# ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES: BROMINATED CHEMICALS

## PART I

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# ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES: BROMINATED CHEMICALS

PART I

by

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ABSTRACT

Sampling and analysis was designed to determine ambient concentrations of ethylene dibromide and other brominated chemicals near production facilities in El Dorado and Magnolia, AK. A characterization was made of the environmental matrices - air, water, soil, sediment and biota - for the presence and levels of ethylene dibromide, vinyl bromide and other related chemicals surrounding the bromine industry.

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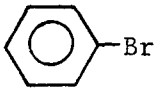
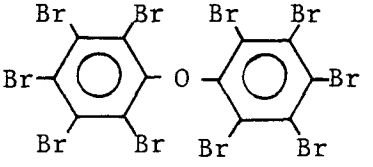
NAMES, ABBREVIATIONS, AND STRUCTURAL FORMULAS OF BROMINATED COMPOUNDS

| | |
|---|---|
| Methyl Bromide (MB) | $CH_3Br$ |
| Vinyl Bromide (VB) | $CH_2=CH-Br$ |
| Bromoform (BF) | $CHBr_3$ |
| Bromoethane (BE) | $CH_3CH_2-Br$ |
| 1,2-Dibromoethane (EDB) | $Br-CH_2CH_2-Br$ |
| 1-Chloro-2-bromoethane (CBE) | $ClCH_2CH_2-Br$ |
| Allyl Bromide (AB) | $CH_2=CH-CH_2-Br$ |
| 1-Chloro-3-bromopropane (CBP) | $Cl-CH_2CH_2CH_2-Br$ |
| 1-Chloro-2,3-dibromopropane (DBCP) | $Cl-CH_2CHBrCH_2-Br$ |

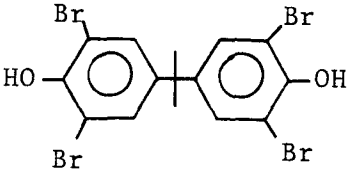
Bromobenzene (BB)



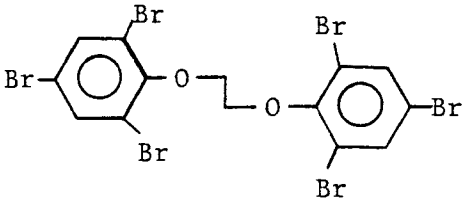
Decabromobiphenyl ether (Decabrom)
syn.-decabromobiphenyl oxide



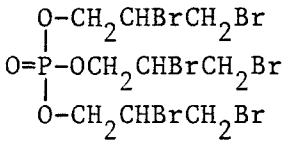
2,2'-Bis(dibromo-4-hydroxyphenyl)propane
(Tetrabrom)
trivial name - Tetrabromobisphenol A



1,2-Bis(2,4,6-tribromophenoxy)ethane
trade name - Firemaster 680®



Tris-(2,3-dibromopropyl)phosphate (TRIS)
trade name - Firemaster LVT23P®



ACKNOWLEDGEMENTS

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Most importantly, we wish to thank EPA personnel who assisted in the many facets of this program, both from EPA Region VI, specifically Drs. Frank Hall, Oscar Ramierez, Paul Fahrenthold and Tim Matzke and Dr. Vincent DeCarlo of the Office of Toxic Substances.

Most assuredly the success of this program stemmed from the invaluable help provided by Mr. Gerald Southall and John Mitchell of the State of Arkansas Department of Pollution and Ecology who were responsible for gaining access to the areas of interest for study and for their public relations in El Dorado and Magnolia, AK. A special thanks is in order to them.

We also wish to thank the various companies that were visited in El Dorado and Magnolia and express our deep appreciation in their assistance during our visit on their plant sites. A special thanks to Mr. Dick Karkannien and the personnel at Arkansas Chemical Inc. for assisting in the acquisition of power for the ozone measurements conducted on plant property.

## 1.0 SUMMARY AND CONCLUSIONS

Development and/or validation of methods for the collection and analysis of brominated chemicals (inorganic and organic) in environmental samples - air, water, soil, sediment, and biota - was conducted and these techniques were applied to the characterization of the environment surrounding the bromine industry in El Dorado and Magnolia, AK. The final analytical protocols which were adopted in this research program are given in Appendix A.

Evaluation of a miniature impinger train for the collection of halides and halogens indicated that if molecular chlorine and bromide ion were present in air the displacement of bromide from the first impinger would occur. Thus, false high values of molecular bromine would be observed. Determination of chloride and bromide was conducted by turbidimetric measurements; the detection limit was approximately 10 $\mu g/m^3$. Differentiation of chloride and bromide ions was accomplished by ion-exchange techniques or, in some cases, the bromide was detected by a fluorescence quench method using fluorescein. Inorganic fluoride was directly determined using a fluoride ion-specific electrode and the detection limit was $\sim$2 $\mu g/m^3$.

Collection of volatile brominated organics in ambient air utilized Tenax GC® and carbon sorbents. In some cases aluminum vacuum cannisters were used as alternatives to the sorbent methods for obtaining methyl chloride, methyl bromide, vinyl chloride and vinyl bromide. Airborne particulates were trapped on glass fiber and cellulose filters. Methods for recoverying of brominated organics from air particulates, water, soil, sediment and biota were developed and/or validated. Techniques such as inert gas purging or solvent extraction were used to isolate the brominated materials from the condensed phases.

The principal method for the identification of brominated organics was gas chromatography/mass spectrometry/computer (gc/ms/comp). Quantitation

was performed by gc/ms/comp and gc/ec. Alternate detection methods such as neutron activation, spectrophotometry, and scanning electron microscopy/X-ray dispersion were used for exploration and confirmation of the presence of brominated substances.

A total of 26 brominated organic compounds was identified in environmental samples collected from a geographical area associated with the bromine industry (Table 1.1). Many of the chemicals were detected in environmental matrices off plant property indicating that their transport into the neighboring environment was occurring. Quantification of most of the chemicals in various environmental media (Table 1.1) was also conducted.

Examples of selected results exhibitng highest concentrations observed in environmental samples are given in Tables 1.2 and 1.3. These preliminary results indicate a spatial spreading of brominated compounds into the environment.

Additional research would be required to establish the extent of environmental contamination and man's exposure and body burden.

Table 1.1. HALOGENATED AND OTHER CHEMICALS IDENTIFIED IN THE ENVIRONMENT

| Substance | Matrix |
|---|---|
| chlorodibromopropane | air |
| 1-chloro-2,3-dibromopropane | air, water, soil, sediment, front and tail brine |
| 1,2-dibromoethane | air, water, soil, sediment |
| difluorodibromomethane | air |
| methyl bromide | air |
| bromobenzene | air, soil, sediment |
| bromoethane | air |
| bromoform | air, sediment, front and tail brine |
| 1-chloro-2-bromoethane | air, water, sediment |
| 1-chloro-3-bromopropane | air |
| 1,3-dichloropropane | air |
| vinyl bromide | air |
| bromodichloromethane | air, tail and front brine |
| allyl bromide | air |
| 1 or 2-bromopropane | air |
| bromopropene | air, water |
| chlorobromopropene | air |
| 1,1-dibromo-2-chloropropane | air |
| dibromopropane | air |
| dibromoethene | water |
| chlorobutene | water |

(continued)

Table 1.1 (cont'd)

| Substance | Matrix |
|---|---|
| bromodichloropropane | water |
| 1,2-dichloroethane | water, soil, sediment |
| trichloroethylene | water |
| Decabrom® | air particulate, soil, sediment, human hair |
| Tetrabromobisphenol A | air particulate, soil, sediment, human hair |
| Tris | air particulate, soil |
| Firemaster 680® | air particulate, soil |
| dibromochloromethane | front and tail brine |
| styrene | air |
| benzene | front and tail brine |
| toluene | front and tail brine |
| dimethyldisulfide | front and tail brine |
| thiacyclopentane | front and tail (?) brine |
| dithiol propane isomer | front and tail brine |
| ethylbenzene | front brine |
| n-undecane | front and tail brine |
| n-dodecane | front and tail brine |

Table 1.2. MAXIMUM CONCENTRATIONS OF BROMINATED CHEMICALS OBSERVED IN SELECTED ENVIRONMENTAL SAMPLES

| Company/Community | Chemical | Medium | Quantity |
|---|---|---|---|
| Great Lakes Chemical Corp. | $Cl_2/Br_2$ | Air | 183,000 $ng/m^3$ |
| | $Cl^-/Br^-$ | Air | 876,000 $ng/m^3$ |
| | EDB | Air | 271,283 $ng/m^3$ |
| | Decabrom | Air | 94,118 $ng/m^3$ |
| | Decabrom | Soil | >>225,000 µg/Kg |
| Velsicol Inc. | $Cl^-/Br^-$ | Air | 91,000 $ng/m^3$ |
| | $Cl_2/Br_2$ | Air | 158,000 $ng/m^3$ |
| | EDB | Air | 2,425 $ng/m^3$ |
| | Firemaster 680 | Air | 183 $ng/m^3$ |
| | Tris | Air | 60 $ng/m^3$ |
| | Decabrom | Air | 72 $ng/m^3$ |
| Ethyl Corp. | EDB | Air | 20,250 $ng/m^3$ |
| | DBCP | Air | 1,688 $ng/m^3$ |
| Dow Chemical | $Cl_2/Br_2$ | Air | 64,000 $ng/m^3$ |
| | EDB | Air | 62,484 $ng/m^3$ |
| | DBCP | Air | 6,653 $ng/m^3$ |
| Parkers Chapel | EDB | Air | 1,260 $ng/m^3$ |
| El Dorado, AK | 1-Chloro-2-bromoethane | Air | 4,200 $ng/m^3$ |

Table 1.3. MAXIMUM CONCENTRATIONS OF BROMINATED CHEMICALS OBSERVED IN ENVIRONMENTAL SAMPLES TAKEN IN THE VICINITY OF INDUSTRY

| Vicinity of-- | Chemical | Medium | Quantity |
|---|---|---|---|
| Great Lakes Chemical Corp. | Decabrom | Sediment | 19,000 µg/Kg |
| | Bisphenol A | Sediment | 22,000 µg/Kg |
| | Bisphenol A | Soil | 150,000 µg/Kg |
| | Decabrom | Soil | 25,000 µg/Kg |
| | Pentabromophenol | Soil | 200 µg/Kg |
| | Bisphenol A | Sediment | 330,000 µg/Kg |
| | Decabrom | Sediment | ∿1,000,000 µg/Kg |
| Velsicol Inc. | Tetrabrom | Soil | 118 µg/Kg |
| | Firemaster 680 | Soil | 253 µg/Kg |
| | Tris | Soil | 840 µg/Kg |
| | Tetrabrom | Sediment | 30 µg/Kg |
| | Firemaster 680 | Sediment | 466 µg/Kg |
| | Tris | Sediment | 2,000 µg/Kg |
| El Dorado, AK | Bisphenol A | Human hair | >13 µg/Kg |
| | Decabrom | Human hair | 5 µg/Kg |

## 2.0 INTRODUCTION

Ethylene dibromide is a colorless non-flammable liquid of high density and chloroform-like odor. It is a particularly good solvent for non-polar materials such as gums, waxes and many other organic chemicals,[1] but its major use is as an additive in leaded gasoline. It is miscible with benzene, carbon tetrachloride, ether, alcohols and other non-polar solvents. Its low vapor pressure and slight water solubility suggest that it would tend to be persistent in water and soil in cases where it is released into the environment. The brominated hydrocarbons are less volatile than their chlorine analogs. Ethylene dibromide melts at about 10°C. Ethylene dibromide is commercially produced by reaction of ethylene and bromine.

The compound is generally regarded to be inert at normal temperatures and pressures with slight decomposition resulting from exposure to light.[1] At elevated temperatures, it can be hydrolyzed to ethylene glycol and bromoethanol. When heated to 340-370°C, it decomposes into vinyl bromide and hydrobromic acid. It is considered a useful synthetic intermediate since the terminal halogen atoms are reactive.

Studies indicate that ethylene dibromide is resistant to atmospheric oxidation by peroxides and ozone and a half-life of 100 days or more has been reported.[2] It is generally regarded to be less reactive in the atmosphere than the corresponding alkanes or olefins. Ethylene dibromide has a half-life of ~5-10 days in water; its hydrolysis is favored by acid conditions.[2]

Ethylene dibromide is a major industrial chemical by virtue of its use in leaded motor fuel which accounts for 85% of its demand. Domestic production of the chemical by direct combination of ethylene and bromine totaled 331 million pounds in 1973.[3] As a fuel additive (~0.025% wt/vol) ethylene dibromide serves to scavenge lead oxide residues from combustion chambers of gasoline engines.[3] Lead oxide residues result from the use

of fuels containing tetra-alkyl lead compounds as anti-knock agents. The ethylene dibromide undergoes combustion with fuel. As a consequence of combustion, the bromine content of the chemical is released to the atmosphere as lead bromide through the engine exhaust. As the use of leaded fuel is abandoned, the use of ethylene dibromide in this capacity will probably also be reduced.

Another important use of ethylene dibromide has been as a fumigant for disinfecting fruits, vegetables, food grains and in warehouses.[4] It is also commonly used in conjunction with methyl bromide as a nematicide in tobacco fields where it is injected into the shank of tobacco plant stalks.[5] It also has commonly been used in citrus groves in Florida. Ethylene dibromide may be used by itself or even frequently in combination with fumigants such as carbon disulfide, ethylene dichloride and carbon tetrachloride.[6,7]

Ethylene dibromide is also a useful synthetic intermediate for the synthesis of dyes, pharmaceuticals and other organics, but these applications account for ~5% of its current demand.

Similarly to ethylene dibromide, fumazone and methyl bromide are commonly used to control soil nematodes. Fumazone is a mixed halogenated hydrocarbon, i.e., dibromochloropropane.

Another extremely important area of usage of brominated organics is as fire retardants. Examples of these which are important to this program are TRIS, Decabrom and Firemaster 680. In contrast to ethylene dibromide, methyl bromide or fumazone, these are high molecular weight materials with extremely low vapor pressures and high thermal, biological and chemical stability. For these reasons these chemicals, if present, exhibit a long-term persistence in the environment and would be associated with the condensed phase matrices. Also, gradual accumulation might be anticipated with continued emissions.

The broad overview of this program has been to examine the potential prevalence of chemicals emanating from the bromine industry in the El Dorado and Magnolia, AK areas. The program was concerned with the acquisition of information about the types of chemicals associated with this industry which were in the environment for subsequent studies on their

environmental impact. Although the focus has been on the monitoring of ethylene dibromide (1,2-dibromoethane) and vinyl bromide, other chemicals which might occur were also of prime interest.

The specific aims of this study were to examine environmental matrices surrounding the bromine industry in El Dorado and Magnolia, AK and to identify as much as possible all brominated chemicals resulting from industrial activities. Prior to this study a limited analysis had been conducted in this area for ethylene dibromide. However, other chemicals were not sought. For this reason, whether other brominated chemicals were being released to the environment reamined unknown. It was the objective of this study to acquire a maximum amount of information concerning the potential pollution related to the bromine industry. As part of the broad-based concept, the program was divided into a survey phase under which a limited amount of monitoring was conducted for airborne materials and the chemicals present in the environment were identified. A more in-depth study of these chemicals was to follow by examining all environmental matrices. In the survey study it was the principal objective to establish the types of chemicals associated with the bromine industry which might be released to the environment, while, in the second phase, the purpose was to determine their occurrence and quantities both immediate and distant from the plant sites. Furthermore, the specific aims eventually included determining the potential prevalence and occurrence of brominated chemicals in environmental matrices which might eventually expose local populations. However, it was beyond the scope of this program to establish a direct environmental impact by the identified brominated substances on the local vegetation and human population.

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# 3.0 METHOD DEVELOPMENT AND VALIDATION

## 3.1 INORGANICS IN AMBIENT AIR

### 3.1.1 Chloride/Bromide and Chlorine/Bromine Sampling and Analysis in Ambient Air

The method for collection and analysis of halides and halogens in ambient air was initially specified in the Task request as the Texas Air Control Board Method[1] for chloride and chlorine. The performance of this procedure and several supplementary analytical methods was evaluated in this laboratory for utility in the proposed study.

#### 3.1.1.1 Evaluation of the Impinger Train for the Collection of Halides and Halogens

The impinger train specified by the Texas Air Control Board Method[1] is comprised of a midget impinger containing deionized water (20 ml) followed by an impinger containing 0.005M $NaAsO_2$ in 0.1M NaOH (20 ml). The performance of this collection system had only been evaluated for chloride and chlorine and its performance with respect to bromide/bromine was unknown. Artifacts due to the presence of chlorine or other oxidants may affect the distribution of the various halide species through the impinger train. Thus it was necessary to examine these potential problems and to validate the method prior to its implementation in this program.

The following species were tested for their distribution in the impinger train: HCl, HBr, $Br_2$ and $Cl_2$. Hydrochloric acid and HBr were introduced as aqueous solutions into an empty impinger at the beginning of the train. Volatilization occurred during the course of the experiment. The halogens were introduced by permeation tubes (Metronics Assoc., Inc., Palo Alto, CA). The permeation rates were determined gravimetrically for each tube at the temperature used for the experiments. The results are shown in Table 3.1. The last experiment in the table included the spiking of the deionized water impinger with HBr before initiating the experiment. The effluent from the

Table 3.1. EVALUATION OF HALIDE IMPINGER TRAIN PERFORMANCE

| Halide species | Flow rate (ℓ/min) | Vol. (ℓ) | Midget Impingers (20 ml each) AI[a,b] (% recovery) | AII[a,b] (% recovery) | BI[c] (% recovery) | BII[c] (% recovery) | Overall recovery |
|---|---|---|---|---|---|---|---|
| HCl | 1.9 | 65.6 | 688 ± 48 | <12 | | | |
| HCl | 1.9 | 119 | 3640 ± 56 | <12 | | | 108 |
| HCl | 1.68 | 267 | 725 ± 4 | < 6 | | | |
| HBr | 1.65 | 59.4 | 1176 ± 120 | 12 | | | |
| HBr | 1.63 | 116 | 2392 ± 136 | 12 | | | 89 |
| HBr | 1.98 | 283 | ≤1788<br>1700 | 178<br>164[c] | | | |
| $Cl_2$ | 0.5 | 31.1 | 94 ± 5<br>(84) | - | 32<br>(29) | | 113 |
| $Cl_2$ | 1.62 | 283 | 44 ± 7<br>(14) | - | 274 ± 10<br>(87) | <5<br>(<2) | 101 |
| $Br_2$ | 1.02 | 28.3 | 27 ± 7<br>(54) | - | 18 + 0<br>(40) | - | 97 |
| $Br_2$ | 0.6 | 28.3 | 33 ± 6<br>(43) | - | 35 ± 0<br>(46) | | 89 |
| $Br_2$ | 1.82 | 300 | 61 ± 6<br>(23) | - | 182 ± 0<br>(69) | <5<br>(<2) | 92 |
| $Br_2$ | 1.44 | 302 | 27 ± 6<br>(8) | - | 29 ± 7<br>(85) | 11 ± 1<br>(3) | 96 |
| HBr/ $Cl_2$ | 1.78 | 283 | 24 ± 2[d,e]<br>(6)<br>348 ± 11[f]<br>(108) | | | | |

[a] Analysis by turbidity except where stated otherwise

[b] Impingers contained deionized water

[c] Chloride determined by ion exchange chromatography

[d] Determined by fluorescein fluorescence quench

[e] Bromide determined by ion exchange chromatography

[f] Impinger AI was initially doped with 400 μg HBr

chlorine permeation tube was sampled and the deionized water analyzed by ion exchange chromatography (see Section 3.1.1.2).

3.1.1.2 Analysis of Halides and Halogens

The turbidimetric method of detection of halides in the impinger solutions is one of the more sensitive methods readily available. However, it does not differentiate between chloride and bromide. When this method is used alone, the results must be reported as total halide and in terms of the halide used for calibration (usually chloride). The response is halide-dependent as can be seen from the calibration curves shown in Figure 3.1. By using chloride for calibration purposes, the results will be underestimated by not more than 20% if the sample is pure bromide.

Separation of Chloride and Bromide.--In order to determine the specific halides present in a sample the development of an ion exchange chromatographic separation similar to that described by DeGeiso et al.[2] was undertaken. Following this chromatography, halide detection was made turbidimetrically.

The chromatography described by DeGeiso[2] was miniaturized and the performance evaluated as a function of column length and resin type for five 1 cm diameter columns as indicated in Table 3.2.

Table 3.2. COLUMNS EVALUATED FOR RESOLUTION OF CHLORIDE AND BROMIDE

| Column | Resin Type | Mesh Size | Column Length |
|---|---|---|---|
| 1 | Bio-Rad AG-1 X8 | 100-200 | 4.6 cm |
| 2 | Bio-Rad AG-1 X8 | 100-200 | 6.4 cm |
| 3 | Bio-Rad AG-1 X8 | 100-200 | 10.2 cm |
| 4 | Bio-Rad AG-1 X8 | 100-200 | 13.5 cm |
| 5 | Bio-Rad AG-1 X10 | 200-400 | 8.9 cm |

The resins were converted from the chloride form to the nitrate form using 0.5M $NaNO_3$. After equilibration, 5 ml of a $1.0 \times 10^{-2}$M NaCl solution was then placed on each column and allowed to drain, and the sides of the columns washed with 2 x 1.0 ml portions of deionized water. The column

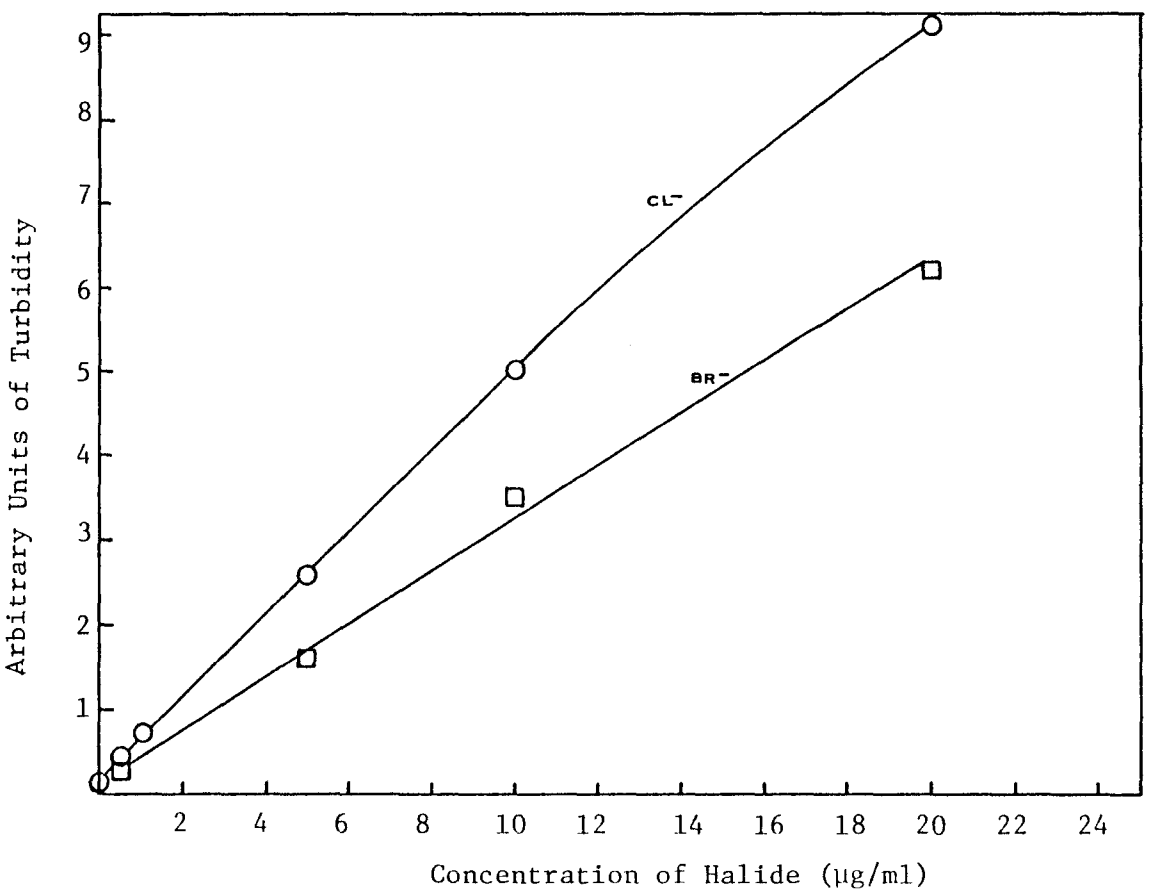


Figure 3.1. Calibration Curves for Turbidimetric Determination of Chloride and Bromide

was eluted with 0.5M $NaNO_3$ at ~1 ml/min and 2 ml fractions were collected until all the chloride was removed. Chloride concentrations were measured with a Beckmann Expandomatic 55-2 pH meter using a Beckmann chloride ion selective electrode.

The void volume of column 1 was small enough to allow breakthrough of the chloride before any of the 0.5M $NaNO_3$ eluant was passed through the column. For columns 2-5, a longer length provided a greater retention of the chloride on the column, but with only a very minor increase in peak broadness (10 ml peak width for column 2 vs. 12 ml peak width for column 4). Work proceeded with columns 2 and 3, which required less time and eluant per analysis.

The procedure above was repeated for columns 2 and 3 using 5 ml of a $1 \times 10^{-2}$M NaBr solution in 0.5M $NaNO_3$ and washing with 2 x 1.0 ml 0.5M $NaNO_3$. Each column was eluted with 0.5M $NaNO_3$ to the point where all the chloride had been removed as determined in the previous experiment. Then 2.0M $NaNO_3$ was passed through the column at the same 1 ml/min rate until all the bromide had been removed. Two ml fractions were collected. The bromide concentrations were measured in the same manner.

It was apparent that the use of the initial eluant, 0.5M $NaNO_3$, as the medium for application of the sample resulted in premature elution of bromide and extreme band broadening. Since adding $NaNO_3$ to the sample represents one additional step this approach was deleted from further studies.

Next to be evaluated was deionized water as the sample medium on column 3. The procedure was identical to that described above, except that the 5 ml aliquot first placed on the column was both $1 \times 10^{-2}$M NaCl and $1.0 \times 10^{-2}$M NaBr. The column sides were washed with 2 x 1.0 ml of deionized water, not 0.5M $NaNO_3$.

The bromide ion on this 10.2 cm long column began to elute just prior to changing $NaNO_3$ concentrations (see Figure 3.2). Baseline resolution was not quite attained. For this reason it was decided to lengthen the column to 15 cm.

Two impinger solutions, deionized water and 0.1M NaOH-0.005M $NaAsO_2$, were evaluated where both contained $10^{-2}$M NaCl and $10^{-2}$M NaBr. Two newly

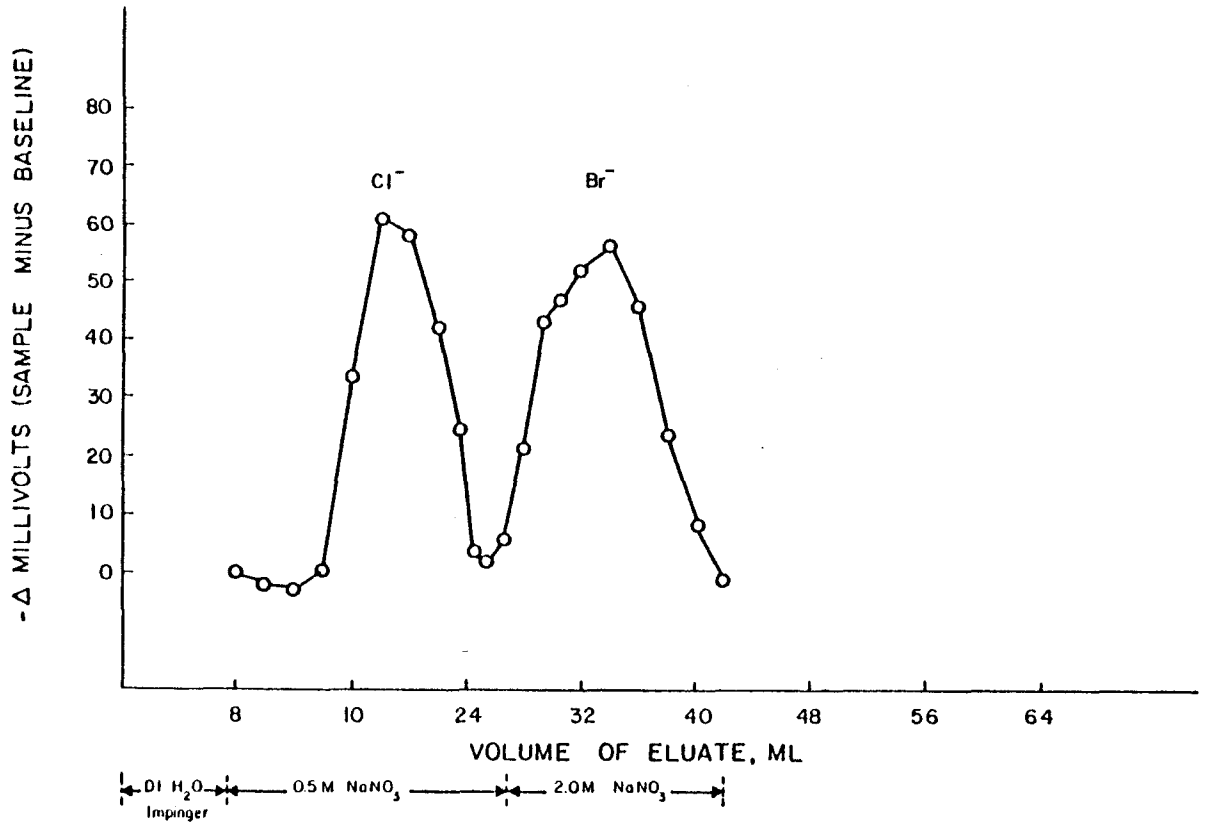


Figure 3.2. Anion exchange chromatography of $Cl^-$ and $Br.^-$ AG-1 X8
Column: 1 cm i.d. x 10.2 cm
Concentration: $10^{-2}$M

prepared AG-1 X10 columns 15 cm in length were used. Halide concentrations of each fraction were measured turbidimetrically.[1] The Texas Air Control Board Method was used with the reagent volumes reduced by 1/4 to accommodate 2 ml samples. Examples of the chromatograms obtained are shown in Figures 3.2 and 3.3 and water baseline is shown in Figure 3.4. The greatest difference in the elution pattern using the two different impinger solutions was the amount of chloride recovered from each column (see Table 3.3).

Table 3.3. RECOVERIES OF CHLORIDE AND BROMIDE FROM IMPINGER SOLUTIONS

| Impinger Solution | % Recovery $Cl^-$ | % Recovery $Br^-$ |
|---|---|---|
| Deionized water | ∿50 | ∿20 |
| 0.005M $NaAsO_2$-0.1M NaOH | ∿180 | ∿20 |

A contributing factor to the amount of chloride recovered using the arsenite solution may have been the use of a prepared 0.1M NaOH solution with an unspecified chloride content (contamination). Subsequently all solutions were prepared using NaOH electrolytic pellets with a maximum chloride contaminant of .003% which corresponds to 0.12 μg/ml in the impinger solution.

A thorough assessment of the halide recoveries using ten 1-cm diameter columns of Bio-Rad AG-1 X10 (100-200 mesh) equilibrated with 0.5M $NaNO_2$ was made. Each column was 15 cm in length. Because of problems with poor recovery encountered in previous work, all of these columns were pre-equilibrated with 15 ml of solution of $10^{-2}$M chloride and $10^{-2}$M bromide in $H_2O$. The 5 ml of halide solution was drained to the top of the column, washed with 1 ml of deionized water twice, eluted with 26 ml of 0.5M $NaNO_3$, then 15 ml of 2.0M $NaNO_3$, as if an analysis were to be performed. Each column was then re-equilibrated with 0.5M $NaNO_3$ by passing 100 ml of the eluant through the column.

Five ml of the following solutions were placed on each column as indicated in Table 3.4.

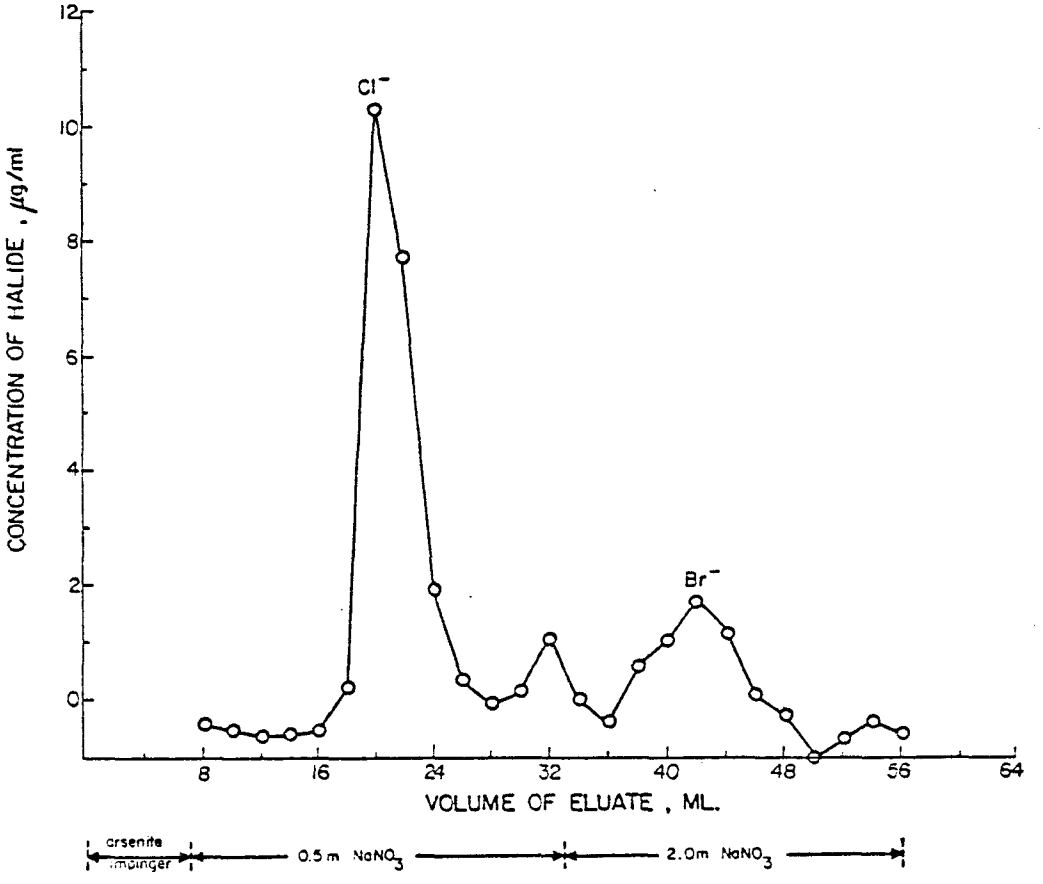


Figure 3.3. Anion exchange chromatography on AG-1 XI - Arsenite impinger solution containing chloride and bromide.
Column: 1 cm i.d. x 15 cm
Concentration: $10^{-4}$M

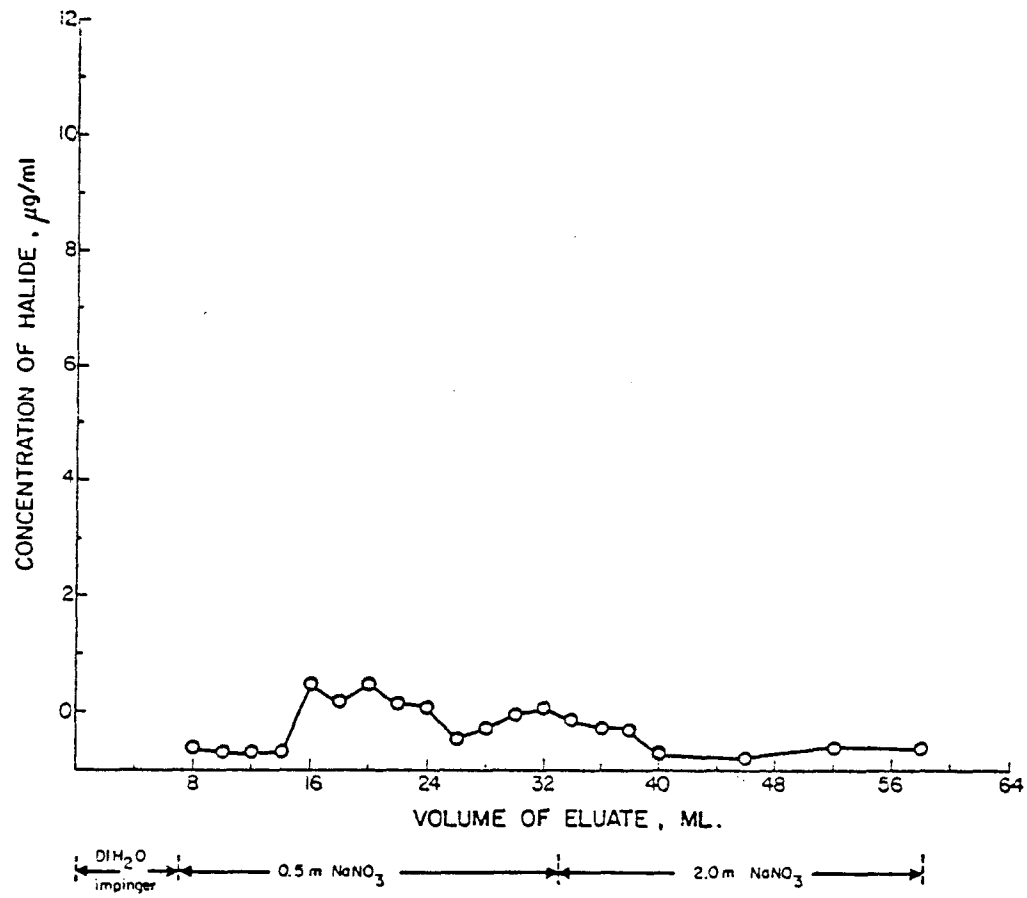


Figure 3.4. Anion exchange chromatography on AG-1 X8 - Water Blank. Column: 1 cm i.d. x 15 cm

For each column, the procedure was to place the 5 ml of halide solution on the column and allow it to drain at 1 ml/min to the top of the column. The sides were then washed with 1 ml of deionized water twice. Twelve ml of 0.5M $NaNO_3$ were put through the column and discarded. Another 12 ml of

Table 3.4. SOLUTIONS APPLIED TO ION EXCHANGE COLUMNS

| Sample No. | Chloride (M) | Bromide (M) |
|---|---|---|
| 1 & 8 | $10^{-2}$ | - |
| 2 & 9 | - | $10^{-2}$ |
| 3 & 10 | $10^{-4}$ | - |
| 4 & 11 | - | $10^{-4}$ |
| 5 & 12 | $10^{-2}$ | $10^{-4}$ |
| 6 & 13 | $10^{-4}$ | $10^{-2}$ |
| 7 & 14 | - | - |

0.5M $NaNO_3$ were put through the column, and this was saved for analysis, as it contained the chloride fraction. Then, two more ml of this same eluant was run through and this was again discarded. The eluant was changed to 2.0M $NaNO_3$, and 15 ml was passed through the column and saved. This fraction contained the bromide. The column was then re-equilibrated with 0.5M $NaNO_3$ and was ready for further use.

Analysis was done as previously described[1] using the turbidimetric method.

After work was completed with the halides in deionized water, the same array of solutions was prepared using halides made up in 0.1M NaOH and 0.005M $NaAsO_2$, the halogen impinger solution. The procedure described above was followed exactly. The results are reported in Table 3.5.

The recoveries at low concentration were low and the lowest concentration tested did not approach the required level for environmental samples.

Table 3.5. RECOVERIES OF CHLORIDE AND BROMIDE FROM ION-EXCHANGE CHROMATOGRAPHY ON AG-1 X10 (100-200 MESH) 1 x 15 cm COLUMNS

| Sample No. | Chloride | | | Bromide | | |
|---|---|---|---|---|---|---|
| | Added (μg)[a] | Found (μg) | Recovery (%) | Added (μg)[a] | Found (μg) | Recovery (%) |
| 1[a] | 1773 | 940 | 53 | - | 0.05 | - |
| 2[a] | - | -0.05 | - | 3950 | 4050 | 102 |
| 3[a] | 17.7 | 4.3 | 24 | - | -0.04 | - |
| 4[a] | - | 0.03 | - | 39.5 | 42.7 | 108 |
| 5[a] | 1773 | 1060 | 60 | 39.5 | 21.3 | 54 |
| 6[a] | 17.7 | 4.7 | 26 | 3950 | 3750 | 95 |
| 7[a] | - | 0.45 | - | - | 0.10 | - |
| 8[b] | 1773 | 1139 | 64 | - | 0.10 | - |
| 9[b] | - | 1.1 | - | 3950 | 3675 | 93 |
| 10[b] | 17.7 | 19.5 | 109 | - | 0.3 | - |
| 11[b] | - | 12.1 | - | 39.5 | 11.2 | 29 |
| 12[b] | 1773 | 950 | 54 | 39.5 | 18.0 | 45 |
| 13[b] | 17.7 | 16.2 | 92 | 3950 | 3675 | 93 |
| 14[b] | - | 0.54 | - | - | 0.16 | - |

[a]Sample was applied in 5 ml of deionized water

[b]Sample was applied in 5 ml of 0.1M NaOH/0.005M $NaAsO_2$ (impinger solution)

In an effort to improve the recoveries indicated above, new ion exchange chromatographic conditions were investigated. The rationale of the new approach was to increase specific interactions with respect to nonspecific interactions: the first system explored was DEAE Sephadex (Pharmacia, Uppsala, Sweden). The backbone of this ion exchange resin is subject to many fewer nonspecific interactions than the polystyrene-divinylbenzene backbone of the Dowex resins. The benefit of this type of backbone was not realized due to two problems: (1) the DEAE (diethyl-aminoethyl) functional group is weakly basic and as such does not show sufficient discrimination between chloride and bromide, and (2) the resin undergoes extreme volume changes (factors of 2 to 3) with relatively small changes in ionic strength. Another approach to increasing specific to nonspecific adsorption was to continue the use of the polystyrene-divinyl-benzene type (AG-1 X10, 100/200 mesh), but to decrease the amount and use less severe conditions for developing the chromatogram. The column diameter was reduced from 1.0 cm to 0.4 cm and the length from 15 cm to 7 cm. The resin in prepared columns was converted to the nitrate form and equilibrated with deionized water. The sample was applied in 4 ml of deionized water and washed on with 0.5 ml water. The elution was begun with 0.1M $NaNO_3$ and changed to 0.5M $NaNO_3$ after the chloride had eluted (see Figure 3.5). Using the profile in Figure 3.5 a standard elution scheme was adopted: 4 ml 0.1M $NaNO_3$ for chloride and 2 ml 0.5M $NaNO_3$ for bromide. An evaluation of recoveries over a range of concentrations was instituted. The results are shown in Table 3.6. All of these samples were applied in deionized water. Certain difficulties are encountered in 0.1M NaOH/0.005M $NaAsO_2$ impinger solution. The presence of such a high anion concentration even through it is the weakly adsorbing hydroxide ion diminishes the binding of the halides during sample application and causes premature elution of the chloride and bromide peaks.

Bromide by Fluorescein Fluorescence Quench.--The method of Axelrod, Bonelli and Lodge[3] was evaluated for the analysis of impinger solutions containing bromide. The method employs hydrogen peroxide for the oxidation of bromide in an acidic medium (glacial acetic acid) to give elemental bromine. The bromine substitutes on the phenolic rings of the fluorescent

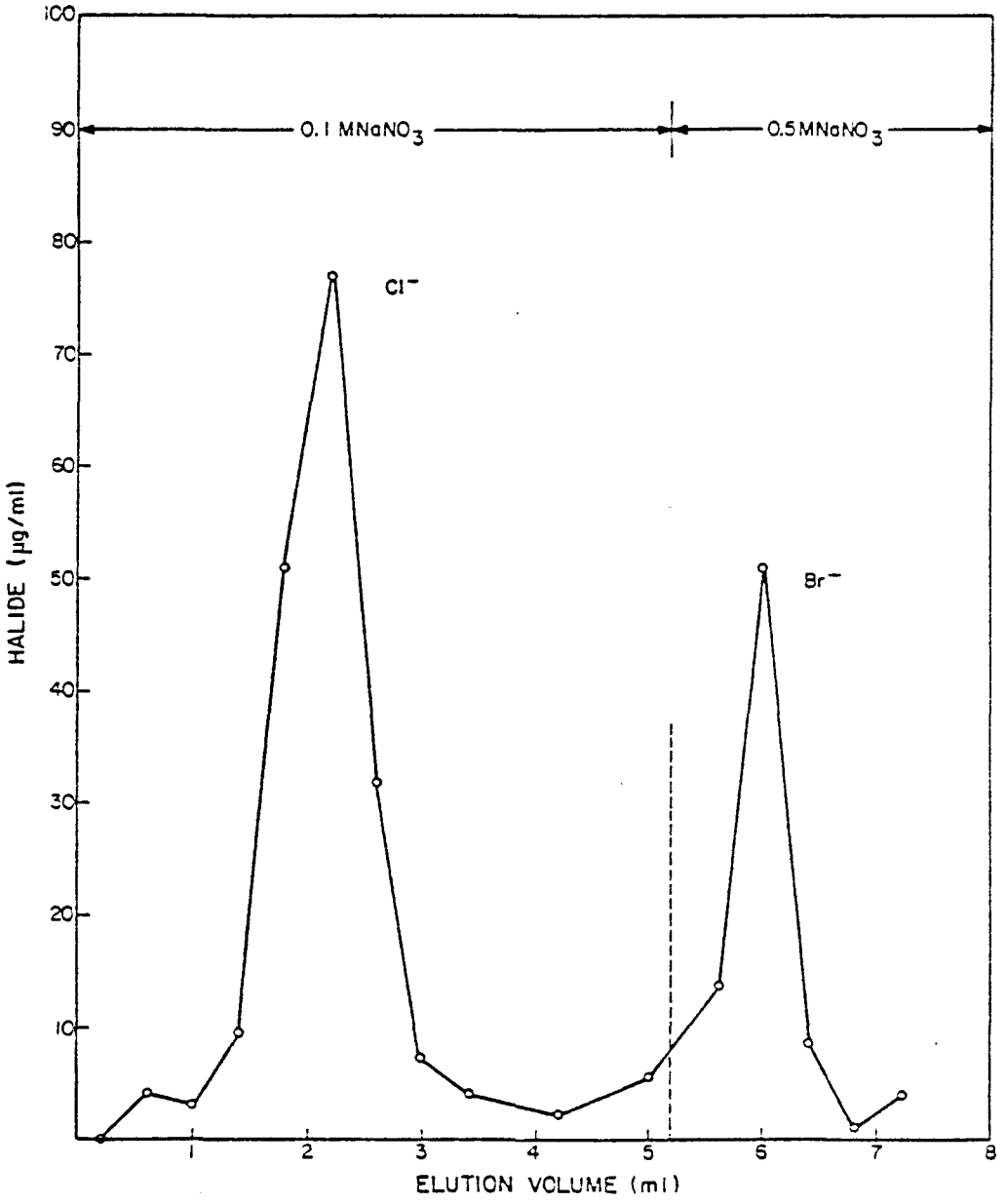


Figure 3.5. Anion exchange chromatography of chloride and bromide ions on AG-1 X10 (100/200 mesh) 4 x 70 mm column.

Table 3.6. RECOVERIES OF CHLORIDE AND BROMIDE FROM ION-EXCHANGE CHROMATOGRAPHY ON AG-1 X10 (100-200 MESH) 4 x 70 mm COLUMNS

| Sample No. | Chloride | | | Bromide | | |
|---|---|---|---|---|---|---|
| | added (μg)[a] | found (μg) | Recovery (%) | added (μg)[a] | found (μg) | Recovery (%) |
| 1 | 500 | 570 ± 60 | 114 ± 12 | 0 | 17.8 ± 3 | - |
| 2 | 400 | 336[b] | 84[b] | 0 | - | - |
| 3 | 400 | 397 | 99.2 | 0 | 30.1 | - |
| 4 | 0 | 1.2 | - | 400 | 401 ± 2 | 100 ± 0.5 |
| 5 | 0 | 16.8 | - | 400 | - | - |
| 6 | 40 | - | - | 40 | 40.8 ± 1.2 | 102 ± 2 |
| 7 | 40 | 34.4[b] | 86[b] | 0 | - | - |
| 8 | 40 | 33.6 | 84 | 40 | 31.0 | 77.6 |
| 9 | 4 | - | - | 4 | 4.0 ± 0.2 | 100 ± 5 |
| 10 | 4 | 1.6[b] | 40[b] | 0 | - | - |
| 11 | 4 | 4.0 | 100 | 4 | 6.2 | 155 |
| 12 | 0 | 1.1 ± 0.1 | - | 0 | 1.5 ± 0.2 | - |
| 13 | 0 | <0.8[b] | - | 0 | - | - |
| 14 | 0 | <0.8 | - | 0 | - | - |

[a]Sample was applied in 4.0 ml deionized water

[b]Collected fractions stored 48 hrs before analysis

dye, fluorescein, to yield a nonfluorescent eosin-type product. The decrease in fluorescence is measured. This procedure works well on standards in deionized water. The above authors[3] have evaluated potential interferences and found 5% or less interference due to 100 fold excess of $SO_3^{2-}$, $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$, $Fe^{3+}$, $Cu^{2+}$, $Pb^{2+}$, HCOOH, $CH_3COCH_3$, HCOOH and $CH_3CH_2OH$. Chloride does not interfere at $10^5$ molar excess over bromide. Greater than 5% error was found when $I^-$, $NO_2^-$, $Fe^{2+}$ were present in 100 fold excess on a molar basis. Brominated organics may interfere.

Suitable conditions for the analysis of bromide in the 0.1M NaOH/ 0.005M $NaAsO_2$ impinger solution were not found. Neutralization with nitric acid and addition of 30% hydrogen peroxide before the addition of the fluorescein reagent gave no response to bromide. Some response (~70%) was observed when the bromide in impinger solution was added to the peroxide and followed immediately by the fluorescein reagent. This response is not quantitative and results would not be reliable. A cation exchange resin AG-50W-X8 was used in an attempt to neutralize the sample, but bromide recoveries from this resin were low at the 1 ppm level tested.

The final analytical protocol which was adopted for this study is given in Appendix A.

3.1.2 Determination of Inorganic Fluoride in Ambient Air

The sampling and analytical method for inorganic fluoride was specified in the research request as that adopted by the Texas State Department of Health, Air Pollution Control Board.[1]

The fluoride ion selective electrode (Orion Model 96-09 combination fluoride electrode) was evaluated over the range 1.27 to 19 ppm and found to give a linear response. Initially the samples were evaluated directly without distillation. If significant fluoride concentrations were found, then verification would have been made using the steam distillation procedure.

The final analytical protocol for collection and analysis of fluoride in ambient air which was adopted for this study is given in Appendix A.

3.1.3 Acid Mist Analysis in Ambient Air

The "acid mist" procedure[4] was verified by confirming the sensitivity of the titration to <1 μg as $H_2SO_4$. The residual acid on the extracted cellulose discs was <1 μg/disc as $H_2SO_4$.

The analytical protocol for collection and analysis of acid mist which was adopted for this research program is given in Appendix A.

3.2 Brominated Organics in Environmental Media

3.2.1 Air

3.2.1.1 Volatile Organics

Determination of Breakthrough Volumes.--The techniques for determining breakthrough volumes on solid sorbents have previously been described.[5,6] The breakthrough volumes for several halogenated compounds which had been subsequently identified in ambient air samples taken from El Dorado and Magnolia, AK were determined. It is necessary to determine the breakthrough volumes if one wishes to subsequently quantify the components identified in ambient air.

The breakthrough volumes for several brominated compounds on Tenax GC were determined at several temperatures ranging from 10-38°C (50-100°F). These results are shown in Table 3.7. Since the ambient air temperature was carefully determined during the field sampling, then the breakthrough volumes could be used for the quantification of the compounds in the samples. The breakthrough volumes were estimated at several different temperatures in the event that ambient air temperature fluctuations were experienced during sampling.

It is evident from these data (Table 3.7) that the breakthrough volumes for methyl chloride, methyl bromide, vinyl chloride and vinyl bromide are too low for utilizing this sorbent for their collection and quantification.[5] If methyl chloride, methyl bromide or vinyl bromide are detected on Tenax GC cartridges, the concentrations would be at rather elevated levels. These halogenated hydrocarbons are more suitably quantified either directly by gas chromatography with electron capture detection, or by their entrapment on carbon cartridges and subsequently detection by mass fragmentography (Ref. 5, Section E, Appendix A).

Table 3.7. ESTIMATED BREAKTHROUGH VOLUMES FOR SEVERAL HALOGENATED COMPOUNDS ON TENAX GC

| Compound | BP (°C) | Ambient Temperatures | | | | | |
|---|---|---|---|---|---|---|---|
| | | 50°F (10°C) | 60°F (15°C) | 70°F (21°C) | 80°F (27°C) | 90°F (32°C) | 100°F (38°C) |
| Allyl bromide* | 70 | 37 | 27 | 20 | 15 | 11 | 8 |
| Bromobenzene | 155 | 2,144 | 1,521 | 1,079 | 764 | 542 | 384 |
| Bromodichloromethane* | 89-90 | 138 | 102 | 75 | 54 | 40 | 29 |
| Bromoform | 149 | 507 | 386 | 294 | 224 | 171 | 130 |
| 1-Bromopropane* | 70 | 128 | 94 | 70 | 51 | 38 | 28 |
| 1-Chloro-2-bromoethane* | 107 | 920 | 676 | 500 | 367 | 270 | 198 |
| 1-Chloro-3-bromopropane* | 141 | 1,122 | 856 | 656 | 500 | 382 | 291 |
| 1-Chloro-2,3-dibromopropane* | - | 1,460 | 1,114 | 850 | 649 | 496 | 378 |
| 1,1-Dibromo-2-chloropropane* | - | 1,593 | 1,216 | 928 | - | 510 | 413 |
| Dibromochloromethane* | 135 | 263 | 200 | 153 | 117 | 89 | 68 |
| 1,2-Dibromoethane | 131 | 348 | 255 | 188 | 138 | 101 | 74 |
| 1,2-Dibromopropane* | 141 | 1,142 | 871 | 665 | 508 | 387 | 296 |
| Methyl chloride | -24 | 0.8 | 0.6 | 0.5 | 0.4 | 0.3 | 0.25 |
| Methyl bromide | 3.59 | 3 | 2 | 2 | 1 | 1 | 0.9 |
| Vinyl chloride | 13 | 2 | 1.5 | 1.25 | 1.0 | 0.8 | 0.6 |
| Vinyl bromide | 16 | 8 | 6 | 4 | 3 | 2 | 1.8 |

(continued)

Table 3.7 (cont'd)

| Compound | BP (°C) | Ambient Temperatures | | | | | |
|---|---|---|---|---|---|---|---|
| | | 50°F (10°C) | 60°F (15°C) | 70°F (21°C) | 80°F (27°C) | 90°F (32°C) | 100°F (38°C) |
| Epichlorohydrin (1-chloro-2,3-epoxypropane) | 116 | 200 | 144 | 104 | 74 | 54 | 39 |
| Epibromohydrin (1-bromo-2,3-epoxypropane) | 134-6 | 678 | 479 | 337 | 237 | 168 | 118 |
| Trimethylene chlorobromide | 142-5 | 1,130 | 927 | 656 | 465 | 329 | 233 |
| Bromine | 58.7 | 0.032 | 0.028 | 0.024 | 0.020 | 0.016 | 0.012 |
| Chlorine | - | 0.030 | 0.025 | 0.020 | 0.015 | 0.012 | 0.010 |
| Iodine | 184.3 | 0.032 | 0.028 | 0.024 | 0.020 | 0.016 | 0.012 |
| Water | 100 | 0.060 | 0.050 | 0.040 | 0.030 | 0.010 | 0.002 |

*Values estimated on mathematical extrapolation from slop of linear regression in a homologous series and boiling point of compound.

Also, the breakthrough volumes for bromine, chlorine, iodine and water are given. These inorganic gases have extremely low breakthrough volumes. This is an important feature, for if they accumulate on the sorbent, then potential in situ reactions could occur between the inorganic gases, olefinic and aromatic compounds.

Determination of Relative Molar Response Factors for Quantification.-- The relative molar response (RMR) values were determined for several halogenated compounds using unique ions for each compound. The methods employed for determining the RMR values have previously been described.[5] These results are given in Table 3.8. In many cases, the RMR value for a second ion was determined in the event it would be necessary to establish the identity of the halogenated hydrocarbon by the theoretical ion cluster intensity ratio. The RMR for the second ion was calculated using authentic compounds. Thus each compound can be quantitated in the event that the first ion is not sufficiently specific for that substance.

These data (Table 3.8) also indicate that as the degree of halogenation increases, so does the RMR value, and thus a decrease in sensitivity for the compound is experienced by the mass spectrometer.

The limits of detection (LOD) for several halogenated hydrocarbons utilizing the technique of glass capillary gc/ms/comp are given in Table 3.9. The LOD's are estimated values using an average sampling volume of 150 ℓ at an ambient temperature of 27°C. The limit of detection is based upon either the breakthrough volume or volume of air sampled, whichever is less, and the measured RMR value. As shown in Table 3.9, the limits of detection for the halogenated hydrocarbons of interest range, from 0.2-2.0 $ng/m^3$ (sub-ppt). Table 3.9 thus provided a guideline as to the anticipated sensitivity of the overall analytical technique and was the basis for establishing the non-detectable levels. For the purpose of quantification, generally 10-20 times the amounts listed in this table were required.

The analytical protocol for collection and analysis of volatile brominated organics which was adopted for this research program is given in Appendix A.

Table 3.8. RELATIVE MOLAR RESPONSE VALUES FOR SEVERAL HALOGENATED COMPOUNDS BASED UPON SELECTED IONS

| Compound | M.W. | R.R.T | 1st Ion | | 2nd Ion | |
|---|---|---|---|---|---|---|
| | | | m/e (I) | RMR | m/e (I) | RMR |
| Allyl bromide | 120 | 1.167 | 120 (25) | 3.25 | 122 (25) | 3.25 |
| Bromobenzene | 156 | 2.771 | 156 (8) | 2.18 | 158 ( ) | - |
| Bromodichloromethane | 162 | 1.389 | 129 (12) | 1.54 | 85 (60) | 6.16 |
| Bromoform | 250 | 2.361 | 173 (100) | 2.75 | 252 (10) | 0.30 |
| 1- or 2-Bromopropane | 122 | 1.085 | 124 (20) | 3.25 | 122 (20) | 3.25 |
| 1-Chloro-2-bromoethane | 142 | 1.657 | 144 (15) | 1.12 | 63 (100) | 7.39 |
| 1-Chloro-3-bromopropane | 156 | 2.278 | 158 (60) | 4.48 | 160 (120) | 1.12 |
| 1-Chloro-2,3-dibromopropane | 234 | 3.472 | 157 (100) | 9.46 | 159 (25) | 2.37 |
| 1,1-Dibromo-2-chloropropane | 234 | 3.416 | 157 (100) | 9.46 | 159 (25) | 2.37 |
| Dibromochloromethane | 206 | - | 129 (100) | 6.53 | 208 (10) | 0.70 |
| 1,2-Dibromoethane | 186 | 2.000 | 109 (95) | 3.34 | 188 (2) | 0.50 |
| 1,2- or 1,3-Dibromopropane | 200 | 2.250 | 123 (99) | 3.37 | 202 (65) | 2.21 |
| Methyl chloride | 50 | 0.628 | 50 ( ) | 1.7 | 52 ( ) | 0.66 |
| Methyl bromide | 94 | 0.888 | 94 ( ) | 1.9 | 81 ( ) | - |
| Vinyl bromide | 106 | 0.667 | 108 (75) | 2.2 | 110 (10) | 0.30 |

Table 3.9. ESTIMATED LIMITS OF DETECTION FOR SEVERAL HALOGENATED HYDROCARBONS

| Compound | Fragment ion (1st) | LOD[a] ng/m$^3$ |
|---|---|---|
| Allyl bromide | 120 | 1.6 |
| Bromobenzene | 156 | 0.6 |
| Bromodichloromethane | 129 | 2.0 |
| Bromoform | 173 | 0.8 |
| 1-Bromopropane | 124 | 0.9 |
| 1-Chloro-2-bromoethane | 144 | 0.2 |
| 1-Chloro-3-bromopropane | 158 | 0.5 |
| 1-Chloro-2,3-dibromopropane | 157 | 0.4 |
| 1,1-Dibromo-2-chloropropane | 157 | 0.4 |
| Dibromochloromethane | 129 | 0.5 |
| 1,2-Dibromoethane | 109 | 0.7 |
| 1,2-Dibromopropane | 123 | 0.5 |

[a]Assuming an average sampling volume of 150 ℓ and 27°C which was experienced during the Phase I survey study.

Analysis of Ethylene in the Presence of Other Gases.--During the preliminary phases of this study an analytical protocol was developed for the gas chromatographic analysis of ethylene in ambient air. To effect separation of ethylene from other atmospheric hydrocarbons (e.g., ethane), the air samples were chromatographed at -78°C on an OV-101 glass SCOT capillary. Maintenance of a -78°C oven temperature was accomplished by placing small blocks of dry ice in and above the oven. This successfully lowered the oven temperature, but also resulted in the accumulation of considerable water vapor condensate in the oven and surrounding electronic components. Consequently, repeated instrument failure resulted.

Efforts to minimize condensation in the instrument centered on introduction of a dry, cold gas stream and maintenance of adequate ventilation in the oven. Initially this was accomplished by blowing a stream of nitrogen gas through a liquid nitrogen-cooled cold trap and ultimately into the gas chromatograph. This design proved troublesome as the gas line tended to freeze in the cold trap, causing the flow to be erratic. This system was modified by introducing nitrogen gas into an aspirator fixed to a metal liquid nitrogen dewar, thereby spraying a gentle, fine mist of liquid nitrogen into the oven. This technique was employed for maintaining a cryogenic oven temperature during the ethylene analyses. Difficulty was encountered in eliminating leaks from the column connections since sealed connections at 20°C tended to leak at temperatures below -60°C. Consequently, the oven was operated at -60°C with the temperature controlled by the nitrogen flow and monitored with a calibrated iron-constantan thermocouple connected with reversed polarity.

The ambient air samples, contained in stainless steel, septum-capped bottles, were introduced into a 1.7 mm i.d. x 842 mm length stainless steel gas sampling loop with a gas syringe. A minimum of 10 ml of sample was passed through the loop to insure that no contamination from previous samples would occur. The sample was injected onto a 60 m glass SCOT 1% OV-101 capillary column by changing the position of a six-way valve to direct the carrier gas (~5 ml/min) through the sampling loop. The valve and oven injection port temperatures were 170 and 0°C, respectively. Injection was sustained until the ethylene had eluted from the capillary

column (approximately 2 min). Detection was achieved with a flame ionization detector operated at 150°C. Standard ethylene-nitrogen mixtures, contained in Tedlar bags, were injected every third sample for quantitation.

The final analytical protocol for collection and analysis of ethylene which was adopted for this study is given in Appendix A.

3.2.1.2 Semi-volatile Organics Associated with Particulates

Collection of Tris-(2,3-dibromopropyl)phosphate (TRIS) on Glass Fiber and Cellulose Filters -- The sampling method used for the collection of TRIS is given in Appendix A. The procedure was developed under a separate Task Order of this contract.[7] Two types of filter material, glass fiber and cellulose, were field-tested during preliminary sampling in Arkansas and the glass fiber was found to be definitely superior. Two Hi-Vol samplers in parallel were used - one fitted with cellulose filters and the other with glass fiber filters. This parallel sampling demonstrated several reasons for the choice of glass fiber.

Gas-Liquid Chromatography-Electron Capture (GLC/ECD) and Gas-Liquid Chromatography-Mass Spectrometry-Computer (GLC/MS/COMP) Analysis for TRIS -- The analytical methods used are given in Appendix A. The method was developed under a separate Task Order of this contract.[7] The approach is based upon the use of a short glass column (0.2 cm i.d. x 42 cm) packed with a nonpolar phase. The same type columns were used for both GLC/ECD and GLC/MS/COMP analyses. Three liquid phases have been used, SE-30, OV-101 and OV-17 with benzyltriphenylphosphonium chloride as a surfactant. Detection limits upon GLC/MS/COMP were very poor; hence, multiple ion detection was used almost exclusively. In this method the mass filter is stepped through discrete ion masses repetitively instead of scanning the entire mass range. The selected ions are detected for proportionately more of the total time thereby improving signal-to-noise for those ions. Confirmation of identity when required was accomplished either by monitoring several selected ions and comparing ion intensities with standards of TRIS or by direct probe MS.

Other Semi-volatile Organics Associated with Particulates -- The sampling and solvent extraction procedures developed for TRIS were used to screen for the presence of other brominated compounds. Several compounds

were identified in the particulate samples by the use of direct probe mass spectrometry. Quantitation, however, requires the combination of GLC/MS/COMP analysis. In order to improve the sensitivity of the Finnigan 3300 for these high molecular weight compounds, multiple ion detection was used. Table 3.10 lists these compounds, the ions used and the instrumental limit of detection. Other factors such as collection efficiency and recovery also affect these values. First of all, the flow rate through the cellulose filter was 60% of that through the glass fiber filters and, secondly, visual inspection of the filters revealed considerable breakthrough of the particulate through the cellulose. The unexposed side of the cellulose filter was colored and a glass fiber filter which was used to support the cellulose was darkened. Mechanical strength was also a problem. The breakthrough problem was further evidenced by consistently lower values for TRIS and other brominated compounds in the cellulose filters (see 4.2.3.2). On this basis glass fiber filters were used in all subsequent sampling.

Other Analytical Methods -- Thin layer chromatography (TLC) may be used for many of the compounds which are of interest here for either a qualitative or quantitative analysis. These techniques have been used here primarily as screening methods to supplement other analytical methods. For some brominated compounds such as TRIS, the detection system reported by Weichsel[8] is useful. This method is based upon the reaction of fluorescein with elemental bromine released through peroxide oxidation. An evaluation in our laboratory of this TLC detection system has indicated that semi-quantitative results may be obtained using the technique of fluorescence quench thin-layer scanning. The basis for this detection method is the conversion of fluorescein impregnated in the thin-layer to the brominated analog, eosin. The resulting loss of fluorescence is then detected by scanning the thin-layer in the reflectance mode.[8] An example of a chromatogram obtained in this manner is shown in Figure 3.6. This detection system is highly specific for brominated compounds. However, the limit of detection is of the order of 0.5 μg/spot. Some improvement in sensitivity may be obtained by optimizing the chromatographic conditions. Basic elements of the reaction are acidic medium (glacial acetic acid), an

Table 3.10. LIMITS OF DETECTION OF BROMINATED ORGANICS IN AIR

| Compound | Ions (m/e) | Limit of Detection[a,b] ($ng/m^3$) |
|---|---|---|
| TRIS[c] | 417*, 419*, 337 | 614 |
| Tetrabrom[d] | 529*, 531* | 10 |
| Pentabromophenol | 488*, 490* | 25 |
| Firemaster 680[e] | 357*, 688, 690 | 10, 90[f] |
| Decabrom[g] | 800*, 802, 804 | 20-100[h] |

[a]Octachloronaphthalene was used as an external standard (m/e 404).

[b]These limits of detection are computed based upon the extract analyzed representing 2 $ml/m^3$ air sampled according to the procedure in Appendix A.

[c]Tris-(2,3-dibromopropyl)phosphate.

[d]2,2-Bis(dibromo-4-hydroxyphenyl)propane.

[e]1,2-Bis(2,4,6-tribromophenoxy)ethane.

[f]This value is based on mass 688 which was required due to interferences with mass 357.

[g]Confirmed from full scan mass spectrum.

[h]Substantial day-to-day variation of sensitivity to Decabrom.

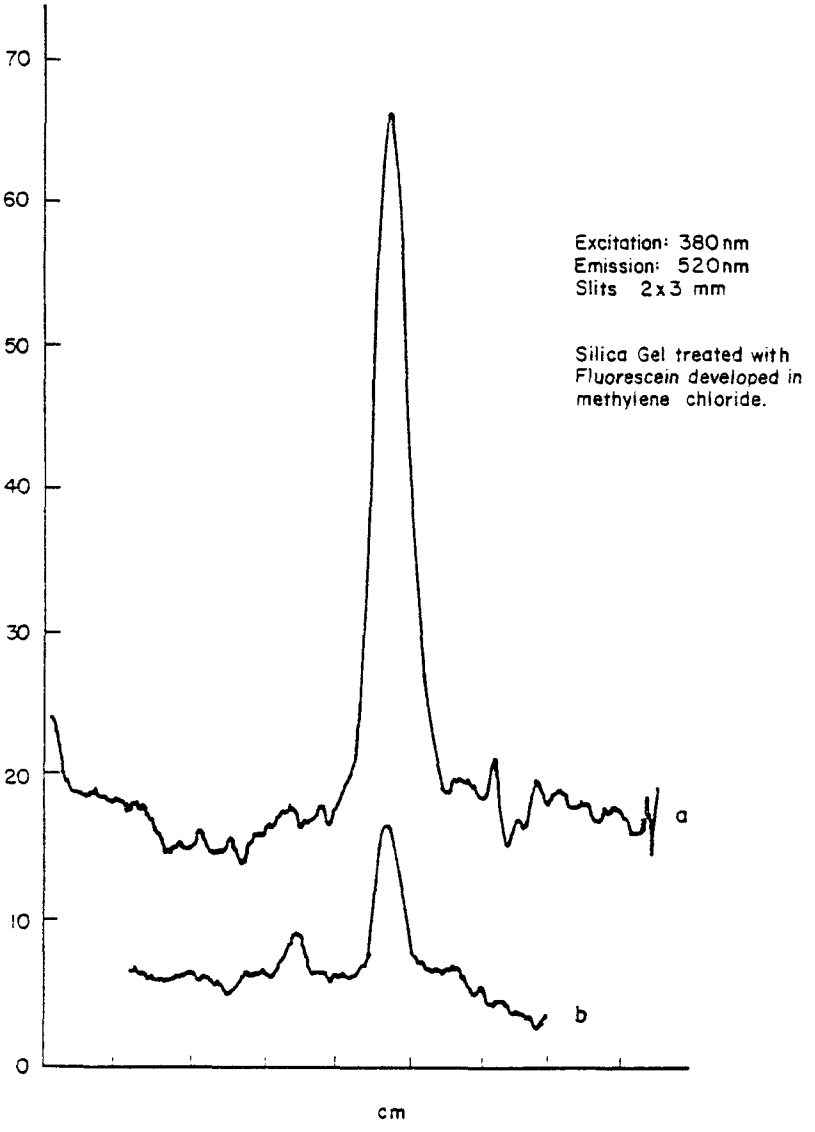


Figure 3.6. Thin layer chromatogram of tris(2,3-dibromopropyl)-phosphate on fluorescein impregnated silica gel; solvent: methylene chloride. Scan in fluorescence quench mode. a. 3.7 μg TRIS, b. 0.44 μg TRIS.

oxidant [either $H_2O_2$ or chloramine-T (N-chloro-p-toluene-sulfonamide)-sodium] and fluorescein. Thin-layer parameters for several semi-volatile brominated organics used throughout the program are given in Table 3.11.

Table 3.11. THIN-LAYER PARAMETERS FOR SEMI-VOLATILE BROMINATED ORGANICS ON SILICA GEL

| Compound | Solvent | $R_f$ |
|---|---|---|
| Decabrom | Hexane/Toluene (95:05) | 0.7 |
| 2,4,6-Tribromophenol | Toluene | 0.65 |
| Pentabromophenol | Toluene | 0.5 |
| Tetrabrom | Toluene | 0.4 |
| 4-Bromophenol | Toluene | 0.2 |
| Firemaster 680 | Hexane/Toluene (60/40) | 0.6 |

### 3.2.2 Water and Sediment

#### 3.2.2.1 Volatile Brominated Organics

An adaptation and validation of the Volatile Organic Analysis (VOA) method was employed for the more volatile brominated compounds.

Recovery studies were performed to determine the efficiency of the purge procedure in removing various volatile organic species at approximately the 1 μg level from water and sediment. The final analytical protocols adopted are presented in Appendix A. Samples were spiked by the addition of 5 μl of a standard mixture containing ~200 ng each of six halogenated compounds in methanol. The loaded cartridges were analyzed by GC/FID on a silanized OV-101 SCOT column (0.36 mm i.d. x 100 m length) using helium carrier at 2 ml/min. The sample was injected by thermal desorption with purging of the compounds loaded on the Tenax GC cartridge into a liquid nitrogen-cooled nickel-capillary trap. The condensed vapors are then introduced onto the high resolution gas chromatographic column by raising the temperature of the nickel capillary trap. The analytical conditions are summarized in Table 3.12. The results are given in Table 3.13.

Table 3.12. CONDITIONS FOR ANALYSIS OF TENAX CARTRIDGES FROM VOA PURGE -- RECOVERY STUDIES

| | |
|---|---|
| **GC Conditions -** | |
| Column: | OV-101 (2.5%) SCOT column (0.36 mm i.d.) |
| Column Temperature: | Programmed from 30° to 220°C at 4°/min |
| Detector: | FID |
| Carrier gas: | Helium |
| Flow rate: | 2 ml/min |
| **Thermal Desorption Conditions -** | |
| Desorption temperature: | 270°C |
| Purge gas: | helium |
| Flow rate: | 30 ml/min |
| Purge time: | 5 min |
| Ni capillary temperatures: | -77°C during purge<br>150°C during injection |

Table 3.13. RECOVERY STUDIES - VOA METHOD

| Compound | Amount Spiked (µg) | Medium | Amount Recovered (µg) (1) | (2) | (3) | Average % Recovery | Standard Deviation |
|---|---|---|---|---|---|---|---|
| 1-chloro-1-butene | 0.926 | dist. $H_2O$ | 0.710 | 0.743 | Data | 78.5 | 0.0233 |
| 1,2-dichloroethane | 0.853 | dist. $H_2O$ | 0.739 | 0.654 | Not | 81.6 | 0.0601 |
| 1-bromo-2-chloroethane | 1.137 | dist. $H_2O$ | 0.922 | 0.913 | Available- | 80.7 | 0.00636 |
| 1,2-dibromoethane | 2.253 | dist. $H_2O$ | 1.839 | 1.655 | Intrumental | 77.5 | 0.130 |
| bromobenzene | 1.663 | dist. $H_2O$ | 1.435 | 1.927 | Error | 101.8 | 0.347 |
| m-chlorotoluene | 1.400 | dist. $H_2O$ | 1.355 | 1.358 | | 96.9 | 0.00212 |
| 1-chloro-1-butene | 0.880 | stream $H_2O$ | 0.651 | 0.628 | 0.554 | 69.4 | 0.0507 |
| 1,2-dichloroethane | 0.810 | stream $H_2O$ | 0.593 | 0.556 | 0.255 | 57.8 | 0.185 |
| 1-bromo-2-chloroethane | 1.080 | stream $H_2O$ | 1.041 | 1.022 | 1.099 | 96.6 | 0.0401 |
| 1,2-dibromoethane | 2.140 | stream $H_2O$ | 1.969 | 1.850 | 2.643 | 100.7 | 0.428 |
| bromobenzene | 1.580 | stream $H_2O$ | 1.657 | 1.326 | 1.810 | 101.1 | 0.247 |
| m-chlorotoluene | 1.330 | stream $H_2O$ | 1.337 | 0.999 | 1.074 | 85.5 | 0.178 |
| 1-chloro-1-butene | 0.880 | soil | 0.266 | 0.238 | 0.392 | 33.9 | 0.0820 |
| 1,2-dichloroethane | 0.810 | soil | 0.436 | 0.481 | 0.611 | 62.9 | 0.0909 |
| 1-bromo-2-chloroethane | 1.080 | soil | 0.679 | 0.625 | 0.978 | 70.4 | 0.190 |
| 1,2-dibromoethane | 2.140 | soil | 1.471 | 1.600 | 1.922 | 77.8 | 0.232 |
| bromobenzene | 1.580 | soil | 0.968 | 1.254 | 1.417 | 76.8 | 0.227 |
| m-chlorotoluene | 1.330 | soil | 0.881 | 0.830 | 1.134 | 71.3 | 0.163 |

3.2.2.2 Semi-Volatile Brominated Organics

Sample Preparation.--Two approaches to the recoveries of semi-volatile organics from water were evaluated: one, the extraction of trace organics with a macroreticular resin (XAD-2) and elution with an organic solvent (diethyl ether), and the other direct solvent partitioning. Using the procedure described by Junk et al. [9], recoveries of EDB and TRIS were determined using GC/ECD by comparison of peak areas with standard solutions chromatographed at the same time. The extraction method was as follows: methanol-extracted XAD-2 was placed in a column 6 mm i.d. to a height of 10 cm. The column was rinsed free of methanol with distilled water (3 x 20 ml). An aliquot (200 ml) of sample, spiked water or blank was filtered through the resin bed. The adsorbed organics were eluted with diethyl ether (25 ml) added in two portions, 15 ml and 10 ml, allowing each to equilibrate for 10 min. The ether extract was then dried over sodium sulfate and analyzed by GC/ECD. The recoveries are shown in Table 3.14. Extraction of the filtered water with diethyl ether recovered ∿ 40% of the added EDB indicating poor extraction efficiency by the resin.

Table 3.14. RECOVERIES OF BROMINATED COMPOUNDS FROM WATER USING XAD-2 RESIN

| Compound | Concentration µg/ℓ | % Recoveries |
|---|---|---|
| EDB | 1.45 | 12 |
| | 13.4 | 12 |
| | 134 | 8 |
| TRIS | 2.09 | 115 |
| | 19.3 | 44 |
| | 193 | 57 |

Three solvents have been screened for their extraction efficiency for EDB and TRIS. The results are given in Table 3.15. Of those tested the best solvent for EDB is hexane. Toluene is best for TRIS. A sequential extraction procedure was evaluated in which 20 ml of sample water (or spiked water) was partitioned first with 20 ml of hexane and then with 20

Table 3.15. EXTRACTION EFFICIENCY OF SEVERAL ORGANIC SOLVENTS FOR EDB AND TRIS[a]

| | | | EDB | | TRIS | |
|---|---|---|---|---|---|---|
| | Volume (ml) | No. of Extractions | Amount added (µg) | % Recovery | Amount added (µg) | % Recovery |
| Diethyl ether | 40[b] | 1 | 2.00 | 86 | 20.0 | 46 |
| | 20 | 2 | | <2.5 | | <7.5 |
| Hexane | 20 | 1 | 2.00 | 80 | 20.0 | 49 |
| | 20 | 2 | | <5 | | <15 |
| Toluene | 20 | 1 | 2.00 | 87 | 20.0 | 111 |
| | 20 | 2 | | <5 | | <15 |

[a]200 ml of distilled water was spiked with the indicated amounts of EDB and TRIS.

[b]Diethyl ether was partially soluble and 40 ml was required to recover 20 ml of extract.

ml of toluene. The recoveries for each stage of this sequence are shown in Table 3.16 for TRIS and EDB. There is a problem, however, with merely combining the fractions when analyzing a volatile compound such as EDB. Toluene severely "tails" during GC analysis which affects the response of the EC detector to EDB. For this reason a parallel extraction scheme was selected for the analytical protocol (Appendix A). To verify the need to use a volatile solvent such as hexane for the analysis of volatile constituents, EDB losses upon evaporation of three solvents were compared (Table 3.17). In actual practice, only a five-fold concentration of the sample is required to detect EDB at the ppb level by GC/ECD when hexane was used.

Sediment samples were treated in the same manner as soils described in Section 3.2.3.2 except that the sample size was 10 g.

GLC/ECD and GLC/MS/COMP Analysis -- GLC/ECD methods for the semi-volatile brominated organics were developed for the purpose of method validation and sample screening. Two types of packed columns were used. A short 42 cm non-polar column (Section 3.2.1.2) for TRIS and a semi-polar column [170 cm x 0.2 cm i.d., Carbowax 20M on Chromosorb G AW/DMCS, (100/120 mesh)] for more volatile compounds such as EDB. A 42 cm x 0.2 cm i.d. column coated with 2% OV-101 on Supelcoport was used for all the GLC/MS/COMP analyses. The analytical procedure for the mass spectral analysis was the same as that described in Section 3.2.1.2. The limits of detection varied as indicated in Table 3.18.

### 3.2.3 Soil

#### 3.2.3.1 Volatile Brominated Organics

The same general procedure was used for soil (and sediment) as for water except the sample size is 20 g in 450 ml of distilled water added to suspend the solids. The additional requirement for mechanical stirring to maintain the suspension was met by using a 500 ml round bottom flask and a magnetic stirrer (see Appendix A). Recovery studies were performed for soil in the same manner as for water. The results are shown in Table 3.13.

#### 3.2.3.2 Semi-volatile Brominated Organics

Sample Preparation -- The recovery of a wide variety of compounds from a matrix such as soil poses a difficult problem. If the solvent is

Table 3.16. RECOVERIES FROM SEQUENTIAL SOLVENT EXTRACTION OF WATER[a]

| | % Recovery | | | | | |
|---|---|---|---|---|---|---|
| | Distilled Water | | | Stream Water | | |
| | Hexane[b] | Toluene[c] | Total | Hexane[b] | Toluene[c] | Total |
| TRIS[d] | 72 | 15 | 87 | 91 | 24 | 115 |
| EDB[e] | 91 | <10 | 91 | 82 | <10 | 82 |

[a]200 ml of sample extracted with 20 ml of each solvent.

[b]First extraction of the series.

[c]Second extraction.

[d]TRIS was added to give 100 ppb in water.

[e]EDB was added to give 10 ppb in water.

Table 3.17. LOSSES OF ETHYLENE DIBROMIDE DURING SOLVENT EXTRACTION[a]

| Solvent | Concentration Factor | % Loss |
|---|---|---|
| diethyl ether[b] | 122 | 14 |
| hexane[b] | 93 | 50 |
| toluene[c] | 15 | 33 |

[a]100 ml of the test solvent containing 11.6 µg of EDB.

[b]Concentrated in Kuderna-Danish (K-D) apparatus and micro K-D on steam bath. Snyder columns were used throughout.

[c]Concentrated in flat bottom flask using Snyder column and a hot plate for heat.

Table 3.18. LIMITS OF DETECTION OF BROMINATED ORGANICS IN WATER

| Compound | Method | | |
|---|---|---|---|
| | GLC/ECD (µg/ℓ) | GLC/MS (µg/ℓ) | Other (µg/ℓ) |
| EDB | 1 | -[a] | - |
| TRIS | 0.2 | 500-1000 | 20[b] |
| Tetrabrom | - | 50 | - |
| Pentabromophenol | - | 100 | - |
| Firemaster 680 | - | 50[c], 800[d] | - |
| Decabrom | - | 10 | 2.5 |

[a]Not determined.

[b]Thin-layer chromatography.

[c]Based upon m/e 257, a non-specific ion.

[d]Based upon m/e 688, the parent ion.

not selective for the compound of interest the background may be seriously elevated and extensive clean-up procedures required. With this in mind, two soil extraction procedures were evaluated. One employed a water/acetonitrile/ ethyl ether partition and the other water/acetone/toluene. A soil sample (50 g) was wetted with 50 ml of water and extracted with 50 ml of acetonitrile/ ethyl ether (1:1) followed by two 50 ml ethyl ether extractions. Recoveries from the first solvent combination were very low (<10%) for decabromobiphenyl ether (Decabrom) and EDB, two of the three compounds selected as "marker" compounds for this evaluation. The latter solvent combination proved more satisfactory. In this procedure, 50 g of soil was extracted with 50 ml of diethyl ether; 10% of this extract was reserved for volatiles (EDB) analysis with the remainder combined with subsequent fractions. Ether extraction was followed by the addition of water (5 ml), acetone (40 ml) and toluene (80 ml) and mixing. The organic layer was removed and filtered. The acetone and toluene extraction was repeated two more times and the volume reduced before GC/ECD analysis. Table 3.19 gives the recoveries for selected compounds.

Table 3.19. RECOVERIES OF SEMI-VOLATILE HALOGENATED ORGANICS FROM SOIL BY SOLVENT EXTRACTION[a]

| Compound | Concentration µg/ℓ | % Recoveries |
|---|---|---|
| 1,2-Dibromoethane | 1000 | 52 |
| | 100 | 7.9[b] |
| Tris-(2,3-dibromo-propyl)phosphate | 1000 | 81 |
| | 100 | 77 |
| Decabromobiphenyl ether | 1000 | 85 |
| | 100 | 84 |

[a]Method of extraction described in the text.

[b]An evaporation step was employed which may be responsible for the loss of EDB. This step has since been found to be unnecessary for GC/ECD analysis.

GLC/ECD and GLC/MS/COMP Analysis of Soil Extracts -- The GLC/ECD methods described in Section 3.2.2.2 were applicable to screening of soil samples for TRIS. Where very high levels were present, TLC methods for

Decabrom were used. In general, however, GLC/MS/COMP was used in the MID mode for the analysis of soil sample extracts. The same conditions were used as those described in Section 3.2.1.2. Limits of detection were higher than for water by a factor of 2 to 3.

3.2.4 Other Media

3.2.4.1 Hair

Samples were extracted in a Soxhlet apparatus with toluene for 16 hrs and the volume reduced to 5-10 ml using a Snyder column. Aliquots (0.5 ml) were evaporated to dryness and weighed to determine total solids (oil). Octachloronaphthalene was added to each sample as an internal standard. These aliquots were redissolved and purified using high performance liquid chromatography on a μStyragel (500Å) column with toluene as a solvent. Prior to sample analysis the elution volumes of several marker compounds were established (Decabrom and Firemaster 680) and these elution volumes were used to select the fraction collected. Two chromatographs of 50 to 100 μl of extract (∿4-8 mg of hair oil) were performed on each sample. The fractions from each sample were combined and the volume reduced for submission to GC/MS/COMP analysis. The same GLC/MS analysis conditions were used as for the soil and sediment samples.

3.2.4.2 Milk

Several attempts at direct solvent extraction were unsuccessful due to emulsion formation. However, the following procedure was successful. A well-mixed weighed sample (10 g) was mixed with clean glass wool and the proteins precipitated by the addition of 100 ml of acetone. Separation of the precipitate was sometimes facilitated by centrifugation. The acetone was decanted and filtered as were two additional 25 ml acetone fractions. The volume of the acetone was reduced to ∿20 ml using a Snyder column. The precipitate was washed two times with 10 ml of toluene. The toluene fractions were combined with the acetone. Two phases formed due to the water in the acetone and the aqueous phase was removed. The organic phase was dried over sodium sulfate and the volume reduced to 5-10 ml. This procedure was followed using blank raw cows' milk and milk which was spiked in the amounts given in Table 3.20.

Table 3.20. AMOUNTS OF BROMINATED ORGANICS ADDED TO MILK

| Compound | Sample | | |
|---|---|---|---|
| | MB | M1 (μg/g) | M10 (μg/g) |
| 2,4,6-Tribromophenol | 0 | 1.2 | 12 |
| Tetrabrom | 0 | 1.0 | 10 |
| TRIS | 0 | 2.4 | 24 |
| Decabrom | 0 | 1.0 | 10 |

Figure 3.7 shows the elution volumes of several brominated compounds relative to sample MB (Figure 3.7-F). Figure 3.8 shows the chromatogram for M10 with both uv (300 nm) and refractive index (RI) detection. The chromatogram of the M1 extract showed some of the appropriate peaks on the UV detector but the RI detector is too insensitive to detect TRIS at this level (1.1 μg). The other brominated compounds such as Decabrom and tribromophenol, were clearly present in the expected amounts.

3.2.4.3 Placenta

The placenta samples were extracted by the same procedure as used for the milk samples with the addition of homogenization with a Virtis Blender after the addition of acetone. HPLC clean-up was attempted on the placenta extracts; however, the lipids in this case appeared to be relatively low molecular weight compared to milk (see Figure 3.9).

3.3 References

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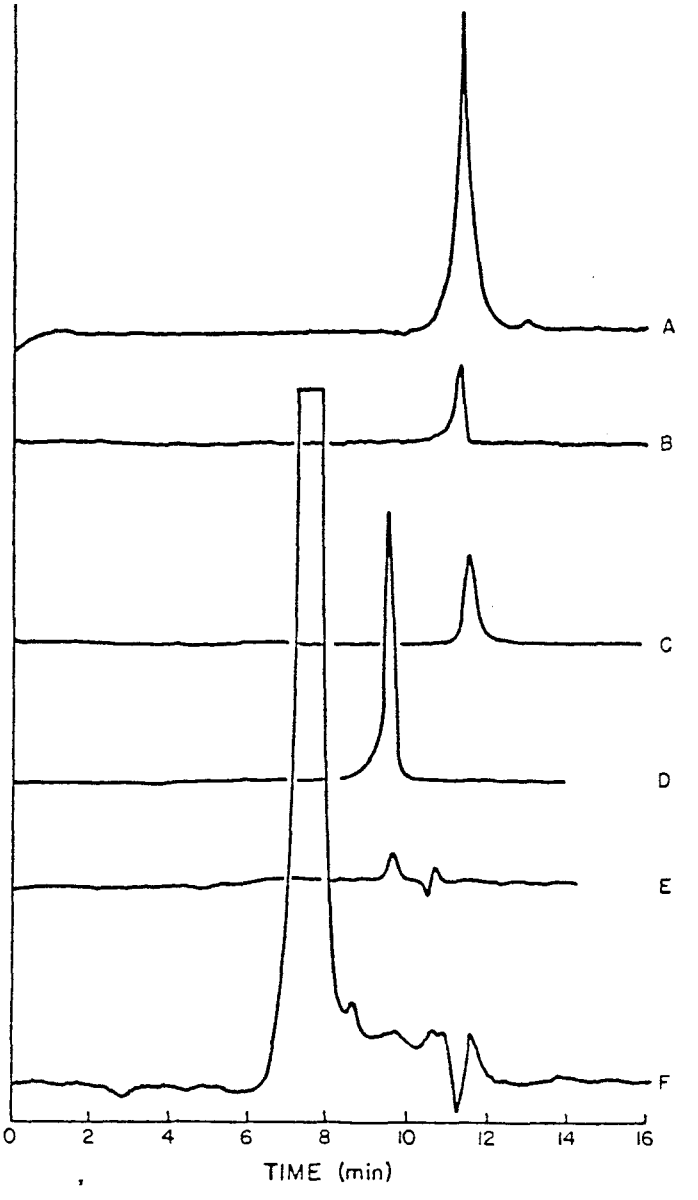
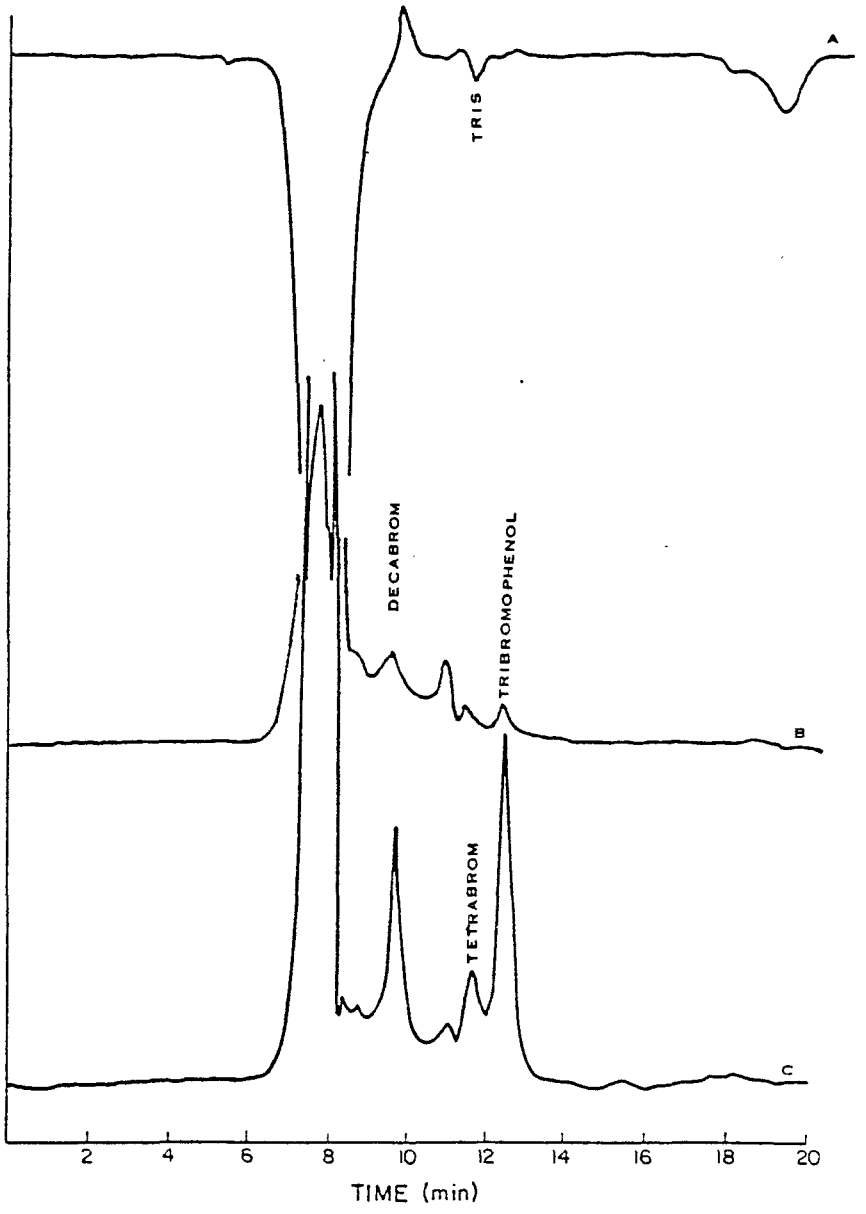



Column: μStragel (28 cm); Solvent: Toluene
Flow rate: 1 ml/min; UV: 300 mm

Figure 3.7. Retention volumes of some brominated compounds on HPLC. A - TRIS (466 μg), RI detector, x8; B - 1-chloro-2,3-dibromopropane (118 μg), RI detector, x8; C - tetrabrom (40 μg), uv detector, 0.4 AUFS; D - decabrom (40 μg), uv detector, 0.4 AUFS; E - hexabromodiphenyl (2 μg), uv detector, 0.1 AUFS; F - blank milk extract.




Column: μStyragel (28 cm); Solvent: toluene;
Flow rate: 1 ml/min; UV: 300 nm - 0.1 AUFS;
RI: 8X

Figure 3.8. High performance liquid chromatography of spiked milk extracts: A - extract M10 (200 μl injected or 4% of extract); RI detector; B - Extract M1 (100 μl injected or 4% of extract), UV detector; C - Extract M10 (200 μl injected or 4% of extract), UV detector.

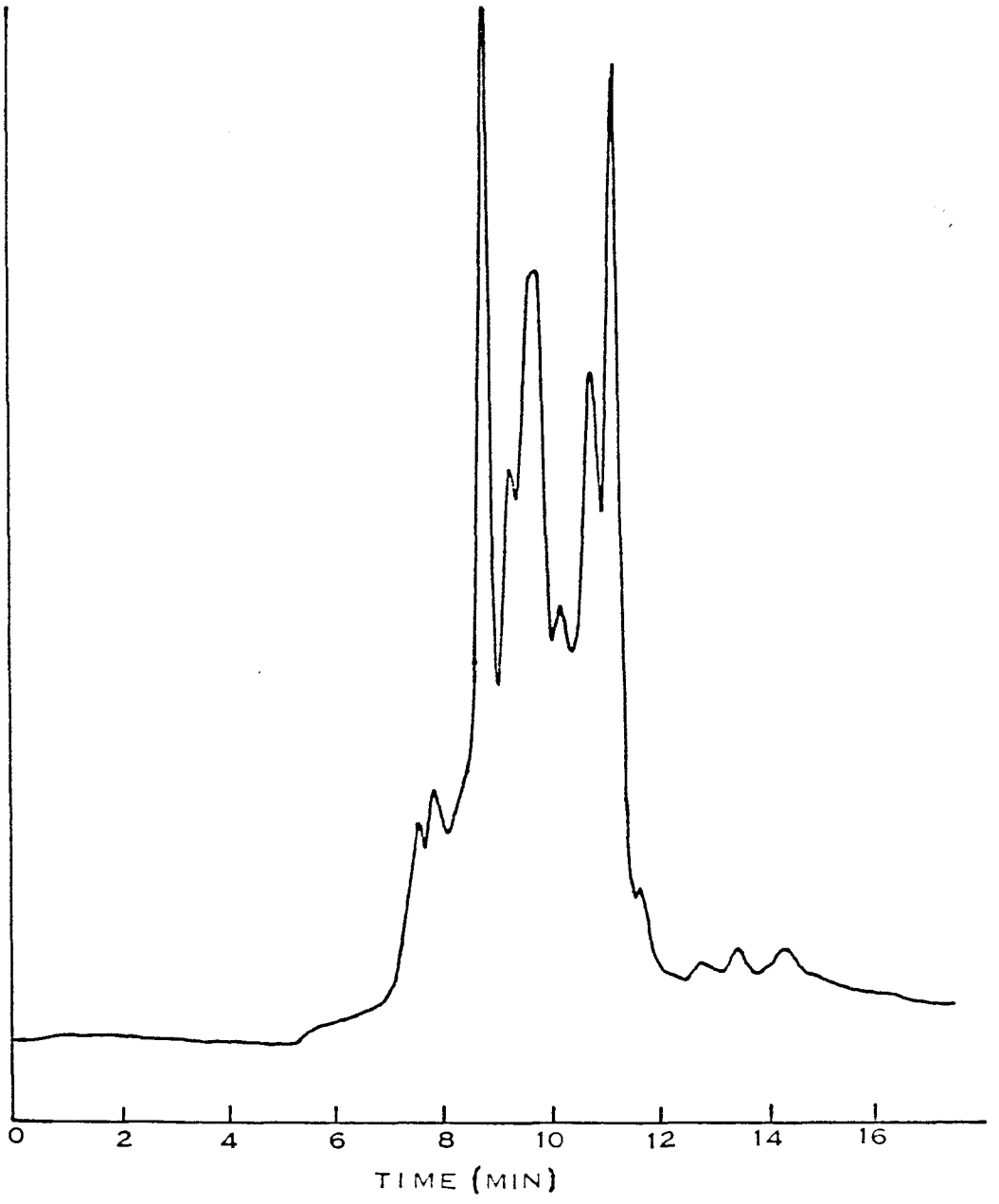



Figure 3.9. Placenta extract - hplc chromatogram of μStyragel column.

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## 4.0 SURVEY OF ENVIRONMENTAL MEDIA FOR CHEMICALS ASSOCIATED WITH BROMINE INDUSTRY

### 4.1 TECHNICAL STRATEGY

The strategy which was adopted for the Survey Phase attempted simultaneously to evaluate the analytical techniques employed for characterizing the ambient air and to acquire a maximum amount of information about the chemicals surrounding the bromine industry.

The analytical methods utilized in this study are given in Table 4.1. Scanning electron microscope (SEM) equipped with energy dispersing X-ray (EDX) capabilities (Section A, Appendix A) was used for element mapping of particles collected on glass and cellulose fiber filters. Primary application of SEM and EDX was for detecting the presence and relative amounts of Cl, Br, S, and counterions (Na, K, Ca, etc.).

Table 4.1. ANALYTICAL TECHNIQUES EMPLOYED FOR STUDYING POLLUTANTS IN AMBIENT AIR SURROUNDING BROMINE INDUSTRY IN ARKANSAS

| Technique | Information Type |
|---|---|
| Scanning Electron Microscope and Energy Dispersive X-ray Analysis | Cl, Br, counterions, particle topography |
| Neutron Activation Analysis | Total Cl, Br |
| Spectrophotometric Techniques | $Cl^- + Br^-$, $Cl^-$, $Br^-$ |
| Gas Chromatography Flame Ionization Detection | Ethylene |
| Gas Chromatography Electron Capture Detection | Methyl chloride, Methyl bromide |
| High Resolution Gas Chromatography/ Mass Spectrometry/Computer | Structural characterization and quantification of volatile organics |

Neutron activation analysis (Section B, Appendix A) was employed for determining the total Cl and Br content in various collected sample matrices. Depending on the information type desired semi-quantitative and quantitative data were obtained where possible.

Turbidity measurements (Section G, H, Appendix A) were made for total halide (and halogen) and when feasible individual species were quantitated after applying ion-exchange methods. In some cases neutron activation, SEM, and EDX were used in concert with spectrophotometric methods (Sections I, J, and Appendix A).

A variety of gas chromatographic methods was employed with specific detectors for organic analysis. Flame ionization was employed for ethylene analysis (Section C, Appendix A). Methyl chloride and methyl bromide were detected by electron capture (Section D, Appendix A).

For obtaining a broad overview of the types of organics and the levels present in ambient air, high resolution gas chromatography/mass spectrometry/computer techniques were used (Section E, F, Appendix A).

4.1.1 Sampling

In order to cross-check the analytical techniques, sampling efforts were designed to acquire sufficient quantities of samples (replicates) for multi-analyses. Figure 4.1 depicts a schematic of the cartridge sampling train used for fractionating non-volatile, semi-volatile and volatile components from ambient air. A glass fiber filter preceded the Tenax GC cartridge. The filter was used for removing non-volatile or particulate material from the air. The volatiles were trapped on Tenax GC. In tandem with the Tenax GC cartridge we used an SKC carbon as a back-up material for stopping the very volatile organics (e.g., vinyl chloride, vinyl bromide, methyl chloride and methyl bromide).

Molecular chlorine, bromine and the halides, chloride and bromide, were collected in midget impingers (Figure 4.2) in a tandem arrangement (Sections G, H, Appendix A). Sufficient impinger volumes were used in the collection scheme for subsequent multi-analyses. Fluoride was collected in a separate, single midget impinger concomitantly and in parallel with the Cl/Br devices (Section I, Appendix A).

Acid mist was collected on cellulose filters and in duplicate (Section J, Appendix A).

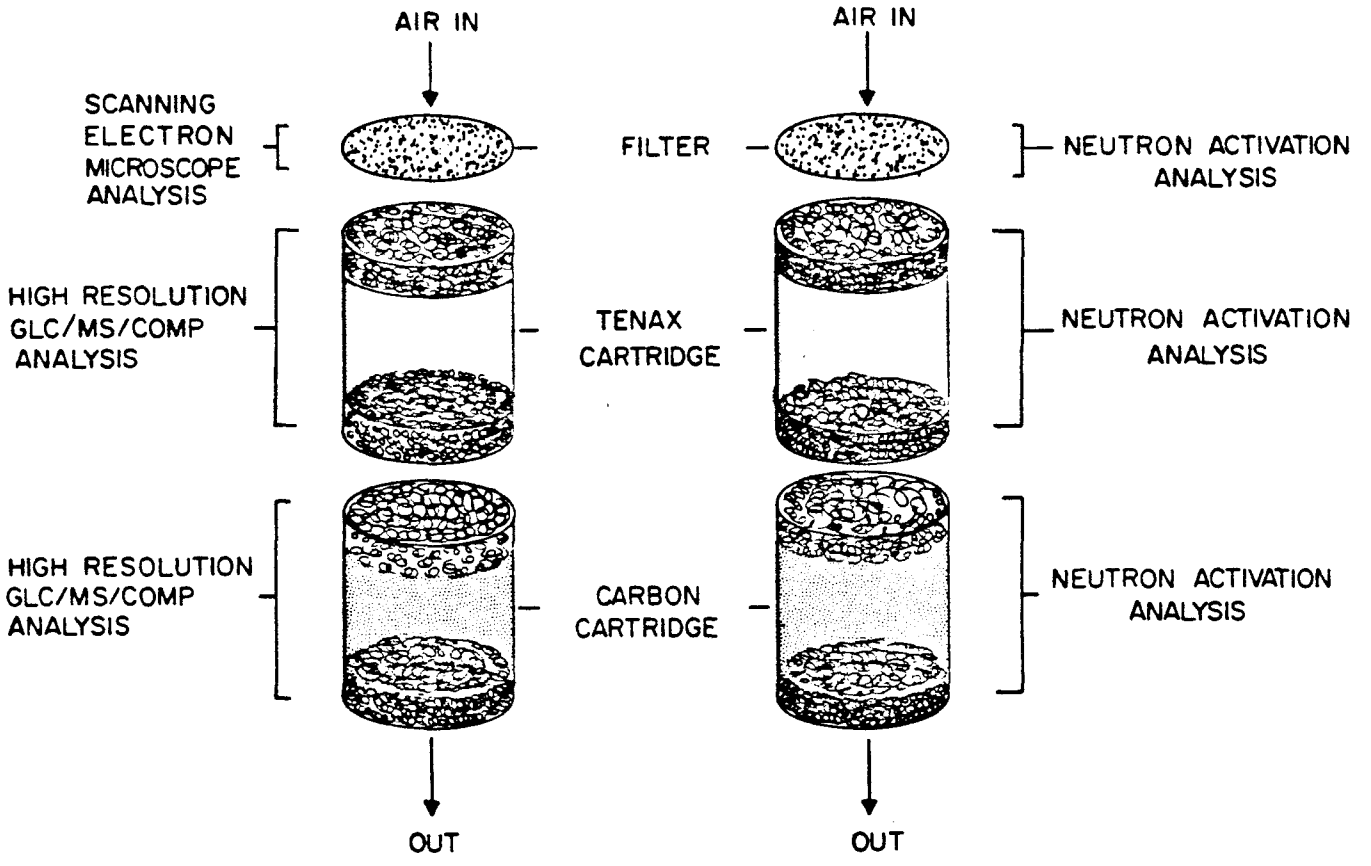



Figure 4.1. Schematic of duplicate (parallel) cartridge sampling and designated sample analysis

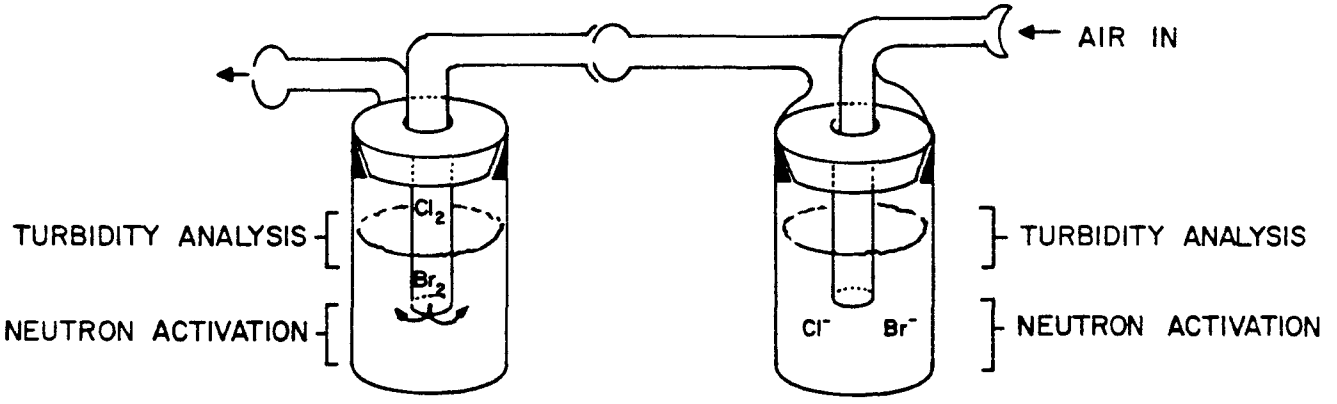



Figure 4.2. Tandem midget impingers for collection and designated sample analysis for halogenated substances

Hi-Vol glass and cellulose fiber filters (Figure 4.3) were used for collecting particulates for SEM and EDX analysis. As part of the sampling protocols in each of these cases, "Hi" and "low" volume cartridge sampling was performed with the intent of collecting adequate quantities of material for characterization by high resolution GLC/MS/COMP. A Nutech Model 221-A sampler (Nutech Corp., Durham, NC) was utilized for "Hi" volume sampling and a DuPont personal sampler (Section F, Appendix A) for "low" volume sampling. The DuPont sampler was also evaluated for potential long-term sampling (24-36 hr) and sampling in highly remote and distant locations from the plant sites.

The DuPont samplers were located off the property of the Great Lakes Corp. and Arkansas Chemical, Inc. area. They were placed on the water tower in Parker's Chapel and on a water tower in downtown El Dorado, Arkansas. The purpose of this sampling was to determine whether it was possible to detect and quantify halogenated organic volatiles during an overnight period. We intended to demonstrate whether halogenated organic vapors were transported from the plant sites to populated areas resulting in potential exposure. The Parker's Chapel water tower is located between Great Lakes Corp. and Arkansas Chemical, Inc. on Arkansas Highway 15. It is approximately one mile from Great Lakes (line of sight) and about 1.5 miles from Arkansas Chemical, Inc.

Inorganics were collected during separate sampling periods at the same locations as for organics.

During all sampling periods, meteorological data were recorded continuously at one sampling location with a Meteorological Research, Inc. instrument (temperature, wind direction and speed). Every 30-60 min, wind speed and direction, temperature, barometric pressure and humidity were recorded using hand-held instrumentation. These parameters were estimated with a Dwyer Wind Meter (Dwyer Inst. Inc., Michigan City, IN), a pocket altimeter (Gischard, West Germany), and a sling psychrometer (Taylor Inst. Co., Rochester, NY). Direction bearings and distances were measured with a lensatic compass and a Rangematic Distance Finder (Ranging Inc., Rochester, NY), respectively.

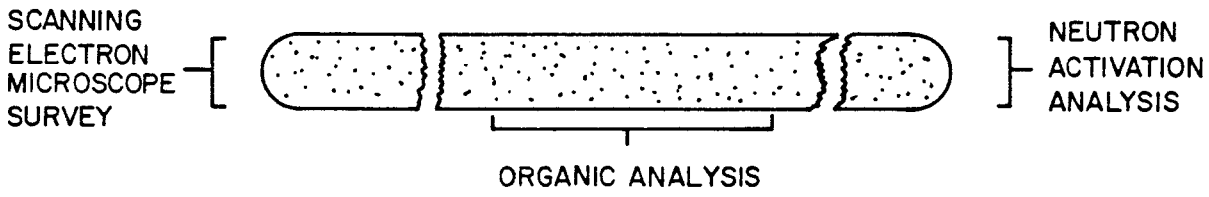



Figure 4.3. Hi-Vol filter and designated sample analysis

Other subjective observations were also made.

4.1.2 Analytical Cross-Checking

In order to evaluate the analytical methodology and to obtain a broad spectrum of information concerning potential pollutants, several instrumental techniques were used in a cross-check fashion. The glass fiber filters (Figure 4.3) from the cartridge sampling train were examined by SEM, EDX (when feasible) and NA techniques. Using this approach it would be possible to determine the relative amounts of Cl, Br, and S occurring in the non-volatile fraction (particulate) and to a certain degree whether these elements are predominantly organic or inorganic by counterion studies using SEM-EDX. The use of SEM-EDX and NA also serves as a rapid preliminary screening technique to determine whether analysis for organics, inorganics or both is justified by other more definitive (but time-consuming) methods.

The volatile organic compounds trapped on the Tenax cartridge were designated for analysis by high resolution GC/MS/COMP techniques and by neutron activation (Figure 4.1). High resolution GC/MS/COMP analysis of the Tenax cartridge allowed the identification and quantification of organic volatiles which were emitted by the bromine extraction or synthetic organic units at the plant facility. In some cases duplicate analysis of the Tenax cartridges by high resolution GC/MS/ COMP was conducted in order to determine the reproducibility of analysis. In other cases, a second cartridge was not subjected to high resolution GC/MS/COMP analysis, but instead submitted for neutron activation. In this manner, it was possible to determine whether chlorinated and brominated compounds escaped detection by the high resolution GC/MS/COMP analysis since it was possible by the more general technique of neutron activation to obtain total equivalents of Cl and Br. Carbon cartridges (Figure 4.1) were analyzed similarly to the Tenax cartridges, by high resolution GC/MS/COMP and by neutron activation analysis.

Although high resolution GLC/MS/COMP was used for unequivocal identification of vinyl chloride, vinyl bromide, methyl chloride and methyl bromide from Tenax GC cartridges, these halogenated compounds were also quantified by independent methods, i.e., GC with electron capture (Section D, Appendix A) and mass fragmentography (Section E, Appendix A).

In addition to the sampling of low volumes (~75-150ℓ) of air with the cartridge train, Hi-Vol sampling was employed (Figure 4.3). Glass and cellulose filters were subjected to SEM-EDX and NA analysis.

The first impinger solution contained primarily halides (Figure 4.2) and was examined by NA and turbidity methods. In some cases, ion-exchange separation of $Cl^-$ and $Br^-$ was performed to determine individual halide concentrations in air. The second impinger trapped molecular chlorine and bromine; it was treated in the identical manner to the first.

4.1.3 Prioritization of Sample Analyses

Many samples were taken for organic and inorganic analyses. Since the major objectives of this study were to obtain a broad overview of the major pollutants occurring from the bromine industry and to evaluate analytical techniques for collection and analysis, samples were prioritized and "best samples" were examined. These were selected on the basis of the best sampling conditions as reflected by the meteorological parameters during the sampling period. Also, consideration was given to significant potential emissions during the most active periods of the plant facility operations. Lower priority was given to those cases where the plant operations were believed to be unfavorable for collection of adequate amounts of chemicals for study. Furthermore, when meteorological conditions were unstable or when emissions from the plant sites were not continuously carried to the sampling locations, the samples were given a low analysis priority.

The prioritization scheme for the Survey Phase was necessary to obtain a maximum amount of information with the expenditure of only a moderate level of effort.

## 4.2 RESULTS AND DISCUSSION

### 4.2.1 Arkansas Chemical Incorporated

#### 4.2.1.1 Sampling

The sampling protocol and sample descriptions for Arkansas Chemical Inc. are given in Table 4.2. The corresponding Figures 4.4 and 4.5 designate the sampling locations for September 20 and 21, 1976. Soil and water samples were also collected on April 4, 1977. These protocols are given in Table 4.3 and Figure 4.6.

Table 4.2. SAMPLING PROTOCOL FOR ARKANSAS CHEMICAL INCORP., HIGHWAY 15, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/20/76 | C1 | L1 | 1330-1523 | 103 | HHC[a] | 25-26 | 95 | 270°/6 | Full Cloud Cover, rain |
| P1 | | L2 | 1330-1525 | 102 | HHC[a] | 25-26 | 95 | 270°/6 | Full Cloud Cover, rain |
| | | L3 | 1330-1530 | 137 | HHC[a] | 25-26 | 95 | 270°/6 | Full Cloud Cover, rain |
| | | L4 | 1325-1524 | 148 | HHC[a] | 25 | 95 | 270°/6 | Full Cloud Cover, rain |
| | C2 | L1 | 1545-1614 | 44 | F, CBN, CBD | | | | |
| | | L2 | 1545-1614 | 54 | F, CBN, CBD | | | | |
| | | L3 | 1545-1615 | 43 | F, CBN, CBD | | | | |
| | | L4 | 1545-1615 | 81 | F, CBN, CBD | | | | |
| | C3 | L1 | 1637-1800 | 272 | AM | | | | |
| | | L2 | 1637-1757 | 154 | AM | | | | |
| | | L3 | 1640-1758 | 137 | AM | | | | |
| | | L4 | 1636-1758 | 90 | AM | | | | |
| | | L1 | 1720 | 1 | TED | | | | |
| | | L2 | 1742 | 1 | TED | | | | |
| | | L5 | 1748 | 1 | TED | | | | |
| | | L1 | 1723 | 0.28 | VAC | | | | |
| | | L5 | 1727 | 0.28 | VAC | | | | |
| | | L6 | 1727-1742 | 0.28 | VAC | | | | |
| 9/21/76 | C1 | L1 | 1805-1835 | 184 | HHC[a] | 27 | 44 | | |
| P2 | | L2 | 1808-1826 | 235 | HHC[a] | | | | Odor of $H_2S$, $Br_2$ |
| | | L3 | 1808-1835 | 243 | HHC[a] | | | | Clear |

[a]Nutech Model 220 sampler 3-6 ft elevation.

Locations shown in Figures 4 and 5.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can

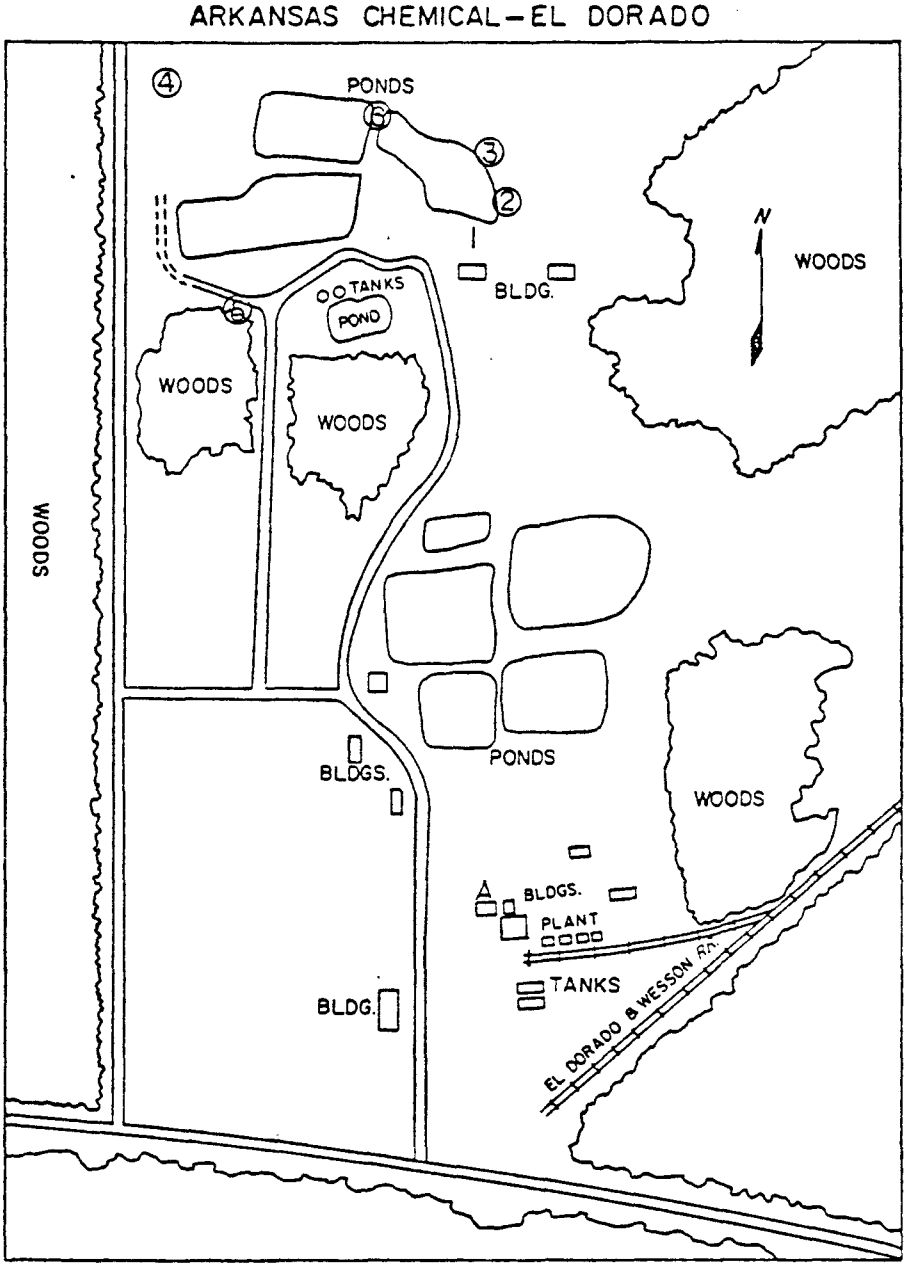



Figure 4.4. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for P1 - 9/20/76.

A - $Br_2$ facility

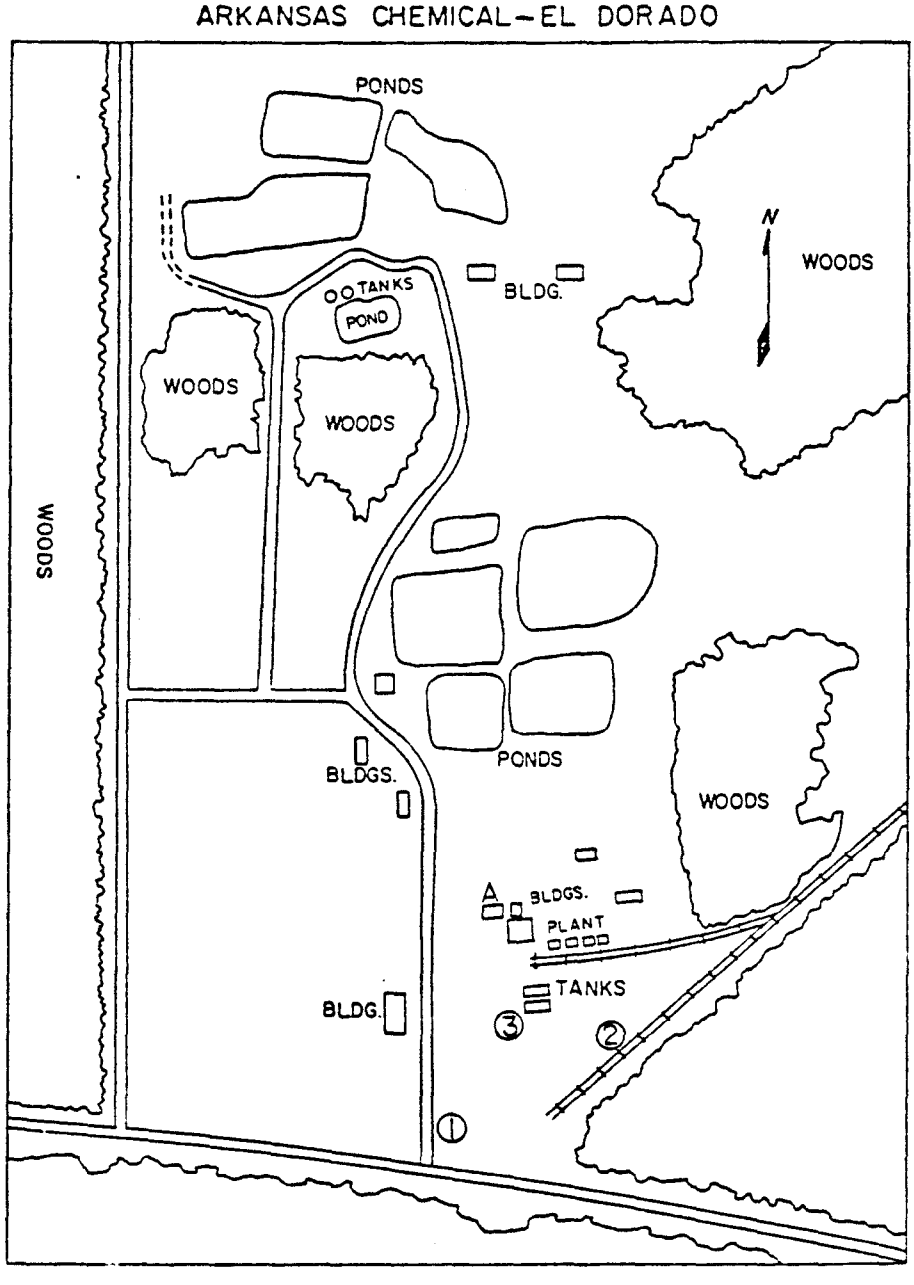



Figure 4.5. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for P2 - 9/21/76.

A - $Br_2$ facility.

Table 4.3. SAMPLING PROTOCOL FOR ARKANSAS CHEMICAL INCORP., EL DORADO

| Period | Cycle | Location | Sample Size | Type of Sample |
|---|---|---|---|---|
| 1 | C1 | L1 | 2 cores | SHHC-V |
| 4/7/77 | | | 2 cores | SHHC-SV |
| | | L2 | 2 cores | SHHC-V |
| | | | 2 cores | SHHC-SV |
| | | L3 | 2 cores | SHHC-V |
| | | | 2 cores | SHHC-SV |
| | | | 1 ℓ | WHHC-V/SV[a,b] |

[a]Stream 30 cm wide, 10 cm deep in drainage ditch.

[b]Water was collected from standing puddles.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

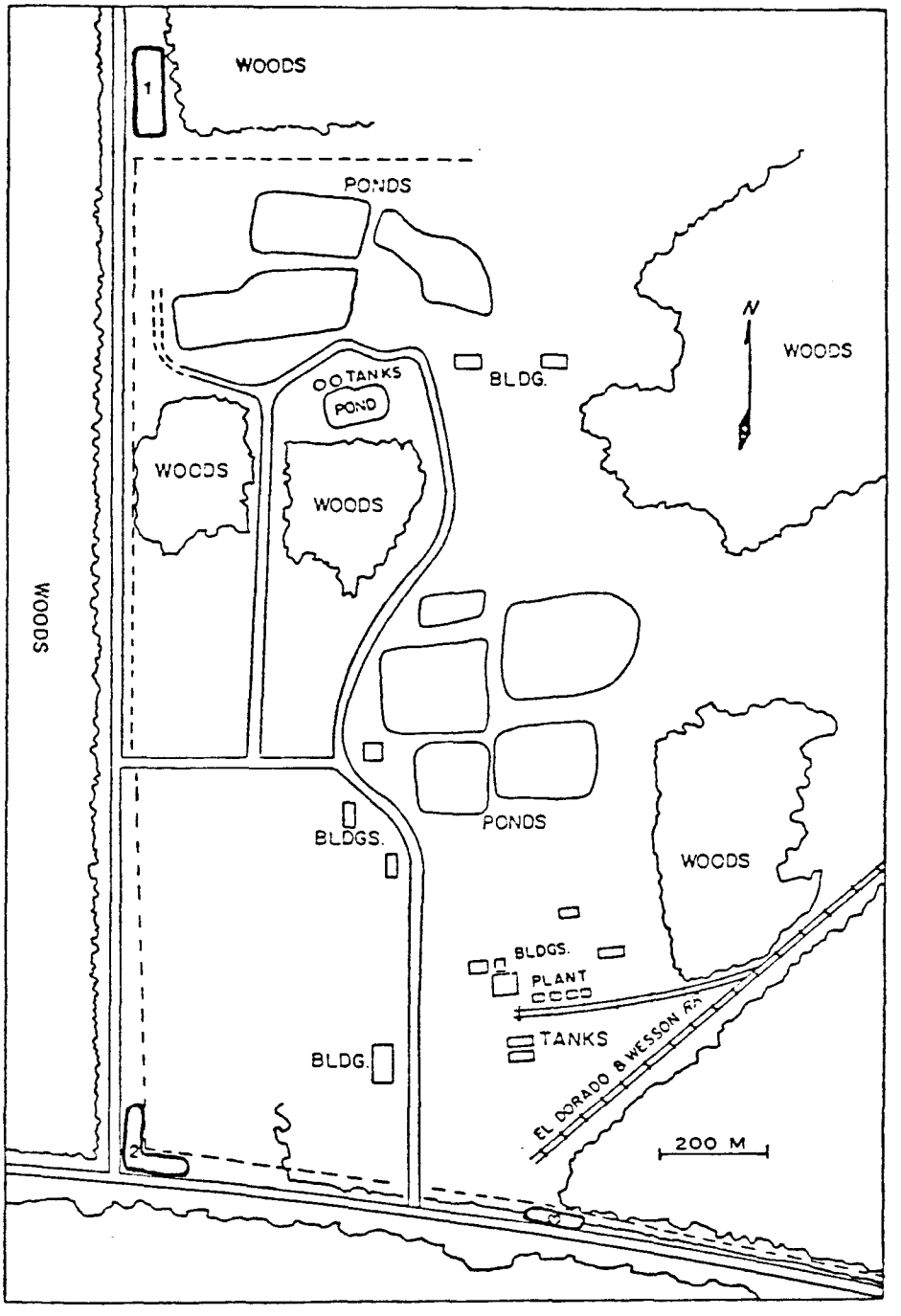



Figure 4.6. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for P1 - 4/7/77.

4.2.1.2 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by turbidimetric determination of total halide are given in Table 4.4. The site, period and cycle designation are given in the sampling protocols and the location on the schematic maps (Fig. 4.4).

Table 4.4. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INC.[a,b]

| | Locations | | | |
|---|---|---|---|---|
| Species | L1 | L2 | L3 | L4 |
| $Cl_2/Br_2$[c] | <109 | <92 | <100 | <61 |
| $Br_2$[d] | - | 238 | - | 28 |
| $Cl^-/Br^-$[c] | <75 | <61 | 69 | 49 ± 53 |
| $Br^-$[d] | - | <19 | - | <12 |

[a]Samples are from P1/C2.

[b]Values are in $\mu g/m^3$.

[c]By turbidity.

[d]By neutron activation analysis.

Arkansas Chemical Inc. showed only one detectable concentration of halide by turbidity at L4 (downwind of a group of ponds, see Fig. 4.4). Neutron activation analysis of that location indicated no bromide. A high bromide level was found at L2 which is inconsistent with the total halide determination. Cellulose filters used in the sampling cycle immediately following the impinger sampling cycle showed no detectable bromine.

Fluoride/Fluorine.--No fluoride or fluorine was detected in any of the samples in ambient air surrounding Arkansas Chemical Inc. The limits of detection are based upon the background levels observed in control solutions and are indicated by "less than" values. A detection limit of 0.02 ppm in the impinger solution was achieved for the volume of air sampled.

Acid Mist.--No titratable acid was detected in any samples (Table 4.5). Table 4.5 summarizes the upper limit of acid mist concentration in these samples. Again, they are represented as "less than values".

Table 4.5. ACID MIST IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INCORP. AS $H_2SO_4$[a]

| Period | Cycle | Locations | | | |
|---|---|---|---|---|---|
| | | L1 | L2 | L3 | L4 |
| P1 | C3 | -[b] | <30 | - | <52 |

[a]Values in $\mu g/m^3$.

[b]Not determined.

Table 4.6. CONCENTRATION OF BROMINE IN BRINE SAMPLES

| Site | Sample Type | µg Br/ml |
|---|---|---|
| Arkansas Chemical Incorp. | Front brine | 6588.2 |
| | Tail brine | 418.2 |

4.2.1.3 Bromine and Brominated Organics in Brine

Neutron Activation Analysis.--Table 4.6 lists the concentrations of bromine (molecular plus halides) in front and tail brine samples. A 93% reduction of the bromine concentration was observed between front and tail brines. Significant quantities of bromine were detected in the tail brine samples; however, the technique of neutron activation does not distinguish whether the bromine is present as molecular bromine, bromide ion or brominated organics. Furthermore, the number of bromine atoms per molecule cannot be delineated. The importance of these results is primarily attributed to the presence of substantial quantities of "bromine" even after bromine extraction.

GC/MS/COMP Analysis for Volatile Organics.--The front brine from Arkansas Chemical Inc. was purged (Appendix A) to recover volatile brominated organics for subsequent identification by GC/MS/COMP and estimation of concentrations. The front brine sample from Arkansas Chemical Inc. (Fig. 4.7) contained benzene, dimethyldisulfide, toluene, thiacyclopentane, dithiopropane isomer, ethylbenzene, cyclooctatetraene, undecane and n-dodecane. The tail brine sample (Fig. 4.8) contained benzene, dimethyldisulfide, toluene and 1-chloro-2,3-dibromopropane (Fig. 4.9).

In Table 4.7 the concentrations of halogenated and other organics in brine samples from Arkansas Chemical Inc. are provided. In general the concentration of halogenated hydrocarbons did not appreciably increase after recovery of bromine from brine.

The above results represent the analysis of only a single sample in each case. For this reason the concentration of volatile organics in these samples may not be representative of the change in composition between front and tail brine. The results do, however, give an indication of the types of compounds which are present as volatile organics. It would be interesting in future studies to also include the examination of semi-volatile brominated organics in brine samples.

4.2.1.4 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Analysis was conducted according to the protocols given in Appendix A.

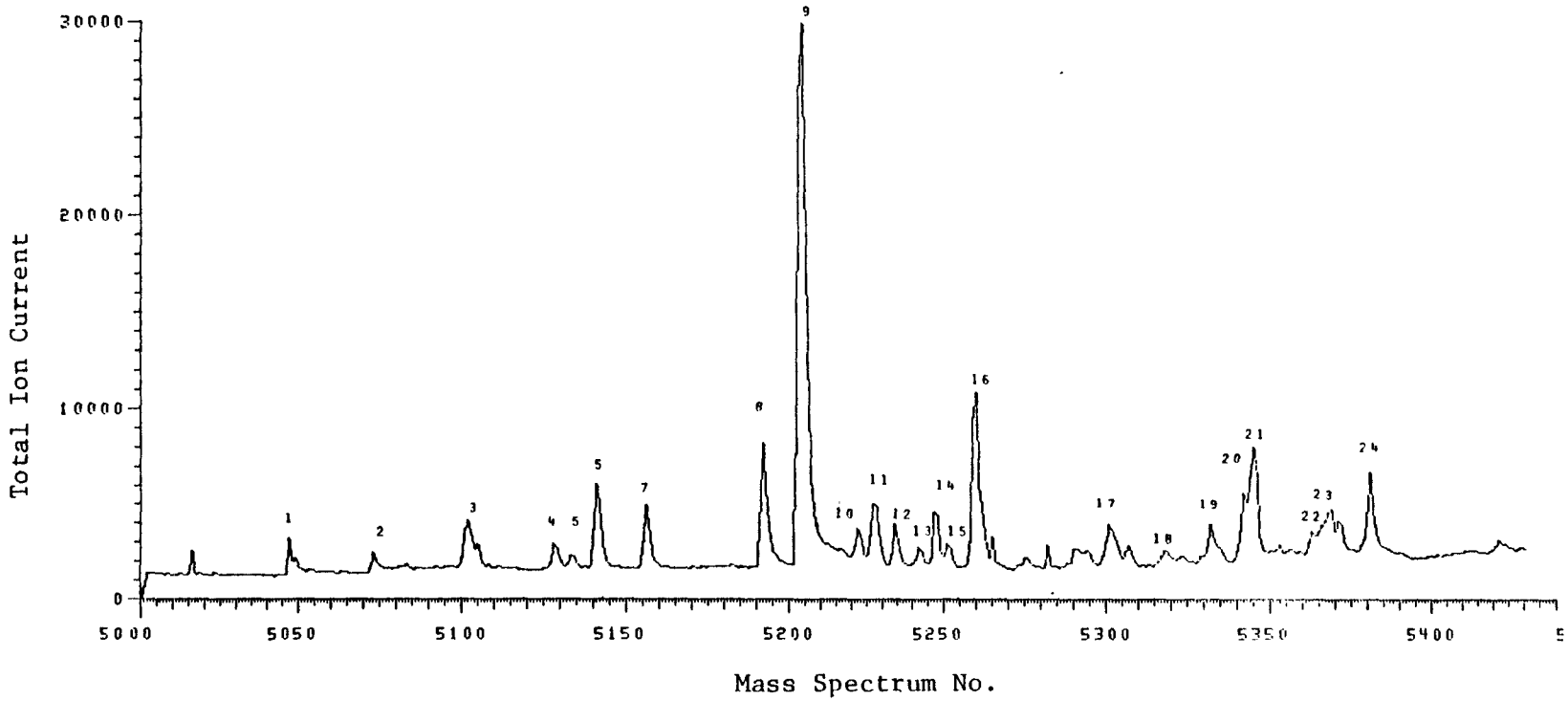



Figure 4.7. Total ion current profile of volatile organics in front brine from Arkansas Chemical Incorp. Peak No. 4 = hexafluorobenzene (e$), 5 = chloroform, 6 = perfluorotoluene (e$), 7 = benzene, 8 = dimethyldisulfide, 9 = toluene, 10 = thiacyclopentane, 12 = dithiopropane, 14 = ethylbenzene, 19 = cyclooctatetraene, 21 = n-undecane, 22 = $C_{12}H_{26}$ isomer, and 24 = n-dodecane.

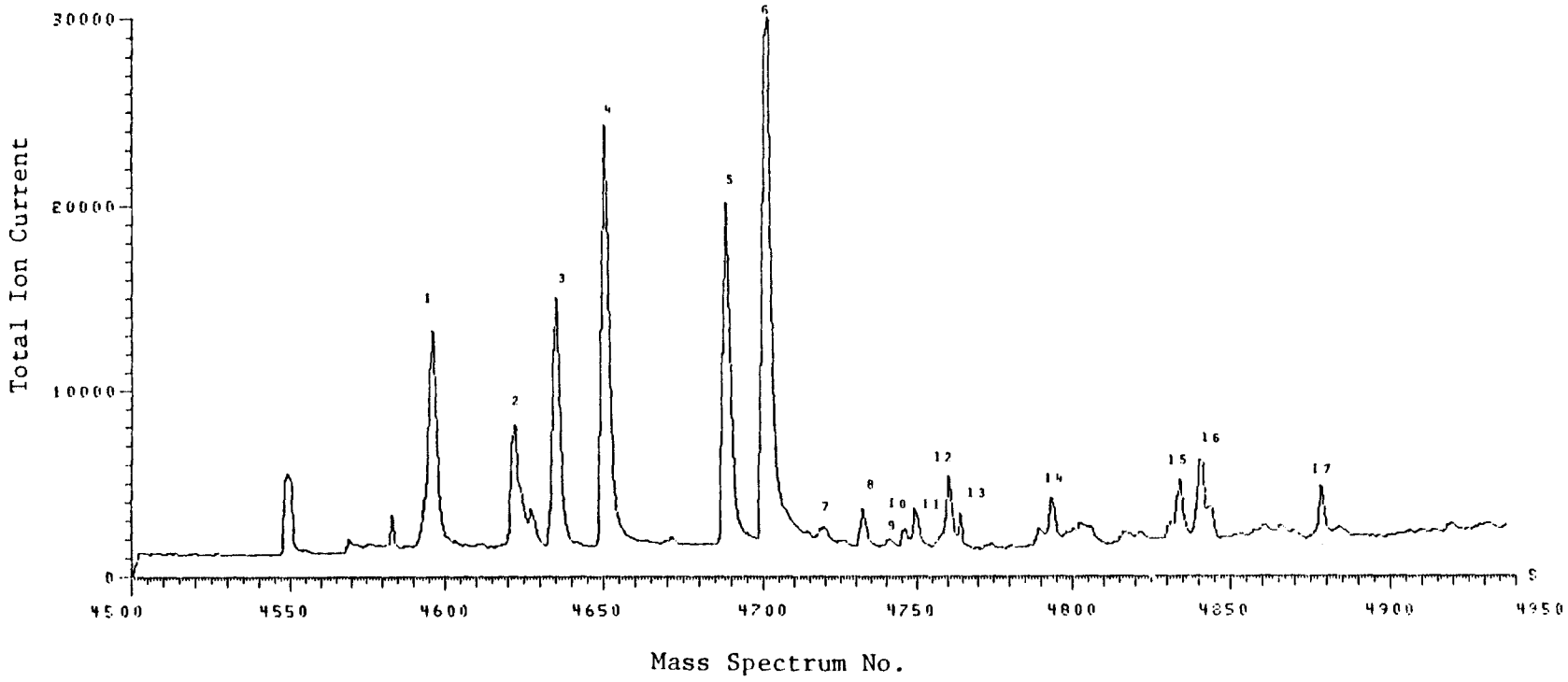



Figure 4.8. Total ion current profile of volatile organics in tail brine from Arkansas Chemical Incorp. Peak No. 2 = hexafluorobenzene (e₹), 3 = perfluorotoluene (e₹), 4 = benzene, 5 = dimethyldisulfide, 6 = toluene, and 15 = 1-chloro-2,3-dibromopropane.

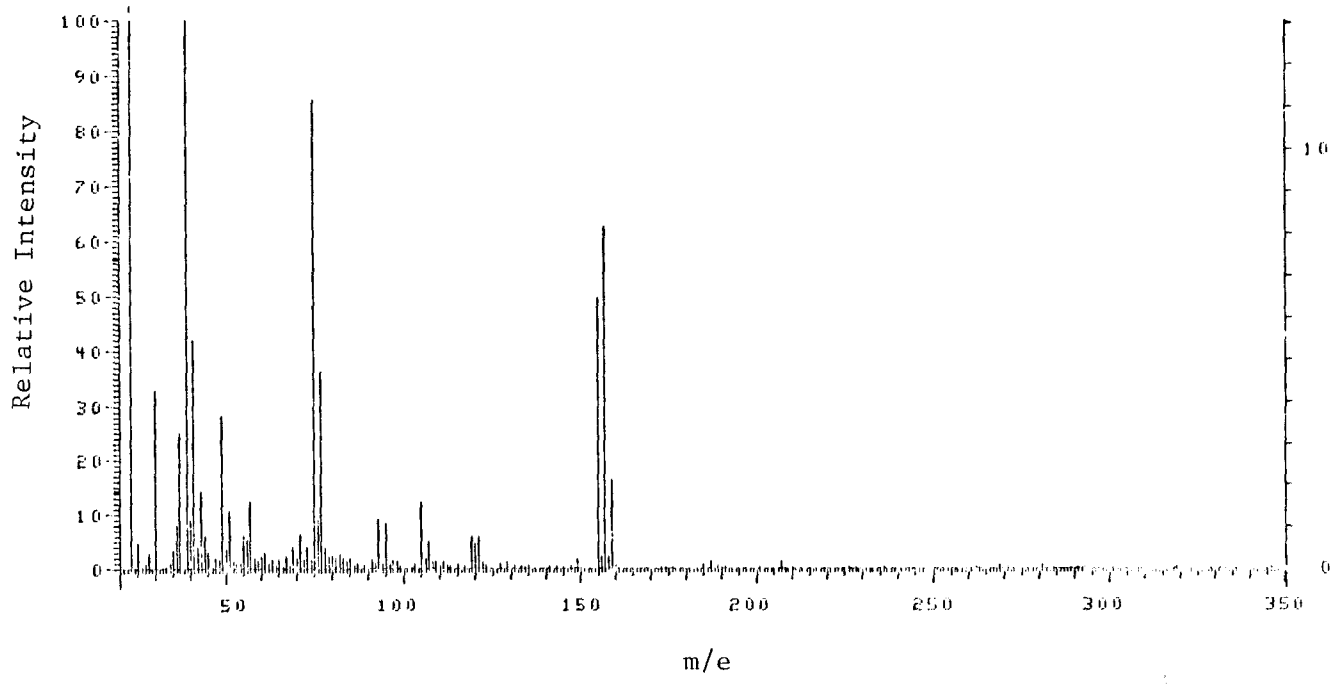



Figure 4.9. Mass spectrum of 1-chloro-2,3-dibromopropane in tail brine sample (ACI). Peak No. 15 in Figure 4.8.

Table 4.7. HALOGENATED AND OTHER ORGANICS IDENTIFIED AND QUANTITATED IN BRINE SAMPLES FROM ARKANSAS CHEMICAL INCORP.[a]

| | Sample Type | |
|---|---|---|
| | Front Brine | Tail Brine |
| Dibromochloromethane | 540 | N.D. |
| 1-Chloro-2,3-dibromopropane | 40 | 56 |
| Hexafluorobenzene (e$)[b] | | - |
| Perfluorotoluene (e$)[b] | | - |
| Ethylene dibromide | | T(?) |
| Benzene | 600 | 2,285 |
| Toluene | 10,000 | 3,200 |
| Dimethyldisulfide | 1,600 | 1,714 |
| Thiacyclopentane | 800 | T |
| Dithiopropane isomer | 1,600 | 1,400 |
| Ethylbenzene | 1,200 | N.D. |
| n-Undecane | 3,200 | 1,600 |
| n-Dodecane | 1,600 | 850 |
| Cyclooctatetraene (tent.) | 800 | N.D. |

[a]Concentrations are in ppt.

[b]e$ = external standard, 200 ng.

Figures 4.10 and 4.11 depict the total ion current profile and ion chromatograms for the volatile ambient air pollutants which were collected on the Tenax GC cartridges at Location No. 1 on the bank of the spent brine ponds at ACI. Figure 4.11 clearly depicts the presence of 1,2-dibromoethane and 1-chloro-2,3-dibromopropane. No bromoform was detected in this sample. The profile for the volatile organics at Location No. 2 on this site is given in Figure 4.12. This sample was found to contain a trace of allyl bromide and 1,2-dibromoethane.

1,2-Dibromoethane was also identified at Location No. 3 (Table 4.8, Figure 4.13). No other halogenated compounds which were unique were found in this sample. An ambient air sample taken at Location No. 4 (Table 4.9, Figure 4.14) contained a new compound which was tentatively identified as difluorodibromomethane. 1,2-Dibromoethane was also present.

The use of ion chromatograms or mass fragmentography (Fig. 4.11) is highly advantageous once the identity of the compound has been established in samples. The selection of the unique ion in a mass spectrum of a compound and the display of the intensity of that ion vs. the mass spectrum number (retention time) allows further deconvolution of the complex ambient air profile. This technique has been utilized throughout the study for displaying the relative intensities of the halogenated organics that were identified in the samples. The mass spectrum number of the halogenated compound is also related to the retention time in the chromatographic run. From this information it is possible to locate the peak which corresponds to the compound of interest by its retention time and the intensity of this ion is directly proportional to the concentration of the compound in the sample.

Table 4.10 summarizes the halogenated compounds which were identified by GC/MS/COMP in ambient air at Arkansas Chemical Inc. in El Dorado, Arkansas.

Table 4.10. HALOGENATED COMPOUNDS IDENTIFIED BY GC/MS/COMP IN AMBIENT AIR AT ARKANSAS CHEMICAL INCORP., EL DORADO, ARKANSAS

| Compound | Compound |
|---|---|
| Chlorodibromopropane | Difluorodibromomethane (tent.) |
| 1-Chloro-2,3-dibromopropane | Methyl Bromide |
| 1,2-Dibromoethane | |

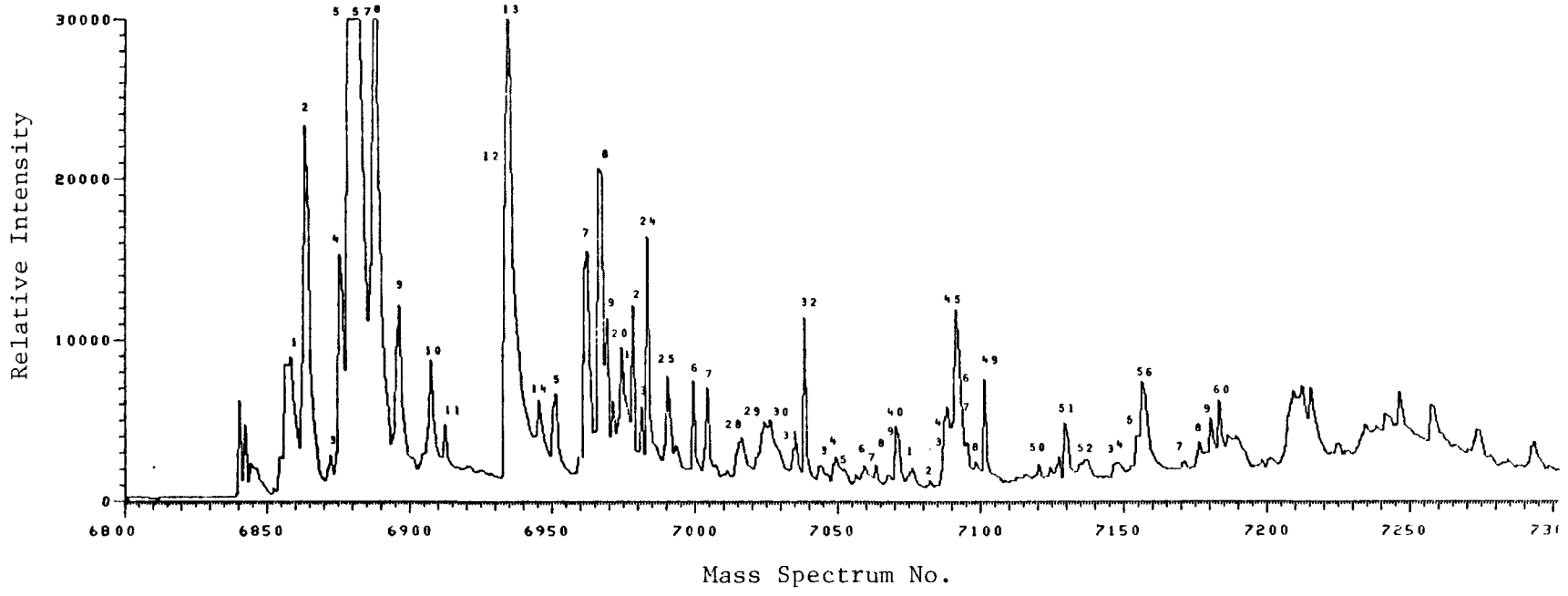



Figure 4.10. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L1).

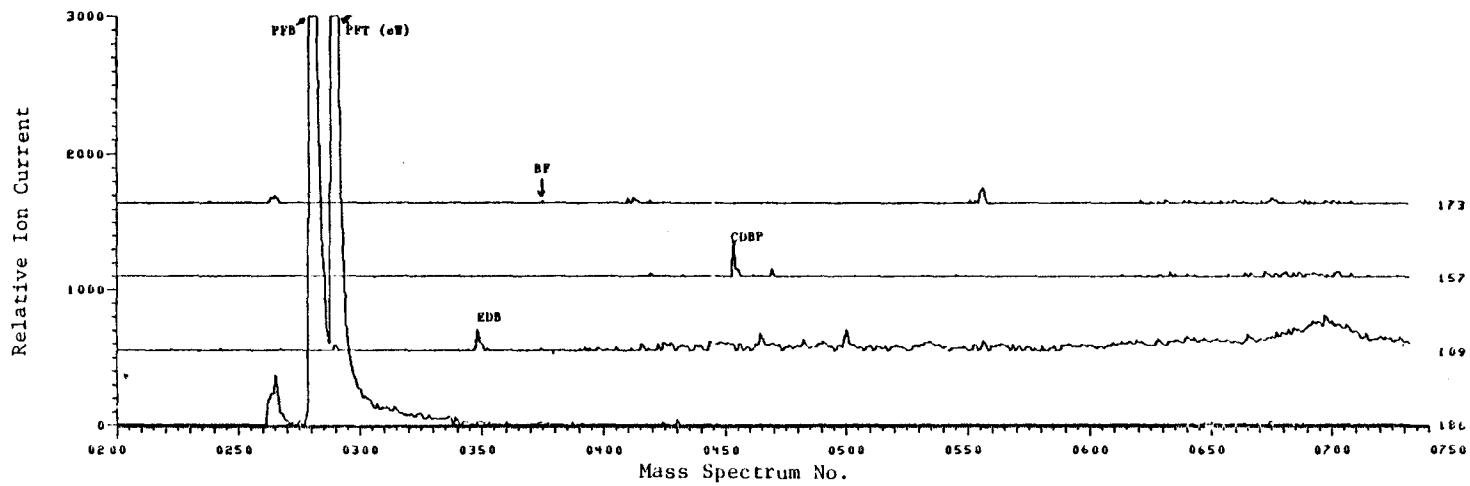



Figure 4.11. Ion chromatograms for ambient air sample from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L1). BF = bromoform, CDBP = 1-chloro-2,3-dibromopropane, EDB = ethylene dibromide.

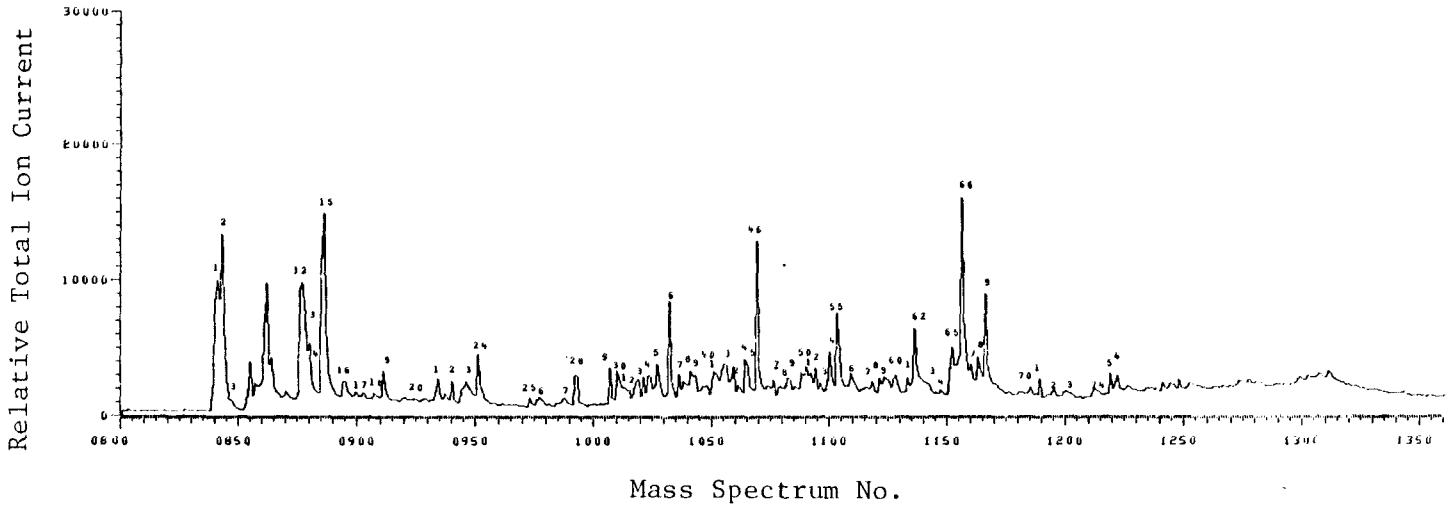



Figure 4.12. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L2).

Table 4.8. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM ARKANSAS CHEMICAL INC. SITE IN EL DORADO, ARKANSAS (P1/C1/L3)[a]

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 1 | 45 | dichlorodifluoromethane |
| 1A | 46 | acetaldehyde |
| 2 | 47 | trichlorofluoromethane |
| 2A | 48 | acetone |
| 2B | 50 | dichloromethane |
| 3 | 51 | freon 113 (BKG) |
| 3A | 53 | isopropanol |
| 3B | 55 | butenal isomer |
| 3C | 56 | 2-methylpentane |
| 3D | 57 | 3-methylpentane |
| 3E | 57 | butanal (tent.) |
| 4 | 58 | hexafluorobenzene (eS) |
| 4A | 59 | n-hexane |
| 5 | 60 | chloroform |
| 6 | 63 | perfluorotoluene (eS) |
| 6A | 64 | methylcyclopentane |
| 6B | 65 | 1,1,1-trichloroethane |
| 6C | 67 | benzene |
| 7 | 68 | carbon tetrachloride |
| 7A | 68 | cyclohexane |
| 7B | 69 | $C_7H_{16}$ isomer |
| 7C | 70 | methylbutanal isomer |
| 8 | 73 | n-pentanal |
| 9 | 75 | n-heptane |
| 9A | 79 | $C_7H_{14}$ isomer |
| 9B | 79 | $C_8H_{18}$ isomer |
| 9C | 80 | methylcyclohexane |
| 9D | 84 | 4-methyl-2-pentanone |
| 9E | 85 | methylpentanal isomer |
| 10 | 87 | toluene |
| 10A | 90 | $C_8H_{18}$ isomer |
| 11 | 93 | n-hexanal + 1,2-dibromoethane |
| 11A | 94 | $C_8H_{16}$ isomer |
| 11B | 96 | silane compound (BKG) |
| 12 | 96 | n-octane |
| 12A | 97 | tetrachloroethylene |
| 12B | 100 | $C_8H_{16}$ isomer |
| 13 | 101 | hexamethylcyclotrisiloxane (BKG) |
| 13A | 103 | ethylcyclohexane |
| 13B | 104 | $C_9H_{20}$ isomer |
| 14 | 106 | ethylbenzene |
| 15 | 108 | p-xylene |
| 16 | 109 | $C_9H_{20}$ isomer |
| 16A | 110 | $C_{10}H_{22}$ isomer |
| 17 | 111 | styrene |
| 18 | 112 | 2,2,4-trimethylheptane |
| 18A | 112 | m-xylene |
| 18B | 113 | n-heptanal |
| 19 | 113 | $C_{10}H_{22}$ isomer |
| 19A | 115 | $C_9H_{18}$ isomer |
| 20 | 116 | n-nonane |
| 21 | 118 | $C_{10}H_{20}$ isomer |
| 21A | 119 | $C_{10}H_{22}$ isomer |
| 22 | 120 | dimethyl-ethylbenzene isomer |
| 23 | 121 | $C_{10}H_{22}$ isomer |
| 24 | 122 | $C_{10}H_{20}$ isomer |
| 25 | 123 | $C_{10}H_{22}$ isomer |
| 25A | 123 | $C_{10}H_{16}$ isomer |
| 25B | 124 | $C_{10}H_{22}$ isomer |
| 26 | 125 | benzaldehyde |
| 26A | 126 | n-propylbenzene |
| 27 | 127 | p-ethyltoluene |
| 28 | 128 | $C_{10}H_{22}$ isomer |
| 29 | 129 | $C_{11}H_{24}$ isomer |
| 30 | 130 | $C_{11}H_{24}$ isomer |
| 31 | 132 | $C_{11}H_{24}$ isomer |
| 32 | 133 | $C_3$-alkyl benzene isomer |
| 32A | 134 | $C_{10}H_{20}$ isomer |
| 33 | 135 | 4-methyldecane |
| 34 | 136 | n-decane |
| 35 | 137 | $C_{11}H_{22}$ isomer |
| 35A | 138 | $C_{10}H_{16}$ isomer |
| 36 | 138 | $C_{11}H_{24}$ isomer |
| 37 | 139 | $C_4$-alkyl benzene isomer |
| 38 | 140 | $C_{11}H_{24}$ isomer |
| 39 | 141 | $C_{10}H_{16}$ isomer |
| 40 | 142 | $C_{11}H_{24}$ isomer |
| 41 | 144 | $C_{11}H_{24}$ isomer |
| 42 | 145 | acetophenone |
| 43 | 147 | $C_{11}H_{24}$ isomer |
| 44 | 149 | $C_4$-alkyl benzene isomer |

(continued)

Table 4.8 (cont'd)

| Chromato-graphic Peak No. | Elution Temp. (°C) | Compound | Chromato-graphic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|---|---|---|
| 44A | 150 | $C_{12}H_{24}$ isomer | 48 | 164 | $C_{12}H_{26}$ isomer |
| 45 | 152 | n-nonanal | 48A | 165 | $C_{13}H_{28}$ isomer |
| 45A | 153 | $C_{11}H_{22}$ isomer | 49 | 169 | n-decanal |
| 46 | 154 | n-undecane | 49A | 170 | $C_{12}H_{24}$ isomer |
| 46A | 157 | $C_4$-alkyl benzene isomer | 50 | 171 | n-dodecane |
| 46B | 157 | $C_{12}H_{26}$ isomer | 50A | 174 | $C_{13}H_{28}$ isomer |
| 46C | 159 | $C_{12}H_{26}$ isomer | 50B | 184 | $C_{13}H_{28}$ isomer |
| 47 | 160 | 3-phenylpropenal | 50C | 188 | $C_{13}H_{28}$ isomer |
| 47A | 163 | $C_5$-alkyl benzene isomer | | | |

[a]See Table 4.2 for sampling protocol.

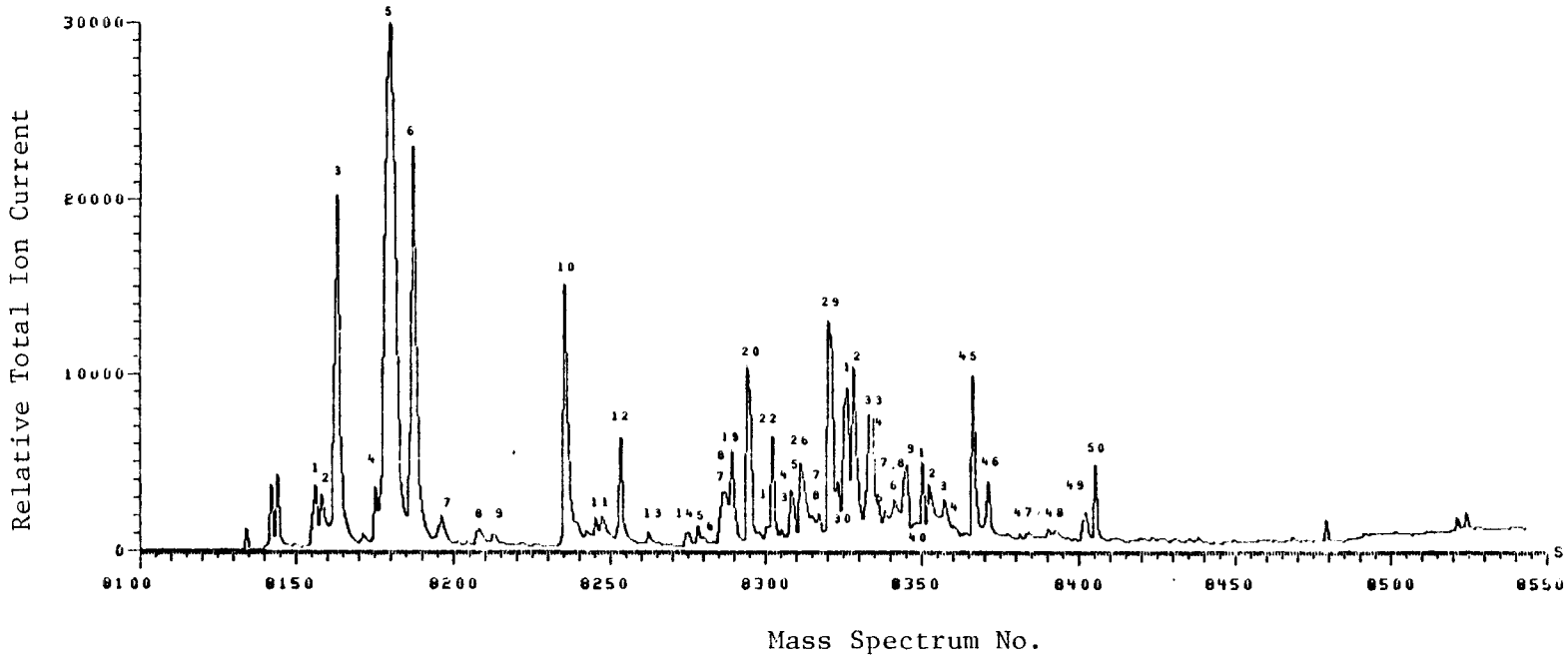



Figure 4.13. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L3).

Table 4.9. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM ARKANSAS CHEMICAL INC. SITE IN EL DORADO, ARKANSAS (P1/C1/L4)[a]

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 2 | 41 | $CO_2$ |
| 2A | 46 | acetaldehyde |
| 2B | 47 | difluorodibromomethane (tent.) |
| 3 | 48 | trichlorofluoromethane |
| 3A | 49 | isopentane |
| 4 | 50 | acetone |
| 4A | 51 | dichloromethane |
| 5 | 52 | freon 113 (BKG) |
| 5A | 53 | isopropanol |
| 5B | 54 | ter-butanol |
| 5C | 55 | butenal |
| 6 | 56 | 2-methylpentane |
| 7 | 58 | 3-methylpentane |
| 8 | 59 | hexafluorobenzene (es) |
| 9 | 60 | n-hexane |
| 9A | 61 | chloroform |
| 10 | 64 | methylcyclopentane |
| 10A | 65 | perfluorotoluene (es) |
| 10B | 67 | 1,1,1-trichloroethane |
| 11 | 68 | benzene |
| 11A | 69 | carbon tetrachloride |
| 11B | 70 | cyclohexane |
| 12 | 71 | $C_7H_{16}$ isomer |
| 12A | 71 | methylbutanal isomer |
| 12B | 72 | $C_7H_{16}$ isomer |
| 12C | 73 | hexamethyldisiloxane (BKG) |
| 13 | 74 | n-pentanal |
| 14 | 76 | n-heptane |
| 14A | 80 | methylcyclohexane |
| 14B | 84 | 4-methyl-2-pentanone |
| 14C | 85 | methylpentanal isomer |
| 15 | 87 | toluene |
| 15A | 92 | $C_8H_{16}$ isomer |
| 16 | 93 | 1,2-dibromoethane |
| 16A | 93 | n-hexanal |
| 17 | 95 | n-octane |
| 17A | 96 | tetrachloroethylene |
| 17B | 96 | $C_8H_{16}$ isomer |
| 17C | 102 | $C_8H_{16}$ isomer |
| 17D | 103 | $C_9H_{20}$ isomer |
| 18 | 106 | ethylbenzene |
| 18A | 106 | $C_9H_{20}$ isomer |
| 19 | 107 | p-xylene |
| 20 | 108 | $C_9H_{20}$ isomer |
| 20A | 100 | $C_9H_{20}$ isomer |
| 21 | 111 | styrene |
| 22 | 112 | $C_{10}H_{20}$ isomer |
| 22A | 112 | m-xylene |
| 23 | 113 | m-heptanal |
| 23A | 113 | $C_{10}H_{22}$ isomer |
| 23B | 114 | $C_9H_{18}$ isomer |
| 24 | 115 | n-nonane |
| 24A | 117 | $C_9H_{18}$ isomer |
| 25 | 118 | tetramethylhexane isomer |
| 25A | 119 | $C_3$-alkyl benzene isomer |
| 26 | 119 | trimethylheptane isomer |
| 27 | 120 | dimethyl-ethylhexane isomer |
| 28 | 121 | $C_{10}H_{22}$ isomer |
| 29 | 122 | trimethylheptane isomer |
| 29A | 122 | $C_{10}H_{16}$ isomer |
| 30 | 123 | benzaldehyde |
| 31 | 125 | $C_{10}H_{20}$ isomer |
| 32 | 126 | m-ethyltoluene |
| 33 | 128 | $C_{11}H_{24}$ isomer |
| 34 | 129 | $C_{11}H_{24}$ isomer |
| 35 | 131 | $C_{10}H_{16}$ isomer |
| 36 | 132 | $C_{10}H_{22}$ isomer |
| 37 | 134 | $C_{11}H_{24}$ isomer |
| 38 | 134 | n-decane + dichlorobenzene isomer |
| 39 | 135 | $C_{11}H_{24}$ isomer |
| 40 | 136 | $C_{10}H_{16}$ isomer |
| 41 | 138 | $C_4$-alkyl benzene isomer |
| 41A | 138 | $C_{11}H_{24}$ isomer |
| 41B | 139 | $C_{10}H_{16}$ isomer |
| 42 | 140 | $C_{11}H_{24}$ isomer |
| 43 | 141 | $C_{11}H_{24}$ isomer |
| 44 | 142 | $C_{11}H_{24}$ isomer |
| 45 | 144 | acetophenone |
| 46 | 145 | $C_{12}H_{26}$ isomer |
| 46A | 147 | $C_{10}H_{12}$ isomer |
| 47 | 148 | $C_9H_{11}O$ isomer |

(continued)

Table 4.9 (cont'd)

| Chromatographic Peak No. | Elution Temp. (°C) | Compound | Chromatographic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|---|---|---|
| 47A | 149 | $C_{10}H_{12}$ + $C_{11}H_{20}$ isomer | 49C | 161 | dimethylphenol isomer |
| 48 | 150 | n-nonanal | 49D | 165 | dimethylphenol isomer |
| 48A | 151 | $C_{11}H_{22}$ isomer | 49E | 167 | n-decanal |
| 49 | 152 | n-undecane | 50 | 168 | $C_{12}H_{24}$ isomer |
| 49A | 155 | $C_4$-alkyl benzene isomer | 51 | 169 | n-dodecane |
| 49B | 158 | 3-phenylpropenal | 51A | 177 | $C_{12}H_{24}$ isomer |

[a]See Table 4.2 for sampling protocol.

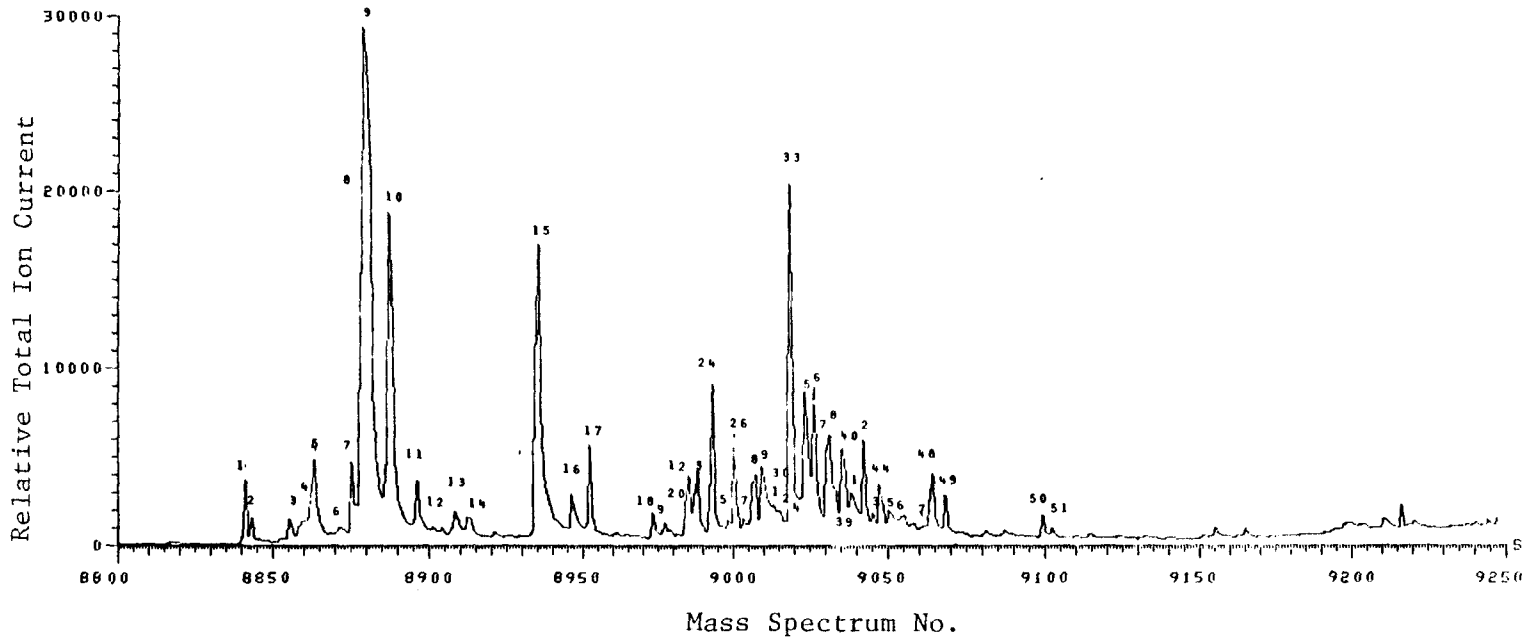



Figure 4.14. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L4).

Quantification of Halogenated Hydrocarbons.--The identified halogenated hydrocarbons were quantified (Section F, Appendix A). Table 4.11 presents the levels of halogenated hydrocarbon in samples taken near the spent brine pond on the Arkansas Chemical Inc. site. The highest level observed was 133 ng/$m^3$ (1,2-dibromoethane). This sample was taken at L4 and it actually represented an upwind sample from the brine pond and the bromine extraction facility. For this reason it was believed that the brominated compound had been transported from another facility since the analysis of spent brine indicated only a trace of EDB.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--Methyl chloride was detected by GC/EC in one sample (P1/C3/L1) at a level of 200 μg/$m^3$. The detection limit was about 200 μg/$m^3$ for methyl chloride and 120 μg/$m^3$ for methyl bromide. No other halogenated species (of these four) were detected at ACI.

Ethylene.--The levels of ethylene found at ACI are given in Table 4.12. These values were typical background levels observed in most samples taken in this area.

Table 4.12. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR[a]

| Site | Period/Cycle/Location | ppm |
|---|---|---|
| ACI | P1/C3/L1 | 0.76 ± 0.16 |
| | P1/C3/L2 | 0.85 ± 0.15 |
| | P1/C3/L5 | 0.76 ± 0.16 |

[a]See Table 4.2 for sampling protocol and Fig. 4.4 for locations.

4.2.1.5 Brominated Organics in Soil and Water

All of the soil and water samples were screened by the VOA method (Appendix A) for the presence of EDB and other volatile brominated compounds, and none were found. One of the soil samples [P1/C1/L1 (April 4, 1977)] was selected for analysis for semi-volatile brominated organics. The results are given in Table 4.13.

The spectrum of Tetrabrom obtained from the soil sample P1/C1/L1 is shown in Figure 4.15.

Table 4.11. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INCORP., EL DORADO, AK

| Period/Cycle/Location[a] | Allyl bromide | Bromoform | 1 or 2-Bromopropane | 1-Chloro-2,3-Dibromo-propane | 1,2-Ethylene dibromide | Difluorodibromomethane |
|---|---|---|---|---|---|---|
| P1/C1/L1 | 70 | T[b] | - | 1.87 | 3.10 + 0.8 | - |
| L2 | T | -[c] | - | - | 5.30 | - |
| L3 | 29.7 | - | 5.5 | - | 81 | - |
| L4 | - | - | 6.7 | - | 133 | T |

[a]Refer to Table 4.2 for sampling protocol, values are in $ng/m^3$.

[b]T = trace detected.

[c]- = not detected.

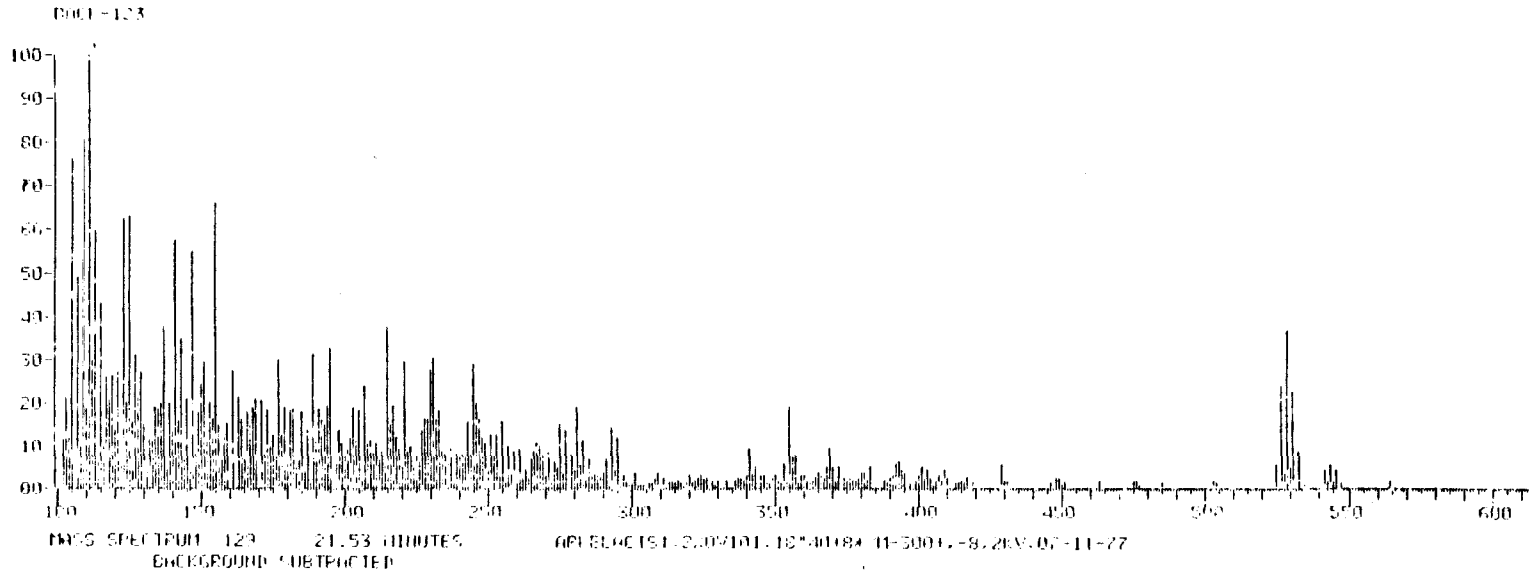



Figure 4.15. Mass spectrum of Tetrabrom in soil sample P1/C1/L1.

Table 4.13. ANALYSIS OF A SOIL SAMPLE COLLECTED NEAR ARKANSAS CHEMICALS, INCORPORATED, EL DORADO, AK

| Period/Cycle/Location | EDB (µg/k) | Decabrom (g/k) | Tetrabrom (µg/kg) |
|---|---|---|---|
| P1/C1/L1 | ND | 260[a,b] | 4,100[a,c] |

[a]Quantitated by GC/MS/COMP with multiple ion detection (MID).

[b]Confirmed by GC/MS/COMP-MID using ion intensity ratios; m/e 800:960 was 3.0 for standards and 2.7 for the sample.

[c]Confirmed by GC/MS/COMP in full scan mode.

### 4.2.2 Great Lakes Chemical Corporation

#### 4.2.2.1 Sampling

The sampling protocol and sample descriptions for Great Lakes Chemical Corporation are given in Table 4.14. The corresponding Figures 4.16-4.18 designate the sampling locations for September 22-24, 1976. The sampling protocols for April 7, 22, and 29 and May 17, 1977 are given in Table 4.15 and their locations in Figures 4.19 and 4.20.

#### 4.2.2.2 Survey of Chemicals on Glass Fiber and Cellulose Filters

Scanning Electron Microscopy (SEM) and Electron Microprobe (EM) Analysis.--Samples were collected at Great Lakes Chemical Corp. by the State of Arkansas Air Pollution Control Division using Hi-Vol samplers. Glass fiber filters (GFF) and cellulose filters (CF) were sampled in parallel. Each site was sampled for three 24 hour periods. One period from each site has been analyzed by SEM and EM. Both types of filter material were examined. Sufficient sample was concentrated on the surface of the GFF to permit direct analysis without the usual carbon-coating to prevent charge buildup on the sample.

Initially, an examination for the presence of bromine and its subsequent mapping was performed. In Figure 4.21 the EM spectrum shown is expanded for the greatest sensitivity in the bromine region. Traces were detectable in both samples when compared to the background in Figure 4.22. However, these traces are insufficient to produce an elemental map.

Table 4.14. SAMPLING PROTOCOL FOR GREAT LAKES CHEMICAL CORPORATION, HIGHWAY 15, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/22/76 P1 | C1 | L1 | 1026-1234 | 109 | HHC[a] | 24-26 | 51-46 | 130/3-230/3-6 | Clear |
| | | L2 | 1026-1234 | 122 | HHC[a] | | | | |
| | | L3 | 1026-1234 | 140 | HHC[a] | 26 | | variable/light | Clear, slight odor of $Br_2$ |
| | | L4 | 1026-1233 | 100 | HHC[a] | 24 | 51 | | Clear, odor of bromobenzene Brine Pit-heavy odor |
| | C2 | L5 (ELV) | 1010-1702 | - | HHC[c] | 26 | | | |
| | | L2 (ELV) | 945-1702 | - | HHC[c] | | | | |
| | | L2 | 945-1702 | - | HHC[b] | | | | |
| | | L3 | 1026-1700 | - | HHC[b] | 26 | | calm | Clear, odor of $Br_2$ |
| | | L4 | 1026-1602 | - | HHC[b] | 28-30 | | calm | |
| | C3 | L1 | 1238-1337 | 46.7 | F, CBN, CBD | 27 | | 230/3-6 | |
| | | L2 | 1236-1336 | 54.6 | F, CBN, CBD | | | | |
| | | L3 | 1236-1336 | 48.1 | F, CBN, CBD | 28 | | | Clear, slight odor of $Br_2$ |
| | | L4 | 1233-1336 | 77.8 | F, CBN, CBD | | | shifted to South | |
| | C4 | L1 | 1340-1450 | 123 | AM | | | 230/3-6 | No drift |
| | | L2 | 1337-1451 | 137 | AM | | | | |
| | | L3 | 1337-1451 | 103 | AM | | | | |
| | | L4 | 1340-1453 | 125 | AM | 28 | | | Clear |
| | | L5 | 1130 | 1 | TED | | | | |
| | | L6 | 1138 | 1 | TED | | | | |
| | | L7 | 1143 | 1 | TED | | | | |

(continued)

Table 4.14 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmbh) | Other |
| 9/22/76 | | L6 | 1130 | 0.28 | VAC | | | | |
| P1 | | L8 | 1143 | 0.28 | VAC | | | | |
| 9/22/76 | C1 | L1 | 1553-1802 | 116 | HHC[a] | 22 | 65 | South/3 | Clear |
| P2 | | L2 | 1548-1608 | 96 | HHC[a] | | | | |
| | | L3 | 1600-1831 | 160 | HHC[a] | 33-30 | 38 | clear | Clear, odor of brine steam |
| | | L4 | 1549-1823 | 191 | HHC[a] | | | 270°/5-5KTS | Clear, light $Br_2$ odor |
| 9/22,23/76 | C2 | Parkers Chapel Water Tower | 1730-1030 | - | HHC[c] | | | | |
| | C3 | L1 | 1813-1913 | 36.8 | F, CBN, CBD | | | | |
| | | L2 | 1827-1932 | 73.6 | F, CBN, CBD | | | | |
| | | L3 | 1803-1916 | 59.4 | F, CBN, CBD | 30 | | 240°/5-8 | |
| | C4 | L5 | 1930 | - | VAC | | | | |
| 9/24/76 | C1 | L1 | 1200-1420 | 229 | HHC[a] | 29 | 38 | North/8 | |
| P3 | | L2 | 1200-1420 | 178 | HHC[a] | | | | |
| | | L3 (ELV) | 1200-1420 | 205 | HHC[e] | | | | Clear, odor phenol, slight $Br_2$ |
| | | L4 | 1200-1420 | 216 | HHC[f] | | | | Upset at 1304-1309 |
| | C2 | L3 (ELV) | 1740-948 | - | HHC[d] | | | 30°/3-10 | |
| | | L5 (ELV) | 1745-945 | - | HHC[d] | | | 180°/3-11 | |

(continued)

Table 4.14 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/24/76 | C3 | L4 | 1018-1818 | - | HHC[d] | | | 30°/3-10 | |
| P3 | | L6 (ELV) | 1145-1824 | - | HHC[c] | | | | |
| | C4 | L7 | 1428-1536 | 62 | F, CBN, CBD | 28-29 | 38-42 | ENE-NNE/8-13 | Clear, visible $Br_2$ plume SE, Black smoke NE, odor of $H_2S$ |
| | | L2 | 1430-1536 | 59 | F, CBN, CBD | | | | Clear, strong odor of $Br_2$ and phenol |
| | | L3 | 1430-1536 | 85 | F, CBN, CBD | | | | |
| | | L4 | 1430-1536 | 74 | F, CBN, CBD | | | | |
| | C5 | L7 | 1540-1652 | 119 | AM | | | | |
| | | L2 | 1540-1652 | 147 | AM | | | | |
| | | L3 | 1542-1652 | 110 | AM | | | | Clear, slight odor of $Br_2$ |
| | | L4 | 1540-1652 | 143 | AM | | | | |
| | C6 | L7 | 1657-1806 | 51 | F, CBN, CBD | | | | |
| | | L2 | 1657-1758 | 54 | F, CBN, CBD | | | | |
| | | L3 | 1659-1706 | 64 | F, CBN, CBD | | | | Odor of phenol |
| | | L4 | 1657-1803 | 68 | F, CBN, CBD | | | | |

[a] Nutech Model 220 sampler 3-6 ft elevation

[b] DuPont sampler 3-6 ft elevation

[c] DuPont sampler 15-18 ft elevation

[d] Overnight sampling

[e] Sampling done on top of 3 story tower

[f] Sampling done on top of Tank

Locations shown in Figures 7, 8, and 9.

Key to Sample Type:
HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Bromide
CBD - Chlorine and Chloride
AM - Acid Mist
TED - Tedlar bag
VAC - Aluminum Vacuum Can

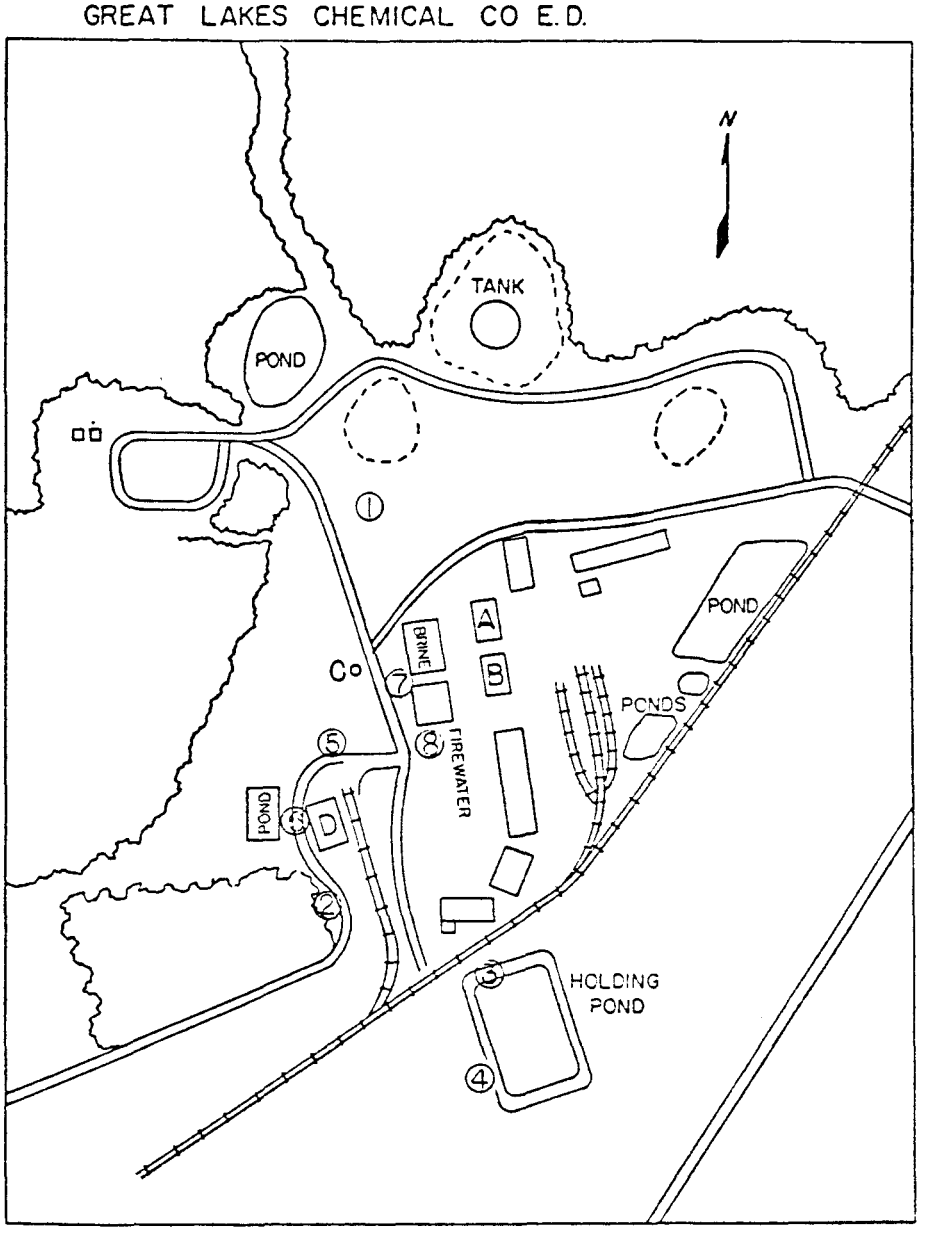



Figure 4.16. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P1 - 9/22/76

A - EDB facility

B - $Br_2$ facility

C - $H_2S$ stripper

D - Tetrabrom facility

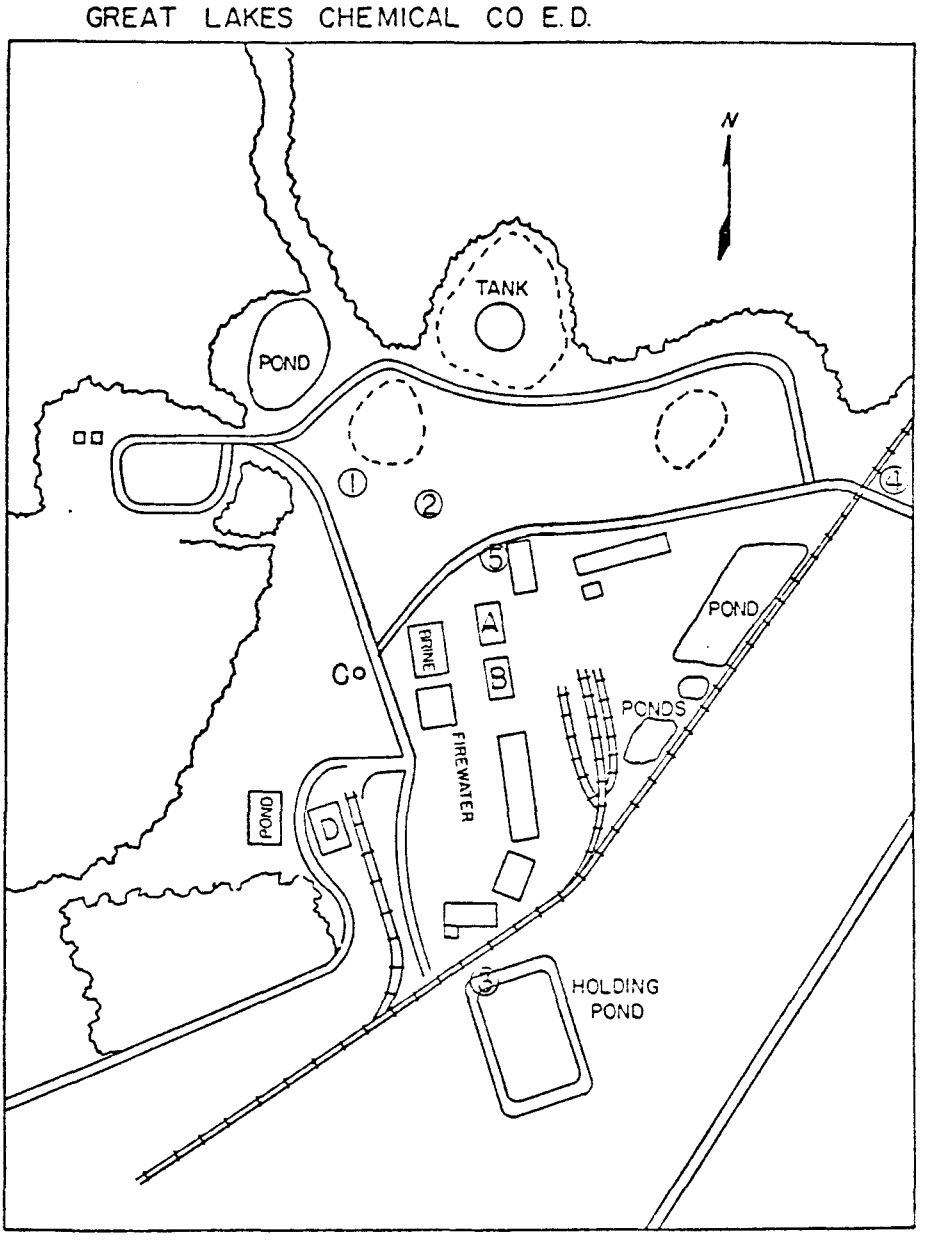



Figure 4.17. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P2 - 9/22/76.

A - EDB facility

B - $Br_2$ facility

C = $H_2S$ facility

D = Tetrabrom facility

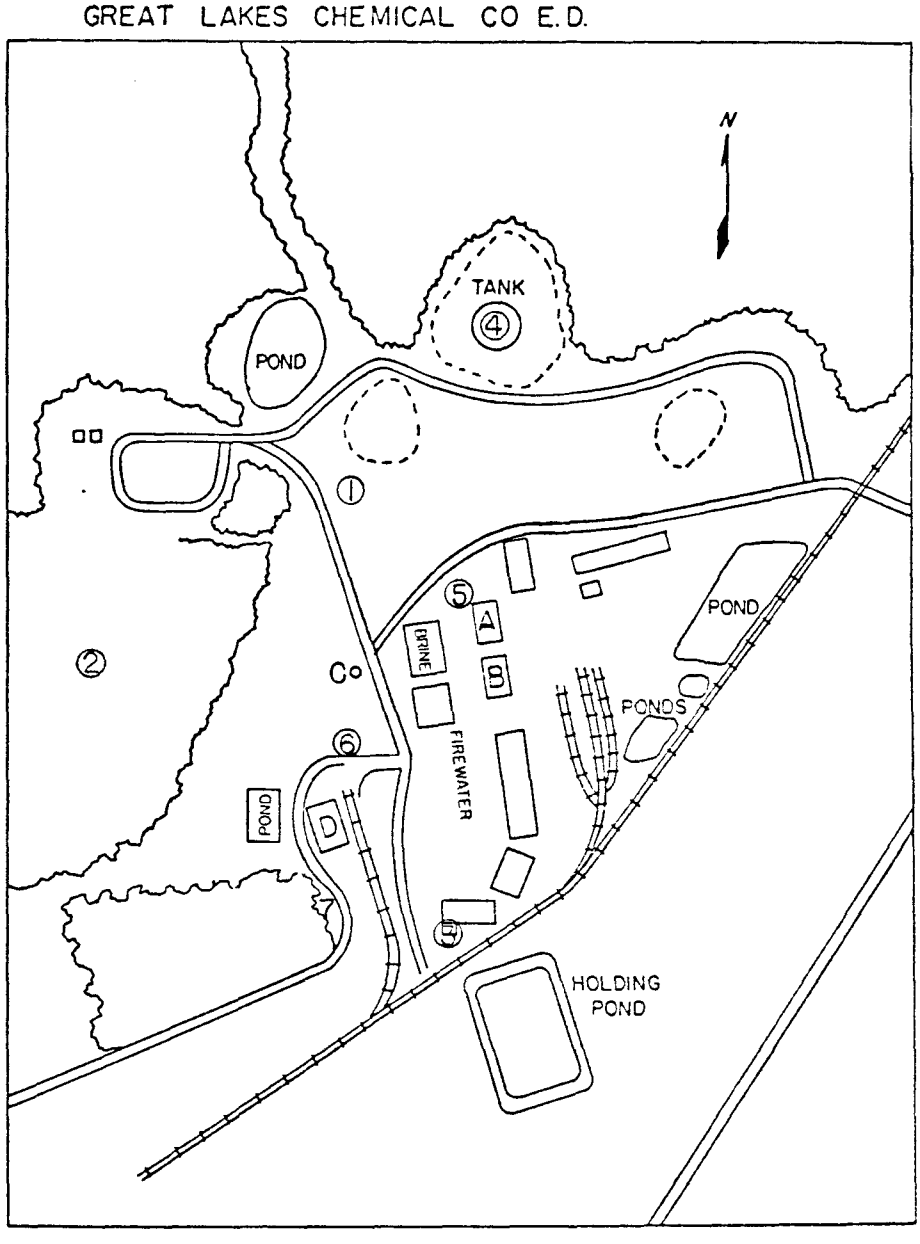



Figure 4.18. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P3 - 9/24/76.

A - EDB facility

B - $Br_2$ facility

C - $H_2S$ stripper

D - Tetrabrom facility

Table 4.15. SAMPLING PROTOCOL FOR GREAT LAKES CORPORATION, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Size | Type of Sample |
|---|---|---|---|---|
| P1 | C1 | L1 | 2 core[a] | SHHC-V |
| 4/7/77 | | | 2 core | SHHC-SV |
| | | | 1 ℓ | WHHC-V/SV[b] |
| | | | | VHHC-V[c] |
| | | | | VHHC-SV[b] |
| | | L2 | 2 core | SHHC-V |
| | | | 2 core | SHHC-SV |
| | | | 1 ℓ | WHHC-V/SV[d] |
| | | L3 | 2 core | SHHC-V |
| | | | 2 core | SHHC-SV |
| | | L4 | -- | VHHC-V |
| | | | | VHHC-SV |
| P2 | C1 | L1 | | SEHHC-V/SV |
| 4/22/77 | | L2 | | SCHHC-V/SV |
| | | L3 | | SEHHC-V/SV |
| | | L4 | | SCHHC-V/SV |
| P3 | | Parkers Chapel | 1 ℓ | MHHC-V/SV |
| 4/29/77 | | | | |
| P4 | C1 | Parkers Chapel | | VHHC-V/SV[e] |
| 5/17/77 | | | | |

[a]Core ∿5 cm diameter, 13 cm depth.

[b]∿2/3 m wide, ∿1 cm deep in dry weather (no rain for 1 week).

[c]Needles stripped from 40 cm of pine bough sampled at ∿5 m above ground from trees showing damage.

[d]Stream ∿30 cm wide, ∿5 cm deep in dry weather (no rain for 1 week).

[e]Apples.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

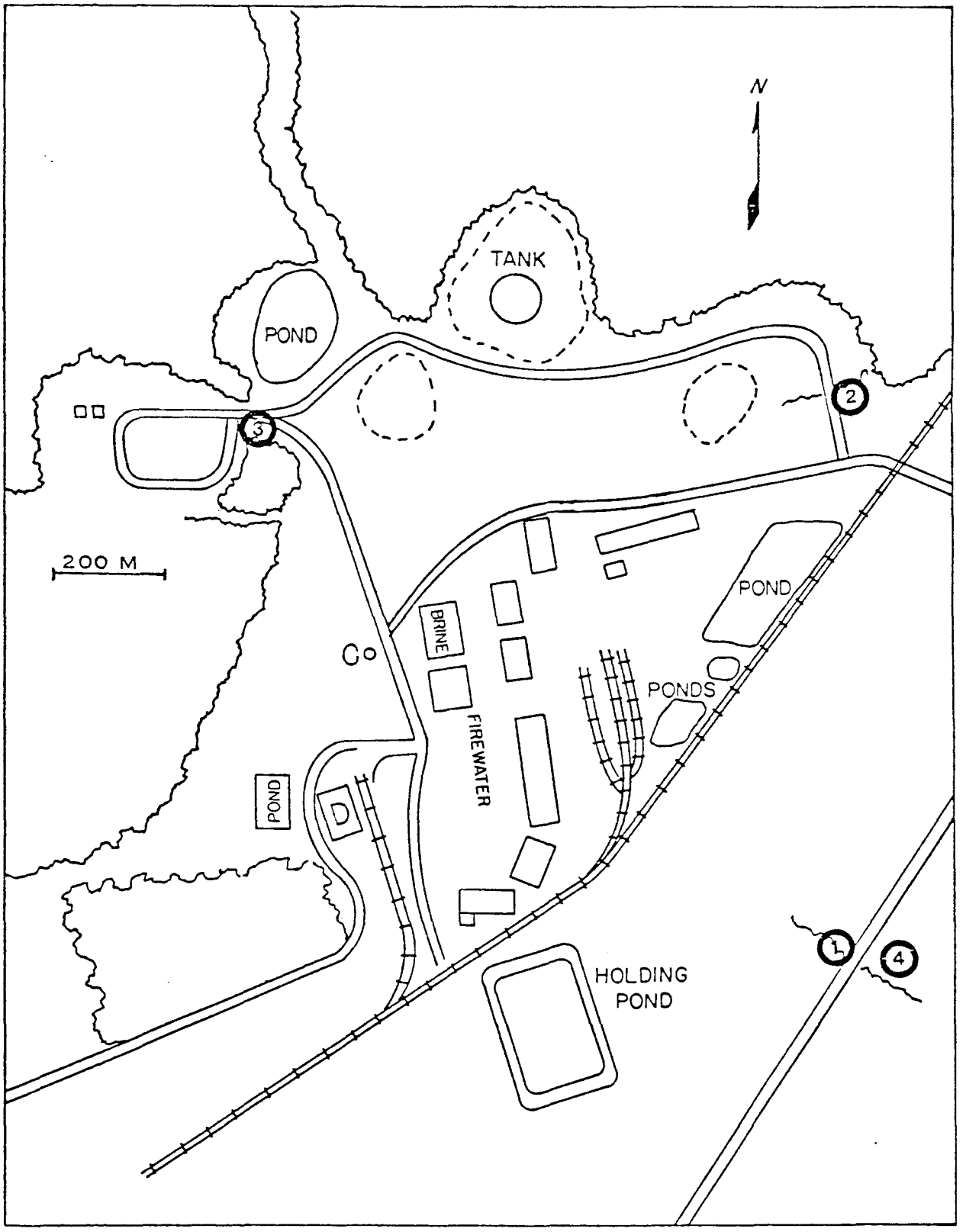



Figure 4.19. Schematic map of Great Lakes Chemical Corporation, El Dorado - sampling locations for P1 - 4/7/77.

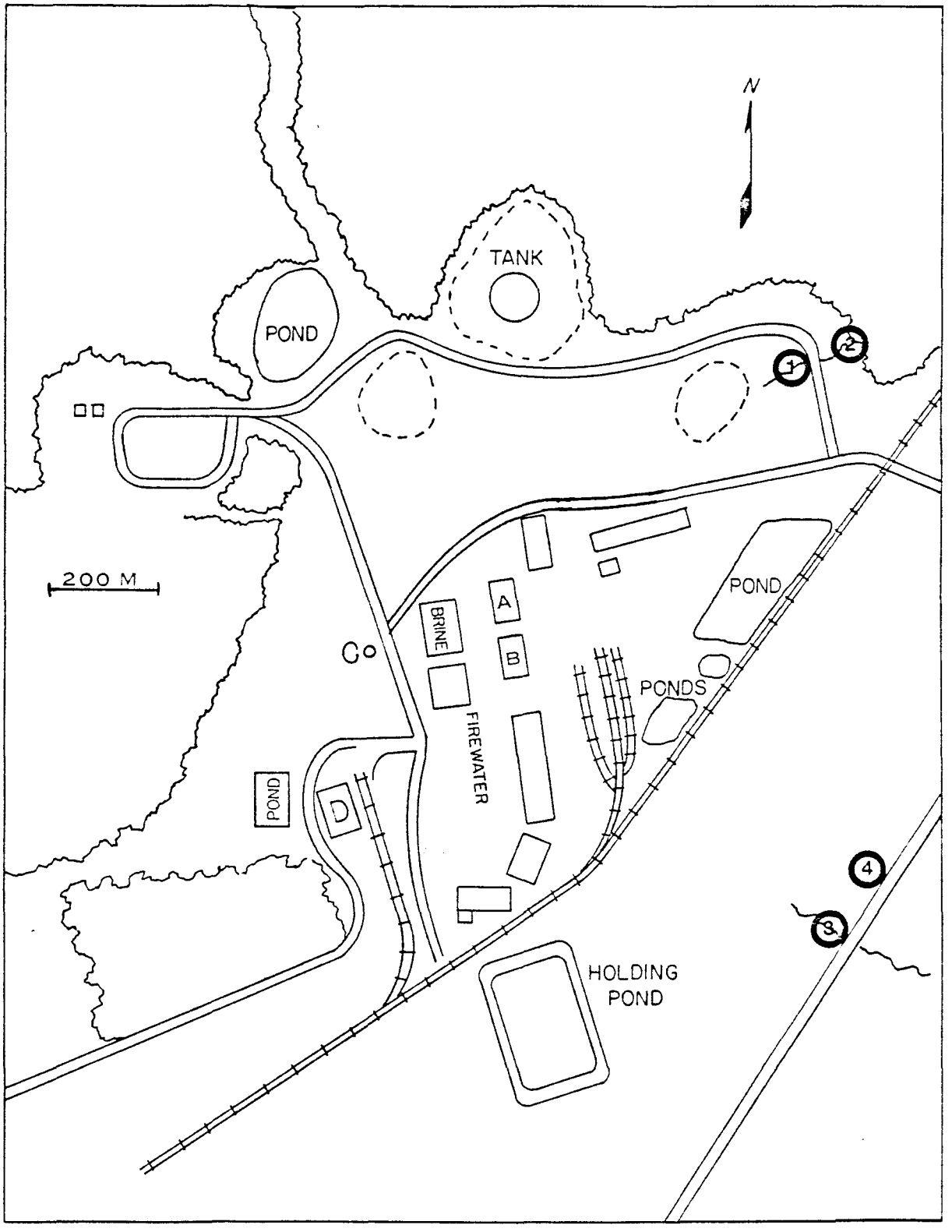
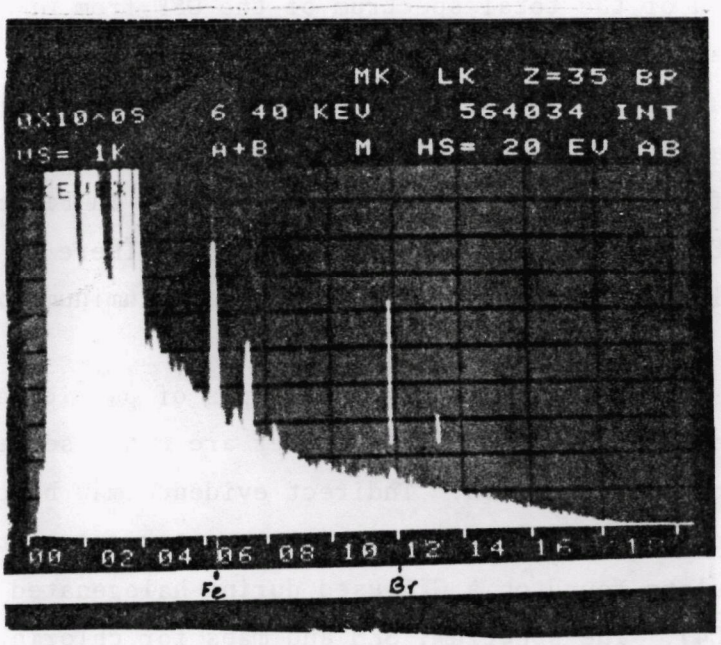
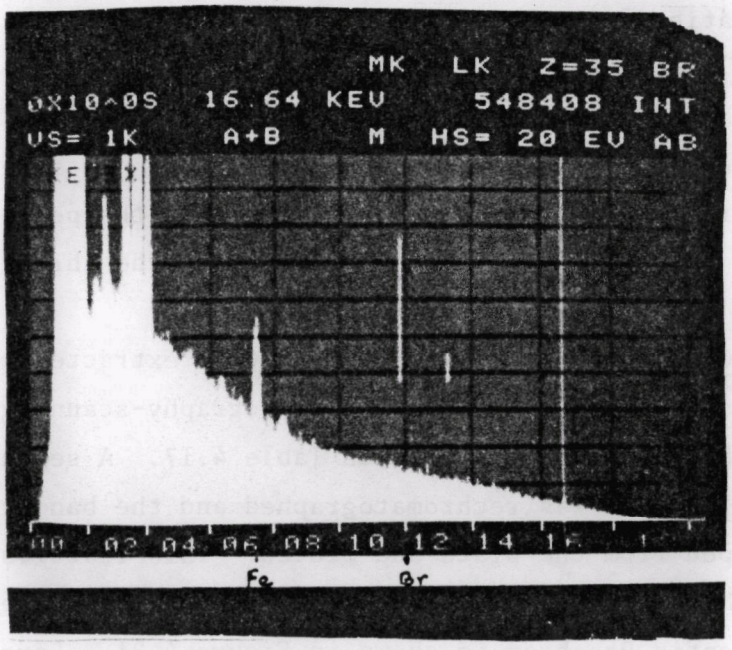



Figure 4.20. Schematic map of Great Lakes Chemical Corporation, El Dorado - sampling locations for P2 - 4/22/77.




a

Figure 4.21. Great Lakes Chemical Corporation, El Dorado, Arkansas on 12/17/76 - 12/18/76. Volume sampled 2,733.6 $m^3$ air.




b

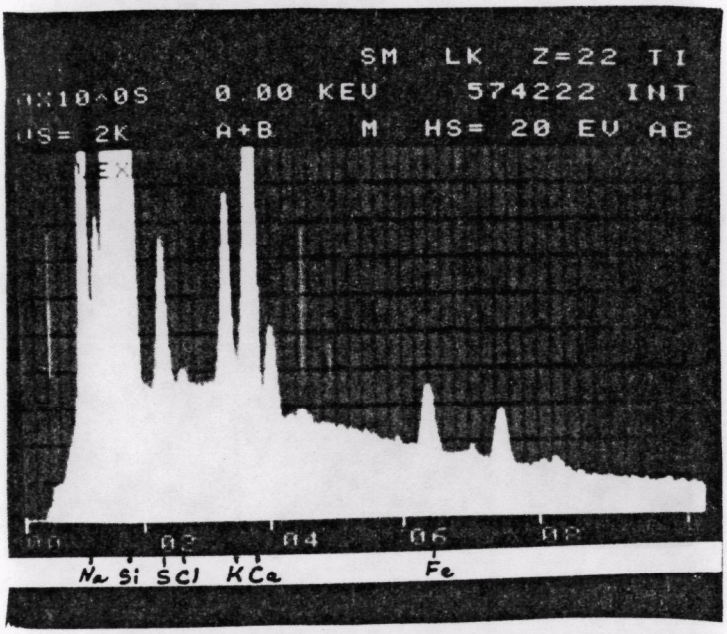
Figure 4.22. Electron microprobe spectrum of blank glass fiber filter.

An inspection of the total spectrum of the GFF from Great Lakes Chemical Corp. (Fig. 4.23a) reveals several other elements which were significantly above background (that is, chlorine, aluminum, and iron). The amount of sulfur is especially high compared to chlorine. Electron microprobe maps of chlorine, sulfur, aluminum, and silicon are shown in Figures 4.23-4.25 along with the SEM maps of the region (Fig. 4.23). There is some degree of coincidence of aluminum and silicon indicating an aluminum silicate particulate is probably present.

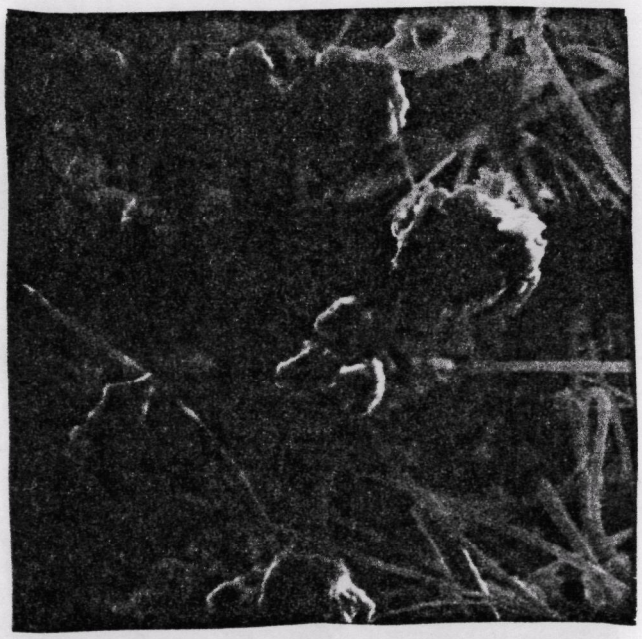
In general, this analysis surveys the types of particulate which were present. Since elements of low atomic number are not observed, carbon and its compounds escape observation. Indirect evidence may be obtained for halogenated organics by eliminating possible counterions. Such was the case of a particulate found on a GFF used during halogenated hydrocarbon sampling (P1/C1/L4). The spectrum, SEM and maps for chlorine, sodium, potassium, calcium and magnesium are shown in Figures 4.26-4.29. There were relatively low amounts of counterions as compared to the chlorine. Calcium is at background. Magnesium shows the greatest intensity, but even so it is weak compared to chlorine.

Neutron Activation Analysis.--A segment of each filter was submitted to neutron activation analysis. The segment was 2 x 2 cm cut from the medium fold with the distal edge of the segment 3 cm from the filter edge. The results of the neutron activation analysis are shown in Table 4.16. The highest concentration of bromine (20.2 $\mu g/m^3$) was detected in a sample taken on December 17, 1976. Also, this represented the period for the highest chlorine value (1.7 $\mu g/m^3$) observed during the three day sampling period.

Brominated Organics.--The filters above were extracted as described in Appendix A and analyzed by thin layer chromatography-scanning densitometry for Decabrom. The results are listed on Table 4.17. A second extraction of the GFF from 12/18/76 was rechromatographed and the band corresponding to Decabrom scraped from the plate and eluted. This fraction was submitted to direct probe MS analysis. The spectrum is shown in Figure 4.30. A spectrum of authentic Decabrom is shown in Figure 4.31. Large amounts of a yellow material remained near the origin on the GLC plate. This material




a



b

1280

Figure 4.23. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on glass fiber filter. Sample Volume: 2,733.6 $m^3$; Location: Great Lakes Chemical Corporation, El Dorado, Arkansas. Collected 12/17/76 - 12/18/76.

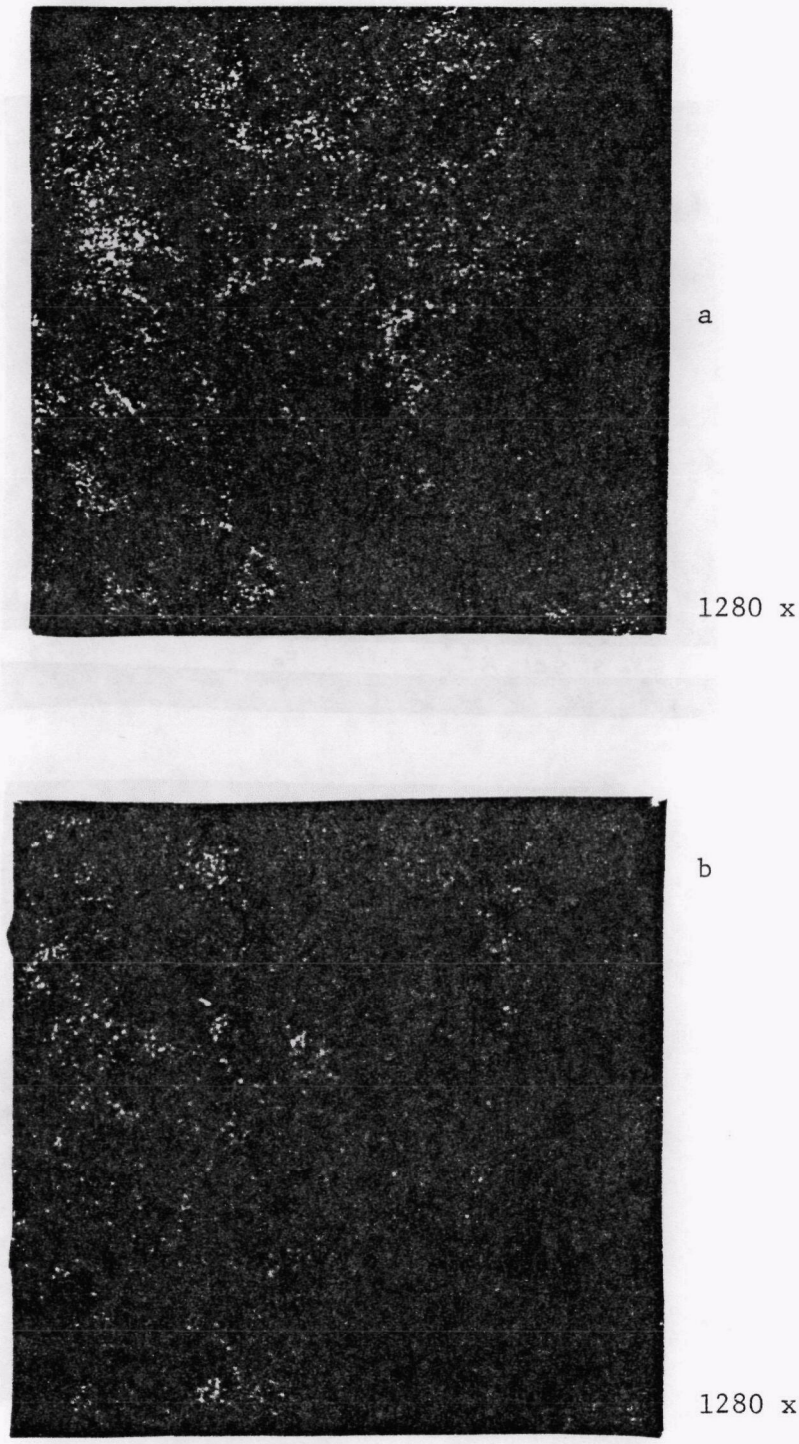
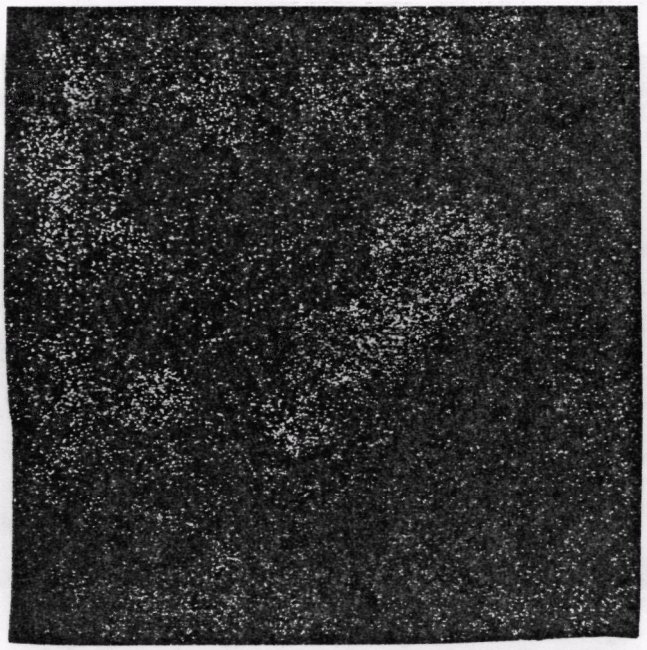
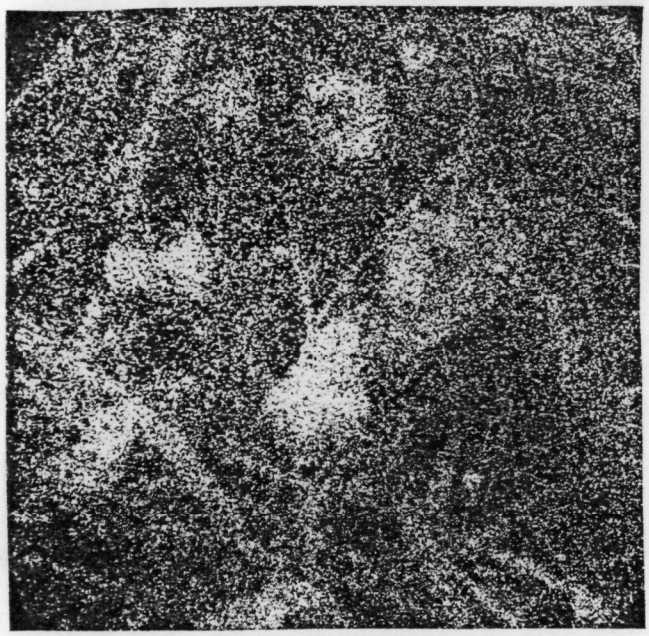



Figure 4.24. Electron microprobe element map of region shown in Figure 4.23.
(a) Chlorine map; (b) Sulfur map.



a

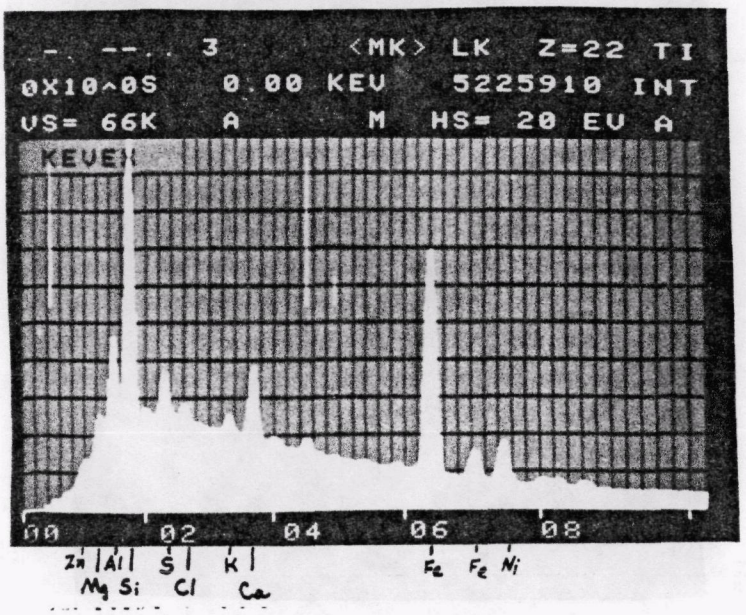
1280 x



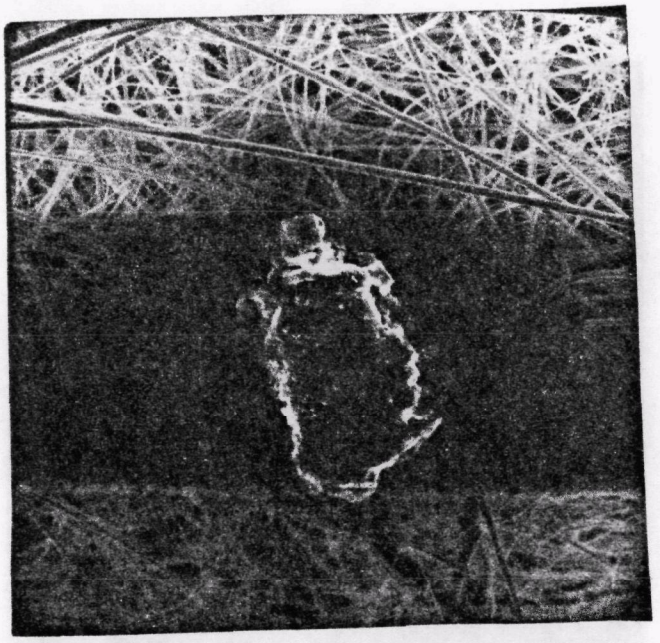
b

1280 x

Figure 4.25. Electron microprobe element map of region shown in Figure 4.23.
(a) Aluminum map; (b) Silicon map.

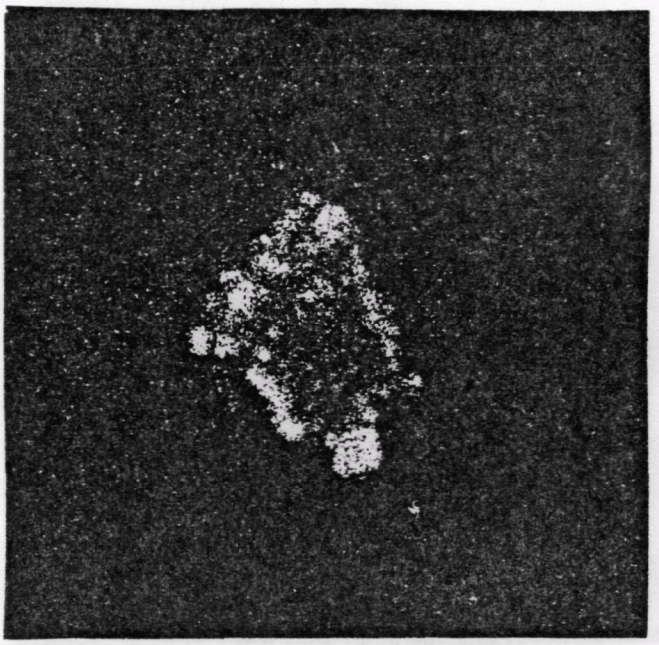



a



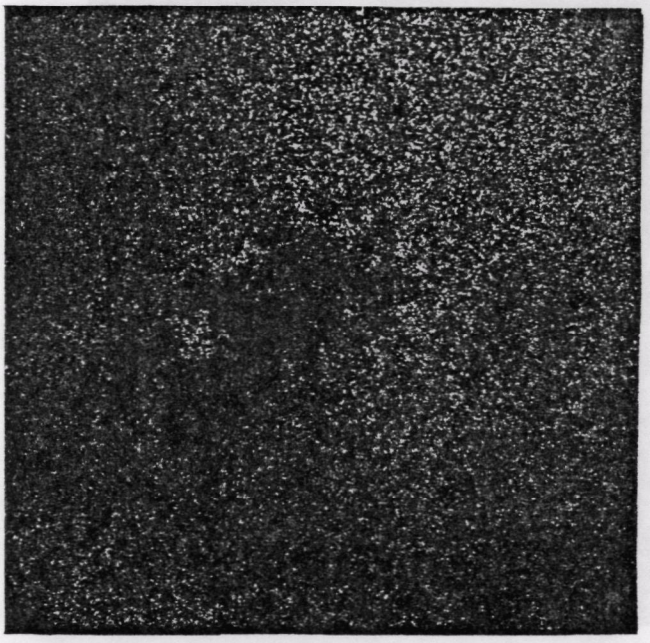
b

Figure 4.26. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on a glass fiber filter. Sample Volume: 0.1 $m^3$ air. Location: Great Lakes Chemical Corp., El Dorado, Arkansas. Collected 9/22/76



a

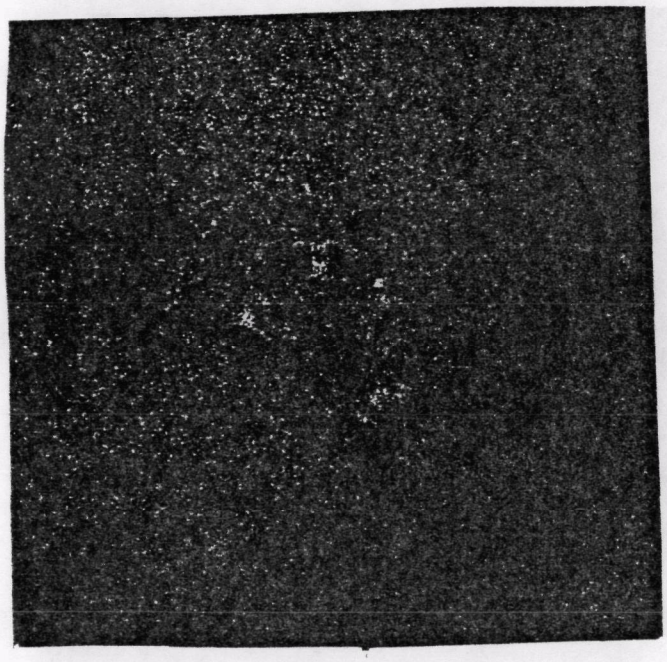
520 x



b

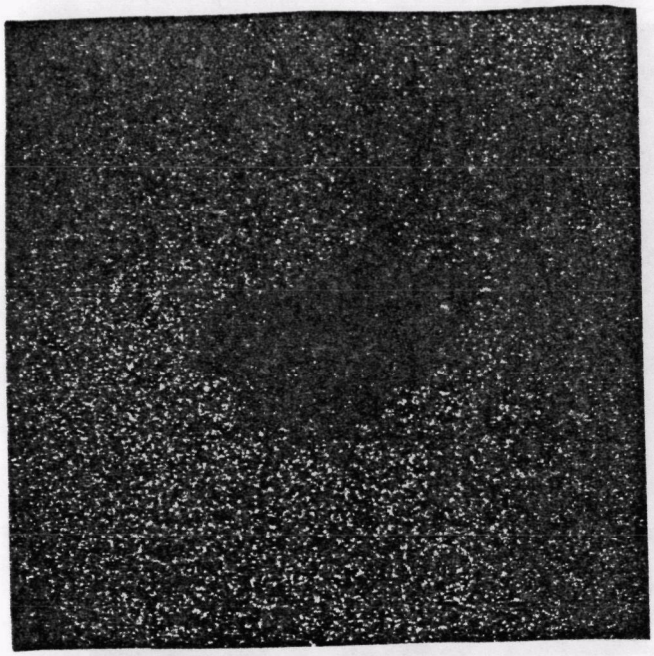
520 x

Figure 4.27. Electron microprobe element map of region shown in Figure 4.26.
(a) Chlorine map; (b) Sodium map.



a

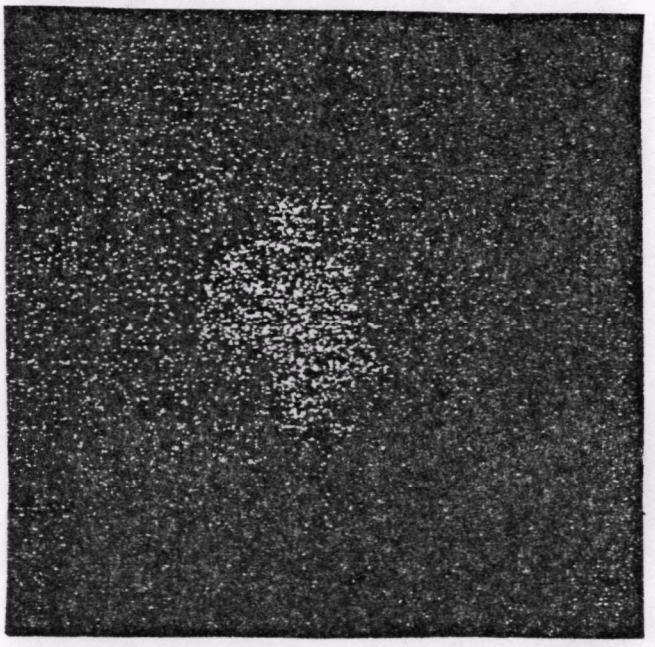
520 x



b

520 x

Figure 4.28. Electron microprobe element map of region shown in Figure 4.26.
(a) Potassium map; (b) Calcium map.



520 x

Figure 4.29. Electron microprobe element map of region shown in Figure 4.26.
Magnesium map.

Table 4.16. NEUTRON ACTIVATION ANALYSIS OF AMBIENT AIR HI-VOL SAMPLES

| Site | Date | Medium | Br ($\mu g/m^3$) | Cl ($\mu g/m^3$) |
|---|---|---|---|---|
| GRL[a] | 12/13/76- | GFF[b] | 0.089 | N.D. |
| | 12/14/76 | CF[c] | 0.230 | 0.043 |
| GRL | 12/16/76- | GFF | 0.574 | 0.345 |
| | 12/17/76 | CF | 0.24 | 0.086 |
| GRL | 12/17/76- | GFF | 20.2 | 1.70 |
| | 12/18/76 | CF | 2.44 | 0.40 |

[a]All were 24 hr samples.

[b]GFF = glass fiber filter.

[c]CF = cellulose filter.

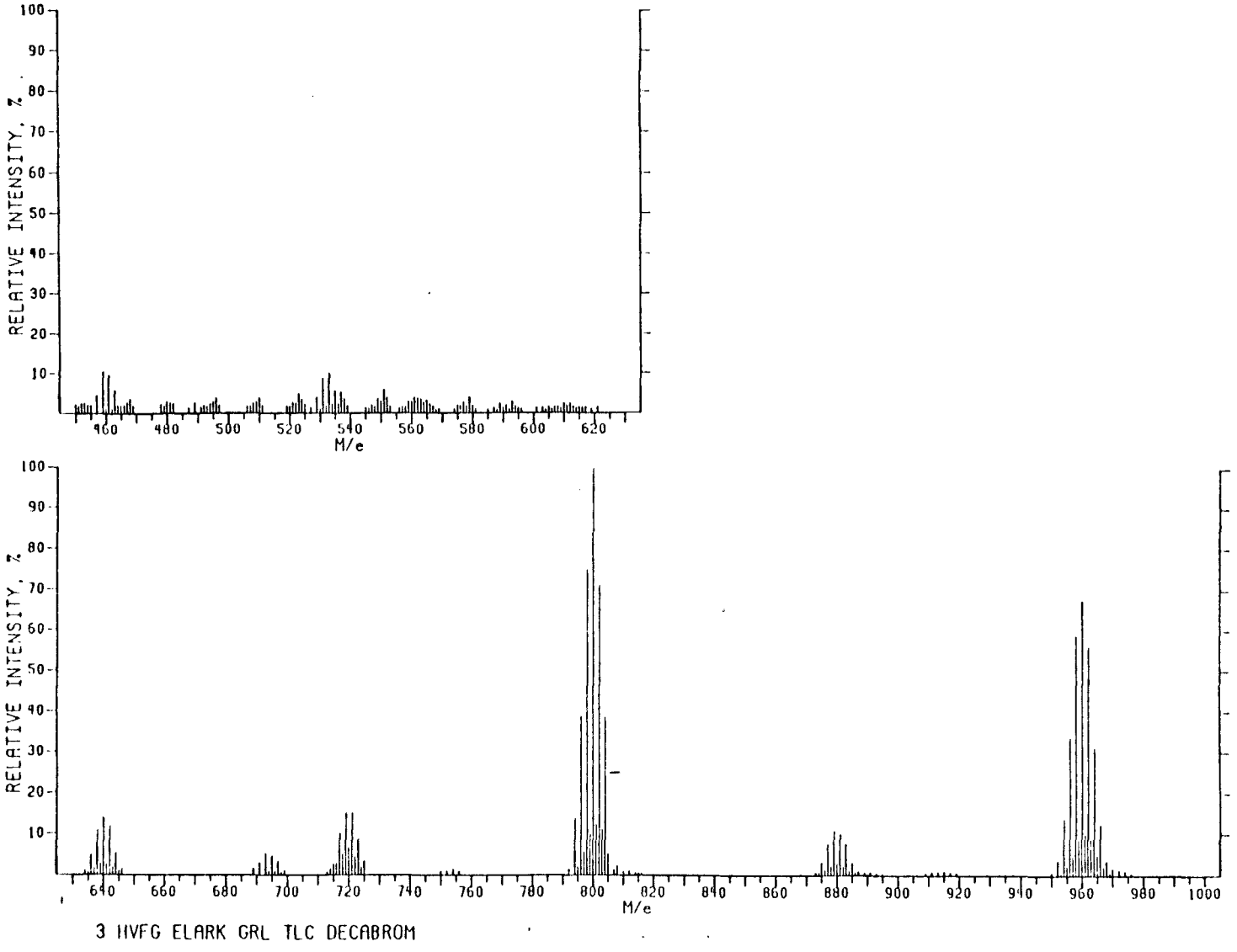



Figure 4.30. Mass spectrum of GFF-TLC Extract Obtained by Direct Probe.

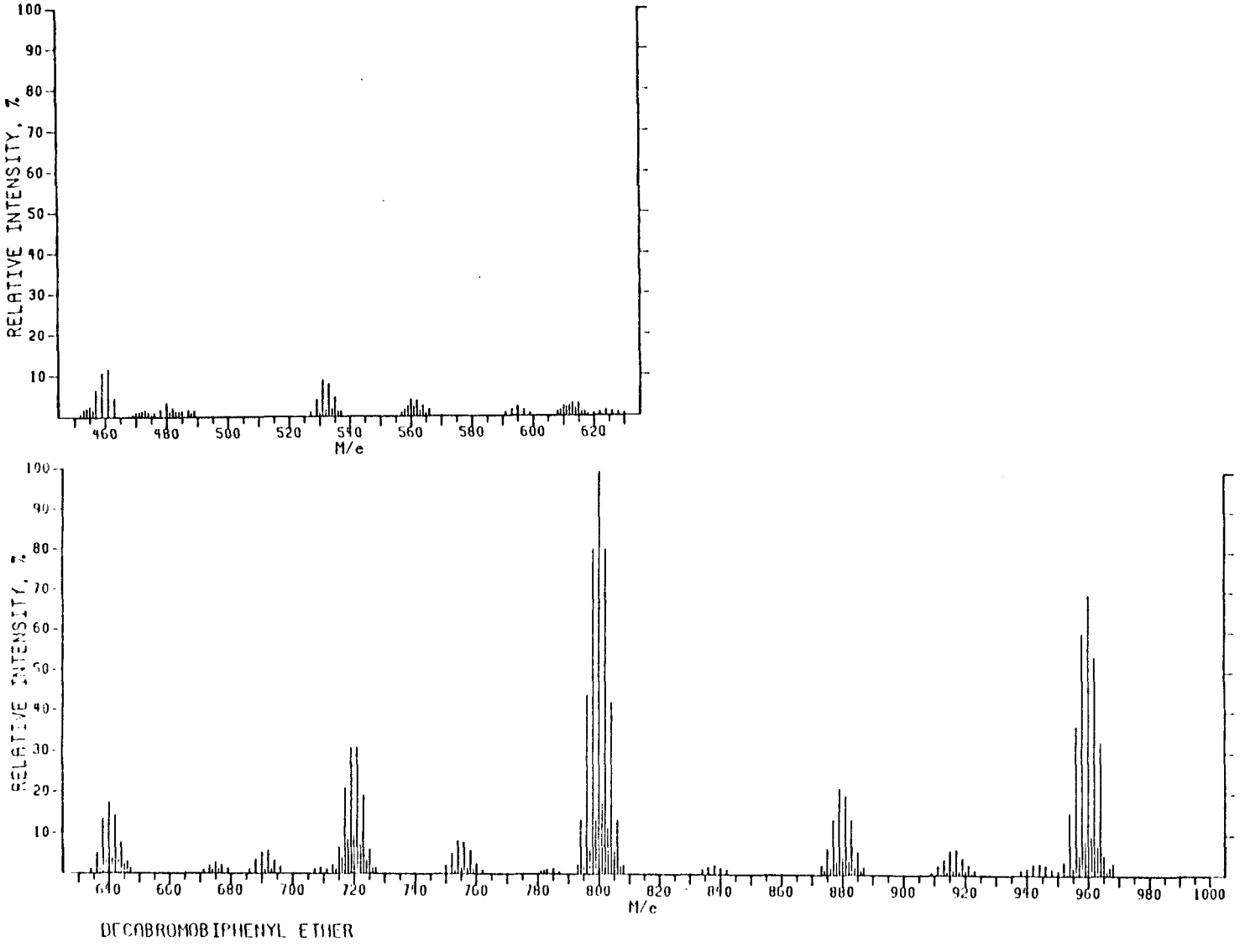



Figure 4.31. Mass spectrum of authentic Decabrom.

was eluted and subjected to GC/MS/COMP. The GC/MS spectrum is shown in Figure 4.32 along with the spectrum of authentic Tetrabrom.

Table 4.17. ANALYSIS OF HI-VOL FILTERS FOR DECABROM

| Date | Filter Type | Decabrom ($ng/m^3$) |
|---|---|---|
| 12/13, 14/76 | GFF[a] | <13.3 |
| | CF[b] | <16.5 |
| 12/16, 17/76 | GFF | 94.3 |
| | CF | 22.9 |
| 12/17, 18/76 | GFF | 118 |
| | CF | 113 |

[a]GFF = glass fiber filter

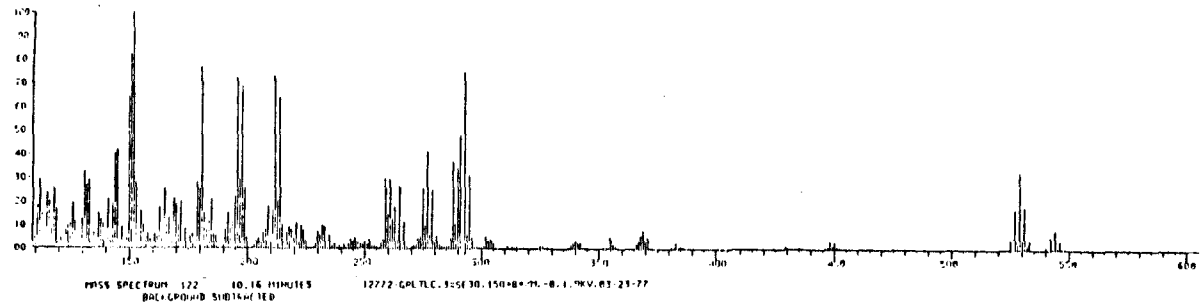
[b]CF = cellulose filter

4.2.2.3 Inorganics in Ambient Air

*Chloride/Bromide and Chlorine/Bromine*.--The results obtained by turbidimetric determination of total halide and halogen are given in Table 4.18. The site, period and cycle designation were given in the sampling protocols (Table 4.13) and the location on the schematic maps (Fig. 4.16-4.18).

Sampling was performed on two days yielding a total of three sets of impinger samples. During Period 1, halides were detected at L4 (Fig. 4.16) adjacent to the holding pond. During Period 2 halides were found at L2 (Fig. 4.17) downwind of the bromine extraction and ethylene dibromide facilities. At 1304 to 1309 hours an upset occurred. At 1430 hours Cycle 4 for halides and halogens was initiated (Fig. 4.18). Both halides and halogens were found in some of these samples. Neutron activation analysis indicated low, but detectable, amounts of bromide in L3 and L4 (Table 4.19); however, the NAA bromine value for L2 is inconsistent with both the orientation with respect to the meteorological conditions and of course the halide and total halogen value. Cycle 6 which was taken four hours after the upset showed the highest halide values at L3 and L4 (Fig. 4.18), but no detectable halogens. Neutron activation analysis depicted no detectable bromine or bromide at L3 which gave the highest total halide values. There

(a)



(b)

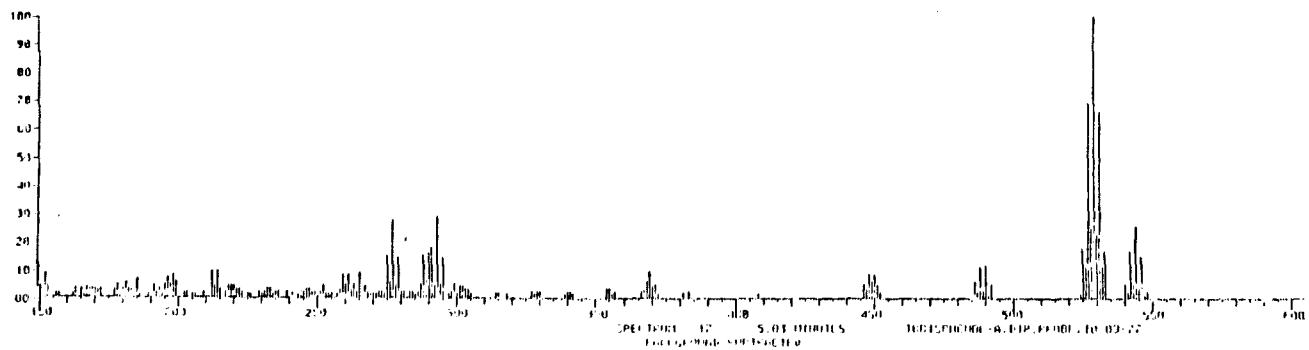


Figure 4.32. Mass spectrum of (a) GFF-TLC extract and (b) authentic Decabrom obtained by GC/MS/COMP.

Table 4.18. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

| | | $Cl_2/Br_2$ | | | | | $Cl^-/Br^-$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Period | Cycle | L1 | L2 | L3 | L4 | L7 | L1 | L2 | L3 | L4 | L7 |
| P1 | C3 | -[c] | - | <103 | <62 | - | - | - | <65 | 53 ± 8 | - |
| P2 | C3 | <130 | <65 | <81 | - | - | <90 | 140 ± 0 | <56 | - | - |
| P3 | C4 | | <79 | 60 ± 12 | <67 | 183 ± 17 | - | - | 186 ± 4 | 137 ± 37 | 61 ± 86 |
| P3 | C6 | | - | <77 | <71 | <94 | - | - | 876 ± 11 | 324 ± 20 | <61 |

[a]Values in $\mu g/m^3$.

[b]Determined by turbidity.

[c]Not analyzed.

Table 4.19. CONCENTRATIONS OF BROMIDE AND BROMINE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

| | | $Br_2$ | | | | | $Br^-$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Period | Cycle | L1 | L2 | L3 | L4 | L7 | L1 | L2 | L3 | L4 | L7 |
| P1 | C3 | -[c] | - | <42 | - | - | - | - | <21 | - | - |
| P2 | C3 | - | - | - | - | - | - | - | - | - | - |
| P3 | C4 | - | 484 | <24 | <27 | <16 | - | <17 | 28 | 26 | <47 |
| P4 | C6 | - | - | <32 | - | - | - | - | <16 | - | - |

[a]Values in $\mu g/m^3$.

[b]By Neutron Activation Analysis.

[c]Not analyzed.

is some question about this value since ion exchange chromatographs showed at least 80% of the halide at L3 was bromide. In addition, glass filters and cellulose filters used in sampling cycles before and after the P3, C4 impinger sampling cycle showed high halogen concentrations at L3. There is apparently a change in the prevalent species between Cycle 4 and 6 from halogens to halide. More detailed studies should be required to verify this change and determine its etiology.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples taken of ambient air surrounding Great Lakes Chemical Corp. (Table 4.20). The limits of detection were 0.012 ppm in the impinger solution based on the volume of air sampled and the sensitivity of the turbidimetric method.

Table 4.20. CONCENTRATIONS OF FLUORIDE/FLUORINE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

| Period | Cycle | Locations | | | | |
|---|---|---|---|---|---|---|
| | | L1 | L2 | L3 | L4 | L7 |
| P1 | C3 | - | - | <4.2 | <2.6 | - |
| P2 | C3 | <5.4 | <2.7 | <3.4 | - | - |
| P3 | C4 | - | <3.4 | <2.4 | <2.7 | <3.2 |
| P3 | C6 | - | - | <2.8 | <2.6 | <3.9 |

[a]Values in $\mu g/m^3$.

[b]Determined by ion specific electrode method.

Acid Mist.--No titratable acid was found in any samples. Table 4.21 summarizes the upper limit of ambient air concentration of acid mist.

Table 4.21. ACID MIST IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP. AS $H_2SO_4$[a]

| Period | Cycle | Location |
|---|---|---|
| | | L3 |
| P1 | C4 | <45 |
| P2 | C5 | <43 |

[a]Values in $\mu g/m^3$.

4.2.2.4 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Figures 4.33 and 4.34 depict the total ion current and ion chromatograms of organic volatiles which were collected at L3 on the Great Lakes Corp. site (Fig. 4.18 for sampling location). Several halogenated compounds were identified. They were bromopropane, 1,2-chlorobromoethane, 1,2-dibromoethane, 1-chloro-3-bromopropane, bromoform and bromobenzene. The sampling location was on top of a three-story facility which was not in operation and is normally used

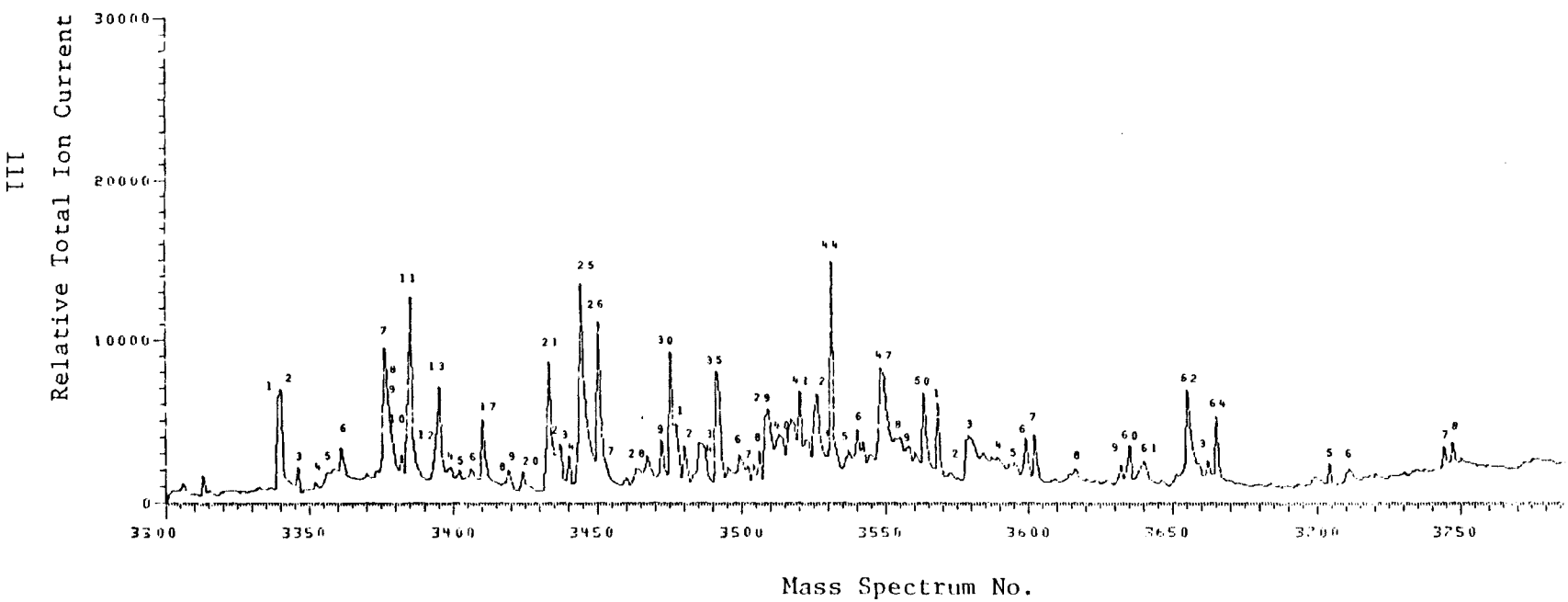



Figure 4.33. Total ion current profile of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C1/L3).

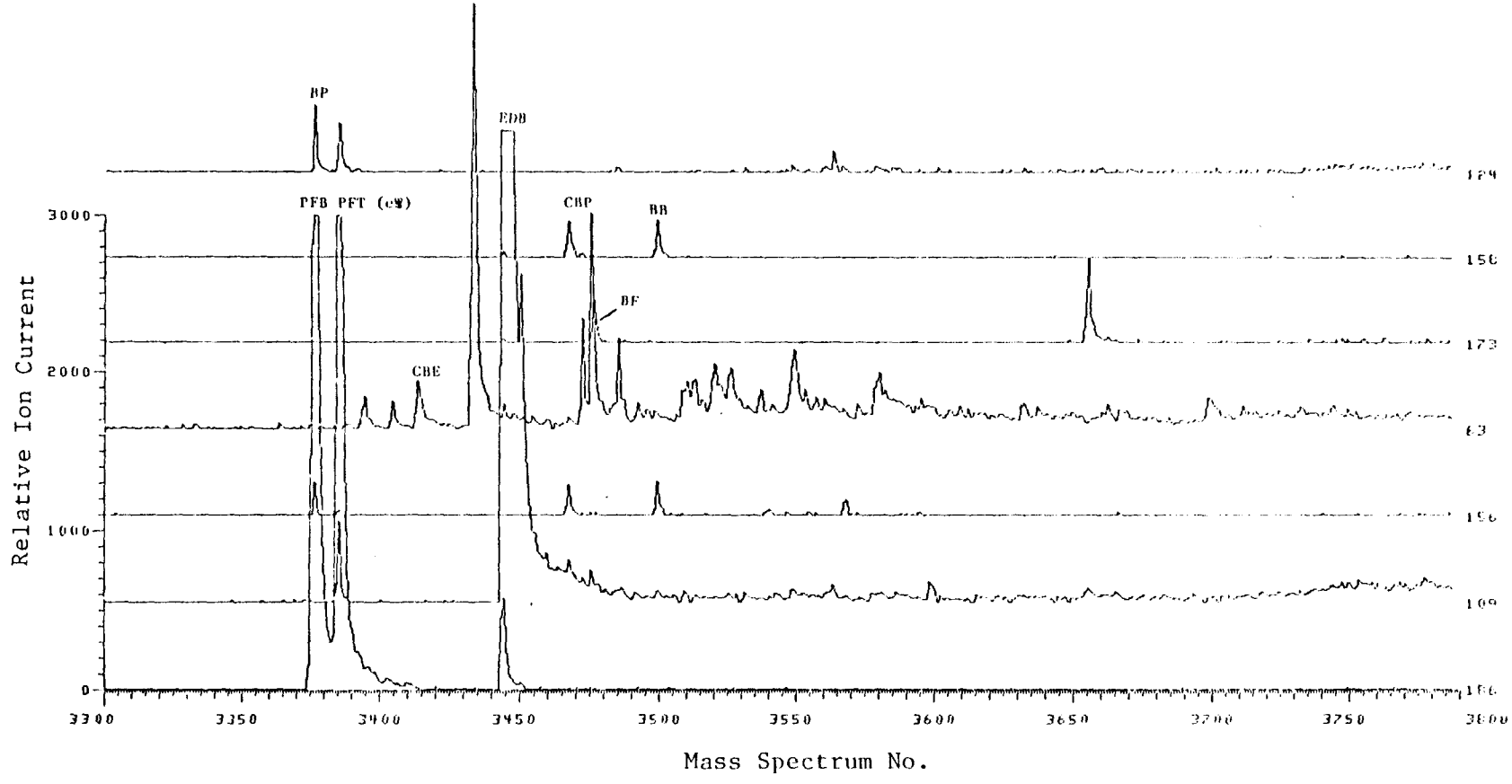



Figure 4.34. Ion chromatograms of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C1/L3). BP = bromopropane, CBE = 1-chloro-2-bromoethane, EDB = ethylene dibromide, CBP = 1-chloro-3-bromopropane, BF = bromoform, BB = bromobenzene.

for the production of sodium bromide. Another sampling period was between 1740 to 945 hours (overnight) using a DuPont personal sampler. At L3 (ELV), EDB was clearly identified (Peak No. 34, Fig. 4.35 and 4.36). The results corresponding to L5 (ELV) are depicted in Figures 4.37-4.38.

On the night of September 24, 1976, two DuPont personal samplers were deployed on two water towers, one located in El Dorado and the second in Parker's Chapel on Highway 15. Samplers were set to sample at ~110 ml/min/ cartridge during the 13 hour sampling period. The sampling period began at approximately 0500 hrs.

Table 4.22 lists the volatile organics which were identified in ambient air taken on the El Dorado city water tower. No halogenated compounds were identified in this sample. Most compounds appeared to be from auto exhaust. Figure 4.39 depicts the total ion current profile for this sample. Figure 4.40 represents the ion chromatogram for this ambient air sample. No brominated compounds were detected.

Table 4.23 lists the volatile organics in the ambient air at the Parker's Chapel water tower. Although we were unable to identify in the sample any brominated compounds from full mass spectral interpretation, we were able to detect them by mass fragmentography. Figure 4.41 depicts the total ion current profile for this sample and Figure 4.42 depicts the ion chromatograms. Allyl bromide, bromopropane and 1,2-dibromoethane were clearly detected.

Table 4.24 summarizes the halogenated hydrocarbons which were identified by GLC/MS/COMP in ambient air surrounding and in the vicinity of Great Lakes Chemical Corp.

Quantification of Halogenated Hydrocarbons.--Table 4.25 presents the concentrations of halogenated hydrocarbons surrrounding the Great Lakes Corp. site. Also presented in this table are the concentration of allyl bromide, 1- or 2-bromopropane and 1,2-dibromoethane which had been detected in the ambient air samples taken on Parker's Chapel water tower. The highest concentration observed were for 1,2-dibromoethane which reached a level of 1,837 $ng/m^3$ in a sample taken at Location 3 which was on the sodium bromide production facility.

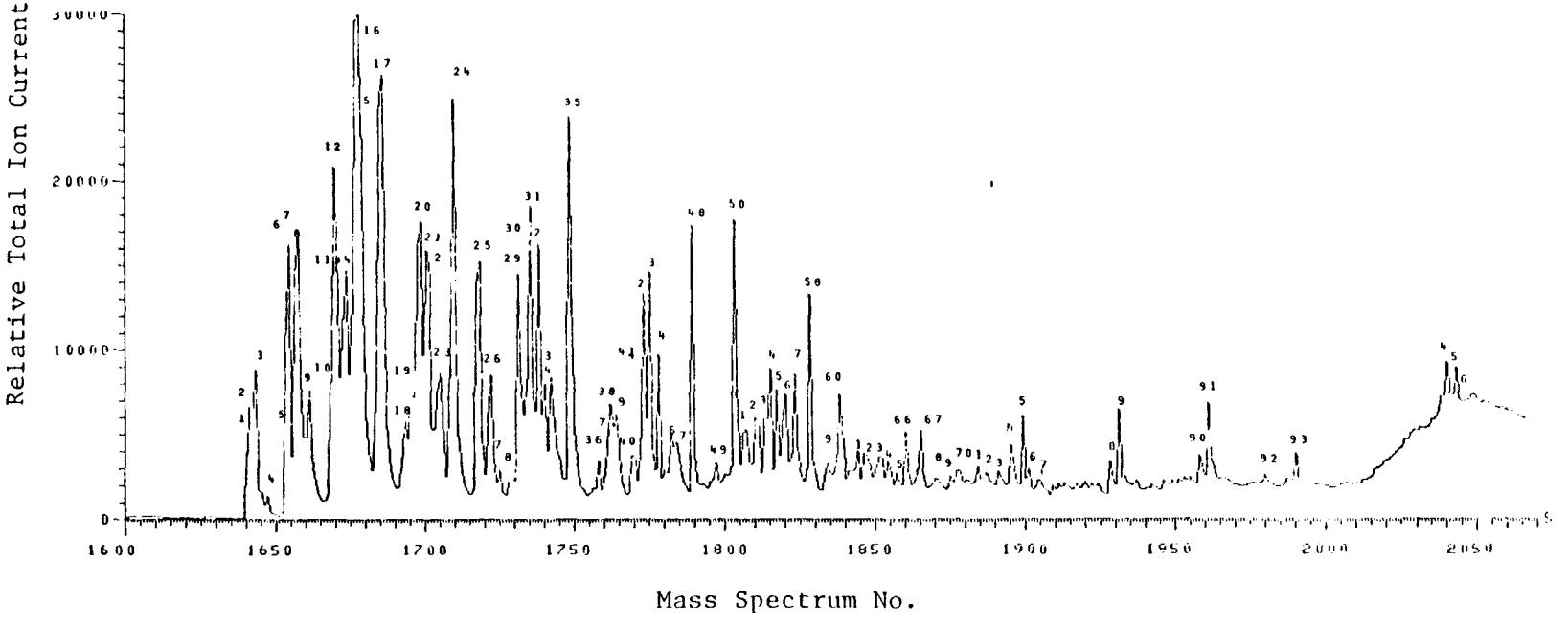



Figure 4.35. Total ion current profile of volatile ambient air pollutants from Great Lakes Corp. site, El Dorado, Arkansas (P3/C3/L3 ELV).

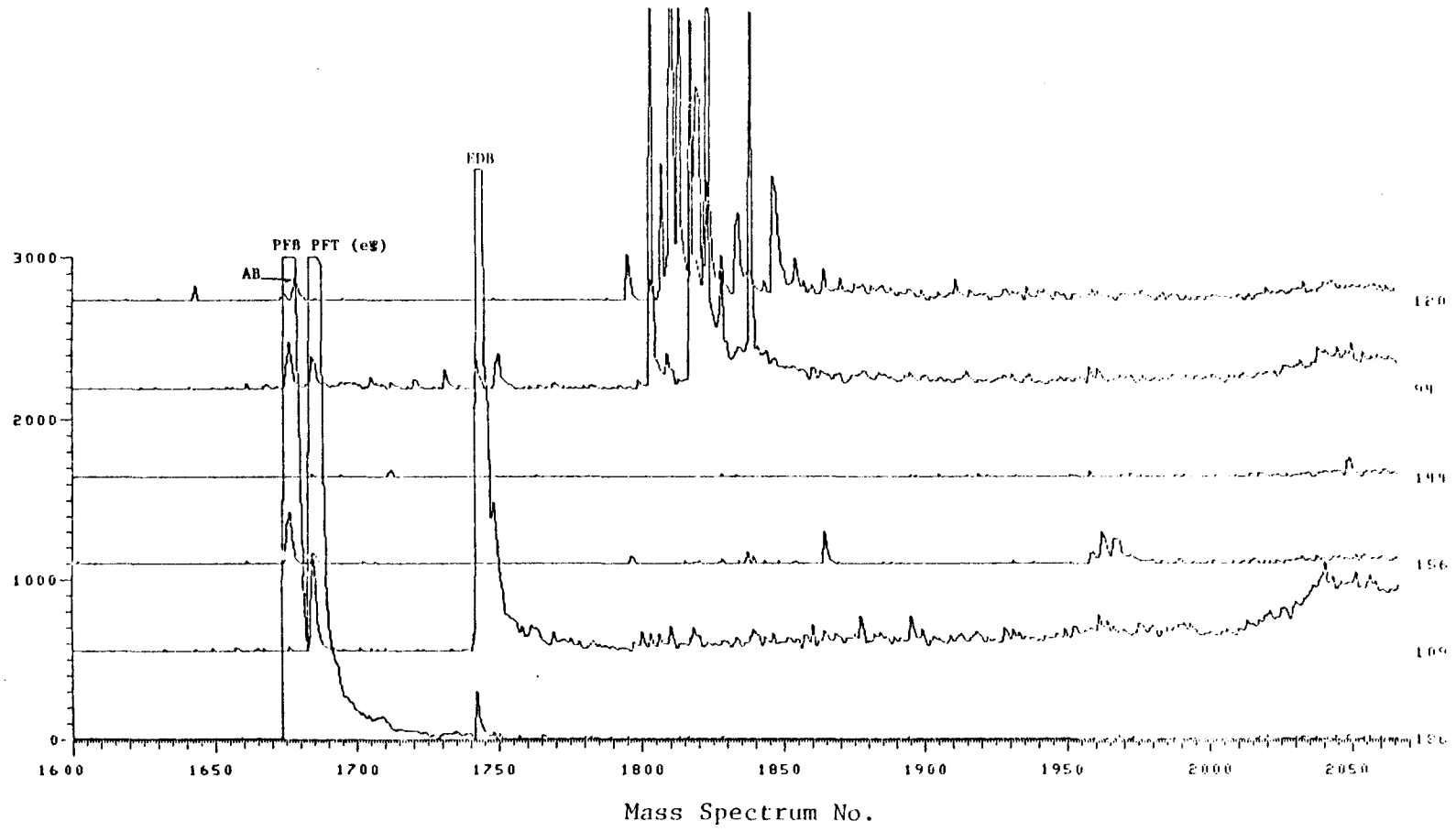



Figure 4.36. Ion chromatograms of ambient air sample from Great Lakes Corp. site, E1, Dorado, Arkansas (P3/C3/L3 ELV). AB = allyl bromide, EDB = 1,2-dibromoethane.

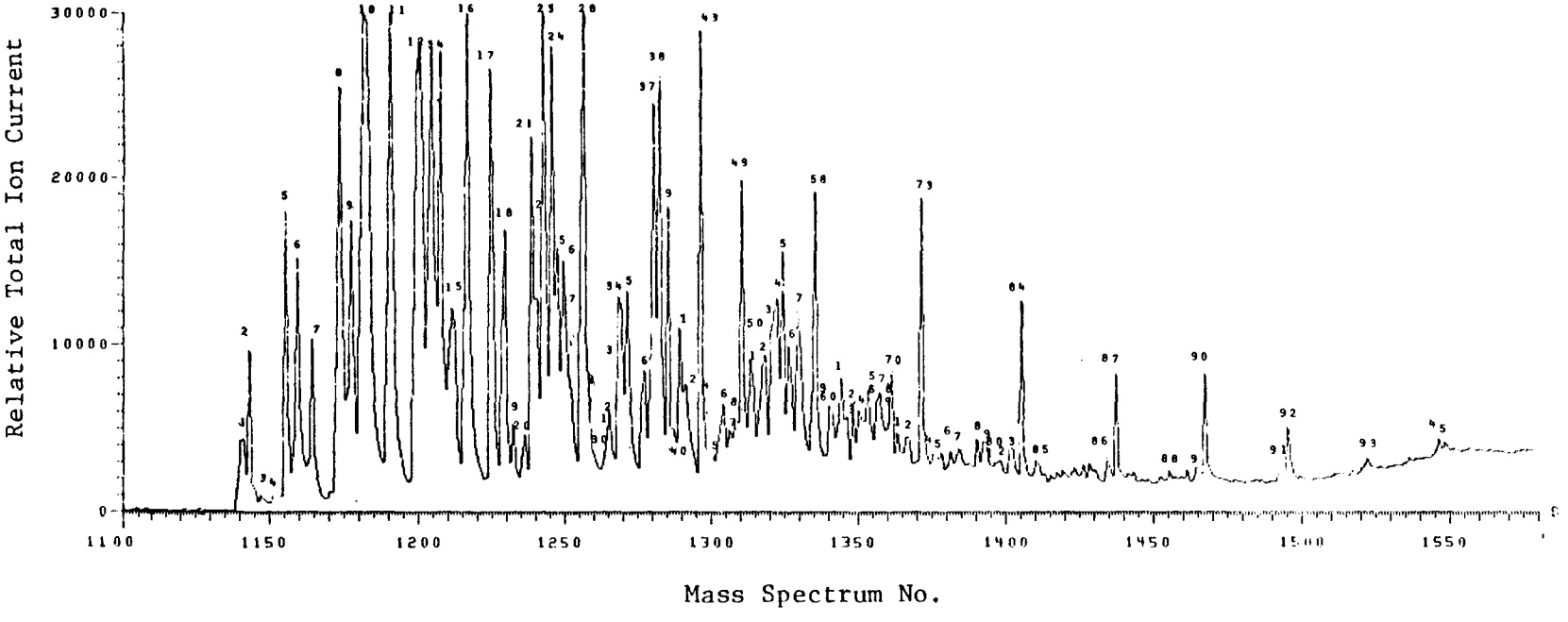



Figure 4.37. Total ion current profile of volatile ambient air pollutants from Great Lakes Corp., El Dorado, Arkansas (P3/C3/L5 ELV).

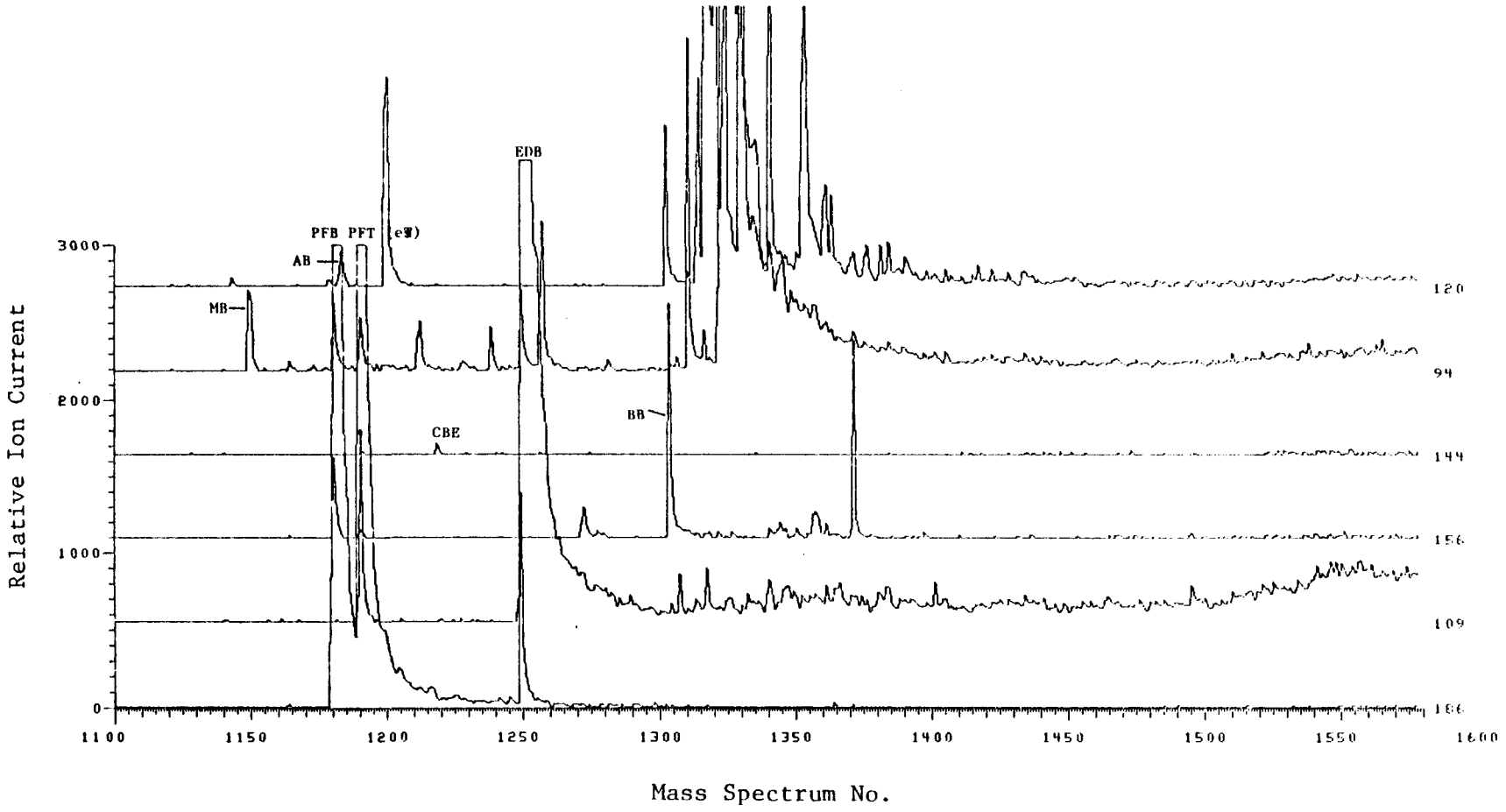



Figure 4.38. Ion chromatograms of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C3/L5 ELV). MB = methyl bromide, AB = allyl bromide, CBE = 1-chloro-2-bromoethane, EDB = ethylene dibromide, BB = bromobenzene.

Table 4.22. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR TAKEN ON EL DORADO, ARKANSAS CITY WATER TOWER[a]

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 1 | 44 | dichlorodifluoromethane |
| 1A | 44 | n-butane |
| 2 | 46 | acetaldehyde |
| 3 | 47 | isopentane |
| 4 | 47 | trichlorofluoromethane |
| 5 | 48 | acetone + $C_5H_{10}$ isomer |
| 6 | 50 | dichloromethane + freon 113 (BKG) |
| 6A | 51 | n-pentane |
| 6B | 52 | isopropanol |
| 7 | 54 | 2-methylpentane |
| 7A | 54 | butenal isomer |
| 8 | 55 | 3-methylpentane |
| 8A | 56 | n-butanal |
| 9 | 57 | hexafluorobenzene (es) |
| 9A | 57 | n-hexane |
| 9B | 58 | chloroform |
| 10 | 61 | methylcyclopentane + perfluorotoluene (es) |
| 10A | 64 | $C_7H_{14}$ isomer |
| 10B | 65 | $C_7H_{16}$ isomer |
| 10C | 66 | benzene |
| 10D | 66 | carbon tetrachloride |
| 10E | 67 | cyclohexane |
| 10F | 68 | 2-methylhexane |
| 10G | 68 | 2,3-dimethylpentane |
| 10H | 69 | 3-methylhexane |
| 10I | 71 | n-pentanal |
| 10J | 72 | $C_7H_{14}$ isomer |
| 11 | 73 | n-heptane |
| 12 | 78 | methylcyclohexane |
| 12A | 80 | $C_8H_{16}$ isomer |
| 13 | 81 | $C_8H_{18}$ isomer |
| 13A | 84 | $C_7H_{14}$ isomer |
| 13B | 84 | $C_8H_{18}$ isomer |
| 14 | 85 | toluene |
| 15 | 87 | $C_8H_{18}$ isomer |
| 15A | 89 | $C_8H_{18}$ isomer |
| 15B | 90 | 4-methyl-2-pentanone |
| 16 | 91 | n-hexanal + 3-methylpentanal |
| 17 | 94 | n-octane |
| 17A | 95 | tetrachloroethylene |
| 18 | 95 | $C_8H_{16}$ isomer |
| 19 | 98 | $C_8H_{16}$ isomer |
| 20 | 101 | ethylcyclohexane |
| 21 | 103 | $C_9H_{18}$ isomer |
| 22 | 105 | ethylbenzene |
| 23 | 107 | p-xylene |
| 23A | 108 | $C_9H_{20}$ isomer |
| 23B | 109 | $C_9H_{18}$ isomer |
| 24 | 110 | $C_9H_{20}$ isomer |
| 25 | 111 | styrene + $C_9H_{20}$ isomer |
| 25A | 111 | 2,3-dimethylpentanal |
| 26 | 112 | n-heptanal |
| 26A | 114 | $C_9H_{18}$ isomer |
| 27 | 115 | n-nonane |
| 28 | 119 | isopropylbenzene |
| 28A | 119 | $C_9H_{18}$ + $C_{10}H_{22}$ isomer |
| 28B | 122 | $C_{10}H_{20}$ isomer |
| 28C | 122 | $C_{10}H_{12}$ isomer |
| 29 | 123 | $C_{11}H_{24}$ isomer |
| 29A | 124 | $C_9H_{18}$ isomer |
| 30 | 125 | benzaldehyde |
| 30A | 127 | $C_{10}H_{22}$ + $C_3$-alkyl benzene isomers |
| 31 | 128 | $C_{10}H_{22}$ + $C_{10}H_{20}$ isomers |
| 31A | 129 | $C_{11}H_{24}$ isomer |
| 31B | 130 | $C_{10}H_{22}$ isomer |
| 32 | 131 | octanone isomer |
| 33 | 133 | n-octanal |
| 34 | 134 | $C_{10}H_{20}$ isomer |
| 35 | 135 | n-decane |
| 35A | 136 | $C_{10}H_{20}$ isomer |
| 35B | 137 | $C_{10}H_{20}$ isomer |
| 36 | 138 | $C_{11}H_{24}$ isomer |
| 37 | 140 | $C_{11}H_{24}$ isomer |
| 38 | 142 | $C_{11}H_{24}$ isomer |
| 39 | 143 | $C_{10}H_{20}$ isomer |
| 40 | 144 | acetophenone |
| 41 | 146 | $C_{11}H_{24}$ isomer |
| 42 | 148 | $C_{11}H_{24}$ isomer |
| 43 | 149 | 2-nonanone |
| 44 | 151 | n-nonanal |

(continued)

Table 4.22 (cont'd)

| Chromato-graphic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|
| 44A | 152 | $C_{11}H_{22}$ isomer |
| 45 | 153 | n-undecane |
| 46 | 155 | $C_4$-alkyl benzene isomer |
| 46A | 160 | phenylpropenal isomer |
| 47 | 162 | dimethylphenol isomer |
| 48 | 167 | 2-decanone |
| 49 | 169 | n-decanal |
| 50 | 171 | n-dodecane |
| 50A | 172 | $C_{13}H_{28}$ isomer |
| 50B | 173 | $C_{12}H_{24}$ isomer |
| 51 | 173 | $C_{10}H_{16}$ isomer |

[a]Ambient air sampled with DuPont personal sampler (ca. 110 ml/min) on 9/24-9/25/76 from 2000-900 hr.

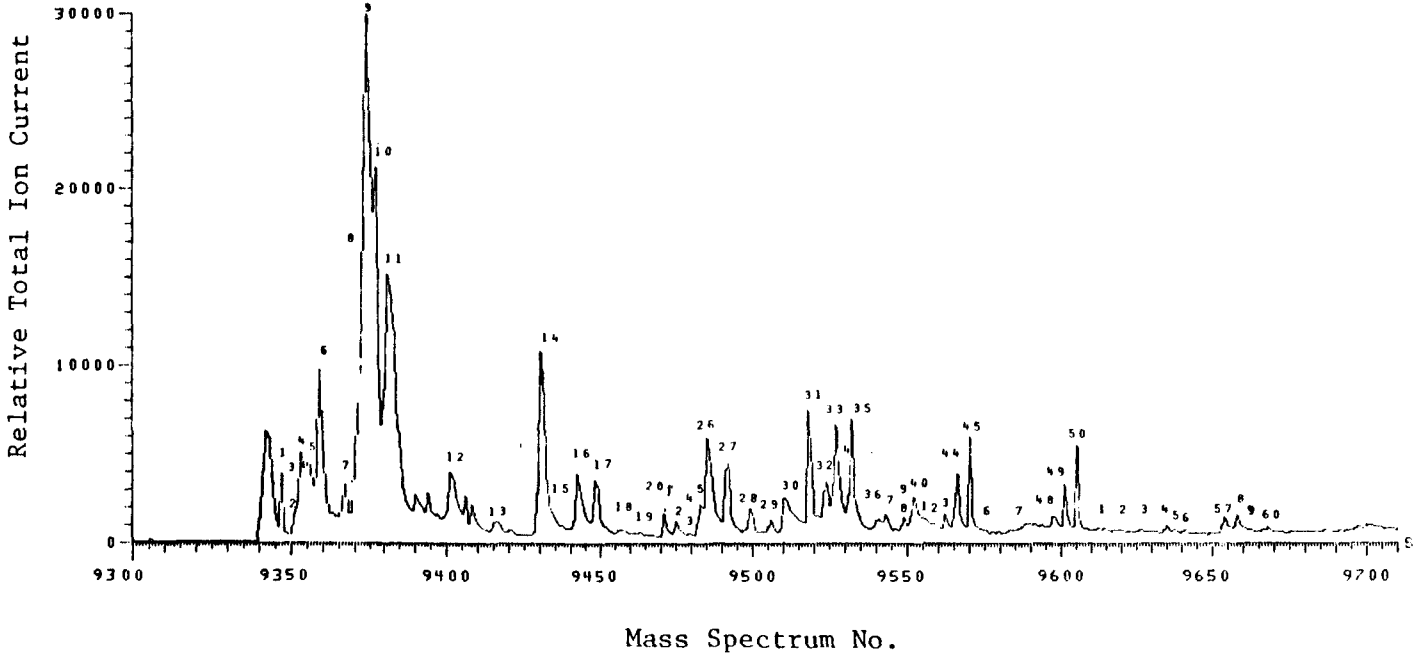



Figure 4.39. Total ion current profile of volatile ambient air pollutants taken on El Dorado, Arkansas city water tower.

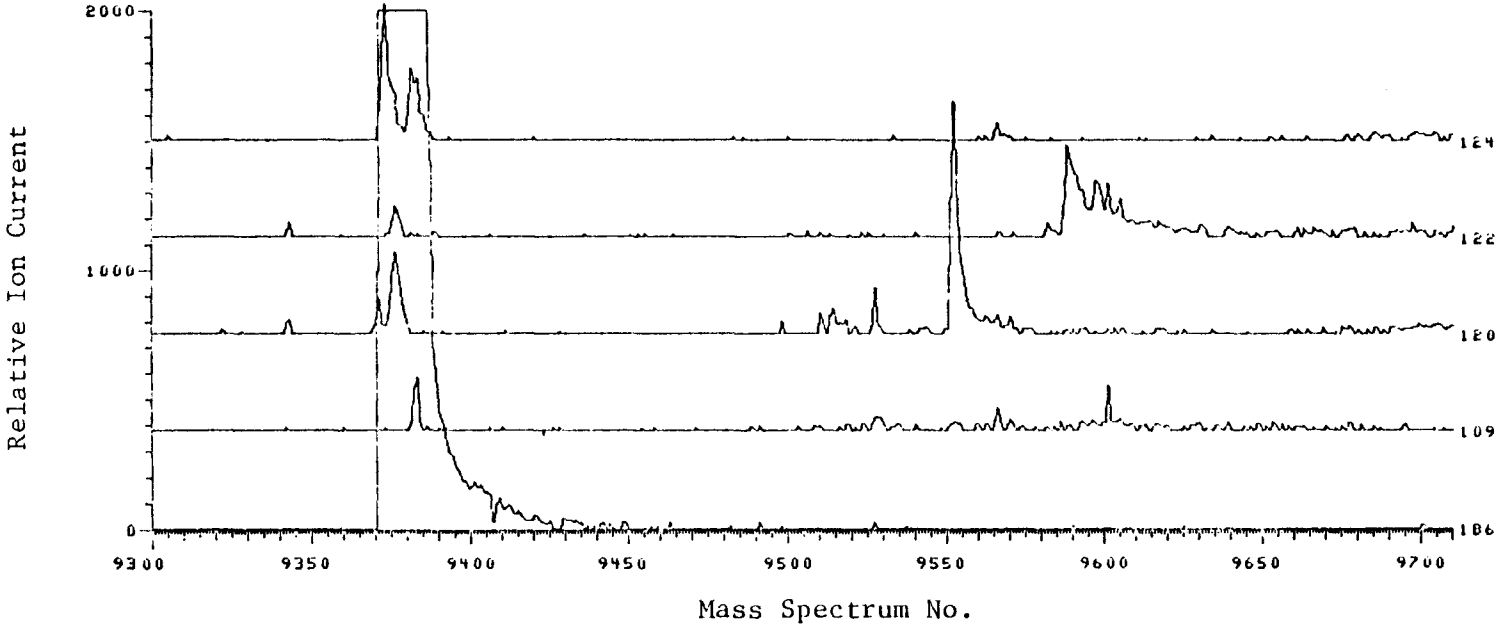



Figure 4.40. Ion chromatograms of ambient air sample from top of El Dorado city water tower in Arkansas.

Table 4.23. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR TAKEN ON PARKER'S CHAPEL WATER TOWER NEAR EL DORADO, ARKANSAS[a]

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 1 | 45 | butane + dichlorodifluoromethane |
| 2 | 47 | acetaldehyde |
| 2A | 47 | isopentane |
| 3 | 48 | trichlorofluoromethane |
| 4 | 49 | propanal + $C_5H_{10}$ isomer |
| 5 | 49 | n-pentane |
| 5A | 50 | acetone |
| 5B | 50 | $C_5H_{10}$ isomer |
| 6 | 51 | dichloromethane + fluorotrichloromethane |
| 6A | 52 | isopropanol |
| 6B | 54 | $C_6H_{12}$ isomer |
| 7 | 55 | 2-methylpentane |
| 8 | 57 | 3-methylpentane |
| 8A | 57 | $C_6H_{12}$ isomer |
| 9 | 58 | hexafluorobenzene (eS) |
| 10 | 59 | n-hexane |
| 10A | 59 | chloroform |
| 11 | 62 | perfluorotoluene (eS) |
| 11A | 63 | methylcyclopentane |
| 12 | 64 | 1,1,1-trichloroethane |
| 12A | 65 | butanal isomer |
| 12B | 66 | $C_7H_{14}$ isomer |
| 12C | 66 | $C_6H_{10}$ isomer |
| 13 | 67 | benzene |
| 13A | 67 | carbon tetrachloride |
| 14 | 68 | cyclohexane |
| 14A | 69 | $C_7H_{14}$ isomer |
| 15 | 69 | 2-methylhexane |
| 15A | 70 | 2,3-dimethylpentane |
| 16 | 71 | 3-methylhexane |
| 16A | 72 | methyl isopropyl ketone |
| 17 | 72 | dimethylcyclopentane isomer + pentanal |
| 18 | 73 | methylhexane isomer + trichloroethylene |
| 19 | 73 | $C_7H_{14}$ isomer |
| 20 | 75 | n-heptane |
| 20A | 77 | $C_7H_{14}$ isomer |
| 21 | 79 | methylcyclohexane |
| 21A | 80 | $C_8H_{16}$ isomer |
| 22 | 81 | 2,4-dimethylhexane |
| 23 | 83 | 1,2,3-trimethylcyclopentane |
| 23A | 83 | $C_8H_{16}$ isomer |
| 24 | 85 | trimethylpentane isomer |
| 24A | 85 | $C_8H_{16}$ isomer |
| 25 | 86 | toluene |
| 25A | 87 | 2,3-dimethylhexane |
| 26 | 88 | 2-methylheptane |
| 26A | 88 | 4-methylheptane |
| 27 | 89 | 3-methylheptane |
| 27A | 90 | 1,trans-2-dimethylcyclohexane |
| 28 | 91 | 1,cis-2-dimethylcyclohexane |
| 29 | 92 | $C_9H_{20}$ isomer |
| 29A | 92 | hexanal |
| 30 | 93 | $C_8H_{16}$ isomer |
| 30A | 94 | $C_8H_{16}$ isomer |
| 31 | 95 | n-octane |
| 31A | 96 | tetrachloroethylene |
| 31B | 96 | $C_8H_{16}$ isomer |
| 31C | 98 | $C_8H_{16}$ isomer |
| 32 | 99 | $C_9H_{20}$ isomer |
| 32A | 100 | silane compound (BKG) |
| 33 | 101 | 2,4-dimethylheptane |
| 34 | 102 | 2-methyloctane or 2,6-dimethylheptane |
| 35 | 102 | ethylcyclohexane |
| 36 | 103 | $C_9H_{20}$ isomer |
| 36A | 104 | $C_9H_{18}$ isomer |
| 36B | 105 | trimethylcyclohexane isomer |
| 36C | 106 | $C_9H_{20}$ isomer |
| 37 | 107 | ethylbenzene |
| 37A | 107 | trimethylcyclohexane isomer |
| 37B | 108 | 4-methyloctane |
| 38 | 109 | p-xylene |
| 38A | 110 | $C_9H_{20}$ isomer |
| 39 | 110 | m-xylene |
| 40 | 111 | 3-methyloctane |

(continued)

Table 4.23 (cont'd)

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 40A | 112 | styrene + $C_9H_{18}$ isomer |
| 40B | 112 | dimethylpentanal (tent.) isomer |
| 41 | 113 | o-xylene |
| 41A | 114 | n-heptanal |
| 42 | 115 | methyl ethylcyclohexane isomer |
| 42A | 116 | $C_9H_{18}$ isomer |
| 43 | 117 | n-nonane |
| 44 | 118 | $C_9H_{18}$ isomer |
| 44A | 119 | $C_{10}H_{20}$ isomer |
| 45 | 120 | isopropylbenzene |
| 45A | 120 | dimethyloctane isomer |
| 46 | 121 | tetramethylhexane isomer |
| 47 | 122 | $C_{10}H_{22}$ isomer |
| 47A | 123 | $C_{10}H_{20}$ isomer |
| 48 | 123 | propylcyclohexane |
| 49 | 124 | $C_{10}H_{22}$ isomer |
| 49A | 125 | $C_{10}H_{20}$ isomer |
| 50 | 125 | n-propylbenzene + benzaldehyde + $C_{10}H_{22}$ isomer |
| 50A | 126 | $C_{10}H_{20}$ isomer |
| 51 | 127 | p-ethyltoluene |
| 51A | 127 | $C_{10}H_{22}$ isomer |
| 52 | 128 | m-ethyltoluene |
| 52A | 129 | $C_{10}H_{22}$ isomer |
| 53 | 129 | $C_{11}H_{24}$ isomer |
| 54 | 130 | $C_{11}H_{24}$ isomer |
| 55 | 131 | 3-methylnonane |
| 56 | 133 | dimethyloctane isomer |
| 56A | 133 | $C_{11}H_{24}$ isomer |
| 57 | 134 | o-ethyltoluene |
| 57A | 135 | $C_{10}H_{20}$ isomer |
| 57B | 136 | $C_{11}H_{22}$ isomer |
| 58 | 137 | n-decane |
| 58A | 138 | $C_4$-alkyl benzene isomer |
| 59 | 138 | $C_{11}H_{24}$ isomer |
| 59A | 139 | $C_{11}H_{22}$ isomer |
| 59B | 139 | 1,2,3-trimethylbenzene |
| 60 | 140 | $C_{11}H_{24}$ + $C_4$-alkyl benzene isomers |
| 60A | 140 | $C_{12}H_{26}$ isomer |
| 61 | 141 | $C_{11}H_{24}$ isomer |
| 62 | 142 | $C_{12}H_{26}$ isomer |
| 63 | 143 | butylcyclohexane |
| 63A | 144 | $C_{12}H_{26}$ isomer |
| 64 | 145 | $C_4$-alkyl benzene isomer |
| 64A | 145 | $C_{12}H_{26}$ isomer |
| 64B | 146 | n-butylbenzene + propyltoluene isomer |
| 64C | 146 | $C_{11}H_{22}$ isomer |
| 65 | 147 | $C_{12}H_{26}$ isomer |
| 66 | 148 | $C_{11}H_{24}$ isomer |
| 67 | 149 | $C_{12}H_{26}$ isomer |
| 68 | 149 | $C_{12}H_{26}$ isomer |
| 69 | 150 | $C_{11}H_{22}$ isomer |
| 70 | 151 | $C_{11}H_{24}$ isomer |
| 70A | 151 | $C_{12}H_{24}$ isomer |
| 71 | 152 | $C_{11}H_{22}$ isomer |
| 71A | 153 | $C_{11}H_{24}$ isomer |
| 72 | 153 | nonanal |
| 72A | 154 | $C_{11}H_{22}$ isomer |
| 73 | 155 | n-undecane |
| 73A | 157 | $C_{12}H_{24}$ isomer |
| 73B | 163 | $C_{12}H_{26}$ isomer |
| 73C | 165 | $C_{13}H_{28}$ isomer |
| 73D | 170 | $C_{12}H_{26}$ isomer |
| 73E | 173 | n-dodecane (tent.) |
| 73F | 191 | $C_{15}H_{32}$ isomer |

[a]Ambient air sampled with DuPont personal sampler (ca. 110 ml/min) on 9/24-9/25/76 from 2130-930 hr.

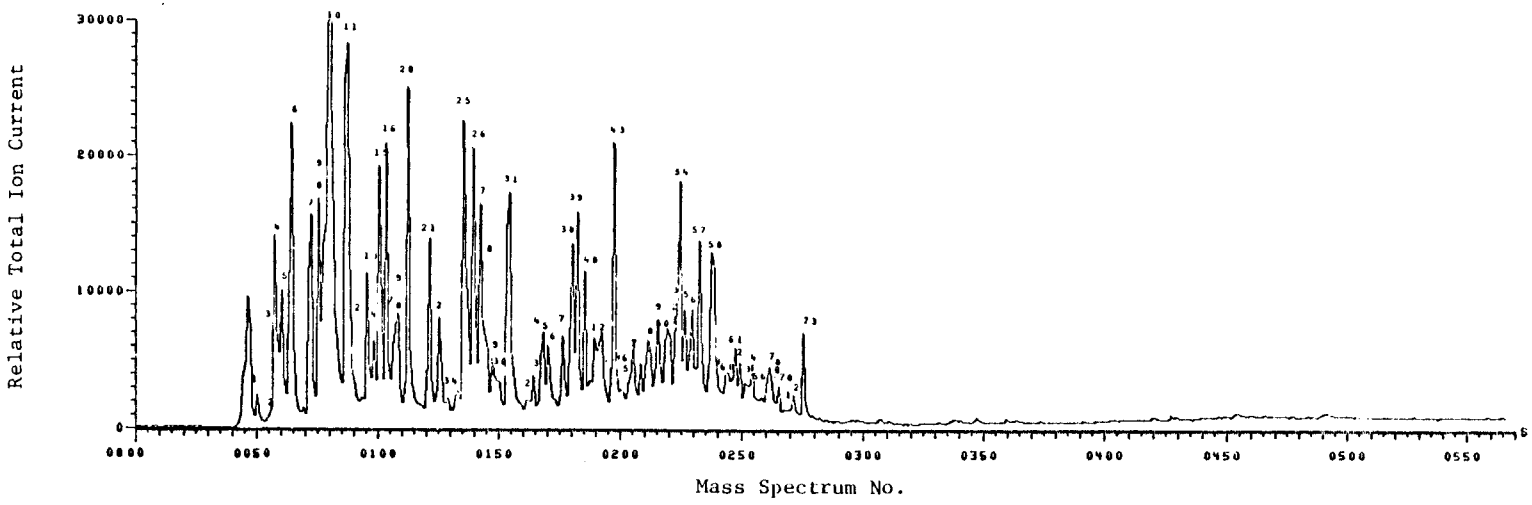



Figure 4.41. Total ion current profile of volatile ambient air pollutants taken on Parker's Chapel water tower near El Dorado, Arkansas.

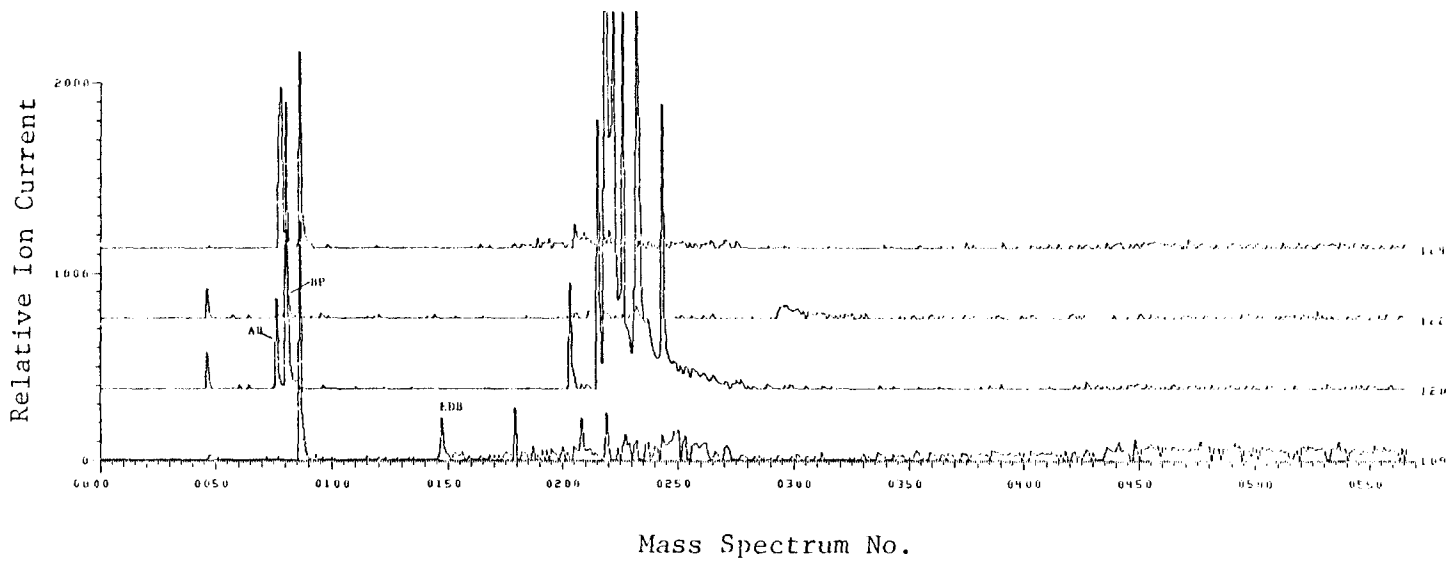



Figure 4.42. Ion chromatograms of ambient air sample from top of Parker's Chapel water tower near El Dorado, Arkansas. AB = allyl bromide, BP = bromopropane, and EDB = 1,2-dibromoethane.

Table 4.24. HALOGENATED HYDROCARBONS IDENTIFIED BY GC/MS/COMP IN AMBIENT AIR AT GREAT LAKES CORP., EL DORADO, ARKANSAS

| Compound | Compound |
|---|---|
| Bromobenzene | 1,2-Dibromoethane |
| Bromoethane | 1,3-Dichloropropane |
| Bromofluoromethane (tent.) | Methyl Bromide |
| Bromoform | Methyl Chloride |
| 1-Chloro-2-bromoethane | Pentachloroethane (tent.) |
| 1-Chloro-3-bromopropane | Vinyl Bromide |

Table 4.25. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING GREAT LAKES CORP., EL DORADO, AK

| Period/Cycle/Location[a] | Allyl bromide | Bromobenzene | Bromodichloromethane | Bromoform | 1 or 2-Bromopropane | 1-Chloro-2-bromoethane | 1-Chloro-3-bromopropane | 1-Chloro-2,3-dibromopropane | 1,2-Ethylene dibromide | Methyl bromide | Vinyl bromide |
|---|---|---|---|---|---|---|---|---|---|---|---|
| P3/C1/L1 | -[b] | - | 1.9 | - | 13.4 | - | - | - | 7.4 | - | - |
| L2 | 8.4 | 20.7 | 9.6 | 15.1 | 10.8 | 2.8 | - | - | 1,107 | - | - |
| L3 | - | 60 | 15 | 11.96 | 16.8 | 6.6 | 23.7 | - | 1,837 | - | - |
| L4 | - | - | - | - | 15.4 | - | - | T[c] | - | - | - |
| P3/C3/L4 | T | - | T(?) | - | 55 | - | - | - | - | ? | - |
| L6 (ELV) | 8 | - | 26.4 | - | 16 | 13 | - | - | 430 | - | - |
| P3/C3/L3 (ELV) | - | - | - | - | 4 | - | T | - | 89 | - | - |
| L5 (ELV) | 2.5 | 25 | - | - | 11.8 | 0.3 | T | - | 500 | ? | ? |
| E.D., AK water tower | - | - | - | - | - | - | - | - | - | - | - |
| P.C., AK water tower | 24.8 | - | - | - | 25.2 | - | - | - | 7.2 | - | - |

[a] Refer to Table 4.13 for sampling protocol, values are in $ng/m^3$.
[b] - = not detected
[c] T = trace detected

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--None of these substances occurred at levels which were quantifiable by GC/ECD or mass fragmentography. The LOD for methyl chloride and methyl bromide was 200 and 120 $\mu g/m^3$, respectively, by GC/ECD. For mass fragmentography the LOD was about 20 ppb.

Ethylene.--The levels of ethylene detected represented typical background levels as observed for all samples (Table 4.26).

Table 4.26. ETHYLENE LEVELS IN AMBIENT AIR

| Site | Period/Cycle/Location | ppm |
|---|---|---|
| GRL | P1/C4/L5 | 1.20 ± 0.10 |
| | P1/C4/L6 | 0.90 ± 0.10 |
| | P1/C4/L7 | 0.90 ± 0 |

4.2.2.5 Brominated Organics in Water, Sediment and Soil

The samples were screened by the VOA method for the presence of EDB and other volatile brominated organics and selected samples were analyzed for semi-volatile brominated organics. The results are summarized in Table 4.27. Confirming spectra for EDB and Tetrabrom are shown in Figures 4.43 and 4.44, respectively.

4.2.3 Michigan Chemical Corporation (Velsicol)

4.2.3.1 Sampling

The sampling protocol and sample descriptions for Michigan Chemical Corp. are given in Table 4.28. The corresponding figure 4.45 designates the sampling locations for September 21, 1976. Table 4.29 and Figure 4.46 present the protocol for April 7, 1977.

4.2.3.2 Survey of Chemicals on Glass Fiber and Cellulose Filters

Scanning Electron Microscopy (SEM) and Electron Microprobe (EM) Analysis.--Samples consisting of three sampling periods, each 24 hours in length were collected at the Michigan Chemical Corp. plant site. Glass fiber filters (GFF) and cellulose filters (CF) were used in parallel sampling. Both types of filter material were examined. Sufficient sample was concentrated on the surface of the GFF to permit direct analysis without the usual carbon coating to prevent charge buildup on the sample.

Table 4.27. RESULTS OF ANALYSIS OF SOIL, SEDIMENT AND WATER SAMPLES FOR BROMINATED ORGANICS--SURVEY SAMPLING NEAR GREAT LAKES CHEMICAL CORPORATION, EL DORADO, AK

| Period/Cycle/Location | Sample Type | Ethylene dibromide (µg/kg) | Decabromo-biphenyl ether (µg/kg) | Tetrabromo-bisphenol A (µg/kg) | Polybrominated biphenyls |
|---|---|---|---|---|---|
| P1/C1/L1 (4/7/77) | S/HHC | ND | 16,000[a,b] | >>225,000[a,b,c] | * (tent.)[b] |
| | W/HHC | 22[c,d] | ND[c] | ND[c] | -- |
| L2 | S/HHC | *[c] | -- | -- | -- |
| | W/HHC | 620[c,d] | ND[c] | ND[c] | -- |
| L3 | S/HHC | *[c] | -- | -- | -- |
| P2/C1/L1 (4/22/77) | SD/HHC | ND | 19,000[a,b,c] | 22,000[a,b,c] | ND[b,c] |
| L2 | W/HHC[e] | *[c] | -- | -- | -- |
| L3 | SD/HHC | ND | -- | -- | -- |
| | W/HHC | ND | -- | -- | -- |
| L4 | W/HHC | ND | -- | -- | -- |

[a] Quantitated by gas chromatography-mass spectrometry with multiple ion detection (GC-MS-MID).

[b] Identity confirmed by direct probe-mass spectrometry.

[c] Confirmed by gas chromatography-mass spectrometry in the full scan mode.

[d] Quantitation by gas chromatography-electron capture detection.

[e] Scum on water.

Key:
* = Identified but not quantitated
ND = not detected
S = soil
W = water
SD = sediment
HHC = for halogenated hydrocarbon analysis

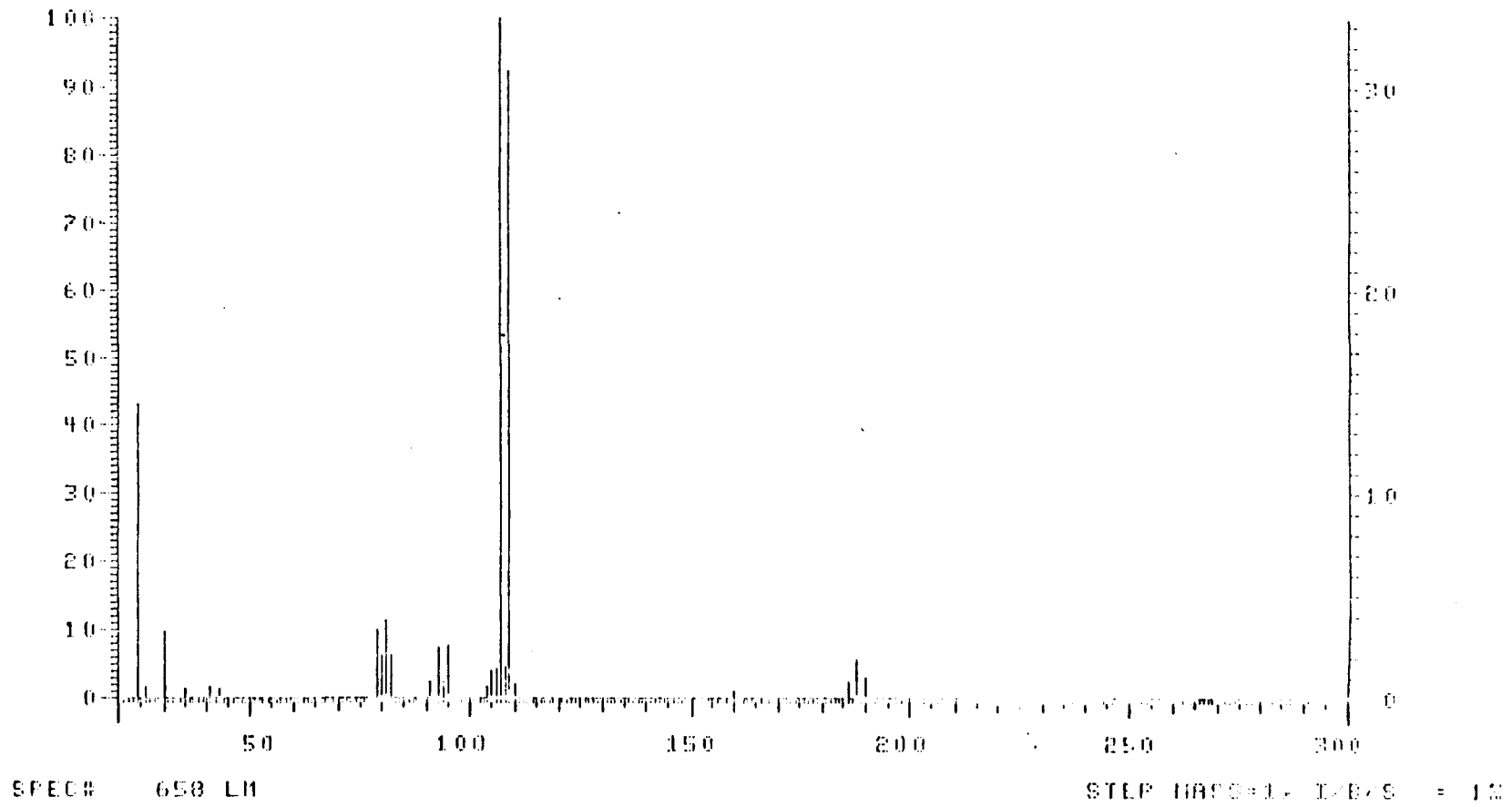



Figure 4.43. Gas chromatography/mass spectrometric analysis of volatiles purged from water collected near Great Lakes Chemical Corp., El Dorado, Arkansas (P1/C1/L2) - mass spectrum of ethylene dibromide.

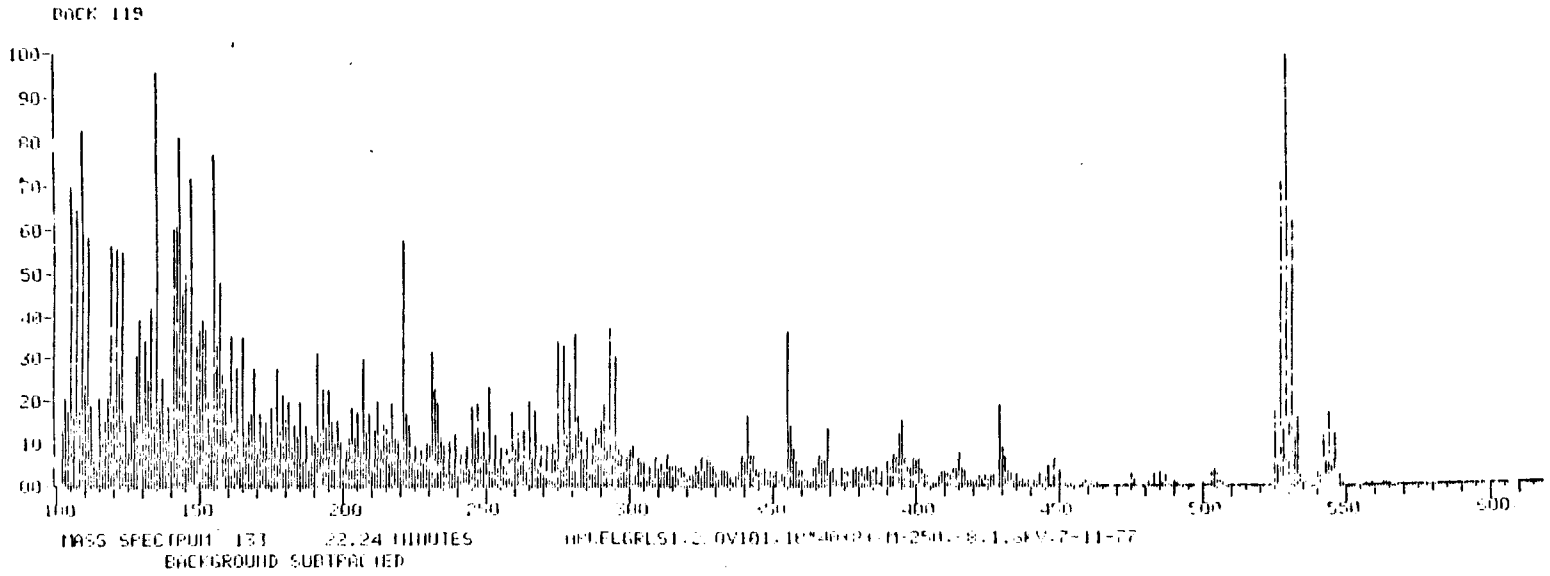



Figure 4.44. Mass spectrum of soil extract (P1/C1/L1) exhibiting Tetrabrom.

Table 4.28. SAMPLING PROTOCOL FOR MICHIGAN CHEMICAL CORPORATION, HIGHWAY 167, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/21/76 | C1 | L1 | 1140-1415 | 130 | HHC[a] | | | | |
| | | L2 | 1140-1411 | 123 | HHC[a] | 27-30 | 56 | 350°/8-010°/8 | Clear, slightly cloudy[d] |
| | | L3 | 1140-1415 | 171 | HHC[a] | 31 | | | Clear, odor of $H_2S$ + $Br_2$[d] |
| | | L4 | 1140-1415 | 175 | HHC[a] | | | | d |
| | C2 | L2 | 1140-1614 | - | HHC[b] | 29 | | 358/8 | Clear[d] |
| | | L3 | 1140-1614 | - | HHC[b] | 31 | | | d |
| | | L4 | 1124-1625 | - | HHC[b] | | | | d |
| | | L4 (ELV) | 1120-1625 | - | HHC[c] | | | | |
| | | L5 (ELV) | 1105-1742 | - | HHC[c] | | | | |
| | C3 | L1 | 1419-1513 | 48 | F, CBN, CBD | | | | $Br_2$ plume visible |
| | | L2 | 1415-1513 | 30 | F, CBN, CBD | | | | |
| | | L3 | 1415-1513 | 59 | F, CBN, CBD | | | | Clear, odor of $Br_2$ |
| | | L4 | 1415-1513 | 58 | F, CBN, CBD | | | | |
| | C4 | L1 | 1516-1614 | 93 | AM | | | | |
| | | L2 | 1513-1614 | 107 | AM | | | | |
| | | L3 | 1516-1614 | 93 | AM | 31 | | | Clear, odor of $Br_2$ |
| | | L4 | 1516-1614 | 91 | AM | | | | |
| | | L3 | 1335 | 0.28 | VAC | | | | |
| | | L4 | 1330 | 0.28 | VAC | | | | |
| | | L5 | 1340 | 0.28 | VAC | | | | |
| | | L1 | 1335 | 1 | TED | | | | |
| | | L2 | 1330 | 1 | TED | | | | |
| | | L3 | 1330 | 1 | TED | | | | |
| | | L4 | 1343 | 1 | TED | | | | |

(continued)

Table 4.28 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/21/76 | C4 | L1 | 1540 | 0.28 | VAC | | | North West/11 | |
| | | L2 | 1548 | 0.28 | VAC | | | | |
| | | L5 | 1548 | 1 | TED | | | | |
| | | L6 | 1600 | 1 | TED | | | | |

[a] Nutech Model 220 sampler 3-6 ft elevation

[b] DuPont sampler 3-6 ft elevation

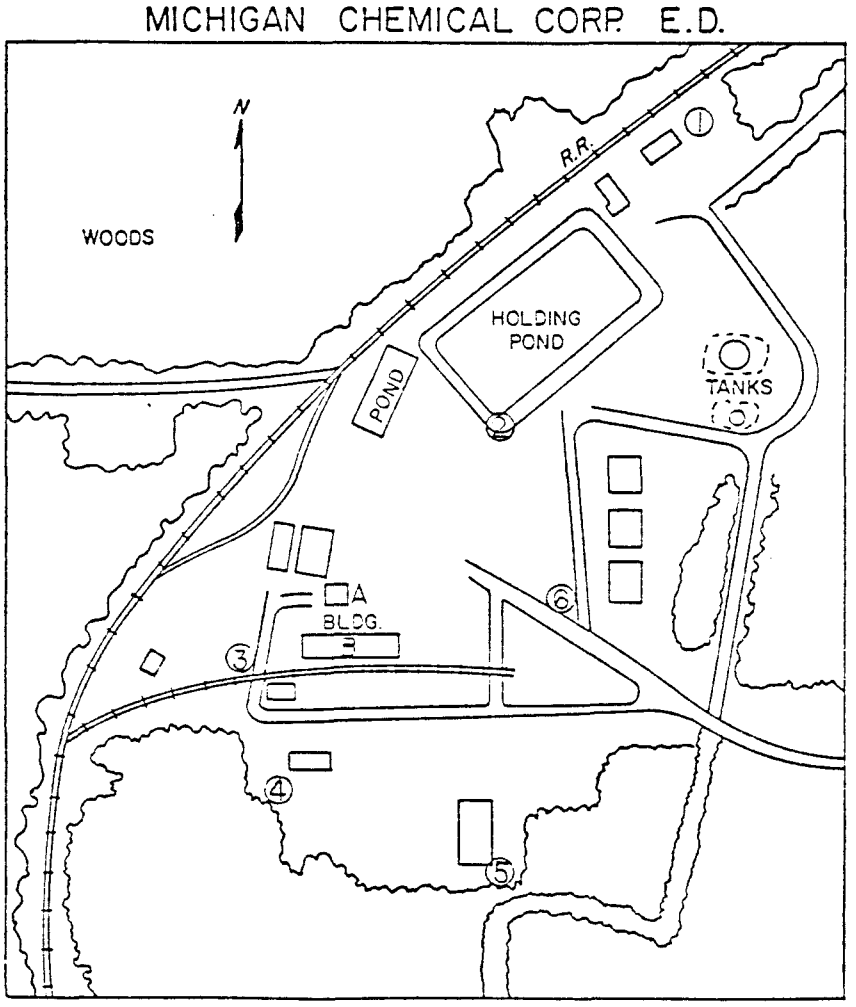
[c] DuPont sampler 15-18 ft elevation

[d] $Br_2$ emission visible at 1408

Locations shown in Figure 37.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
F - Fluoride and Fluorine
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can




APPROX. SCALE 1 cm = 110 m

Figure 4.45. Schematic map of Michigan Chemical Corp., El Dorado - sampling locations for P1-9/21/76.

A = $Br_2$ facilities

B = EDB facilities

Table 4.29. SAMPLING PROTOCOL FOR MICHIGAN CHEMICAL CORPORATION, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Size | Type of Sample |
|---|---|---|---|---|
| P1 4/7/77 | C1 | L1 | 2 cores[a] | SHHC-V |
| | | | 2 cores | SHHC-SV |
| | | | 1 ℓ | WHHC-V/SV[b] |
| | | | --c | VHHC-V |
| | | | | VHHC-SV |
| | | L2 | 2 cores | SHHC-V |
| | | | 2 cores | SHHC-SV |
| | | | 1 ℓ | WHHC-V/SV[b] |
| | | | --[c] | VHHC-V |
| | | | | VHHC-SV |

[a]Core ∿ 5 cm diameter, 13 cm.

[b]Water was collected from standing puddles.

[c]Needles stripped from 40 cm of pine bough sampled ∿5 m above ground from trees showing damage.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

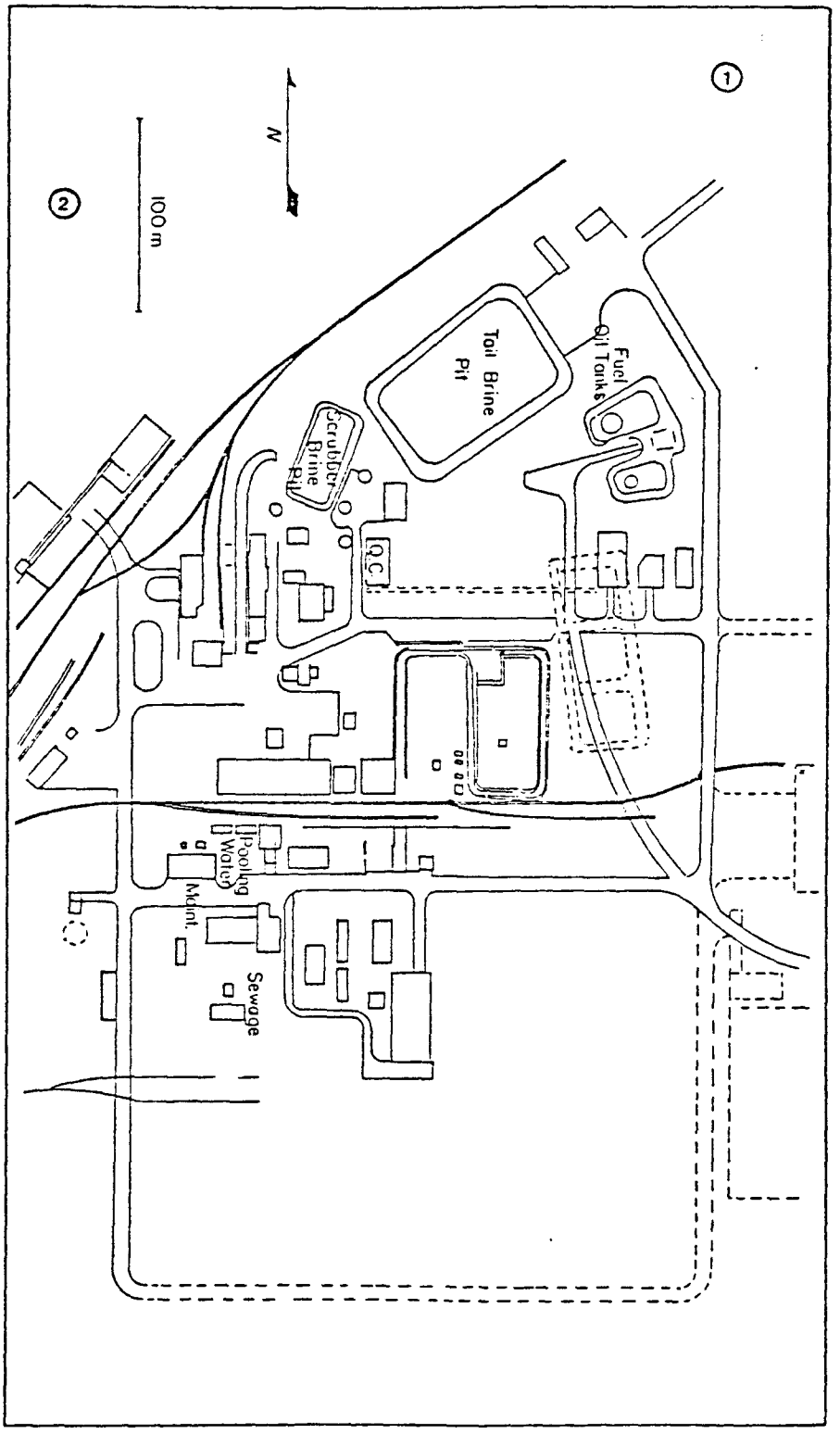


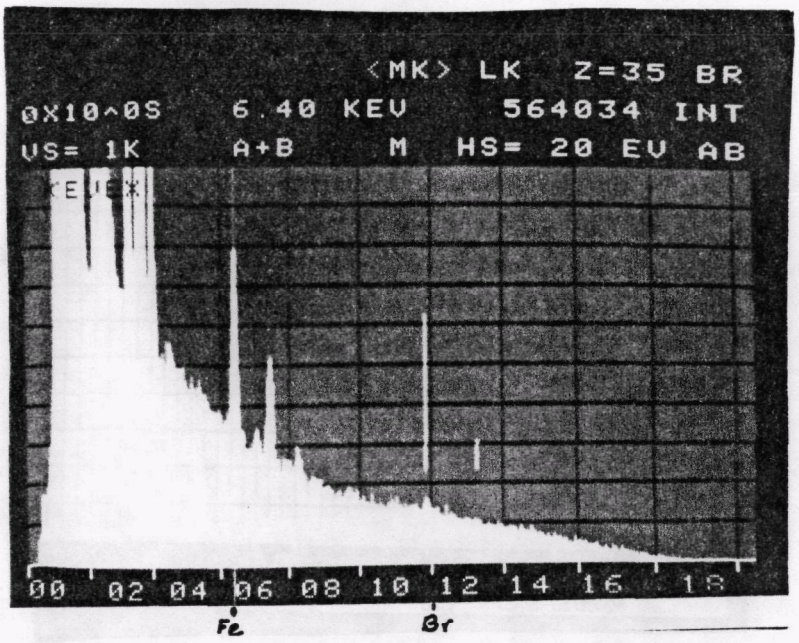

Figure 4.46. Schematic map of Michigan Chemical Corp. - sampling locations for 4/7/77.

Initially a search for the presence of bromine and its potential for mapping was made. In Figure 4.47, the EM spectrum from this site was expanded for greatest sensitivity in the bromine region. Traces were detectable when compared to the background in Figure 4.47. These traces were not sufficient, however, to produce an elemental map.

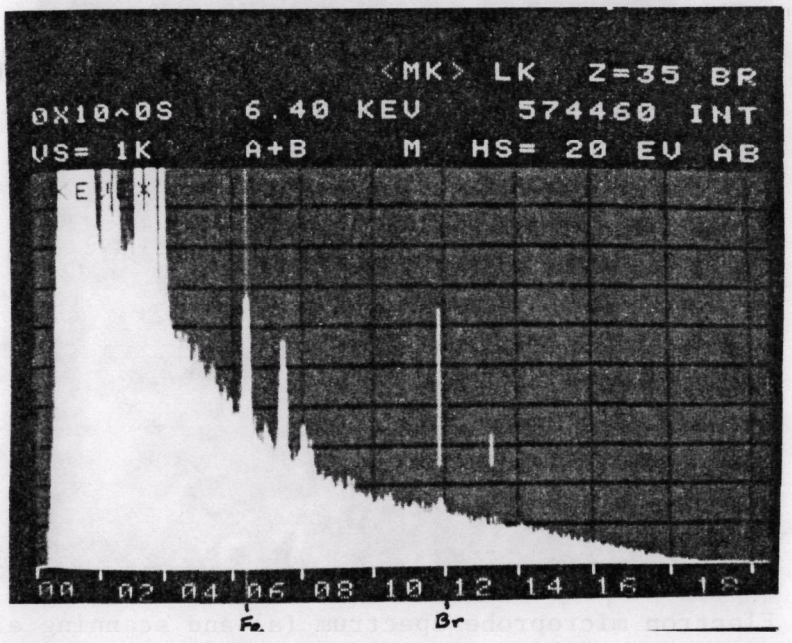
Electron microprobe maps for chlorine, sulfur, aluminum, and silicon are shown in Figures 4.49-4.52 along with the SEM map of the region (Fig. 4.48) for the cellulose filter from Michigan Chemical Corp. The spectrum (Fig. 4.48) depicted a higher chlorine peak than sulfur peak, the reverse of what was observed for Great Lakes Chemical Corp. In addition, aluminum, silicon and calcium are above background levels. This region was micrographed (Fig. 4.53) and mapped for chlorine, sodium, sulfur, calcium, silicon and aluminum. There was a significant substantial coincidence for sodium and chlorine, calcium and sulfur, but very little for silicon and aluminum (Fig. 4.54). Another region of the sample was carbon coated, and in this region there was almost no chlorine, but substantial amounts of calcium and sulfur appeared together. Many silicon particles appeared, but the majority are unassociated with aluminum.

Neutron Activation Analysis.--Samples of airborne particulates which had been collected by the State of Arkansas Air Pollution Control Division using a Hi-Vol sampler were examined by neutron activation for the presence of halogens, halides, etc. A segment of each filter was submitted to neutron activation analysis. The segment was 2 x 3 cm, cut from the median fold with the distal edge of the segment 3 cm from the filter edge. The results of the neutron activation analysis are shown in Table 4.30. On the third day of sampling the highest concentration of bromine and chlorine were observed for both types of filters used. The analysis of these samples for the presence of brominated organics is discussed under Section 4.2.3.5.

Gas-Liquid Chromatography/Electron Capture.--The Hi-Vol filters which were used in sampling at the Michigan Chemical Corp. site were analyzed for tris-(2,3-dibromopropyl)phosphate. Two by five cm segments from the central portion of the filters were cut out. Filter segments were placed in silanized 3 dram vials and extracted with 5 ml of acetone for two hours on a reciprocal shaker at approximately 120 cycles/min. These extracts were

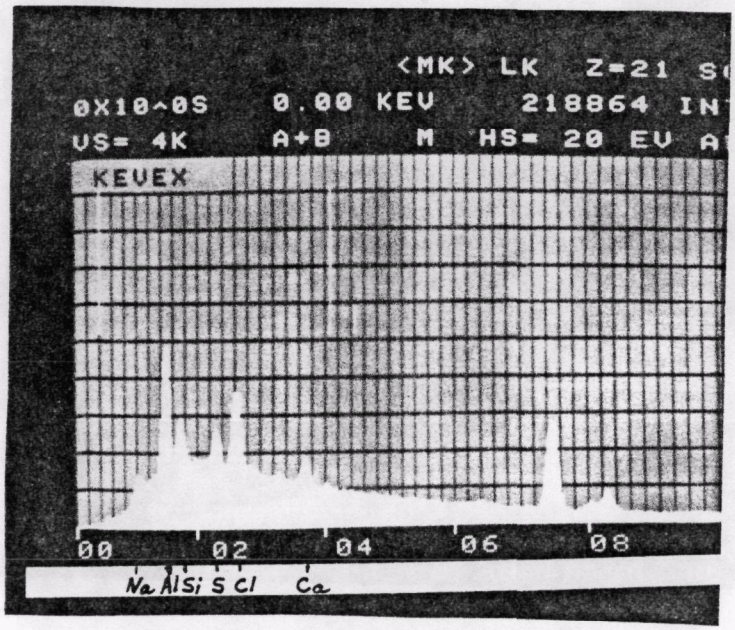



a



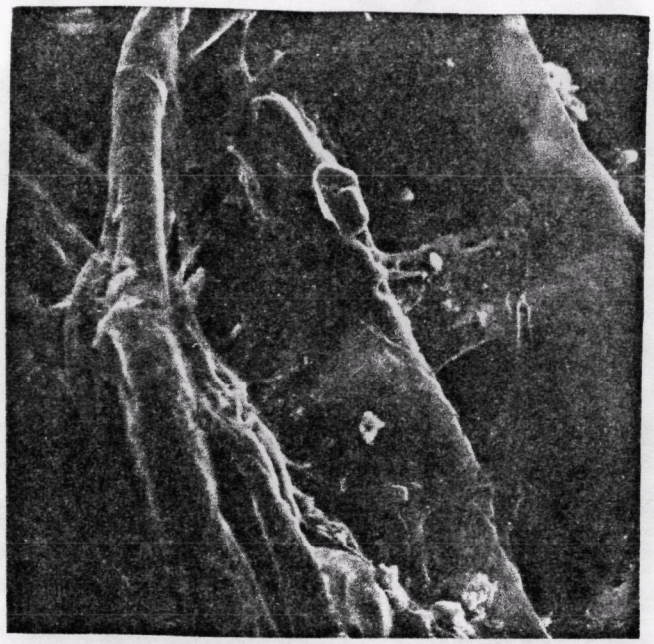

b

Figure 4.47. Electron microprobe spectrum of a 24 hr Hi-Vol glass fiber filter air sample taken at (a) Michigan Chemical Corporation, El Dorado, Arkansas on 12/22/76 - 12/23/76. Volume sampled 2603.6 $m^3$ air; (b) Great Lakes Chemical Corporation, El Dorado, Arkansas on 12/17/76 - 12/18/76. Volume sampled 2,733.6 $m^3$ air.




a

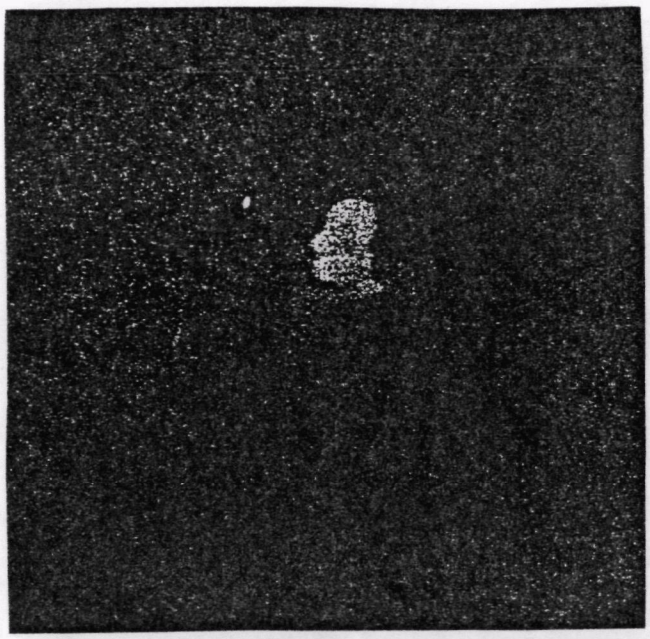
1200 x



b

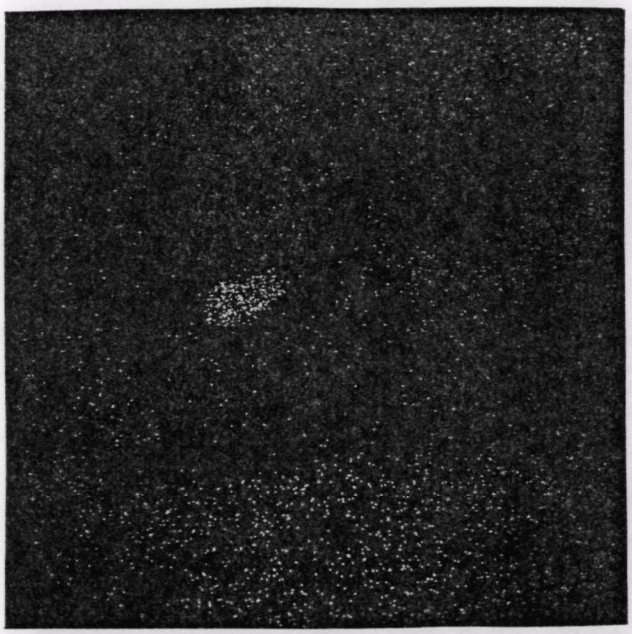
1200 x

Figure 4.48. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on a cellulose filter. Sample Volume: 1463.9 $m^3$ air. Location - Michigan Chemical Corp., El Dorado, Arkansas. Collected 12/22/76 - 12/23/76.



a

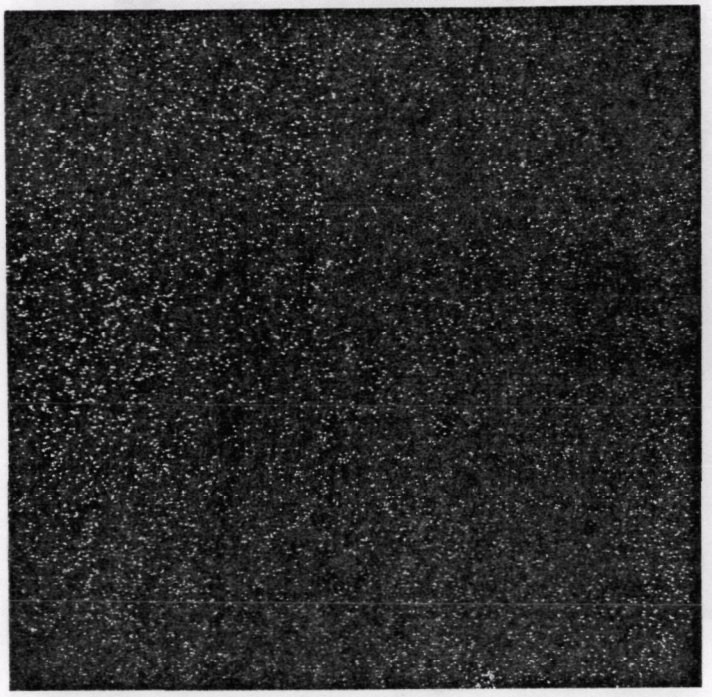
1200 x



b

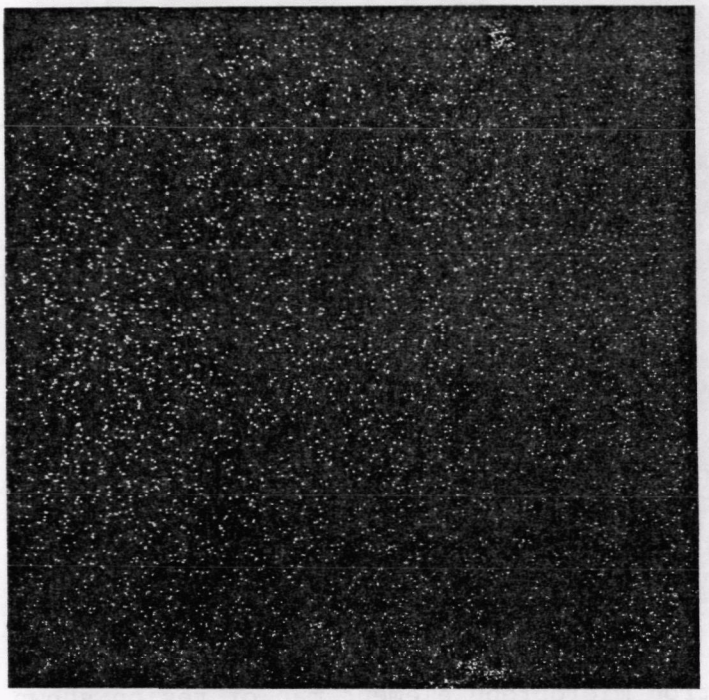
1200 x

Figure 4.49. Electron microprobe element map of region shown in Figure 4.48.
(a) Chlorine map; (b) Sodium map.



a

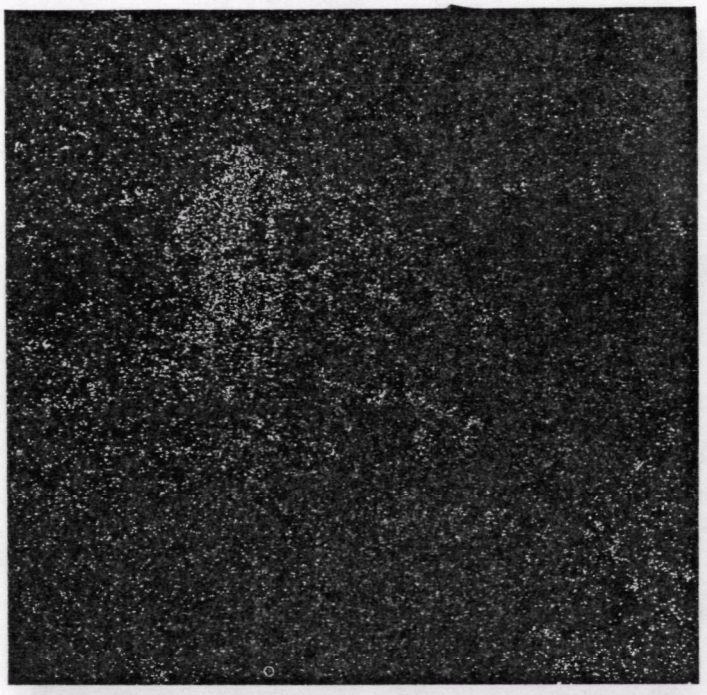
1200 x



b

1200 x

Figure 4.50. Electron microprobe element map of region shown in Figure 4.48.
(a) Sulfur map; (b) Calcium map.



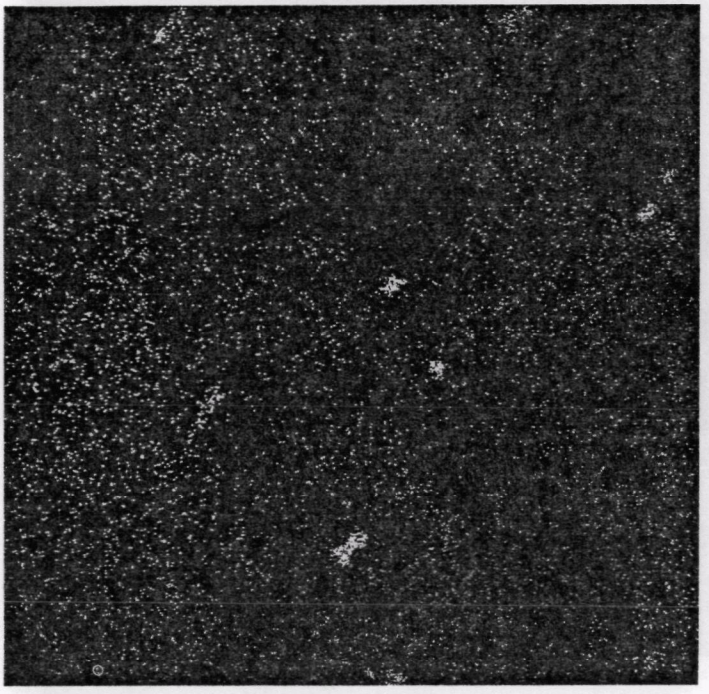
a

300 x

b

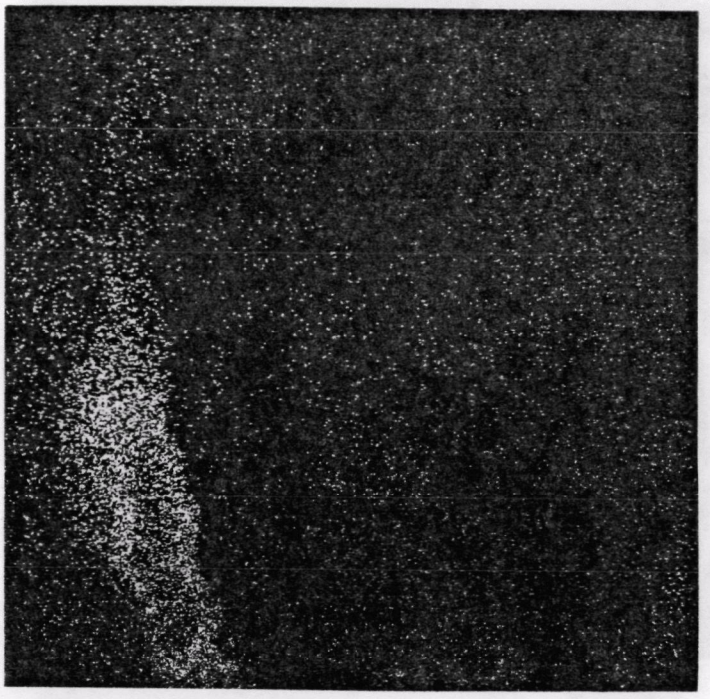
300 x

Figure 4.51. Electron microprobe element map of region shown in Figure 4.48.
(a) Calcium map; (b) Sulfur map.



a

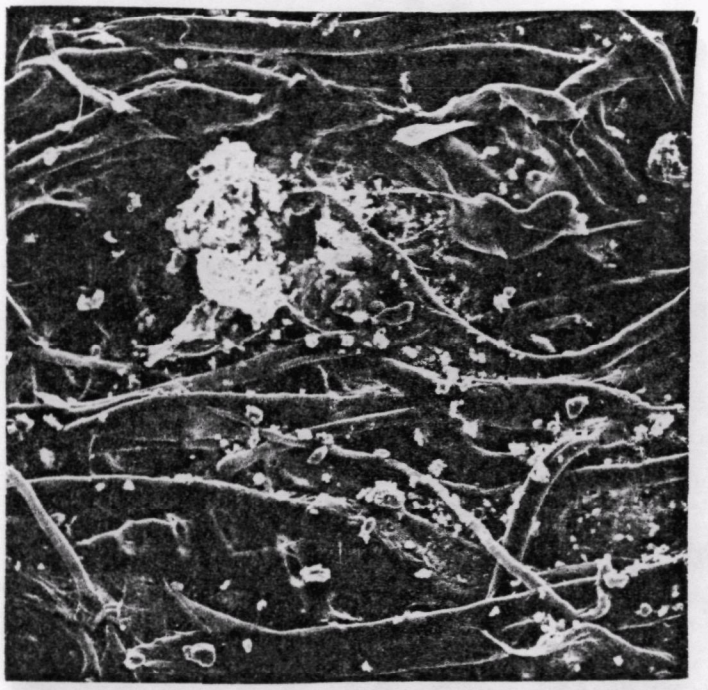
1200 x



b

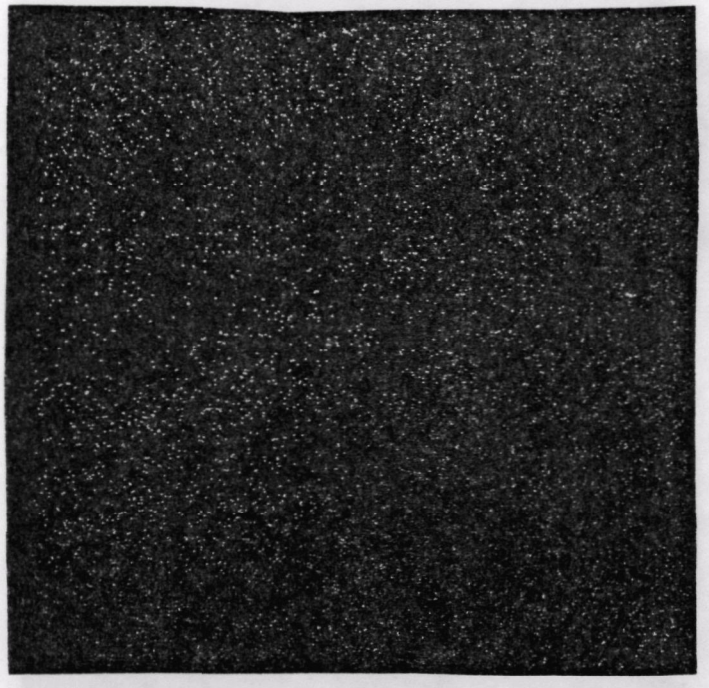
1200 x

Figure 4.52. Electron microprobe element map of region shown in Figure 4.48.
(a) Silicon map; (b) Aluminum map.



a

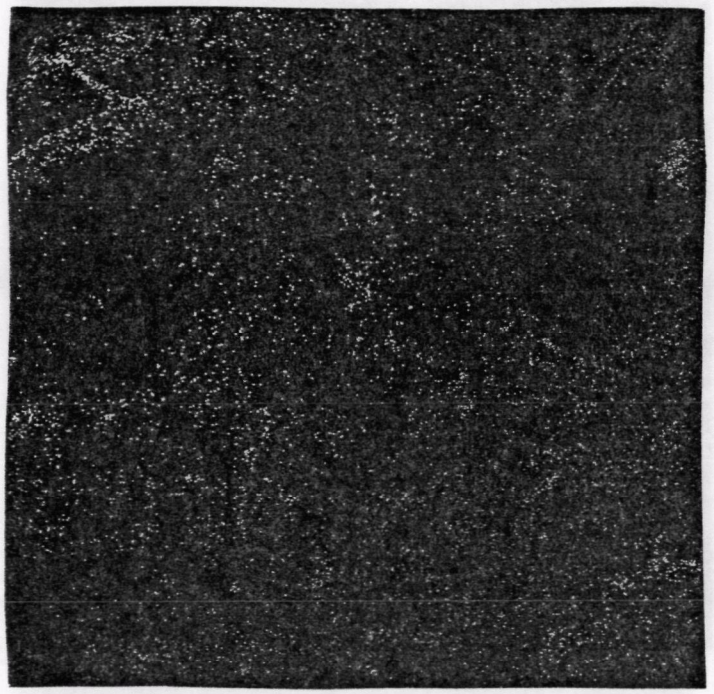
300 x



b

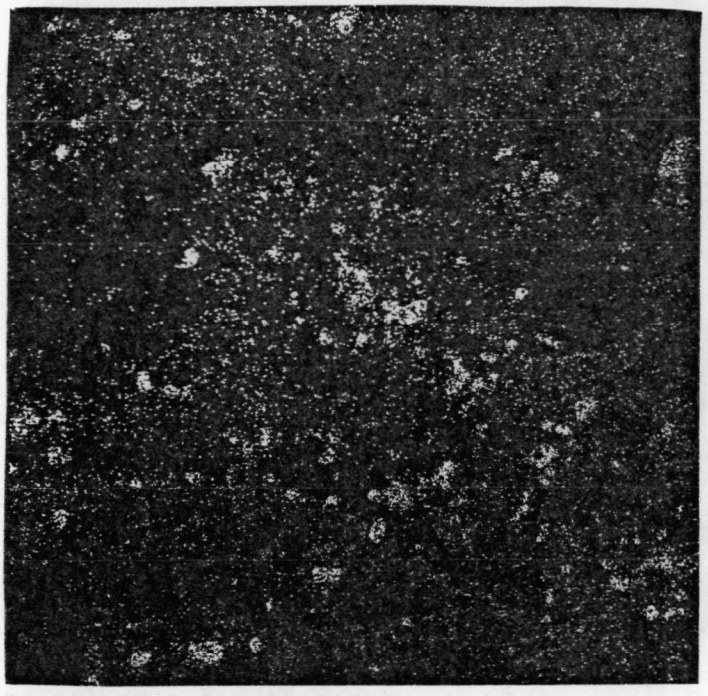
300 x

Figure 4.53. (a) Scanning electron micrograph of a region on an air sample collected on a cellulose filter. Sample Volume: 1463.9 $m^3$. Location - Michigan Chemical Corp., El Dorado, Arkansas. Collected 12/22/76 - 12/23/76; (b) Electron microprobe chlorine map of the region shown in a.



a

300 x



a

300 x

Figure 4.54. Electron microprobe element map of region shown in Figure 4.53.
(a) Aluminum map; (b) Silicon map.

Table 4.30. NEUTRON ACTIVATION ANALYSIS OF AMBIENT AIR HI-VOL SAMPLES

| Site | Date | Medium | Br ($\mu g/m^3$) | Cl ($\mu g/m^3$) |
|---|---|---|---|---|
| MIC[a] | 12/19/76- | GFF[b] | 2.05 | 0.91 |
| | 12/20/76 | CF[c] | 0.18 | 0.062 |
| MIC | 12/21/76- | GFF | 0.16 | 0.37 |
| | 12/22/76 | CF | 0.16 | 0.31 |
| MIC | 12/22/76- | GFF | 6.23 | 28.25 |
| | 12/23/76 | CF | 19.6 | 8.25 |

[a]All were 24 hr samples.

[b]GFF = glass fiber filter.

[c]CF = cellulose filter.

analyzed by GLC/ECD. The resulting chromatogram for one such sample is shown in Figure 4.55, along with the standard. The chromatograms were surprisingly free of interferences using the described conditions. An evaluation of the completeness of extraction was performed for both glass fiber filter samples and cellulose filters. A second extraction with a fresh 5 ml portion of acetone was performed. The recoveries of 20 and 10% in the second extract for glass fiber and cellulose filters, respectively, are consistent with solvent holdup of each filter. Extraction efficiency was greater than 90% for a single extraction.

The results of the GLC/ECD analysis were negative for TRIS in samples collected from 12/18/76-12/22/76; however, 70 $\pm$ 0.12 $ng/m^3$ and 50 $\pm$ 0.11 $ng/m^3$ of TRIS were found on glass fiber filter and cellulose filter, respectively, collected from 12/22/76-12/23/76. These must be regarded as minimum values since collection efficiencies and recoveries have not been vigorously established for Hi-Vol filters. The determinations reported above were replicates performed on two days on a different segment of the filters.

GLC/MS/COMP.--Confirmation of the presence of TRIS was achieved by GLC/MS using multiple ion detection. The chromatograms of an extract and a TRIS standard are shown in Figure 4.56 and the peak areas of the selected ions are given in Table 4.31.

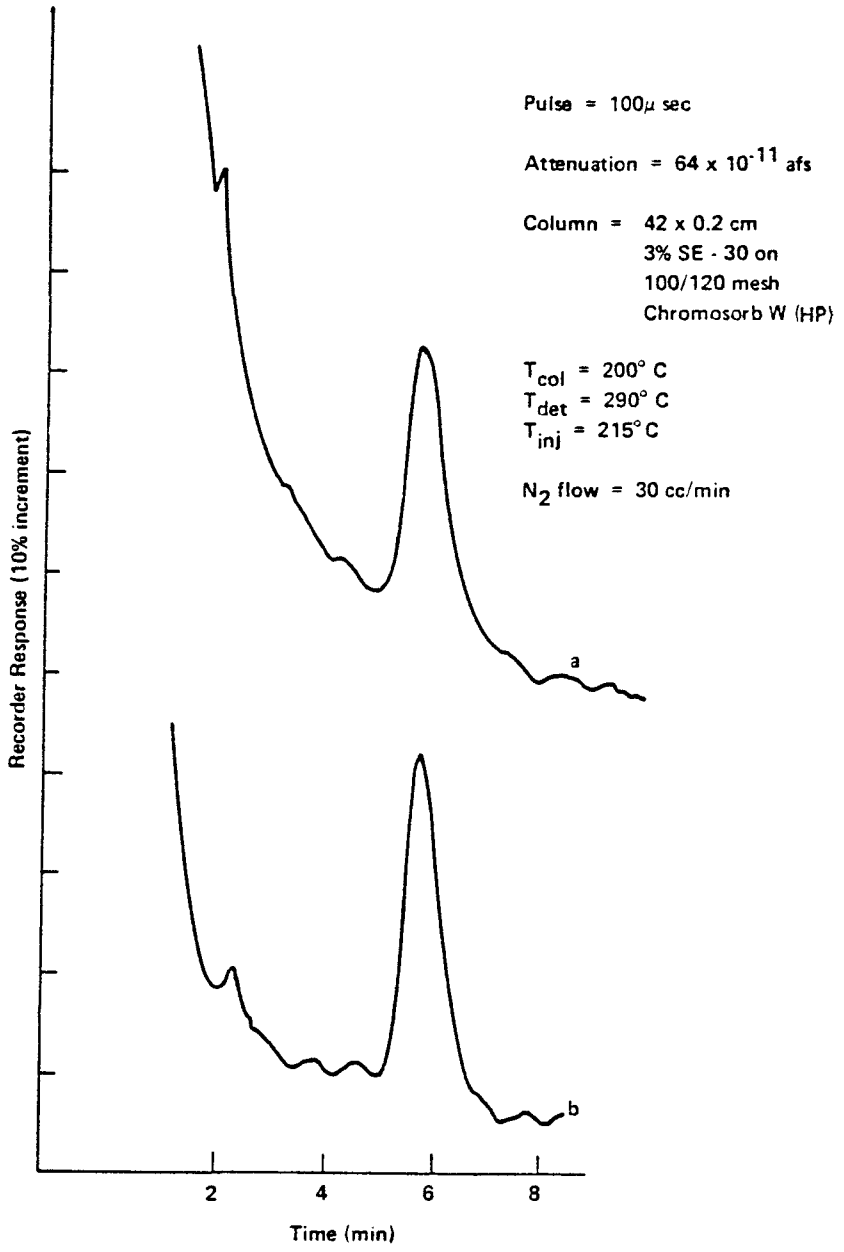
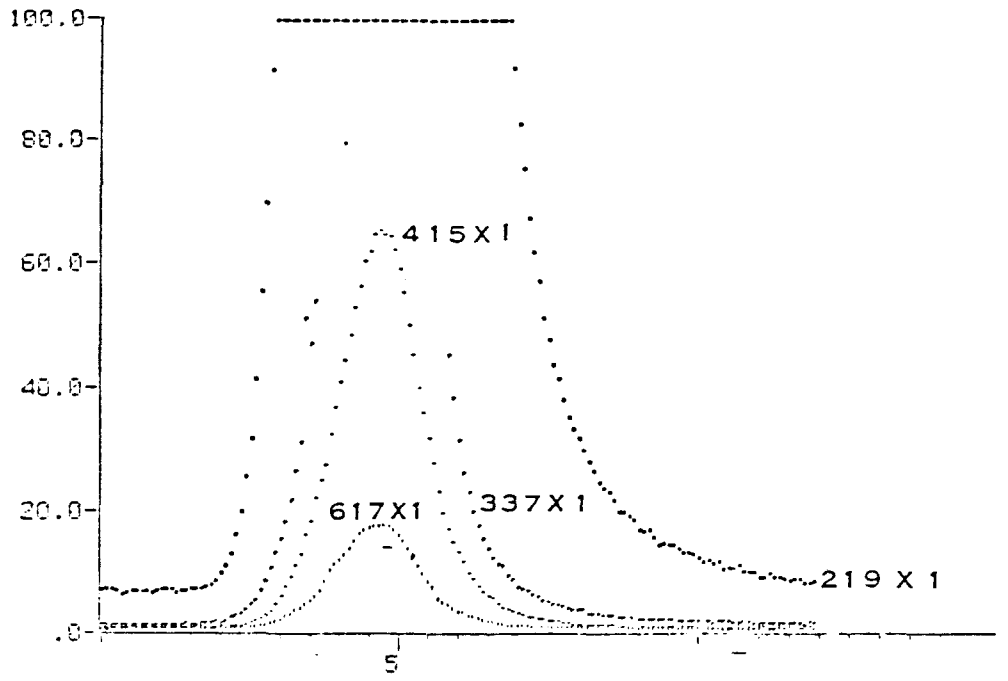



Figure 4.55. Gas liquid chromatography/electron capture detection ($^{63}Ni$) of (a) an acetone extract of the Hi-Vol glass fiber filter sample collected 12/22/76 - 12/23/76 at Michigan Chemical Corp., El Dorado, AK; and, (b) a TRIS standard (0.8 ng).



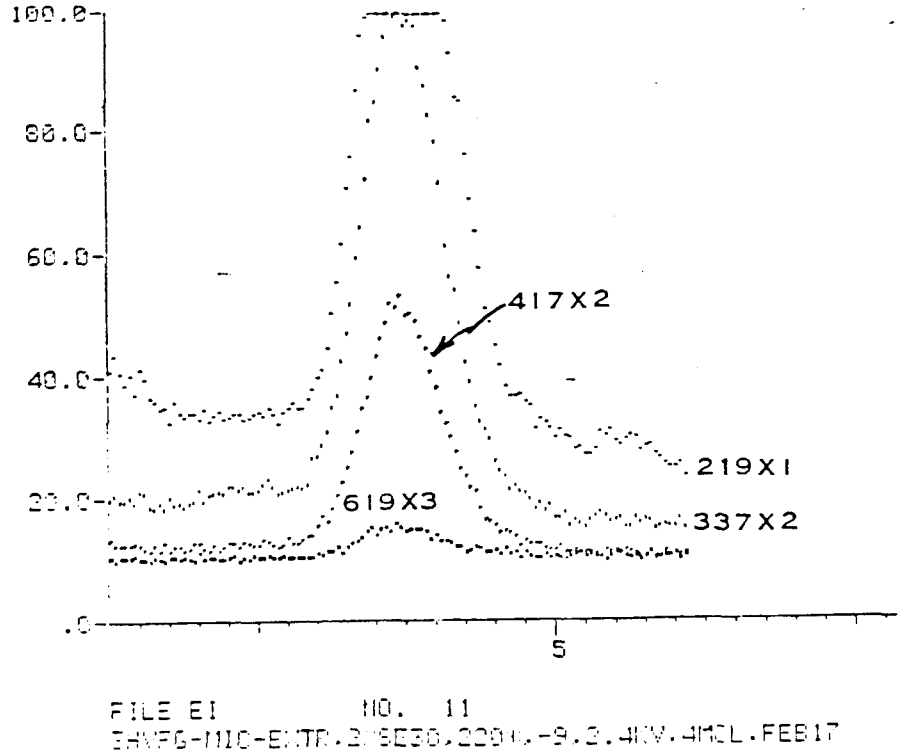




Figure 4.56. Gas chromatography/mass spectrometry analysis with multiple ion detection of (a) TRIS standard and, (b) extract of Hi-Vol glass fiber filter sample collected at Michigan Chemical Company 12/22/76 - 12/23/76.

Table 4.31. PEAK AREAS AND RATIOS OF SELECTED IONS OBTAINED FROM ANALYSIS OF TRIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN MULTIPLE ION DETECTION MODE

| Sample | m/e[a] | RT (min)[b] | Peak Area | Background | Ratio of m/e Values | | Ion Ratioed |
|---|---|---|---|---|---|---|---|
| | | | | | Observed | Predicted | |
| TRIS standard | 217 | 4.69 | 1150.78 | 05.18 | 1.08 | 1.01 | 217/219 |
| | 219 | 4.68 | 1063.84 | 04.54 | | | |
| | 335 | 4.69 | 114.98 | 01.34 | 0.52 | 0.51 | 335/337 |
| | 337 | 4.63 | 219.62 | 01.14 | | | |
| | 415 | 4.68 | 37.60 | 00.90 | 0.36 | 0.34 | 415/417 |
| | 417 | 4.68 | 103.72 | 01.00 | | | |
| | 617 | 4.71 | 08.72 | 00.88 | 0.91 | 1.02 | 617/619 |
| | 619 | 4.61 | 09.46 | 00.84 | | | |
| Extract of HI Vol sample collected at Michigan Chemical Co., 12/22/76-12/23/76 (G.F.F.) | 217 | 4.56[c] | 2059.92 | 26.44 | 1.09 | 1.01 | 217/219 |
| | 219 | 4.61 | 1888.80 | 31.54 | | | |
| | 335 | 4.46 | 413.10 | 10.30 | 0.49 | 0.51 | 335/337 |
| | 337 | 4.44 | 837.44 | 09.58 | | | |
| | 415 | 4.48 | 144.92 | 07.38 | 0.36 | 0.34 | 415/417 |
| | 417 | 4.48 | 389.50 | 06.06 | | | |
| | 617 | 4.43 | 36.60 | 03.46 | 1.00 | 1.02 | 617/619 |
| | 619 | 4.46 | 36.74 | 03.44 | | | |

a) These m/e values were selected as most characteristic of TRIS.

b) Retention time on gc column (3% SE-30 on Supelcoport 100/120 mesh; 42 x 0.2 cm col; Tcol = 220; flow rate 30 ml/min.

c) Slight variation in retention time represents day to day variation as the retention time for an extract run on the same day was 4.76 $\pm$ 0.08 min.

4.2.3.3 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by turbidimetric determination of total halide are given in Table 4.32. The site, period and cycle designation were given in the sampling protocol (Table 4.28) and the locations on the schematic maps (Fig. 4.45).

Table 4.32. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. (VELSICOL)[a,b]

| Species | Locations | | | |
|---|---|---|---|---|
| | L1 | L2 | L3 | L4 |
| $Cl_2/Br_2$[c] | 300 ± 99 | 293 ± 280 | <80 | <82 |
| $Br_2$[d] | <42 | <68 | <17 | <35 |
| $Cl^-/Br^-$[c] | <69 | 300 ± 110 | <56 | <57 |
| $Br^-$[d] | <21 | <34 | 35 | 50 |

[a]Samples are from P1/C3.

[b]Values are in $\mu g/m^3$.

[c]By turbidity.

[d]By neutron activation analysis.

At Michigan Chemical Corp., detectable quantities of halogens were found at L1 (downwind from the holding pond) and L2 (Fig. 4.45). Detectable quantities of halide were found at L2 only. Comparable data for bromine obtained by neutron activation analysis (Table 4.32) indicate the predominant element is probably chlorine and/or chloride. Neutron activation analysis performed on cellulose filters (acid mist) used in sampling immediately following the impinger sampling showed significant amounts of bromine collected at L3 and L4.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples (Table 4.33). The limits of detection were approximately 0.012 ppm in the impinger solution based on the volume of air sampled and the sensitivity of the turbidimetric technique.

Table 4.33. CONCENTRATIONS OF FLUORIDE/FLUORINE IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. (VELSICOL)[a,b]

| | | Locations | | | |
|---|---|---|---|---|---|
| Period | Cycle | L1 | L2 | L3 | L4 |
| P1 | C3 | <4.2 | <6.7 | <3.2 | <3.1 |

[a]Values in $\mu g/m^3$.

[b]Determined by ion specific electrode.

Acid Mist.--No titratable acid was found in any sample. Table 4.34 summarizes the upper limit of ambient air concentration of acid mist.

4.2.3.4 Bromine and Brominated Organics in Brine

Neutron Activation Analysis.--Table 4.35 lists the concentration of bromine (molecular plus halide) in brine samples. A reduction of 90% of the bromine concentration was observed between the front and tail brine. Significant quantities of bromine were still detected in the tail brine samples. However, the technique of neutron activation did not distinguish whether the bromine is present as molecular bromine, bromide ion or brominated organics. Furthermore, the number of bromines per organic molecule could not be delineated by this technique. The importance of these results is primarily attributed to the presence of substantial quantities of "bromine" even after bromine extraction.

GLC/MS/COMP Analysis for Volatile Organics.--Volatile halogenated organics were recovered from water using previously described methods (Appendix A). Figures 4.57 and 4.58 depict the total ion current chromatograms for the volatile organics which were observed in front and tail brine samples. The unequivocal identification of benzene and toluene was established in Michigan Chemical Corp. front brine sample (Fig. 4.57). In the tail brine sample (Fig. 4.58) from the same site we identified bromodichloromethane (Fig. 4.59), toluene, dibromochloromethane (Fig. 4.60) and bromoform.

The halogenated and other organics which were identified and quantitated in brine samples from Michigan Chemical Corp. are shown in Table 4.36. The

Table 4.34. ACID MIST IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. AS $H_2SO_4$[a]

| Period | Cycle | Locations | | | |
|---|---|---|---|---|---|
| | | L1 | L2 | L3 | L4 |
| P1 | C4 | <50 | <44 | <50 | <51 |

[a]Values as $\mu g/m^3$.

Table 4.35. CONCENTRATION OF BROMINE IN BRINE SAMPLES

| Site | Sample Type | µg Br/ml |
|---|---|---|
| Michigan Chemical Corp. | Front brine | 6421.5 |
| | Tail brine | 645.8 |

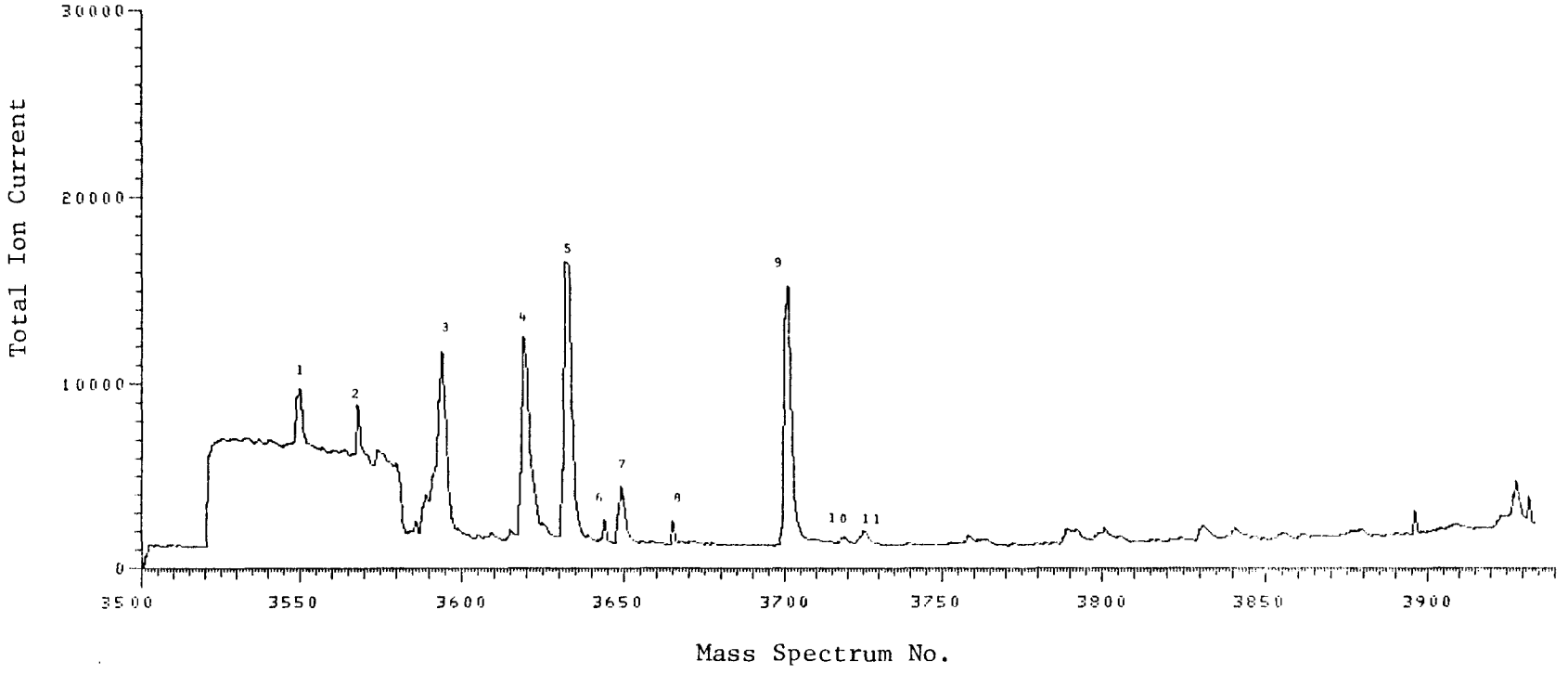



Figure 4.57. Total ion current profile of volatile organics in front brine sample from Michigan Chemical Corp. Peak No. 4 = hexafluorobenzene (e$), 5 = perfluorotoluene (e$); 7 = benzene and 9 = toluene.

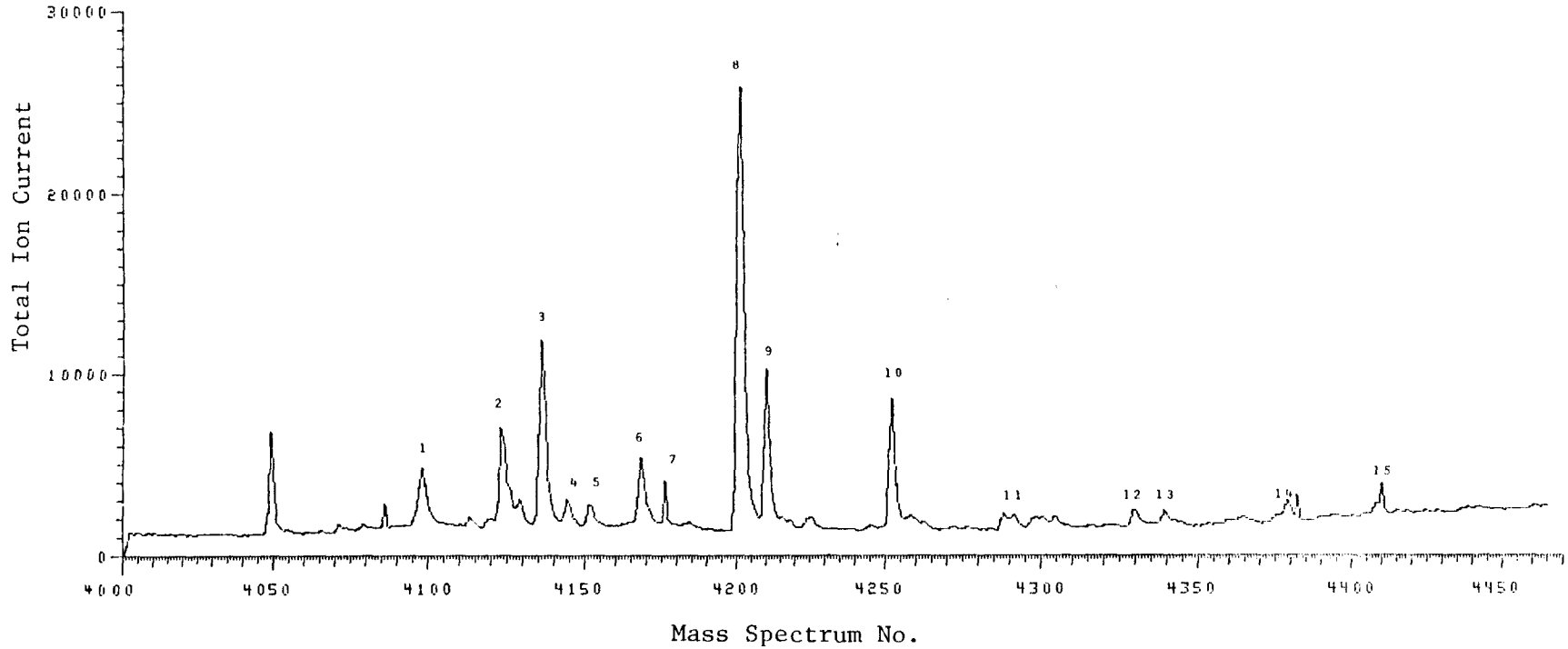



Figure 4.58. Total ion current profile of volatile organics in tail brine sample from Michigan Chemical Corp. Peak No. 2 = hexafluorobenzene (e$), 3 = perfluorotoluene (e$), 5 = benzene, 6 = bromodichloromethane, 8 = toluene, 9 = dibromochloromethane, and 10 = bromoform.

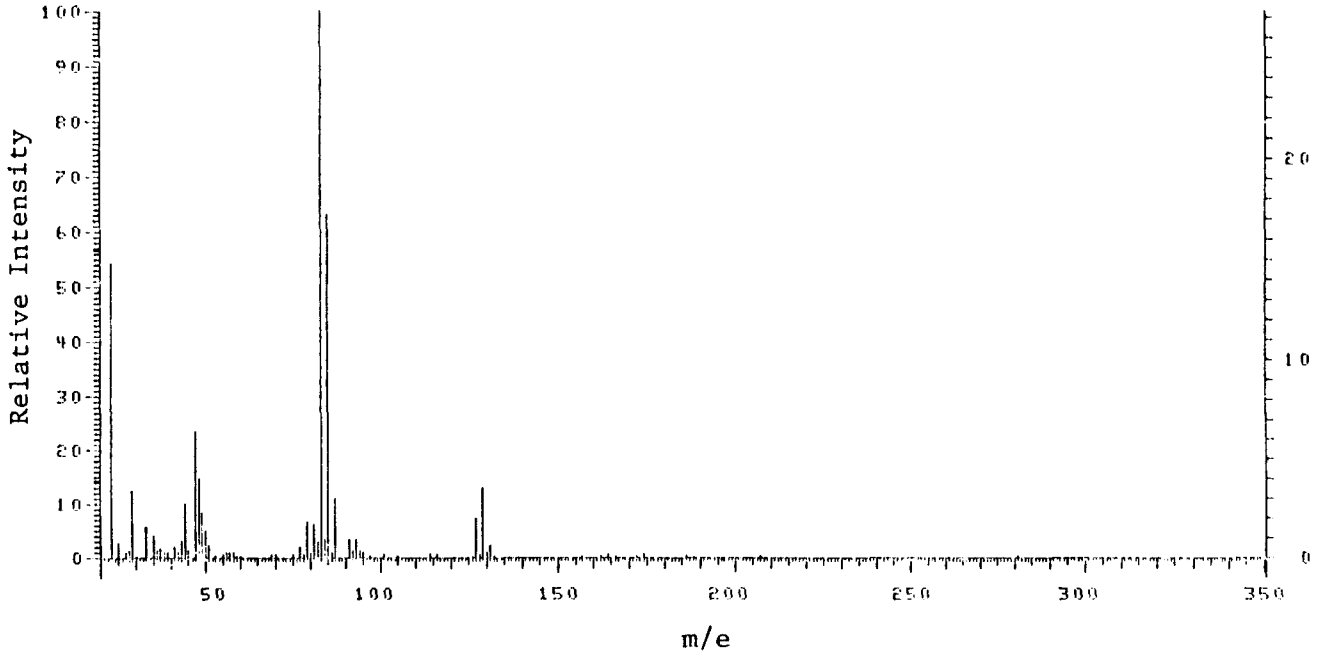



Figure 4.59. Mass spectrum of bromodichloromethane in tail brine sample (MCI). Peak No. 6 in Figure 4.58

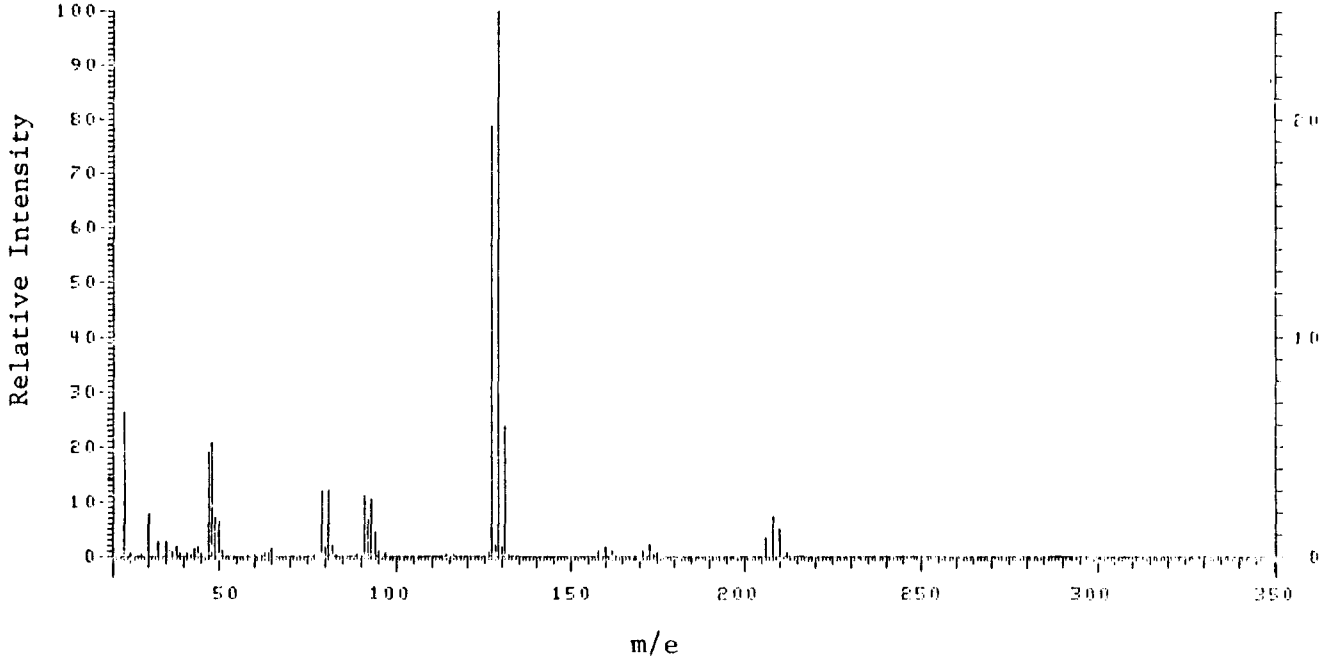



Figure 4.60. Mass spectrum of dibromochloromethane in tail brine sample (MCI). Peak No. 9 in Figure 4.58.

Table 4.36. HALOGENATED AND OTHER ORGANICS IDENTIFIED AND QUANTITATED IN BRINE SAMPLES FROM MICHIGAN CHEMICAL CORP.[a]

| Compound | Sample Type | |
|---|---|---|
| | Front brine | Tail Brine |
| Methyl Chloride | 5.3 | N.D. |
| Bromoform | 8.0 | 752 |
| Bromodichloromethane | 6.7 | 52 |
| Dibromochloromethane | 1.3 | 800 |
| Hexafluorobenzene (eS)[b] | - | - |
| Perfluorotoluene (eS)[b] | - | - |
| Toluene | 1,120 | 3,200 |
| Benzene | 240 | 120 |

[a]Concentrations are in ppt.

[b]eS = external standard, 200 ng.

concentrations of bromoform, bromodichloromethane and dibromochloromethane were observed to increase significantly after the brine passed through the bromine extraction process.

4.2.3.5 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GLC/MS/COMP.--Table 4.37 lists the volatile organics which were identified in ambient air taken from the Michigan Chemical Corp. site. This sample represents the sampling location upwind from the bromine extraction and organic synthesis facilities. The compounds listed in this table are representative of the many components that are generally found in ambient air with the primary contribution from fossil fuel and its combustion. Several halogenated compounds, for example, dichlorodifluoromethane, trichlorofluoromethane, dichloromethane, chloroform, 1,1,1-trichloroethane, carbon tetrachloride and methyl chloride are commonly found as background compounds in ambient air samples taken throughout the Continental United States. Figures 4.61 and 4.62 depict the total ion

Table 4.37. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L1)[a]

| Chromatographic Peak No. | Elution Temperature (°C) | Compound |
|---|---|---|
| 1 | 40 | $CO_2$ |
| 2 | 41 | dichlorodifluoromethane |
| 2A | 42 | chloromethane |
| 2B | 43 | 1-butene |
| 3 | 44 | acetaldehyde |
| 3A | 46 | isopentane |
| 4 | 46 | trichlorofluoromethane |
| 5 | 47 | propanal + n-pentane + furan |
| 5A | 47 | $C_5H_8$ isomer + acetone |
| 5B | 48 | dimethyl ether + diethyl ether (tent.) |
| 5C | 48 | dichloromethane |
| 6 | 49 | freon 113 (BKG) |
| 6A | | 2-methylpropanal |
| 7 | 53 | 2-methylpentane |
| 7A | 54 | crotonaldehyde |
| 7B | 54 | vinyl acetate (tent.) |
| 8 | 55 | 3-methylpentane |
| 8A | 55 | n-butanal |
| 8B | 56 | methyl vinyl ketone |
| 9 | 56 | methyl ethyl ketone + methylfuran isomer |
| 9A | 57 | n-hexane |
| 10 | 57 | chloroform |
| 10A | 59 | $C_6H_{12}$ isomer |
| 11 | 61 | methylcyclopentane |
| 11A | 62 | 1,1,1-trichloroethane |
| 11B | 64 | 3-methylbutanal |
| 11C | 65 | benzene |
| 11D | 66 | carbon tetrachloride |
| 11E | 66 | cyclohexane |
| 12 | 67 | 2-methylhexane |
| 12A | 67 | 2,3-dimethylpentane |
| 13 | 68 | 3-methylhexane |
| 13A | 69 | $C_7H_{14}$ isomer |
| 14 | 70 | n-pentanal |
| 15 | 72 | n-heptane |
| 16 | 77 | methylcyclohexane |
| 16A | 78 | $C_8H_{18}$ isomer |
| 17 | 83 | toluene |
| 18 | 85 | $C_8H_{18}$ isomer |
| 19 | 87 | $C_8H_{18}$ isomer |
| 19A | 88 | $C_8H_{16}$ isomer |
| 20 | 89 | n-hexanal |
| 20A | 90 | $C_8H_{16}$ isomer |
| 21 | 92 | n-octane |
| 21A | 97 | $C_9H_{20}$ isomer |
| 22 | 98 | $C_9H_{20}$ isomer |
| 22A | 99 | $C_8H_{16}$ isomer |
| 23 | 100 | $C_9H_{20}$ isomer |
| 24 | 103 | ethylbenzene |
| 25 | 105 | p-xylene |
| 26 | 106 | $C_9H_{20}$ isomer |
| 26A | 107 | $C_9H_{20}$ isomer |
| 26B | 108 | styrene |
| 27 | 110 | n-heptanal |
| 27A | 111 | $C_9H_{18}$ isomer |
| 28 | 113 | n-nonane |
| 29 | 120 | $C_{10}H_{22}$ isomer |
| 29A | 120 | $C_{10}H_{16}$ isomer |
| 30 | 121 | benzaldehyde |
| 30A | 123 | $C_3$-alkyl benzene isomer |
| 31 | 125 | $C_{10}H_{22}$ isomer |
| 32 | 127 | $C_{10}H_{22}$ isomer |
| 32A | 129 | $C_3$-alkyl benzene isomer |
| 33 | 129 | n-octanal |
| 33A | 130 | $C_{10}H_{20}$ isomer |
| 34 | 132 | n-decane |
| 34A | 135 | 1,2,3-trimethylbenzene |
| 35 | 138 | $C_{11}H_{24}$ isomer |
| 35A | 141 | $C_4$-alkyl benzene |
| 36 | 142 | acetophenone |
| 37 | 144 | $C_{11}H_{24}$ isomer |
| 37A | 147 | unknown |
| 38 | 149 | $C_{11}H_{22}$ isomer + n-nonanal |
| 39 | 151 | n-undecane |
| 40 | 162 | diethyl phthalate |
| 41 | 164 | decanone isomer |
| 42 | 166 | $C_{12}H_{24}$ isomer |
| 43 | 168 | n-dodecane |
| 47 | 189 | n-tridecane |

[a]See Table 4.28 for sampling protocol.

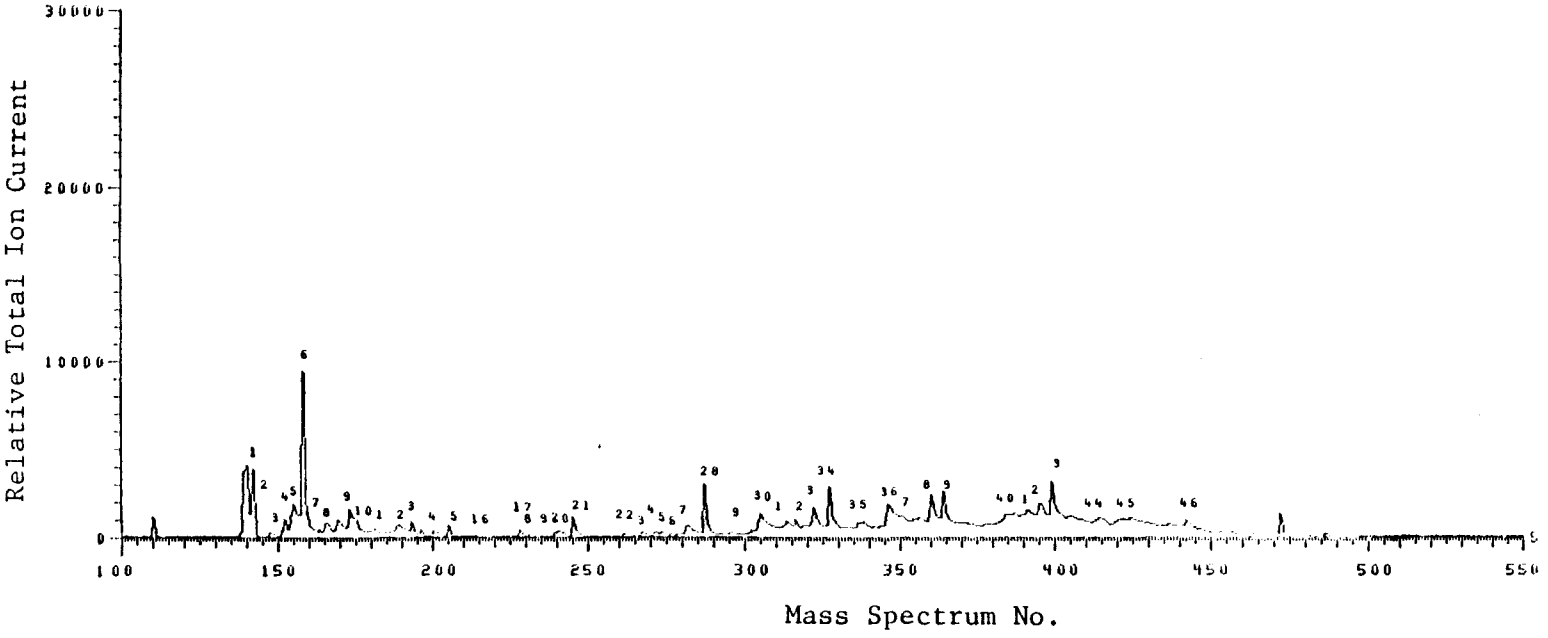



Figure 4.61. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L1).

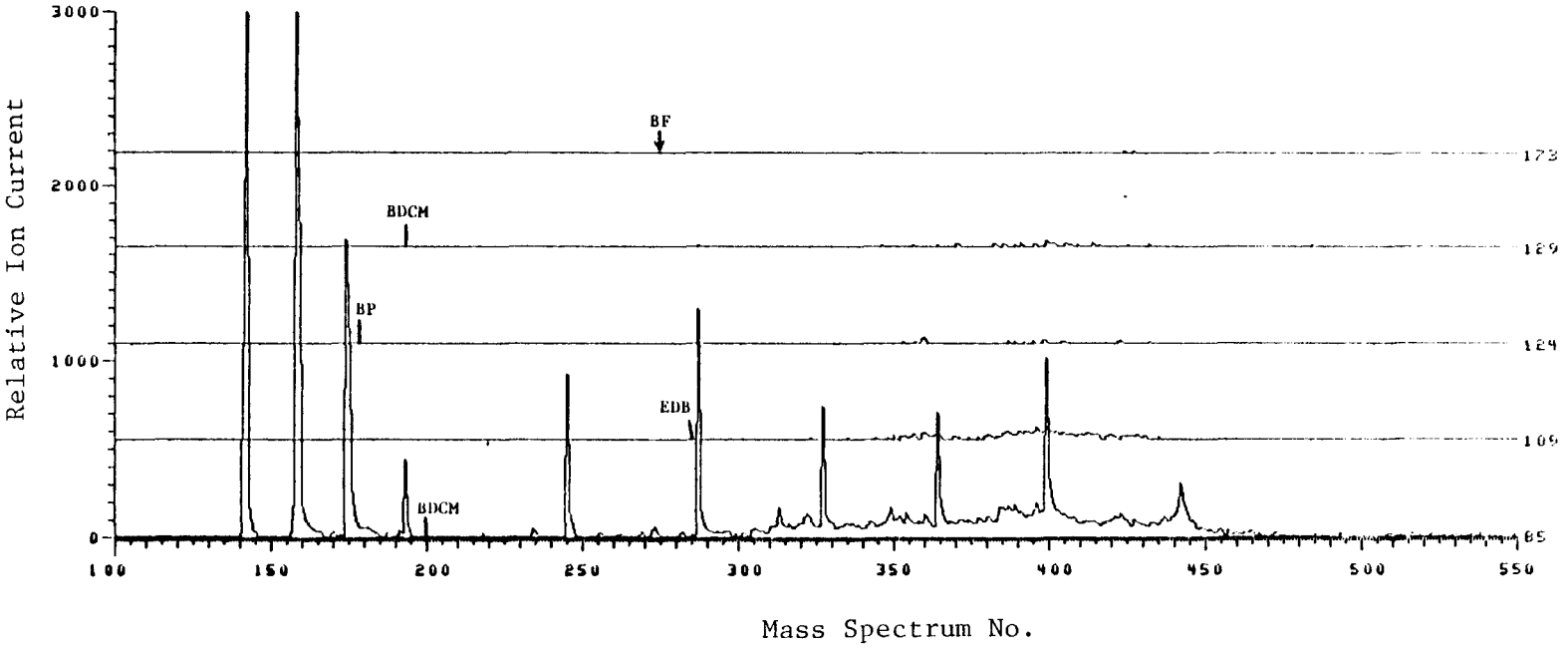



Figure 4.62. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L1). BF = bromoform, BP = bromopropane, EDB = ethylene dibromide, BDCM = bromodichloromethane.

current profile and ion chromatogram generated by the GLC/MS/COMP system of the volatile ambient air pollutants which were identified in Table 4.37. The relative total ion current axis is fully attenuated to allow the comparison of overall intensity of the pollution profiles.

In Figure 4.62 ion chromatograms are depicted for the ambient air sample taken from the upwind location at Michigan Chemical Corp. The ions chosen - m/e 85, m/e 109, m/e 124, m/e 129 and m/e 173 - correspond to bromodichloromethane (BDCM), ethylene dibromide (EDB), bromopropane (BP), bromodichloromethane (BDCM) and bromoform (BF), respectively.

Table 4.38 lists the volatile organics identified in ambient air sample taken at L2 on the Michigan Chemical Corp. site. The sampling location in this case was on the bank of the pond and downwind from the spent brine pond, but upwind from the bromine extraction and organic synthesis facilities. During the entire sampling period, the wind direction was toward the main plant facility. Dibromochloromethane and bromoform were identified. Figure 4.63 depicts the total ion current profile of the volatile ambient air pollutants listed in Table 4.38. Figure 4.64 shows the ion chromatograms for m/e 186, m/e 173, m/e 129 and m/e 124. In this figure the peaks which correspond to DBCM and BF are marked.

Table 4.39 lists the volatile organics which were identified at L3 on the Michigan Chemical Corp. site. In this sample, bromomethane, a chlorobromopropene isomer, 1,2-dibromoethane, and 1,1-dibromo-2-bromochloropropane were identified. Figure 4.65 represents the profile of the volatile ambient air pollutants which were listed in Table 4.39. The relatively large peaks (46 and 47) which appeared in this chromatogram could not be identified, however, based upon the mass spectra of these two chromatographic peaks, it was concluded that they did not contain halogen. A series of ion chromatograms for Figure 4.65 is shown in Figure 4.66. The ions at m/e 186, m/e 109, m/e 157, m/e 85 and m/e 124 represent the external standards, perfluorobenzene and perfluorotoluene, and 1,2-dibromoethane, dibromochloropropane, bromodichloromethane and bromopropane, respectively. The identities of the components of a sample taken at L4 are given in Table 4.40. The relationship of this location to the brine ponds, bromine extraction, and organic synthesis facilities is shown in Figure 4.45. In this sample we

Table 4.38. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L2)[a]

| Chromatographic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|
| 1 | 39 | $CO_2$ |
| 1A | 40 | dichlorodifluoromethane |
| 1B | 41 | chloromethane |
| 1C | 41 | 1-butene |
| 1D | 42 | n-butane |
| 1E | 44 | acetaldehyde |
| 2 | 45 | trichlorofluoromethane |
| 2A | 46 | $C_5H_{10}$ isomer |
| 2B | 46 | $C_5H_8$ isomer |
| 2C | 47 | isopentane |
| 3 | 47 | acetone + dimethyl ether + diethyl ether (tent.) |
| 3A | 48 | dichloromethane (tent.) |
| 4 | 48 | freon 113 (BKG) |
| 4A | 51 | n-pentane |
| 5 | 52 | 2-methylpentane |
| 5A | 53 | 2-methylpropenal |
| 5B | 54 | 3-methylpentane |
| 5C | 54 | n-butanal |
| 6 | 55 | hexafluorobenzene (ef) |
| 6A | 56 | n-hexane |
| 7 | 56 | chloroform |
| 7A | 57 | methyl ethyl ketone |
| 8 | 59 | perfluorotoluene (ef) |
| 8A | 60 | methycyclopentane |
| 8B | 61 | 1,1,1-trichloroethane |
| 9 | 63 | benzene |
| 9A | 64 | carbon tetrachloride |
| 10 | 65 | 2-methylhexane |
| 10A | 66 | 2,3-dimethylpentane |
| 10B | 67 | 3-methylhexane |
| 10C | 68 | $C_7H_{14}$ isomer |
| 11 | 69 | 3-methylbutanal + $C_7H_{14}$ isomer |
| 11A | 70 | bromodichloromethane |
| 11B | 71 | n-pentanal |
| 12 | 71 | n-heptane |
| 13 | 76 | methylcyclohexane |
| 14 | 78 | 4-methyl-2-pentanone |
| 15 | 83 | toluene |
| 16 | 85 | $C_8H_{18}$ isomer |
| 17 | 80 | dibromochloromethane |
| 17A | 87 | $C_8H_{16}$ isomer |
| 18 | 89 | n-hexanal + $C_8H_{16}$ isomer |
| 19 | 91 | n-octane |
| 19A | 92 | tetrachloroethylene |
| 19B | 93 | $C_8H_{16}$ isomer |
| 20 | 102 | ethylbenzene |
| 20A | 103 | $C_9H_{20}$ isomer |
| 21 | 104 | p-xylene |
| 21A | 105 | bromoform |
| 21B | 106 | $C_9H_{20}$ isomer |
| 22 | 107 | $C_9H_{20}$ isomer |
| 22A | 108 | styrene |
| 23 | 109 | o-xylene |
| 23A | 110 | $C_9H_{18}$ isomer |
| 23B | 111 | heptanal |
| 24 | 112 | n-nonane |
| 24A | 116 | $C_{10}H_{22}$ isomer |
| 24B | 118 | $C_{10}H_{20}$ isomer |
| 25 | 120 | $C_{10}H_{22}$ isomer |
| 25A | 121 | $C_9H_{18}$ isomer |
| 26 | 121 | benzaldehyde |
| 27 | 123 | p-ethyltoluene |
| 28 | 125 | $C_{10}H_{22}$ isomer |
| 29 | 127 | $C_{10}H_{22}$ + $C_3$-alkyl benzene isomers |
| 29A | 129 | methylheptanal isomer |
| 30 | 130 | n-octanal |
| 30A | 131 | $C_{10}H_{20}$ + $C_3$-alkyl benzene isomers |
| 31 | 132 | n-decane |
| 31A | 134 | $C_{11}H_{24}$ isomer |
| 31B | 135 | $C_4$-alkyl benzene isomer |
| 32 | 137 | $C_{11}H_{24}$ isomer |
| 33 | 142 | acetophenone |
| 34 | 144 | cresol isomer |
| 34A | 145 | $C_{11}H_{24}$ isomer |
| 34B | 147 | $C_{11}H_{22}$ isomer |
| 35 | 149 | n-nonanal |
| 35A | 150 | $C_{11}H_{22}$ isomer |
| 36 | 151 | n-undecane |
| 37 | 154 | $C_{12}H_{26}$ isomer |
| 37A | 155 | $C_{10}H_{26}$ isomer |
| 38 | 156 | dimethylphenol isomer |
| 38A | 160 | $C_{12}H_{26}$ isomer |
| 39 | 177 | $C_{12}H_{26}$ isomer |
| 40 | 179 | $C_{13}H_{28}$ isomer |
| 40B | 185 | $C_{13}H_{28}$ isomer |
| 40C | 188 | $C_{14}H_{30}$ isomer |

[a]See Table 4.27 for sampling protocol.

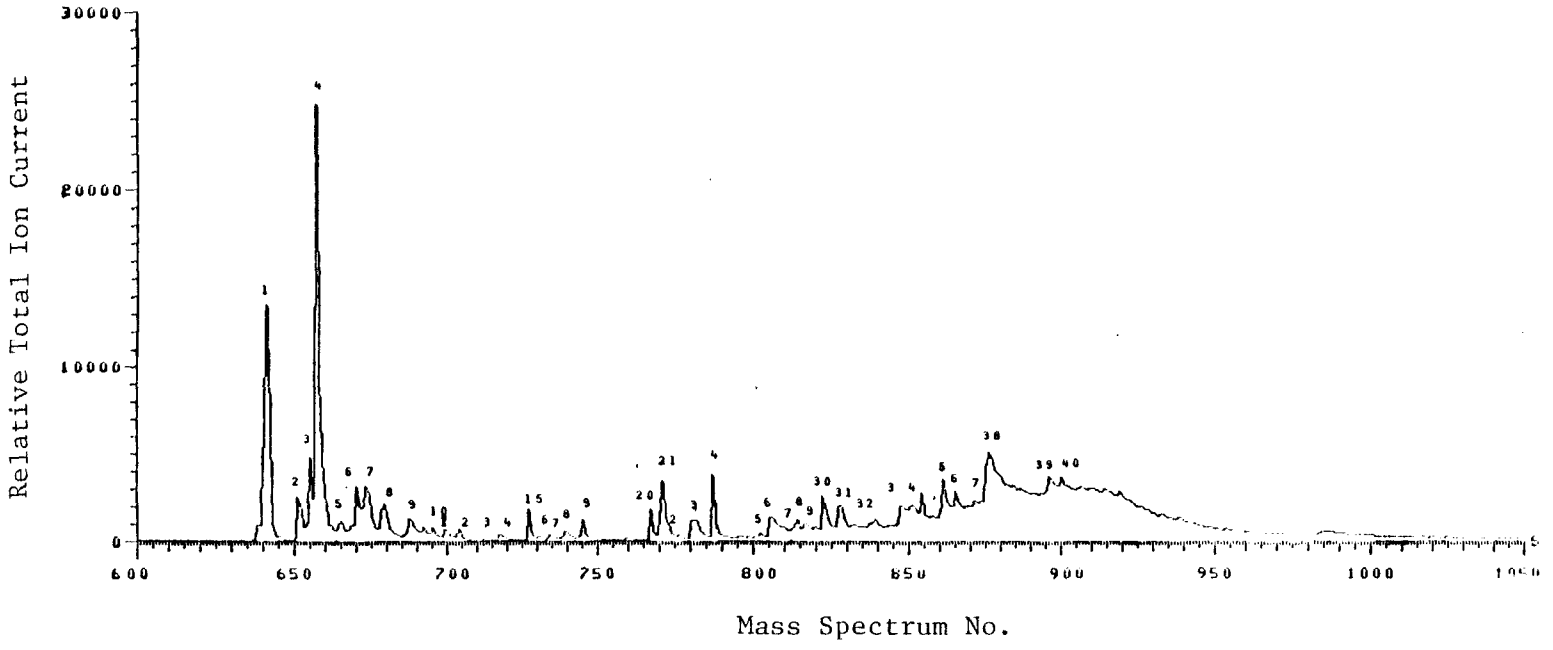



Figure 4.63. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L2).

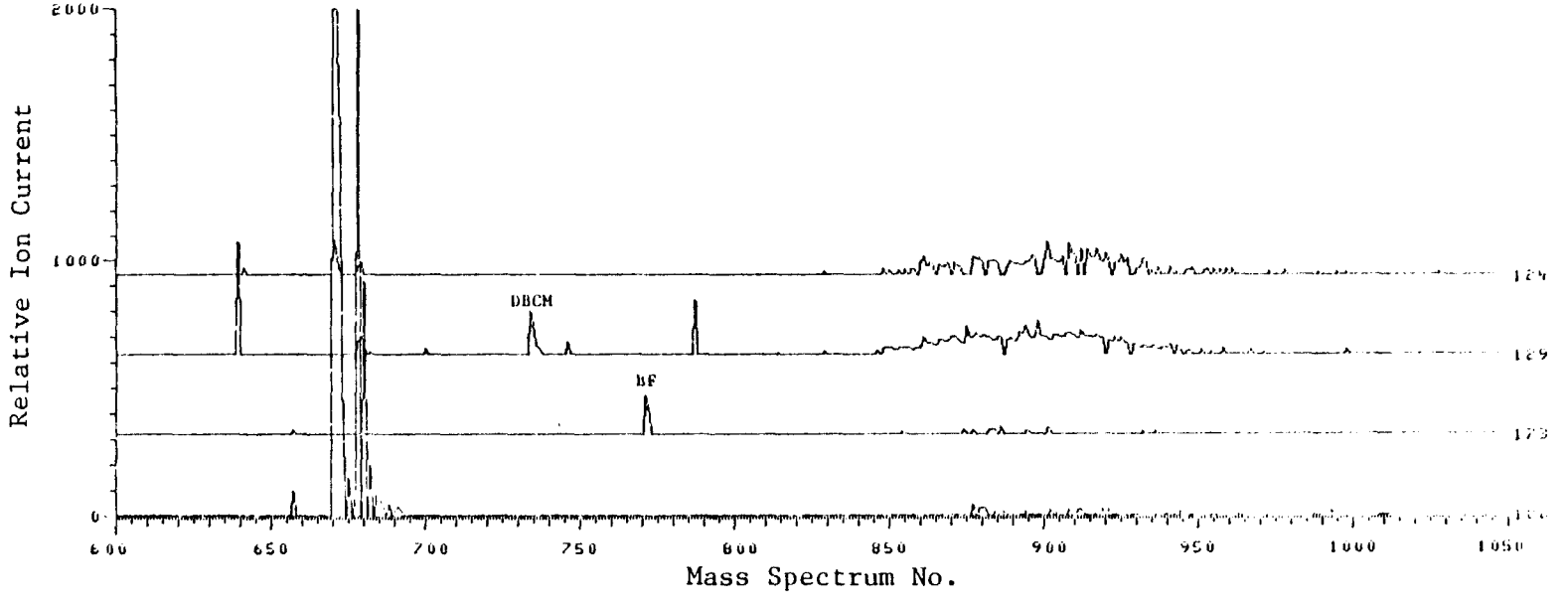



Figure 4.64. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L2). BF = bromoform, DBCM = dibromochloromethane.

Table 4.39. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L3)[a]

| Chromatographic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|
| 1 | 39 | $CO_2$ |
| 1A | 41 | dichlorodifluoromethane |
| 1B | 43 | 1-butene + n-butane |
| 2 | 43 | acetaldehyde |
| 2A | 44 | bromomethane |
| 3 | 46 | trichlorofluoromethane |
| 4 | 47 | $C_5H_{10}$ isomer |
| 4A | 47 | propanal + propenal + furan |
| 5 | 48 | acetone |
| 5A | 48 | $C_5H_8$ isomer |
| 5B | 49 | dichloromethane |
| 6 | 50 | freon 113 (BKG) |
| 6A | 52 | n-pentane |
| 6B | 53 | 2-butenal |
| 7 | 54 | 2-methylpentane |
| 7A | 55 | 2-methylpropenal |
| 8 | 56 | n-butanal + 3-methylpentane |
| 9 | 57 | hexafluorobenzene (ES) |
| 10 | 58 | n-hexane |
| 11 | 59 | chloroform |
| 11A | 61 | methyl ethyl ketone |
| 12 | 62 | perfluorotoluene (ES) |
| 14 | 66 | benzene |
| 14A | 66 | carbon tetrachloride |
| 14B | 67 | cyclohexane |
| 15 | 68 | 2-methylhexane |
| 15A | 69 | 2,3-dimethylpentane |
| 16 | 70 | 3-methylhexane |
| 16A | 70 | $C_6H_8$ isomer |
| 17 | 71 | 3-methylbutanal |
| 17A | 73 | n-pentanal |
| 18 | 74 | n-heptane |
| 18A | 75 | $C_7H_{14}$ isomer |
| 18B | 75 | $C_7H_{14}$ isomer |
| 19 | 81 | $C_6H_{12}O$ isomer |
| 20 | 86 | toluene |
| 21 | 88 | $C_8H_{18}$ isomer + chlorobromopropene isomer (tent.) |
| 22 | 89 | $C_8H_{18}$ isomer |
| 22A | 91 | 2-methylpentanal |
| 22B | 91 | $C_8H_{16}$ isomer |
| 23 | 92 | n-hexanal |
| 23A | 92 | dibromoethane |
| 23B | 93 | $C_8H_{18}$ isomer |
| 23C | 93 | $C_8H_{16}$ isomer |
| 24 | 94 | n-octane |
| 25 | 95 | tetrachloroethylene |
| 25A | 98 | $C_9H_{20}$ isomer |
| 25B | 99 | $C_8H_{16}$ isomer |
| 25C | 99 | $C_9H_{20}$ isomer |
| 26 | 104 | ethylbenzene |
| 27 | 106 | p-xylene |
| 27A | 107 | $C_9H_{20}$ isomer |
| 28 | 108 | $C_9H_{20}$ isomer |
| 28A | 109 | 2-heptanone |
| 29 | 110 | styrene |
| 30 | 111 | o-xylene + n-heptanal |
| 30A | 112 | $C_9H_{18}$ isomer |
| 31 | 114 | n-nonane |
| 31A | 116 | $C_9H_{18}$ isomer |
| 31B | 118 | isopropylbenzene |
| 31C | 119 | $C_{10}H_{22}$ isomer |
| 31D | 120 | $C_{10}H_{22}$ isomer |
| 32 | 121 | propylcyclohexane |
| 32A | 122 | $C_{10}H_{16}$ isomer |
| 33 | 123 | benzaldehyde + $C_{10}H_{22}$ isomer |
| 33A | 124 | n-propylbenzene |
| 34 | 125 | p-ethyltoluene |
| 35 | 126 | $C_{10}H_{22}$ isomer |
| 36 | 127 | $C_{11}H_{24}$ isomer |
| 37 | 128 | $C_{10}H_{22}$ isomer |
| 37A | 129 | $C_{10}H_{22}$ isomer |
| 37B | 130 | $C_{10}H_{20}$ isomer |
| 38 | 131 | octanal |
| 38A | 131 | o-ethyltoluene |
| 38B | 132 | $C_{10}H_{20}$ isomer |
| 39 | 133 | n-decane |
| 39A | 135 | $C_{10}H_{20}$ isomer |
| 40 | 136 | 1,2,3-trimethylbenzene |
| 40A | 136 | $C_4$-alkyl benzene isomer |
| 40B | 137 | $C_{11}H_{24}$ isomer |
| 40C | 137 | $C_{10}H_{20}$ isomer |
| 41 | 138 | $C_{11}H_{24}$ isomer |
| 41A | 139 | $C_{10}H_{20}$ isomer |
| 41B | 140 | $C_{11}H_{24}$ isomer |
| 41C | 141 | $C_4$-alkyl benzene isomer |
| 41D | 141 | $C_{11}H_{24}$ isomer |

(continued)

Table 4.39 (cont'd)

| Chromato-graphic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|
| 41E | 142 | $C_2$-alkyl benzene isomer |
| 42 | 143 | $C_{11}H_{24}$ + 1,1-dibromo-2-chloropropane |
| 43 | 145 | $C_{11}H_{24}$ isomer |
| 44 | 149 | $C_{11}H_{22}$ isomer |
| 45 | 151 | n-undecane |
| 45A | 152 | $C_{12}H_{26}$ isomer |
| 46 | 212 | unknown |
| 47 | 217 | unknown |

[a]See Table 4.28 for sampling protocol.

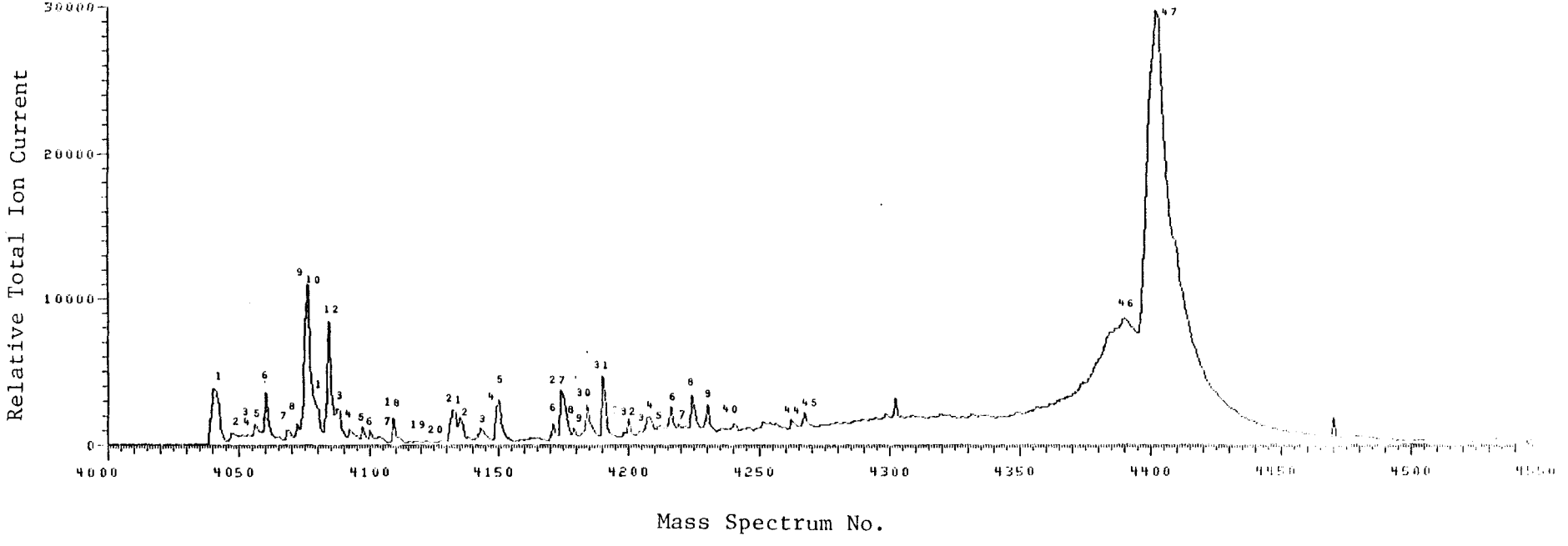



Figure 4.65. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L3).

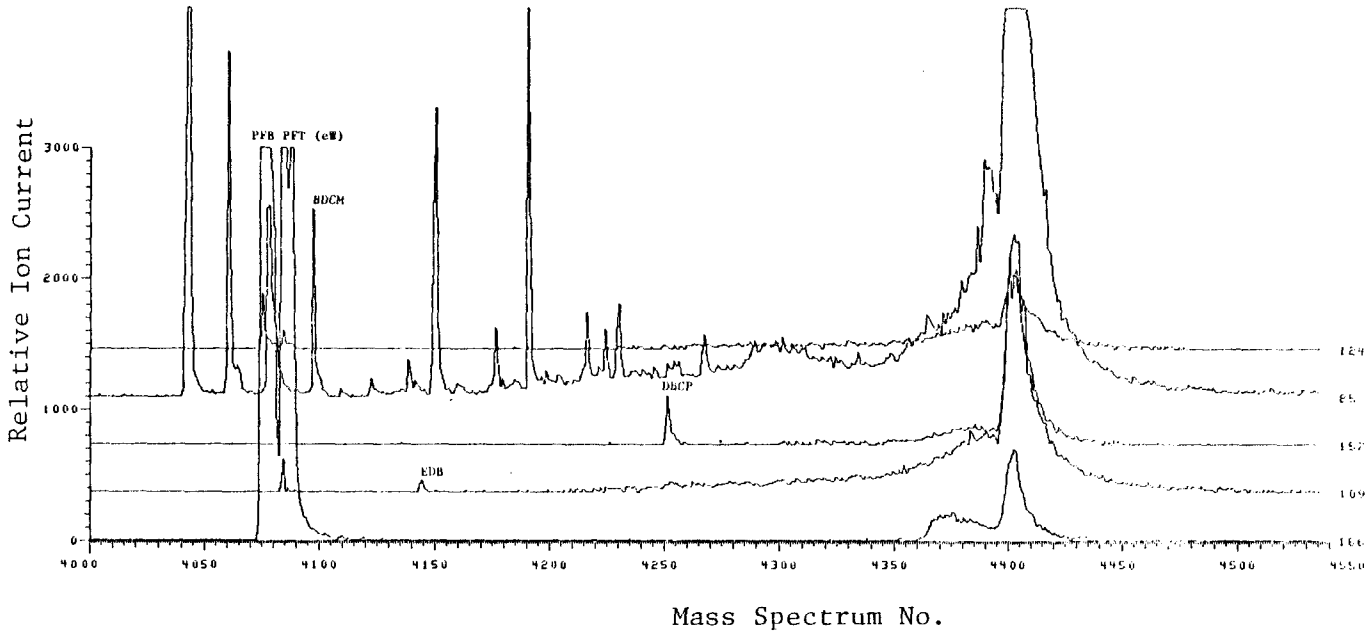



Figure 4.66. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L3). BDCM = bromodichloromethane, EDB = ethylene dibromide, DBCP = 1,1-dibromo-2-chloropropane.

Table 4.40. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L4)[a]

| Chromatographic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|
| 1 | 39 | $CO_2$ |
| 3 | 41 | dichlorodifluoromethane |
| 4 | 42 | 1-butene |
| 4A | 43 | bromoethane (tent.) |
| 5 | 44 | acetaldehyde |
| 5A | 45 | isopentane |
| 6 | 46 | trichlorofluoromethane |
| 6A | 46 | propenal + propanal + furan |
| 7 | 47 | n-pentane + $C_5H_8$ isomer |
| 7A | 47 | acetone |
| 8 | 49 | dichloromethane + freon 113 (BKG) |
| 8A | 51 | 2-methylpropenal |
| 9 | 53 | 2-methylpentane |
| 9A | 54 | 2-methylpropenal |
| 10 | 55 | 3-methylpentane |
| 10A | 55 | n-butanal |
| 11 | 56 | hexafluorobenzene (es) |
| 11A | 57 | n-hexane |
| 11B | 58 | chloroform |
| 11C | 59 | methyl ethyl ketone |
| 11D | 59 | bromopropane isomer (tent.) |
| 12 | 60 | perfluorotoluene (es) |
| 12A | 61 | methylcyclopentane |
| 13 | 62 | 1,1,1-trichloroethane |
| 13A | 62 | allyl bromie |
| 14 | 64 | benzene |
| 14A | 65 | carbon tetrachloride |
| 14B | 65 | cyclohexane |
| 15 | 66 | 2-methylhexane |
| 15A | 67 | 2,3-dimethylpentane |
| 16 | 67 | 3-methylhexane |
| 17 | 69 | n-pentanal |
| 18 | 72 | n-heptane |
| 20 | 77 | methylcyclohexane |
| 21 | 79 | 4-methyl-2-pentanone |
| 22 | 84 | toluene |
| 23 | 85 | chlorobromopropene isomer (tent.) + $C_8H_{18}$ isomer |
| 24 | 87 | 3-methylheptane |
| 24A | 88 | $C_8H_{16}$ isomer |
| 25 | 89 | 2-methylpentanal + diisobutylene |
| 26 | 90 | n-hexanal |
| 26A | 90 | dibromoethane isomer |
| 26B | 92 | $C_8H_{16}$ isomer |
| 27 | 93 | n-octane |
| 28 | 94 | tetrachloroethylene |
| 29 | 100 | $C_9H_{20}$ isomer |
| 29A | 100 | ethylcyclohexane |
| 29B | 101 | dibromopropane isomer |
| 30 | 102 | 1-chloro-3-bromopropane |
| 31 | 104 | ethylbenzene |
| 31A | 105 | $C_{10}H_{22}$ isomer |
| 32 | 106 | p-xylene |
| 33 | 107 | $C_9H_{20}$ isomer |
| 34 | 108 | $C_9H_{20}$ isomer |
| 35 | 110 | styrene + 2,4-dimethylpentanal |
| 36 | 111 | o-xylene |
| 36A | 111 | n-heptaldehyde |
| 36B | 112 | $C_9H_{18}$ isomer |
| 37 | 114 | n-nonane |
| 37A | 116 | $C_9H_{18}$ isomer |
| 37B | 117 | isopropylbenzene |
| 38 | 118 | $C_{10}H_{22}$ isomer |
| 39 | 119 | $C_{10}H_{22}$ isomer |
| 40 | 120 | propylcyclohexane |
| 41 | 121 | $C_{10}H_{22}$ + $C_{10}H_{16}$ isomers |
| 42 | 123 | benzaldehyde |
| 42A | 123 | n-propylbenzene |
| 43 | 125 | p-ethyltoluene |
| 43A | 126 | $C_{10}H_{22}$ isomer |
| 44 | 127 | $C_{10}H_{22}$ isomer |
| 45 | 128 | $C_3$-alkyl benzene isomer |
| 46 | 130 | dimethylhexanal or $C_8H_{16}O$ isomer |
| 47 | 131 | n-octanal |
| 47A | 132 | $C_3$-alkyl benzene isomer |
| 47B | 133 | $C_3$-alkyl benzene isomer |
| 47C | 133 | $C_{10}H_{20}$ isomer |
| 48 | 134 | n-decane |
| 49 | 136 | $C_{10}H_{16}$ isomer |
| 50 | 137 | $C_4$-alkyl benzne isomer |
| 50A | 139 | $C_{11}H_{24}$ isomer |
| 51 | 140 | $C_{11}H_{24}$ isomer |
| 52 | 141 | $C_{11}H_{22}$ isomer |
| 53 | 142 | $C_4$-alkyl benzene isomer |
| 54 | 144 | $C_4$-alkyl benzene isomer |
| 55 | 145 | 1-chloro-2,3-dibromopropane |
| 56 | 147 | $C_4$-alkyl benzene isomer |
| 57 | 149 | $C_9$-alkyl aldehyde isomer |
| 58 | 150 | n-nonanal |

(continued)

Table 4.40 (cont'd)

| Chromatographic Peak No. | Elution Temp. (°C) | Compound | Chromatographic Peak No. | Elution Temp. (°C) | Compound |
|---|---|---|---|---|---|
| 58A | 152 | $C_{11}H_{22}$ isomer | 62 | 167 | $C_{12}H_{24}$ isomer |
| 59 | 153 | n-undecane | 62A | 169 | $C_{12}H_{26}$ isomer |
| 61 | 163 | dimethylphenol isomer | | | |

[a]See Table 4.28 for sampling protocol.

identified bromomethane, bromopropane, allyl bromide, chlorobromopropene, 1,2-dibromoethane, a dibromopropane isomer, 1-chloro-3-bromopropane and 1-chloro-2,3-dibromopropane. In all of the samples which contained bromopropane, we were unable to determine whether it was a 1- or 2-bromopropane (identical mass spectra) since the authentic material was not available to us for establishing the chromatographic retention time.

Table 4.41 summarizes the halogenated hydrocarbons which were identified by GLC/MS/COMP in ambient air surrounding the Michigan Chemical Corp. plant site.

Table 4.41. HALOGENATED HYDROCARBONS IDENTIFIED BY GC-MS-COMP IN AMBIENT AIR AT MICHIGAN CHEMICAL CORPORATION, EL DORADO, ARKANSAS

| Compound | Compound |
|---|---|
| Allyl Bromide | 1-Chloro-3-bromopropane |
| Bromobenzene | 1-Chloro-2,3-dibromopropane |
| Bromodichloromethane | Dibromochloromethane |
| Bromoform | 1,1-Dibromo-2-Chloropropane |
| 1- or 2-Bromopropane | 1,2-Dibromomethane |
| Bromopropene | Dibromopropane |
| Chlorobromopropene | Methyl Bromide |
| | Methyl Chloride |

Quantification of Halogenated Hydrocarbons.--Table 4.42 lists the halogenated hydrocarbons which were identified and quantitated in ambient air surrounding the Michigan Chemical Corp. site. In this case, the concentrations were generally in the ng/$m^3$ range. The highest detected was chlorobromopropene at L5 where a personal sampler was placed at an elevation of 15 feet from ground level. This location was between two buildings which provided a wind corridor coming directly from the organic synthesis facilities. The sampler was approximately 100 meters from that facility. At L4, another

Table 4.42. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP., EL DORADO, AK

| Period/Cycle/Location[a] | Allyl bromide | Bromobenzene | Bromodichloromethane | Bromoform | 1- or 2-Bromopropane | Chlorobromopropane | 1-Chloro-2,3-Dibromo-propane | 1-Chloro-3-bromopropane | 1-Chloro-2,3-Dibromopro-pane or 1,1-Dibromo-2-chloropropane | Dibromochloromethane | 1,1-Dibromo-2-chloro-propane | 1,2- or 1,3-Dibromo-propane | Ethylene dibromide | Methyl bromide |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1/C1/L1 | -[b] | - | - | - | - | - | - | - | - | - | - | - | - | - |
| L2 | - | - | 6.4 | 26.4 | T[c] | - | - | - | - | 7.2 | - | - | - | - |
| L3 | - | - | 5.2 | - | 47.2 | - | - | - | - | - | 2.6 | - | 1.7 | - |
| L4 | T | - | - | - | T | T | - | 2.0 | 17 | - | - | 1.1 | 34 | T |
| P1/C2/L2 | 3.2 | - | - | T | 20.8 | - | - | T | 5.4 | - | - | - | - | - |
| L4 | - | - | - | - | 24.8 | - | - | - | 6.5 | 39.8 | - | - | - | - |
| L4 (ELV) | 32.9 | - | - | - | 35 | 4 | 20.6 | 63 | - | - | - | - | T | T |
| L5 (ELV) | - | 28 | - | 4.0 | T | 83 | - | - | - | - | - | - | - | - |

[a]See Table 4.28 for sampling protocol, values are in $ng/m^3$.

[b]- = not detected.

[c]T = trace detected.

DuPont personal sampler was approximately 10 feet from ground level, whereas the remaining samplers were approximately 4 feet above ground.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--None of these chemicals were detected in ambient air by GC/ECD or mass fragmentography. The LOD of methyl chloride and methyl bromide was 200 and 120 $\mu g/m^3$ by GC/ECD.

Ethylene.--The levels of ethylene determined at the Michigan Chemical Corp. site are given in Table 4.43. The observed concentrations were generally regarded as background quantities.

Table 4.43. ETHYLENE LEVELS IN AMBIENT AIR

| Site[a] | Period/Cycle/Location | ppm |
|---|---|---|
| MCI | P1/C4/L1 | 0.85 ± 0.15 |
| | P1/C4/L2 | 0.85 ± 0.05 |
| | P1/C4/L3 | 0.80 ± 0 |
| | P1/C4/L4 | 0.75 ± 0.05 |
| | P1/C4/L5 | 0.85 ± 0.05 |
| | P1/C4/L6 | 0.85 ± 0.05 |

[a]See Table 4.28 and Figure 4.45 for sampling protocol and locations.

4.2.3.6 Brominated Organics in Soil and Water

The soil and water samples were screened for EDB and other volatile brominated organics by the VOA method. None were found in any of these samples. The soil sample P1/C1/L1 was extracted and analyzed for semi-volatile brominated organics by direct probe high resolution mass spectrometry and GC/MS/COMP. The results are given in Table 4.44.

Table 4.44. ANALYSIS OF A SOIL SAMPLE FROM THE VICINITY OF MICHIGAN CHEMICAL CORPORATION

| Period/Cycle/Location | Decabrom (μg/kg) | Tetrabrom (μg/kg) |
|---|---|---|
| P1/C1/L1 | ND[a] | 1,100[a] |

[a]Quantitation by GC/MS/COMP-MID.

4.2.4 Ethyl Corporation

4.2.4.1 Sampling

The sampling protocol and sample descriptions for Ethyl Corp. are given in Table 4.45. The corresponding Figure 4.67 designates the sampling locations for September 23, 1976. Table 4.46 and Figure 4.68 present the protocol and locations for May 17, 1977.

4.2.4.2 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by the turbidimetric determination of a total halide are given in Table 4.47. The site, period and cycle designation were given in the sampling protocols (Table 4.45) and the locations on schematic map (Fig. 4.67). No detectable halogens and halides were observed in samples of ambient air surrounding Ethyl Corp.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples. The limit of detection was less than 2.7 $\mu g/m^3$ based on the volume of air sampled and the sensitivity of the ion selective electrode.

Acid Mist.--No titratable acid was found in any samples. The upper limit of ambient air concentration of acid mist was 41 $\mu g/m^3$ when standardized as $H_2SO_4$.

4.2.4.3 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Sampling locations 2 and 3 were 200-250 yards from the bromine extraction and organic synthesis facilities. Location 1 represented an upwind sample near a large storage tank area (see Fig. 4.67 for sampling locations). Figure 4.69 depicts the total ion current profile of the volatile organic pollutants collected at L2 on the Ethyl Corp. site. The large peak (No. 19) was identified as toluene

Table 4.45. SAMPLING PROTOCOL FOR ETHYL CORPORATION, HIGHWAY 79, MAGNOLIA, ARKANSAS

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | T (°C) | % RH | Wind Dir./ Speed (kmph) | Other |
| 9/23/76 | C1 | L1 | 1427-1726 | 143 | HHC[a] | 24-30 | 40-70 | 180/4-calm | Clear |
| P1 | | L2 | 1427-1726 | 140 | HHC[a] | | | | |
| | | L3 | 1422-1726 | 197 | HHC[a] | | | 8-13 | Clear, slight $Br_2$ + $H_2S$ odor |
| | C2 | L4 | 1355-1903 | | HHC[b] | | | | |
| | C3 | L1 | 1729-1830 | 50.9 | F, CBN, CBD | | | | |
| | | L2 | 1729-1830 | 28.3 | F, CBN, CBD | | | | |
| | | L3 | 1729-1830 | 70.8 | F, CBN, CBD | | | | Clear |
| | C4 | L1 | 1835-1944 | 11 | AM | | | | |
| | | L2 | 1834-1944 | 115 | AM | | | | |
| | | L3 | 1832-1944 | 115 | AM | | | | |
| | | L4 | 1508 | 1 | TED | | | | |
| | | L5 | 1502 | 1 | TED | | | | |
| | | L6 | 1512 | 1 | TED | | | | |
| | | L7 | 1517 | 1 | TED | | | | |
| | | L5 | 1502 | 0.28 | VAC | | | | |

[a]Nutech Model 220 sampler 3-6 ft elevation.

[b]DuPont sampler 3-6 ft elevation.

Locations shown in Figure 10.

Key to Sample Type:
HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can

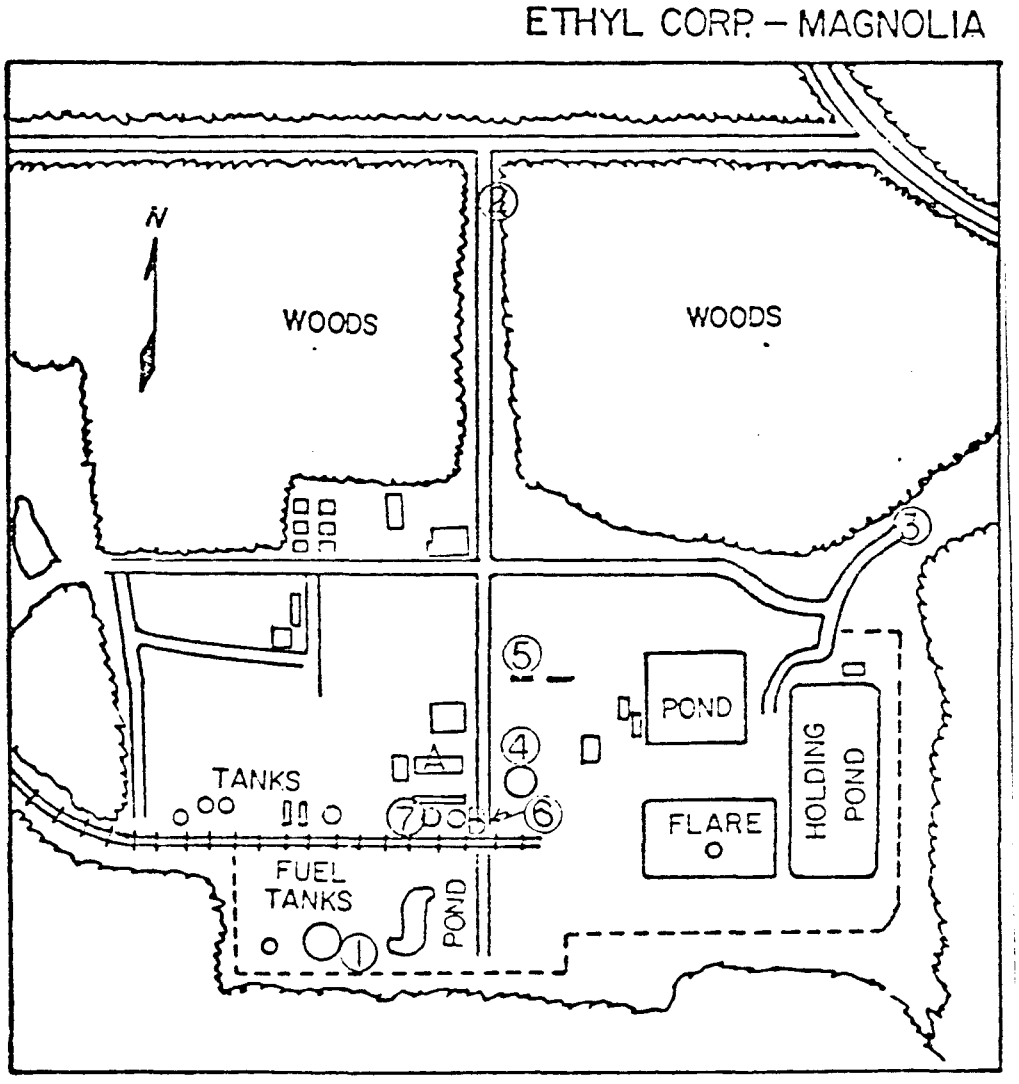



Figure 4.67. Schematic map of Ethyl Corporation, Magnolia - sampling locations for P1 - 9/23/76.

A - EDB and $Br_2$ facilities

B = EDB facilities

Table 4.46. SAMPLING PROTOCOL FOR ETHYL CORPORATION, MAGNOLIA, ARKANSAS

| Period | Cycle | Location | Sample Size | Type of Sample |
|---|---|---|---|---|
| P1 | C1 | L1 | 2 core[a] | SHHC-V |
| 5/17/77 | | L1 | 2 core | SHHC-SV |
| | | L2 | | VHHC-V/SV[b] |
| | | L3 | | VHHC-V/SV[d] |
| | | L4 | 1 ℓ | WHHC-V/SV[c] |
| | | L5 | 1 ℓ | WHHC-V/SV[e] |
| | | L5 | | VHHC-V/SV[f] |
| | | L6 | 2 core | SHHC-V |
| | | L6 | 2 core | SHHC-SV |
| | | L6 | 1 ℓ | WHHC-V/SV[e] |
| | | L7 | 2 core | SHHC-V |
| | | L7 | 2 core | SHHC-SV |

[a]Core ∿5 cm diameter, 13 cm depth.

[b]Needles stripped from 40 cm of pine bough sampled at ∿5 m above ground from trees showing damage.

[c]Wide, slow moving portion of stream.

[d]Blackberries.

[e]Well water.

[f]Peaches.

Key to sample type: SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

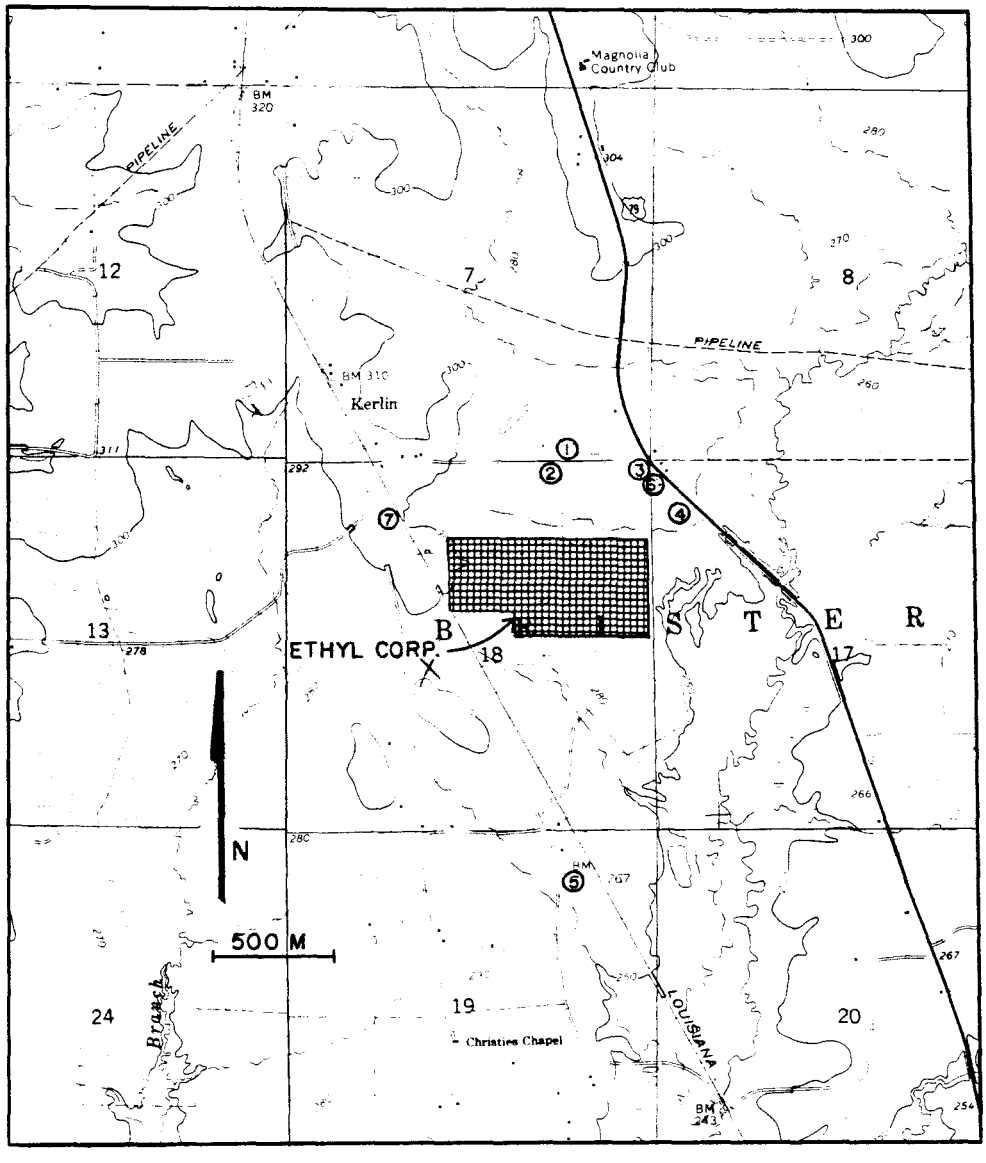



Figure 4.68. Map of area in vicinity of Ethyl Corporation, Magnolia, Arkansas - sampling locations for water, soil, sediment, and vegetation for P1 - 5/17/77.

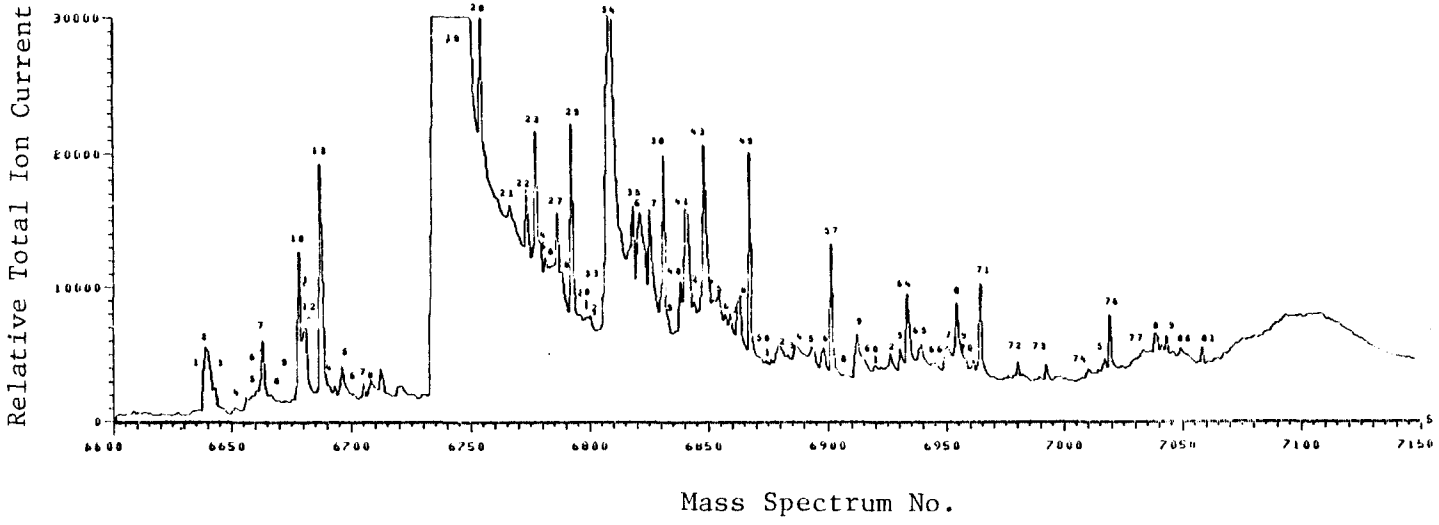



Figure 4.69. Total ion current profile of volatile ambient air pollutants from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2).

Table 4.47. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING ETHYL CORP.[a,b]

| Species | Location L3 |
|---|---|
| $Cl_2/Br_2$[c] | <70 |
| $Br_2$[d] | <29 |
| $Cl^-/Br^-$[c] | <44 |
| $Br^-$[d] | <14 |

[a]Samples are from P1/C3.

[b]Values are in $\mu g/m^3$.

[c]By turbidity.

[d]By neutron activation analysis.

and the large concentration probably occurred because a diesel powered tank trailer passed by the sampling location. On the backside of this large peak (Peak No. 20), 1,2-dibromoethane was detected. This is more clearly presented in Figure 4.70 which presents the ion chromatograms for m/e 85, m/e 109, m/e 120 and m/e 124. The peaks corresponding to allyl bromide and 1,2-dibromoethane which were identified in this sample are also noted in this figure.

At L3 (see Fig. 4.67) several halogenated organics were detected. The profile for this location is shown in Figure 4.71 and the ion chromatograms are shown in Figure 4.72. In Figure 4.72 the presence of bromopropane, chlorobromoethane, bromodichloromethane and 1,2-dibromoethane are clearly evident. Table 4.48 summarizes the halogenated hydrocarbons identified by GC/MS/COMP in ambient air samples from Ethyl Corp.

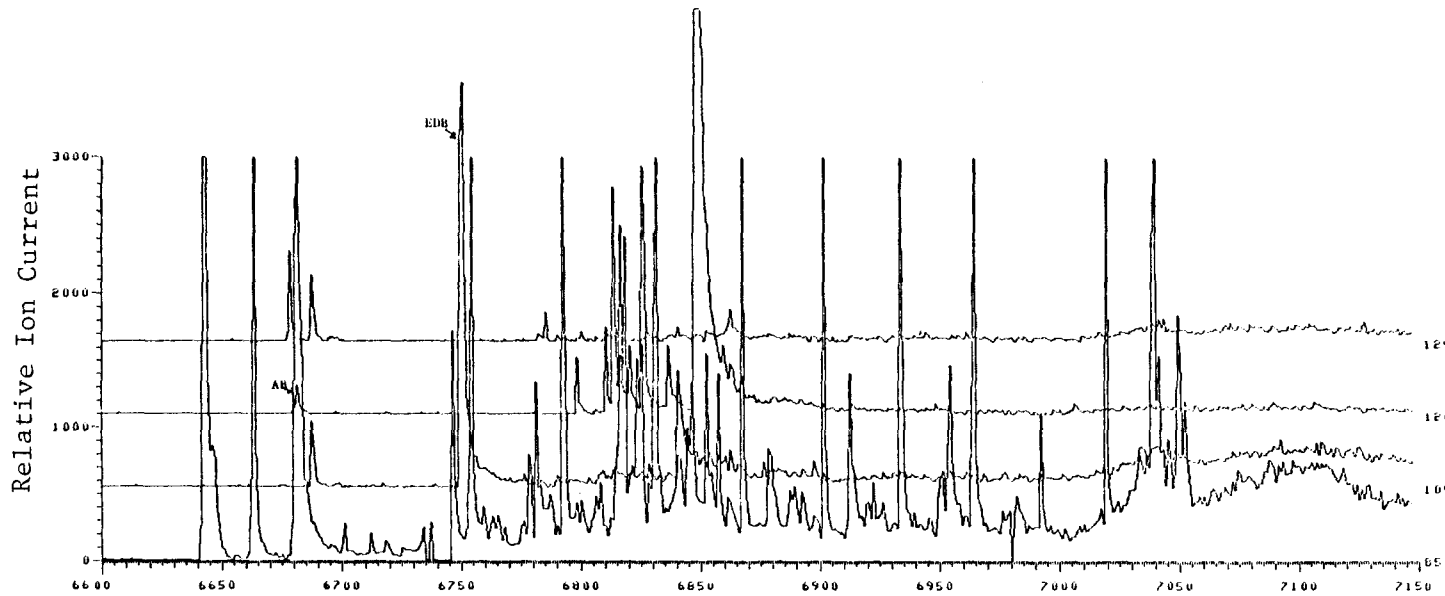



Figure 4.70. Ion chromatograms of ambient air sample from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2). AB = alkyl bromide, EDB = ethylene dibromide.

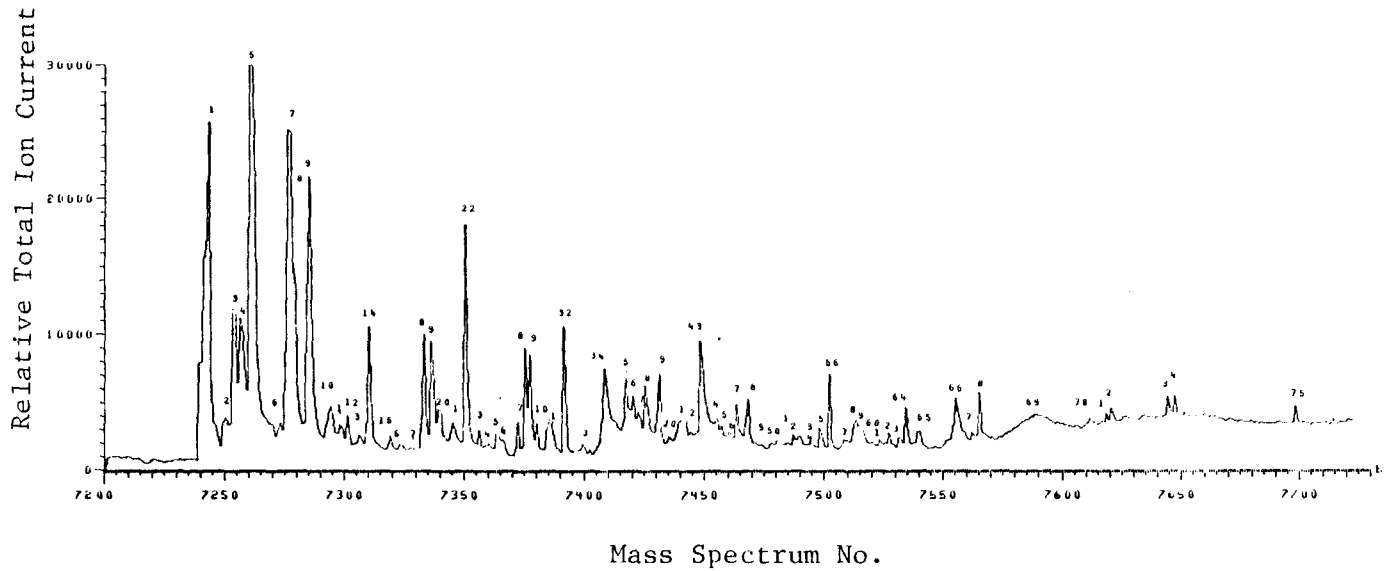



Figure 4.71. Total ion current profile of volatile ambient air pollutants from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L3).

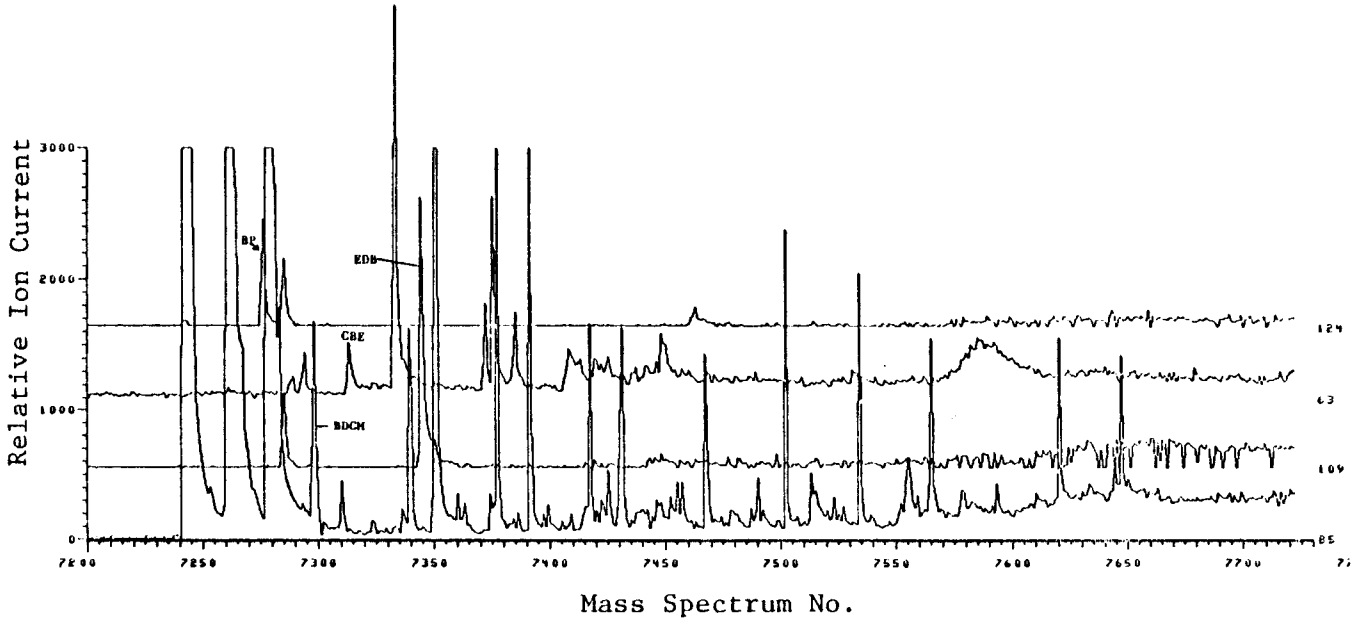



Figure 4.72. Ion chromatograms of ambient air sample from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2). BP = bromopropane, CBE = chlorobromoethane, BDCM = bromodichloromethane and EDB = 1,2-dibromoethane.

Table 4.48. HALOGENATED HYDROCARBONS IDENTIFIED BY GC/MS/COMP IN AMBIENT AIR AT ETHYL CORP., MAGNOLIA, ARKANSAS

| Compound | Compound |
|---|---|
| 1-chloro-2-bromoethane | 1,2-dibromoethane |
| bromopropane | vinyl bromide |
| bromodichloromethane | allyl bromide |

Quantification of Halogenated Hydrocarbons.--The levels of halogenated hydrocarbons in the ambient air samples surrounding Ethyl Corp. are given in Table 4.49. The highest concentration of any halogenated hydrocarbon of all the samples which were collected at all the sites occurred in the sample taken at L4. The sampling location was approximately 20 yards from the 1,2-dibromoethane synthesis facility. The level of 1,2-dibromoethane was 20,215 $ng/m^3$.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride, and Vinyl Bromide.--None of these chemicals were detected by GC/ECD or mass fragmentography.

Ethylene.--The ethylene levels observed are given in Table 4.50. Typical background values were seen.

4.2.4.4 Brominated Organics in Soil, Water and Vegetation

All of the samples described in Table 4.46 were analyzed by the VOA procedure for EDB and other halogenated organics. No EDB was detected in any of the samples nor were any other volatile halogenated organics identified. A soil sample P1/C1/L1 was extracted for semi-volatile organics and submitted to high resolution mass spectral analysis (direct probe) and no halogenated organics were found.

4.2.5 Dow Chemical Co. and Vicinity

During the survey study ambient air monitoring for brominated organics was not conducted at this plant site. However, condensed phase samples were collected and some of these data are presented here.

Table 4.49. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTIFIED IN AMBIENT AIR SURROUNDING ETHYL CORP., MAGNOLIA, AK

| Period/Cycle/Location[a] | Allyl bromide | Bromodichloromethane | 1- or 2-Bromopropane | 1-Chloro-2-bromo-propane | Ethylene dibromide | Methyl bromide |
|---|---|---|---|---|---|---|
| P1/C1/L1 | 9.4 | -[b] | - | - | 227 | ? |
| L2 | 15.8 | 3.4 | 16.2 | - | 174 | - |
| L3 | - | 6.8 | 26.6 | 1.2 | 21.2 | - |
| P1/C2/L4 | - | - | - | - | 20,250 | T[c] |

[a]Refer to Table 4.45 for sampling protocol, values are in $ng/m^3$

[b]- = not detected

[c]T = trace detected

Table 4.50. ETHYLENE LEVELS IN AMBIENT AIR

| Site[a] | Period/Cycle/Location | ppm |
|---|---|---|
| EC | P1/C4/L4 | 0.76 ± 0.06 |
| | P1/C4/L5 | 0.60 ± 0 |
| | P1/C4/L6 | 0.70 ± 0.10 |
| | P1/C4/L7 | 0.73 ± 0.13 |

[a]See Table 4.45 and Figure 4.67 for protocol and locations.

4.2.5.1 Sampling

Samples of soil, water and vegetation were collected in the vicinity of Dow Chemical Co., Magnolia, AK. The sampling protocol is given in Table 4.51 and Figure 4.73.

4.2.5.2 Brominated Organics in Soil, Water and Vegetation

Environmental samples were analyzed by the VOA procedure for the presence of EDB and other volatile halogenated organics. The results are given in Table 4.52.

Table 4.51. SAMPLING PROTOCOL FOR DOW CHEMICAL CO.
MAGNOLIA, ARKANSAS

| Period | Cycle | Location | Sample Size | Type of Sample |
|---|---|---|---|---|
| P1 | C1 | L1 | 2 cores[a] | SHHC-V |
| 5/17/77 | | L1 | 2 cores | SHHC-SV |
| | | L1 | | VHHC-V/SV |
| | | L2 | 1 ℓ | WHHC-V/SV[b] |
| | | L3 | 1 ℓ | WHHC-V/SV[c] |
| | | L4 | 2 cores | SHHC-V |
| | | L4 | 2 cores | SHHC-SV |
| | | L5 | 1 ℓ | WHHC-S/SV[d] |
| | | L5 | | VHHC-S/SV[e] |
| | | L5 | | VHHC-S/SV[f] |
| | | L6 | 2 cores | SHHC-S |
| | | L6 | 2 cores | SHHC-SV |
| | | L7 | 1 ℓ | WHHC-S/SV[b] |

[a] Core ∿5 cm diameter, 13 cm depth.

[b] ∿2 m wide, ∿15 cm deep in dry weather (no rain for 1 week).

[c] Farm ponds.

[d] Lake.

[e] Leaves of pecan tree.

[f] Potatoes.

Key to sample type: SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

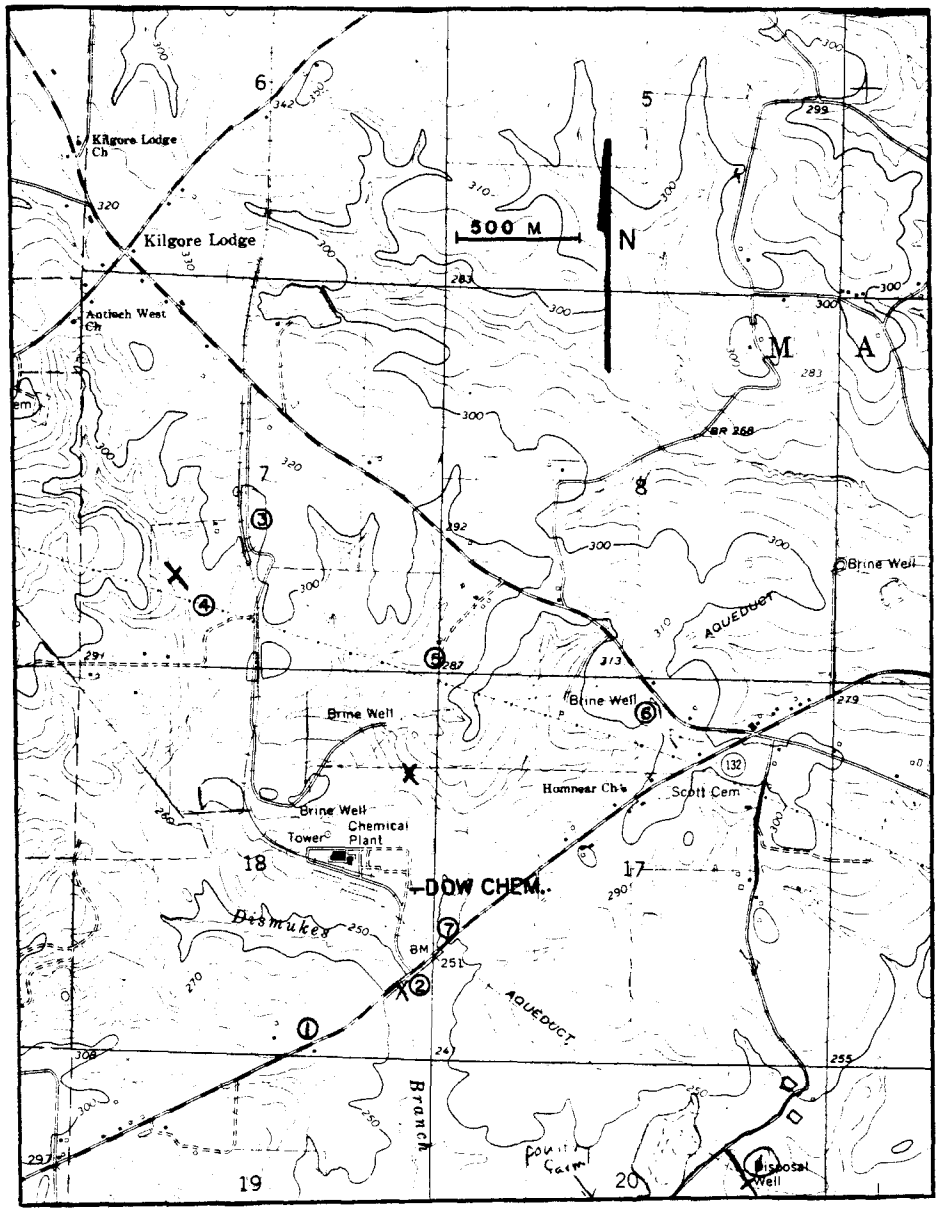



Figure 4.73. Map of area in vicinity of Dow Chemical Company, Magnolia, Arkansas - sampling locations for water, soil, sediment and vegetation for P1 - 5/17/77.

Table 4.52. VOA ANALYSIS OF ENVIRONMENTAL SAMPLES FROM THE VICINITY OF DOW CHEMICAL CO., MAGNOLIA, AK

| Period/Cycle/Location | Sample Type | EDB |
|---|---|---|
| P1/C1/L1 | Soil | ND |
| L2 | Water | ND |
| L3 | Water | ND |
| L4 | Soil | Detected |
| L5 | Vegetation (potatoes) | ND |
| | Vegetation (pecan leaves) | ND |
| | Water | ND |
| L6 | Soil | ND |

## 5.0 LONG-TERM MONITORING FOR VOLATILE BROMINATED ORGANICS

Sites were selected in the El Dorado and Magnolia areas to continuously monitor for volatile brominated organics in ambient air. The objective was to determine whether significant levels of brominated organics in ambient air were being transported from the bromine industry to populated areas. Thus the specific aim was to assess potential exposure to volatile brominated organics, specifically, 1,2-dibromoethane.

### 5.1 SAMPLING AND ANALYSIS

Two sites were selected in El Dorado - one on the water tower at Parker's Chapel and the other on a water tower in El Dorado. Figure 5.1 shows the location of these sites with respect to Great Lakes Chemical Corporation and Arkansas Chemical Inc. Three sites were selected in Magnolia and their locations are shown in Figures 5.2-5.4 with respect to the city of Magnolia, Dow Chemical Co. and Ethyl Corporation, respectively.

The sampling and analysis methodology employed in this study is given in Appendix A, Section F.

### 5.2 RESULTS AND DISCUSSION

The sampling protocols for ambient air samples collected in El Dorado are given in Tables 5.1 and 5.2. 1,2-Dibromoethane was detected on three different days at the Parkers Chapel water tower (Table 5.1). On the first day of sampling, a level of 700 $ng/m^3$ was measured and the highest value was found during the 26th sampling period at which time it achieved a level of 1,260 $ng/m^3$. As can be seen in Table 5.1, during these three days of sampling the predominant wind direction was from the general area of the Great Lakes Chemical Corp. Low concentrations of 1-chloro-2-bromoethane, dibromopropane and allyl bromide were found in samples taken on the El Dorado water tower (Table 5.2). In general, these sampling periods represented times when the wind direction was generally from the west to southwest direction.

Tables 5.3-5.5 present the sampling protocols for the air monitoring conducted in Magnolia, AK near Dow Chemical Co. and near Ethyl Corporation,

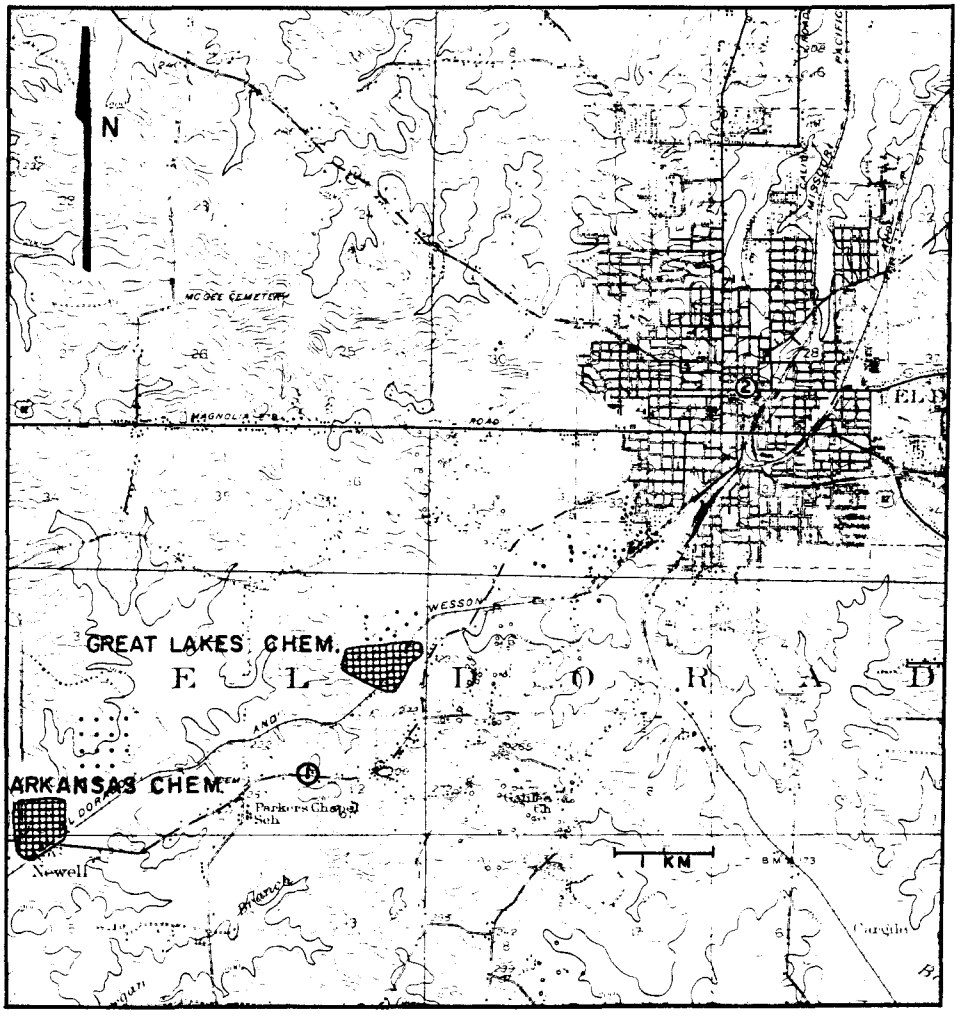



Figure 5.1. Map of El Dorado area - sampling locations for continuous air monitoring.

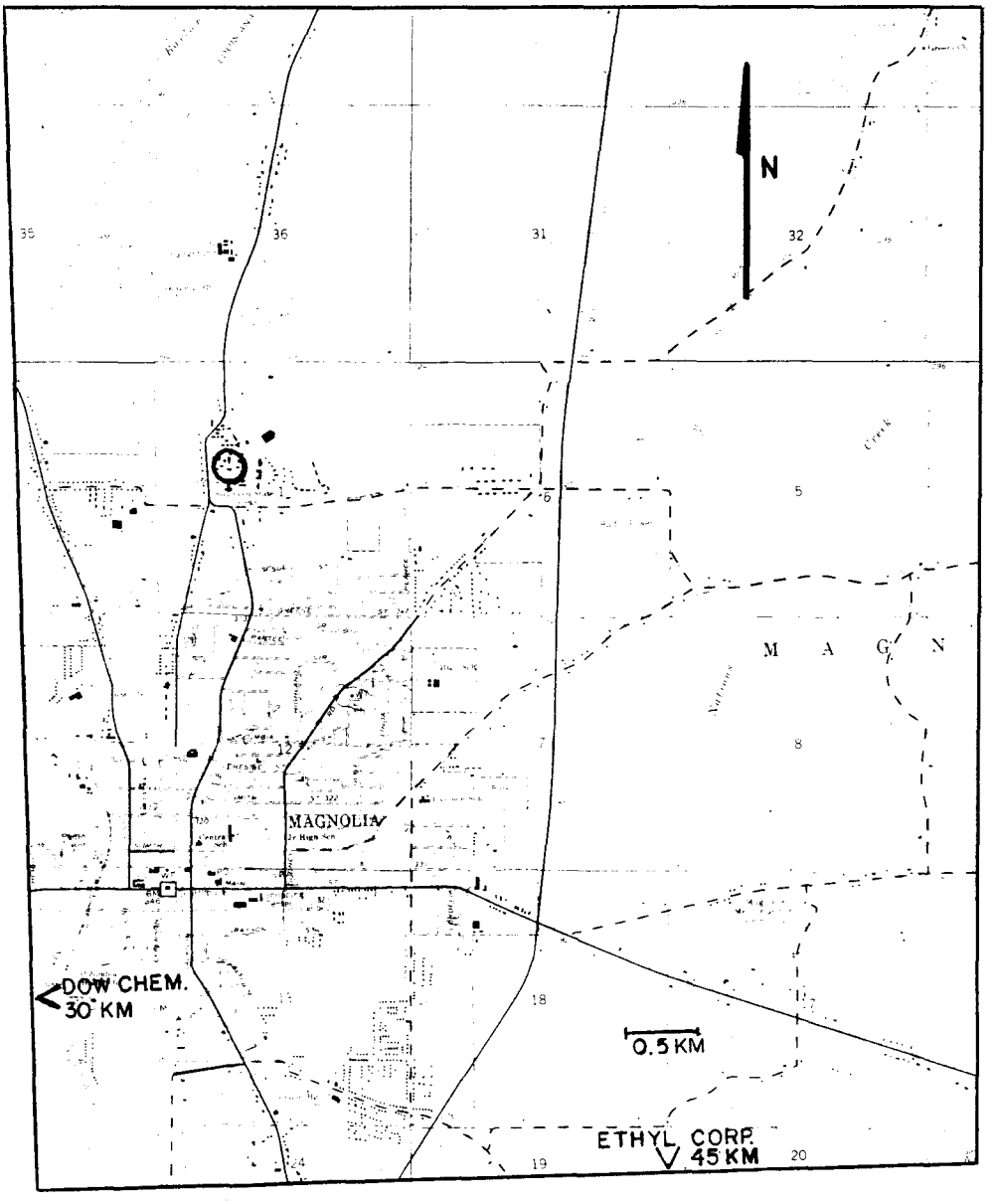



Figure 5.2. Map of Magnolia area - sampling locations for continuous air monitoring.

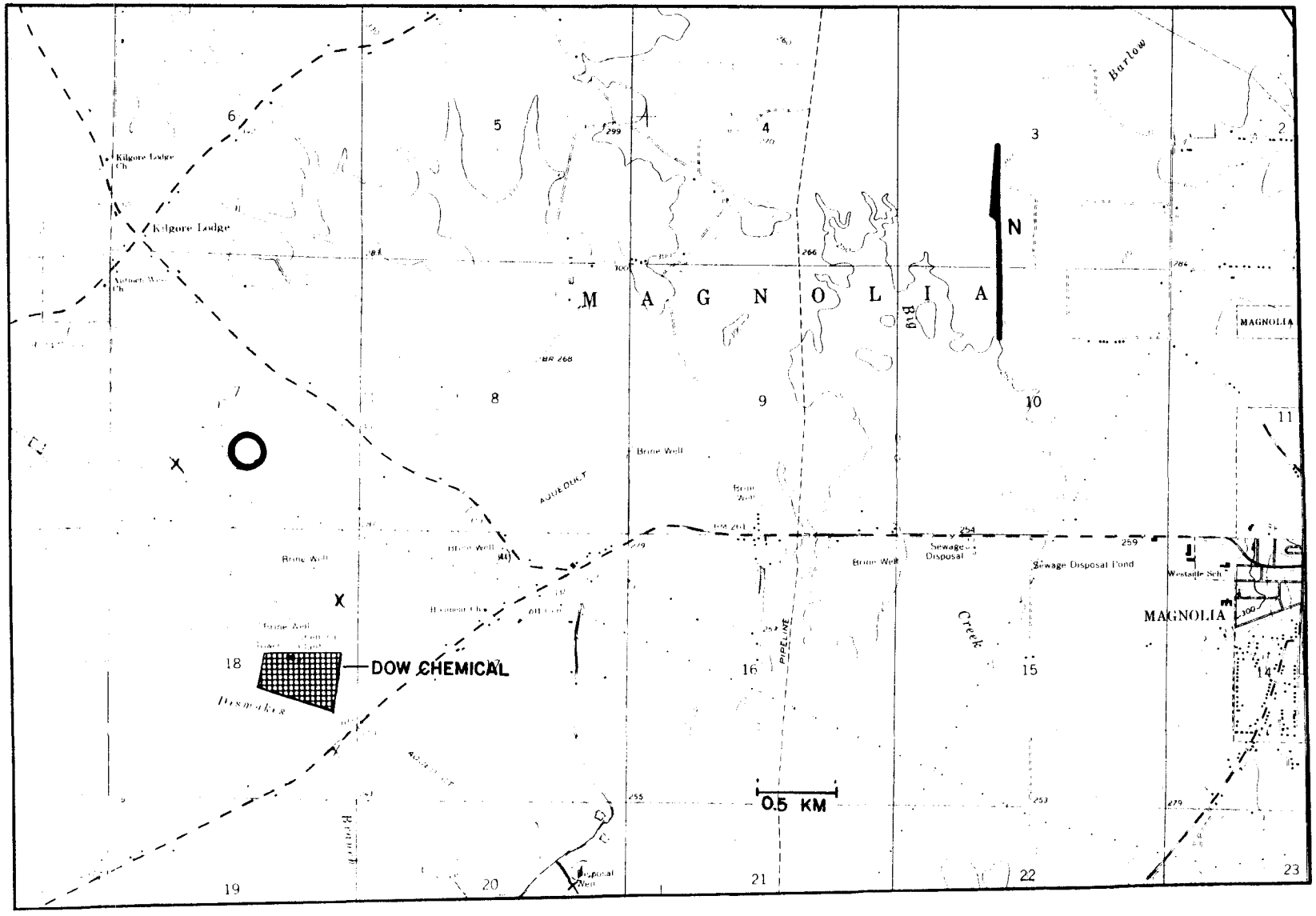



Figure 5.3. Map of area in vicinity of Dow Chemical Company, Magnolia, Arkansas - sampling location for continuous air monitoring.

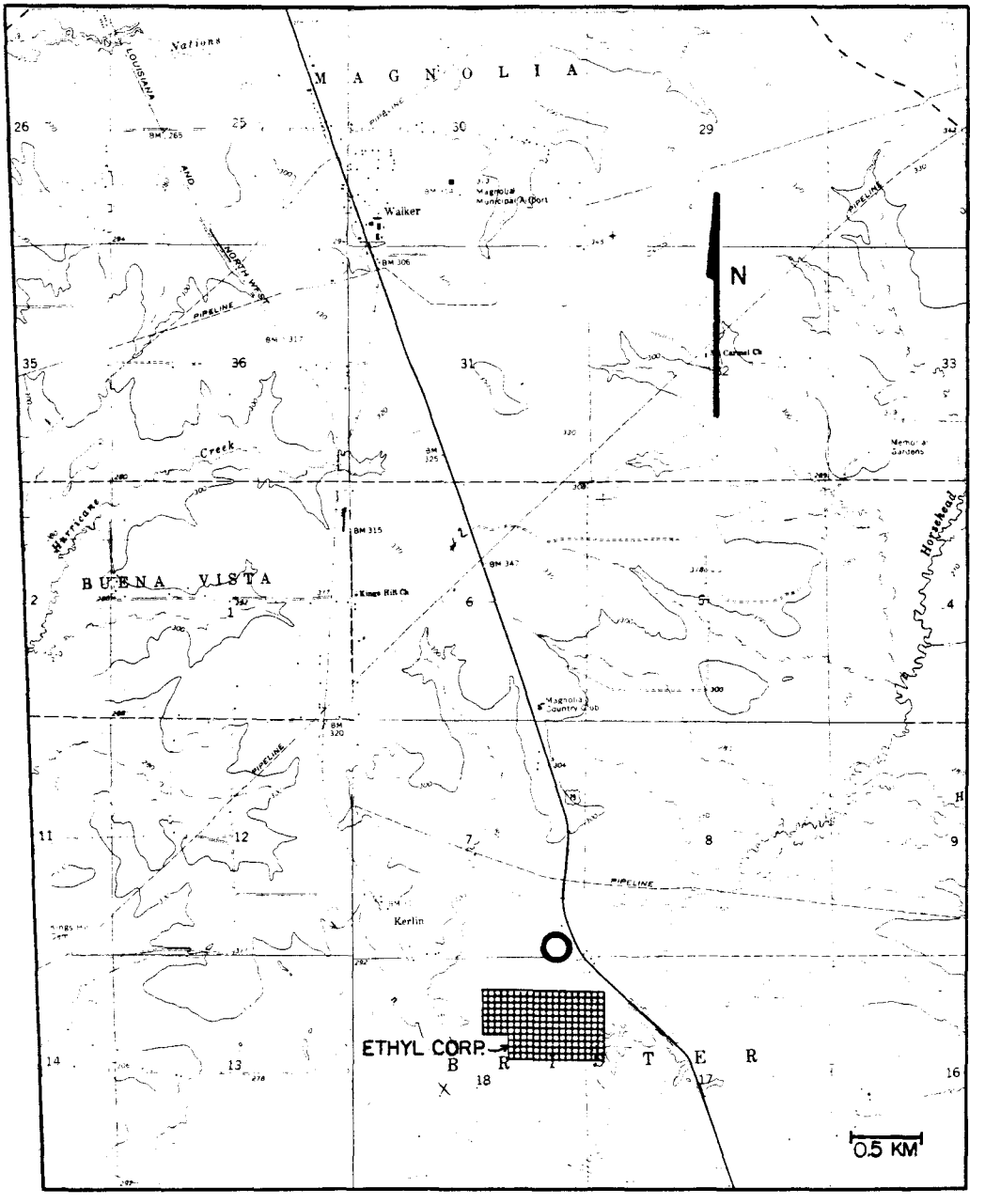



Figure 5.4. Map of area in the vicinity of Ethyl Corporation, Magnolia, Arkansas - sampling location for continuous air monitoring.

Table 5.1. SAMPLING PROTOCOL FOR CONTINUOUS AIR MONITORING IN THE EL DORADO, ARKANSAS VICINITY - LOCATION 1: PARKERS CHAPEL WATER TOWER

| Period | Volatile Brominated Organics $ng/m^3$ | Time/Date | Volume ($m^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind speed (Knts) | Precipitation | |
| P1 | 700[b] | 1425, 3/5/77-1625, 3/6/77 | 0.131 | 17/1° | NE-NW | 0-10 | | |
| P2 | ND | 1635, 3/6/77-1706, 3/7/77 | 0.147 | 20/-2 | NW-SW calm | 0-10 | | |
| P3 | ND | 1706, 3/7/77-1550, 3/8/77 | 0.136 | 23/1 | calm NW, SW | 0-15 | | |
| P4 | ND | 1550, 3/8/77-1725, 3/9/77 | 0.153 | 21/5 | calm, SW,S,SE | 0-15 | | |
| P5 | ND | 1725, 3/9/77-1555, 3/10/77 | 0.134 | 24/4 | SE | 5-10 | | |
| P6 | ND | 1555, 3/10/77 1715, 3/12/77 | 0.152 | 23/12 | SE,W | 10-15 | 2.06 cm | |
| P7 | ND | 1715, 3/11/77-1700, 3/12/77 | 0.142 | 23/10 | SE,SW,W | 5-15 | | Rain, Wind and water damage to to sampler. Various malodors present. |
| P8 | ND | 1700, 3/12/77-1655, 3/13/77 | 0.143 | 27/10 | SW,W | 5-10 | | |
| P9 | ND | 1655, 3/13/77-1718, 3/14/77 | 0.146 | 29/6 | calm S,SW | 0-15 | | Dust storm coming into area. |
| P10 | ND | 1718, 3/14/77 | 0.138 | 30/17 | SW,W | 0-10 | | |

(continued)

Table 5.1 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology: Temp. °C[a] | Meteorology: Wind Dir. | Meteorology: Wind Speed (Knts) | Meteorology: Precipitation | Comments |
|---|---|---|---|---|---|---|---|---|
| P11 | 280[b] | 1615, 3/15/77-<br>1830, 3/17/77 | 0.158 | 30/12 | N,NE | 5-15 | | |
| P12 | ND | 1830, 3/16/77-<br>1600, 3/17/77 | 0.129 | 25/14 | NE,E,SE,S | 5-10 | | |
| P13 | ND | 1600, 3/17/77-<br>1708, 3/18/77 | 0.151 | 26/16 | S,SW,NW | 5-15 | | |
| P14 | ND | 1708, 3/18/77<br>1705, 3/19/77 | 0.144 | 21/14 | NE,E,SE | 0-10 | | |
| P15 | ND | 1705, 3/19/77-<br>1750, 3/20/77 | 0.148 | 20/-1 | calm NW,E<br>SE | 0-10 | | |
| P16 | ND | 1750, 3/20/77-<br>1535, 3/21/77 | 0.130 | 26/9 | calm SE,E,W | 0-15 | | |
| P17 | ND | 1535, 3/21/77-<br>1530, 3/22/77 | 0.144 | 26/1 | NW,NE | 0-10 | | |
| P18 | ND | 1530, 3/22/77-<br>0900, 3/23/77 | 0.105 | 18/1 | calm | - | | Strong odor, not $H_2S$. |
| P19 | ND | 0900, 3/23/77-<br>1555, 3/24/22 | 0.186 | 23/8 | S, Calm | 0-5 | 0.56 cm | |
| P21 | ND | 1635, 3/25/77-<br>1855, 3/26/77 | 0.158 | 25/16 | SE | 5-10 | | |
| P22 | ND | 1855, 3/26/77-<br>1614, 3/27/77 | 0.128 | 25/18 | SE,S | 5-15 | 2.67 cm | |

(continued)

Table 5.1 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P23 | ND | 1614, 3/27/77-<br>1706, 3/28/77 | 0.149 | 27/13 | S,SE<br>S-SW | -20 G | 2.08 cm | |
| P24 | ND | 1706, 3/28/77-<br>1600, 3/29/77 | 0.144 | 24/14 | S,SW,SE | 5-10 | | |
| P25 | ND | 1600, 3/29/77-<br>1850, 3/30/77 | 0.161 | 29/17 | calm S,SW,W | 5-10 | | |
| P26 | 1,260[b] | 1850, 3/30/77-<br>1353, 3/31/77 | 0.114 | 23/17 | NW,N,NE | 5-10 | | |
| P27 | ND | 1353, 3/31/77-<br>1200, 4/1/77 | 0.190 | 23/11 | NE,E | 5-10 | 0.08 cm | |
| P28 | ND | 1200, 4/1/77<br>1515, 4/2/77 | 0.245 | 24/15 | SE,S,SW | 5-10 | 0.79 cm | |
| P29 | ND | 1515, 4/2/77-<br>1655, 4/3/77 | 0.205 | 22/13 | calm SW,S,NE | 0-15 | 1.40 cm | |
| P30 | ND | 1655, 4/3/77- | 0.164 | 18/15 | E,NE, calm W | 0-15<br>(G 22) | 0.56 cm | |
| P31 | ND | 1752, 4/4/77-<br>1615, 4/5/77 | 0.146 | 18/6 | W,NW | 0-15<br>(G 23) | | |

(continued)

Table 5.1 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P32 | ND | 1615, 4/5/77-<br>1825, 4/6/77 | 0.156 | 18/4 | calm NW,W,SW | 0-10 | | |
| P33 | ND | 1825, 4/6/77- | ~0.135 | 29/9 | calm W | 0-14 | | |

[a]High/low

[b]1,2-dibromoethane

Table 5.2. SAMPLING PROTOCOL FOR CONTINUOUS AIR MONITORING IN THE EL DORADO, ARKANSAS VICINITY - LOCATION 2: EL DORADO WATER TOWER

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P1 | 2,520[b] | 1650, 3/5/77-1700, 3/6/77 | 0.145 | 17/1 | NE-NW | 0-10 | | |
| P2 | 4,200[b] | 1700, 3/6/77-1840, 3/7/77 | 0.134 | 20/-2 | NW-SW calm | 0-10 | | |
| P3 | ND | 1840, 3/7/77-1615, 3/8/77 | 0.129 | 23/1 | calm NW,SW | 0-15 | | |
| P4 | ND | 1516, 3/8/77-1802, 3/9/77 | 0.170 | 21/5 | calm SW,S,SE | 0-15 | | |
| P5 | 560[c] | 1802, 3/9/77-1620, 3/10/77 | 0.120 | 24/4 | SE | 5-10 | | |
| P6 | ND | 1620, 3/10/77-1746, 3/11/77 | 0.129 | 23/12 | SE,W | 10-15 | 2.06 cm | |
| P7 | ND | 1746, 3/11/77-1725, 3/12/77 | 0.142 | 23/10 | SE,SW,W | 5-15 | | |
| P8 | ND | 1725, 3/12/77-1725, 3/13/77 | 0.144 | 27/10 | SW,W | 5-10 | | |
| P9 | ND | 1725, 3/13/77-1816, 3/14/77 | 0.149 | 29/6 | calm S,SW | 0-15 | | |
| P10 | ND | 1816, 3/14/77-1645, 3/15/77 | 0.135 | 30/17 | SW,W | 0-10 | | |

(continued)

Table 5.2 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P11 | ND | 1745, 3/15/77-<br>1855, 3/16/77 | 0.157 | 30/12 | N,NE | 5-15 | | |
| P12 | 700[b] | 1855, 3/16/77-<br>1630, 3/17/77 | 0.129 | 25/14 | NE,E,SE,S | 5-10 | | |
| P13 | ND | 1630, 3/17/77-<br>1745, 3/18/77 | 0.152 | 26/16 | S,SW,NW | 5-15 | | |
| P14 | ND | 1745, 3/19/77-<br>1730, 3/19/77 | 0.142 | 21/14 | NE,E,SE | 0-10 | | |
| P15 | ND | 1730, 3/19/77-<br>1810, 3/29/77 | 0.148 | 20/-1 | calm NW,E,<br>SE | 0-10 | | |
| P16 | ND | 1810, 3/20/77-<br>1600, 3/21/77 | 0.157 | 26/9 | calm SE,S,W | 0-15 | | |
| P17 | ND | 1600, 3/21/77-<br>1455, 3/22/77 | 0.183 | 26/1 | NW,NE | 0-10 | | |
| P18 | ND | 1455, 3/22/77-<br>0925, 3/23/77 | 0.116 | 18/1 | calm | - | | |
| P19 | ND | 0925, 3/23/77-<br>1625, 3/24/77 | 0.203 | 23/8 | S calm | 0-5 | 0.56 cm | |
| P21 | ND | 1600, 3/25/77-<br>1925, 3/26/77 | 0.164 | 25/16 | SE | 5-10 | | Raining |

(continued)

Table 5.2 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P22 | ND | 1925, 3/26/77-<br>1652, 3/27/77 | 0.129 | 25/18 | SE,S | 5-15 | 2.67 cm | Raining |
| P23 | 280[d] | 1652, 3/27/77-<br>1735, 3/28/77 | 0.148 | 27/13 | S,SE,W-SW | 5-20 (G) | 2.08 cm | |
| P24 | ND | 1735, 3/28/77-<br>1625, 3/29/77 | 0.137 | 24/14 | S,SW,SE | 5-10 | | |
| P25 | ND | 1625, 3/29/77-<br>1922, 3/30/77 | 0.162 | 29/17 | calm, S,SW,W | 5-10 | | |
| P26 | ND | 1922, 3/30/77-<br>1415, 3/31/77 | 0.113 | 23/17 | NW,N,NE | 5-10 | | |
| P27 | ND | 1415, 3/31/77-<br>1220, 4/1/77 | 0.132 | 23/11 | NE,E | 5-10 | 0.08 cm | |
| P28 | ND | 1220, 4/1/77-<br>1450, 4/2/77 | -- | 24/15 | SE,S,SW | 5-10 | 0.79 cm | Pump stopped during sampling interval |
| P29 | ND | 1450, 4/2/77-<br>1720, 4/3/77 | 0.136 | 22/13 | calm, SW,S,NE | 0-15 | 1.40 cm | |
| P30 | ND | 1720, 4/3/77- | 0.180 | 18/15 | E,NE,calm,W | 0-15<br>(G 22) | 0.56 cm | |
| P31 | 280 | 1824, 4/4/77-<br>1740, 4/5/77 | 0.152 | 18/6 | W,NW | 0-15<br>(G 23) | | |

(continued)

Table 5.2 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P32 | T | 1740,4/5/77- | -- | 18/4 | calm,NW,W,SW | 0-10 | | Pump stopped during sampling interval |
| P33 | 260 | 1856, 4/6/77- | ∿0.135 | 29/9 | calm W | 0-14 | | |

[a] High/low

[b] 1-chloro-2-bromoethane

[c] dibromopropane

[d] allyl bromide

Table 5.3. PROTOCOL FOR CONTINUOUS AIR MONITORING, MAGNOLIA, ARKANSAS

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P1 | ND | 1740, 4/9/77-<br>1900, 4/11/77 | 0.148 | 29/10 | calm S,SW,SE | 0-10 | | |
| P2 | ND | 1900, 4/11/77-<br>1150, 4/13/77 | 0.123 | 29/11 | calm S,SE | 0-10<br>(G 16) | | |
| P3 | ND | 1150, 4/13/77-<br>1605, 4/15/77 | 0.157 | 29/11 | calm SE | 0-10<br>(G 19) | | |
| P4 | T[b] | 1605, 4/15/77-<br>1705, 4/17/77 | 0.147 | 29/14 | calm SE | 0-15 | | |
| P5 | ND | 1705, 4/17/77-<br>1700, 4/19/77 | 0.144 | 28/14 | SE,S | 5-10 | 4.98 cm | |
| P6 | ND | 1700, 4/19/77-<br>1750, 4/21/77 | 0.146 | 28/18 | calm SE | 0-10 | 0.30 cm | |
| P7 | ND | 1750, 4/21/77-<br>2025, 4/23/77 | 0.152 | 26/11 | E,SE,SW,W<br>calm | 0-10 | 1.37 cm | |
| P8 | T[c] | 2025, 2/23/77-<br>1130, 4/25/77 | 0.116 | 26/9 | N,NW calm | 0-10 | trace | |
| P9 | T[b] | 1130, 4/25/77-<br>1450, 4/28/77 | 0.137 | 29/7 | calm, NW<br>S,SW | 0-15 | | |
| P10 | ND | 1450, 4/28/77-<br>1700, 5/1/77 | 0.150 | 28/11 | - | 0-8 | | |
| P11 | ND | 1700, 5/1/77-<br>2220, 5/8/77 | 0.488 | 29/10 | - | 0-10 | | |

[a] High/low

[b] dibromochloropropane

[c] allyl bromide

Table 5.4. PROTOCOL FOR CONTINUOUS AIR MONITORING NEAR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS

| Period | Volatile Brominated Organics $ng/m^3$ | Time/Date | Volume ($m^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P1 | ND | 1315, 4/9/77-<br>1825, 4/11/77 | 0.012 | 29/10 | calm,S,SW,SE | 0-10 | | |
| P2 | ND | 1825, 4/11/77-<br>1120, 4/13/77 | 0.123 | 29/11 | calm,S,SW | 0-10<br>(G 16) | | |
| P3 | T[b] | 1120, 4/13/77-<br>1935, 4/15/77 | 0.078 | 29/11 | calm, SE | 0-10<br>(G 19) | | Sharp odor in air 4/15/77 |
| P4 | ND | 1935, 4/15/77-<br>1540, 4/17/77 | 0.127 | 29/14 | calm, SE | 0-15 | | Flare at Dow emitting grey smoke which was drifting northeast of sampler. Wind from southeast. |
| P5 | ND | 1540, 4/17/77-<br>1620, 4/19/77 | 0.146 | 28/14 | SE,S | 5-10 | | |
| P6 | ND | 1620, 4/19/77-<br>1925, 4/2/77 | <0.153[a] | 28/18 | calm, SE | 0-10 | 4.98 cm | |
| P7 | ND | 1925, 4/2/77-<br>1905, 4/23/77 | 0.145 | 26/11 | E,SE,SW,W<br>calm | 0-10 | 0.30 cm | Plume seen over plant site with very weak wind blowing in direction of sampler. |
| P8 | ND | 1905, 4/23/77-<br>1100, 4/25/77 | 0.120 | 26/9 | N,NW,calm | 0-10 | 1.37 cm | |
| P9 | 142,[c] 21[d] | 1130, 4/25/77-<br>2010, 4/28/77 | 0.209 | 29/7 | calm,NW,S,SW | 0-15 | trace | |

(continued)

Table 5.4 (cont'd)

| Period | Volatile Brominated Organics ng/m$^3$ | Time/Date | Volume (m$^3$) | Meteorology: Temp. °C[a] | Meteorology: Wind Dir. | Meteorology: Wind Speed (Knts) | Meteorology: Precipitation | Comments |
|---|---|---|---|---|---|---|---|---|
| P10 | 81,[c] 24[d] | 2010, 4/28/77-1740, 4/30/77 | 0.167 | 29/13 | calm,SW,SE | 0-10 | | Odor in air, wind from plant direction. |
| P11 | ND | 1740, 4/30/77-1130, 5/2/77 | 0.097 | 29/12 | - | 0-8 | | Faint odor from plant, winds from plant direction. |
| P12 | 35,[c] 18[d] | 1130, 5/2/77-1200, 5/4/77 | 0.146 | 29/11 | - | 0-10 | | |

[a] High/low

[b] allyl bromide

[c] 1,2-dibromoethane

[d] dibromochloropropane

Table 5.5. PROTOCOL FOR CONTINUOUS AIR MONITORING NEAR ETHYL CORPORATION, MAGNOLIA, ARKANSAS

| Period | Volatile Brominated Organics $ng/m^3$ | Time/Date | Volume ($m^3$) | Meteorology | | | | Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Temp. °C[a] | Wind Dir. | Wind Speed (Knts) | Precipitation | |
| P1 | ND | 1130, 4/9/77<br>1130, 4/11/77 | <0.144[a] | 29/10 | calm, S,SW,SE | 0-10 | | |
| P2 | ND | 1800, 4/11/77-<br>1050, 4/13/77 | 0.122 | 29/11 | calm S,SE | 0-10<br>(G 16) | | |
| P3 | ND | 1050, 4/13/77-<br>1900, 4/15/77 | 0.202 | 29/11 | calm SE | 0-10<br>(G 19) | | |
| P4 | ND | 1900, 4/15/77-<br>1425, 4/17/77 | 0.130 | 29/14 | calm SE | 0-15 | | |
| P5 | ND | 1435, 4/17/77<br>1535, 4/19/77 | 0.147 | 28/14 | SE,S | 5-10 | | |
| P6 | ND | 1535, 4/19/77-<br>1845, 4/21/77 | 0.134 | 28/18 | calm, SE | 0-10 | 4.98 cm | Odor of bromine. |
| P7 | ND | 1845, 4/21/77-<br>1750, 4/23/77 | 0.141 | 26/11 | E,SE,SW,W | 0-10 | 0.3 cm | |
| P8 | ND | 1750, 4/23/77-<br>1100, 4/23/77 | 0.123 | 26/9 | N,NW,calm | 0-10 | 1.37 cm | |
| P9 | ND | 1100, 4/25/77-<br>1905, 4/28/77 | <0.120[a] | 29/7 | calm, NW<br>SW,S | 0-15 | trace | |
| P10 | 57[b] | 1905, 4/28/77-<br>1625, 4/30/77 | 0.130 | 29/13 | calm,SW | 0-10 | | |

[a] High/low

[b] 1,2-dibromoethane

respectively. In a few of the ambient air samples taken from these sites, dibromochloropropane (DBCP), allyl bromide and 1,2-dibromoethane were detected. Traces of DBCP and allyl bromide were detected at the air montoring station on the Southern Arkansas University campus. 1,2-Dibromoethane and DBCP were detected in ambient air samples taken at a sampling station located north of Dow Chemical Co. (Table 5.4). During the periods in which the brominated organics were detected, the wind direction was generally from the southeast, and south to southwest directions (Table 5.4). During one sampling period, a low concentration of 1,2-dibromoethane was detected in an ambient air sample taken north of Ethyl Corporation (Table 5.5).

# 6.0 CHARACTERIZATION OF ENVIRONMENTAL MEDIA ASSOCIATED WITH BROMINE INDUSTRY

## 6.1 TECHNICAL STRATEGY

### 6.1.1 Sampling

As pointed out in Section 4.1, the strategy of the Survey Study was to evaluate the analytical techniques employed for characterizing ambient air and to acquire a maximum amount of information about the chemicals surrounding the bromine industry. With this information in hand as well as the information which was acquired during the long-term continuous monitoring for volatile organic vapors and from condensed phase media for semi-volatile and volatile brominated organics, we proceeded to design a sampling and analysis regime to more extensively study the environmental media surrounding the bromine industry. The concept included extensive sampling of air, water, soil, sediment and biota on the plant sites as well as off-site. Subsequent prioritization of the samples for analysis was necessary in order to best characterize the potential contamination of environmental media by the activities associated with the bromine industry in El Dorado and Magnolia, AK. The sampling strategy included collection of samples immediate and distant from the various industrial sites in order to possibly demonstrate the transport of brominated organics. The sampling strategy was designed not only to investigate transport of brominated organics but also the potential impact on populated areas.

The sampling methods employed during this phase of the program were as described in Appendix A which provides the analytical protocols.

### 6.1.2 Prioritization of Sample Analysis

Table 6.1 presents the inventory of samples which were collected in Southern Arkansas between July 15 and August 5, 1977. As indicated in the table, a total of 439 samples was collected. However, samples were selected for analysis based upon several criteria which were used to provide a guideline in prioritizing these samples for analysis. The samples of ambient air were selected on the basis of the most favorable meteorological

Table 6.1. INVENTORY OF SAMPLES COLLECTED IN SOUTHERN ARKANSAS (7/15/77 to 8/5/77)[a]

| Type of Sample | Great Lakes, El Dorado | Velsicol[b] El Dorado | Ethyl Corp. Magnolia | Dow Chemical Magnolia | Great Lakes Marysville | Other | Arkansas Chemical Co. - El Dorado | Total |
|---|---|---|---|---|---|---|---|---|
| Tenax GC/Carbon (air)[c] | 21 | 19 | 15 | 13 | 1 | 1 | 0 | 70 |
| Impingers (halides, air)[c] | 16 | 16 | 12 | 16 | 4 | 0 | 0 | 64 |
| Hi-Vol Filters (air) | 4 | 4 | 6 | 6 | 2 | 0 | 8 | 30 |
| Vacuum Can. (air)[c] | 18 | 15 | 14 | 6 | 4 | 0 | 0 | 57 |
| Soil | 20 | 19 | 20 | 20 | 0 | 8 | 0 | 87 |
| Water | 25 | 5 | 3 | 11 | 0 | 0 | 0 | 44 |
| Vegetation | 23 | 5 | 5 | 4 | 0 | 0 | 0 | 37 |
| Sediment | 14 | 5 | 2 | 4 | 0 | 0 | 0 | 25 |
| Milk | 3 | 1 | 1 | 0 | 0 | 0 | 0 | 5 |
| Miscellaneous | 9 | 2 | 1 | 0 | 0 | 8 | 0 | 20 |
| | | | | | | | | 439 |

[a]Samples indicated for an industrial site include both on property and vicinity samples.

[b]Formerly Michigan Chemical Co.

[c]Each sampling train counted as a sample even though two analyses were made.

conditions with respect to the sampling locations and the proximity of the industrial facility. Other environmental media such as soil, water, sediment and biota were selected for analysis in the initial phases of the program based upon samples taken in the immediate vicinity of the plant area but off-site. When environmental samples collected off-site indicated the presence of brominated compounds, then additional samples more distant from the plant sites were selected for analysis.

6.1.3 Ozone Measurements in El Dorado, AK

During the period from July 22-August 12, hourly ozone concentrations were tabulated. Appendix A, Section M describes the techniques used for determining the ozone concentration. The results are given in Appendix D.

6.2 RESULTS AND DISCUSSION

6.2.1 Great Lakes Chemical Corporation and Vicinity

6.2.1.1 Sampling

The sampling protocols for ambient air, water, soil, etc. surrounding Great Lakes Chemical Corporation in El Dorado, AK are given in Tables 6.2-6.4. The sampling period, cycle, location, sampling time, volume and type of sample as well as meteorological conditions are described; the corresponding locations are shown on Figures 6.1-6.5.

6.2.1.2 Inorganics in Ambient Air

The halides and halogens which were quantitated in ambient air surrounding Great Lakes Chemical Co. are given in Table 6.5. The turbidimetric method was used for determining halide and halogen. The values given in Table 6.5 are expressed as chloride and molecular chlorine. However, if bromide or bromine was the predominant species, the values would be multiplied by 1.5. The highest concentration of halide was observed at location 2 at which time it reached a level of 274 $\mu g/m^3$. For this period L4 represents the upwind sample.

6.2.1.3 Brominated and Other Organics

Air.--Table 6.6 presents the ambient air levels of volatile brominated organics which were detected during the five day period. The highest concentration was 271,283 $ng/m^3$ of 1,2-dibromoethane which occurred at location 2 during the second sampling period. This represented a downwind sampling station approximately 200 yds from the organic synthesis facility.

Table 6.2. SAMPLING PROTOCOL FOR AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.,

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions T(°C) | %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P1 7/17/77 | C1 | L0 | 1955-1420 (7/18/77) | 100 | HHC[ab] | | | | |
| P2 7/18/77 | C1 | L1 | 1139-1240 (7/19/77) | 202 | HHC[ab] | | | | |
| | | L2 | 1155-1305 (7/19/77) | 204 | HHC[ab] | | | | |
| | | L3 | 1242-1315 (7/19/77) | 199 | HHC[ab] | | | | |
| | | L4 | 1543-1352 (7/19/77) | 129 | HHC[ab] | | | | |
| | | L5 | 1514-1334 (7/19/77) | 208 | HHC[ab] | 20-35 | | E,SE, calm, N | |
| | | L1 | 1438-1800 | 246 | CBD,CBN[c] | | | | |
| | | L2 | 1444-1807 | 238 | CBD,CBN[c] | | | | |
| | | L3 | 1244-1815 | 356 | CBD,CBN[c] | | | | |
| | | L4 | 1359-1824 | 265 | CBD,CBN[c] | | | | |
| | | L5 | 1530-1335 (7/19/77) | 1,949,000 | Hi-Vol[b] | | | | |
| P3 7/19/77 | C1 | L1 | 1256-1110 (7/20/77) | 192 | HHC[ab] | | | | |
| | | L2 | 1310-1121 (7/20/77 | 180 | HHC[ab] | | | | |
| | | L3 | 1321-1131 (7/20/77) | 188 | HHC[ab] | | | | Strong odor of $H_2S$ |
| | | L4 | 1400-1147 (7/20/77) | 123 | HHC[ab] | | | | |
| | | L5 | 1347-1139 (7/20/77) | 185 | HHC[ab] | 20-32 | 90 | N, NE, calm | |
| | | L1 | 1250-1725 | 204 | CBD,CBN[c] | | | NE to W/3-7 | |
| | | L2 | 1310-1735 | 247 | CBD,CBN[c] | | | | |
| | | L3 | 1317-1738 | 266 | CBD,CBN[c] | | | N, calm | Strong odor of $H_2S$ |
| | | L4 | 1355-1747 | 254 | CBD,CBN[c] | | | | |
| | | L6 | 1855 | 0.5 | VAC | | | | |
| | | L7 | 1858 | 0.5 | VAC | | | | |
| | | L5 | 1345-1455 (7/20/77) | 2,051,000 | Hi-Vol[b] | | | | |
| P4 7/20/77) | C1 | L1 | 1118-1032 (7/21/77) | 188 | HHC[ab] | 20-27 | 60-90 | S,with periods of calm | Upset 1730 |
| | | L2 | 1127-1047 (7/21/77) | <189 | HHC[ab] | | | 3-6 | Pump stopped during interval |
| | | L3 | 1137-1130 (7/21/77) | 193 | HHC[ab] | | | | Upset 1730 |
| | | L4 | 1152-1150 (7/21/77) | 129 | HHC[ab] | | | | Raining 1150 |
| | | L5 | 1147-1143 (7/21/77) | 194 | HHC[ab] | | | | |
| | | L1 | 1018-1520 | 220 | CBD,CBN[c] | | | gusty unstable | |
| | | L2 | 1024-1527 | 216 | CBD,CBN[c] | | | pattern | |
| | | L3 | 1031-1533 | 247 | CBD,CBN[c] | | | | |
| | | L4 | 1058-1540 | 279 | CBD,CBN[c] | | | | |

(continued)

Table 6.2 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions T(°C) | %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P4 | C1 | (Continued) | | | | | | | |
| 7/20/77 | | L1 | 1520 | 0.5 | VAC | | | | |
| | | L2 | 1530 | 0.5 | VAC | | | | |
| | | L3 | 1533 | 0.5 | VAC | | | | |
| | | L4 | 1540 | 0.5 | VAC | | | | |
| | | L5 | 1512 | 0.5 | VAC | | | | |
| | | L8 | 1730 | 0.5 | VAC | | | | Middle of Methylchloride storage tanks |
| | | L9 | 1732 | 0.5 | VAC | | | | Upwind of Methylchloride storage tanks |
| | | L5 | 1500-1520 (7/21/77) | 1,928,000 | Hi-Vol[b] | | | | |
| P5 | C1 | L1 | 1042-0845 (7/22/77) | 179 | HHC[ab] | 20-30 | 60-90 | S,NW-NE,calm/1-8 | |
| 7/21/77 | | L2 | 1115-0900 (7/22/77) | 176 | HHC[ab] | | | | |
| | | L3 | 1138-0910 (7/22/77) | 174 | HHC[ab] | | | | |
| | | L4 | 1210-0950 (7/22/77) | 117 | HHC[ab] | | | | |
| | | L5 | 1150-0925 (7/22/77) | 175 | HHC[ab] | | | | |
| | | L1 | 1010-1455 | 205 | CBD,CBN[c] | | S,SW/5-6 | | |
| | | L2 | 1016-1500 | 216 | CBD,CBN[c] | | | | Bromine upset at N1045 |
| | | L3 | 1025-1504 | 249 | CBD,CBN[c] | | | | |
| | | L4 | 1031-1507 | 221 | CBD,CBN[c] | | | | Near cooling water tower |
| | | L1 | 1230 | 0.5 | VAC | | | | |
| | | L2 | 1230 | 0.5 | VAC | | | | |
| | | L3 | 1230 | 0.5 | VAC | | | | |
| | | L4 | 1212 | 0.5 | VAC | | | | |
| | | L1 | 0845 (7/22/77) | 0.5 | VAC | | | | |
| | | L2 | 0900 (7/22/77) | 0.5 | VAC | | | | |
| | | L3 | 0910 (7/22/77) | 0.5 | VAC | | | | |
| | | L4 | 0950 (7/22/77) | 0.5 | VAC | | | | |
| | | L5 | 0925 (7/22/77) | 0.5 | VAC | | | | |
| | | L5 | 1525-0931 (7/22/77) | 1,475,000 | Hi-Vol[b] | | | | |

[a]DuPont sampler 3-6 ft elevation.

[b]Overnight sampling.

[c]Nutech Model 220 sampler 3-6 ft elevation.

Locations shown in Figures 6.1 and 6.2

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

Table 6.3. SOIL SAMPLING PROTOCOLS SURROUNDING AND ON GREAT LAKES CHEMICAL CORP., EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Type | Sample Size | Comments |
|---|---|---|---|---|---|
| P1 | C1 | L1[a] | S/HHC | 2 cores | Taken ∿6 M from the road in school yard |
| 7/17/77 | | L2[a] | S/HHC | 2 cores | Parkers Chapel School |
| | | L3[a] | S/HHC | 2 cores | Samples from dry ditch beside railroad |
| P4 | C1 | L4[a] | S/HHC | 2 cores | |
| 7/20/77 | | L5[a] | S/HHC | 2 cores | |
| | | L6[a] | S/HHC | 2 cores | West of methyl bromide storage in a swampy area |
| | | L7[a] | S/HHC | 2 cores | |
| P5 | C1 | L8[b] | S/HHC | 2 cores | |
| 7/21/77 | | L9[b] | S/HHC | 2 cores | Northeast ∿30 M from laboratory building |
| | | L10[b] | S/HHC | 2 cores | On road to south dump |
| | | L11[b] | S/HHC | 2 cores | ∿20 M west of holding pond on south edge of property |
| | | L12[b] | S/HHC | 2 cores | |
| | | L13[a] | S/HHC | 2 cores | |
| | | L14[a] | S/HHC | 2 cores | |
| | | L15[a] | S/HHC | 2 cores | |
| | | L16[a] | S/HHC | 2 cores | |
| P7 | C1 | L17[a] | S/HHC | 2 cores | |
| 7/23/77 | | | | | |
| P8 | C1 | L18[a] | S/HHC | 2 cores | |
| 7/24/77 | | L19[a] | S/HHC | 2 cores | |

[a]See Figure 6.3 for map of sample locations.

[b]See Figure 6.4 for map of sample locations.

S = soil samples
HHC = for halogenated hydrocarbon analysis.

Table 6.4. WATER AND SEDIMENT SAMPLING PROTOCOL SURROUNDING AND ON GREAT LAKES CHEMICAL CORPORATION AND THE EL DORADO, ARKANSAS AREA

| Period | Cycle | Location | Sample Type | Sample Size (ℓ) | Comments |
|---|---|---|---|---|---|
| P1 | C1 | L1 | SD/HHC | 2 | In swampy area |
| 7/17/77 | | L2 | SD/HHC | 2 | |
| | | | W/HHC | 2 | |
| P3 | C1 | L3 | W/HHC | 2 | Roof run off during rain |
| 7/19/77 | | L4 | W/HHC | 2 | |
| P4 | C1 | L5 | W/HHC | 2 | Hard bottom ∿ 21 M east (downstream) |
| 7/20/77 | | | SD/HHC | 2 | of culvert under road - directly draining from Great Lakes |
| | | L6 | SD/HHC | 2 | Puddle east side of Lion oil tank |
| | | | W/HHC | 2 | |
| | | L7 | W/HHC | 2 | Pond ∿ 60 M in diameter with oil slick |
| | | L8 | W/HHC | 2 | Clear running water |
| | | | SD/HHC | 2 | |
| | | L9 | W/HHC | 2 | Creek |
| | | | SD/HHC | 2 | |
| P5 | C1 | L10 | W/HHC | 2 | Out fall of Great Lakes [a] |
| 7/21/77 | | | SD/HHC | 2 | |
| | | L11 | W/HHC | 2 | Upstream of out fall[a] |
| | | | SD/HHC | 2 | |
| | | L12 | W/HHC | 2 | |
| | | | SD/HHC | 2 | Hard clay (grey) |
| | | L13 | W/HHC | 2 | Water backed up in reclaimation area |
| | | | SD/HHC | 2 | Clay/sand bottom, probably new since the entire area was recently graded. |
| | | L14 | SD/HHC | 2 | Pond 200 M north of Parker's Chapel water tower |
| | | | W/HHC | 2 | |
| P7 | C1 | L15 | W/HHC | 4 | Creek |
| 7/23/77 | | | SD/HHC | 4 | |
| P8 | C1 | L16 | W/HHC | 2 | |
| 7/24/77 | | | SD/HHC | 2 | Stream |
| | | L17 | W/HHC | 2 | Well water (9 M deep) |
| | | L18 | W/HHC | 2 | Pond |
| | | | SD/HHC | 2 | |
| | | L19 | W/HHC | 2 | Well water |
| P13 | C1 | L10 | W/HHC | 2 | Out fall of Great Lakes |
| 7/29/77 | | L11 | W/HHC | 2 | Upstream of out fall |

[a]Identified by Jarrell Southall, Arkansas State Pollution Control and Ecology.

Locations are shown in Figure 6.5.

W = Water sample
SD = Sediment sample
HHC = for halogenated hydrocarbon analysis

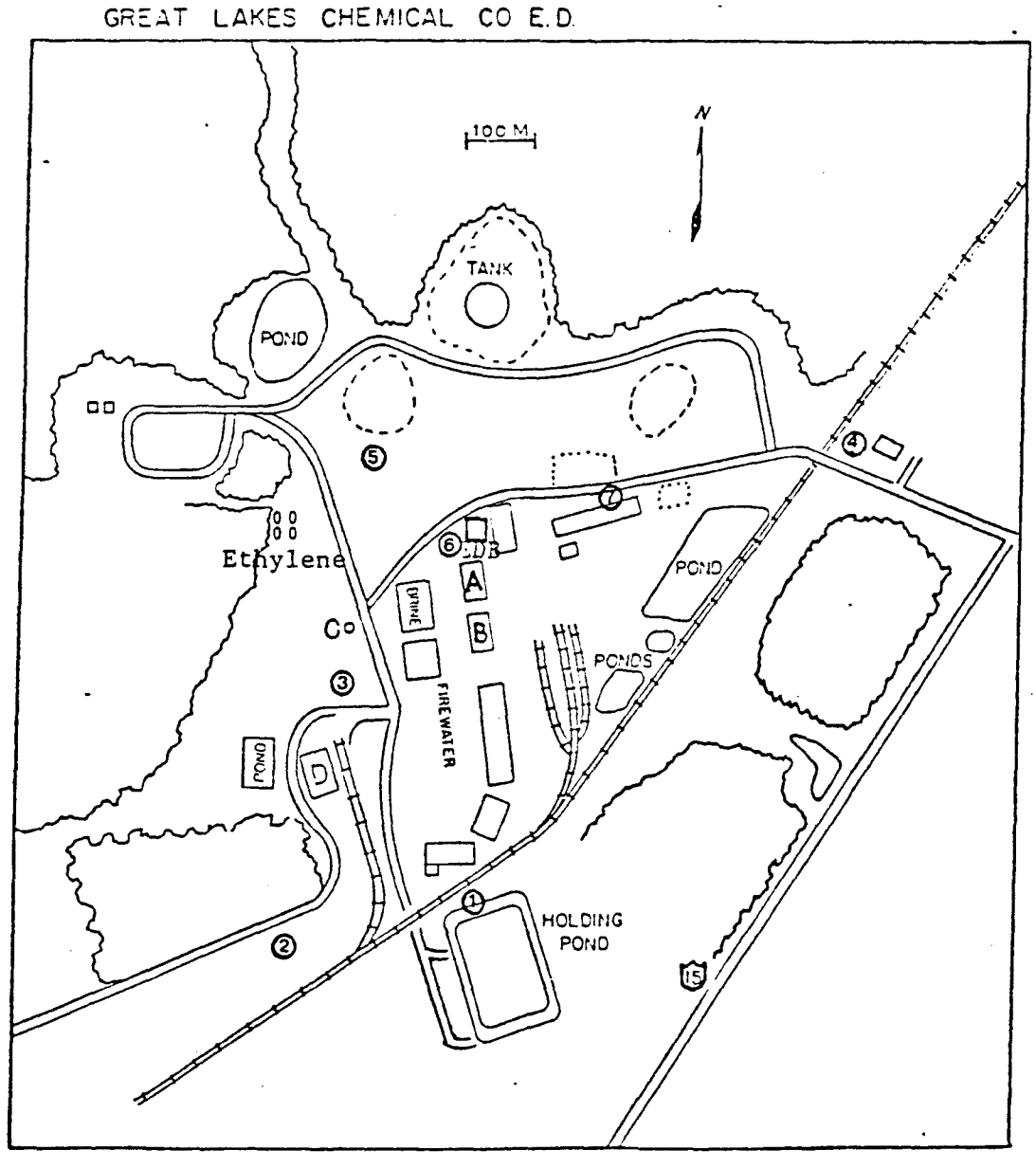



Figure 6.1. Schematic map of Great Lakes Chemical Company, El Dorado, AK - Air sampling locations for P2 (7/18/77) through P5 (7/21/77).

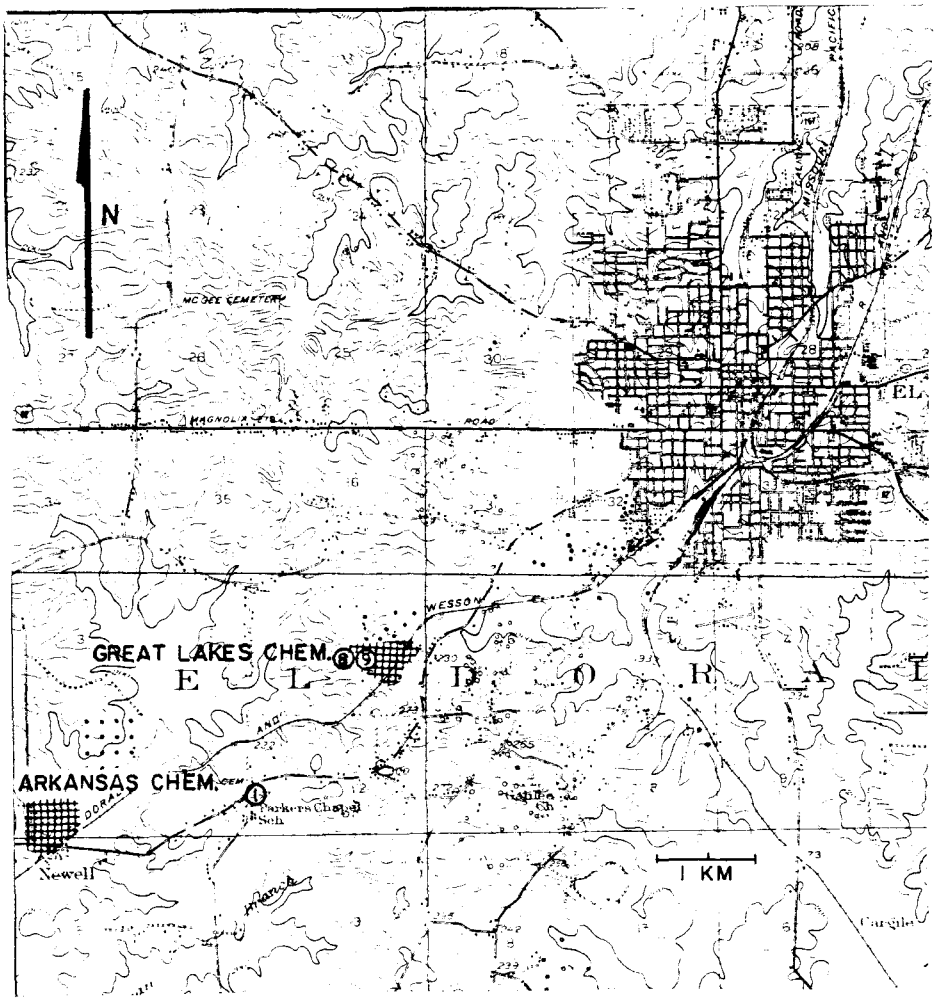



Figure 6.2. Map of Great Lakes Chemical Co. Vicinity, El Dorado, Arkansas - air sampling locations (7/17/77 - 7/24/77).

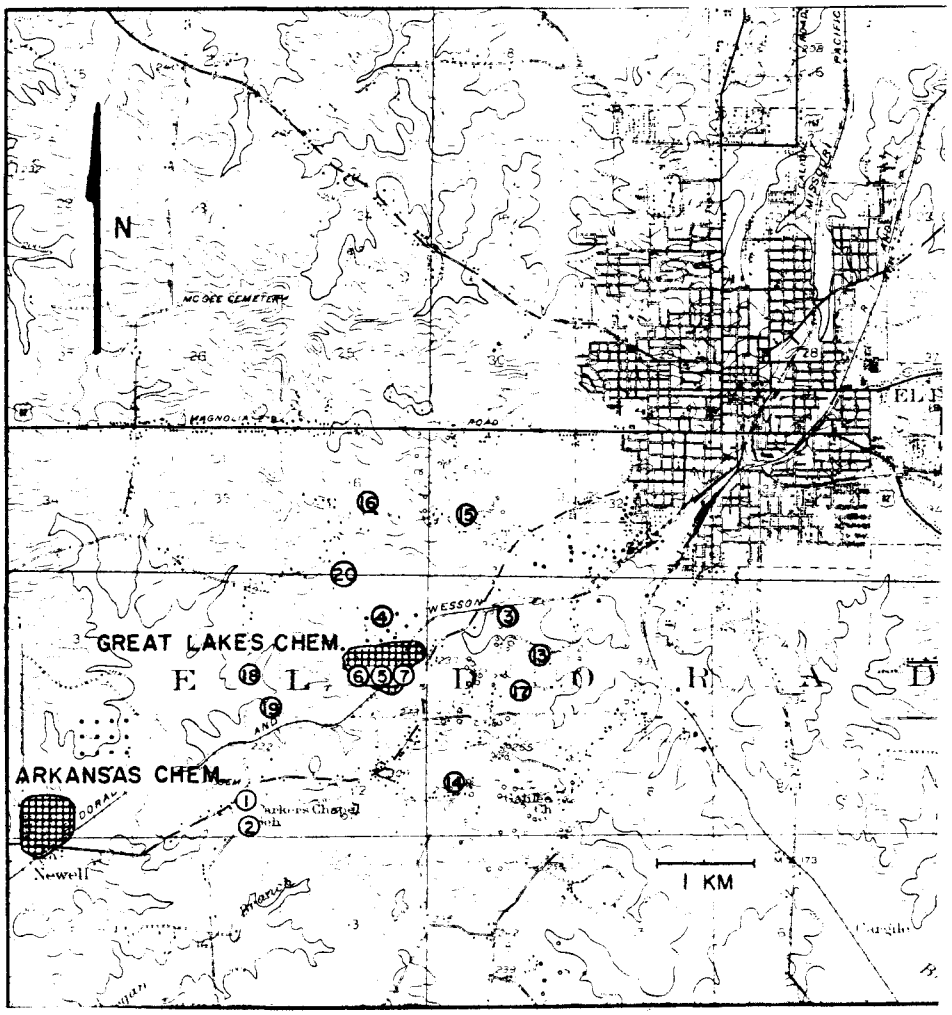



Figure 6.3. Map of Great Lakes Chemical Co. Vicinity, El Dorado, Arkansas - soil sampling locations (7/17/77 - 7/20/77).

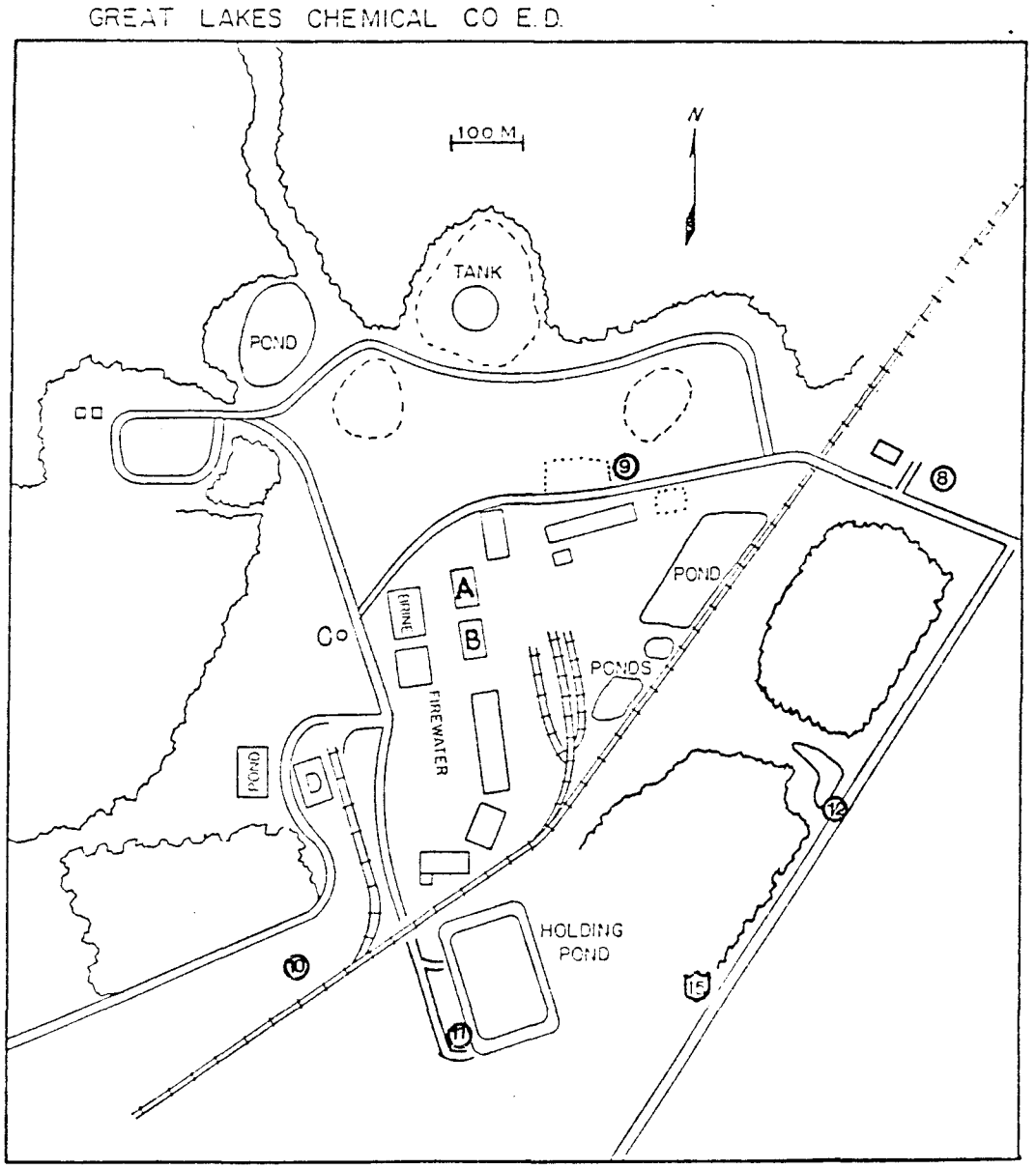



Figure 6.4. Schematic map of Great Lakes Chemical Company, El Dorado, Arkansas -- Soil Sampling Locations. (7/21/77)

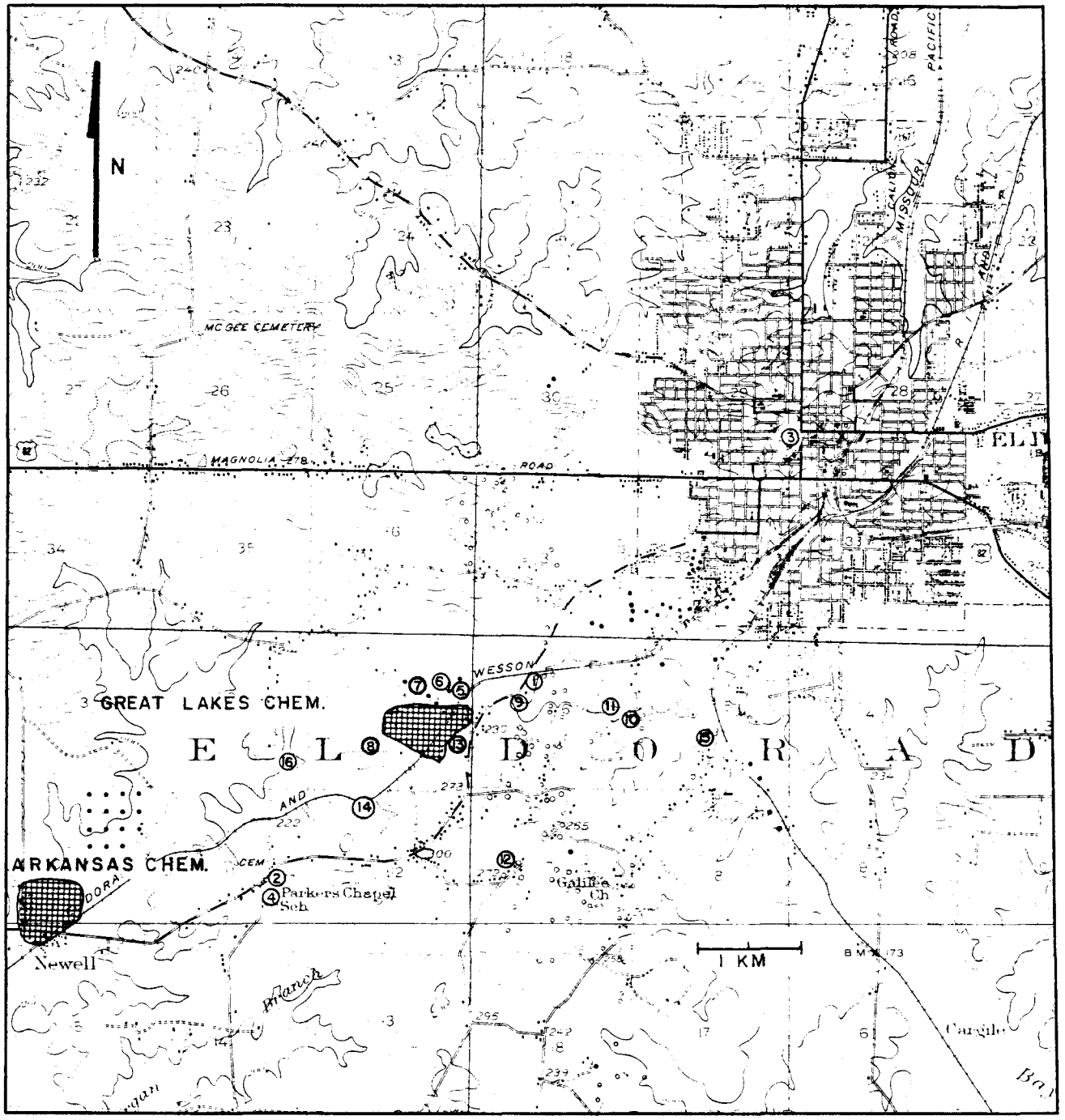



Figure 6.5. Vicinity map of Great Lakes Chemical Company, El Dorado, Arkansas - Water and sediment sampling locations (7/17/77 - 7/24/77).

Table 6.5. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP., EL DORADO, AK

| Period/Cycle/Location[a] | Halide as $Cl^{-}$[b] $\mu g/m^3$ | Halogen as $Cl_2$[b] $\mu g/m^3$ |
|---|---|---|
| P2/C1/ L1 | 244 ± 120 | 58 ± 9 |
| L2 | 274 ± 184 | 217 ± 16 |
| L4 | < 9 | 34 ± 8 |
| P3/C1/ L1 | 151 ± 34 | 49 ± 2 |
| L2 | 26 ± 13 | 63 ± 2 |
| L3 | 13 ± 8 | 71 ± 21 |
| P5/C1/ L1 | 54 ± 16 | 88 ± 15 |
| L3 | 113 ± 53 | 56 ± 9 |

[a] Refer to Table for sampling protocol

[b] Values are expressed as $Cl^{-}$ or $Cl_2$, however if $Br^{-}$ or $Br_2$ is the predominate species, the values should be multiplied by 1.5.

Table 6.6. AMBIENT AIR LEVELS OF VOLATILE BROMINATED ORGANICS SURROUNDING GREAT LAKES CORP., EL DORADO, AK[a]

| Period/Cycle/Location | Bromobenzene | 1-Chloro-2-Bromoethane | 1,2-Dibromoethane | Dibromochloropropanes | Bromoform | 1-Chloro-3-Bromopropene | Bromodichloromethane | Allyl bromide | Bromopropanes | Dibromopropanes | Chlorodibromomethane | Dibromomethane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1/C1/L1 | 5.3 | ND | 1.7 | ND | ND | ND | T | ND | ND | N | N | ND |
| P2/C1/L1 | ND | ND | 95 | ND | T | ND | T | ND | T | ND | ND | ND |
| L2 | 470 | 73 | 271,283 | 1.4 | 25 | ND | T | ND | T | ND | ND | ND |
| L3 | 3,842 | 70 | 2,408 | 1.4 | 20 | T | ND | T | ND | T | ND | ND |
| L4 | 188 | 34 | 20 | ND | ND | ND | ND | ND | T | ND | ND | ND |
| L5 | 1,131 | 2.8 | T | T | 22 | ND | ND | ND | ND | ND | ND | ND |
| P3/C1/L1 | ND | ND | 2.8 | T | T | T | T | T | T | ND | ND | ND |
| L2 | 29 | T | 8,092 | T | T | ND | T | ND | ND | ND | ND | ND |
| L3 | 4,276 | ND | 39,060 | T | T | ND | ND | ND | ND | ND | ND | ND |
| L4 | 20 | ND | 3,352 | T | T | ND | ND | ND | T | ND | ND | ND |
| L5 | 51 | ND | 32,872 | 2.8 | 98 | ND | T | ND | ND | ND | ND | ND |
| P4/C1/L1 | ND | T | ND | T | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 280 | ND | 118 | ND | T | T | T | ND | ND | T | ND | ND |
| L3 | 1,041 | T | 896 | ND | 104 | ND | T | T | ND | T | ND | ND |
| L4 | 22 | ND | 190 | ND | ND | ND | ND | T | ND | ND | ND | ND |
| L5 | 980 | 22 | 35,056 | 5.6 | 37 | ND | T | ND | ND | T | ND | ND |

(continued)

Table 6.6 (cont'd)

| Period/Cycle/Location | Bromobenzene | 1-Chloro-2-Bromoethane | 1,2-Dibromoethane | Dibromochloropropanes | Bromoform | 1-Chloro-3-Bromopropene | Bromodichloromethane | Allyl bromide | Bromopropanes | Dibromopropanes | Chlorodibromomethane | Dibromomethane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P5/C1/L1 | 4.5 | ND | T | T | ND | ND | ND | T | T | T | ND | ND |
| L2 | 428 | T | 1,056 | ND | T | T | T | ND | ND | ND | ND | ND |
| L3 | 95 | ND | 526 | ND | 22 | T | ND | T | T | ND | ND | ND |
| L4 | 4.8 | ND | T | ND | T | ND | ND | ND | ND | T | ND | ND |
| L5 | 4.8 | T | 270 | T | T | T | ND | ND | T | T | T | ND |

[a]Values are in $ng/m^3$.

Bromobenzene, 1-chloro-2-bromoethane, dibromochloropropanes and bromoform were also measured. Trace levels of several other brominated organics were detected. However, in contrast to the survey sampling phase, chlorodibromomethane and dibromomethane were not detected.

Tables 6.7 and 6.8 present the concentration of ethylene in ambient air surrounding the Great Lakes Chemical Corp. plants in El Dorado and Marysville. The background levels of ethylene were approximately 1 ppm and, in some cases, reached 6-7 ppm at locations 3 and 4 at the El Dorado plant site. Elevated concentrations of ethylene were not detected at the Marysville plant.

Analysis of the particulate material collected on Hi-Vol glass fiber filters revealed the presence of traces of tetrabromobisphenol A (Table 6.9). The highest level was observed during the fourth sampling period when it reached 1.8 $\mu g/m^3$. Also at this time Decabrom was detected at a level of 25 $\mu g/m^3$. This sampling period generally favored a downwind position from the Tetrabrom facility.

Sediment.--Samples of sediment which were selected for analysis did not contain detectable levels of pentabromophenol. However, relatively large quantities of Tetrabrom and Decabrom were found (Table 6.10). In fact, these samples represented the most contaminated of those examined. A level of 1 g/kg of Decabrom was found in sediment taken from near an "outfall pipe" which presumably came from Great Lakes Chemical Corp.

Soil.--Pentabromophenol was quantified in a soil sample taken ~1 mile off property of Great Lakes Chem. Significant quantities of Tetrabrom and Decabrom were found in other soil samples, one of which (L4) contained 150 mg/kg and 25 mg/kg of these chemicals, respectively (Table 6.11).

### 6.2.2 Michigan Chemical Corporation (Velsicol) and Vicinity

#### 6.2.2.1 Sampling

The ambient air sampling protocol for Velsicol Chemical Corporation in El Dorado, AK is given in Table 6.12. A schematic map of Velsicol showing the air sampling locations is given in Figure 6.6. Table 6.13 presents the sampling protocols for water and sediment surrounding and on Velsicol, Inc. Figures 6.7 and 6.8 present the water and sediment sampling locations. Table 6.14 presents the soil sampling protocol and Figures 6.9 and 6.10, the

Table 6.7. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.

| Period/Cycle/Location | ppm Ethylene |
|---|---|
| P4/C1/L1 | 4.4 |
| P4/C1/L2 | 1.0 |
| P4/C1/L3 | 7.2 |
| P4/C1/L4 | 6.3 |
| P4/C1/L5 | 4.8 |
| P4/C1/L9 | 2.6 |
| Lab-1[a] | 0.1 |
| Lab-2[a] | 2.2 |
| Field-1[b] | 0.3 |
| Field-2[b] | 0.9 |
| Field-3[b] | 0.4 |
| Lab-1[a,c] | 3.8 |
| Lab-2[a,d] | 10.1 |
| Field-1[b,c] | 1.7 |
| Field-2[b,c] | 4.9 |
| Field-3[b,d] | 6.5 |
| Field-4[b,d] | 10.0 |

[a]Stored @ 4°C in the lab.

[b]Transported to the sampling area and returned to the lab.

[c]Spiked with 0.9 ppm ethylene.

[d]Spiked with 9.7 ppm ethylene.

Table 6.8. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL, INC. - MARYSVILLE PLANT

| Period/Cycle/Location | ppm Ethylene |
|---|---|
| P1/C1/L2 | 1.4 |
| P1/C1/L3 | 1.1 |
| P1/C1/L4 | 2.1 |
| P1/C1/L5 | 1.7 |
| Lab-1[a] | 0.1 |
| Lab-2[a] | 2.2 |
| Field-1[b] | 0.3 |
| Field-2[b] | 0.9 |
| Field-3[b] | 0.4 |
| Lab-1[a,c] | 3.8 |
| Lab-2[a,d] | 10.1 |
| Field-1[b,c] | 1.7 |
| Field-2[b,c] | 4.9 |
| Field-3[b,d] | 6.5 |
| Field-4[b,d] | 10.0 |

[a]Stored at 4°C in the lab.

[b]Transported to the sampling area and returned to the lab.

[c]Spiked with 0.9 ppm ethylene.

[d]Spiked with 9.7 ppm ethylene.

Table 6.9. RESULTS OF THE ANALYSIS OF HI-VOL FILTERS FOR SEMI-VOLATILE BROMINATED ORGANICS - GREAT LAKES CHEMICAL CORPORATION, EL DORADO, ARKANSAS

| Period/Cycle/Location[a] | Tetrabromobisphenol A[b] ($\mu g/m^3$) | Decabromobiphenyl ether ($\mu g/m^3$) |
|---|---|---|
| P2/C1/L5 | 0.08[c] | 8.0[c] |
| P3/C1/L5 | 1.2[c] | 1.0[c] |
| P4/C1/L5 | 1.8[c,d] | 25[c,e] |
| P5/C1/L5 | ND[c] | 2.0[c] |

[a] See Table 6.2 and Figure 6.2 for locations of samples.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] Quantitation by gas chromatography-mass spectrometry with multiple ion detection.

[d] Confirmed by ion intensity ratio of 1.7 for the sample vs. 1.5 for the standard for 529/531.

[e] Confirmed by ion intensity ratio for the sample of 2.8 compared to 2.7 for the sample for ion pair 800/804.

Table 6.10. RESULTS OF ANALYSIS OF SEDIMENT SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS GREAT LAKES CHEMICAL CORPORATION, EL DORADO, ARKANSAS

| Period/Cycle/Location[a] | Pentabromophenol (µg/Kg) | Tetrabromobisphenol A[b] (µg/Kg) | Decabromobiphenyl ether (µg/Kg) |
|---|---|---|---|
| P4/C1/L5 | ND[c,d] | 630[d] | ND[c,d] |
| P4/C1/L8 | ND[d] | 24,000[d] | 14,000[d] |
| P5/C1/L10 | - | - | 1,000,000[e] |
| P5/C1/L13 | ND[d] | 330,000[d] | 6,300[d] |
| P6/C1/L14 | ND[d] | 300[d] | ND[d] |

[a]See Table 6.4 and Figure 6.4 for locations of samples.

[b]2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c]Not detected - approximately 100 µg/Kg is required to detect these compounds.

[d]Quantitation by gas chromatography - mass spectrometry using multiple ion detection.

[e]Quantitation by thin layer chromatography.

Table 6.11. RESULTS OF ANALYSIS OF SOIL SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS GREAT LAKES CORPORATION, EL DORADO, ARKANSAS

| Period/Cycle/Location | Pentabromophenol (µg/Kg) | Tetrabromobisphenol A[b] (µg/Kg) | Decabromobiphenyl ether (µg/Kg) |
|---|---|---|---|
| P1/C1/L1 | ND[c] | ND[c] | ND[c] |
| P4/C1/L4 | ND | 150,000[e] | 25,000[d] |
| P4/C1/L7 | ND | 8,000 | 1,400 |
| P8/C1/L18 | 200 | 2,000 | 120 |
| P8/C1/L20 | ND | ND | ND |

[a]See Table 6.3 and Figure 6.1 for location of samples.

[b]2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c]Not detected - approximately 50 µg/kg is required for detection of these compounds.

[d]Quantitation by gas chromatography/mass spectrometry using multiple ion detection.

[e]Identity confirmed by full scan gc/ms analysis.

Table 6.12. AMBIENT AIR SAMPLING PROTOCOL SURROUNDING VELSICOL CHEMICAL CORP., EL DORADO, AK

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions T(°C) | %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P1 | C1 | L1 | 1130-0925 (9/23/77) | 179 | HHC[ab] | | | | |
| 7/22/77 | | L2 | 1140-0945 (9/23/77) | <162 | HHC[ab] | 18-38 | 52-88 | NW-5-8 (4 hrs.) | Pump stopped |
| | | L3 | 1205-1000 (9/23/77) | 191 | HHC[ab] | | | S/0-3 (18 hrs.) | |
| | | L4 | 1105-1015 (9/23/77) | 81 | HHC[ab] | | | | |
| | | L5 | 1220-1040 (9/23/77) | 116 | HHC[ab] | | | | |
| | | L1 | 1010-1455 | 205 | CBD,CBN[c] | | | | |
| | | L2 | 1016-1500 | 216 | CBD,CBN[c] | | | Variable | Bromine upset ~1045 |
| | | L3 | 1025-1504 | 249 | CBD,CBN[c] | | | SE,W,NW,/7 | |
| | | L4 | 1031-1507 | 221 | CBD,CBN[c] | | | | |
| | | L1 | 1547 | 0.5 | VAC | | | | |
| | | L2 | 1550 | 0.5 | VAC | | | | |
| | | L6 | 1540 | 0.5 | VAC | | | | |
| | | L7 | 1554 | 0.5 | VAC | | | | |
| | | L8 | 1600 | 0.5 | VAC | | | | |
| | | L4 | 1115-1025 (9/23/77) | 1,573,000 | Hi-Vol | | | | |
| P2 | C1 | L1 | 0935-0925 (9/24/77) | 138 | HHC[ab] | 21-40 | 50-92 | N,NW,variable/0-8 (13 hrs.) | |
| 7/23/77 | | L2 | 1400-0945 (9/24/77) | 150 | HHC[ab] | | | S/2-8 (12 hrs.) | |
| | | L3 | 1010-1000 (9/24/77) | 150 | HHC[ab] | | | | |
| | | L4 | 1020-1010 (9/24/77) | 26 | HHC[ab] | | | | |
| | | L5 | 1040-1025 (9/24/77) | 114 | HHC[ab] | | | | |
| | | L1 | 0930-1350 | 214 | CBD,CBN[c] | | | Variable/3-5 | |
| | | L2 | 0945-1355 | 187 | CBD,CBN[c] | | | | |
| | | L3 | 1000-1405 | 247 | CBD,CBN[c] | | | | |
| | | L4 | 1015-1405 | 197 | CBD,CBN[c] | | | | |
| | | L1 | 0930 | 0.5 | VAC | | | | |
| | | L2 | 0950 | 0.5 | VAC | | | | |
| | | L3 | 1005 | 0.5 | VAC | | | | |
| | | L4 | 1018 | 0.5 | VAC | | | | |
| | | L5 | 1040 | 0.5 | VAC | | | | |
| | | L4 | 1030-1010 (9/24/77) | 1,587,000 | Hi-Vol | | | | |

(continued)

Table 6.12 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions T(°C) | %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P3 | C1 | L1 | 0940-1002 (9/25/77) | 121 | HHC[ab] | | | | |
| 7/24/77 | | L2 | 0950-1017 (9/25/77) | 176 | HHC[ab] | 21-38 | 45-92 | S/3-11 (15 hrs.) | |
| | | L3 | 1005-1033 (9/25/77) | 149 | HHC[ab] | | | NE,N/4-5 (5 hrs.) | |
| | | L4 | 1055-1045 (9/25/77) | 97 | HHC[ab] | | | Variable/5 (5 hrs.) | |
| | | L5 | 1055-1040 (9/25/77) | 26 | HHC[ab] | | | | |
| | | L1 | 0925-1400 | 224 | CBD,CBN[c] | | | S, variable/4-7 | |
| | | L2 | 0945-1402 | 189 | CBD,CBN[c] | | | | |
| | | L3 | 1005-1405 | 208 | CBD,CBN[c] | | | | |
| | | L4 | 1018-1410 | 199 | CBD,CBN[c] | | | | |
| | | L4 | 1015-1040 | 1,617,000 | Hi-Vol | | | | |
| P4 | C1 | L1 | 1010-1019 (7/26/77) | 218 | HHC[ab] | 20-37 | 56-90 | S,SE/2-12 (~16 hrs.) | |
| 7/25/77 | | L2 | 1026-0830 (7/26/77) | <200 | HHC[ab] | | | NE/4-10 (~5 hrs.) | Pump stopped |
| | | L3 | 1040-0840 (7/26/77) | 170 | HHC[ab] | | | | |
| | | L4 | 1055-0850 (7/26/77) | 119 | HHC[ab] | | | | |
| | | L1 | 1005-1432 | 218 | CBD,CBN[c] | | | S,SE/10-12 | |
| | | L2 | 1025-1436 | 181 | CBD,CBN[c] | | | | |
| | | L3 | 1045-1440 | 206 | CBD,CBN[c] | | | | |
| | | L4 | 1052-1445 | 188 | CBD,CBN[c] | | | | |
| | | L1 | 1005 | 0.5 | VAC | | | | |
| | | L2 | 1023 | 0.5 | VAC | | | | |
| | | L3 | 1035 | 0.5 | VAC | | | | |
| | | L4 | 1055 | 0.5 | VAC | | | | |
| | | L5 | 1100 | 0.5 | VAC | | | | |
| | | L4 | 1050-0850 (7/26/77) | 1,438,000 | Hi-Vol | | | | |

[a] DuPont sampler 3-6 ft elevation.

[b] Overnight sampling.

[c] Nutech Model 220 sampler 3-6 ft elevation.

Locations shown in Figure 6.6.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

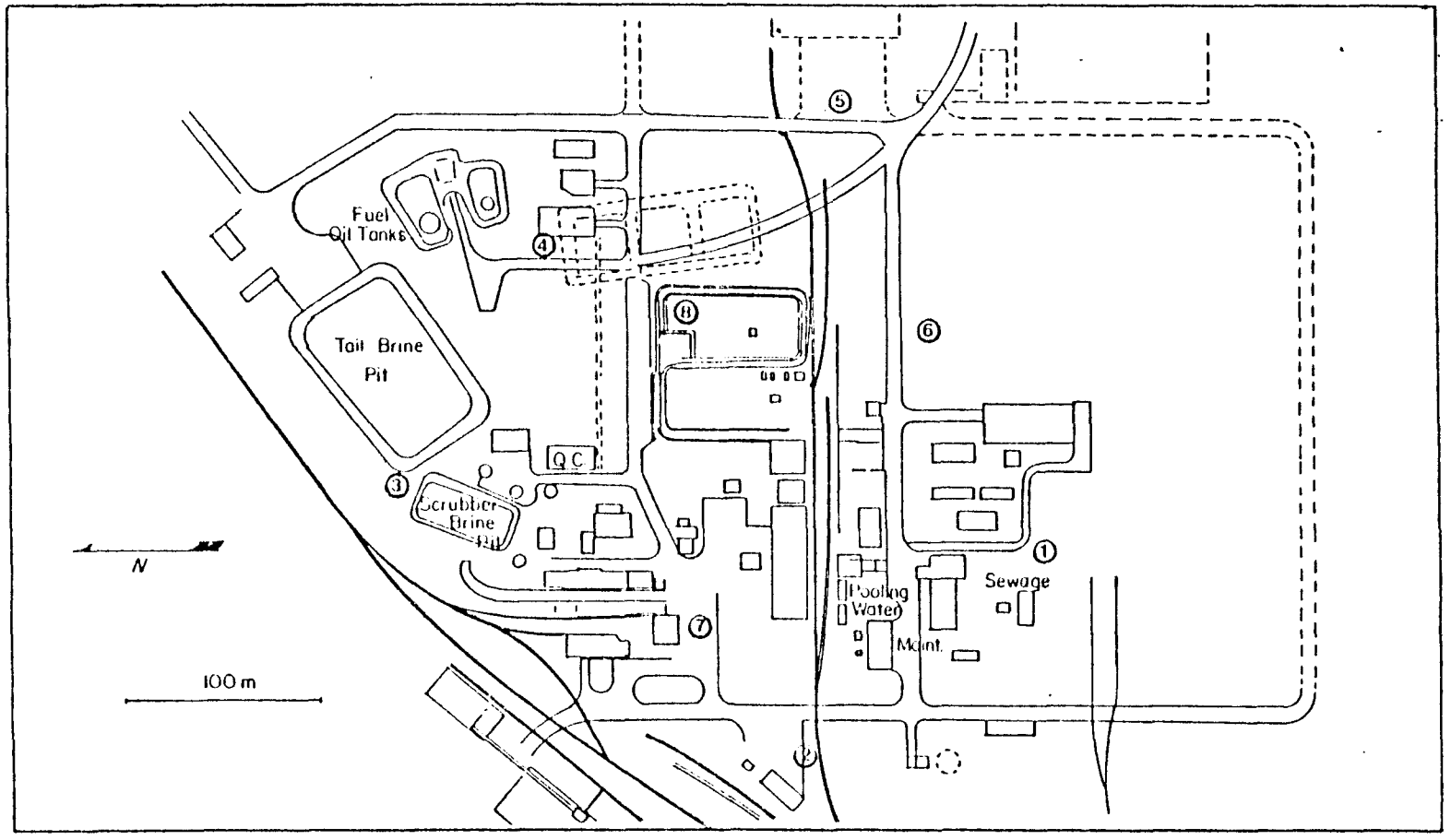



Figure 6.6. Schematic map of Velsicol, Inc., El Dorado, AK. Air sampling locations P1 (7/22/77) through P4 (7/25/77).

Table 6.13. WATER AND SEDIMENT SAMPLING PROTOCOL SURROUNDING AND ON VELSICOL, INCORPORATED, EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Type | Sample Size (ℓ) | Comments |
|---|---|---|---|---|---|
| P1 | C1 | L1 | W/HHC[a] | 2 | ∿1/2 km north of plant in power line |
| 7/22/77 | | | SD/HHC[a] | 2 | corridor |
| | | L2 | W/HHC[a] | 2 | Sessile water |
| | | L3 | W/HHC[a] | 2 | Walker Creek |
| P2 | C1 | L4 | W/HHC[b] | 2 | ∿400 m west of Firemaster 680 facility |
| 7/23/77 | | | SD/HHC[b] | 2 | |
| P4 | C1 | L5 | W/HHC[a] | 2 | Creek dried up except for a puddle |
| 7/25/77 | | | SD/HHC[a] | 2 | |

[a]See Figure 6.7 for map of sample locations.

[b]See Figure 6.8 for map of sample locations.

W = water
SD = sediment
HHC = for halogenated hydrocarbon analysis

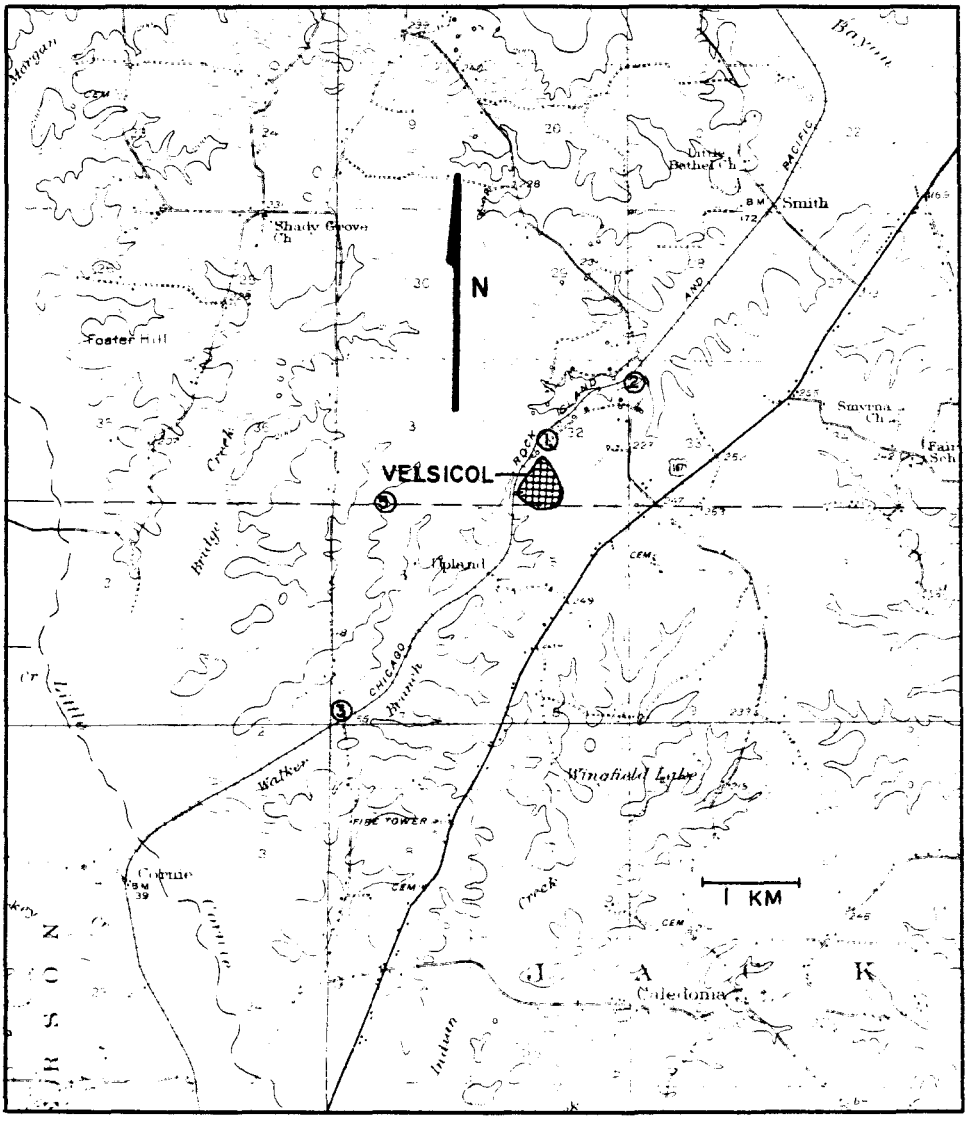



Figure 6.7. Vicinity map of Velsicol, Inc., El Dorado, Arkansas - Water and sediment sample locations (7/22/77 - 7/25/77).

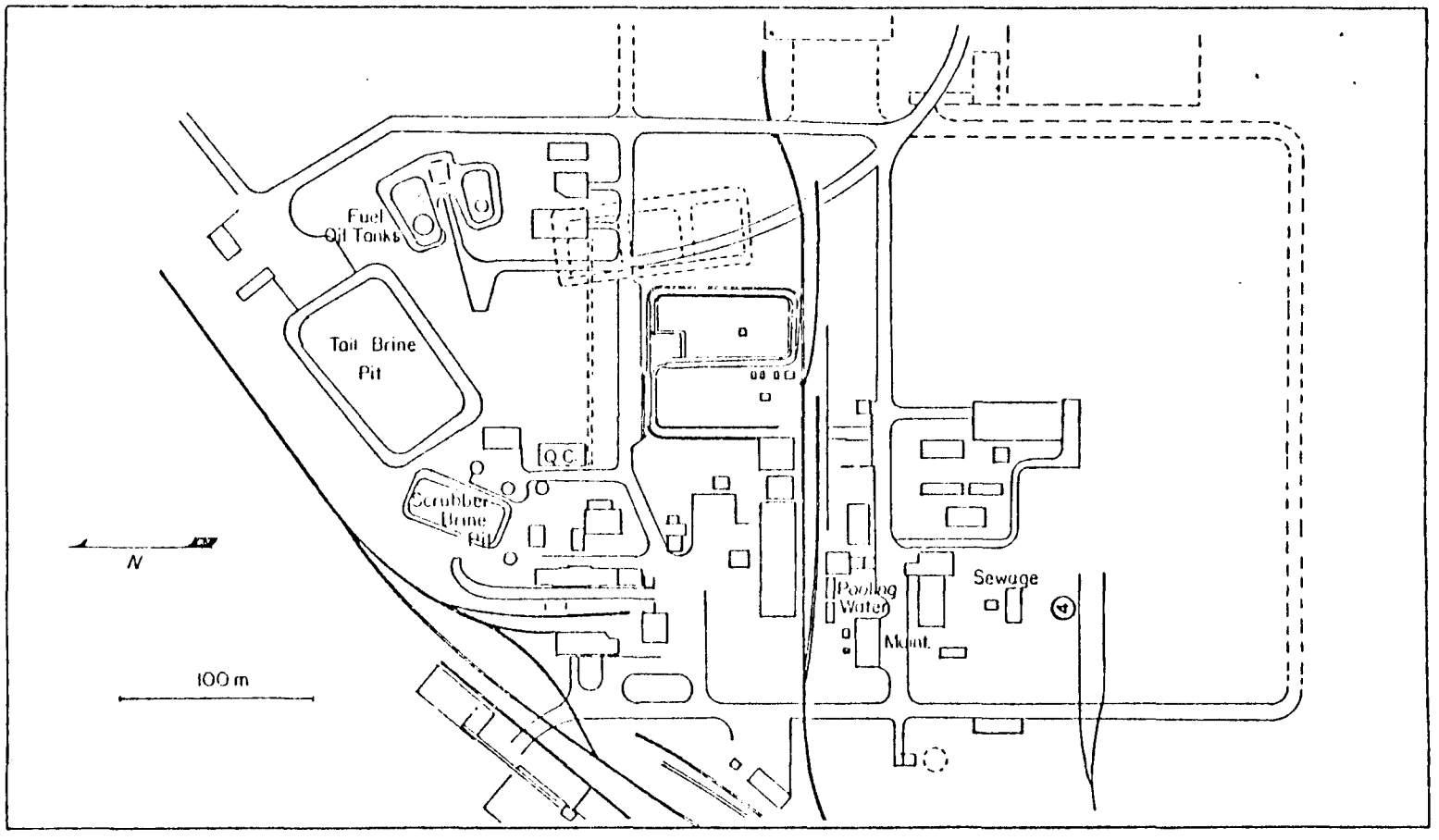



Figure 6.8. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Water and sediment sampling location (7/23/77).

Table 6.14. SOIL SAMPLING PROTOCOLS SURROUNDING AND ON VELSICOL, INC., EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Type | Sample Size | Comments |
|---|---|---|---|---|---|
| P1 | C1 | L1 | S/HHC[a] | 2 cores | Near r.r. tracks (fill dirt). |
| 7/22/77 | | L2 | S/HHC[a] | 2 cores | Between r.r. tracks and sewage treatment facility in a dry stream bed. |
| | | L3 | S/HHC[a] | 2 cores | Near r.r. tracks. |
| | | L4 | S/HHC[a] | 2 cores | Near r.r. tracks. |
| | | L5 | S/HHC[a] | 2 cores | In power line right of way - woods on either side. |
| | | L6 | S/HHC[a] | 2 cores | Near a service road. |
| | | L7 | S/HHC[a] | 2 cores | West of plant beyond a fill area - woods on west side of location. |
| | | L8 | S/HHC[a] | 2 cores | Near service road. |
| | | L9 | S/HHC[a] | 2 cores | From clearing next to car wash at entrance. |
| | | L10 | S/HHC[b] | 2 cores | ∿500 M from bromine extraction in power line corridor. |
| | | L11 | S/HHC[b] | 2 cores | ∿20 M north of road in a grassy area. |
| | | L12 | S/HHC[b] | 2 cores | ∿2 KM WSW of Velsicol on trail through woods. |
| | | L13 | S/HHC[b] | 2 cores | Between dirt road and r.r. tracks near power substation. |
| P2 | C1 | L14 | S/HHC[b] | 2 cores | ∿1/2 KM east of plant at a power substation. |
| 7/23/77 | | L15 | S/HHC[b] | 2 cores | ∿1/2 KM north of plant. |
| | | L16 | S/HHC[b] | 2 cores | ∿2 KM due south of plant. |
| P4 | C1 | L17 | S/HHC[a] | 2 cores | From ditch with water probably run off next to Firemaster 680 warehouse. |
| 7/25/77 | | L18 | S/HHC[a] | 2 cores | From the hill above the ditch (L17). |
| | | L19 | S/HHC[b] | 2 cores | ∿1 KM due east of plant on power line right of way. |

[a]See Figure 6.9 for map of sample locations.

[b]See Figure 6.10 for map of sample locations.

S = soil sample
HHC = for halogenated hydrocarbon analysis

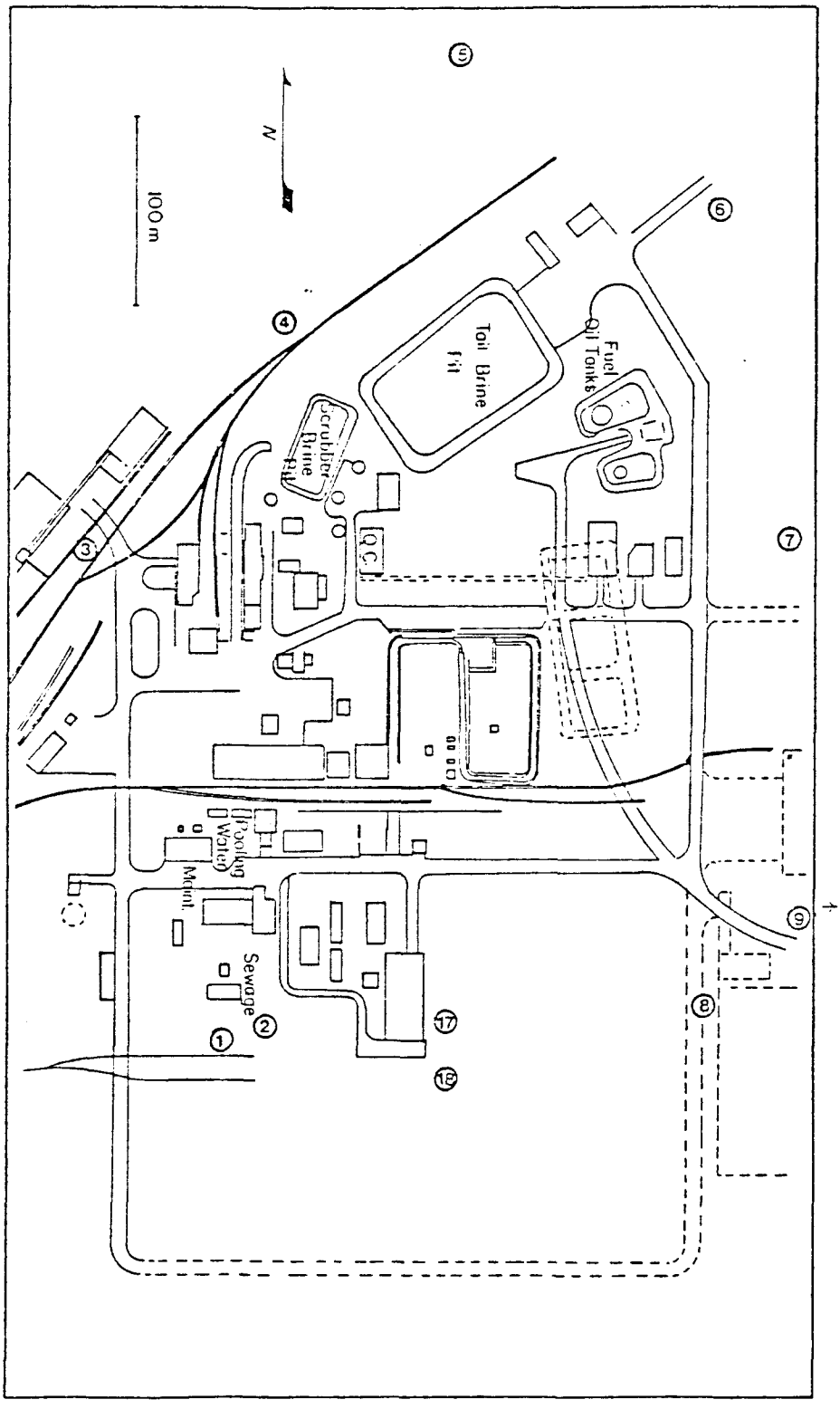



Figure 6.9. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Soil sampling locations (7/22/77 to 7/25/77).

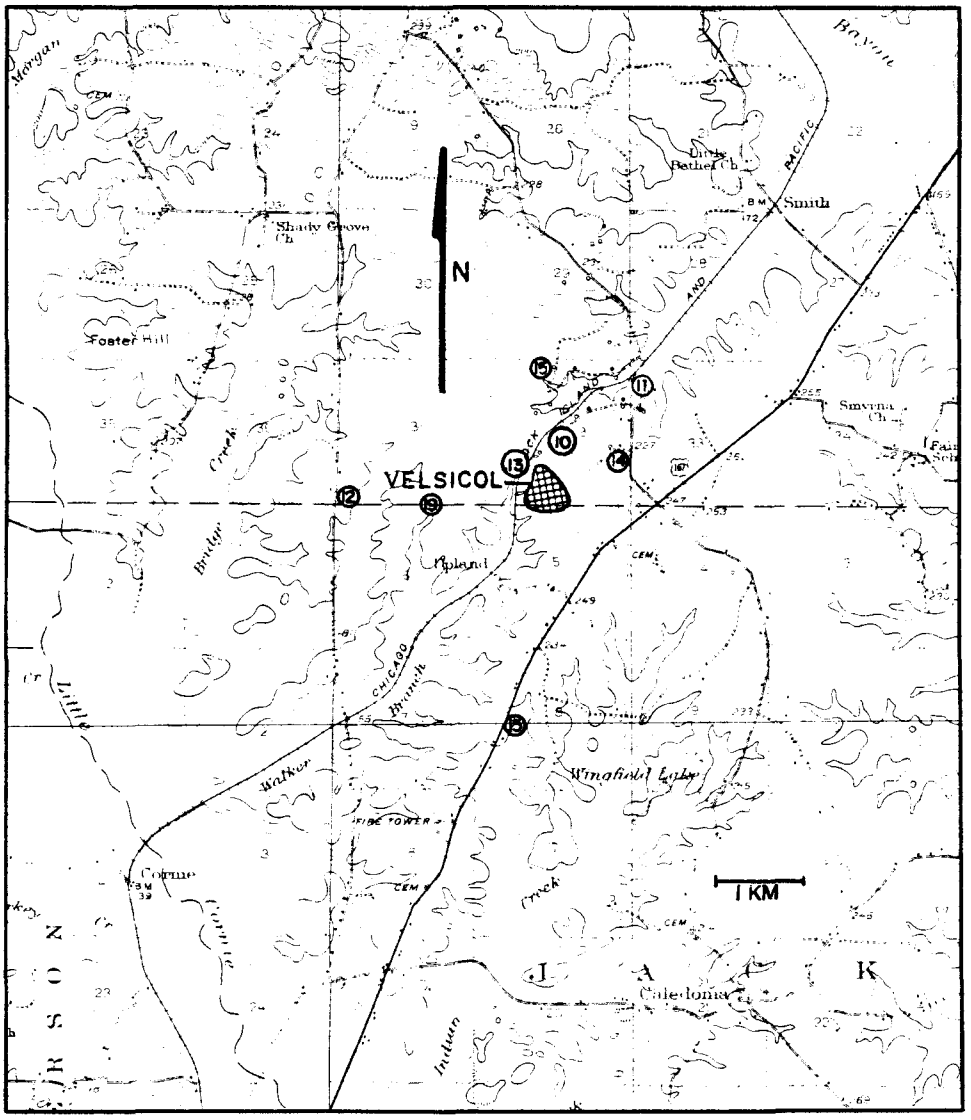



Figure 6.10. Vicinity map of Velsicol, Inc., El Dorado, Arkansas - Soil sampling locations (7/22/77 to 7/25/77).

corresponding sampling locations. Table 6.15 gives the sampling protocols for the biota which were taken surrounding and on Velsicol, Inc. while Figures 6.11 and 6.12 depict the locations of sampling.

6.2.2.2 Inorganics in Ambient Air

Table 6.16 gives the concentrations of halides and halogens in ambient air surrounding Velsicol. The samples were selected for analysis on the basis of meteorological conditions. The detection limit for halide was approximately <10 $\mu g/m^3$. The highest halide level detected occurred during the fourth sampling period at L3 when a level of 91 $\mu g/m^3$ was reached. The concentration of halogen, on the other hand, was observed to be 219 $\mu g/m^3$ at the third location during the third sampling period. Inspection of these data indicate a concomitant increase and decrease in the levels of halides and halogen during the various sampling periods.

6.2.2.3 Brominated and Other Organics

Air.--The ambient air levels of volatile brominated organics surrounding Velsicol, Inc. are given in Table 6.17. Many brominated organics which were detected during the Survey Phase (see Section 4.2.3.5) were not detected during this phase. Ethylene dibromide, dibromochloropropane (DBCP) and chlorodibromomethane were detected at relatively low concentrations throughout each of the four sampling periods.

Table 6.18 gives the concentrations of ethylene in ambient air. Recalling that the background concentration is ~0.6 - 1.0 ppm, the highest level of ethylene was found at L7 at which time it reached 6.8 ppm.

The glass fiber filters were analyzed according to the procedures in Appendix A for semi-volatile brominated organics. The results are presented in Table 6.19. With the particulate samples collected by Hi-Vol samplers the interpretation of a positive finding is complicated by the possibility that the compounds found may not be current emissions. They may be adsorbed onto soil particles which continue to be resuspended in the air. The primary counterindication of the above is the presence of varying combinations of material from day to day especially TRIS and Firemaster 680 with very similar meteorology.

A control filter was spiked with TRIS, Tetrabrom and Decabrom using a matrix of 10 $cm^2$ (2 cm x 5 cm) alternating spiked areas with blank areas. A

Table 6.15. VEGETATION AND MISCELLANEOUS SAMPLING PROTOCOLS SURROUNDING AND ON VELSICOL, INC., EL DORADO, ARKANSAS

| Period | Cycle | Location | Sample Type | Sample Size (ℓ) | Comments |
|---|---|---|---|---|---|
| P1 7/22/77 | C1 | L1 | V/HHC[a] | | Fern type leaves |
| | | L2 | V/HHC[a] | | |
| | | L3 | V/HHC[b] | | Corn |
| | | L4A | V/HHC[b] | | Tomato |
| | | L4B | V/HHC[b] | | Cabbage |
| P2 7/23/77 | C1 | L5 | M/HHC[b] | 0.5 | Cow's milk |

[a]See Figure 6.11 for map of sample locations.

[b]See Figure 6.12 for map of sample locations.

V = vegetation
M = miscellaneous samples
HHC = for halogenated hydrocarbon analysis

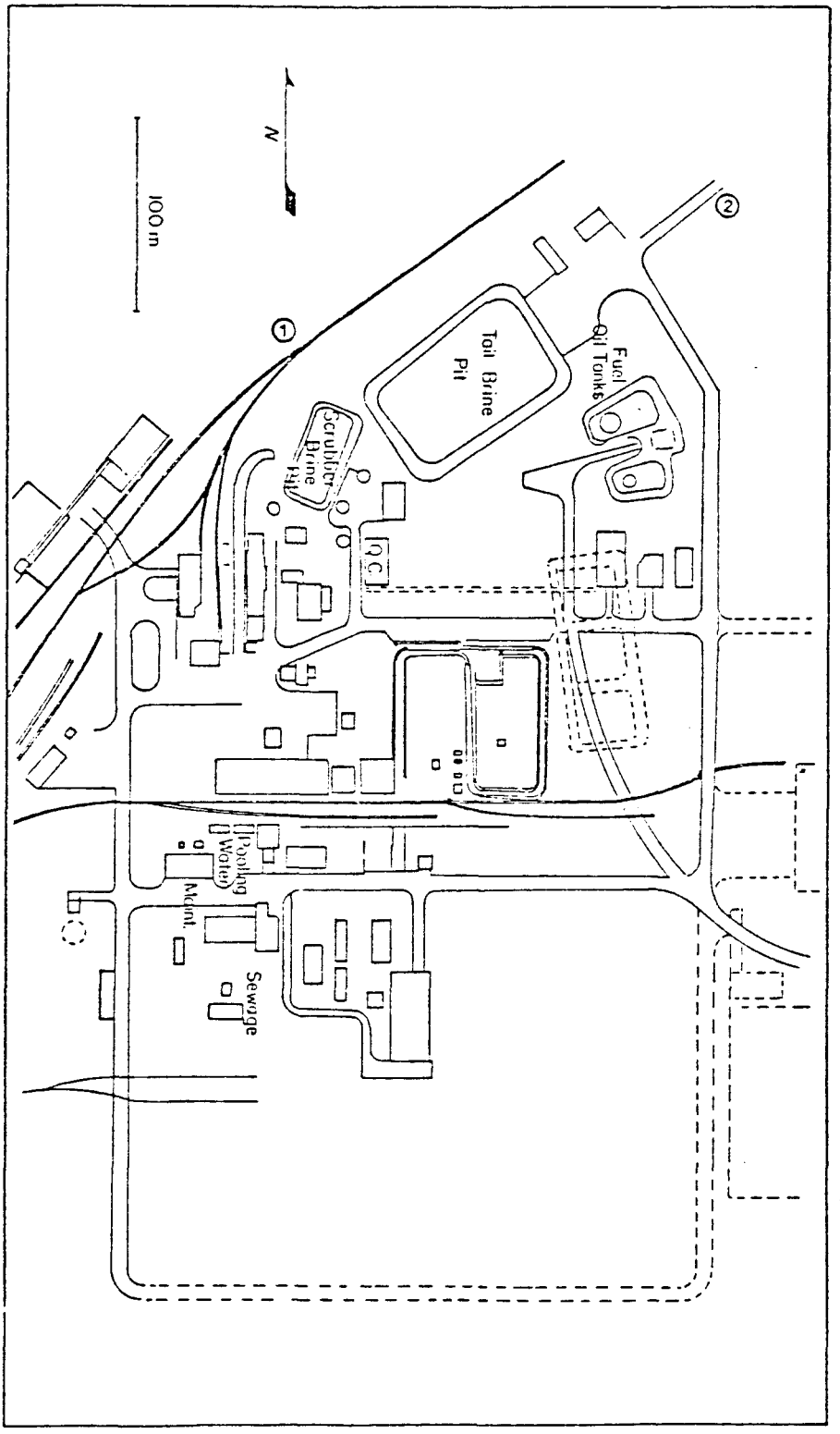



Figure 6.11. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Vegetation and miscellaneous sampling locations (7/22/77 - 7/23/77).

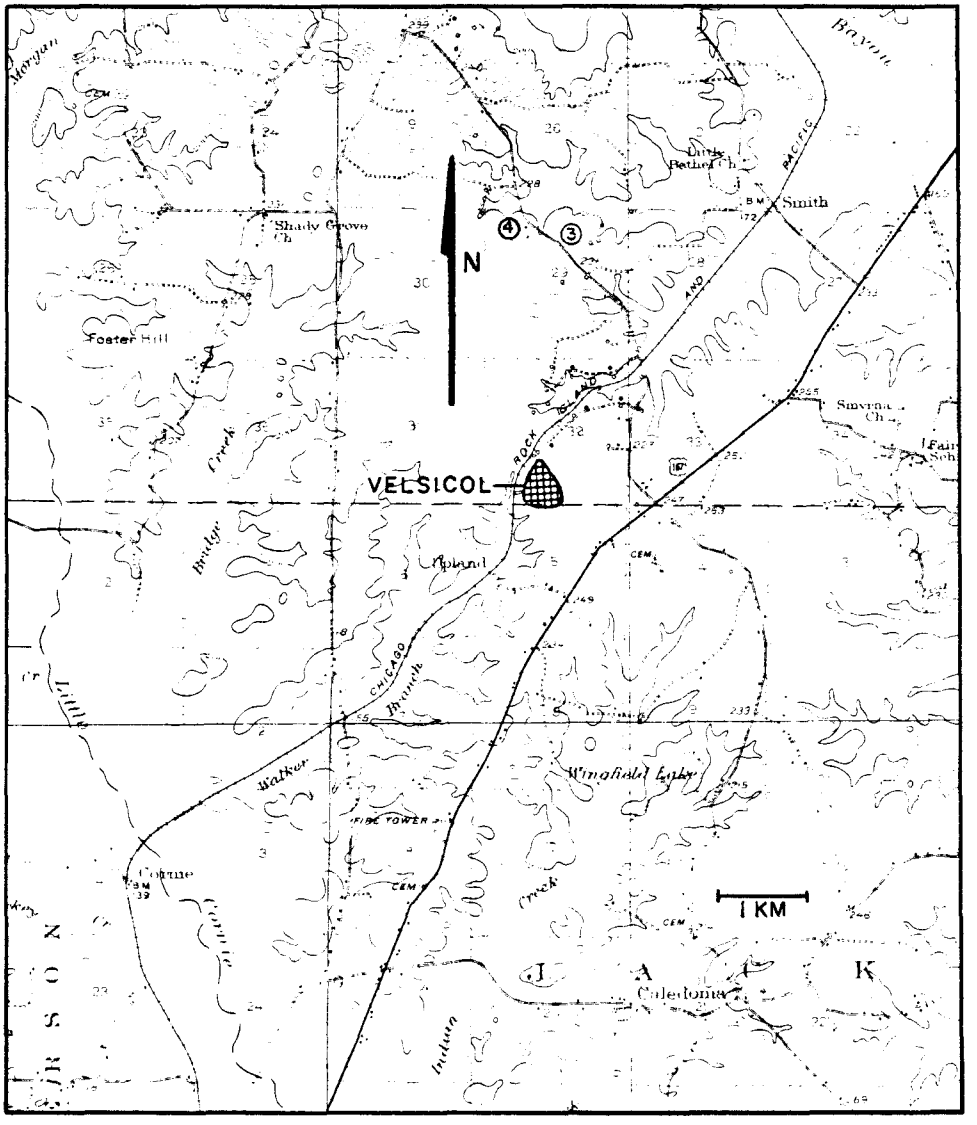



Figure 6.12. Map of the vicinity of Velsicol, Inc., El Dorado, Arkansas - Vegetation and miscellaneous sample locations (7/22/77 - 7/23/77).

Table 6.16. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING VELSICOL, INC., EL DORADO, AK

| Period/Cycle/Location[a] | Halide as $Cl^-$[b] $\mu g/m^3$ | Halogen as $Cl_2$[b] $\mu g/m^3$ |
|---|---|---|
| P1/C1/L1 | 83 ± 18 | 41 ± 10 |
| L3 | 27 ± 6 | 75 ± 45[c] |
| L4 | 51 ± 7 | 75 ± 30 |
| P2/C1/L1 | <21 | < 8 |
| L3 | 35 ± 7 | 81 ± 38[c] |
| L4 | <18 | <20 |
| P3/C1/L1 | <15 | <17 |
| L3 | 63 ± 8 | 219 ± 9 |
| L4 | <10 | <20 |
| P4/C1/L1 | < 8 | 41 ± 16 |
| L3 | 91 ± 8 | 158 ± 44[c] |
| L4 | <18 | 74 ± 21 |

[a]Refer to Table 6.12 for sampling protocol.

[b]Values are expressed as $Cl^-$ or $Cl_2$. However, if $Br^-$ or $Br_2$ is the predominant species, the values should be multiplied by 1.5.

[c]An amber color developed when $AgNO_3$ was added in the procedure.

Table 6.17. AMBIENT AIR LEVELS OF VOLATILE BROMINATED ORGANICS SURROUNDING VELSICOL CHEMICAL CORP., EL DORADO, AK[a]

| Period/Cycle/Location | 1,2-Dibromoethane | Dibromochloro-propane | Bromoform | 1-Chloro-3-bromo-propane | Bromodichloro-methane | Allyl bromide | Bropropanes | Dibromopropanes | Chlorodibromo-methane | Dibromomethane |
|---|---|---|---|---|---|---|---|---|---|---|
| P1/C1/L1 | 493 | 93 | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 227 ± 45 | 174 | T | ND | ND | ND | ND | ND | 8.4 ± 2.8 | ND |
| L3 | 501 | 7.8 | T | ND | ND | ND | ND | ND | ND | ND |
| L4 | 45 | 34 | ND | ND | ND | ND | ND | ND | T | ND |
| L5 | 448 | 14 | ND | ND | ND | ND | ND | ND | 31 | ND |
| P2/C1/L1 | T | 12 | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 868 | 187 | T | ND | ND | ND | ND | ND | T | ND |
| L3 | T | 37 | ND | ND | ND | ND | ND | ND | ND | ND |
| L4 | 280 | 32 | T | ND | ND | ND | ND | ND | T | ND |
| L5 | 120 | T | ND | ND | ND | ND | ND | ND | 22 | ND |
| P3/C1/L1 | T | ND | T | ND | ND | ND | ND | ND | T | ND |
| L2 | T | T | ND | ND | ND | ND | ND | ND | 23 | ND |
| L3 | 2,425 | T | T | ND | ND | ND | ND | ND | ND | ND |
| L4 | ND | T | ND | ND | ND | ND | ND | ND | 81 | ND |
| L5 | 342 | T | ND | ND | ND | ND | ND | ND | ND | ND |
| P4/C1/L1 | 67 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L3 | 193 | T | ND | ND | ND | ND | ND | ND | ND | ND |
| L4 | 171 | T | ND | ND | ND | ND | ND | ND | ND | ND |

[a]Values are in $ng/m^3$

Table 6.18. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING VELSICOL CHEMICAL INC.

| Period/Cycle/Location | ppm Ethylene |
|---|---|
| P1/C1/L1 | 0.6 |
| P1/C1/L2 | 3.8 |
| P1/C1/L6 | 2.3 |
| P1/C1/L7 | 6.8 |
| P1/C1/L8 | 5.3 |
| Lab-1[a] | 0.1 |
| Lab-2[a] | 2.2 |
| Field-1[b] | 0.3 |
| Field-2[b] | 0.9 |
| Field-3[b] | 0.4 |
| Lab-1[a,c] | 3.8 |
| Lab-2[a,d] | 10.1 |
| Field-1[b,c] | 1.7 |
| Field-2[b,c] | 4.9 |
| Field-3[b,d] | 6.5 |
| Field-4[b,d] | 10.0 |

[a]Stored at 4°C in the laboratory.

[b]Transported to the sampling area and returned to the lab.

[c]Spiked with 0.9 ppm ethylene.

[d]Spiked with 9.7 ppm ethylene.

Table 6.19. BROMINATED ORGANICS FOUND ON GLASS FIBER FILTERS FROM HI-VOL SAMPLERS

| Period/Cycle/Location | Tetrabromobis-phenol A $ng/m^3$ | Firemaster 680 $ng/m^3$ | Tris(2,3-dibromo-propyl)phosphate $ng/m^3$ | Decabromobiphenyl ether $ng/m^3$ |
|---|---|---|---|---|
| P1/C1/L4 | 28[a,b] | 39[a,c] | 60[d] | ND |
| P2/C1/L4 | ND[a] | ND[a] | 44[d] | ND[a] |
| P3/C1/L4 | ND[a] | 172[a,c] | 51[d] | ND[a] |
| P4/C1/L4 | ND[a] | 183[a,c] | ND[d] | 72[a,c] |

[a] GLC/MS/COMP analysis in the multiple ion detection mode.

[b] Ion intensity ratio of m/e 529/531 was 1.42 vs. 1.48 for standard tetrabromobisphenol A.

[c] One ion monitored, no confirmation.

[d] Analysis by GLC/ECD. Results are uncorrected for recovery which was 87% at an equivalent to 27 $ng/m^3$ and 91% at an equivalent to 287 $ng/m^3$ of TRIS.

24 hr Hi-Vol air sample of 2000 $m^3$ was collected at RTI, RTP. Recoveries of 2 areas analyzed for TRIS are given in Table 6.20.

Table 6.20. TRIS RECOVERY STUDY

| Amount of TRIS added (µg) | Amount of TRIS found[a] (µg) | % Recovered |
|---|---|---|
| 11.1 | 10.2 | 91 |
| 1.04 | 0.90 | 87 |

[a]Analysis by GLC/ECD.

This filter was transported to the field and returned before analysis.

Water and Sediment.--Water samples P1/C1/L1 and P4/C1/L5 (see Table 6.13 and Figures 6.6 and 6.8) were analyzed by the VOA method for qualitative information. No brominated compounds were identified by this method.

Water and sediment samples from Velsicol were analyzed for semi-volatile brominated organics according to the protocol in Appendix A. The results are shown in Table 6.21. The TRIS found in the water sample P1/C1/L3 is indicative of water transport since the creek sampled is part of the Velsicol watershed. The origin of Firemaster 680 and TRIS at P4/C1/L5 is less obvious. This location is 1.5 km from the facility and airborne contamination may contribute. The watershed for this stream extends to within 0.6 km of the facility. At the time the sample was collected drought had reduced the stream to a pool approximately 2 x 5 m. The combination of airborne dispersion and collection and dispersion of runoff water may have resulted in the TRIS and Firemaster 680 levels observed.

Soil.--Qualitative analysis of soil samples near Velsicol Chemical Corp. was performed on two samples. The findings are presented in Table 6.22.

Analysis of soil samples was by GLC/MS/COMP according to the protocol in Appendix A. The results are given in Table 6.23. Soil sample P1/C1/L3 was further analyzed in the full scan mode. The results of the spectral interpretation are given in Table 6.24. Spectra of three peaks are included as Figures 6.13, 6.14, 6.15, and 6.16 along with the spectra of standards

Table 6.21. RESULTS OF ANALYSIS OF SEDIMENT AND WATER SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS - VELSICOL, INC., EL DORADO, ARKANSAS

| Period/Cycle/Location[a] | Sample Type | Tetrabromo-bisphenol A[b] µg/kg | Firemaster 680[c] µg/kg | Tris(2,3-dibromo-propyl)phosphate µg/kg |
|---|---|---|---|---|
| P1/C1/L1 | SD/HHC | 30[d] | 466[e] | ND[f] |
| | | | | 2600[g] |
| | W/HHC | | | ND[g] |
| P1/C1/L3 | SD/HHC | ND[f] | ND[f] | ND[f] |
| | W/HHC | | | 10[g] |
| P4/C1/L5 | SD/HHC | ND[f] | 10[h] | ND[f,g] |
| | W/HHC | | | 2[g] |

[a] See Table 6.13 and Figures 6.7 and 6.8.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] 1,2-bis(2,4,6-tribromophenoxy)ethane.

[d] Quantitation by gas chromatography-mass spectrometry with multiple ion detection. The ions 529 and 531 were monitored giving an intensity ratio of 1.57 for the sample compared to 1.5 ± 0.1 for standards under the same conditions.

[e] Quantitation by gas chromatography-mass spectrometry with multiple ion detection. The ion 357 and retention time were used for identification. This ion is not very specific; however, it is the most prominent in the mass spectrum of Firemaster 680.

[f] Not detected by gas chromatography-mass spectrometry with multiple ion detection.

[g] Quantitation by gas chromatography-electron capture detection.

[h] Quantitation by gas chromatography-mass spectrometry with multiple ion detection using three ions, m/e 690 and 688 which are very specific for Firemaster 680 although less sensitive than m/e 357.

Table 6.22. QUALITATIVE ANALYSIS OF VOLATILE HALOGENATED ORGANICS IN SOIL SAMPLES COLLECTED NEAR VELSICOL CHEMICAL CORPORATION, EL DORADO, AK

| Period/Cycle/Location | Halogenated Compounds Identified |
|---|---|
| P1/C1/L2 | bromobenzene<br>1-chloro-2,3-dibromopropane[a]<br>1,2-dichloroethane |
| P1/C1/L3 | None detected |

[a]Tentative identification

Table 6.23. RESULTS OF ANALYSIS OF SOIL SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS - VELSICOL, INC., EL DORADO, ARKANSAS

| Period/Cycle/Location[a] | Tetrabromo-bisphenol A[b] µg/Kg | Firemaster 680[c] µg/Kg | Tris(2,3-dibromo-propyl)phosphate µg/Kg |
|---|---|---|---|
| P1/C1/L2 | ND | 5900[d]<br>6400[e] | ND[k,l] |
| P1/C1/L3 | 130[f]<br>90[h] | 400[d]<br>330[h] | 100 - 500[g]<br>1300[i,j] |
| P1/C1/L5 | ND | ND | ND[k]<br>300[i] |
| P1/C1/L7 | 60[f] | <6 | ND[k,l] |
| P1/C1/L9 | ND | 166[d] | ND[k,l] |
| P1/C1/L10 | 118[f] | 253[d] | ND[k,l]<br>840[i,j] |
| P1/C1/L13 | ND | 68[d] | ND[k,l] |
| P2/C1/L14 | ND | 100[d] | ND[k,l] |

[a] See Table 1 and Figures 2 and 3 for location of samples.
[b] 2,2-Bis(dibromo-4-hydroxyphenyl)propane.
[c] 1,2-Bis(2,4,6-tribromophenoxy)ethane.
[d] This compound was quantitated by gas chromatography-mass spectrometry with multiple ion detection. Rentention time and the m/e 357 ion was used. Note should be made that this is not a particularly specific ion and may be subject to some interference.
[e] Quantitation by thin-layer chromatography - scanning spectro-densitometry.
[f] Quantitation is based on two ions, m/e 529 and 531 in the proper intensity ratio of 1.5 ± 0.1 (529/531).
[g] Quantitation and verification was attempted by gas chromatography-mass spectrometry with multiple ion detection. Three of the most prominent ions were used, m/e 419, 417 and 337. The standards gave ion intensities ratios of 0.8 ± 0.2; 1.0; 1.9 ± 0.2, respectively, compared to the sample intensity ratios of 0.4; 1.0; 3.8. This is not very good agreement and indicates further sample purification would be required for a rigorous confirmation.
[h] Confirmed by full scan gas chromatography-mass spectrometry. Additional ions were used for the quantitation of Firemaster 680 (m/e, 688 and 690).
[i] Quantitation by gas chromatography-electron capture.
[j] An attempt to gain additional confirmation by thin-layer chromatography with fluorescein indicator for bromine containing compounds indicated many bromocompounds. There were so many different compounds that no conclusions concerning TRIS could be made.
[k] Not detected by gas chromatography-mass spectrometry with multiple ion detection (< ~ 5000 µg/Kg).

Table 6.24. BROMINATED COMPOUNDS IDENTIFIED FROM GAS CHROMATOGRAPHY - MASS SPECTROMETRY ANALYSIS OF SOIL SAMPLE P1/C1/L3[a] FROM VELSICOL, INC., EL DORADO, ARKANSAS

| Retention[b] Time (min) | Compound |
|---|---|
| 0.19 | $C_{12}H_6Br_2O$ (tent.) |
| 0.33 | [m/e 360, 362; Br = 3] |
| 0.39 | $C_6H_2Br_4$ (tent.) and $C_9H_{14}O_4P\ Br_3$ (tent.) |
| 2.06 | $C_{15}H_{12}O_2\ Br_4$[2,2-Bis(dibromo-4-hydroxyphenyl)propane] |
| | $C_9H_{15}O_4P\ Br_6$[Tris(2,3-dibromopropyl)phosphate] |
| 3.33 | $C_{14}H_8O_2Br_6$[1,2-bis(2,4,6-tribromophenoxy)ethane] |
| 6.06 | $C_{12}H_5Br_5O$ (tent.)[c] and $C_{12}H_5Br_5$ (tent.)[c] |
| 6.59 | [m/e 690 ± 1, 576 ± 1 and 439 ± 1 containing halogens] |
| 6.86 | [m/e 626 ± 1, 609 ± 1, 594 ± 1, 576 ± 1, 429 ± 1 and 339 ± 1 containing halogens] |
| 7.06 | $C_{12}Br_{10}O$ [decabromobiphenyl ether] |

[a] See Table 6.14 and Figures 6.8 and 6.9 for sample location.
[b] Gas chromatography conditions: 2% OV-101 on Gas Chrom Q; column, 45 cm x 0.2 cm i.d.; 20 cc/min helium; initial temperature 220°C, programmed at 12°/min to 300°C.
[c] The identification represents the empirical formula for the highest mass observed in the mass spectrum; however, the higher brominated homologs in this series also give these ions. The retention time is similar to that of the octa- or nona- brominated biphenyl or biphenyl ether.

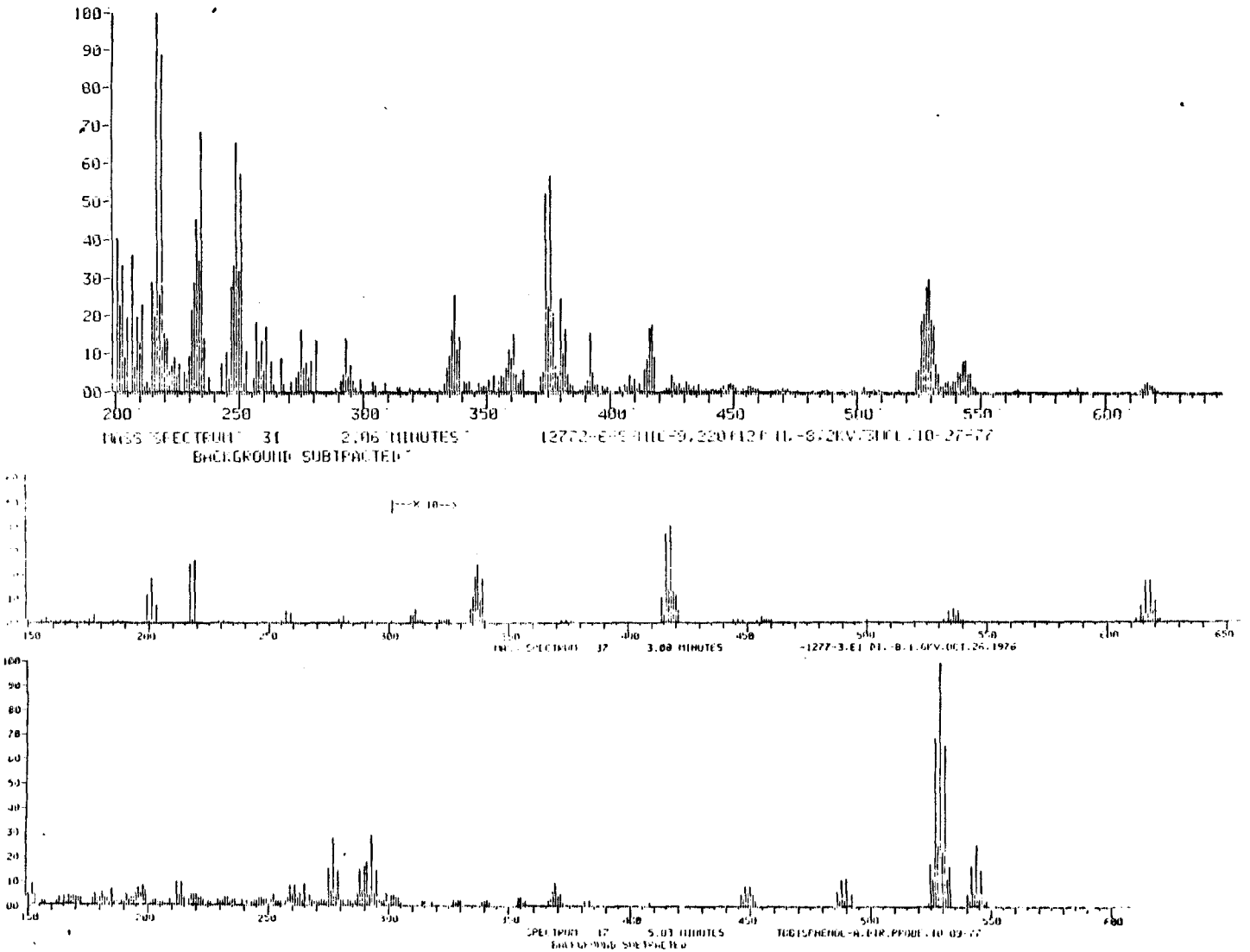



Figure 6.13. Mass spectrum of GC peak eluting at 2.06 min from soil sample L1/C1/L3. (a) Sample spectrum (GLC); (b) TRIS spectrum (Direct probe); (c) Tetrabrom spectrum (Direct probe).

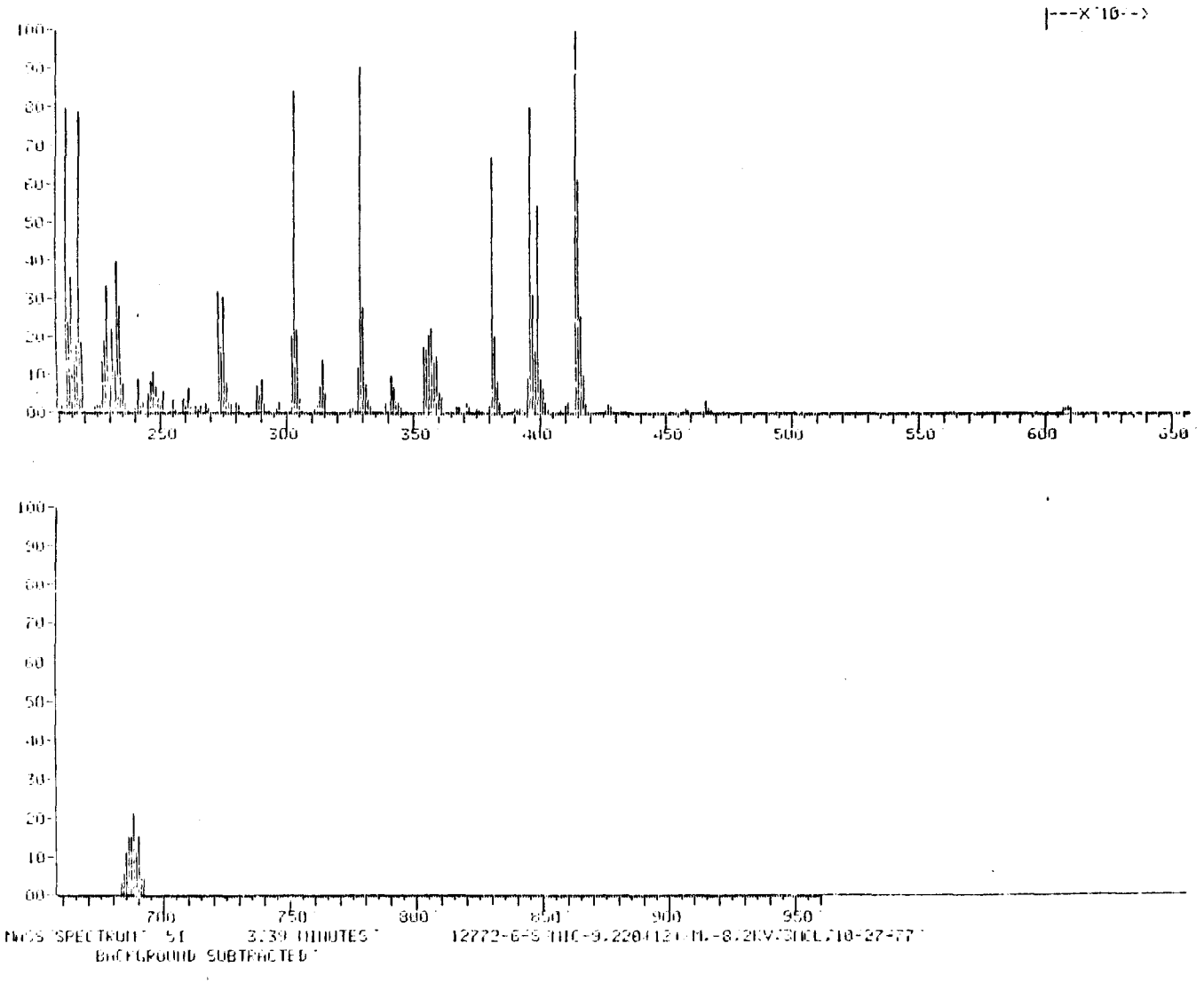



Figure 6.14. Mass spectrum of GC peak eluting at 3.4 min from soil sample P1/C1/L3.

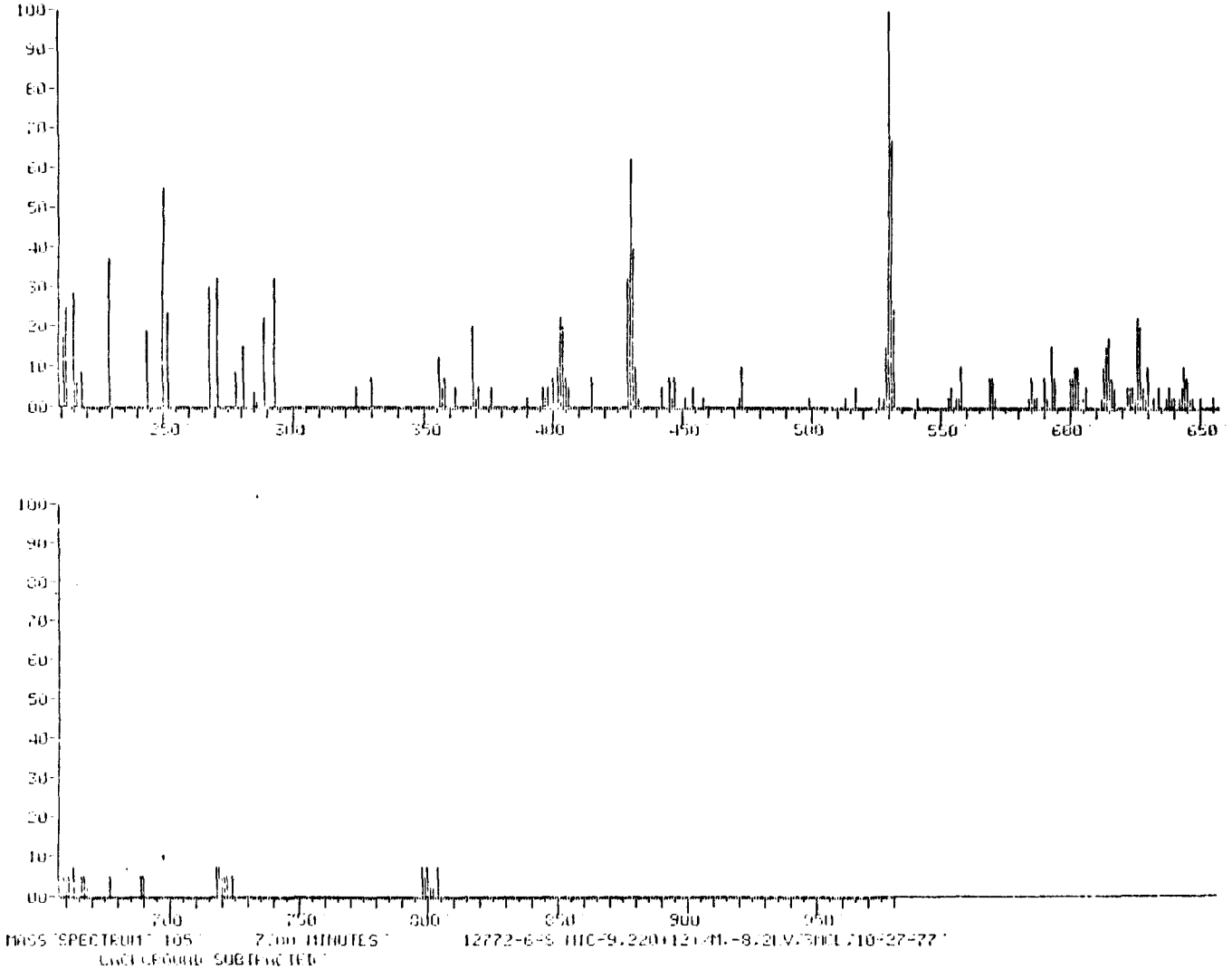



Figure 6.15. Mass spectrum of GC peak eluting at 7.00 min from soil sample P1/C1/L3 identified as decabrom•biphenyl ether.

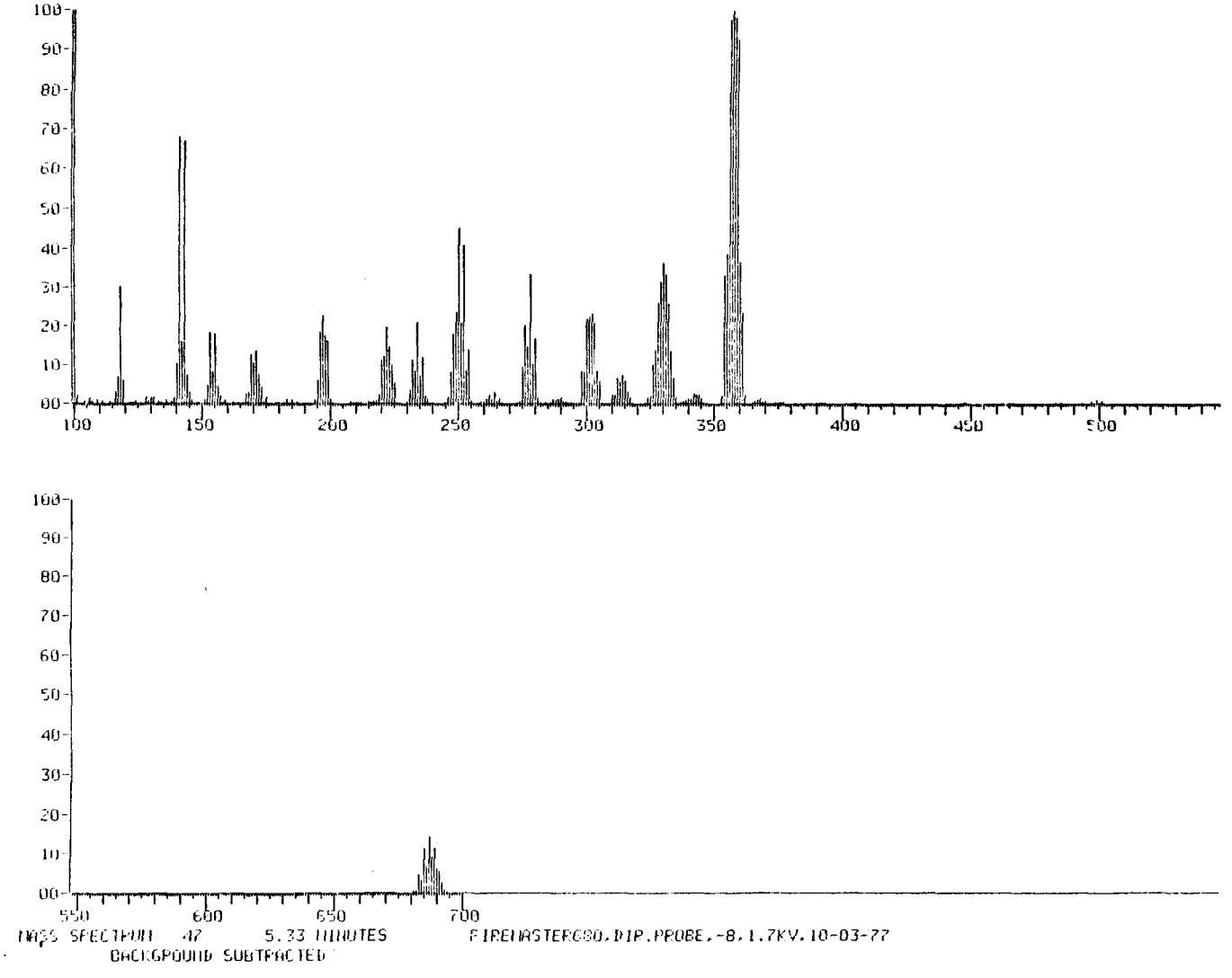



Figure 6.16. Mass spectrum of authentic Firemaster 680 (direct probe).

of the brominated compounds identified. This is the first occasion where TRIS could be confirmed by full scan rather than ion intensity ratios.

Soil sample P1/C1/L2 and P1/C1/L3 represent contamination by facility activities such as loading and processing the materials found. The samples at locations 5, 7 and 9, although within the facility, are not in areas obviously involved in processing or handling brominated compounds. Locations 10 and 14 are even more remote from the process area and there is no obvious activity which should lead to contamination except for airborne dispersion. (The watershed drains the opposite direction.)

6.2.3 Ethyl Corporation and Vicinity

6.2.3.1 Sampling

Table 6.25 presents the sampling protocol for ambient air surrounding Ethyl Corporation in Magnolia, AK. The corresponding air sampling locations for these periods are given in Figure 6.17.

6.2.3.2 Inorganics in Ambient Air

Table 6.26 presents the halides and halogens which were quantified in ambient air surrouding Ethyl Corporation. Relative to other bromine industrial units, the concentrations of halide and halogen which were detected at Ethyl Corporation were much lower and nearer the detection limit of the analytical methods.

6.2.3.3 Brominated and Other Organics

Air.--The ambient air levels for several volatile brominated organics surrounding Ethyl Corporation are given in Table 6.27. Only three brominated organics, ethylene dibromide, a bromopropane and 1-chloro-3-bromopropane were detected. The highest concentrations observed were for 1,2-dibromoethane which was generally at levels of 1-5 $\mu g/m^3$. No other brominated organics were detected in ambient air (Table 6.27).

Table 6.28 gives the concentrations of ethylene in ambient air that were detected at Ethyl Corporation. Except for Location 1 (9.8 ppm), the concentrations of ethylene were near background levels.

Soil.--No brominated organics were detected.

Table 6.25. AMBIENT AIR SAMPLING PROTOCOL SURROUNDING ETHYL CORP., MAGNOLIA, AK

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | Meteorological Conditions T(°C) | %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P1 (7/26/77) | C1 | L1 | 1620-0935 (7/27/77 | 99 | HHC[ab] | 17-33 | 50-90 | N,NE/6-10 | |
| | | L2 | 1655-1000 (7/27/77) | 126 | HHC[ab] | | | | |
| | | L3 | 1708-1018 (7/27/77) | 79 | HHC[ab] | | | | |
| P2 (7/27/77) | C1 | L1 | 0945-0845 (7/28/77) | 120 | HHC[ab] | 19-32 | 65-90 | E/5-6 (2 1/2 hrs) | |
| | | L2 | 1005-0900 (7/28/77) | 184 | HHC[ab] | | | N/7-20 (2 hrs.) | |
| | | L3 | 1020-1000 (7/28/77) | 113 | HHC[ab] | | | E to N shifting/4-6 (5 hrs) | |
| | | L4 | 1055-1012 (7/28/77) | ∿ 40 | HHC[ab] | | | N, NW/1-3 (12 1/2 hrs) | pump not fully functional |
| | | L1 | 0945-1400 | 181 | CBD,CBN[c] | | | | |
| | | L2 | 1005-1405 | 311 | CBD,CBN[c] | 19-34 | 65-92 | E/5-6 (2 1/2 hrs) | |
| | | L3 | 1020-1410 | 200 | CBD,CBN[c] | | | N/7-20 (2 hrs) | |
| | | L4 | 1045-1415 | 175 | CBD,CBN[c] | | | | |
| | | L1 | 0940 | 0.5 | VAC | | | | |
| | | L2 | 1000 | 0.5 | VAC | | | | |
| | | L3 | 1022 | 0.5 | VAC | | | | |
| | | L4 | 1040 | 0.5 | VAC | | | | |
| | | L5 | 1300 | 0.5 | VAC | | | | |
| | | L1 | 0940-0850 (7/28/77) | 1,475,000 | Hi-Vol | | | | |
| | | L2 | 1002-0900 (7/28/77) | 2,187,000 | Hi-Vol | | | | |
| P3 (7/28/77) | C1 | L1 | 0850-0845 (7/29/77) | 70 | HHC[ab] | 22-32 | 68-92 | SE to W/4-5 (4 hrs) | |
| | | L2 | 0915-0915 (7/29/77) | 177 | HHC[ab] | | | E to W/8-10 (7 hrs) | |
| | | L3 | 1002-1005 (7/29/77) | 118 | HHC[ab] | | | N, calm (7 hrs) with intermittant NE/5 (1 hr) and SE/8 (1 hr) SE/5 (2 hrs) | |
| | | L4 | 1035-0955 (7/29/77) | ∿210 | HHC[ad] | | | | battery dead at end of period |
| | | L1 | 0845-1245 | 167 | CBD,CBN[c] | | | | |
| | | L2 | 0930-1245 | 178 | CBD,CBN[c] | | | | |
| | | L3 | 0955-1420 | 225 | CBD,CBN[c] | | | | |
| | | L4 | 1010-1455 | 171 | CBD,CBN[c] | | | | |
| | | L1 | 0845 | 0.5 | VAC | | | | |
| | | L2 | 0900 | 0.5 | VAC | | | | |
| | | L3 | 0955 | 0.5 | VAC | | | | |
| | | L4 | 1010 | 0.5 | VAC | | | | near tank car marked allyl chloride |
| | | L6 | 1050 | 0.5 | VAC | | | | |
| | | L1 | 0855-0855 (7/29/77) | 1,467,000 | Hi-Vol | | | | |
| | | L2 | 1247-0905 (7/29/77) | 1,792,000 | Hi-Vol | | | | |

(continued)

Table 6.25 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | T(°C) | Meteorological Conditions %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| P4 (7/29/77) | C1 | L1 | 0900-1125 (7/30/77) | 126 | HHC[ab] | 19-32 | 60-92 | SW to W/9-12 (9 hrs) mostly calm (11 hrs) with occasional gust (S and SE at 3-5) S/4-15 (5 hrs) | |
| | | L2 | 0925-1130 (7/30/77) | 192 | HHC[ab] | | | | |
| | | L3 | 1015-1150 (7/30/77) | 118 | HHC[ab] | | | | |
| | | L4 | 1000-1150 (7/30/77) | <418 | HHC[ad] | | | | pump stopped |
| | | L1 | 0900-1315 | 170 | CBD,CBN[c] | | | SW to W/9-12 | upset at 0915, orange clouds moving toward location 1 |
| | | L2 | 0930-1350 | 187 | CBD,CBN[c] | | | | |
| | | L3 | 0830-1245 | 171 | CBD,CBN[c] | | | | |
| | | L4 | 0950-1405 | 177 | CBD,CBN[c] | | | | |
| | | L1 | 1340 | 0.5 | VAC | | | | |
| | | L2 | 1350 | 0.5 | VAC | | | | |
| | | L3 | 1415 | 0.5 | VAC | | | | |
| | | L4 | 1405 | 0.5 | VAC | | | | |
| | | L1 | 0900-1245 (7/30/77) | 1,673,000 | Hi-Vol | | | | |
| | | L2 | 0910-1205 (7/30/77) | 2,331,000 | Hi-Vol | | | | |

[a] DuPont sampler 3-6 ft elevation

[b] Overnight sampling

[c] Nutech Model 220 sampler 3-6 ft elevation

[d] A field adapted Walker Minnow aeration pump.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

Locations shown in Figure 6.17.

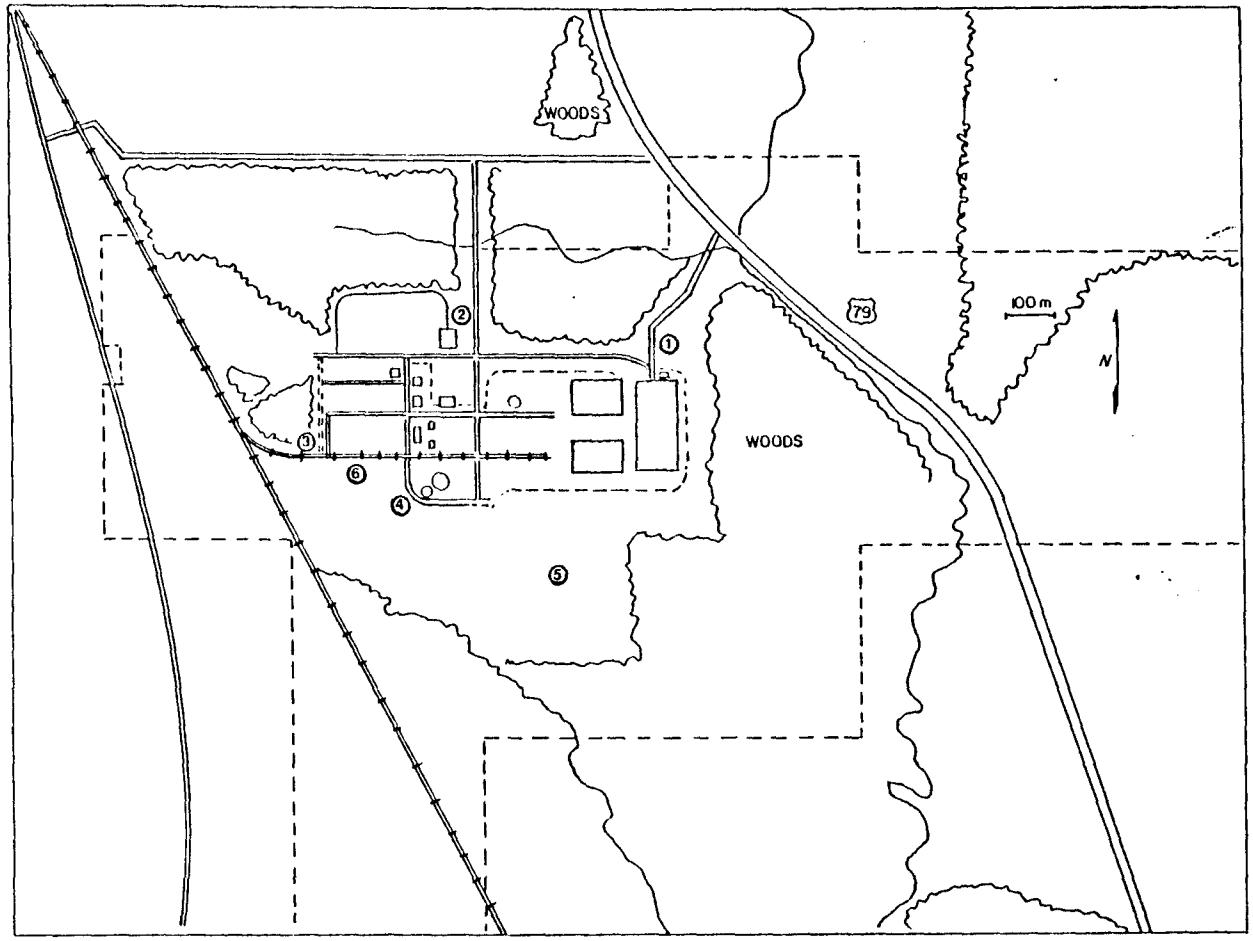



Figure 6.17. Schematic map of Ethyl Corporation, Magnolia, AK - Air sampling locations P1-P6 (7/26/77 through 7/30/77).

Table 6.26. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING ETHYL CORPORATION, MAGNOLIA, AK[a]

| Period/Cycle/Location | Halide as $Cl^{-}$[b] $\mu g/m^3$ | Halogen as $Cl_2$[b] $\mu g/m^3$ |
|---|---|---|
| P2/C1/L1 | <14 | <22 |
| L2 | 18 ± 12 | 19 ± 6 |
| L3 | <17 | <20 |
| L4 | 39 ± 20 | <22 |
| P3/C1/L1 | 36 ± 12 | 96 ± 36 |
| L2 | 45 ± 23 | 34 ± 23 |
| L4 | <12 | 46 ± 23 |
| P4/C1/L1 | 57 ± 23 | 45 ± 11 |
| L2 | <20 | 40 ± 20 |
| L4 | 41 ± 51 | 45 ± 22 |

[a] Refer to Table 6.25 for sampling protocol.

[b] Values are expressed as $Cl^{-}$ or $Cl_2$; however, if $Br^{-}$ or $Br_2$ is the predominant species, the values should be multiplied by 1.5.

Table 6.27. AMBIENT AIR LEVELS FOR SEVERAL VOLATILE BROMINATED ORGANICS SURROUNDING ETHYL CORP., MAGNOLIA, AK

| Period/Cycle/Location | 1,2-Dibromoethane | 1-Chloro-3-bromo-propane | Bromopropanes | Bromobenzene | 1-Chloro-2-bromo-ethane | Dibromochloro-propanes | Bromoform | Bromodichloro-methane | Allyl bromide | Dibromopropanes | Chlorodibromo-methane | Dibromomethane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1/C1/L1 | ND | T | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 2,957 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L3 | 216 | 39 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| P2/C1/L1 | 818 | 482 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 1,008 | 64 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L3 | 1,411 | 241 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L4 | 2,520 | 678 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| P3/C1/L1 | 1,638 | 36 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 1,868 | 14 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L3 | 26 | T | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L4 | 5,012 | T | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| P4/C1/L1 | 3,791 | 1,688 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L2 | 2,800 | 20 | 734 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L3 | 356 | ND | T | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| L4 | 2,366 | 171 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

Table 6.28. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING ETHYL CORPORATION, MAGNOLIA, AK

| Period/Cycle/Location | ppm Ethylene |
|---|---|
| P3/C1/L1 | 9.8 |
| P3/C1/L2 | 2.9 |
| P3/C1/L3 | 3.5 |
| P3/C1/L4 | 3.4 |
| P3/C1/L6 | 2.1 |
| Lab-1[a] | 0.1 |
| Lab-2[a] | 2.2 |
| Field-1[b] | 0.3 |
| Field-2[b] | 0.9 |
| Field-3[b] | 0.4 |
| Lab-1[a,c] | 3.8 |
| Lab-2[a,d] | 10.1 |
| Field-1[b,c] | 1.7 |
| Field-2[b,c] | 4.9 |
| Field-3[b,d] | 6.5 |
| Field-4[b,d] | 10.0 |

[a]Stored at 4°C in the laboratory.

[b]Transported to the sampling area and returned to the lab.

[c]Spiked with 0.9 ppm ethylene.

[d]Spiked with 9.7 ppm ethylene.

### 6.2.4 Dow Chemical Company and Vicinity

#### 6.2.4.1 Sampling

Table 6.29 gives the ambient air sampling protocol for Dow Chemical Company. Figures 6.18-6.20 depict the air sampling locations described in Table 6.29. Table 6.30 presents the sampling protocols for water and sediment for this area. Figure 6.21 depicts the sampling locations for water and sediment on and in the vicinity of Dow Chemical Co. in Magnolia. Table 6.31 lists the sampling protocols for soil and the locations are given in Figure 6.22.

#### 6.2.4.2 Inorganics in Ambient Air

The concentrations of halides and halogens determined in ambient air surrounding Dow Chemical Co. is given in Table 6.32. No halide was detected in any of these samples with a detection limit of ~5 $\mu g/m^3$. Relatively low concentrations of halogen were detected in samples at locations 3 and 4 during cycles 1 and 2.

#### 6.2.4.3 Brominated and Other Organics

Air.--Table 6.33 presents the concentrations of volatile brominated organics which were estimated in ambient air surrounding Dow Chemical Co. The most prevalent brominated species was 1,2-dibromoethane and the highest concentration observed was 62,848 $ng/m^3$ during the second sampling period at location No. 4. Included are the concentrations of styrene which were detected in the air samples taken at Dow Chemical Co. The most prevalent occurrence of styrene was observed at L2 during the third sampling period at which time it reached a level of 19,656 $ng/m^3$.

Table 6.34 presents the concentrations of ethylene in ambient air surrounding Dow. As indicated in this table, the levels of ethylene were generally near background concentrations.

Water and Sediment.--Water and sediment samples were analyzed by the VOA procedure given in Appendix A. The results are presented in Table 6.35. Among the sediment and water samples, P3/C1/L7 contained an extensive number of halogenated organics. These samples were taken in an area subject to overflow runoff from the settling ponds nearby.

Soil.--Soil samples were analyzed by the VOA procedure in Appendix A for the identification of halogenated organics. The results are given in Table 6.36.

Table 6.29. AMBIENT AIR SAMPLING PROTOCOL FOR DOW CHEMICAL CO., MAGNOLIA, AK

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | T(°C) | Meteorological Conditions %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| 8/1/77 P1 | C1 | L1 | 1055-0950 (8/2/77) | 169 | HHC[ab] | 17-32 | 70-90 | N,NE,NW,/2-7 | |
| | | L2 | 1130-1030 (8/2/77) | 89 | HHC[ab] | | | | |
| | | L3 | 1208-1100 (8/2/77) | 169 | HHC[ab] | | | | |
| | | L1 | 1045-1510 | 198 | CBN,CBD[c] | | | | |
| | | L3 | 1200-1535 | 168 | CBN,CBD[c] | | | | |
| | | L4 | 1150-1530 | 161 | CBN,CBD[c] | 30-32 | 70 | N,NW/5-7 | |
| | | L1 | 1045-1000 (8/2/77) | 1,520,000 | Hi-Vol[b] | | | | |
| | | L4 | 1210-1155 (8/2/77) | 1,996,000 | Hi-Vol[b] | | | | |
| 8/2/77 P2 | C1 | L1 | 1000-1005 (8/3/77) | 130 | HHC[ab] | 14-33 | 55-92 | NE,NW/2-9 | |
| | | L2 | 1040-1025 (8/3/77) | 77 | HHC[ab] | | | | |
| | | L3 | 1150-1105 (8/3/77) | 729 | HHC[cb] | | | | |
| | | L4 | 1110-1045 (8/3/77) | 75 | HHC[ab] | | | | |
| | | L5 | 1230-0945 (8/3/77) | 670 | HHC[cb] | | | | |
| | | L1 | 1015-1440 | 223 | CBN,CBD[c] | 27-33 | 60-80 | NE/9 | |
| | | L3 | 1155-1450 | 183 | CBN,CBD[c] | | | | |
| | | L4 | 1115-1455 | 169 | CBN,CBD[c] | | | | |
| | | L5 | 0955-1355 | 183 | CBN,CBD[c] | | | | |
| | | L3 | 1100-1040 (8/3/77) | 1,950,000 | Hi-Vol[b] | | | | |
| | | L5 | 1005-0950 (8/3/77) | 1,472,000 | Hi-Vol[b] | | | | |
| | | L1 | 1020 | - | VAC | | | | |
| | | L2 | 1030 | - | VAC | | | | |
| | | L3 | 1230 | - | VAC | | | | |
| | | L4 | 1200 | - | VAC | | | | |
| | | L5 | 1400 | - | VAC | | | | |

[ab] DuPont sampler 3-6 ft elevation
[b] Overnight sampling
[c] Nutech Model 220 sampler 3-6 ft elevation

Locations shown in Figures 6.18-6.20

Key to Sample Type:
HHC - Halogenated Hydrocarbon
CBN - Bromine and chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

(continued)

Table 6.29 (cont'd)

| Period | Cycle | Location | Sampling Time | Sampling Volume (ℓ) | Type of Sample | T(°C) | Meteorological Conditions %RH | Wind Direction Speed (kmph) | Other |
|---|---|---|---|---|---|---|---|---|---|
| 8/3/77 P3 | C1 | L1 | 1015-0830 (8/4/77) | 180 | HHC[ab] | 16-35 | 45-92 | E Var, NW/2-9 | |
| | | L2 | 1035-0840 (8/4/77) | 59 | HHC[ab] | | | | |
| | | L3 | 1120-0846 (8/4/77) | 640 | HHC[bc] | | | | |
| | | L4 | 1100-0900 (8/4/77) | 178 | HHC[ab] | | | | |
| | | L5 | 1000-0820 (8/4/77) | 652 | HHC[bc] | | | | |
| | | L1 | 1005-1615 | 302 | CBN,CBD[c] | 32-34 | 48 | E Var/5-8 | |
| | | L3 | 1045-1630 | 280 | CBN,CBD[c] | | | | Upset of $Br_2$ during at least the last 1/2 hr. Odor of $Br_2$ |
| | | L4 | 1100-1645 | 275 | CBN,CBD[c] | | | | |
| | | L5 | 0950-1600 | 287 | CBN,CBD[c] | | | | |
| | | L6 | 1600 | - | VAC | | | | |
| | | L3 | 1050-0850 (8/4/77) | 1,793,000 | Hi-Vol[b] | | | | |
| | | L5 | 1000-0825 (8/4/77) | 1,313,000 | Hi-Vol[b] | | | | |
| | C2 | L1 | 1625-0830 (8/4/77) | 506 | CBN,CBD[bc] | 16-34 | 45-92 | E/3-5 (4 hrs.) | Upset of $Br_2$ just before Sampling |
| | | L3 | 1640-0850 (8/4/77) | 424 | CBN,CBD[bc] | | | NW/<2 (12 hrs.) | |
| | | L4 | 1650-0900 (8/4/77) | 518 | CBN,CBD[bc] | | | | Odor noticeable, possibly HBr |
| | | L5 | 1615-0820 (8/4/77) | 392 | CBN,CBD[bc] | | | | |

[ab] DuPont sampler 3-6 ft elevation
[b] Overnight sampling
[c] Nutech Model 220 sampler 3-6 ft elevation

Location shown in Figures 6.18-6.20

Key to Sample Type:
HHC - Halogenated Hydrocarbon
CBN - Bromine and chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

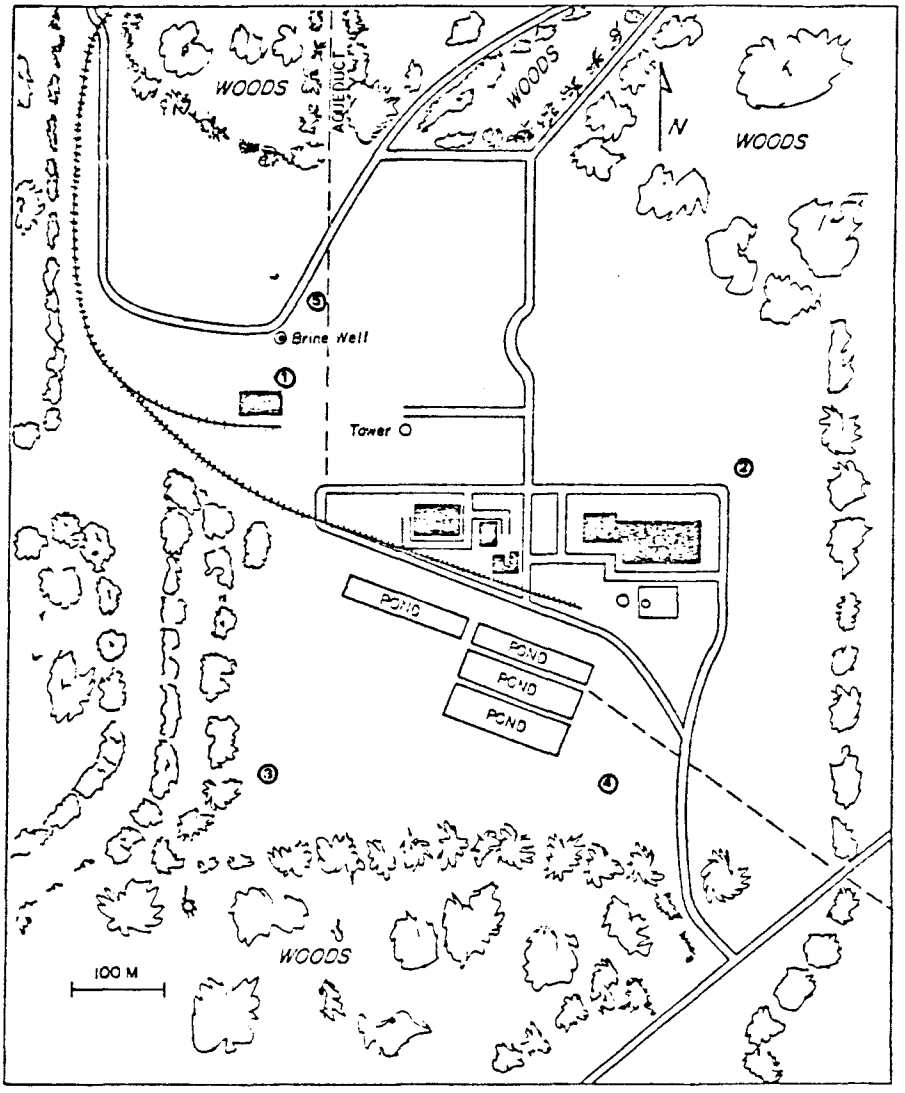



Figure 6.18. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P1 - 8/1/77

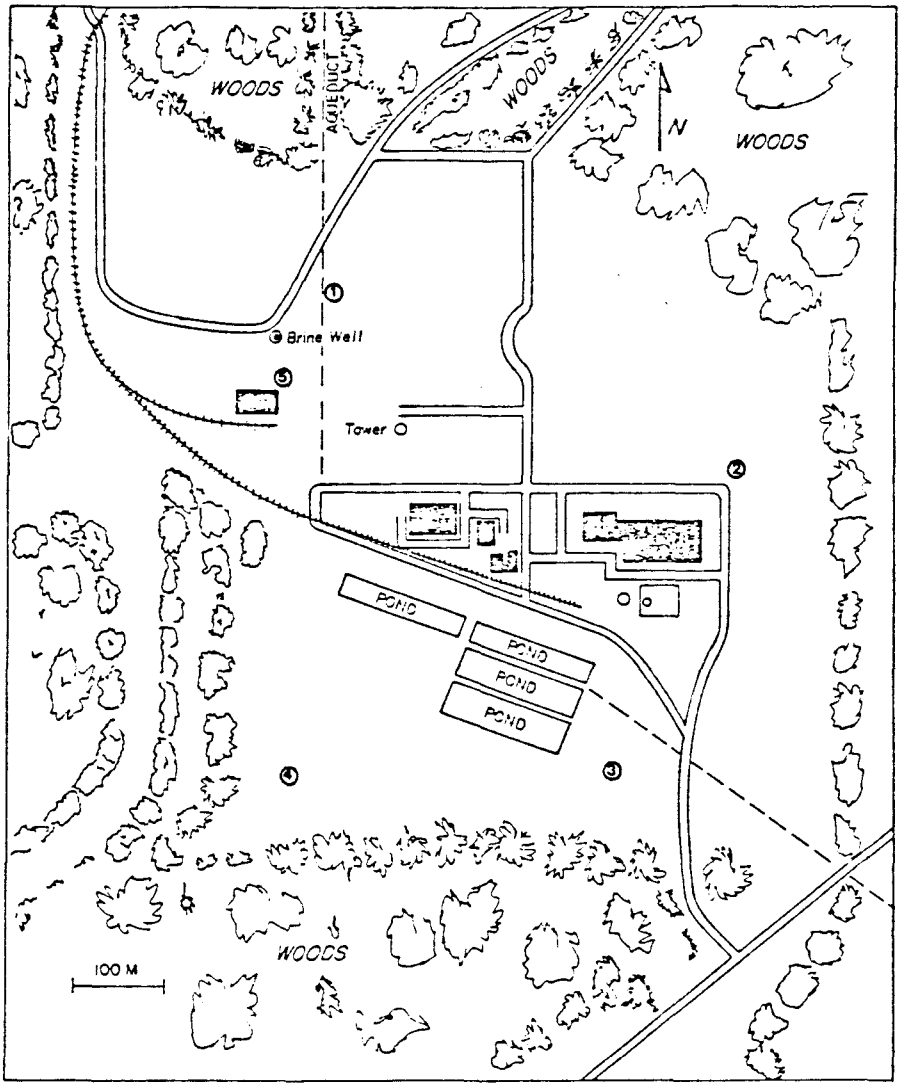



Figure 6.19. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P2 - 8/2/77.

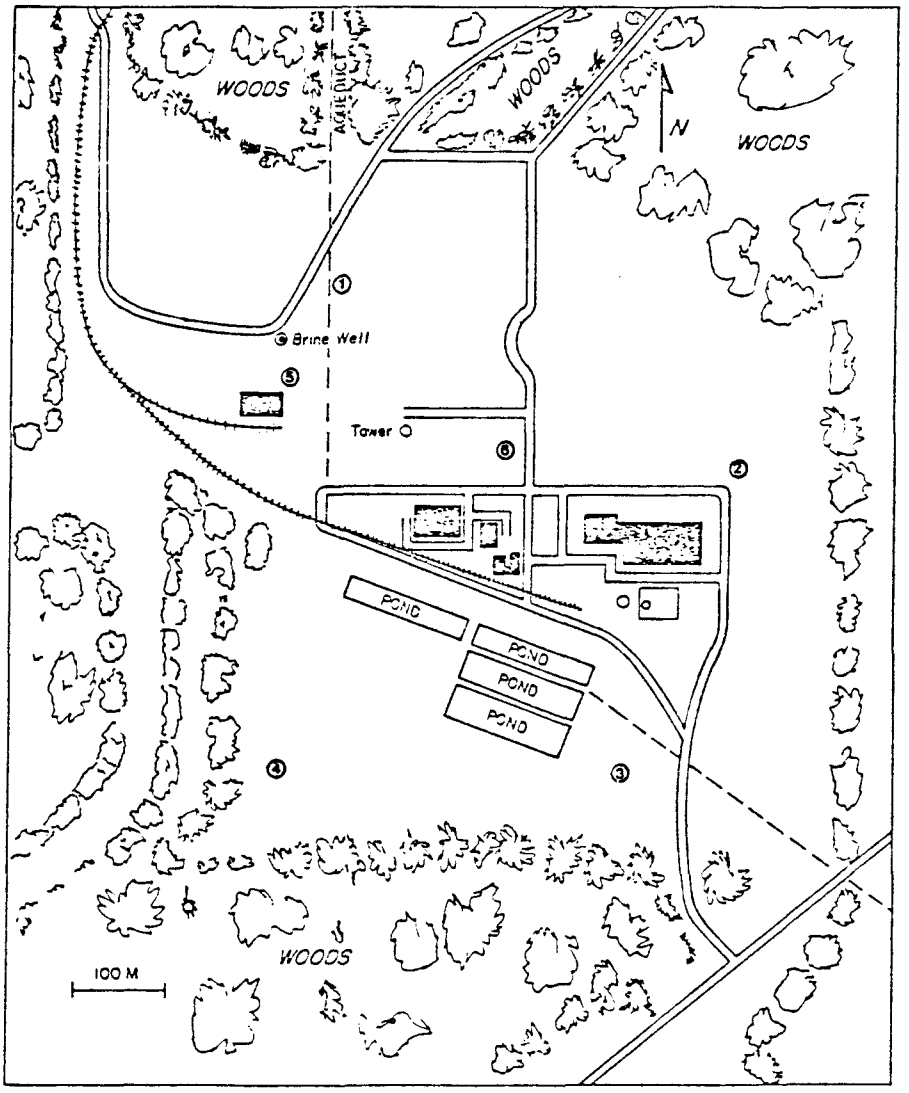



Figure 6.20. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P3 - 8/3/77

Table 6.30. WATER AND SEDIMENT SAMPLING PROTOCOLS FOR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS

| Period | Cycle | Location | Sample Type | Sample Size | Comments |
|---|---|---|---|---|---|
| P1 | C1 | L1 | W/HHC | 2 ℓ | water from small pond - runoff after rain |
| 7/30/77 | | L2 | W/HHC | 2 ℓ | pond water |
| | | | SD/HHC | 2 ℓ | pond sediment (drainage from pond) |
| | | L3 | W/HHC | 2 ℓ | drainage from pond |
| | | L4 | W/HHC | 2 ℓ | stream water |
| | | | SD/HHC | 2 ℓ | stream sediment |
| P2 | C1 | L5 | W/HHC | 2 ℓ | runoff (after rain) from Dow settling ponds |
| 8/1/77 | | L6 | W/HHC | 2 ℓ | stream water |
| P3 | C1 | L7 | W/HHC | 2 ℓ | standing water |
| 8/2/77 | | | SD/HHC | 2 ℓ | |
| | | L8 | W/HHC | 2 ℓ | stream water |
| | | L9 | W/HHC | 2 ℓ | small stream |
| P4 | C1 | L10 | W/HHC | 2 ℓ | pond beside road |
| 8/3/77 | | | SD/HHC | 2 ℓ | pond beside road |
| | | L11 | W/HHC | 2 ℓ | very slow stream |

Locations are shown in Figure 6.21.
W = water samples
SD = sediment samples
HHC = for halogenated hydrocarbon analysis

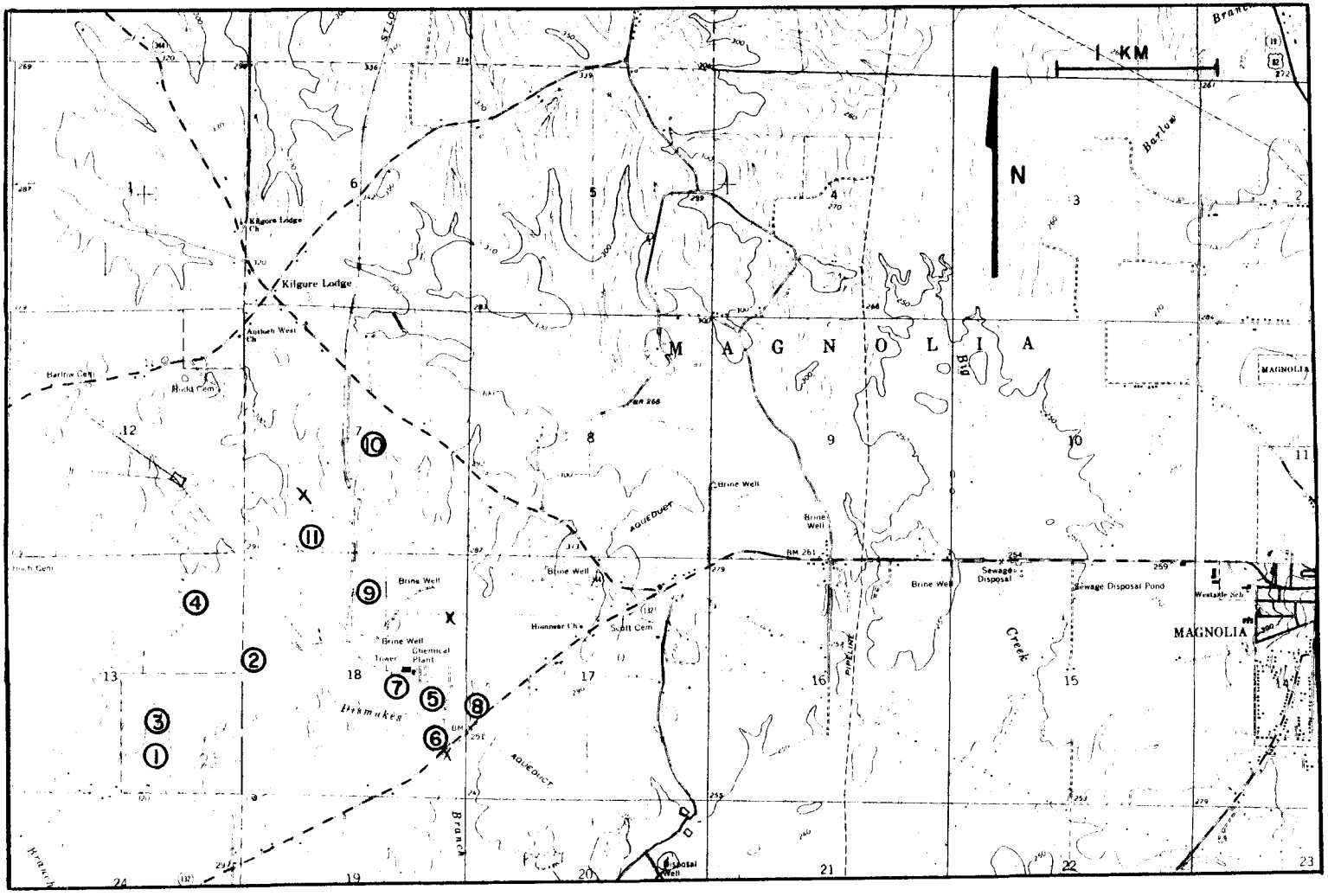



Figure 6.21. Water sampling locations in the vicinity of Dow Chemical Co., Magnolia, Arkansas (7/29/77 - 8/3/77).

Table 6.31. SOIL SAMPLING PROTOCOLS FOR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS[a]

| Period | Cycle | Location | Sample Size | Comments |
|---|---|---|---|---|
| P1 | C1 | L1 | 2 cores | |
| 7/30/77 | | L2 | 2 cores | Box Springs Road |
| P3 | C1 | L3 | 2 cores | Near air sampler |
| 8/2/77 | | L4 | 2 cores | Near air sampler |
| | | L5 | 2 cores | At NE corner of drive into plant |
| | | L6 | 2 cores | Rt. 344 at Rt. 132 |

[a]Locations of sampling are shown in Figure 6.22.

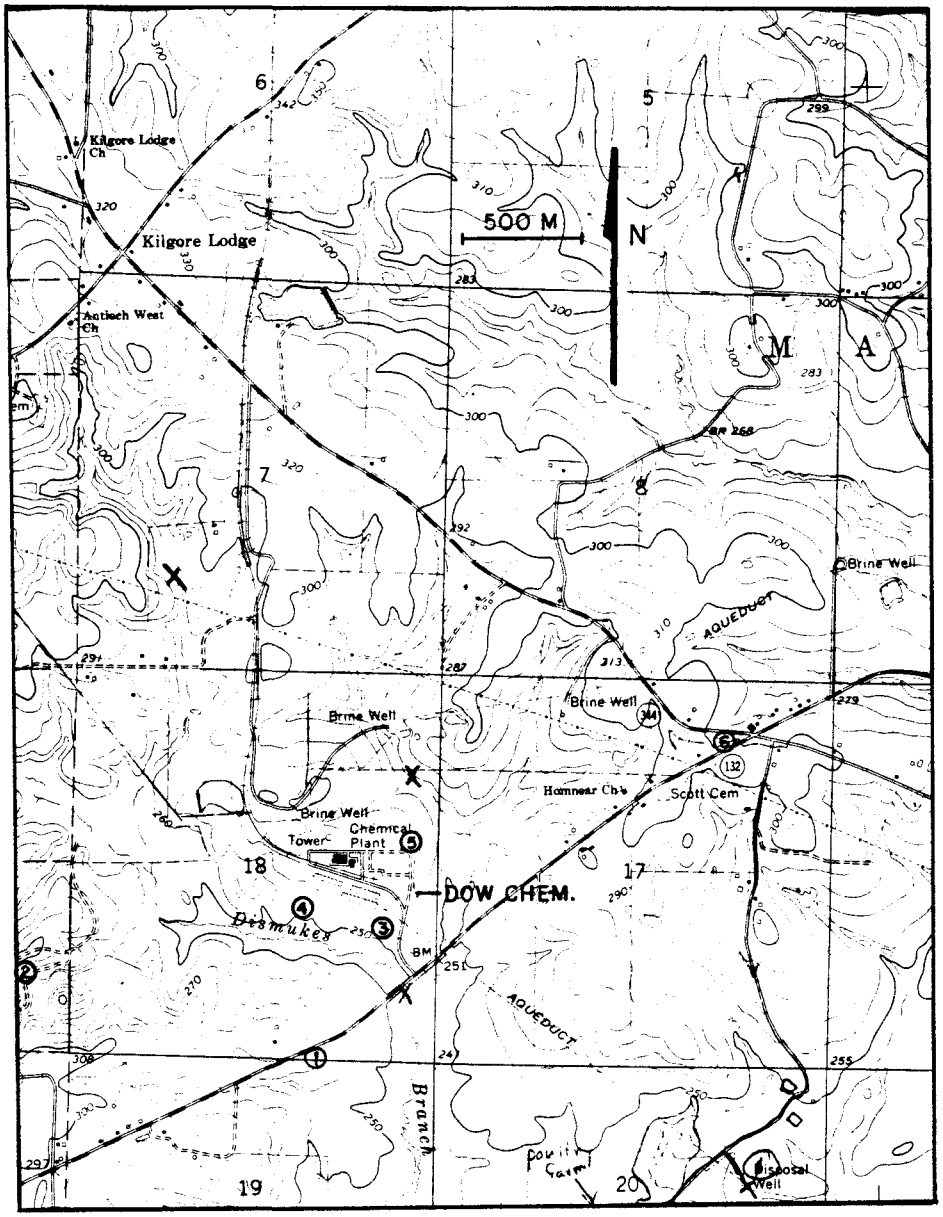



Figure 6.22. Sampling locations for soil samples collected in the vicinity of Dow Chemical Co. (7/30/77 - 8/2/77).

Table 6.32. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING DOW CHEMICAL COMPANY MAGNOLIA, AK

| Period/Cycle/Location[a] | Halide as $Cl^{-}$[b] $\mu g/m^3$ | Halogen as $Cl_2$[b] $\mu g/m^3$ |
|---|---|---|
| P3/C1/L2 | < 5 | < 12 |
| L3 | < 5 | 64 ± 5 |
| L4 | < 6 | < 6 |
| P3/C2/L2 | < 5 | < 10 |
| L3 | < 6 | 14 ± 7 |
| L4 | < 4 | 18 ± 9 |

[a] Refer to Table 6.29 for sampling protocol.

[b] Values are expressed as $Cl^{-}$ or $Cl_2$; however, if $Br^{-}$ or $Br_2$ is the predominant species, the values should be multiplied by 1.5.

Table 6.33. ESTIMATED LEVELS OF VOLATILE BROMINATED ORGANICS IN AMBIENT AIR SURROUNDING DOW CHEMICAL CO., MAGNOLIA, AK[a]

| Period/Cycle/Location | Bromobenzene | 1-Chloro-2-bromo-ethane | 1,2-Dibromoethane | Dibromochloropropane | Bromoform | 2-Chloro-3-bromo-propane | Dibromopropane | Dibromochloro-methane | Styrene |
|---|---|---|---|---|---|---|---|---|---|
| P1/C1/L1 | ND | ND | 62 | 25 | ND | ND | ND | ND | 907 |
| L2 | ND | ND | 462 | 75 | ND | ND | ND | ND | 694 |
| L3 | ND | 445 | 40,415 | 1,996 | 8 | ND | ND | ND | 12,158 |
| P2/C1/L1 | ND | ND | 1,509 | 99 | ND | ND | T | ND | 1,103 |
| L2 | ND | ND | ND | ND | ND | ND | ND | ND | |
| L3 | ND | 163 | 30,156 | 624 | ND | ND | T | ND | 10,016 |
| L4 | ND | 1,089 | 62,484 | 6,653 | ND | ND | T | ND | 15,978 |
| L5 | ND | 32 | 14,028 | 300 | ND | ND | T | ND | 1,758 |
| P3/C1/L1 | ND | ND | 179 | 36 | ND | ND | T | ND | 960 |
| L2 | 66 | ND | 1,744 | 100 | 380 | ND | ND | ND | 19,656 |
| L3 | 23 | 304 | 30,172 | 795 | ND | ND | ND | ND | 5,089 |
| L4 | 140 | 251 | 921 | 188 | ND | ND | T | ND | 130 |
| L5 | 35 | 403 | 59,438 | 2,002 | 50 | ND | T | ND | 14,272 |

[a]Concentrations are in $ng/m^3$.

Table 6.34. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING DOW CHEMICAL CO.

| Period/Cycle/Location | ppm Ethylene |
|---|---|
| P2/C1/L1 | 1.6 |
| P2/C1/L2 | 2.4 |
| P2/C1/L3 | 1.8 |
| P2/C1/L4 | 2.2 |
| P2/C1/L5 | 1.9 |
| Lab-1[a] | 0.1 |
| Lab-2[a] | 2.2 |
| Field-1[b] | 0.3 |
| Field-2[b] | 0.9 |
| Field-3[b] | 0.4 |
| Lab-1[a,c] | 3.8 |
| Lab-2[a,d] | 10.1 |
| Field-1[b,c] | 1.7 |
| Field-2[b,c] | 4.9 |
| Field-3[b,d] | 6.5 |
| Field-4[b,d] | 10.0 |

[a]Stored at 4°C in the laboratory.

[b]Transported to the sampling area and returned to the lab.

[c]Spiked with 0.9 ppm ethylene.

[d]Spiked with 9.7 ppm ethylene.

Table 6.35. QUALITATIVE ANALYSIS OF WATER AND SEDIMENT SAMPLES COLLECTED NEAR DOW CHEMICAL COMPANY, MAGNOLIA, AK

| Period/Cycle/Location | Sample Medium | Halogenated Compounds Identified[a] |
|---|---|---|
| P1/C1/L2 | water | ND[b] |
| L4 | water | ND |
| P2/C1/L5 | water | tetrachloroethylene |
| P3/C1/L7 | water | bromopropene<br>1,2-dichloroethane<br>dibromoethene<br>trichloroethene<br>chlorobromoethane<br>1,2-dibromoethane<br>chlorobutene<br>bromodichloropropane<br>1-chloro-2,3-dibromopropane |
| | sediment | bromobenzene<br>bromoform<br>1,2-dibromoethane<br>1-chloro-2-bromoethane[c]<br>1-chloro-2,3-dibromopropane[c]<br>1,2-dichloroethane[c] |
| P4/C1/L11 | water | 1,2-dichloroethane[c] |

[a] Analysis by VOA method with GC/MS/COMP detection.

[b] None detected.

[c] Tentative identification.

Table 6.36. QUALITATIVE ANALYSIS OF SOIL SAMPLES COLLECTED NEAR DOW CHEMICAL COMPANY, MAGNOLIA, AK

| Period/Cycle/Location | Halogenated Compounds Identified[a] |
|---|---|
| P1/C1/L1 | ND[b] |
| L2 | 1,2-dichloroethane |
| P3/C1/L3 | chloroform |
| L4 | ND |
| L5 | 1,2-dichloroethane[c] |
| L6 | ND |

[a]Analysis by VOA method with GC/MS/COMP detection.

[b]None detected.

[c]Tentative identification.

### 6.2.5 Samples from Human Population

#### 6.2.5.1 Sampling

Samples of human hair were obtained from El Dorado and Magnolia barber shops (Table 6.37). In order to obtain enough material for analysis, composite samples were made.

In conjunction with a local pediatrician (Dr. James Sykes), human placenta and cord were obtained from six deliveries in El Dorado, AK during the period of July 22 to August 5, 1977.

#### 6.2.5.2 Brominated Organics

Composites of human hair from each of the barber shops were analyzed as three separate samples (Table 6.38). Two of the three composites had detectable quantities of Decarbrom. Since the three composites surveyed a total of ~40 individuals, these findings mean that a minimum of 5% (2 out of 40) of the population had detectable levels of Decabrom. Tetrabrom was confirmed in one sample but interferences prevented confirmation in either of the other two composites.

Eight of the placenta samples were extracted and four were submitted to GC/MS/COMP analysis. The level of background was so high that mg/kg concentrations would have had to be present for detection. No brominated compounds could be identified in these samples. Further purification would no doubt improve the sensitivity of the analysis.

## 6.3 QUALITY ASSURANCE

The validity of the data generated under this task depended directly upon the quality of the analytical procedures. As such, a strict quality assurance program was established as discussed below. The heart of the quality assurance program was the division of the task into subtasks which focused upon the medium or analysis to be performed. Each subtask had a leader who was responsible for its execution including method validation, sampling, sample analysis, quality control, and data interpretation. The definite delineation of responsibilities reduced the chances of error through poor communication.

### 6.3.1 Analytical Protocol Validation

Depending on the exact nature of the analytical scheme, each step of a protocol was validated through the use of blanks and spiked samples. The

Table 6.37. SAMPLING PROTOCOL FOR SAMPLES OF THE HUMAN POPULATION

| Period | Cycle | Location | Site | Sample Type | Comments |
|---|---|---|---|---|---|
| P1 7/23/77 | C1 | L1 | El Dorado | Hair | approximately 16 individuals |
| | | L2 | El Dorado | Hair | approximately 20 individuals |
| | | L3 | El Dorado | Hair | 7 individuals |
| P2 7/27/77 | C1 | L1 | Magnolia | Hair | unknown number of individuals |
| P3 7/30/77-8/4/77 | C1 | L1 | Union County Hospital | Placenta/ Cord | tissue from normal deliveries at the hospital during the period shown |
| | | L2 | | | |
| | | L3 | El Dorado | | |
| | | L4 | | | |
| | | L5 | | | |
| | | L6 | | | |
| | | L7 | | | |
| | | L8 | | | |

Table 6.38. ANALYSIS OF HUMAN HAIR COLLECTED IN EL DORADO, ARKANSAS FOR SEMI-VOLATILE BROMINATED ORGANICS[a]

| Period/Cycle/Location | Tetrabromobisphenol A[c] (μg/Kg) | Decabromobiphenyl ether (μg/Kg) |
|---|---|---|
| P7/C1/L14 | 2.0[d] | 5[e] |
| P7/C1/L15 | >13[f] | 0.3[g] |
| P7/C1/L16 | >0.7[f] | ND[h] |

[a]Quantitation by gas chromatography/mass spectrometry using multiple ion detection.

[b]See Table 6.37 for protocol.

[c]2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[d]The two ions, 528 and 530, were observed at the correct gc retention time with the correct intensity ratio, 1.6 vs. 1.5 for the standard.

[e]Confirmed by full scan gas chromatography/mass spectrometry.

[f]The two ions, 528 and 530, were observed at the correct gc retention time; however, the ion intensity ratios were 2.3 and 0.94 for P7/C1/L15 and P7/C1/L16, respectively, compared to 1.5 for the standard. These samples would require further purification in order to determine whether tetrabromobisphenol A is or is not present.

[g]Unconfirmed.

[h]Not detected - approximately 0.1 μg/g is required to detect this compound.

validations were conducted using sufficient replication to provide statistically reliable recovery data.

The specific details of the validation experiments and their results are discussed in Section 3.0.

6.3.2 Field Sampling Quality Assurance

6.3.2.1 Quality Control Samples

Blank and spiked samples were created to assure that compounds identified in field samples are not artifacts and to assure that compounds collected in the field are retained in the sample through storage and analysis. For most of the sample matrices, duplicate blank and spiked samples were taken to the field to approximate the conditions to which the samples were subjected. In addition, duplicate blank and control samples remained in the laboratory to monitor storage efficiency and to provide a crosscheck on the field blank and control samples. Blanks and control samples for each medium are summarized in Table 6.39.

6.3.2.2 Sample Identification Protocol

During sample collection, a sample data sheet (Figures 6.23 and 6.24) was maintained for each sample. The sampling locations for each sampling period were recorded on a detailed area map. The coded form contained information such as date and time of sampling, locations, sampling parameters and meteorological information. The alpha-numeric sample code was also fixed directly to the sample container at that time.

Following each day's sample collection, the protocol sheets and sample labels were independently reviewed by two field personnel to assure that all information was logged in, that the codes were self-consistent and that there was no duplication. Upon returning to the laboratory, the samples were again checked for proper labeling.

6.3.2.3 Sample Containers

Sample containers were selected for inertness and ability to maintain sample integrity. Screw caps were lined with foil or teflon and plastic bags were made of Tedlar®. No polyethylene or other standard commercial plastic was allowed to come in contact with the samples. Prior to field sampling, each container was scrupulously cleaned as discussed in Section 3.3.3.1.

Table 6.39. INVENTORY OF CONTROLS AND BLANKS FOR QUALITY ASSURANCE FOR ARKANSAS FIELD SAMPLING - JULY AND AUGUST, 1977

| Sample Type | Blanks | | Controls | | Compound | Concentrations |
|---|---|---|---|---|---|---|
| | Laboratory | Field | Laboratory | Field | | |
| Charcoal cartridges | 2 | 7 | 2 | 8 | methyl chloride | 309 ng |
| | | | | | methyl bromide | 100 ng |
| | | | | | vinyl chloride | 254 ng |
| | | | | | vinyl bromide | 250 ng |
| Tenax cartridges | 2 | 3 | 2 | 4 | perfluorobenzene ‡ | 201 ng |
| | | | | | perfluorotoluene ‡ | 85 ng |
| | | | | | ethylene dibromide | 350 ng |
| | | | | | bromobenzene | 250 ng |
| | | | | | 1,2-dibromopropane | 304 ng |
| | | | | | 1-bromo-2-chloroethane | 308 ng |
| | | | | | dibromomethane | 150 ng |
| | | 2 | | 2 | perfluorobenzene ‡ | 250 ng |
| | | | | | perfluorotoluene ‡ | 105 ng |
| | | | | | dibromomethane | 155 ng |
| | | | | | 1,2-dibromopropane | 314 ng |
| | | | | | 1-bromo-2-chloroethane | 320 ng |
| Vacuum canisters | 2 | 3 | 3 | 4 | methyl chloride | 6, 60 and 300 ppb |
| | | | | | methyl bromide | 35, 350 and 1750 ppb |
| | 2 | 3 | 2 | 4 | ethylene | 0.884 and 9.72 ppm |
| | | | | | ethane | 0.880 and 9.69 ppm |
| Impinger solutions | 4 | 4 | 8 | 8 | chloride, bromide in deionized water | 0.5 and 1.0 ppm each ion |
| | 4 | 4 | 8 | 8 | chloride, bromide in alkaline arsenite solution | 0.5 and 1.0 ppm each ion |

(continued)

Table 6.39 (cont'd)

| Sample Type | Blanks | | Controls | | Compound | Concentrations |
|---|---|---|---|---|---|---|
| | Laboratory | Field | Laboratory | Field | | |
| Glass fiber filters | 2 | 3 | | 2 | tetrabromobisphenol A | 49, 198, 260, 520 ng/cm$^2$ |
| | | | | | decabromobiphenyl ether | 49, 198, 260, 520 ng/cm$^2$ |
| | | | | | tris-(2,3 dibromopropyl) phosphate | 101, 202, 540, 1080 ng/cm$^2$ |
| Water | 2[a] | 3[a] | 2 | 4 | 1-chloro-1-butene | 1 and 5 µg/100 ml |
| | | | | | 1,2-dichloroethane | 1 and 5 µg/100 ml |
| | | | | | 1-bromo-2-chloroethane | 1 and 5 µg/100 ml |
| | | | | | 1,2-dibromoethane | 1 and 5 µg/100 ml |
| | | | | | bromobenzene | 1 and 5 µg/100 ml |
| | | | | | m-chlorotoluene | 1 and 5 µg/100 ml |
| | | | 2[b] | 4 | tris(2,3-dibromopropyl) phosphate | 21 and 210 ppb |
| | | | | | pentabromophenol | 9.6 and 95 ppb |
| | | | | | 2,4,6-tribromophenol | 10.7 and 107 ppb |
| | | | | | tetrabromobisphenol A | 9.8 and 100 ppb |
| | | | | | decabromobiphenyl ether | 9.6,96 and 105 ppb |
| | | | | | tetrabromophthalic anhydride | 10 and 100 ppb |
| | | | | | 2,3-dibromopropanol | 20 and 200 ppb |
| | | | | | bromobenzene | 10.8 and 108 ppb |
| | | | | | 1,2-dibromo-3-chloro-propane | 11.2 and 112 ppb |
| | | | | | hexabromocyclododecane | 10 and 100 ppb |
| | | | | | bromoform | 12.2 and 122 ppb |
| | | | | | 1,2,-dibromoethane | 14.5 and 145 ppb |
| | | | | | 2,2',4,4',6,6'-hexabromo biphenyl | 9.6 and 96 ppb |

(continued)

Table 6.39 (cont'd)

| Sample Type | Blanks | | Controls | | Compound | Concentrations |
|---|---|---|---|---|---|---|
| | Laboratory | Field | Laboratory | Field | | |
| Vegetation | 2 | 3 | 2 | 4 | 1-chloro-1-butene<br>1,2-dichloroethane<br>1-bromo-2-chloroethane<br>1,2-dibromoethane<br>bromobenzene<br>m-chlorotoluene | 10 and 50 µg/2 g Vegetation |
| | 2 | 3 | 2 | 4 | tris(2,3-dibromopropyl) phosphate | 21 and 210 ppb |
| | | | | | pentabromophenol | 9.6 and 96 ppb |
| | | | | | 2,4,6-tribromophenol | 10.7 and 107 ppb |
| | | | | | tetrabromobisphenol A | 10.0 and 100 ppb |
| | | | | | decabromobiphenyl ether | 10.5 and 105 ppb |
| Milk | 2[a] | 2[a] | 4[c] | 2 | 1-chloro-1-butene [a] | 5 µg/100 ml |
| | | | | | 1,2-dichloroethane [a] | 5 µg/100 ml |
| | | | | | 1-bromo-2-chloroethane [a] | 5 µg/100 ml |
| | | | | | 1,2-dibromoethane a | 5 µg/100 ml |
| | | | | | bromobenzene [a] | 5 µg/100 ml |
| | | | | | m-chlorotoluene [a] | 5 µg/100 ml |
| | | | | | tris(2,3-dibromopropyl) phosphate [b] | 42 and 4.2 µg/200 ml |
| | | | | | pentabromophenol [b] | 1.9 and 19 µg/200 ml |
| | | | | | 2,4,6-tribomophenol [b] | 2.1 and 21 µg/200 ml |
| | | | | | tetrabromobisphenol A[b] | 2.0 and 20 µg/200 ml |
| | | | | | decabromobiphenyl ether[b] | 2.1 and 21 µg/200 ml |

(continued)

Table 6.39 (cont'd)

| Sample Type | Blanks | | Controls | | Compound | Concentrations |
|---|---|---|---|---|---|---|
| | Laboratory | Field | Laboratory | Field | | |
| Soil | 2 | 3 | 2 | 4 | 1-chloro-1-butene<br>1,2-dichloroethane<br>1-bromo-2-chloroethane<br>1,2-dibromoethane<br>bromobenzene<br>m-chlorotoluene | 10 and 50 µg/20 g soil. |
| | 2 | 3 | 2 | 4 | tris(2,3-dibromopropyl) phosphate | 21 and 210 ppb |
| | | | | | pentabromophenol | 9.6 and 96 ppb |
| | | | | | 2,4,6-tribromophenol | 10.7 and 107 ppb |
| | | | | | tetrabromobisphenol A | 10.0 and 100 ppb |
| | | | | | decabromobiphenyl ether | 10.5 and 105 ppb |
| Sediment | 2 | 3 | 2 | 4 | 1-chloro-1-butene<br>1,2-dichloroethane<br>1-bromo-2-chloroethane<br>1,2-dibromoethane<br>bromobenzene<br>m-chlorotoluene | 10 and 50 µg/20 g soil |
| | 2 | 3 | 2 | 4 | tris(2,3-dibromopropyl) phosphate | 21 and 210 ppb |
| | | | | | pentabromophenol | 9.6 and 96 ppb |
| | | | | | 2,4,6-tribromophenol | 10.7 and 107 ppb |
| | | | | | tetrabromobisphenol A | 10.0 and 100 ppb |
| | | | | | decabromobiphenyl ether | 10.5 and 105 ppb |

(continued)

Table 6.39 (cont'd)

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[a] Laboratory and field blanks serve for volatile and semi-volatile analysis.

[b] Two of these contols contained only the first five compounds at the higher concentration.

[c] Two of these controls contained the first six compounds and two contained the last five compounds.

[$] External standard

Abbr. Code: _____

FIELD SAMPLING PROTOCOL SHEET - B

Date: _____ Medium: _____( )

(_____) (_____) (_____) (_____) (____)
Project No. Operator Period Medium/Rationale State

Municipality _____( )

Address _____

Site _____( )

Location _____( )

Sample Code _____

Code Key:
W - Water
S - Soil
SD - Sediment
G - Grab
V - Vegetation
A - Animal
M - Miscellaneous
C - Composited

---

Sample size _____ Sampling rate _____

Time____Temp. Wet.____ Dry _____
Re. Humid____% Wind Dir./Speed __/___
Cloud _____Odor _____
Remarks _____

Time____Temp. Wet.____Dry _____
Rel. Humid____% Wind Dir./Speed __/__
Cloud _____Odor _____
Remarks _____

End: Time _____, Date _____
Start: Time _____, Date _____

Remarks/Map:

Figure 6.23. Field sampling protocol for condensed matrices.

Date:_____

(_____) (_____) (___) (_____) (___)
Project No. Operator Seq. Sampler/Rationale State

Municipality_____( )

Location_____

Site_____( )

Sample Code_____

| No. | Dimensions (cm) | Sorbent | Date/Analytical Procedure |
|---|---|---|---|
| ___ | _____ | ( M) | _____ |
| ___ | _____ | ( M) | _____ |
| ___ | _____ | ( M) | _____ |
| ___ | _____ | ( M) | _____ |

DC Amps_____ Sampling Rate (LPM)_____ Vacuum ("Hg)_____

Rationale: Qual. Anal (F)_____ End: Time_____ $ft^3$___

Quant. Anal. (E)_____ Calibration (C)__ Start: Time _____ $ft^3$___

Experimental: Lab (L)_____ Field (X)__ Total: (min)._____ $ft^3$___

Remarks_____ Volume Air/Cartridge:

_____ $\frac{0.0283\ (ft^3)}{\text{No. Split}} = $_____ $(M^3)$

MAP:

Time_____ Temp. Wet._____ Dry_____
Rel. Humid____% Wind Dir./Speed___/___
Cloud_____Odor_____
Remarks_____

Time_____ Temp. Wet._____ Dry_____
Rel. Humid____% Wind Dir./Speed___/___
Cloud_____ Odor_____
Remarks_____

Time_____ Temp. Wet._____ Dry_____
Rel. Humid____% Wind Dir./Speed___/___
Cloud_____ Odor_____
Remarks_____

Time_____ Temp. Wet._____ Dry_____
Rel. Humid____% Wind Dir./Speed___/___
Cloud_____ Odor_____
Remarks_____

Figure 6.24. Field sampling protocol for ambient air

6.3.2.4 Sample Storage

At the end of each day's sample collection, the samples were sorted, the labels checked, caps and seals were checked for leaks and the containers boxed. The soil, Tenax cartridges, carbon cartridges, milk, vegetation, and tissue samples were transferred to frozen storage. Water and sediment samples, which could not be frozen, were refrigerated. Upon return to the laboratory the samples were again frozen or cooled until analysis.

6.3.3 Analytical Quality Assurance

Samples were extracted, worked up and analyzed according to the detailed procedures outlined in Appendix A. Throughout the entire procedure, the analysts endeavored to maintain sample integrity and assure accurate analytical results. The salient features of the analytical quality assurance are outlined below.

6.3.3.1 Reagent and Glassware Control

Reagent and glassware control was required in order to minimize contamination. Sample containers, glassware, etc. were cleaned with Isoclean®, rinsed with deionized-distilled water and heat treated at 450-500°C to insure the removal of all traces of organic compounds. Solvents were redistilled in glass in our laboratories prior to their use.

6.3.3.2 Sample Logging

In addition to the field sampling protocol sheets prepared during sample collection, records of analysis progress were maintained. Immediately on return from the field, a log book was established for each sample matrix and each sample logged in. The progress of each sample through the analytical protocol was followed in the sample logbook.

Each instrument operator maintained a detailed log book indicating when the sample was run, the conditions under which it was run, the data which were printed out and the mode of data storage.

6.3.3.3 Instrumentation Control

The performance of each instrument used for sample analysis was evaluated daily by running a standard.

6.3.3.4 Analysis of Quality Control Samples

Quality control samples were interspersed with field samples in the queue for analysis. This protocol was designed to detect contaminants or variations in extraction efficiency with time.

Volatile Brominated Organics.--In addition to the analysis of control samples in Table 6.39, the reproducibility of analysis for volatile brominated organics collected on Tenax GC using GC/MS/COMP (mass fragmentography) was examined on several sets of samples. The results are given in Table 6.40. The first sample of a replicate set was analyzed approximately two and one-half weeks after collection in October of 1976. The second sample from the replicate set was analyzed four months later. The second sample had been kept at -20° during the entire period prior to its analysis. It is evident (Table 6.40) that the reproducibility of analysis ranges from a few percent to ±25%. From these results it was concluded that percent reproducibility for analysis of halogenated hydrocarbons by the technique of high resolution gc/ms/comp was more than adequate for the purpose of this study.

Ethylene.--Validation of sample integrity was achieved through the preparation of eleven vacuum cannisters as blanks or controls. These "quality control" samples, either transported to and from the field with the samples or refrigerated in the laboratory, were prepared to insure (1) that no undetected contamination occurred as a result of transport or storage and (2) that any losses due to leakage from the container or adsorption to the interior of the container be detected. The results of the analysis of these samples were presented in Section 6.0.

The average ethylene concentration found in the blank samples is 0.8 ppm (range 0.1-2.2 ppm). This relatively high blank value is reflected in the results of the control samples, particularly of those spiked at the 0.9 ppm level. Consequently, 0.8 ppm represents the approximate limit of detection for ethylene by this technique. Recovery from control samples containing 9.7 ppm ethylene was significantly closer to that expected. The average recovery at this concentration was 91%.

Decabrom and Tetrabrom.--Soil from the Research Triangle Park was spiked with 100 µg/kg each of Decabrom and Tetrabrom. Analysis by GC/MS/COMP found 110 and 162 µg/kg, respectively. These levels are very near the limit of detection.

Other controls per Table 6.39 were analyzed interdispersed with field samples.

Table 6.40. REPRODUCIBILITY OF REPLICATE MEASUREMENTS FOR HALOGENATED HYDROCARBONS ON TENAX GC SAMPLING CARTRIDGES[a]

| Site | Period/Cycle/Location | Allyl bromide | Bromobenzene | Bromoform | 1- or 2-Bromopropane | 1-Chloro-3-Bromopropane | 1-Chloro-2,3-Dibromopropane | 1,2-Dibromoethane |
|---|---|---|---|---|---|---|---|---|
| Great Lakes Corp. | P3/C1/L2 | 8.4 ± 5.6 | 20.7 ± 7 | 15.1 ± 3 | 10.8 ± 4.4 | - | - | 1107 ± 32 |
| | P3/C1/L3 | - | 60 ± 20 | 11.96 ± 0 | - | 23.7 ± 4.6 | - | 1837 ± 162 |
| Ethyl Corp. | P1/C1/L2 | - | - | - | - | - | - | 174 ± 44 |
| Arkansas Chem. Inc. | P1/C1/L3 | 29.7 ± 1 | - | - | - | - | - | 81 ± 15 |
| Michigan Chem. Inc. | P1/C2/L4 | 32.9 ± 1.5 | - | - | 35 ± 15 | 63 ± 6 | 20.6 ± 5.5 | - |

[a]The first sample of replicate set was analyzed in October, 1976, the second sample 4 mo. later; all values are in ng/m$^3$.

6.3.3.5 Data Quality Assessment

The data generated by each analysis were thoroughly examined by the instrument operator to assure quality. In the case of mass spectral data, the data were screened by the instrument supervisor before release. This screen assured data quality and also that the sample had been run according to the request of the analyst.

6.3.3.6 Quality Assurance in Data Interpretation

Both qualitative interpretations and quantitation were spot checked by a second person.

6.4 METHYL CHLORIDE AND METHYL BROMIDE ANALYSIS BY GC/ECD AND MASS FRAGMENTOGRAPHY

6.4.1 Apparatus

Aluminum sample containers were evacuated with a vacuum pump for 15 minutes, flushed with helium, then evacuated again for 15 minutes. They were then checked with a vacuum gauge, and were deemed satisfactory if they showed a vacuum >29".

A stainless steel column (6 ft x 1/8" i.d.) packed with Durapak n-octane/Porasil C (100/120 mesh) was used for the analysis. A 1 ml aliquot of each sample was transferred from the container to the column with a 1 ml Pressure-lok® gas syringe (Precision Instrument Corp.). The lower limit of measurement for MeCl and MeBr was 35 ppm and 5 ppm, respectively.

6.4.2 Quality Control

Standards were prepared using the permeation line system. A flow rate was set across the permeation tubes of MeCl and MeBr to create a certain concentration of MeCl and MeBr in $N_2$. An evacuated aluminum cannister was then attached to a permeation line and allowed to equilibrate with the system, after which the cannister was sealed. Blanks were prepared by filling an evacuated cannister with helium at 1 atm.

The following blanks and controls were prepared:

| | Type | Number |
|---|---|---|
| Blank | Lab | 2 |
| | Field | 3 |
| 6 ppm MeBr + 35 ppb MeCl | Lab | 1 |
| | Field | 1 |
| 60 ppm MeBr + 350 ppb MeCl | Lab | 1 |
| | Field | 2 |
| 300 ppb MeBr + 1750 ppb MeCl | Lab | 1 |
| | Field | 1 |

6.4.3 Analysis of Samples

Standards (Fig. 6.25) to be run each day were prepared on the permeation line, with 1 ml of a standard being drawn directly from the line with a gas syringe. All lab blanks (Fig. 6.26), field blanks, lab controls, and field controls were analyzed. All samples from Dow Chemical were also analyzed.

Blanks contained several large peaks eluting in the general area of MeCl and MeBr, but none that interfered directly with the analysis of the two compounds. None of the controls, however, contained any detectable levels of MeCl and MeBr, indicating that these compounds were not stable in the aluminum cannisters for the period of time stored. Blanks and controls had been stored for 8 to 9 weeks.

Samples from Dow showed no detectable levels of MeBr and MeCl. These samples had been stored for 5 1/2 weeks.

A new control, 900 ppb MeCl and 180 ppb MeBr (Fig. 6.27), was prepared in a cannister exactly as before and analyzed immediately. The appropriate levels of MeCl and MeBr were found. Analysis of this new control five days layer showed approximately a 15% loss of MeCl and MeBr.

No methyl chloride or methyl bromide was detected by mass fragmentography from the analysis of carbon cartridges (Appendix A). Vinyl chloride and vinyl bromide were also not detected.

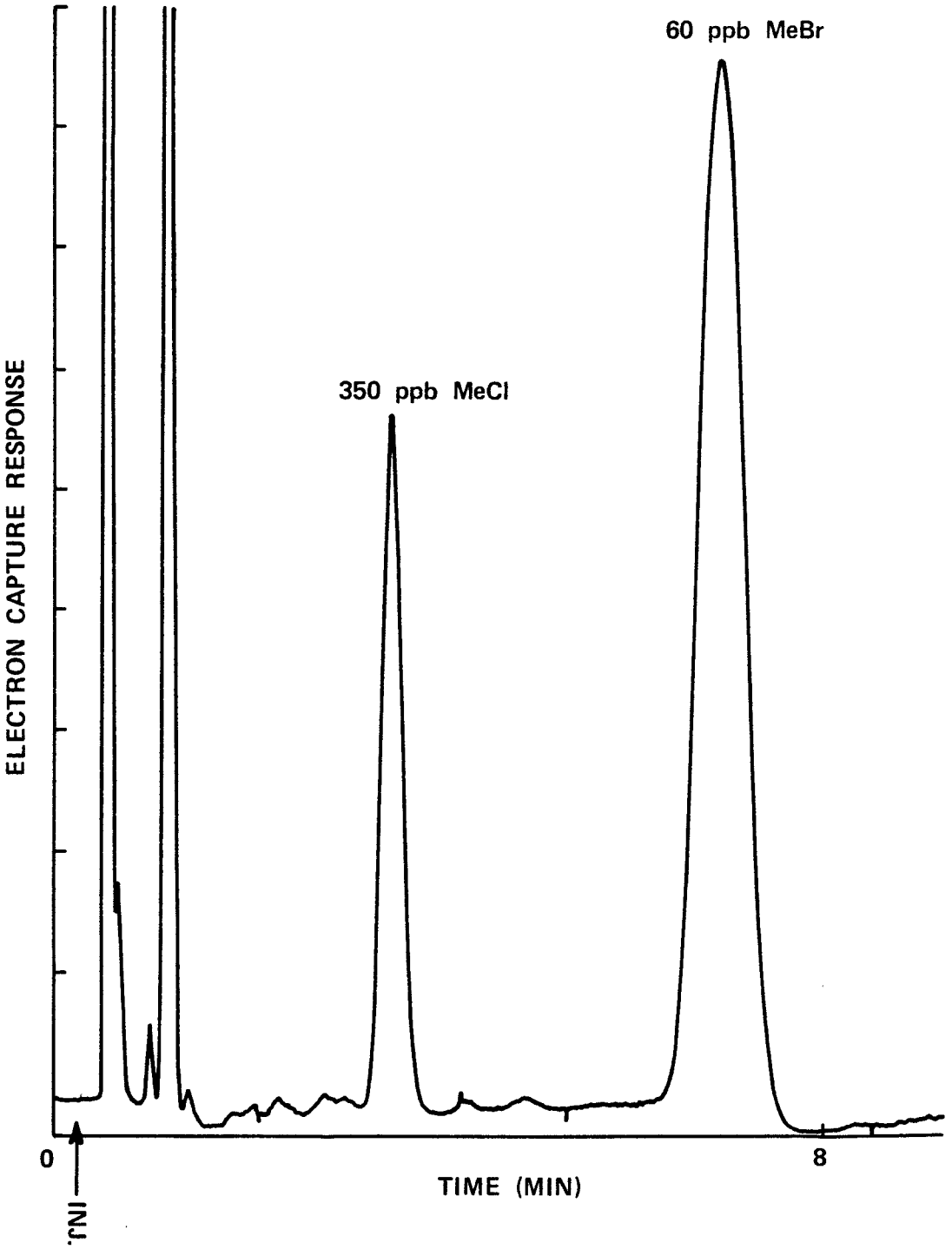


Figure 6.25. GC/ECD of methyl chloride and methyl bromide.

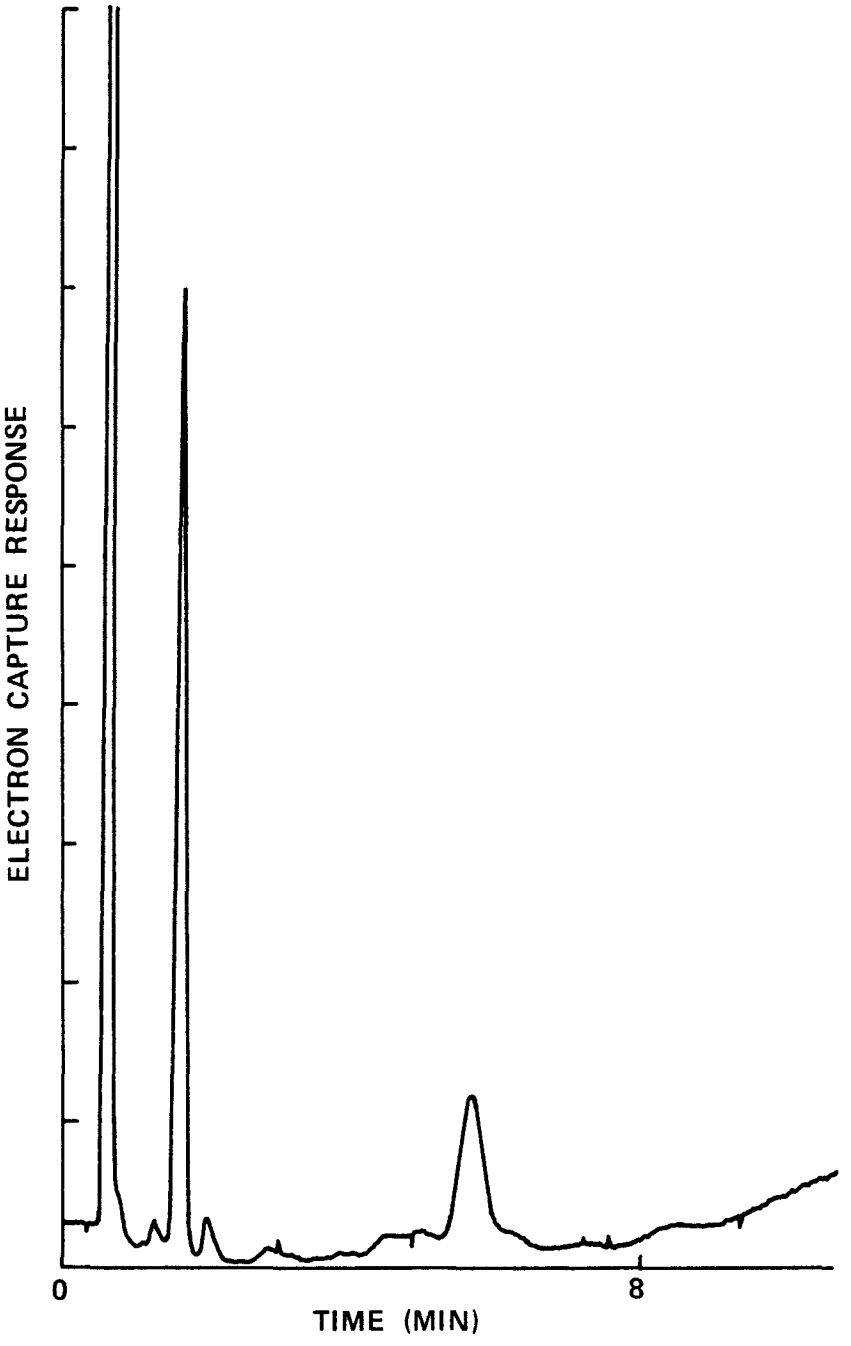


Figure 6.26. GC/ECD of blank control sample.

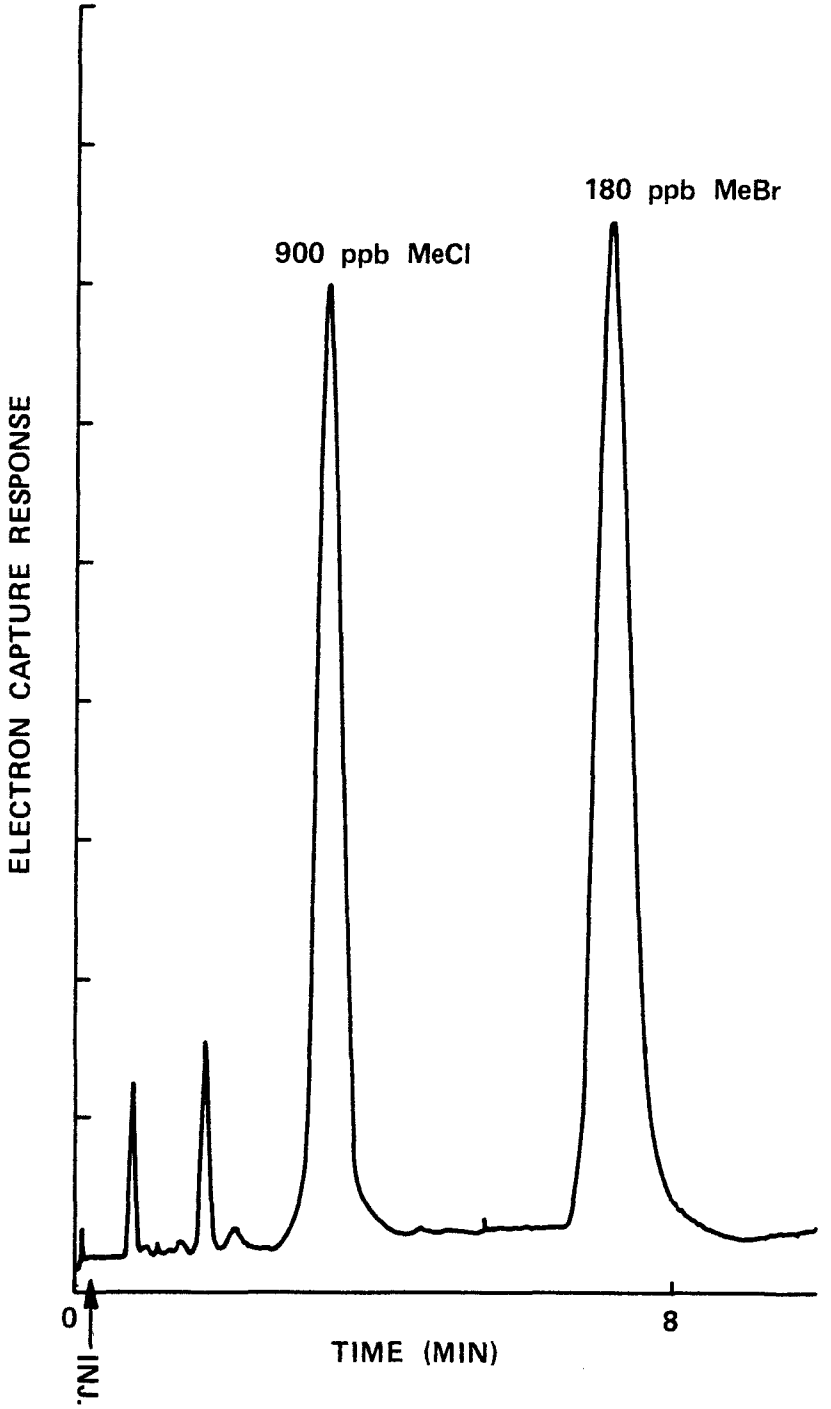


Figure 6.27. GC/ECD of methyl chloride and methyl bromide.

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16. ABSTRACT

Sampling and analysis was designed to determine ambient concentrations of ethylene dibromide and other brominated chemicals near production facilities in El Dorado and Magnolia, AK. A characterization was made of the environmental matrices - air, water, soil, sediment and biota - for the presence and levels of ethylene dibromide, vinyl bromide and other related chemicals surrounding the bromine industry.

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