1983			
Source	Min[b] 6	Max 16	TD 9	TN 22	Min 6	Max 20	TD 9	TN 22	Min 23	Max 11	TD 4	TN 18	Min 4	Max 19	TD 7	TN 17
Area Source																
Drinking Water	65.53	41.72	63.36	47.74	35.34	57.59	33.30	69.06	75.39	30.60	37.98	51.98	23.11	49.39	23.37	30.16
Swimming Pools	32.77	57.00	35.38	50.86	54.04	42.41	56.83	30.04	24.07	69.07	61.42	46.67	76.32	38.40	76.63	69.79
Cooling Towers	1.70	1.27	1.26	1.19	0.07	0.00	0.07	0.19	0.51	0.33	0.53	1.35	0.57	0.06	0.00	0.05
Point Sources																
Cooling Towers	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hyperion WWT	0.00	0.00	0.00	0.00	10.55	0.00	9.81	0.70	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Pomona WWT	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
JWPCP WWT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00
Riverside WWT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.15	0.00	0.00
Ontario-Upland WWT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[a] Some column totals may, because of rounding, not equal 100.

[b] Min = hour of minimum concentration, max = hour of maximum concentration, TD = hour of typical daytime concentration; TN = hour of typical nighttime concentration. Numbers below each heading are modeled hours.

Analysis of model inputs and outputs showed no clear relationship between hourly basinwide emissions and modeled hourly chloroform concentrations at the receptors of interest. Figure 10.2-6 shows, for example, emissions and calculated concentrations for each modeled hour of Run 17. Values have been scaled such that the minimum and maximum of each variable equals 1 and 10, respectively. The variation of total emissions with time clearly reflects the assumed temporal pattern of emissions from swimming pools, which contribute about 65 percent of the chloroform in this run. The peak in the modeled chloroform concentration corresponds to the aforementioned hour when the Riverside wastewater treatment plant was directly downwind of the receptor of interest.

10.2.4 Sensitivity Analysis

In defining the modeling scenarios, it was necessary to assume values for several of the variables used to estimate emissions. 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.

The household use factor (HUF) used to apportion drinking water chlorination emissions between residences and wastewater treatment plants was highly uncertain, although our source tests at wastewater treatment plants indicated that it should be higher than 0.4. Figure 10.2-7 shows the effects of this parameter on the square root of the mean square error between modeled and measured values. As noted earlier, HUF = 0.81 results in the best fit. It should be noted, however, that the error varies relatively little over a wide range of values of HUF.

10.3 DISCUSSION

10.3.1 Emission Inventory

The fact that predicted and observed 24-hour average chloroform concentrations were mostly within a factor of 4 indicates that our emission estimates are, on the whole, reasonably accurate. Our estimates of emissions

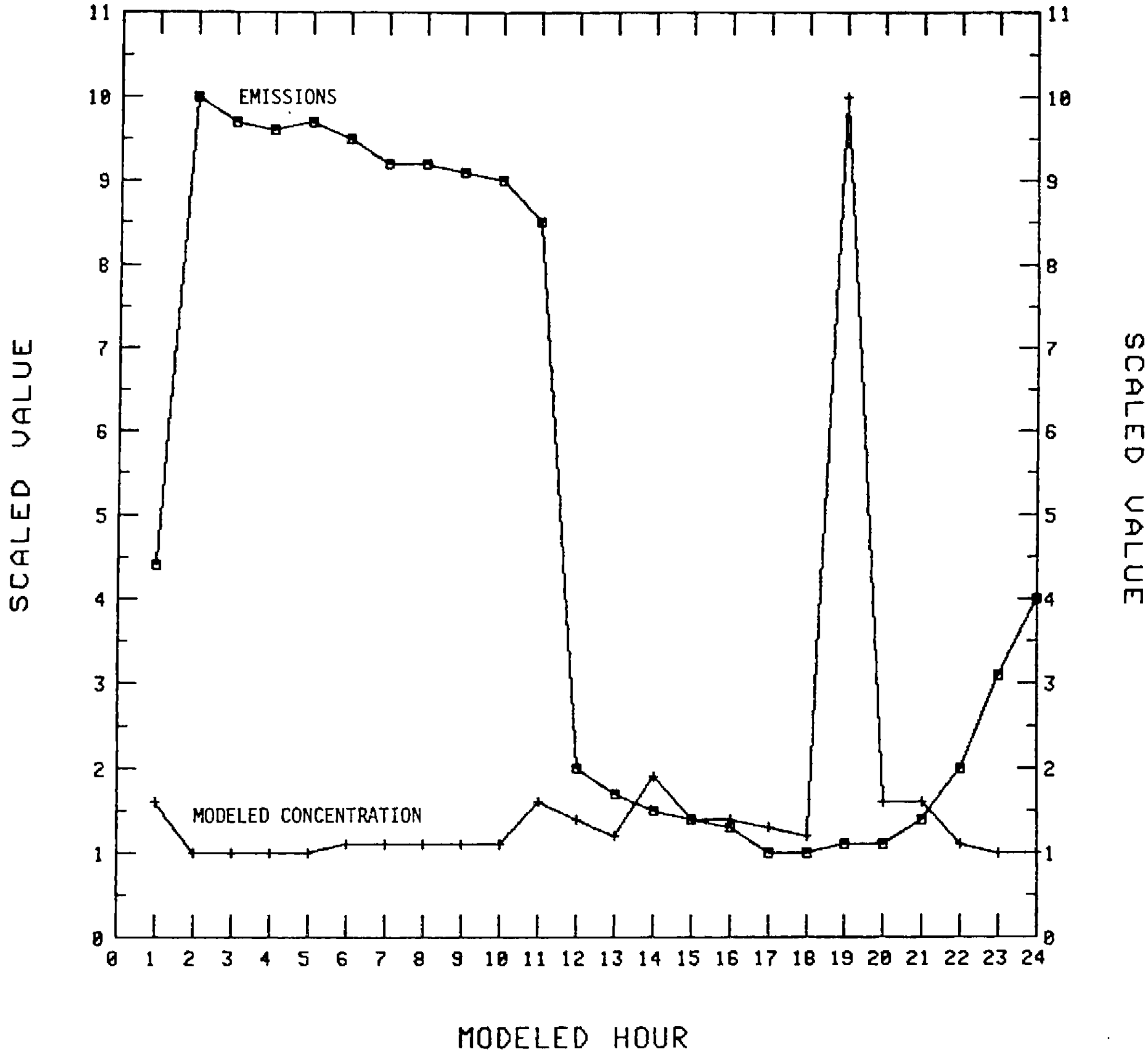

Figure 10.2-6. Emissions vs Calculations for Run 17, by Modeled Hour. Values have been scaled so that minimum and maximum of each variable equals 1 and 10, respectively.

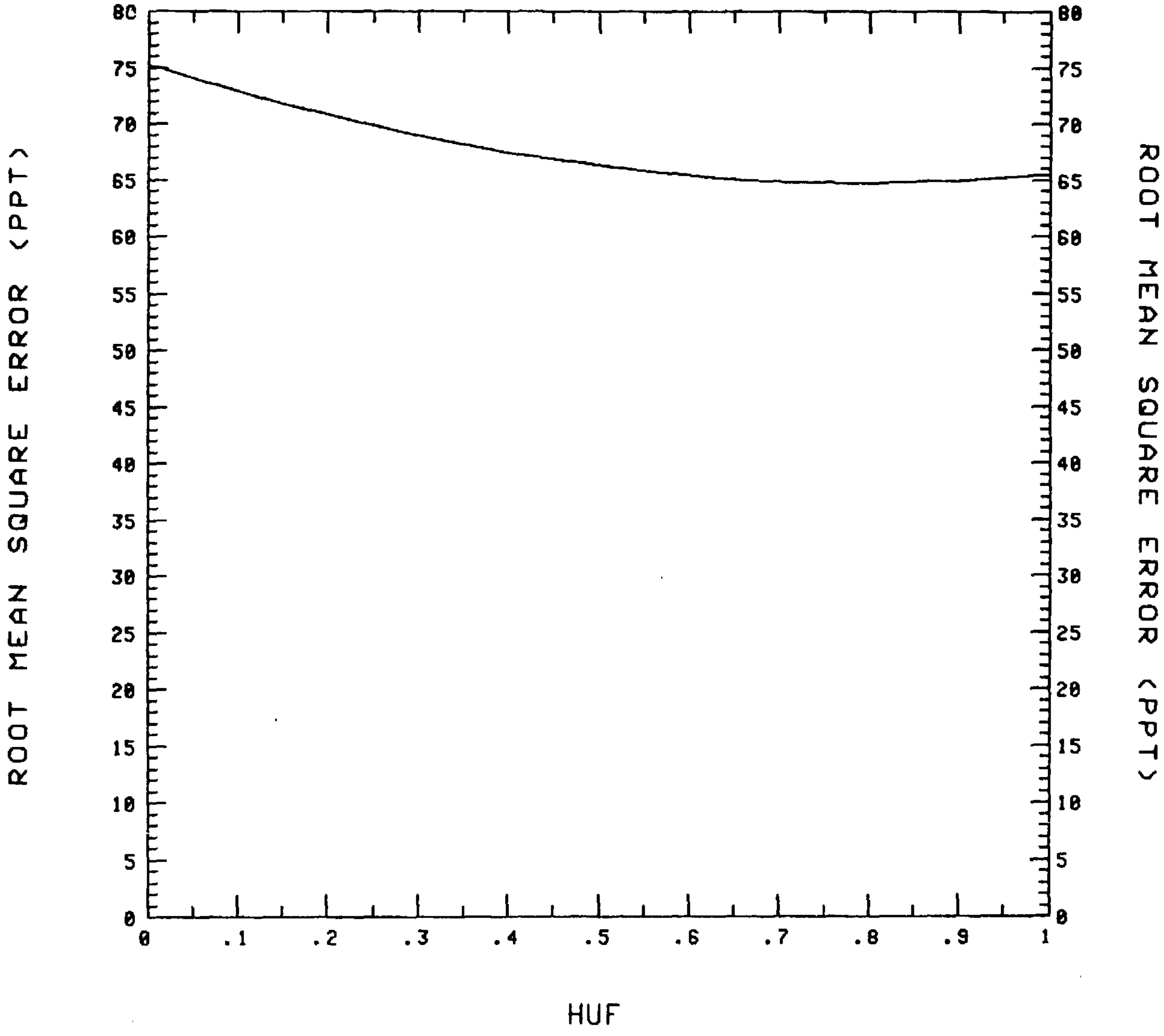

Figure 10.2-7. Effect of Household Use Factor (HUF) on Error Between Modeled and Observed Concentrations.

from drinking water chlorination are probably more accurate than those for swimming pool emissions, as they are based upon more extensive experimental data. However, the pool emission estimates cannot be too far off, inasmuch as (1) removing these emissions would seriously affect the balance between concentrations and emissions and (2) there is no other reasonable chloroform source of the same magnitude.

The model's hour-by-hour or site-by-site predictions could perhaps be improved by using a more sophisticated method of distributing swimming pool emissions spatially and temporally. In view of the uncertainties regarding the pool emission rates, however, an effort of this nature was not warranted.

The example of the Riverside wastewater treatment plant's influence on modeled concentrations at the Riverside receptor suggests the possibility that "hot spots" of chloroform concentrations may exist near point sources and/or in neighborhoods where area sources are particularly strong. Our mobile ambient sampling program (Section 8.2) detected high-exposure areas. As was discussed in Chapter 7, in Phase II we conducted an additional model run to examine the geographic distribution of chloroform concentrations. One prediction of the modeling which corresponds to our ambient sampling results is that chloroform concentrations would vary diurnally along the coast. This variation is consistent with our hypothesis, presented in Section 7.3, that marine air and water act as temporary chloroform "reservoirs," and that onshore flows bring elevated concentrations for a portion of the day.

10.3.2 Atmospheric Concentrations and Chemistry

An explanation why modeled 24-hour chloroform concentrations sometimes exceeded observed values is that chloroform is removed from the atmosphere by some of the mechanisms described in Section 5.3, such as reaction with OH radicals, reaction with chlorine atoms, and dry deposition. None of these removal mechanisms was simulated in the model. However, the smog chamber research described in Chapter 9 confirmed that the removal rate of chloroform is quite low. It is unlikely that significant removal would have occurred on the time scale of the model runs.

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APPENDIX A

INDUSTRIAL COOLING TOWER SURVEY PACKAGE

SAIC
Science Applications International Corporation

10 September 1985

To Whom It May Concern:

Science Applications International Corporation (SAIC) is currently under contract to the California State Air Resources Board (CARB) to evaluate the potential for airborne chloroform emissions from various industrial sources, including cooling towers, in the South Coast Air Basin. We have also been asked by the CARB to obtain information on use of hexavalent chromium in cooling towers.

Your firm has been identified as being in one of the main classes of industrial users of cooling towers in the South Coast Air Basin. Thus, we would greatly appreciate your taking a few minutes to complete the enclosed questionnaire. Your participation is very important for the final results to have scientific validity.

If your firm does not use cooling towers in the South Coast Air Basin, please so indicate and return the questionnaire anyway. A self-addressed, stamped envelope is included for your convenience.

This request for data is a formal one made pursuant to Sections 39607, 39701, and 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code, which authorize the ARB, or its duly appointed representative, to require the submission of air pollution related information from owners and operators of air pollution emission sources. It should be noted that the intent of this request is to provide data for research purposes. The intent of this request is not to provide information to evaluate compliance with regulations.

In accordance with Title 17, California Administrative Code, Sections 91000 et seq., and the California Public Records Act (Government Code Sections 6250 et seq.), the information which you provide may be released (1) to the public upon request, except trade secrets which are not emission data or other information which is exempt from disclosure, or the disclosure of which is prohibited by law, and (2) to the federal Environmental Protection Agency, which protects trade secrets as provided in Section 114(c) of the Clean Air Act and amendments thereto (42 U.S.C. 7401 et seq.) and in federal regulations.

If you wish to claim that any of the information you submit is trade secret or otherwise exempt from disclosure under applicable law, you must identify in writing the portion of the submittal claimed to be confidential and provide the name, address, and telephone number of the individual to be consulted if the ARB receives a request for disclosure or seeks to disclose the data

2615 Pacific Coast Highway, #300, Hermosa Beach, California 90254 · (213) 318-2611
Other SAI Offices: Albuquerque, Ann Arbor, Arlington, Atlanta, Boston, Chicago, Huntsville, La Jolla, Los Angeles, McLean, Palo Alto, Santa Barbara, Sunnyvale, and Tucson.

claimed to be confidential. Emissions data shall not be identified as confidential. Data identified as confidential will not be disclosed unless the ARB determines, in accordance with the above-referenced regulations, that the data do not in fact qualify for a legal exemption from disclosure. The regulations establish substantial safeguards before any such disclosure. Please note that SAIC is in the process of completing a formal agreement with the ARB to protect the disclosures of trade secrets to the public. This agreement will be completed by 1 October 1985.

If you have any other questions, please contact me or Dr. Harvey Rich at (213) 318-2611.

Once again, we would like to emphasize that the participation of every individual facility is important for the results to be scientifically valid.

Thank you for your participation in this important study.

Sincerely,

SCIENCE APPLICATIONS
INTERNATIONAL CORPORATION

Michael B. Rogoz

Michael B. Rogozen, D.Env.
Principal Investigator
CARB Chloroform Emissions Study

STATE OF CALIFORNIA GEORGE DEUKMEJIAN, Governor

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

(916) 445-0753

August 28, 1985

This letter will confirm that Science Applications International Corporation (SAIC) is under contract to the Air Resources Board (ARB) to perform a study entitled "Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin." The contract (No. A4-115-32) requires the contractor to obtain information on production, use, emissions, and atmospheric concentrations of chloroform in the Basin. As part of its research, SAIC will be requesting information from governmental agencies, trade associations and private firms. The Air Resources Board appreciates your firm's cooperation with SAIC in their performance of this research project.

Science Applications International Corporation is required to preserve in strict confidence all information designated "trade secret" which is obtained from business entities during performance of this contract and may not retain, disclose, or in any other manner use such information except to report it to duly authorized members of the Air Resources Board staff. Information supplied to the ARB, other than emissions data, which is found to be trade secret or otherwise entitled to confidential treatment will be kept confidential, although such information may be forwarded to the U. S. Environmental Protection Agency, which protects trade secrets in accordance with Federal law.

If you have any questions concerning this research study or regarding the information requested please call Dr. Michael Rogozen, Principal Investigator for the Project at (213) 318-2611.

Again, thank you for your cooperation.

Sincerly yours,

Frank DiGenova for

John R. Holmes, Ph.D.
Chief, Research Division

ID No. ______

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.			

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?

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

APPENDIX B

METEOROLOGICAL DATA USED IN MODELING

```
                                                                            RUN 01


                                  * METEOROLOGICAL DATA FOR DAY  20 *

                                                        POT. TEMP.
          FLOW        WIND      MIXING                  GRADIENT                     WIND        DECAY
         VECTOR      SPEED      HEIGHT       TEMP.      (DEG. K     STABILITY      PROFILE    COEFFICIENT
HOUR   (DEGREES)     (MPS)     (METERS)    (DEG. K)   PER METER)    CATEGORY      EXPONENT     (PER SEC)
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

  1      180.0        1.34       468.0       286.0      0.0000          2          0.1500    0.000000E+00
  2      180.0        1.34       468.0       288.0      0.0000          2          0.1500    0.000000E+00
  3      203.0        1.34       468.0       289.0      0.0000          2          0.1500    0.000000E+00
  4       90.0        0.89       468.0       290.0      0.0000          2          0.1500    0.000000E+00
  5       90.0        2.68       468.0       290.0      0.0000          3          0.2000    0.000000E+00
  6       90.0        3.58       468.0       289.0      0.0000          3          0.2000    0.000000E+00
  7       90.0        3.13       468.0       289.0      0.0000          3          0.2000    0.000000E+00
  8       90.0        2.68       468.0       287.0      0.0350          6          0.3000    0.000000E+00
  9       90.0        1.34       468.0       286.0      0.0350          6          0.3000    0.000000E+00
 10       68.0        0.89       468.0       286.0      0.0350          6          0.3000    0.000000E+00
 11       45.0        0.89       468.0       286.0      0.0350          6          0.3000    0.000000E+00
 12       90.0        0.89       468.0       284.0      0.0350          6          0.3000    0.000000E+00
 13      203.0        0.89       989.0       283.0      0.0350          6          0.3000    0.000000E+00
 14      225.0        0.89       989.0       282.0      0.0350          6          0.3000    0.000000E+00
 15      248.0        0.89       989.0       281.0      0.0350          6          0.3000    0.000000E+00
 16      180.0        0.89       989.0       280.0      0.0350          6          0.3000    0.000000E+00
 17      225.0        1.34       989.0       280.0      0.0350          6          0.3000    0.000000E+00
 18      248.0        1.34       989.0       279.0      0.0350          6          0.3000    0.000000E+00
 19      225.0        1.34       989.0       279.0      0.0350          6          0.3000    0.000000E+00
 20      248.0        0.89       989.0       279.0      0.0350          6          0.3000    0.000000E+00
 21      248.0        0.89       989.0       280.0      0.0350          6          0.3000    0.000000E+00
 22      248.0        1.34       989.0       280.0      0.0350          6          0.3000    0.000000E+00
 23      248.0        1.34       989.0       281.0      0.0350          6          0.3000    0.000000E+00
 24      248.0        1.79       989.0       284.0      0.0000          4          0.2500    0.000000E+00
```

```
                                                                                    RUN 02

                                   * METEOROLOGICAL DATA FOR DAY 136 *

                                                         POT. TEMP.
          FLOW         WIND        MIXING                GRADIENT                      WIND        DECAY
         VECTOR        SPEED       HEIGHT       TEMP.     (DEG. K      STABILITY     PROFILE    COEFFICIENT
HOUR   (DEGREES)       (MPS)      (METERS)    (DEG. K)  PER METER)     CATEGORY     EXPONENT     (PER SEC)
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

  1       180.0         2.24        807.0       293.0      0.0000          4          0.2500    0.000000E+00
  2       293.0         1.79        807.0       294.0      0.0000          1          0.1000    0.000000E+00
  3       360.0         2.68        807.0       295.0      0.0000          2          0.1500    0.000000E+00
  4       360.0         2.68        807.0       296.0      0.0000          2          0.1500    0.000000E+00
  5       360.0         3.58        807.0       296.0      0.0000          2          0.1500    0.000000E+00
  6        90.0         4.02        807.0       296.0      0.0000          3          0.2000    0.000000E+00
  7        90.0         4.02        807.0       295.0      0.0000          3          0.2000    0.000000E+00
  8        90.0         4.02        807.0       295.0      0.0000          3          0.2000    0.000000E+00
  9        90.0         3.13        807.0       294.0      0.0000          4          0.2500    0.000000E+00
 10        90.0         1.79        807.0       293.0      0.0350          6          0.3000    0.000000E+00
 11        90.0         1.34        807.0       291.0      0.0350          6          0.3000    0.000000E+00
 12        90.0         0.89        807.0       291.0      0.0350          6          0.3000    0.000000E+00
 13       135.0         0.89       1056.0       290.0      0.0350          6          0.3000    0.000000E+00
 14       225.0         0.89       1056.0       289.0      0.0350          6          0.3000    0.000000E+00
 15       180.0         0.89       1056.0       289.0      0.0350          6          0.3000    0.000000E+00
 16       225.0         0.89       1056.0       288.0      0.0350          6          0.3000    0.000000E+00
 17       248.0         0.89       1056.0       287.0      0.0350          6          0.3000    0.000000E+00
 18       270.0         0.89       1056.0       287.0      0.0350          6          0.3000    0.000000E+00
 19       270.0         0.89       1056.0       287.0      0.0350          6          0.3000    0.000000E+00
 20       270.0         0.89       1056.0       286.0      0.0350          6          0.3000    0.000000F+00
 21       203.0         0.89       1056.0       288.0      0.0350          6          0.3000    0.000000E+00
 22       203.0         0.89       1056.0       290.0      0.0000          3          0.2000    0.000000E+00
 23       225.0         1.34       1056.0       293.0      0.0000          2          0.1500    0.000000E+00
 24        90.0         0.89       1056.0       297.0      0.0000          1          0.1000    0.000000E+00
```

```
                                                                       RUN 03


                                * METEOROLOGICAL DATA FOR DAY 192 *

                                                  POT. TEMP.
          FLOW         WIND       MIXING                GRADIENT                  WIND        DECAY
         VECTOR        SPEED      HEIGHT       TEMP.     (DEG. K    STABILITY    PROFILE    COEFFICIENT
 HOUR   (DEGREES)      (MPS)     (METERS)    (DEG. K)  PER METER)   CATEGORY    EXPONENT     (PER SEC)
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

   1      360.0        1.34       531.0       301.0      0.0000         2        0.1500    0.000000E+00
   2      360.0        2.24       531.0       301.0      0.0000         1        0.1000    0.000000E+00
   3      360.0        2.24       531.0       302.0      0.0000         1        0.1000    0.000000E+00
   4      360.0        1.34       531.0       304.0      0.0000         1        0.1000    0.000000E+00
   5       90.0        3.13       531.0       307.0      0.0000         2        0.1500    0.000000E+00
   6       90.0        2.68       531.0       306.0      0.0000         2        0.1500    0.000000E+00
   7       90.0        4.02       531.0       306.0      0.0000         3        0.2000    0.000000E+00
   8       90.0        2.24       531.0       305.0      0.0000         3        0.2000    0.000000E+00
   9       90.0        1.79       531.0       305.0      0.0000         2        0.1500    0.000000E+00
  10       90.0        1.79       531.0       303.0      0.0350         6        0.3000    0.000000E+00
  11       90.0        0.89       531.0       300.0      0.0350         6        0.3000    0.000000E+00
  12       90.0        0.89       531.0       298.0      0.0350         6        0.3000    0.000000E+00
  13      225.0        0.89       564.0       296.0      0.0350         6        0.3000    0.000000E+00
  14      360.0        0.89       564.0       295.0      0.0350         6        0.3000    0.000000E+00
  15      338.0        0.89       564.0       295.0      0.0350         6        0.3000    0.000000E+00
  16      338.0        0.89       564.0       295.0      0.0350         6        0.3000    0.000000E+00
  17      315.0        0.89       564.0       294.0      0.0350         6        0.3000    0.000000E+00
  18      180.0        0.89       564.0       293.0      0.0350         6        0.3000    0.000000E+00
  19      180.0        0.89       564.0       292.0      0.0350         6        0.3000    0.000000E+00
  20      180.0        0.89       564.0       292.0      0.0350         6        0.3000    0.000000E+00
  21      180.0        0.89       564.0       294.0      0.0350         6        0.3000    0.000000E+00
  22       90.0        0.89       564.0       296.0      0.0000         2        0.1500    0.000000E+00
  23      203.0        0.89       564.0       299.0      0.0000         2        0.1500    0.000000E+00
  24       68.0        0.89       564.0       301.0      0.0000         1        0.1000    0.000000E+00
```

* METEOROLOGICAL DATA FOR DAY 79 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	68.0	1.79	468.0	299.0	0.0000	2	0.1500	0.000000E+00
2	45.0	1.34	468.0	301.0	0.0000	2	0.1500	0.000000E+00
3	45.0	2.24	468.0	301.0	0.0000	2	0.1500	0.000000E+00
4	90.0	2.24	468.0	302.0	0.0000	2	0.1500	0.000000E+00
5	90.0	2.68	468.0	302.0	0.0000	2	0.1500	0.000000E+00
6	90.0	3.58	468.0	302.0	0.0000	2	0.1500	0.000000E+00
7	90.0	3.58	468.0	301.0	0.0000	3	0.2000	0.000000E+00
8	90.0	4.02	468.0	298.0	0.0000	3	0.2000	0.000000E+00
9	90.0	3.13	468.0	295.0	0.0350	6	0.3000	0.000000E+00
10	90.0	2.24	468.0	292.0	0.0350	6	0.3000	0.000000E+00
11	90.0	1.79	468.0	291.0	0.0350	6	0.3000	0.000000E+00
12	90.0	1.34	468.0	291.0	0.0350	6	0.3000	0.000000E+00
13	203.0	0.45	989.0	289.0	0.0350	6	0.3000	0.000000E+00
14	203.0	0.45	989.0	288.0	0.0350	6	0.3000	0.000000E+00
15	203.0	0.89	989.0	288.0	0.0350	6	0.3000	0.000000E+00
16	203.0	0.89	989.0	287.0	0.0350	6	0.3000	0.000000E+00
17	225.0	0.89	989.0	286.0	0.0350	6	0.3000	0.000000E+00
18	180.0	0.89	989.0	286.0	0.0350	6	0.3000	0.000000E+00
19	158.0	0.45	989.0	285.0	0.0350	6	0.3000	0.000000E+00
20	225.0	0.45	989.0	284.0	0.0350	6	0.3000	0.000000E+00
21	203.0	0.89	989.0	285.0	0.0350	6	0.3000	0.000000E+00
22	203.0	1.34	989.0	284.0	0.0350	6	0.3000	0.000000E+00
23	225.0	0.89	989.0	286.0	0.0000	2	0.1500	0.000000E+00
24	248.0	0.45	989.0	290.0	0.0000	1	0.1000	0.000000E+00

RUN 05

* METEOROLOGICAL DATA FOR DAY 145 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	23.0	1.34	807.0	294.0	0.0000	4	0.2500	0.000000E+00
2	45.0	1.34	807.0	296.0	0.0000	2	0.1500	0.000000E+00
3	360.0	1.79	807.0	296.0	0.0000	1	0.1000	0.000000E+00
4	360.0	2.68	807.0	296.0	0.0000	1	0.1000	0.000000E+00
5	68.0	2.68	807.0	298.0	0.0000	2	0.1500	0.000000E+00
6	90.0	3.13	807.0	297.0	0.0000	2	0.1500	0.000000E+00
7	90.0	2.68	807.0	296.0	0.0000	2	0.1500	0.000000E+00
8	90.0	2.24	807.0	296.0	0.0000	3	0.2000	0.000000E+00
9	90.0	1.79	807.0	294.0	0.0000	2	0.1500	0.000000E+00
10	113.0	0.89	807.0	292.0	0.0350	6	0.3000	0.000000E+00
11	338.0	1.79	807.0	291.0	0.0350	6	0.3000	0.000000E+00
12	338.0	1.79	807.0	291.0	0.0000	4	0.2500	0.000000E+00
13	315.0	1.34	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
14	315.0	1.34	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
15	293.0	1.79	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
16	315.0	1.34	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
17	315.0	0.89	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
18	293.0	0.89	1056.0	290.0	0.0000	4	0.2500	0.000000E+00
19	315.0	0.89	1056.0	290.0	0.0000	4	0.2500	0.000000E+00
20	315.0	0.89	1056.0	290.0	0.0000	4	0.2500	0.000000E+00
21	270.0	0.45	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
22	225.0	0.45	1056.0	291.0	0.0000	4	0.2500	0.000000E+00
23	45.0	0.45	1056.0	292.0	0.0000	4	0.2500	0.000000E+00
24	360.0	0.45	1056.0	293.0	0.0000	1	0.1000	0.000000E+00

```
                                                                                    RUN 06


                                       * METEOROLOGICAL DATA FOR DAY  11 *


                                                            POT. TEMP.
          FLOW          WIND       MIXING                   GRADIENT                       WIND        DECAY
         VECTOR        SPEED       HEIGHT        TEMP.      (DEG. K      STABILITY      PROFILE    COEFFICIENT
HOUR   (DEGREES)       (MPS)      (METERS)    (DEG. K)    PER METER)     CATEGORY      EXPONENT     (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1       270.0         0.89        468.0       292.0        0.0000           2          0.1500    0.000000E+00
  2       315.0         0.89        468.0       295.0        0.0000           2          0.1500    0.000000E+00
  3        23.0         0.45        468.0       300.0        0.0000           2          0.1500    0.000000E+00
  4        45.0         0.89        468.0       299.0        0.0000           2          0.1500    0.000000E+00
  5        68.0         2.24        468.0       301.0        0.0000           3          0.2000    0.000000E+00
  6        90.0         2.24        468.0       300.0        0.0000           3          0.2000    0.000000E+00
  7        90.0         2.24        468.0       298.0        0.0000           4          0.2500    0.000000E+00
  8       113.0         1.34        468.0       296.0        0.0350           6          0.3000    0.000000E+00
  9       203.0         0.45        468.0       294.0        0.0350           6          0.3000    0.000000E+00
 10       225.0         1.79        468.0       294.0        0.0350           6          0.3000    0.000000E+00
 11       248.0         1.34        468.0       294.0        0.0350           6          0.3000    0.000000E+00
 12       225.0         1.34        468.0       292.0        0.0350           6          0.3000    0.000000E+00
 13       203.0         1.34        989.0       292.0        0.0350           6          0.3000    0.000000E+00
 14       203.0         2.24        989.0       291.0        0.0350           6          0.3000    0.000000E+00
 15       203.0         2.24        989.0       289.0        0.0350           6          0.3000    0.000000E+00
 16       248.0         2.24        989.0       286.0        0.0350           6          0.3000    0.000000E+00
 17       225.0         2.24        989.0       286.0        0.0350           6          0.3000    0.000000E+00
 18       225.0         3.13        989.0       287.0        0.0350           6          0.3000    0.000000E+00
 19       225.0         1.79        989.0       286.0        0.0350           6          0.3000    0.000000E+00
 20       225.0         1.34        989.0       287.0        0.0350           6          0.3000    0.000000E+00
 21       225.0         2.68        989.0       286.0        0.0350           6          0.3000    0.000000E+00
 22       225.0         3.13        989.0       289.0        0.0350           6          0.3000    0.000000E+00
 23       225.0         2.68        989.0       290.0        0.0350           6          0.3000    0.000000E+00
 24       225.0         2.68        989.0       293.0        0.0000           4          0.2500    0.000000E+00
```

```
                                                                                    RUN 07

                                 * METEOROLOGICAL DATA FOR DAY  16 *

                                                             POT. TEMP.
            FLOW         WIND       MIXING                   GRADIENT                     WIND       DECAY
           VECTOR        SPEED      HEIGHT       TEMP.       (DEG. K     STABILITY      PROFILE   COEFFICIENT
  HOUR   (DEGREES)       (MPS)     (METERS)   (DEG. K)     PER METER)    CATEGORY       EXPONENT   (PER SEC)
 * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

    1       270.0        0.45       468.0       291.0        0.0000          2          0.1500   0.000000E+00
    2       360.0        1.34       468.0       291.0        0.0000          2          0.1500   0.000000E+00
    3        23.0        1.79       468.0       292.0        0.0000          2          0.1500   0.000000E+00
    4        45.0        1.79       468.0       292.0        0.0000          2          0.1500   0.000000E+00
    5        68.0        2.24       468.0       291.0        0.0000          3          0.2000   0.000000E+00
    6        68.0        3.13       468.0       291.0        0.0000          3          0.2000   0.000000E+00
    7        90.0        2.68       468.0       291.0        0.0000          3          0.2000   0.000000E+00
    8        90.0        3.58       468.0       289.0        0.0000          4          0.2500   0.000000E+00
    9        68.0        3.13       468.0       289.0        0.0200          5          0.3000   0.000000E+00
   10        90.0        2.24       468.0       289.0        0.0200          5          0.3000   0.000000E+00
   11       113.0        1.34       468.0       289.0        0.0350          6          0.3000   0.000000E+00
   12       158.0        0.89       468.0       288.0        0.0350          6          0.3000   0.000000E+00
   13       113.0        0.45       989.0       287.0        0.0350          6          0.3000   0.000000E+00
   14       180.0        0.45       989.0       287.0        0.0350          6          0.3000   0.000000E+00
   15       203.0        0.45       989.0       286.0        0.0350          6          0.3000   0.000000E+00
   16       225.0        1.34       989.0       286.0        0.0350          6          0.3000   0.000000E+00
   17       225.0        0.89       989.0       286.0        0.0350          6          0.3000   0.000000E+00
   18       225.0        0.89       989.0       285.0        0.0350          6          0.3000   0.000000E+00
   19       225.0        0.89       989.0       285.0        0.0350          6          0.3000   0.000000E+00
   20       203.0        0.89       989.0       285.0        0.0350          6          0.3000   0.000000E+00
   21       203.0        1.79       989.0       284.0        0.0350          6          0.3000   0.000000E+00
   22       203.0        1.79       989.0       285.0        0.0350          6          0.3000   0.000000E+00
   23       203.0        2.68       989.0       285.0        0.0350          6          0.3000   0.000000E+00
   24       225.0        1.79       989.0       286.0        0.0000          3          0.2000   0.000000E+00
```

```
                                                                                    RUN 08

                                  * METEOROLOGICAL DATA FOR DAY 100 *

                                                                 POT. TEMP.
          FLOW         WIND        MIXING                        GRADIENT                           WIND        DECAY
          VECTOR       SPEED       HEIGHT          TEMP.         (DEG. K       STABILITY         PROFILE     COEFFICIENT
HOUR    (DEGREES)      (MPS)      (METERS)       (DEG. K)       PER METER)      CATEGORY         EXPONENT      (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1       270.0        2.68         851.0         287.0           0.0000            3             0.2000     0.000000E+00
  2       293.0        1.34         851.0         288.0           0.0000            2             0.1500     0.000000E+00
  3       109.0        0.89         851.0         289.0           0.0000            3             0.2000     0.000000E+00
  4       270.0        0.89         851.0         288.0           0.0000            3             0.2000     0.000000E+00
  5       270.0        1.79         851.0         288.0           0.0000            3             0.2000     0.000000E+00
  6        45.0        1.79         851.0         288.0           0.0000            4             0.2500     0.000000E+00
  7        90.0        3.58         851.0         288.0           0.0000            4             0.2500     0.000000E+00
  8        68.0        4.02         851.0         286.0           0.0000            4             0.2500     0.000000E+00
  9        90.0        3.13         851.0         286.0           0.0000            4             0.2500     0.000000E+00
 10        68.0        2.68         851.0         286.0           0.0350            6             0.3000     0.000000E+00
 11        68.0        3.58         851.0         285.0           0.0000            4             0.2500     0.000000E+00
 12        90.0        3.13         851.0         285.0           0.0000            4             0.2500     0.000000E+00
 13        90.0        1.79        1085.0         285.0           0.0350            6             0.3000     0.000000E+00
 14        23.0        0.45        1085.0         285.0           0.0350            6             0.3000     0.000000E+00
 15        68.0        1.34        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 16        90.0        1.79        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 17        90.0        2.68        1085.0         285.0           0.0000            4             0.2500     0.000000E+00
 18        68.0        0.89        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 19       203.0        0.45        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 20       135.0        0.45        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 21       158.0        0.45        1086.0         283.0           0.0350            6             0.3000     0.000000E+00
 22       180.0        1.34        1085.0         284.0           0.0350            6             0.3000     0.000000E+00
 23       180.0        0.89        1085.0         285.0           0.0000            3             0.2000     0.000000E+00
 24        68.0        0.45        1085.0         285.0           0.0000            2             0.1500     0.000000E+00
```

RUN 09

* METEOROLOGICAL DATA FOR DAY 144 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	23.0	1.79	807.0	290.0	0.0000	4	0.2500	0.000000E+00
2	23.0	2.24	807.0	290.0	0.0000	4	0.2500	0.000000E+00
3	45.0	2.24	807.0	291.0	0.0000	4	0.2500	0.000000E+00
4	68.0	2.24	807.0	292.0	0.0000	1	0.1000	0.000000E+00
5	68.0	2.24	807.0	292.0	0.0000	1	0.1000	0.000000E+00
6	90.0	3.13	807.0	291.0	0.0000	4	0.2500	0.000000E+00
7	90.0	4.02	807.0	290.0	0.0000	4	0.2500	0.000000E+00
8	90.0	4.02	807.0	292.0	0.0000	4	0.2500	0.000000E+00
9	90.0	3.13	807.0	289.0	0.0000	4	0.2500	0.000000E+00
10	90.0	3.13	807.0	289.0	0.0000	4	0.2500	0.000000E+00
11	90.0	1.79	807.0	289.0	0.0000	4	0.2500	0.000000E+00
12	90.0	1.79	807.0	289.0	0.0000	4	0.2500	0.000000E+00
13	90.0	1.34	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
14	23.0	0.89	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
15	360.0	0.45	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
16	270.0	0.89	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
17	248.0	0.45	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
18	135.0	0.45	1085.0	288.0	0.0350	6	0.3000	0.000000E+00
19	293.0	0.45	1085.0	288.0	0.0000	4	0.2500	0.000000E+00
20	270.0	0.89	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
21	360.0	0.89	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
22	338.0	0.89	1085.0	289.0	0.0000	4	0.2500	0.000000E+00
23	315.0	0.89	1085.0	290.0	0.0000	4	0.2500	0.000000E+00
24	180.0	0.45	1085.0	291.0	0.0000	4	0.2500	0.000000E+00

```
                                                                           RUN 10

                                   * METEOROLOGICAL DATA FOR DAY 211 *

                                                     POT. TEMP.
         FLOW        WIND       MIXING               GRADIENT                   WIND         DECAY
        VECTOR       SPEED      HEIGHT      TEMP.    (DEG. K     STABILITY     PROFILE    COEFFICIENT
 HOUR  (DEGREES)     (MPS)     (METERS)   (DEG. K)  PER METER)    CATEGORY     EXPONENT    (PER SEC)
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

   1     360.0       1.34       531.0      296.0     0.0000          2          0.1500   0.000000E+00
   2     360.0       1.79       531.0      297.0     0.0000          1          0.1000   0.000000E+00
   3      45.0       3.13       531.0      299.0     0.0000          2          0.1500   0.000000E+00
   4      45.0       4.02       531.0      299.0     0.0000          2          0.1500   0.000000E+00
   5      45.0       4.47       531.0      300.0     0.0000          2          0.1500   0.000000E+00
   6      45.0       4.92       531.0      300.0     0.0000          3          0.2000   0.000000E+00
   7      45.0       4.47       531.0      299.0     0.0000          3          0.2000   0.000000E+00
   8      45.0       4.02       531.0      298.0     0.0000          3          0.2000   0.000000E+00
   9      45.0       3.58       531.0      296.0     0.0000          3          0.2000   0.000000E+00
  10      45.0       1.79       531.0      295.0     0.0350          6          0.3000   0.000000E+00
  11      45.0       1.34       531.0      294.0     0.0350          6          0.3000   0.000000E+00
  12     360.0       0.89       531.0      294.0     0.0350          6          0.3000   0.000000E+00
  13     360.0       1.79       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  14      68.0       1.79       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  15      68.0       1.34       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  16      68.0       1.34       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  17      90.0       0.89       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  18      90.0       0.89       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  19      90.0       0.45       564.0      293.0     0.0350          6          0.3000   0.000000E+00
  20      90.0       0.45       564.0      293.0     0.0350          6          0.3000   0.000000E+00
  21     113.0       0.45       564.0      294.0     0.0350          6          0.3000   0.000000E+00
  22      68.0       0.89       564.0      295.0     0.0000          2          0.1500   0.000000E+00
  23      45.0       0.89       564.0      295.0     0.0000          2          0.1500   0.000000E+00
  24      45.0       1.34       564.0      296.0     0.0000          2          0.1500   0.000000E+00
```

```
                                                                                RUN 11


                                 * METEOROLOGICAL DATA FOR DAY 177 *

                                                                POT. TEMP.
            FLOW          WIND        MIXING                    GRADIENT                        WIND        DECAY
           VECTOR         SPEED       HEIGHT        TEMP.       (DEG. K       STABILITY       PROFILE     COEFFICIENT
 HOUR     (DEGREES)       (MPS)      (METERS)     (DEG. K)    PER METER)      CATEGORY        EXPONENT     (PER SEC)
 * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

   1        310.0         1.34        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   2        300.0         1.34        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   3         10.0         1.34        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   4         10.0         1.34        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   5         20.0         1.34        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   6        340.0         2.24        531.0        289.0        0.0000            4            0.2500     0.000000E+00
   7        340.0         3.58        531.0        290.0        0.0000            4            0.2500     0.000000E+00
   8        360.0         3.58        531.0        291.0        0.0000            4            0.2500     0.000000E+00
   9         10.0         3.58        531.0        292.0        0.0000            4            0.2500     0.000000E+00
  10         20.0         2.24        531.0        294.0        0.0200            5            0.3000     0.000000E+00
  11         20.0         2.24        531.0        294.0        0.0200            5            0.3000     0.000000E+00
  12         20.0         1.79        531.0        295.0        0.0350            6            0.3000     0.000000E+00
  13         20.0         1.79        564.0        296.0        0.0350            6            0.3000     0.000000E+00
  14         30.0         1.34        564.0        297.0        0.0350            6            0.3000     0.000000E+00
  15         30.0         1.34        564.0        297.0        0.0350            6            0.3000     0.000000E+00
  16         20.0         1.34        564.0        296.0        0.0350            6            0.3000     0.000000E+00
  17         10.0         1.34        564.0        294.0        0.0350            6            0.3000     0.000000E+00
  18         20.0         1.34        564.0        291.0        0.0350            6            0.3000     0.000000E+00
  19         10.0         1.79        564.0        291.0        0.0350            6            0.3000     0.000000E+00
  20        340.0         1.79        564.0        291.0        0.0350            6            0.3000     0.000000E+00
  21        330.0         2.68        564.0        290.0        0.0000            4            0.2500     0.000000E+00
  22        330.0         3.13        564.0        290.0        0.0000            4            0.2500     0.000000E+00
  23        340.0         3.58        564.0        290.0        0.0000            4            0.2500     0.000000E+00
  24        330.0         3.13        564.0        289.0        0.0000            4            0.2500     0.000000E+00
```

RUN 12

```
                         * METEOROLOGICAL DATA FOR DAY 220 *

                                                         POT. TEMP.
        FLOW        WIND      MIXING                     GRADIENT                     WIND        DECAY
       VECTOR      SPEED      HEIGHT       TEMP.         (DEG. K      STABILITY      PROFILE    COEFFICIENT
HOUR  (DEGREES)    (MPS)     (METERS)    (DEG. K)     PER METER)    CATEGORY      EXPONENT     (PER SEC)
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

  1     135.0       0.45       531.0       295.0        0.0000          1          0.1000    0.000000E+00
  2     338.0       2.24       531.0       294.0        0.0000          1          0.1000    0.000000E+00
  3      23.0       2.68       531.0       294.0        0.0000          1          0.1000    0.000000E+00
  4      45.0       3.13       531.0       294.0        0.0000          2          0.1500    0.000000E+00
  5      68.0       3.13       531.0       294.0        0.0000          2          0.1500    0.000000E+00
  6      68.0       5.36       531.0       297.0        0.0000          3          0.2000    0.000000E+00
  7      45.0       4.47       531.0       300.0        0.0000          3          0.2000    0.000000E+00
  8      68.0       4.02       531.0       302.0        0.0000          3          0.2000    0.000000E+00
  9      45.0       3.13       531.0       304.0        0.0000          3          0.2000    0.000000E+00
 10      68.0       2.24       531.0       307.0        0.0350          6          0.3000    0.000000E+00
 11      45.0       1.79       531.0       308.0        0.0350          6          0.3000    0.000000E+00
 12      68.0       2.24       531.0       310.0        0.0350          6          0.3000    0.000000E+00
 13      23.0       1.79       564.0       310.0        0.0350          6          0.3000    0.000000E+00
 14      45.0       1.34       564.0       309.0        0.0350          6          0.3000    0.000000E+00
 15      68.0       0.89       564.0       307.0        0.0350          6          0.3000    0.000000E+00
 16      45.0       1.79       564.0       307.0        0.0350          6          0.3000    0.000000E+00
 17      45.0       1.79       564.0       305.0        0.0350          6          0.3000    0.000000E+00
 18      45.0       2.24       564.0       303.0        0.0350          6          0.3000    0.000000E+00
 19      23.0       1.34       564.0       301.0        0.0350          6          0.3000    0.000000E+00
 20      45.0       0.89       564.0       302.0        0.0350          6          0.3000    0.000000E+00
 21     158.0       0.45       564.0       302.0        0.0350          6          0.3000    0.000000E+00
 22     225.0       2.24       564.0       300.0        0.0350          6          0.3000    0.000000E+00
 23     225.0       4.47       564.0       299.0        0.0000          3          0.2000    0.000000E+00
 24     248.0       5.36       564.0       299.0        0.0000          3          0.2000    0.000000E+00
```

```
                                                                                RUN 13

                                     * METEOROLOGICAL DATA FOR DAY 258 *

                                                        POT. TEMP.
         FLOW        WIND       MIXING                  GRADIENT                      WIND        DECAY
        VECTOR       SPEED      HEIGHT       TEMP.      (DEG. K      STABILITY      PROFILE    COEFFICIENT
HOUR   (DEGREES)     (MPS)     (METERS)    (DEG. K)   PER METER)     CATEGORY      EXPONENT    (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1      350.0       1.34       531.0       292.0       0.0000          2           0.1500    0.000000E+00
  2      350.0       1.79       531.0       292.0       0.0000          2           0.1500    0.000000E+00
  3      340.0       2.24       531.0       291.0       0.0000          2           0.1500    0.000000E+00
  4      360.0       2.24       531.0       291.0       0.0000          2           0.1500    0.000000E+00
  5       20.0       2.68       531.0       291.0       0.0000          2           0.1500    0.000000E+00
  6       20.0       3.13       531.0       294.0       0.0000          2           0.1500    0.000000E+00
  7       10.0       3.13       531.0       296.0       0.0000          3           0.2000    0.000000E+00
  8       10.0       2.68       531.0       296.0       0.0000          3           0.2000    0.000000E+00
  9      360.0       2.68       531.0       300.0       0.0000          4           0.2500    0.000000E+00
 10      360.0       2.24       531.0       303.0       0.0350          6           0.3000    0.000000E+00
 11      360.0       2.24       531.0       305.0       0.0350          6           0.3000    0.000000E+00
 12      350.0       2.24       531.0       306.0       0.0350          6           0.3000    0.000000E+00
 13      350.0       1.79       564.0       305.0       0.0350          6           0.3000    0.000000E+00
 14      350.0       1.34       564.0       306.0       0.0350          6           0.3000    0.000000E+00
 15      350.0       1.34       564.0       305.0       0.0350          6           0.3000    0.000000E+00
 16      340.0       1.34       564.0       303.0       0.0350          6           0.3000    0.000000E+00
 17      350.0       0.89       564.0       301.0       0.0350          6           0.3000    0.000000E+00
 18       10.0       0.89       564.0       299.0       0.0350          6           0.3000    0.000000E+00
 19      350.0       1.34       564.0       297.0       0.0350          6           0.3000    0.000000E+00
 20      320.0       0.89       564.0       295.0       0.0350          6           0.3000    0.000000E+00
 21      330.0       0.45       564.0       295.0       0.0350          6           0.3000    0.000000E+00
 22      360.0       0.89       564.0       294.0       0.0350          6           0.3000    0.000000E+00
 23      360.0       0.89       564.0       294.0       0.0000          3           0.2000    0.000000E+00
 24      300.0       1.34       564.0       293.0       0.0000          2           0.1500    0.000000E+00
```

RUN 14

* METEOROLOGICAL DATA FOR DAY 334 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	220.0	2.68	558.0	279.0	0.0000	3	0.2000	0.000000E+00
2	230.0	3.13	558.0	280.0	0.0000	4	0.2500	0.000000E+00
3	250.0	3.13	558.0	280.0	0.0000	3	0.2000	0.000000E+00
4	230.0	2.68	558.0	280.0	0.0000	3	0.2000	0.000000E+00
5	220.0	2.68	558.0	280.0	0.0000	3	0.2000	0.000000E+00
6	220.0	2.24	558.0	280.0	0.0000	3	0.2000	0.000000E+00
7	220.0	1.79	558.0	281.0	0.0000	3	0.2000	0.000000E+00
8	230.0	2.68	558.0	282.0	0.0200	5	0.3000	0.000000E+00
9	220.0	1.34	558.0	285.0	0.0350	6	0.3000	0.000000E+00
10	210.0	2.24	558.0	287.0	0.0350	6	0.3000	0.000000E+00
11	210.0	2.68	558.0	288.0	0.0350	6	0.3000	0.000000E+00
12	200.0	2.24	558.0	290.0	0.0350	6	0.3000	0.000000E+00
13	220.0	2.68	819.0	290.0	0.0350	6	0.3000	0.000000E+00
14	230.0	2.68	819.0	290.0	0.0200	5	0.3000	0.000000E+00
15	250.0	1.79	819.0	290.0	0.0350	6	0.3000	0.000000E+00
16	230.0	2.24	819.0	289.0	0.0000	4	0.2500	0.000000E+00
17	240.0	1.34	819.0	288.0	0.0000	4	0.2500	0.000000E+00
18	220.0	1.34	819.0	288.0	0.0000	4	0.2500	0.000000E+00
19	280.0	2.24	819.0	287.0	0.0000	4	0.2500	0.000000E+00
20	220.0	3.13	819.0	287.0	0.0000	4	0.2500	0.000000E+00
21	190.0	1.79	819.0	287.0	0.0000	4	0.2500	0.000000E+00
22	180.0	1.34	819.0	287.0	0.0350	6	0.3000	0.000000E+00
23	190.0	2.24	819.0	286.0	0.0350	6	0.3000	0.000000E+00
24	140.0	0.89	819.0	286.0	0.0000	4	0.2500	0.000000E+00

```
                                                                              RUN 15

                              * METEOROLOGICAL DATA FOR DAY 342 *

                                                        POT. TEMP.
          FLOW       WIND      MIXING                   GRADIENT                    WIND        DECAY
         VECTOR      SPEED     HEIGHT       TEMP.       (DEG. K      STABILITY    PROFILE    COEFFICIENT
 HOUR  (DEGREES)     (MPS)    (METERS)    (DEG. K)    PER METER)     CATEGORY     EXPONENT    (PER SEC)
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

   1     210.0       1.79       558.0       279.0       0.0000           2         0.1500    0.000000E+00
   2     210.0       1.79       558.0       279.0       0.0000           2         0.1500    0.000000E+00
   3     230.0       1.34       558.0       279.0       0.0000           2         0.1500    0.000000E+00
   4     300.0       1.34       558.0       279.0       0.0000           2         0.1500    0.000000E+00
   5     350.0       1.34       558.0       279.0       0.0000           2         0.1500    0.000000E+00
   6     340.0       1.79       558.0       278.0       0.0000           2         0.1500    0.000000E+00
   7     340.0       1.34       558.0       281.0       0.0000           2         0.1500    0.000000E+00
   8     350.0       0.89       558.0       287.0       0.0350           6         0.3000    0.000000E+00
   9     360.0       0.45       558.0       290.0       0.0350           6         0.3000    0.000000E+00
  10     310.0       0.45       558.0       292.0       0.0350           6         0.3000    0.000000E+00
  11     110.0       0.45       558.0       294.0       0.0350           6         0.3000    0.000000E+00
  12      80.0       0.45       558.0       297.0       0.0350           6         0.3000    0.000000E+00
  13      90.0       5.36       819.0       297.0       0.0350           6         0.3000    0.000000E+00
  14     190.0       0.45       819.0       297.0       0.0350           6         0.3000    0.000000E+00
  15     110.0       0.45       819.0       295.0       0.0350           6         0.3000    0.000000E+00
  16      20.0       0.45       819.0       291.0       0.0350           6         0.3000    0.000000E+00
  17     330.0       0.45       819.0       289.0       0.0350           6         0.3000    0.000000E+00
  18     140.0       0.45       819.0       285.0       0.0350           6         0.3000    0.000000E+00
  19     150.0       0.45       819.0       284.0       0.0350           6         0.3000    0.000000E+00
  20     170.0       0.89       819.0       284.0       0.0350           6         0.3000    0.000000E+00
  21     200.0       0.89       819.0       284.0       0.0350           6         0.3000    0.000000E+00
  22     210.0       0.89       819.0       283.0       0.0350           6         0.3000    0.000000E+00
  23     140.0       0.89       819.0       283.0       0.0000           3         0.2000    0.000000E+00
  24     190.0       1.79       819.0       281.0       0.0000           3         0.2000    0.000000E+00
```

RUN 16

* METEOROLOGICAL DATA FOR DAY 129 *

```
                                                              POT. TEMP.
          FLOW        WIND       MIXING                       GRADIENT                      WIND         DECAY
         VECTOR       SPEED      HEIGHT         TEMP.          (DEG. K     STABILITY       PROFILE     COEFFICIENT
HOUR   (DEGREES)      (MPS)     (METERS)      (DEG. K)      PER METER)     CATEGORY       EXPONENT     (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1       135.0        1.34       807.0        287.0          0.0000           2           0.1500     0.000000E+00
  2       158.0        1.79       807.0        288.0          0.0000           2           0.1500     0.000000E+00
  3       158.0        1.79       807.0        287.0          0.0000           1           0.1000     0.000000E+00
  4       135.0        1.79       807.0        288.0          0.0000           1           0.1000     0.000000E+00
  5       180.0        1.79       807.0        287.0          0.0000           4           0.2500     0.000000E+00
  6       158.0        1.79       807.0        287.0          0.0000           4           0.2500     0.000000E+00
  7       180.0        2.24       807.0        287.0          0.0000           4           0.2500     0.000000E+00
  8       180.0        4.47       807.0        287.0          0.0000           4           0.2500     0.000000E+00
  9       180.0        4.47       807.0        287.0          0.0000           4           0.2500     0.000000E+00
 10       158.0        3.58       807.0        287.0          0.0000           4           0.2500     0.000000E+00
 11       180.0        1.79       807.0        290.0          0.0350           6           0.3000     0.000000E+00
 12       180.0        0.89       807.0        291.0          0.0350           6           0.3000     0.000000E+00
 13       180.0        0.89      1056.0        293.0          0.0350           6           0.3000     0.000000E+00
 14       180.0        0.89      1056.0        295.0          0.0350           6           0.3000     0.000000E+00
 15       203.0        0.45      1056.0        296.0          0.0350           6           0.3000     0.000000E+00
 16       180.0        0.89      1056.0        295.0          0.0350           6           0.3000     0.000000E+00
 17       180.0        0.45      1056.0        294.0          0.0350           6           0.3000     0.000000E+00
 18       180.0        1.34      1056.0        292.0          0.0350           6           0.3000     0.000000E+00
 19       180.0        0.89      1056.0        291.0          0.0350           6           0.3000     0.000000E+00
 20       158.0        0.45      1056.0        291.0          0.0350           6           0.3000     0.000000E+00
 21       360.0        0.45      1056.0        290.0          0.0350           6           0.3000     0.000000E+00
 22       158.0        0.45      1056.0        290.0          0.0000           3           0.2000     0.000000E+00
 23       203.0        0.45      1056.0        289.0          0.0000           2           0.1500     0.000000E+00
 24       113.0        0.89      1056.0        287.0          0.0000           2           0.1500     0.000000E+00
```

RUN 17

* METEOROLOGICAL DATA FOR DAY 157 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	113.0	0.89	807.0	287.0	0.0000	2	0.1500	0.000000E+00
2	180.0	2.68	807.0	286.0	0.0000	2	0.1500	0.000000E+00
3	180.0	2.68	807.0	285.0	0.0000	1	0.1000	0.000000E+00
4	158.0	3.13	807.0	285.0	0.0000	1	0.1000	0.000000E+00
5	158.0	4.47	807.0	287.0	0.0000	4	0.2500	0.000000E+00
6	158.0	3.13	807.0	289.0	0.0000	4	0.2500	0.000000E+00
7	158.0	3.13	807.0	290.0	0.0000	4	0.2500	0.000000E+00
8	158.0	2.68	807.0	293.0	0.0000	4	0.2500	0.000000E+00
9	158.0	2.68	807.0	295.0	0.0000	4	0.2500	0.000000E+00
10	180.0	2.24	807.0	299.0	0.0000	4	0.2500	0.000000E+00
11	158.0	1.34	807.0	300.0	0.0350	6	0.3000	0.000000E+00
12	135.0	0.89	807.0	302.0	0.0350	6	0.3000	0.000000E+00
13	180.0	0.89	1056.0	303.0	0.0350	6	0.3000	0.000000E+00
14	203.0	0.45	1056.0	304.0	0.0350	6	0.3000	0.000000E+00
15	225.0	0.89	1056.0	301.0	0.0350	6	0.3000	0.000000E+00
16	225.0	0.89	1056.0	300.0	0.0350	6	0.3000	0.000000E+00
17	203.0	1.34	1056.0	296.0	0.0350	6	0.3000	0.000000E+00
18	180.0	0.89	1056.0	294.0	0.0350	6	0.3000	0.000000E+00
19	113.0	0.45	1056.0	291.0	0.0350	6	0.3000	0.000000E+00
20	135.0	0.45	1056.0	290.0	0.0350	6	0.3000	0.000000E+00
21	135.0	0.45	1056.0	289.0	0.0350	6	0.3000	0.000000E+00
22	45.0	0.45	1056.0	288.0	0.0000	3	0.2000	0.000000E+00
23	360.0	0.45	1056.0	288.0	0.0000	2	0.1500	0.000000E+00
24	158.0	0.45	1056.0	288.0	0.0000	2	0.1500	0.000000E+00

```
                                                                        RUN 18


                          * METEOROLOGICAL DATA FOR DAY 297 *

                                                         POT. TEMP.
         FLOW        WIND      MIXING                    GRADIENT                    WIND        DECAY
        VECTOR       SPEED     HEIGHT        TEMP.       (DEG. K     STABILITY     PROFILE    COEFFICIENT
HOUR   (DEGREES)     (MPS)    (METERS)     (DEG. K)    PER METER)    CATEGORY      EXPONENT    (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1      203.0       5.81      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  2      203.0       5.81      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  3      180.0       7.15      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  4      203.0       4.92      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  5      203.0       4.47      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  6      203.0       3.58      558.0        289.0        0.0000          4          0.2500    0.000000E+00
  7      203.0       4.47      558.0        289.0        0.0000          3          0.2000    0.000000E+00
  8      203.0       3.58      558.0        292.0        0.0000          3          0.2000    0.000000E+00
  9      203.0       4.02      558.0        296.0        0.0200          5          0.3000    0.000000E+00
 10      203.0       4.02      558.0        300.0        0.0200          5          0.3000    0.000000E+00
 11      203.0       4.02      558.0        301.0        0.0200          5          0.3000    0.000000E+00
 12      203.0       4.47      558.0        302.0        0.0200          5          0.3000    0.000000E+00
 13      203.0       4.47      819.0        303.0        0.0200          5          0.3000    0.000000E+00
 14      203.0       4.02      819.0        305.0        0.0200          5          0.3000    0.000000E+00
 15      203.0       4.47      819.0        303.0        0.0200          5          0.3000    0.000000E+00
 16      203.0       4.47      819.0        301.0        0.0200          5          0.3000    0.000000E+00
 17      203.0       4.47      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 18      203.0       3.58      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 19      203.0       3.58      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 20      203.0       3.58      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 21      203.0       4.02      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 22      203.0       4.47      819.0        300.0        0.0200          5          0.3000    0.000000E+00
 23      203.0       4.47      819.0        299.0        0.0200          5          0.3000    0.000000E+00
 24      203.0       4.47      819.0        299.0        0.0000          3          0.2000    0.000000E+00
```

RUN 19

* METEOROLOGICAL DATA FOR DAY 347 *

HOUR	FLOW VECTOR (DEGREES)	WIND SPEED (MPS)	MIXING HEIGHT (METERS)	TEMP. (DEG. K)	POT. TEMP. GRADIENT (DEG. K PER METER)	STABILITY CATEGORY	WIND PROFILE EXPONENT	DECAY COEFFICIENT (PER SEC)
1	23.0	0.89	468.0	283.0	0.0000	2	0.1500	0.000000E+00
2	23.0	0.89	468.0	282.0	0.0000	2	0.1500	0.000000E+00
3	90.0	0.45	468.0	281.0	0.0000	2	0.1500	0.000000E+00
4	113.0	1.79	468.0	282.0	0.0000	2	0.1500	0.000000E+00
5	135.0	1.79	468.0	289.0	0.0000	2	0.1500	0.000000E+00
6	113.0	1.34	468.0	286.0	0.0000	2	0.1500	0.000000E+00
7	23.0	0.89	468.0	289.0	0.0000	2	0.1500	0.000000E+00
8	270.0	0.45	468.0	291.0	0.0350	6	0.3000	0.000000E+00
9	158.0	0.89	468.0	294.0	0.0350	6	0.3000	0.000000E+00
10	203.0	0.45	468.0	295.0	0.0350	6	0.3000	0.000000E+00
11	180.0	0.45	468.0	296.0	0.0350	6	0.3000	0.000000E+00
12	270.0	0.45	468.0	296.0	0.0350	6	0.3000	0.000000E+00
13	203.0	0.45	989.0	297.0	0.0350	6	0.3000	0.000000E+00
14	180.0	0.45	989.0	299.0	0.0350	6	0.3000	0.000000E+00
15	248.0	0.45	989.0	299.0	0.0350	6	0.3000	0.000000E+00
16	270.0	0.45	989.0	298.0	0.0350	6	0.3000	0.000000E+00
17	248.0	0.89	989.0	295.0	0.0350	6	0.3000	0.000000E+00
18	180.0	0.45	989.0	294.0	0.0350	6	0.3000	0.000000E+00
19	203.0	0.89	989.0	290.0	0.0350	6	0.3000	0.000000E+00
20	90.0	0.45	989.0	289.0	0.0350	6	0.3000	0.000000E+00
21	225.0	0.89	989.0	287.0	0.0350	6	0.3000	0.000000E+00
22	248.0	0.89	989.0	287.0	0.0350	6	0.3000	0.000000E+00
23	315.0	0.45	989.0	287.0	0.0350	6	0.3000	0.000000E+00
24	338.0	0.89	989.0	285.0	0.0000	3	0.2000	0.000000E+00

```
                                                                              RUN 20


                                   * METEOROLOGICAL DATA FOR DAY  78 *

                                                    POT. TEMP.
          FLOW        WIND      MIXING              GRADIENT                    WIND        DECAY
         VECTOR       SPEED     HEIGHT      TEMP.    (DEG. K      STABILITY    PROFILE    COEFFICIENT
HOUR   (DEGREES)     (MPS)     (METERS)   (DEG. K)  PER METER)    CATEGORY    EXPONENT     (PER SEC)
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

  1      203.0        4.92      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  2      203.0        5.36      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  3      203.0        5.81      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  4      203.0        5.36      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  5      203.0        5.36      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  6      203.0        5.36      558.0      279.0      0.0000         3         0.2000    0.000000E+00
  7      203.0        5.36      558.0      280.0      0.0000         4         0.2500    0.000000E+00
  8      203.0        4.47      558.0      282.0      0.0000         3         0.2000    0.000000E+00
  9      225.0        4.47      558.0      284.0      0.0000         4         0.2500    0.000000E+00
 10      225.0        2.68      558.0      285.0      0.0200         5         0.3000    0.000000E+00
 11      203.0        4.47      558.0      287.0      0.0200         5         0.3000    0.000000E+00
 12      203.0        4.47      558.0      289.0      0.0200         5         0.3000    0.000000E+00
 13      225.0        3.58      819.0      289.0      0.0200         5         0.3000    0.000000E+00
 14      248.0        2.68      819.0      289.0      0.0350         6         0.3000    0.000000E+00
 15      225.0        3.58      819.0      289.0      0.0200         5         0.3000    0.000000E+00
 16      225.0        3.58      819.0      286.0      0.0200         5         0.3000    0.000000E+00
 17      270.0        2.68      819.0      284.0      0.0350         6         0.3000    0.000000E+00
 18      315.0        0.89      819.0      283.0      0.0350         6         0.3000    0.000000E+00
 19      338.0        0.89      819.0      282.0      0.0350         6         0.3000    0.000000E+00
 20      180.0        1.34      819.0      281.0      0.0350         6         0.3000    0.000000E+00
 21      203.0        4.47      819.0      280.0      0.0200         5         0.3000    0.000000E+00
 22      225.0        4.92      819.0      280.0      0.0200         5         0.3000    0.000000E+00
 23      225.0        4.92      819.0      279.0      0.0000         4         0.2500    0.000000E+00
 24      203.0        5.81      819.0      279.0      0.0000         4         0.2500    0.000000E+00
```

APPENDIX C
QUALITY ASSURANCE DATA

C.1 FIELD QUALITY ASSURANCE

SAIC's field sampling methods were described in detail in Chapters 7 and 8. This appendix discusses quality assurance measures which were taken during the field sampling. Chain-of-custody was documented by SAIC field sampling forms and laboratory submittal forms provided by our subcontractor, Environmental Monitoring and Services, Inc. (EMSI) of Calabasas, CA. In no case was EMSI told which of the samples were blanks, duplicates or triplicates. For the fixed-site sampling, the numbering of the samples was out of chronological sequence, so that the order of analysis would not affect the results.

C.1.1 Fixed-Site Air Sampling

Field blanks were deployed on 2 of the 7 days of fixed-site sampling at Fullerton and Hermosa Beach. The Fullerton blanks had 19.2 and 19.8 ng of chloroform on them. One of the Hermosa Beach blanks could not be analyzed because of problems with the electron capture detector, while the other had 6.9 ng of chloroform. We believe that these relatively high blank levels are due to problems with the analytical method early in the study. Method blank chloroform levels were much lower (generally less than 1 ng of chloroform).

Two field blanks were spiked by SAIC with chloroform vapor, opened briefly during the Hermosa Beach sampling, and then delivered to EMSI for analysis. The recoveries were as follows:

Trap No.	Spike (ng)	Recovery (ng)	Recovery Pct.
34	150	43	28.7
42	25	18.6	74 4

We believe that the relatively poor recoveries were due to uncertainties in the amount spiked, rather than to problems with the analytical method. Analysis of laboratory-spiked samples is discussed in Section C.2.1.3.

Triplicate samples were collected at both Fullerton and Hermosa Beach. However, EMSI was able to analyze only one of the Fullerton trio and two of the three

Hermosa Beach samples. In the latter case, the percentage difference of the pair was 14.7 percent.

C.1.2 Mobile Air Sampling

Duplicate samples were collected at one of the mobile sampling sites. Results were as follows:

Compound	Trap 1 (ng)	Trap 2 (ng)	Pct. Diff.
Chloroform	154	111	16.2
1,1,1-trichloroethane	184	66	47.2
Carbon tetrachloride	40	14	48.1
Trichloroethylene	358	757	35.8
Perchloroethylene	321	40	77.8

C.1.3 Marine Water Sampling

Samples at one of the points along the coast were taken in duplicate. The results of the chloroform analyses were as follows:

Depth (ft)	Sample 1 (ppt)	Sample 2 (ft)	Pct Diff.
0	2.5	12	65.5
9	2.5	10	60.0
18	6	14	40.0
27	8	20	42.9
36	7	8	6.7
45	7	9	12.5

C.2 LABORATORY METHODS AND QUALITY ASSURANCE

Air and water samples collected by SAIC were analyzed by EMSI. The following is adapted from EMSI's laboratory report to SAIC (Levan et al., 1987), which may be obtained as a separate document from the Research Division of the Air Resources Board.

C.2.1 Analysis of Carbon Molecular Sieve (CMS) Traps

C.2.1.1 Overview

CMS traps were analyzed for chloroform, 1,1,1-trichloroethane, carbon tetrachloride, ethylene dichloride, trichloroethylene, tetrachloroethene, and ethylene dibromide, using a modification of EPA Method TO3 (Riggin, 1984). The modification included the replacement of the Nutech Model 320-01 desorber with a Tekmar Model 5010 desorber, and the addition of a Nafion membrane dryer (Permapure Model MD-125-48SF) behind the Tekmar furnace. These modifications in the Tekmar unit provided the hardware equivalent to the Nutech unit that was specified in EPA Method TO3.

The membrane dryer was used to remove water vapor collected on the CMS trap during ambient air sampling. Co-collected water vapor interfered with the analysis by freezing on the capillary column; this blocked low and led to anomalies in the response of the electron capture detector. Using the Nafion dryer tube did not interfere with the analysis of the target compounds and was documented in the literature and in various methods of analysis of volatile organic compounds in air.

The CMS traps were analyzed using a Tekmar Model 5010 desorber and a gas chromatograph equipped with dual electron capture detectors. The data were acquired and stored on the IBM 9001 data system. The quantitation was done using a multipoint calibration by an external standard technique. Details of instrumentation and analytical conditions are summarized in Table C.2-1.

C.2.1.2 Calibration

Preparation of Standards

The primary standards of chloroform, halocarbons, and surrogate compounds were obtained from the EPA repository and Chem Services, Inc. The surrogate standards that were used for the analysis were bromodichloromethane and dibromochloromethane. These compounds were selected because they elute separately from the target compounds, yet have similar physical characteristics. Gaseous standards of chloroform and target halocarbons were made from liquid

Table C.2-1

INSTRUMENTATION AND ANALYTICAL CONDITIONS FOR CHLOROFORM AND HALOCARBONS IN CMS TRAPS

Instrumentation

- IBM 9630 gas chromatograph with dual electron capture detectors
- Tekmar 5010 thermal desorber

Analytical Conditions

Primary Column:	0.53 mm ID x 30 m DB 624 megabore capillary column.
Secondary Column:	0.53 mm ID x 30 m DB 5 megabore capillary column.
Injector Temperature:	Injector was not used. Column was interfaced directly to the Tekmar 5010 desorber.
Detector Temperature:	300°C
Column Temperature:	Multiple ramp program. Ramp 1 - 55°C @ 2 min./4°C per min/75°C Ramp 2 - 75°C/6°C per min/111°C Ramp 3 - 111°C/35° per min/230°C @ 5 min
Flow Rate:	5.7 ml/min helium carrier, 25 ml/min Nitrogen make-up gas.
Sensitivity:	ECD1 = 1 x 1 ECD2 = 1 x 64

Tekmar 5010 Thermal Desorber

PURGE 1	An initial flow of carrier gas to remove air and water vapor.	
	Flow time	5.0 min.
COOL 1	Cooling of Cryo trap 1	
	Temperature	-100°C
DESORB	Heating of tube furnace	
	Furnace temperature	420°C
	Heating time	12.0 min.
COOL 2	Cooling of Cryo trap 2	
	Cryo 2 temperature	-110°C

Table C.2-1

INSTRUMENTATION AND ANALYTICAL CONDITIONS FOR CHLOROFORM AND HALOCARBONS IN CMS TRAPS
(Continued)

TRANSFER	Heat Cryo trap 1 to transfer material to Cryo trap 2	
	Cryo 1 temperature	250°C
	Heating time	3.0 min.
BAKE	Thermal clean-up of tube furnace	
	Furnace temperature	150°C
	Bake time	1.0 min.
	Permapure dryer temperature	70°C

stock mixtures (prepared in-house) by using a simple static dilution system developed by the EPA. Examples of the liquid stock standard preparation are shown in Table C.2-2. The static dilution system is a 2-liter round-bottom flask with a neck threaded to accept a septum and a 2.5-cm Teflon stirring bar. Standards are prepared by injecting a known volume of the liquid stock mixture via the septum while the bottle is agitated on a magnetic stirrer. The surrogate mixture was prepared in a similar manner.

The standard and surrogate mixes were warmed in an oven at 60 ± 5°C for 30 minutes to allow vaporization, then equilibrated at room temperature before use. Aliquots were then withdrawn with a gas-tight syringe for the calibration. Care was taken so that no more than about 5 percent of total volume of the standard was taken out. A fresh standard was remade every four hours for the continuing calibration check.

Generation of Standard Curves

Aliquots from the prepared gaseous standard were withdrawn with a gas-tight syringe, injected through the septa of the Tekmar furnace onto a blank CMS trap and purged with nitrogen for 5 minutes so that the target compounds would deposit on the trap. After the purging, the CMS trap was removed from the furnace, rotated 180 degrees, and re-inserted in the furnace so that the trap would be desorbed in a direction opposite to that of sample collection. The prepared traps were then desorbed under the same analytical conditions as the sample to generate calibration points for the target compounds. The process was repeated for different calibration points to generate the calibration curves. This process minimizes the variation in desorption efficiency of different CMS traps.

C.2.1.3 Quality Control

A set of CMS trap spike and spike duplicate (MS/MSD) was analyzed for every 20 samples. A blank CMS trap was also analyzed every day before sample analysis to check for system contamination and interferences. A standard check was also analyzed at least once for every ten samples to monitor the stability of the electron capture detectors. QA/QC results are summarized in Table C.2-3.

Table C.2-2
STANDARD PREPARATION

HALOCARBONS LIQUID STOCK MIXTURE

Compound	Density (g/ml)	Volume Used (10^{-3} ml)	Final Mixture (ml of pentane)	Concentration (mg/ml)
Chloroform	1.492	67.0	10.0	10.0
1,1,1-Trichloroethylene	1.338	38.0	10.0	5.0
Carbon Tetrachloride	1.594	6.3	10.0	1.0
Ethylene Dichloride	1.255	3980.9	10.0	500.0
Trichloroethene	1.464	68.3	10.0	10.0
BDCM (SS1)	1.980	10.1	10.0	2.0
Tetrachloroethylene	1.623	12.3	10.0	2.0
DBCM (SS2)	2.451	8.2	10.0	2.0
Ethylene Dibromide	2.180	45.9	10.0	10.0

SURROGATE LIQUID STOCK MIXTURE

Compound	Density (g/ml)	Volume Used (10^{-3} ml)	Final Mixture (ml of pentane)	Concentration (mg/ml)
BDCM (SS1)	1.980	10.1	10.0	2.0
DBCM (SS2)	2.451	8.2	10.0	2.0

BDCM (SS1) = Bromodichloromethane (Surrogate #1)
DBCM (SS2) = Dibromochloromethane (Surrogate #2)

Table C.2-3

SUMMARY OF CMS TRAP SPIKED RECOVERY

Date Analyzed: 4/28/87

Compound	Amount Spiked (nanograms)	MS Results (nanograms)	% Recovery	MSD Results (nanograms)	% Recovery	% RPD
Chloroform	2.50	24.10	96	25.90	1021	8
1,1,1-Tricholoroethane	12.50	9.70	78	7.82	63	21
Carbon Tetrachloride	2.50	2.51	100	1.74	70	35
Trichloroethene	25.00	9.50	38	9.60	38	0
Tetrachloroethene	5.00	4.62	92	4.31	86	7
Ethylene Dibromide	25.00	22.10	88	21.60	86	2

Date Analyzed: 5/12/87

Compound	Amount Spiked (nanograms)	MS Results (nanograms)	% Recovery	MSD Results (nanograms)	% Recovery	% RPD
Chloroform	10.00	7.71	77	7.78	78	1.30
1,1,1-Tricholoroethane	5.00	3.12	62	2.62	52	17.10
Carbon Tetrachloride	1.00	0.58	58	0.60	60	3.40
Trichloroethene	10.00	6.40	64	6.90	69	7.50
Tetrachloroethene	2.00	1.02	51	1.11	56	9.30
Ethylene Dibromide	10.00	4.74	47	6.61	66	34

Table C.2-3
(continued)
SUMMARY OF CMS TRAP SPIKED RECOVERY

Date Analyzed: 5/15/87

Compound	Amount Spiked (nanograms)	MS Results (nanograms)	% Recovery	MSD Results (nanograms)	% Recovery	% RPD
Chloroform	5.00	4.96	99	5.10	102	3.0
1,1,1-Tricholoroethane	2.50	1.77	71	1.92	77	8.1
Carbon Tetrachloride	0.50	0.42	84	0.39	78	7.4
Trichloroethene	5.00	4.47	89	4.60	92	3.3
Tetrachloroethene	1.00	0.92	92	0.97	97	5.3
Ethylene Dibromide	5.00	3.45	69	3.52	20	1.4

Date Analyzed: 5/19/87

Compound	Amount Spiked (nanograms)	MS Results (nanograms)	% Recovery	MSD Results (nanograms)	% Recovery	% RPD
Chloroform	5.00	4.24	85	4.06	81	5
1,1,1-Tricholoroethane	2.50	1.31	52	1.32	53	2
Carbon Tetrachloride	0.50	0.29	58	0.25	50	15
Trichloroethene	5.00	3.82	76	3.65	73	4
Tetrachloroethene	1.00	0.60	60	0.56	56	7
Ethylene Dibromide	5.00	3.03	61	2.69	54	12

Table C.2-3
(continued)
SUMMARY OF CMS TRAP SPIKED RECOVERY

Date Analyzed: 5/21/87

Compound	Amount Spiked (nanograms)	MS Results (nanograms)	% Recovery	MSD Results (nanograms)	% Recovery	% RPD
Chloroform	5.00	4.16	83	4.55	91	9.2
1,1,1-Tricholoroethane	2.50	1.50	46	1.22	49	6.3
Carbon Tetrachloride	0.50	0.25	50	0.24	48	4.1
Trichloroethene	5.00	5.39	108	5.22	104	3.8
Tetrachloroethene	1.00	0.96	96	0.86	86	11.0
Ethylene Dibromide	5.00	3.57	71	3.51	70	1.4

C.2.1.4 Sample Analysis

Each CMS trap from the field was spiked with the surrogate standard and desorbed automatically by the Tekmar 5010 desorber. The Tekmar Model 5010 consists of a sorbent trap furnace, an internal cryogenic trap, an eight=port motor-activated valve, a heated transfer line, and a second cryogenic focusing unit for the GC capillary column. (See Figure C.2-1.) The internal cryogenic trap is a blank 10-in x 1/8-in ID nickel tube, while the second cryogenic focusing unit is a 1-ft uncoated megabore fused silica tube. Both cryogenic traps can maintain the trap temperature at -150°C while sorbent media are being desorbed or the sample is revolatilizing.

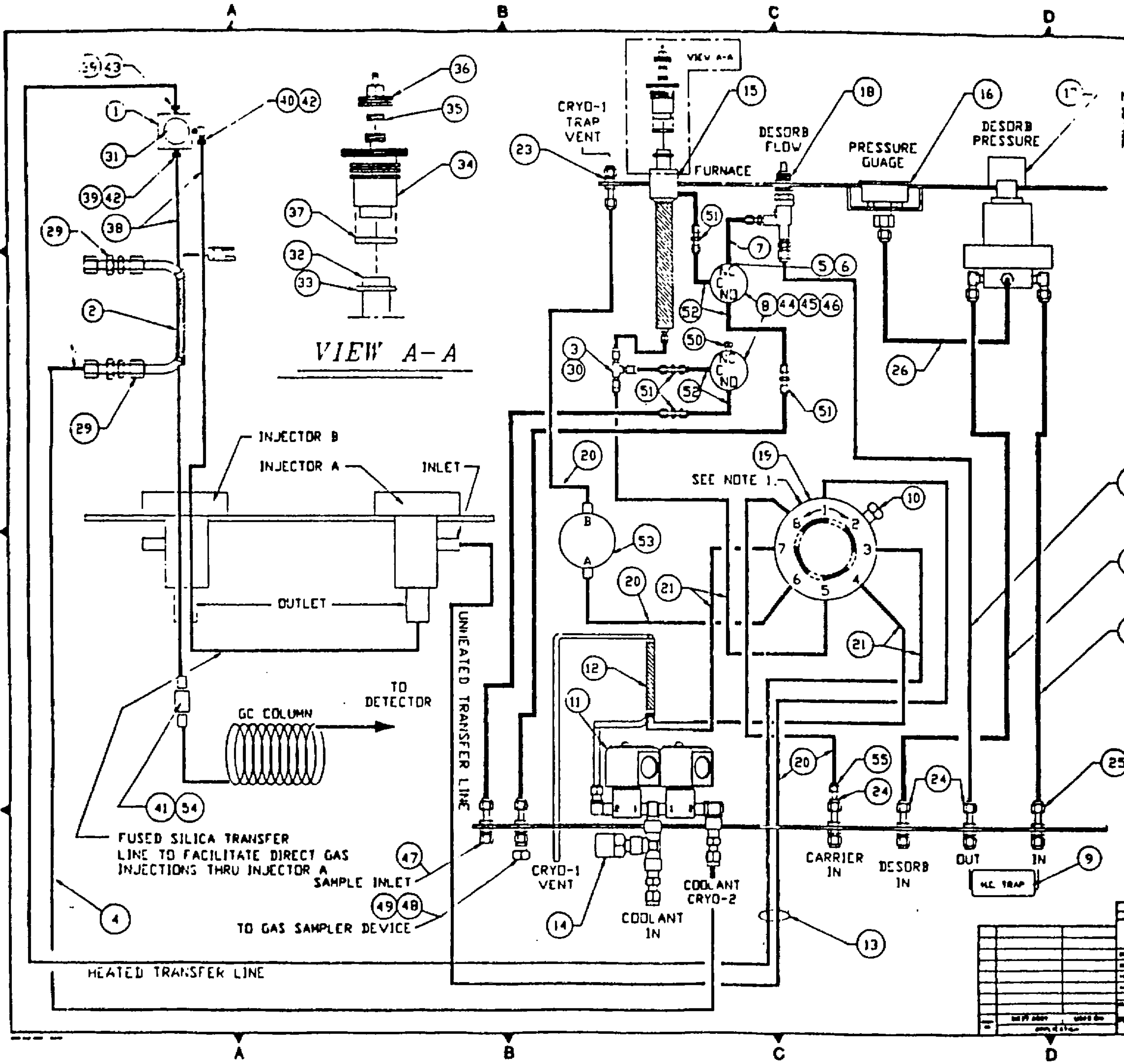
Samples are revolatilized by heating of the internal cryogenic trap from -150°C to 200°C in less than 30 seconds after the completion of the sorbent thermal desorption cycle. The revolatilized sample is cryogenically focused again on the second capillary trap, and subsequently transferred to the analytical columns by heating and backflushing the trap. All of the above steps were programmed into the Tekmar microprocessor and performed automatically by the desorber.

The samples were analyzed simultaneously using two 30 m x -.53 mm ID megabore capillary columns (DB-624 and DB-5). The influent was split equally into the two columns by a tee; the split sample was then fed to two electron capture detectors having different sensitivity settings. With this configuration, the analytical system provided the quantitation and confirmation data at the same time and extended the dynamic range of detection.

C.2.2 Analysis of Aqueous Samples for Chloroform

C.2.2.1 Overview

Seawater and swimming pool water samples were analyzed for chloroform by EPA Method 601, which comprises purge-and-trap gas collection followed by gas chromatography with electron capture detection (GC/ECD). The quantitation column for the analysis was an 0.53-mm ID x 30-m DB-624 megabore capillary column while the confirmation column was an 0.75-mm by 60-m VOCOL capillary column. The data were acquired and stored on the IBM 9001 data system. The



A	ECO 943	
B	PER CN 870	

NOTE:
1) WHEN PORTS 1 AND 8 ARE ALIGNED THIS IS DESORB TO CRYO-1 OR INJECT MODE USING GC CARRIER GAS
2) WHEN PORTS 1 AND 2 ARE ALIGNED THIS IS TRANSFER FROM CRYO-1 TO CRYO-2

1	55	12-0042-016	REDUCER 1/16 TUBE - 1/8 STUB
1	54	14-2071-016	.5mm ID FERRULE
1	53	14-2101-000	VENT VALVE ASSY (2 PORT)
17	52	14-0583-002	TUBING 1/8 (TEFLON)
4	51	12-0398-016	UNION 1/8 S.S.
1	50	14-1749-016	PLUG NUT TEFLON GV
1	49	14-1752-016	F-MALE CONN ADAPTER
1	48	14-1751-016	BULKHD ADAPTER S.S.
1	47	12-0336-016	1/8 SS BULKHD
4	46	12-0072-016	1/8 TEF NUT G.V.
4	45	12-0071-016	INSERT FOR 1/8 TUBE GV
4	44	14-1750-002	TUBE W/GV FLARE
1	43	14-0241-016	FERRULE 1/16 S.S. (VALCO)
1	42	14-0540-016	FERRULE .5mm I.D SGE GV.
1	41	14-2069-016	.5mm GLASS LINED UNION
1	40	14-0159-016	NUT, 1/16 S.S.
2	39	14-0243-016	NUT, 1/16 SHORT (VALCO)
AR	38	14-0539-002	.32mm ID V.S. TUBING
1	37	14-1379-043	O-RING .301 I.D x .070 WTH.
1	36	14-1591-016	NUT, SEPTUM
1	35	14-1387-000	SEPTUM for DESORBER FURN
1	34	14-1375-000	CAP, for DESORBER FURN
1	33	14-1378-043	O-RING .624 I.D. x .070 WTH
1	32	14-1350-002	TRAP TUBE .628 -.623 OD
1	31	14-1443-001	SCREW, SET
1	30	14-1756-016	FERRULE 1/8 TO 1/16
2	29	14-1356-016	BULK HD. UNION 1/4" (BRASS)
1	28	14-1597-200	1/8" COPPER TUBING ASSY.
1	27	14-1597-000	1/8" COPPER TUBING ASSY
44"	26	14-0546-002	TUBING, COPPER 1/8"
1	25	12-0074-016	BULKHEAD 1/8"
3	24	14-0356-016	BULKHEAD 1/8" FILTER ASSY
1	23	14-0264-016	BULKHEAD 1/16" S.S.
1	22	14-1597-100	TUBING 1/8" COPPER ASSY.
9.5	21	14-1643-000	TUBING 1/16" NICKLE HEATED
7.8	20	14-0441-002	TUBING 1/16" NICKLE
1	19	14-1658-000	8 PORT VALVE ASSY.
1	18	14-1155-000	FLOW CONTROL ASSY.
1	17	14-1623-000	PRESSURE REGULATOR ASSY.
1	16	14-1096-000	PRESSURE GUAGE ASSY.
1	15	14-1745-000	DESORBER FURNACE ASSY
1	14	14-0518-050	PRESSURE RELIEF VALVE
1	13	14-1627-000	HEATED TRANS. LINE ASSY.
1	12	14-1594-000	1/16" CRYO-1 ASSY. 110v
1	11	14-1567-000	LN-2 VALVE ASSY.
1	10	14-1590-016	PLUG NUT (VALCO)
1	9	14-1362-000	HYDROCARBON TRAP ASSY.
2	8	14-0029-050	PURGE VALVE 3 PORT
1	7	14-0075-002	LINES (PURGE)
1	6	14-0031-016	NUTS (TEFLON)
1	5	14-0547-016	WASHER (TEFLON)
1	4	14-1668-000	LN2 TRANSFER LINE ASSY
1	3	14-1758-016	TEE SS 1/8"
1	2	14-1601-000	CRYO-2 HEATER ASSY.
1	1	14-1616-000	CRYO-2 TEE ASSY COMP.

APR 2 1995

Tekmar Company

FLOW DIAGRAM 5010
110v Frm Sn. 102

14-1757-000

Figure C.2-1. Diagram of the Tekmar 5010 results of the analyses were calculated using a three-point calibration curve, based on external standards. Details of instrumentation and analytical conditions are summarized in Table C.2-4.

C.2.2.2 Calibration

The primary chloroform and surrogate standards were obtained from Supelco, Inc. and the EPA repository. The working standards for chloroform and the surrogate were prepared by diluting the stock standards with pesticide grade methanol (Burdick and Jackson Laboratories). Prior to the analysis of each sample batch, a three-level standard or a continuing calibration check was performed, followed by a detection limit check and a method blank to ensure the performance of the analytical system. A standard check was also run after every ten samples and the analysis sequence was always completed with a standard.

C.2.2.3 Quality Control

All samples and blanks were spiked with a 2-bromo-1-chloropropane surrogate to monitor the purging efficiency of the system. A set of duplicate and spiked samples was run with every 20 samples. Ten percent of the positive "hit" samples were analyzed for confirmation on the secondary column. QC results are summarized in Tables C.2-5 and C.2-6.

C.2.2.4 Sample Analysis

Prior to analysis, each sample was allowed to warm to room temperature. The sample was then poured into a 5-ml syringe and its final volume was adjusted to 5 ml. Ten microliters of surrogate in methanol were added directly to the syringe. The sample-surrogate combination was then introduced into a glass sparging vessel, where it was purged for 10 minutes with helium. The trap was then desorbed for 4 minutes onto the analytical column. Analysis began at the same time the trap desorption began. Because their chloroform levels were high, swimming pool water samples were diluted to within the range of the calibration curve.

Table C.2-4

INSTRUMENTATION AND ANALYTICAL CONDITIONS FOR CHLOROFORM ANALYSIS

Instrumentation

- Varian 3700 gas chromatograph with an electron capture detector
- Tekmar Model 4000 sample concentrator

Analytical Conditions

	Quantitation	Confirmation
Column:	0.53 mm ID x 30 m DB 624	0.75mm ID x 60m VDCOL
Injector Temperature:	Injector was not used. Column was interfaced directly to the Tekmar 4000.	
Detector Temperature:	280°C	280°C
Column Temperature:	45°C @ 3/6°C per min/100°C	40°C @ 4/1°C per min/135°C
Flow Rate:	8 ml/min helium carrier, 34 ml/min Nitrogen make-up gas.	

Tekmar Model 4000 Sample Concentrator Parameters

Sample Size	5 ml of sample using a fritted disk sparger
PURGE TIME	7 minutes wet purge and 3 minutes dry purge
PURGE FLOW RATE	30 ml/min using nitrogen gas
DESORB PREHEAT TEMPERATURE	175°C
DESORB TEMPERATURE AND TIME	200°C for 3 minutes
BAKE TEMPERATURE AND TIME	210°C for 3 minutes
TRAP MATERIAL	Tenax/charcoal/OV-101

Table C.2-5

QUALITY CONTROL TESTS FOR POOL WATER ANALYSIS

Duplicate Analysis of Pool Water Samples

(Chloroform concentrations in ppt)

Sample	Result	Duplicate Result	%RSD
PW-B-C-6	72	80	11
PW-N-C-3	43	42	2
PW-N-C-7	53	60	12
PW-H-C-8	51	51	0

Spiked Recovery Analysis

(Chloroform concentrations in ppt)

Sample ID	Result	Amount Spiked	Amount Recovered	Percent Recovery
Water Blank	ND	200	213	107
PW-N-C-7	53	50	90	74
PW-H-C-8	51	50	75	48

Table C.2-6

QUALITY CONTROL TESTS FOR SEAWATER SAMPLES

Summary of Duplicate Analysis of Seawater Samples

(Chloroform concentrations in ppt)

Sample	Result	Duplicate Result	%RSD
W014C	4	4	0
W014F	7	10	35
W015C	13	9	36
W09A	6	7	15
W10D	6	8	29
W12B	5	4	22
W02F	7	7	0
W06C	6	3	67
W07D	7	7	0

Summary of Spiked Recovery Analysis

(Chloroform concentrations in ppt)

Sample ID	Result	Amount Spiked	Amount Recovered	Percent Recovery
Method Spike	ND	40	23	60
W015B	9	100	109	100
Method Spike	ND	40	27	68
W09B	5	100	112	107
W10E	11	100	107	96
W12C	6	100	105	99
W04A	4	100	97	93
W06D	8	100	103	95
W07F	12	100	108	96

C.2.2.5 Results

The detection limits of chloroform in seawater and swimming pool water were 5 and 10 parts per trillion (nanograms per liter), respectively. Detection limits were based on a signal-to-noise ratio of approximately 10 to 1. The high chloroform levels in the swimming pool water samples led to some carryover in the purge-and-trap apparatus. Therefore, it was very difficult to obtain "clean" blanks below 5 ppt.

C.2.3 Discussion of Laboratory Results

The detection limit of chloroform and other halocarbons in the CMS trap samples was 0.5 ng per compound per trap; this value was defined by EMSI as ten times the signal-to-noise ratio of the analyte in the lowest standard. However, due to background levels of chloroform and other compounds in the sorbent medium, the *quantitation* limit was 1.0 ng per trap.

There were some difficulties with the analysis of chloroform and halocarbons in the CMS traps. The major problem was the water vapor that was co-collected on the carbon molecular sieve sorbent. The recommended pre-purge of the trap with nitrogen at ambient temperature did not remove the water completely. Therefore, a Nafion dryer tube was installed behind the Tekmar furnace to remove the residual water vapor after the pre-purge step. Once the dryer tube was installed, the response of the electron capture detector showed an increase in sensitivity and stability. The Nafion dryer tube has been used extensively in the analysis of volatile organics in air and does not interfere with most volatile compounds other than aldehydes, ketones, ethers and alcohols.

The second problem was the choice of suitable surrogates for the analysis. The surrogate compounds that were suggested in EPA Method TO3 were used in developing the techniques used here. However, it was found that they interfered with the target compounds. Therefore, bromodichloromethane and dichlorobromomethane were used instead.

The use of dual electron capture detectors provided an extended dynamic range for the quantitation but did not provide an ironclad positive identification of the compounds. For future study of these target compounds, EMSI suggests using an ion trap detector with multiple ion detection mode (ITD/MID) in parallel with the ECD. In this configuration, the ion trap detector would provide confirmation. The detection limit of the target compounds under this arrangement is unknown.

To these observations, SAIC would add that a simple calibration curve and not a working curve was developed for the calibration process. Using a working curve allows for a smaller coefficient of variation and a more precise extrapolation of data to lower concentration levels.

C.3 REFERENCES

Levan, L., D. Cabrey, K. Chen and M. Larson. 1987. Analysis of ambient chloroform and halocarbons in CMS trap and aqueous samples. Prepared by Environmental Monitoring and Services, Inc. for Science Applications International Corporation, Manhattan Beach, CA.

Riggin, R.M. 1984. Compendium of methods for the determination of toxic organic compounds in ambient air. Prepared by Battelle-Columbus Laboratories for the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, EPA-600/4-84-041.

APPENDIX D

TESTS OF LOGNORMALITY OF ARB AMBIENT SAMPLING DATA DISTRIBUTION

D.1 NORMALITY TESTS

Two measures of the normality of a data set are skewness and kurtosis. These are defined as follows (Dixon et al., 1983):

$$\text{Skewness} = \sum(x_j - \bar{x})^3/(Ns^3)$$

$$\text{Kurtosis} = \sum(x_j - \bar{x})^4/(Ns^4)$$

where x_j is an individual sample value, x is the sample mean, and s is the sample variance. These formulas were applied to the original values of the data sets for the four ARB monitoring stations, and then to the logarithms of the values. Table D-1 shows the results.

Skewness is a measure of the symmetry of a distribution, and is zero for a completely symmetric, bell-shaped curve. A positive value indicates that the values are clustered more the the left of the mean, with most of the extreme values to the right. As seen in Table D-1, all the distributions evaluated have a positive skewness. The skewness of the distributions of the logarithms of concentration values are in all cases considerably smaller than those of the original values.

Kurtosis is a measure of the "long-tailedness" of a distribution. A value of kurtosis which is significantly greater than zero indicates a distribution which is longer-tailed than a normal distribution. A negative kurtosis indicates a flatter distribution than a normal one. The kurtosis of the distributions of logarithms is, for all sites, considerably closer to zero than the kurtosis of the distributions of original values.

Table D-1

SKEWNESS AND KURTOSIS OF UNADJUSTED VALUES AND LOGARITHMS OF CHLOROFORM CONCENTRATIONS AT FOUR ARB SAMPLING STATIONS

	Skewness		Kurtosis	
Station	Raw	Log	Raw	Log
Dominguez Hills	2.14	0.59	5.40	0.840
El Monte	1.72	0.38	4.21	0.067
Los Angeles	9.43	1.15	115.50	5.900
Riverside	1.36	0.34	1.75	-0.098

From this analysis we conclude that (1) the data for all sites are distributed approximately lognormally and (2) the El Monte data (whether the original set or the logarithms) depart the most from lognormality.

D.2 REFERENCE

Dixon, W.J., M.B. Brown, L. Engelman, J.W. Frane, M.A. Hill, R.I. Jennrich and J.D. Toporek. 1983. BMDP statistical software. 1983 Printing with additions. University of California Press, Berkeley, CA.