# Urban Air Toxics Concentrations In Downtown Denver

# October 2000 through September 2001

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**Prepared by the Air Pollution Control Division**
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# Urban Air Toxics Concentrations In Downtown Denver

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## Executive Summary

## Executive Summary

This report analyzes one year of urban air toxics data taken at the CAMP station in downtown Denver, Colorado in 2001. Carbonyls, volatile organic compounds, and speciated non-methane organic compounds were all sampled. For carbonyls, twelve compounds were sampled. Formaldehyde, acetone, and acetaldehyde were the most prevalent. The other nine compounds occurred at levels at least one order of magnitude below the top three. Average levels observed during weekdays were greater than the weekend average concentrations. The top eight aldehydes trended together. All compounds except isovaleraldehyde showed strong correlation to formaldehyde. Isovaleraldehyde and 2,5-dimethyl-benzaldehyde were detected in fewer than 35% of the samples. The other carbonyls were all detected in 90% of the samples. Only formaldehyde and acetaldehyde have EPA toxicity "benchmarks", but both these compounds were above their cancer risk benchmarks, indicating cancer risk from these compounds to be greater than one-in-a-million. Formaldehyde risk is about 100 times above the EPA-recommended level. Acetaldehyde risk is about 10 times the EPA-recommended level. Formaldehyde and acetaldehyde were below their EPA benchmarks for chronic health effects, suggesting that non-cancer risks from these compounds are not a concern. The carbonyl method had good repeatability, as shown by duplicate and replicate samples analyzed.

Fifty-eight volatile organic compounds (VOCs) were analyzed from sample canisters. Twenty-nine of these VOCs were never measured at detectable levels. In contrast, nineteen other VOCs were present in Denver air, at measurable levels, in over 90% of the samples. Average levels observed during weekdays were greater than the weekend average concentrations. Statistical correlations between concentrations of individual compounds were not that strong, but acetylene and propylene showed the strongest correlations to other compounds. Thirty-seven of the compounds measured had estimated EPA "benchmark" concentrations. 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene occur at levels believed to represent a greater than one-in-a-million risk of cancer. The single measurable value of acrylonitrile would be above the EPA one-in-a million guideline, if it occurred as an annual mean. None of the compounds had levels greater than the EPA "benchmarks" for non-cancer chronic health risk. The VOC method had good repeatability, as shown by duplicate and replicate samples analyzed.

Seventy-eight speciated non-methane organic compounds (SNMOCs) were analyzed from sample canisters. Sixty-two of the compounds were present in Denver air, at measurable levels, in over 90% of the samples. Six of the compounds were never measured at detectable levels. In general, the average weekday concentration was greater than the average weekend concentration, but some compounds were exceptions to this rule. In contrast to the VOCs, statistical correlations of individual compounds were strong. Only eight of the SNMOCs had EPA-recommended toxicity "benchmarks". Seven of these were among the compounds that were also measured by the VOC method. As with the VOC compounds, 1,3-butadiene and benzene occur at levels believed to represent a greater than one-in-a-million risk of cancer. All eight of these compounds were well below the EPA non-cancer risk "benchmarks". The SNMOC method had good repeatability, as shown by duplicate and replicate samples analyzed. A side-by-side analysis of twelve compounds measured from the same canisters by both the VOC and SNMOC laboratory methods showed that the two analytical techniques yield consistent results.

The majority of the compounds detected in Denver air can be related to automobile emissions. The strong inter-correlations between the carbonyl compounds suggest a common source. The SNMOC compounds were also strongly inter-correlated. Many of the compounds measured do not have EPA-recommended toxicity "benchmarks". Of those that do, formaldehyde, acetaldehyde, 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene are present in Denver air at levels that may create health concerns.

# Section 1 - Introduction

# Introduction

This report discusses results for ambient air toxics monitoring conducted at the downtown Denver CAMP station during the period October 2000 through September 2001. As part of the Environmental Protection Agency's (EPA) Urban Air Toxics Monitoring Program (UATMP), twenty-four hour long samples were collected on a once every six day basis for over a year. Samples were taken with equipment provided by Eastern Research Group, a consulting firm contracted by EPA to provide support to the national network. The sampler collects two different types of samples. A Dinitropheny-hydrazine (DNPH) cartridge collects carbonyl samples by EPA Method TO-11A. Air is also drawn into a stainless steel canister. DNPH cartridges were analyzed for twelve different carbonyls. The canisters were analyzed for 58 volatile organic compounds (VOCs) by EPA method TO-15, and 78 speciated non-methane organic compounds (SNMOCs) by EPA method TO-12. Twelve compounds were analyzed by both the VOC and SNMOC methods, so the total number of chemical compounds assessed by all three methods is 136.

This report presents results according to the monitoring method employed. Thus, one chapter discusses the carbonyls, one presents VOC information, and the last one summarizes the compounds analyzed by the SNMOC method. For consistency, each chapter follows the same format. The chapter begins with a presentation of summary statistics for all compounds analyzed by the method. It then discusses the percentage of samples in which each chemical was detected. Results are split out and analyzed for weekday versus weekend time periods. Some summary graphs of groups of compounds are presented. Correlation coefficients (a statistical measure of how well the presence of some compounds is associated with the presence of other compounds) are developed. The section then presents a brief discussion of quality assurance statistics, such as blank and precision results, that are available under separate cover. Finally, there is a section entitled "Compounds of Significance: Sources and Health Effects". This is one of the most important portions of the report, for it discusses each chemical which has an annual average concentration in Denver air of one part per billion (ppb) or greater, or which has air concentrations above EPA levels of concern. This section gives a brief summary of each chemical's use, its air emission sources, its potential health effects, and concentrations in typical urban air. Where possible, levels are compared to EPA "benchmark" health criteria. (EPA has not developed recommended "benchmark" levels for all compounds). At the end of the chapter is a reference section listing sources of information regarding toxicity and health effects for the chemical compounds that were discussed in the health effects section.

The report ends with a concluding chapter that summarizes results of this study. Compounds most frequently observed were associated with the production, storage, or use of petroleum products. Many of them are emitted from automobile tailpipes. Compounds present in Denver air at levels above EPA "benchmark" levels are formaldehyde, acetaldehyde, 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene. It should be noted that EPA has not developed "benchmark" levels for a number of compounds, and that the effect of combined exposure to these compounds is not known. On the positive side, 30 of the 136 compounds were not detected in Denver air. Seven others were present less than 10 % of the time.

# Section 2 - Carbonyls at CAMP Station

# October 2000 to September 2001

# Summary Statistics - Carbonyls

## Minimum, Maximum, Mean – All Samples

Carbonyl data collected at the downtown CAMP station from October 2000 through September 2001 are presented in this section of the Air Toxics Monitoring Report. For the year-long period, carbonyls were sampled on a one-in-six day basis, for a total of 63 samples attempted. Of these, the laboratory successfully processed 58, for a percentage data recovery rate exceeding 92%. (See Table 2.1).

Table 2.2 summarizes the annual minimum, maximum, and mean concentrations for each carbonyl compound measured during the study. Results show that the most prevalent carbonyls in downtown Denver air are formaldehyde, acetone, and acetaldehyde, in that order. The other nine carbonyl compounds measured occur at concentration levels at least one order of magnitude below these top three compounds.

**Table 2.1 - Percentage Data Recovery For Carbonyl Samples**

| Sample Days Scheduled | Samples Recovered | Percentage Recovered |
|---|---|---|
| 63 | 58 | 92.1 |

# Percentage of Samples For Which Compound Was Detected

Table 2.2 shows that most of these compounds were present in air over 90% of the time the air was sampled. However, isovaleraldehyde and 2,5-dimethylbenzaldehyde were seen less frequently, with detections in only one-quarter to one-third of the air samples taken.

**Table 2.2 – Carbonyl Compounds Data Summary**

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Maximum | Minimum | Mean | Number | Percentage | |
| Formaldehyde | 15.45 | 3.28 | 6.42 | 0 | 0 | 100 |
| Acetaldehyde | 4.75 | 1.07 | 2.43 | 0 | 0 | 100 |
| Acetone | 9.24 | 1.04 | 3.39 | 0 | 0 | 100 |
| Propionaldehyde | 0.54 | 0.05 | 0.23 | 0 | 0 | 100 |
| Crotonaldehyde | 0.18 | 0.01 | 0.07 | 5 | 8 | 92 |
| Butyr/Isobutyraldehyde | 0.58 | 0.06 | 0.21 | 0 | 0 | 100 |
| Benzaldehyde | 0.23 | 0.04 | 0.11 | 1 | 2 | 98 |
| Isovaleraldehyde | 0.31 | 0.00 | 0.05 | 44 | 75 | 25 |
| Valeraldehyde | 0.45 | 0.01 | 0.09 | 0 | 0 | 100 |
| Tolualdehydes | 0.35 | 0.03 | 0.12 | 1 | 2 | 98 |
| Hexaldehyde | 1.30 | 0.07 | 0.40 | 0 | 0 | 100 |
| 2,5-Dimethylbenzaldehyde | 0.06 | 0.00 | 0.02 | 39 | 66 | 34 |

### Weekend Vs. Weekday Results

For the year of carbonyl data, an analysis of weekday versus weekend levels was conducted. Table 2.3 gives summary statistics for minimum, maximum and mean of the weekend samples versus the same statistics for the weekday samples. Figure 2.1 is a graph of these results. For almost all carbonyls, the weekday mean is greater than the weekend one. The exceptions are compounds that were detected infrequently, such as 2,5-dimethylbenz-aldehyde and isovaleraldehyde.

## Graphs - Carbonyls

### Individual Compounds

The most prevalent three carbonyl compounds measured during the study are graphed in Figure 2.2. Formaldehyde showed the highest levels, with most graphed concentrations falling between three and eleven parts per billion. Acetaldehyde was consistently present at levels of one to four parts per billion. Acetone levels generally hovered between two and six parts per billion. The other nine carbonyl compounds were present at levels below two parts per billion. Propionaldehyde, crotonaldehyde, butyr/isobutyraldehyde, benzaldehyde, valeraldehyde, and tolualdehydes were consistently detected at levels below 0.5 ppb. Hexaldehyde was also constantly present, but with many of the spring/ summer samples at levels between 0.5 and 1.0 ppb. This is unlike the other eleven carbonyl compounds, which do not show seasonal effects. Isovaleraldehyde and 2,5-dimethyl-benzaldehyde were detected at levels less than 0.5 ppb.

### Compounds As Groups

Figure 2.2 shows the annual trends for the largest concentration carbonyl compounds: formaldehyde, acetone and acetaldehyde. Generally, concentrations of these compounds rise and fall together, suggesting a common emissions source. In addition, levels remain generally constant throughout the year, suggesting a year-round (non-seasonal) source. The same is true for five of the lower concentration carbonyl compounds, while the four lowest concentration carbonyl compounds do not show any trend.

**Table 2.3 – Weekend Vs. Weekday Statistics for Carbonyls**

| | Summary Statistics WEEKEND (PPB) | | | Summary Statistics WEEKDAY (PPB) | | |
|---|---|---|---|---|---|---|
| | Maximum | Minimum | Weekend Mean | Maximum | Minimum | Weekday Mean |
| Formaldehyde | 9.09 | 3.28 | 5.83 | 15.45 | 3.35 | 6.67 |
| Acetaldehyde | 3.44 | 1.07 | 2.10 | 4.75 | 1.30 | 2.57 |
| Acetone | 4.63 | 1.26 | 2.84 | 9.24 | 1.04 | 3.61 |
| Propionaldehyde | 0.36 | 0.08 | 0.20 | 0.54 | 0.05 | 0.24 |
| Crotonaldehyde | 0.17 | 0.01 | 0.05 | 0.18 | 0.01 | 0.08 |
| Butyr/Isobutyraldehyde | 0.48 | 0.09 | 0.17 | 0.58 | 0.06 | 0.22 |
| Benzaldehyde | 0.13 | 0.04 | 0.09 | 0.23 | 0.06 | 0.11 |
| Isovaleraldehyde | 0.09 | 0.01 | 0.05 | 0.31 | 0.00 | 0.04 |
| Valeraldehyde | 0.17 | 0.03 | 0.08 | 0.45 | 0.01 | 0.10 |
| Tolualdehydes | 0.20 | 0.03 | 0.09 | 0.35 | 0.04 | 0.13 |
| Hexaldehyde | 0.82 | 0.13 | 0.41 | 1.30 | 0.07 | 0.40 |
| 2,5-Dimethylbenzaldehyde | 0.06 | 0.00 | 0.02 | 0.06 | 0.00 | 0.02 |

**Figure 2.1 - Weekday Vs. Weekend Mean For Carbonyls At CAMP**

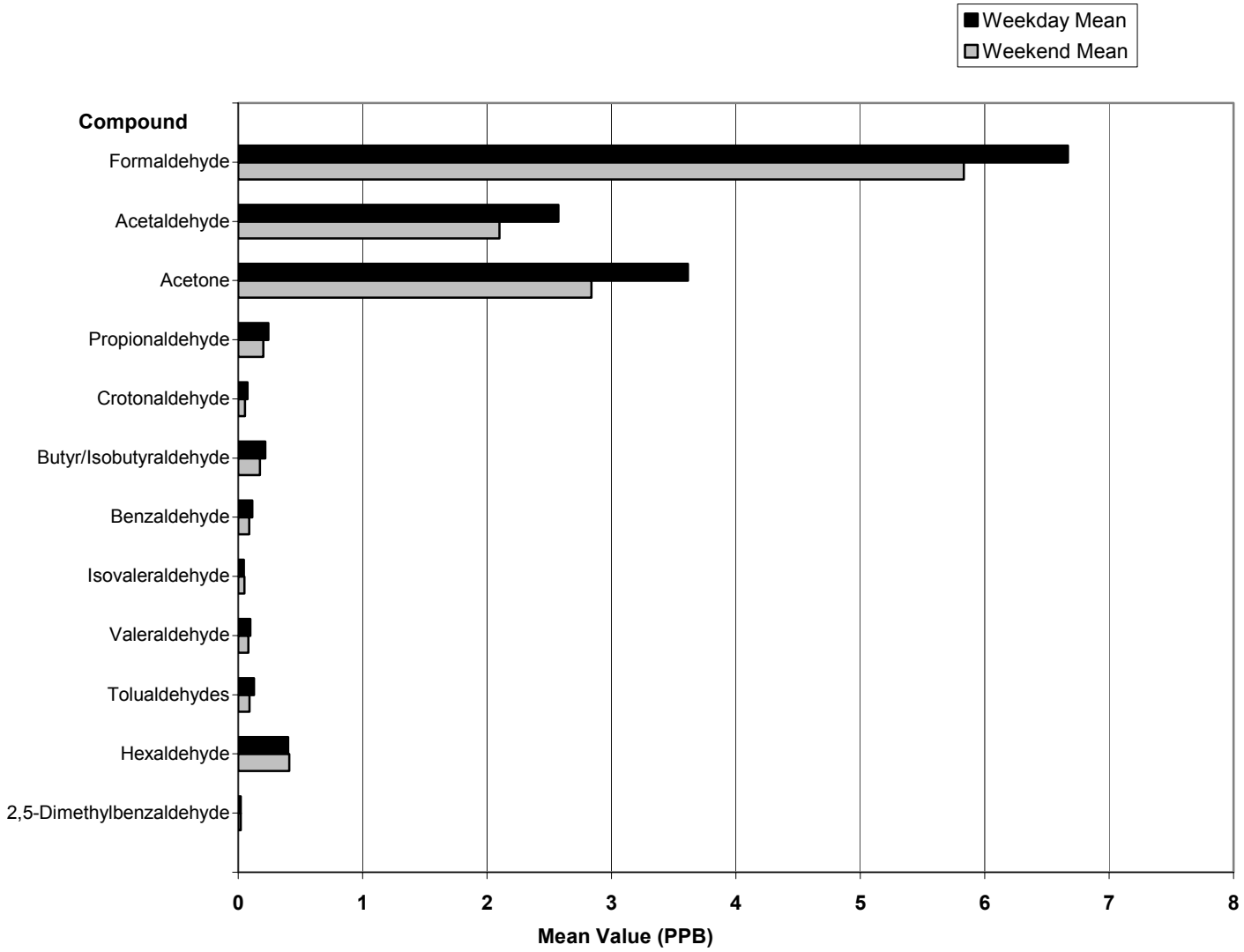
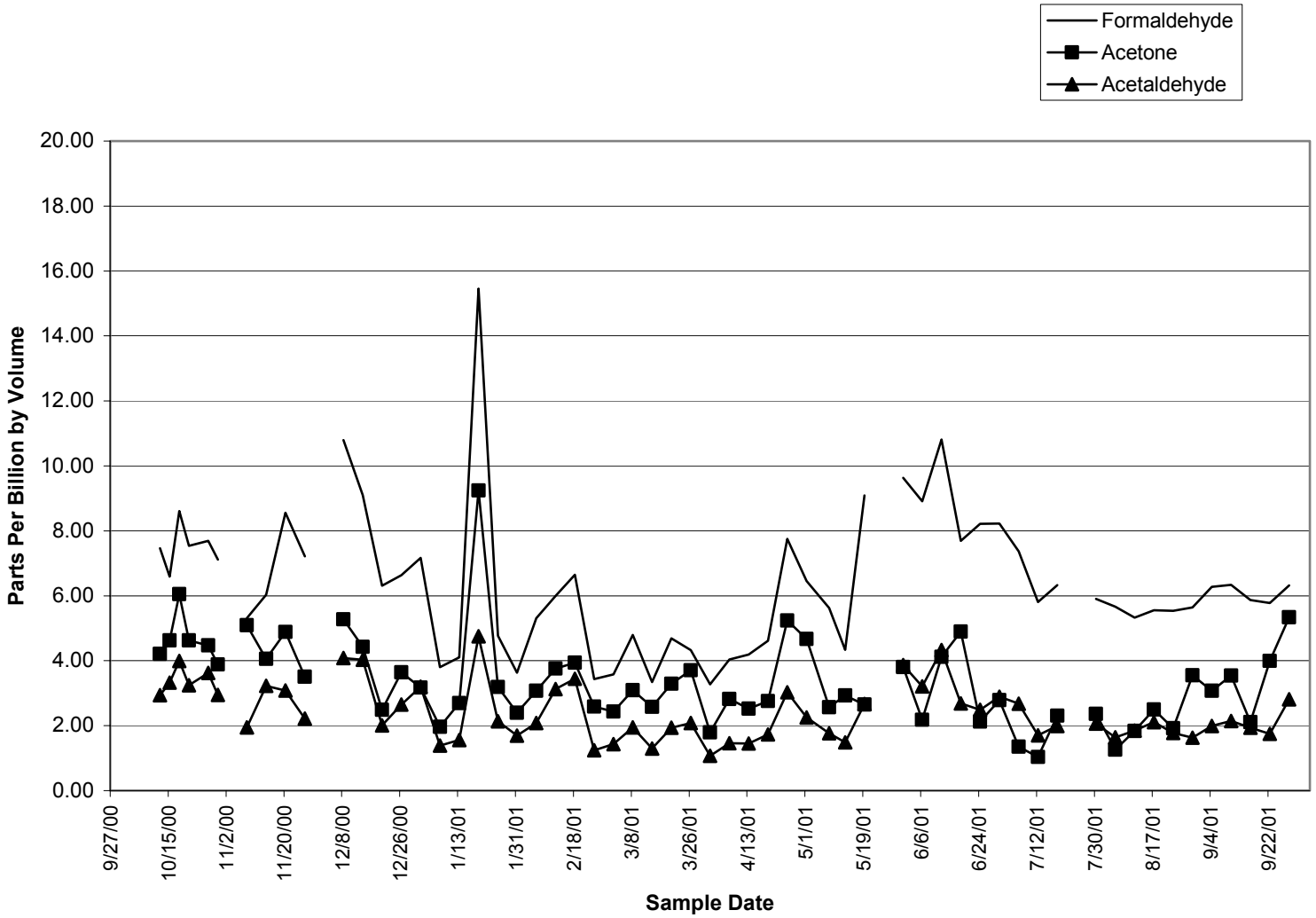


**Figure 2.2 - Largest Concentration Carbonyls At CAMP**



## Correlation Coefficients Between Compounds – Carbonyls

A correlation coefficient analysis conducted for the twelve carbonyl compounds, across the entire year of data, shows that almost all compounds are strongly correlated to formaldehyde and acetaldehyde (Table 2.4). As these are the carbonyls with the largest concentrations in air, it is not that surprising that the lower concentration carbonyls are correlated to them. Acetone shows correlation to the other carbonyls, but the relationship is not as strong as that for formaldehyde and acetaldehyde. Isovaleraldehyde, which was detected 25 % of the time, is negatively correlated with all of the other compounds.

**Table 2.4 - Correlation Coefficients for Carbonyls**

| | Formaldehyde | Acetaldehyde | Acetone | Propionalde. | Crotonalde. | Butyr/Isobutyr. |
|---|---|---|---|---|---|---|
| **Formaldehyde** | 1.0000 | | | | | |
| **Acetaldehyde** | **0.8820** | 1.0000 | | | | |
| **Acetone** | **0.6487** | **0.7069** | 1.0000 | | | |
| **Propionaldehyde** | **0.7385** | **0.8796** | **0.6977** | 1.0000 | | |
| **Crotonaldehyde** | **0.5555** | **0.6055** | 0.3356 | **0.6703** | 1.0000 | |
| **Butyr/Isobutyraldehyde** | **0.5262** | **0.6875** | **0.7039** | **0.6642** | 0.0852 | 1.0000 |
| **Benzaldehyde** | **0.7834** | **0.8439** | **0.5329** | **0.6737** | **0.5368** | 0.4631 |
| **Isovaleraldehyde** | -0.2144 | -0.2474 | -0.2146 | -0.4050 | -0.5060 | -0.3019 |
| **Valeraldehyde** | **0.6574** | **0.5950** | **0.8072** | **0.6224** | 0.3002 | **0.5928** |
| **Tolualdehydes** | **0.7124** | **0.7182** | 0.4892 | **0.7604** | **0.7680** | 0.3421 |
| **Hexaldehyde** | **0.7473** | 0.4979 | 0.2446 | 0.3790 | **0.5632** | -0.0527 |
| **2,5-Dimethylbenzaldehyde** | **0.6546** | **0.5381** | 0.0388 | 0.3733 | 0.4660 | 0.1097 |

| | Benzaldehyde | Isovaleralde. | Valeraldehyde | Tolualdehydes | Hexaldehyde | 2,5-Dimethylben. |
|---|---|---|---|---|---|---|
| **Formaldehyde** | | | | | | |
| **Acetaldehyde** | | | | | | |
| **Acetone** | | | | | | |
| **Propionaldehyde** | | | | | | |
| **Crotonaldehyde** | | | | | | |
| **Butyr/Isobutyraldehyde** | | | | | | |
| **Benzaldehyde** | 1.0000 | | | | | |
| **Isovaleraldehyde** | -0.2451 | 1.0000 | | | | |
| **Valeraldehyde** | 0.4100 | -0.2337 | 1.0000 | | | |
| **Tolualdehydes** | **0.6693** | -0.1552 | 0.4866 | 1.0000 | | |
| **Hexaldehyde** | **0.5366** | -0.4017 | 0.3206 | **0.5439** | 1.0000 | |
| **2,5-Dimethylbenzaldehyde** | **0.6307** | No Correlation | 0.0589 | **0.7767** | **0.6919** | 1.0000 |

Bold = Correlation Greater than + 0.5

No Correlation = These compounds were never detected at the same time.

## Precision of Sample Results – Carbonyls

Periodically throughout the year, a second carbonyl cartridge was sampled simultaneously with the main sample. These additional samples, known as duplicates, were collected in order to assess the precision (repeatability) of the carbonyl sampling method. On the duplicate sampling dates, the laboratory also conducted a test of the precision of the analytical process by injecting two samples of each cartridge's liquid extract into the liquid chromatograph/ mass spectrometer. These samples are known as the laboratory replicates. Thus, this project collected two types of precision data – duplicate data, which assesses both sampling and analysis procedures, and replicate data, which assesses laboratory analytical method repeatability. Detailed information regarding precision and laboratory replicate results is presented in the appendix to this report, which is available as a separate document.

## Field Blanks – Carbonyls

For quality assurance purposes, field blanks were periodically taken by attaching a blank DNPH cartridge to the sampler briefly, and then removing it. The purpose of these blanks was to assess contamination that might exist in the cartridge media, or contamination that might occur in sample installation or shipping. Most cartridges had small amounts of formaldehyde, acetaldehyde, and acetone. The other nine compounds occasionally had detectable amounts on the blanks. Detailed information regarding field blank results is presented in the appendix to this report, which is available as a separate document.

## Compounds of Significance: Sources and Health Effects

Of the twelve carbonyl compounds sampled, three showed annual mean concentrations greater than 1 part per billion (ppb) in Denver air. These are: formaldehyde, acetaldehyde, and acetone. Information regarding the nature, sources, and potential health effects of each of these compounds is given below. Levels observed in Denver are also compared to national EPA "benchmark" concentrations, which are used to evaluate whether areas are meeting national EPA goals for reducing concentrations of hazardous air pollutants. However, unlike national ambient air quality standards governing pollutants such as carbon monoxide or ozone, these EPA "benchmark" values do not have the force of law or regulation. They are simply levels at which EPA believes these pollutants may begin to cause health effects on sensitive members of the population.

### Formaldehyde

Formaldehyde is a hydrocarbon compound with the formula HCHO. It exists in the atmosphere as a colorless gas with a pungent odor. It is used in the manufacture of resins, particleboard, plywood, and glues. It is also employed in chemical manufacturing of pharmaceuticals, herbicides, and sealants. Textile finishes, such as used for "permanent press" clothes, contain formaldehyde (Kirk-Othmer, Vol 11, pages 245 - 246).

Although it is used in industry, the largest source of formaldehyde in outdoor air is combustion. In urban areas, combustion of automotive fuel is the dominant source for much of the year. However, formaldehyde can also photochemically form in the air, as other hydrocarbons and oxides of nitrogen from automobile traffic break down to form ozone. Complicating the situation is the fact that the complex ozone-producing atmospheric reactions may both create and destroy formaldehyde, as the chains of chemical reactions proceed along various pathways.

The Agency for Toxic Substances and Disease Registry (ATSDR), lists a number of possible health effects that may occur from inhalation of formaldehyde. Formaldehyde is an irritant that may cause burning in the eyes, nose, and lungs. At 0.4 – 3 ppm, it may cause the eyes to tear. Formaldehyde is believed to be carcinogenic (cancer-causing) to humans. However, the body can quickly break down formaldehyde, so it does not accumulate in fatty tissue. Currently, ATSDR believes that formaldehyde does not cause birth defects in humans (ATSDR Toxicological Profile for Formaldehyde). Thus, the main concerns with this compound are its irritant properties and its probable ability to cause cancer of the nose and throat.

ATSDR states that typical levels of formaldehyde in urban air are 10 – 20 ppb. The maximum level observed in Denver during this study, 15 ppb, falls right within this range. ATSDR cites concentrations of 0.2 ppb for rural areas, and 2-6 ppb for suburban areas (ATSDR Toxicological Profile for Formaldehyde). The significance of the Denver levels can be assessed by comparing them to national EPA "benchmark" values for formaldehyde.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Tables 2.5 and 2.6 summarize the EPA benchmarks available for formaldehyde. As seen from the table, formaldehyde has benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks have yet to be developed.

Table 2.5 compares the annual mean value of formaldehyde to the EPA " risk factor" for developing cancer. Columns two and three of Table 2.5 give the annual mean, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 2.5 gives the cancer risk associated with breathing a concentration of 1 ug/m3 of the pollutant. Column five, Cancer Risk in Ambient Air, relates the annual concentration of formaldehyde observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, the value of 1.03 X 10-4 for formaldehyde in Denver air is one hundred and three times higher than the EPA goal.

Table 2.6 compares the annual mean values of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 2.6 gives the value below which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For formaldehyde, the value is 0.81, indicating the annual concentration is within the EPA goal.

Therefore, inhalation of formaldehyde in Denver air is believed to be a significant risk factor for contracting cancer of the nose or throat. Formaldehyde in Denver air may also be close to levels that cause irritant effects to the population. As concentrations measured in Denver are typical of large urban areas of the United States, this is a nationwide problem.

**Table 2.5 - Formaldehyde Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 ((1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **Formaldehyde** | **6.42** | **7.89** | **0.000013** | **1.03E-04** |

**Table 2.6 - Formaldehyde Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Formaldehyde** | **6.42** | **7.89** | **9.8** | **0.81** |

## Acetaldehyde

Acetaldehyde is a hydrocarbon with the formula $CH_3CHO$. It is thus closely related to formaldehyde, HCHO. Like formaldehyde, it exists in the atmosphere as a gas with a pungent odor. It is used in the manufacture of acetic acid, acetic anhydride, chloral, glyoxal, and other chemicals. It is employed in the food processing industry as a food and fish preservative, a flavoring agent, and in gelatin fibers. The tanning and paper industries use acetaldehyde, as do the perfume and dye manufacturers (CARB Acetaldehyde Fact Sheet).

Although it is used in industry, the California Air Resource Board believes that the largest sources in outdoor air are combustion and production from photochemical reactions (CARB Acetaldehyde Fact Sheet). Acetaldehyde itself can break down in these complex photochemical reaction pathways, forming formaldehyde. Wood burning and emissions from petroleum refineries are also sources.

The health effects of acetaldehyde are very similar to those of its chemical relative formaldehyde. It irritates the eyes and mucous membranes. It can paralyze the respiratory muscles, act as a narcotic to prevent coughing, and speed up pumping of the heart. Exposure can lead to headaches and sore throat. (Kirk Othmer, Vol 1, page 107). Acetaldehyde is believed to be a probable human carcinogen, leading to cancer of the nose and throat. Acetaldehyde has been shown to cause birth defects in animals, but no human research is available. (CARB Acetaldehyde Fact Sheet).

The California Air Resources Board observed an annual mean of 1.33 ppb acetaldehyde in its state-wide network during 1996 (CARB Acetaldehyde Fact Sheet). The mean observed in this Denver study, 2.4 ppb, is in the same range. The significance of the Denver levels can be assessed by comparing them to national EPA "bench-mark" values for acetaldehyde.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Tables 2.7 and 2.8 summarize the EPA benchmarks available for acetaldehyde. This compound has benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks have yet to be developed.

Table 2.7 compares the annual mean value of acetaldehyde to the EPA " risk factor" for developing cancer. Columns two and three of Table 2.7 give the annual mean of acetaldehyde, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 2.7 gives the risk factor associated with breathing a concentration of 1 ug/m3. Column five, Cancer Risk in Ambient Air, relates the annual concentration observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, the value of 9.65 X 10-6 for acetaldehyde in Denver air is about ten times higher than the EPA goal.

Table 2.8 compares the annual mean values of acetaldehyde to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 2.8 gives the value below which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0.

(That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For acetaldehyde, the hazard index is 0.49, below the EPA goal of 1.0.

Therefore, inhalation of acetaldehyde in Denver air is believed to be a risk factor for contracting cancer of the nose or throat. Acetaldehyde in Denver air does not appear to be at high enough levels to cause irritant effects to the population. Like formaldehyde, acetaldehyde in Denver occurs at levels typical of other large urban areas. Acetaldehyde levels are therefore a national problem related primarily to the use of motor vehicles.

**Table 2.7 - Acetaldehyde Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 ((1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **Acetaldehyde** | **2.43** | **4.38** | **0.0000022** | **9.65E-06** |

**Table 2.8 - Acetaldehyde Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Acetaldehyde** | **2.43** | **4.38** | **9** | **0.49** |

## Acetone

Acetone is a hydrocarbon compound with the formula $CH_3COCH_3$. It is also known as dimethyl ketone or 2-propanone. Like formaldehyde and acetaldehyde, it exists in the atmosphere as a colorless gas with a pungent odor. Its primary industrial use is as a solvent in production of paints, adhesives, cleaners, and inks (Kirk-Othmer, Vol 1, page 189).

Sources of acetone in the ambient air are similar to those of formaldehyde and acetaldehyde. Automobile exhaust, wood burning, and petroleum refining are important sources. For acetone, solvent usage is also a large source of emissions. Unlike the other two carbonyl compounds discussed here, acetone does not readily react in air and can be transported for long distances (ATSDR Toxicological Profile for Acetone).

The Agency for Toxic Substances and Disease Registry lists a number of possible health effects that may occur from inhalation of acetone. Acetone is an irritant that may cause burning in eyes, nose and lungs. At very high levels, it can cause headaches, lightheadedness, dizziness, and confusion (ATSDR Toxicological Profile for Acetone). Currently, there is not enough information to determine whether acetone is carcinogenic (cancer-causing). Research indicates that acetone may cause problems for developing animal fetuses. It is not known whether acetone causes birth defects in humans.

ATSDR cites research suggesting that urban areas of the United States may have mean concentrations of 6.9 ppb (ATSDR Toxicological Profile for Acetone). This is higher than the 3.4 ppb annual mean this study observed in Denver. Unfortunately, the Environmental Protection Agency has not developed "benchmark" values for acetone. Thus, the health significance of these Denver levels is difficult to determine. However, acetone's close association with formaldehyde and acetaldehyde, which are known to be above EPA "benchmark" levels, suggests that emission control strategies directed against the other carbonyls would also reduce acetone concentrations**.**

## References for Carbonyls Section


***Agency For Toxic Substances and Disease Registry. (ATSDR)*** "Toxicological Profiles" for Various Compounds. Web Address: **http://www.atsdr.cdc.gov/toxprofiles/**

Toxicological Profile for Formaldehyde, dated July 1999.
Toxicological Profile for Acetone, dated May 1994.

***California Air Resources Board. (CARB)***
Web Address: **http://www.arb.ca.gov/toxics/cattable.htm**

Acetaldehyde, dated September 1997.

***United States Environmental Protection Agency. (EPA).*** Technology Transfer Network Air Toxics Website. "Dose-Response Assessment for Assessing Health Risks Associated With Exposure To Hazardous Air Pollutants", Table 1, December 2, 2002.
Web Address: **http://www.epa.gov/ttn/atw/toxsource/summary.html**

***Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition.*** (Kirk-Othmer) John Wiley and Sons, New York, New York. USA. 1978.

Acetaldehyde, Volume 1, Pages 97 – 112.
Acetone, Volume 1, Pages 179 – 191.
Formaldehyde, Volume 11, Pages 231 – 250.

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# Section 3 - Volatile Organic Compounds at CAMP Station

# October 2000 to September 2001

# Summary Statistics – Volatile Organic Compounds

## Minimum, Maximum, Mean – All Samples

Volatile organic compound (VOC) data collected at the downtown CAMP station from October 2000 through September 2001 are presented in this section of the Air Toxics Monitoring Report. For the year-long period, volatile organic compounds were sampled on a one-in-six day basis, for a total of 63 samples attempted. Of these, the laboratory successfully processed 58, for a percentage data recovery rate exceeding 92%. (See Table 3.1).

Table 3.2 summarizes the annual minimum, maximum, and mean concentrations for each of the 58 volatile organic compounds measured during the study. Results show that acetylene, propylene, methyl ethyl ketone, benzene, and toluene were the compounds with the highest concentrations in ambient air. These compounds all had sample mean levels greater than one ppb, and were detected in over 98% of the canister samples taken.

**Table 3.1 - Percentage Data Recovery For VOC Samples**

| Sample Days Scheduled | Samples Recovered | Percentage Recovered |
|---|---|---|
| **63** | **58** | **92.1** |

**Table 3.2 - VOC Data Summary**

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| Acetylene | 1.30 | 15.07 | 3.75 | 0 | 0 | 100 |
| Propylene | 0.38 | 2.92 | 1.36 | 0 | 0 | 100 |
| Dichlorodifluoromethane | 0.06 | 0.72 | 0.55 | 0 | 0 | 100 |
| Chloromethane | 0.14 | 0.77 | 0.59 | 0 | 0 | 100 |
| Dichlorotetrafluoroethane | 0.01 | 0.03 | 0.02 | 50 | 86 | 14 |
| Vinyl Chloride | | | | 58 | 100 | 0 |
| 1,3-Butadiene | 0.04 | 0.46 | 0.17 | 2 | 3 | 97 |
| Bromomethane | | | | 58 | 100 | 0 |
| Chloroethane | 0.06 | 0.06 | 0.06 | 57 | 98 | 2 |
| Acetonitrile | 0.27 | 5.53 | 2.49 | 53 | 91 | 9 |
| Trichlorofluoromethane | 0.08 | 1.13 | 0.35 | 0 | 0 | 100 |
| Acylonitrile | 0.27 | 0.27 | 0.27 | 57 | 98 | 2 |
| 1,1-Dichloroethene | | | | 58 | 100 | 0 |
| Methylene Chloride | 0.04 | 1.32 | 0.25 | 0 | 0 | 100 |
| Trichlorotrifluoroethane | 0.02 | 0.15 | 0.09 | 0 | 0 | 100 |
| Trans - 1,2 - Dichloroethylene | | | | 58 | 100 | 0 |
| 1,1 - Dichloroethane | | | | 58 | 100 | 0 |
| Methyl Tert-Butyl Ether | | | | 58 | 100 | 0 |
| Methyl Ethyl Ketone | 0.43 | 2.78 | 1.18 | 1 | 2 | 98 |
| Chloroprene | | | | 58 | 100 | 0 |
| Cis-1,2-Dichloroethylene | | | | 58 | 100 | 0 |
| Bromochloromethane | | | | 58 | 100 | 0 |
| Chloroform | 0.02 | 0.08 | 0.05 | 49 | 84 | 16 |

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| Ethyl Tert-Butyl Ether | | | | 58 | 100 | 0 |
| 1,2 - Dichloroethane | | | | 58 | 100 | 0 |
| 1,1,1 - Trichloroethane | 0.01 | 0.05 | 0.04 | 15 | 26 | 74 |
| Benzene | 0.32 | 2.35 | 1.00 | 0 | 0 | 100 |
| Carbon Tetrachloride | 0.01 | 0.13 | 0.08 | 5 | 9 | 91 |
| tert-Amyl Methyl Ether | | | | 58 | 100 | 0 |
| 1,2 - Dichloropropane | | | | 58 | 100 | 0 |
| Ethyl Acrylate | | | | 58 | 100 | 0 |
| Bromodichloromethane | | | | 58 | 100 | 0 |
| Trichloroethylene | 0.02 | 0.20 | 0.06 | 53 | 91 | 9 |
| Methyl Methacrylate | | | | 58 | 100 | 0 |
| cis -1,3 - Dichloropropene | | | | 58 | 100 | 0 |
| Methyl Isobutyl Ketone | 0.15 | 0.27 | 0.19 | 52 | 90 | 10 |
| trans - 1,3 - Dichloropropene | | | | 58 | 100 | 0 |
| 1,1,2 - Trichloroethane | | | | 58 | 100 | 0 |
| Toluene | 0.56 | 5.41 | 2.22 | 0 | 0 | 100 |
| Dibromochloromethane | | | | 58 | 100 | 0 |
| 1,2-Dibromoethane | | | | 58 | 100 | 0 |
| n-Octane | 0.04 | 0.43 | 0.15 | 1 | 2 | 98 |
| Tetrachloroethylene | 0.02 | 0.19 | 0.07 | 14 | 24 | 76 |
| Chlorobenzene | | | | 58 | 100 | 0 |
| Ethyl benzene | 0.10 | 0.79 | 0.33 | 0 | 0 | 100 |
| m,p - Xylene | 0.13 | 2.41 | 0.95 | 0 | 0 | 100 |
| Bromoform | | | | 58 | 100 | 0 |
| Styrene | 0.04 | 0.26 | 0.09 | 3 | 5 | 95 |
| 1,1,2,2 - Tetrachloroethane | | | | 58 | 100 | 0 |
| O - Xylene | 0.11 | 1.03 | 0.44 | 0 | 0 | 100 |

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| 1,3,5-Trimethylbenzene | 0.05 | 0.49 | 0.21 | 0 | 0 | 100 |
| 1,2,4-Trimethylbenzene | 0.09 | 1.36 | 0.62 | 0 | 0 | 100 |
| M - Dichlorobenzene | | | | 58 | 100 | 0 |
| Chloromethylbenzene | | | | 58 | 100 | 0 |
| P - Dichlorobenzene | 0.01 | 0.05 | 0.03 | 35 | 60 | 40 |
| O - Dichlorobenzene | | | | 58 | 100 | 0 |
| 1,2,4-Trichlorobenzene | | | | 58 | 100 | 0 |
| Hexachloro-1,3-Butadiene | | | | 58 | 100 | 0 |

**Table 3.2, completed.**

## Percentage of Samples For Which Compound Was Detected

Table 3.2 shows the percentage of the samples in which each VOC was detected. Nineteen of the compounds were detected in over 90% of the samples. These compounds are listed in Table 3.3. In contrast, 29 VOCs were never detected at all during the study. This is one-half of the compounds that were sampled. Compounds never detected are listed in Table 3.4. It is interesting to note that vinyl chloride, which is considered to be very toxic, was not detected. Methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME), which are added to automotive fuels to increase oxygen, were not detected.

**Table 3.3 - Compounds Detected in Over 90% of the VOC Air Samples Taken at CAMP**

| |
|---|
| **Acetylene** |
| **Propylene** |
| **Dichlorodifluoromethane** |
| **Chloromethane** |
| **1,3-Butadiene** |
| **Trichlorofluoromethane** |
| **Methylene Chloride** |
| **Trichlorotrifluoroethane** |
| **Methyl Ethyl Ketone** |
| **Benzene** |
| **Carbon Tetrachloride** |
| **Toluene** |
| **n-Octane** |
| **Ethylbenzene** |
| **m,p-Xylene** |
| **Styrene** |
| **o-Xylene** |
| **1,3,5-Trimethylbenzene** |
| **1,2,4-Trimethylbenzene** |

**Table 3.4 - Compounds Never Detected in the VOC Air Samples Taken at CAMP**

| | |
|---|---|
| **Vinyl Chloride** | **Methyl Methacrylate** |
| **Bromomethane** | **cis-1,3-Dichloropropene** |
| **1,1-Dichloroethene** | **Trans-1,3-Dichloropropene** |
| **trans-1,2-Dichloroethylene** | **1,1,2-Trichloroethane** |
| **1,1-Dichloroethane** | **Dibromochloromethane** |
| **Methyl tert-Butyl Ether** | **1,2-Dibromoethane** |
| **Chloroprene** | **Chlorobenzene** |
| **cis-1,2-Dichloroethylene** | **Bromoform** |
| **Bromochloromethane** | **1,1,2,2-Tetrachloroethane** |
| **Ethyl Tert-Butyl Ether** | **m-Dichlorobenzene** |
| **1,2-Dichloroethane** | **Chloromethylbenzene** |
| **tert-Amyl Methyl Ether** | **o-Dichlorobenzene** |
| **1,2-Dichloropropane** | **1,2,4-Trichlorobenzene** |
| **Ethyl Acrylate** | **Hexachloro-1,3-Butadiene** |
| **Bromodichloromethane** | |

## Weekend Vs. Weekday Results

For the year of VOC data, an analysis of weekday versus weekend levels was conducted. Table 3.5 gives summary statistics for minimum, maximum and mean of the weekday samples versus the same statistics for the weekend samples. Figure 3.1 is a graph of these results. For almost all VOCs, the weekday mean is greater than the weekend mean. Carbon tetrachloride and chloromethane are the exceptions. Methyl isobutyl ketone, dichloro-tetrafluoroethane, chloroethane, acetonitrile, and acrylonitrile were only detected on the weekdays. However, Table 3.2 indicates that these weekday-only compounds were detected in fewer than fifteen percent of the air quality samples.

## Graphs – Volatile Organic Compounds

### Individual Compounds

Twenty-nine compounds were detected during the study. Two of the compounds detected at the highest concentrations were graphed with 16 ppbv as the maximum value on the y-axis. These compounds are acetylene and toluene (figure 3.2).

Another group of compounds were detected consistently, but at levels of 4 ppbv or less. These compounds are benzene (figure 3.3), methyl ethyl ketone (figure 3.3), methylene chloride, m,p-xylene, o-xylene, propylene (figure 3.3), trichlorofluoromethane, and 1,2,4-trimethylbenzene. These compounds are emitted from mobile sources.

A number of compounds were regularly present at levels below 1 ppbv. These were 1,3-butadiene, chloromethane, dichlorodifluoromethane, ethylbenzene, methyl isobutyl ketone, styrene, and 1,3,5-trimethyl benzene. Acrylonitrile was unusual, with a single detection at approximately 0.3 ppbv.

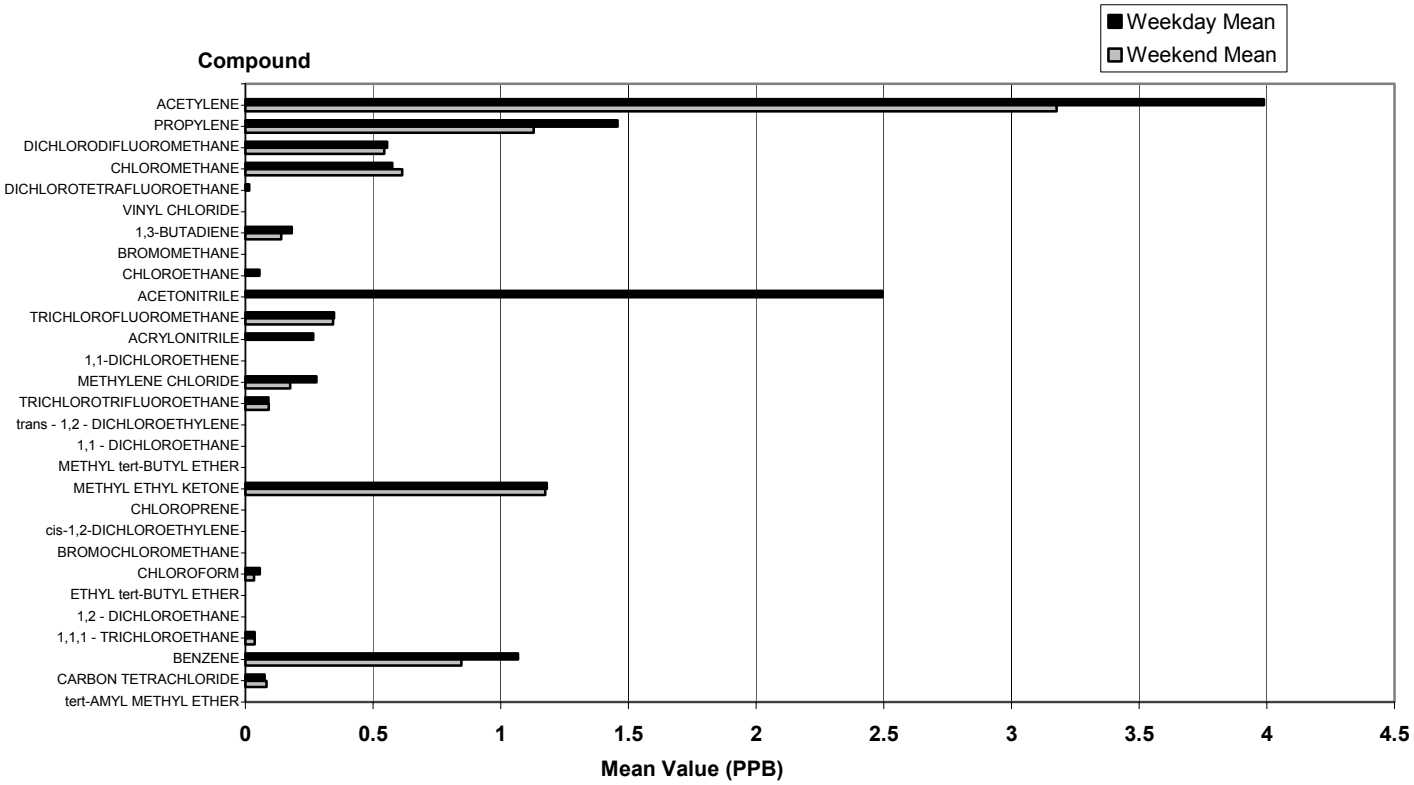
The final group of compounds were measured at levels of less than 0.20 ppbv. Carbon tetrachloride, p-dichlorobenzene, 1,1,1-trichloroethane, and trichlorotrifluoroethane were consistently seen. Detections of chloroethane, chloroform, dichlorotetrafluoroethane, and trichloroethylene were sporadic.

**Table 3.5 - Summary statistics for minimum, maximum and mean of the weekday samples versus the same statistics for the weekend samples**

| | Summary Statistics WEEKDAY (PPB) | | | Summary Statistics WEEKEND (PPB) | | |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Minimum | Maximum | Mean |
| ACETYLENE | 1.39 | 11.22 | 3.99 | 1.30 | 15.07 | 3.18 |
| PROPYLENE | 0.38 | 2.90 | 1.46 | 0.60 | 2.92 | 1.13 |
| DICHLORODIFLUOROMETHANE | 0.19 | 0.72 | 0.56 | 0.06 | 0.67 | 0.54 |
| CHLOROMETHANE | 0.14 | 0.77 | 0.58 | 0.42 | 0.74 | 0.61 |
| DICHLOROTETRAFLUOROETHANE | 0.01 | 0.03 | 0.02 | | | |
| VINYL CHLORIDE | | | | | | |
| 1,3-BUTADIENE | 0.05 | 0.46 | 0.18 | 0.04 | 0.44 | 0.14 |
| BROMOMETHANE | | | | | | |
| CHLOROETHANE | 0.06 | 0.06 | 0.06 | | | |
| ACETONITRILE | 0.27 | 5.53 | 2.49 | | | |
| TRICHLOROFLUOROMETHANE | 0.08 | 1.13 | 0.35 | 0.23 | 0.61 | 0.34 |
| ACRYLONITRILE | 0.27 | 0.27 | 0.27 | | | |
| 1,1-DICHLOROETHENE | | | | | | |
| METHYLENE CHLORIDE | 0.04 | 1.32 | 0.28 | 0.06 | 0.37 | 0.18 |
| TRICHLOROTRIFLUOROETHANE | 0.02 | 0.15 | 0.09 | 0.06 | 0.12 | 0.09 |
| trans-1,2-DICHLOROETHYLENE | | | | | | |
| 1,1-DICHLOROETHANE | | | | | | |
| METHY tert BUTYL ETHER | | | | | | |
| METHYL ETHYL KETONE | 0.48 | 2.25 | 1.18 | 0.43 | 2.78 | 1.17 |
| CHLOROPRENE | | | | | | |
| cis-1,2-DICHLOROETHYLENE | | | | | | |
| BROMOCHLOROMETHANE | | | | | | |
| CHLOROFORM | 0.03 | 0.08 | 0.06 | 0.02 | 0.04 | 0.03 |
| ETHYL tert-BUTYL ETHER | | | | | | |
| 1,2-DICHLOROETHANE | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1,1,1-TRICHLOROETHANE | 0.01 | 0.05 | 0.04 | 0.02 | 0.05 | 0.04 |
| BENZENE | 0.32 | 2.21 | 1.07 | 0.48 | 2.35 | 0.85 |
| CARBON TETRACHLORIDE | 0.01 | 0.12 | 0.08 | 0.04 | 0.13 | 0.08 |
| tert-AMYL METHYL ETHER | | | | | | |
| | | | | | | |
| ETHYL ACRYLATE | | | | | | |
| BROMODICHLOROMETHANE | | | | | | |
| TRICHLOROETHYLENE | 0.02 | 0.20 | 0.07 | 0.02 | 0.02 | 0.02 |
| METHYL METHACRYLATE | | | | | | |
| cis-1,3-DICHLOROPROPENE | | | | | | |
| METHYL ISOBUTYL KETONE | 0.15 | 0.27 | 0.19 | | | |
| trans-1,3-DICHLOROPROPENE | | | | | | |
| 1,1,2-TRICHLOROETHANE | | | | | | |
| TOLUENE | 0.56 | 5.41 | 2.43 | 0.82 | 4.14 | 1.71 |
| DIBROMOCHLOROMETHANE | | | | | | |
| 1,2-DIBROMOETHANE | | | | | | |
| N-OCTANE | 0.05 | 0.43 | 0.16 | 0.04 | 0.28 | 0.11 |
| TETRACHLOROETHYLENE | 0.03 | 0.19 | 0.08 | 0.02 | 0.12 | 0.05 |
| CHLOROBENZENE | | | | | | |
| ETHYLBENZENE | 0.10 | 0.79 | 0.36 | 0.14 | 0.65 | 0.26 |
| m,p-XYLENE | 0.13 | 2.41 | 1.04 | 0.39 | 1.80 | 0.74 |
| BROMOFORM | | | | | | |
| STYRENE | 0.04 | 0.26 | 0.09 | 0.04 | 0.11 | 0.07 |
| 1,1,2,2-TETRACHLOROETHANE | | | | | | |
| o-XYLENE | 0.11 | 1.03 | 0.48 | 0.20 | 0.84 | 0.35 |
| 1,3,5-TRIMETHYLBENZENE | 0.05 | 0.49 | 0.23 | 0.07 | 0.31 | 0.18 |
| 1,2,4-TRIMETHYLBENZENE | 0.09 | 1.36 | 0.65 | 0.23 | 0.96 | 0.54 |
| m-DICHLOROBENZENE | | | | | | |
| CHLOROMETHYLBENZENE | | | | | | |
| p-DICHLOROBENZENE | 0.01 | 0.04 | 0.03 | 0.01 | 0.05 | 0.03 |
| o-DICHLOROBENZENE | | | | | | |
| 1,2,4-TRICHLOROBENZENE | | | | | | |
| HEXACHLORO-1,3-BUTADIENE | | | | | | |

**Figure 3.1 - Weekday Vs. Weekend Mean For VOCs At CAMP**



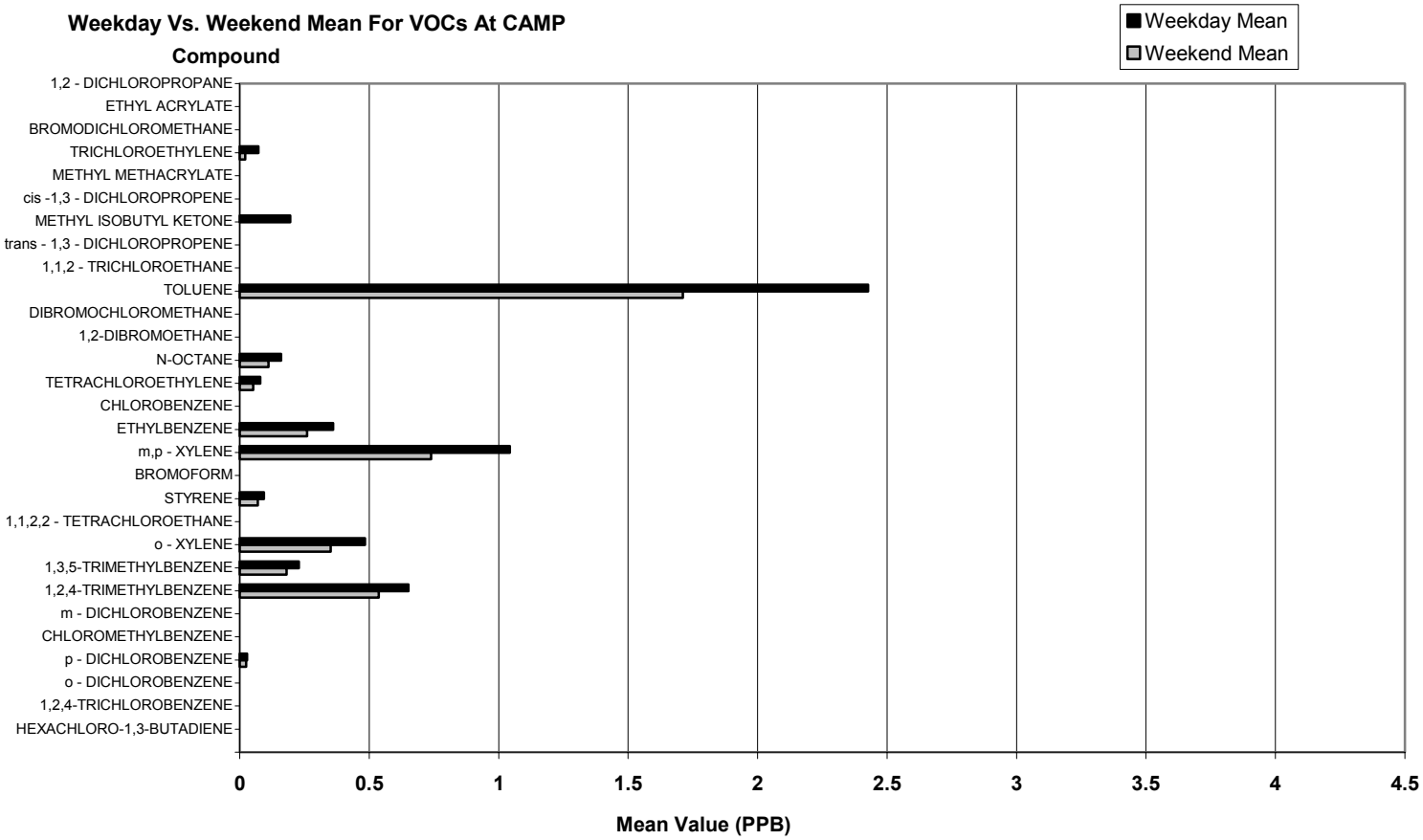



**Figure 3.1, completed.**

**Figure 3.2 - Largest Concentration Volatile Organic Compounds At CAMP**

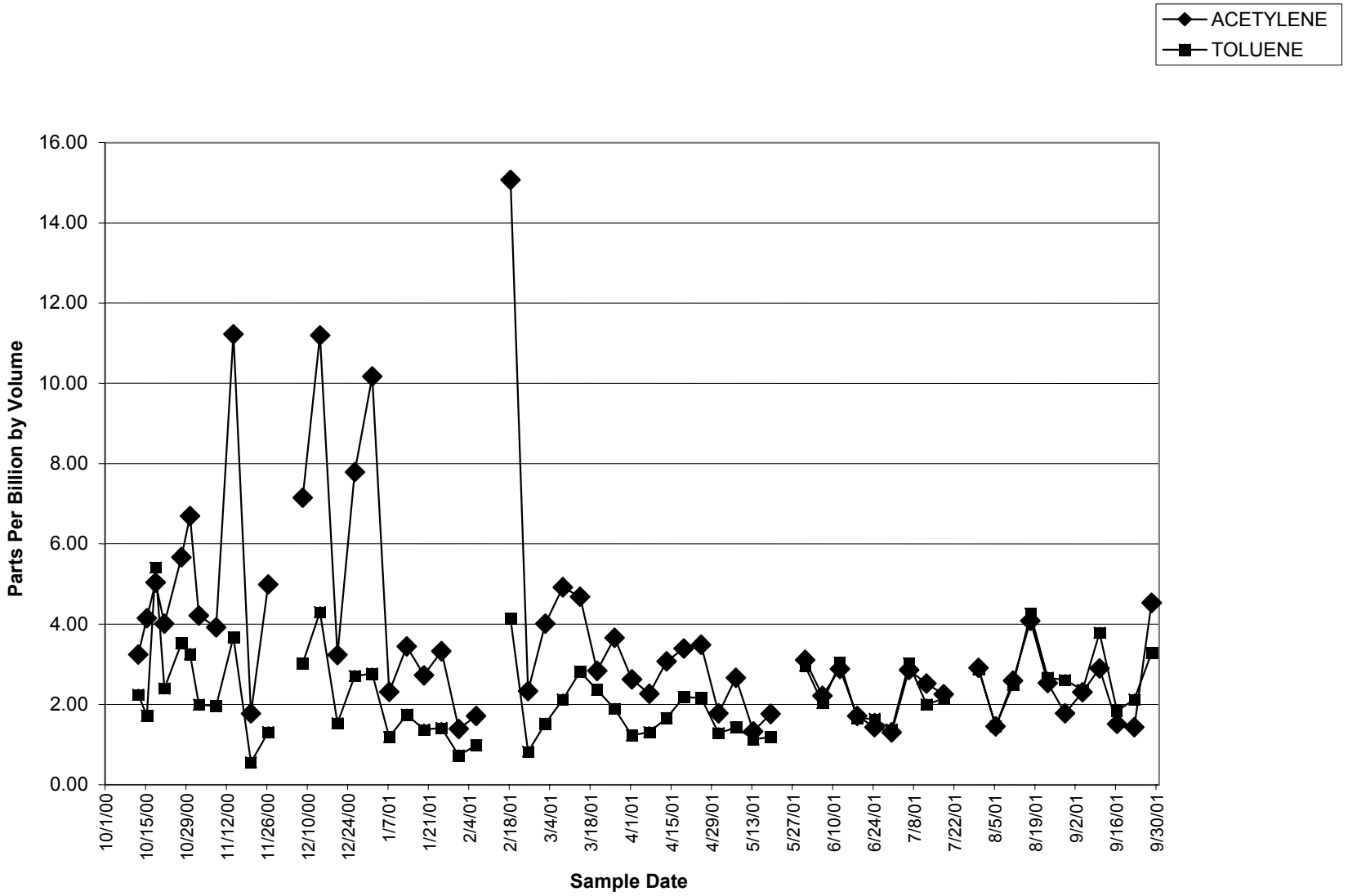


**Figure 3.3 - Largest Concentration Volatile Organic Compounds At CAMP**

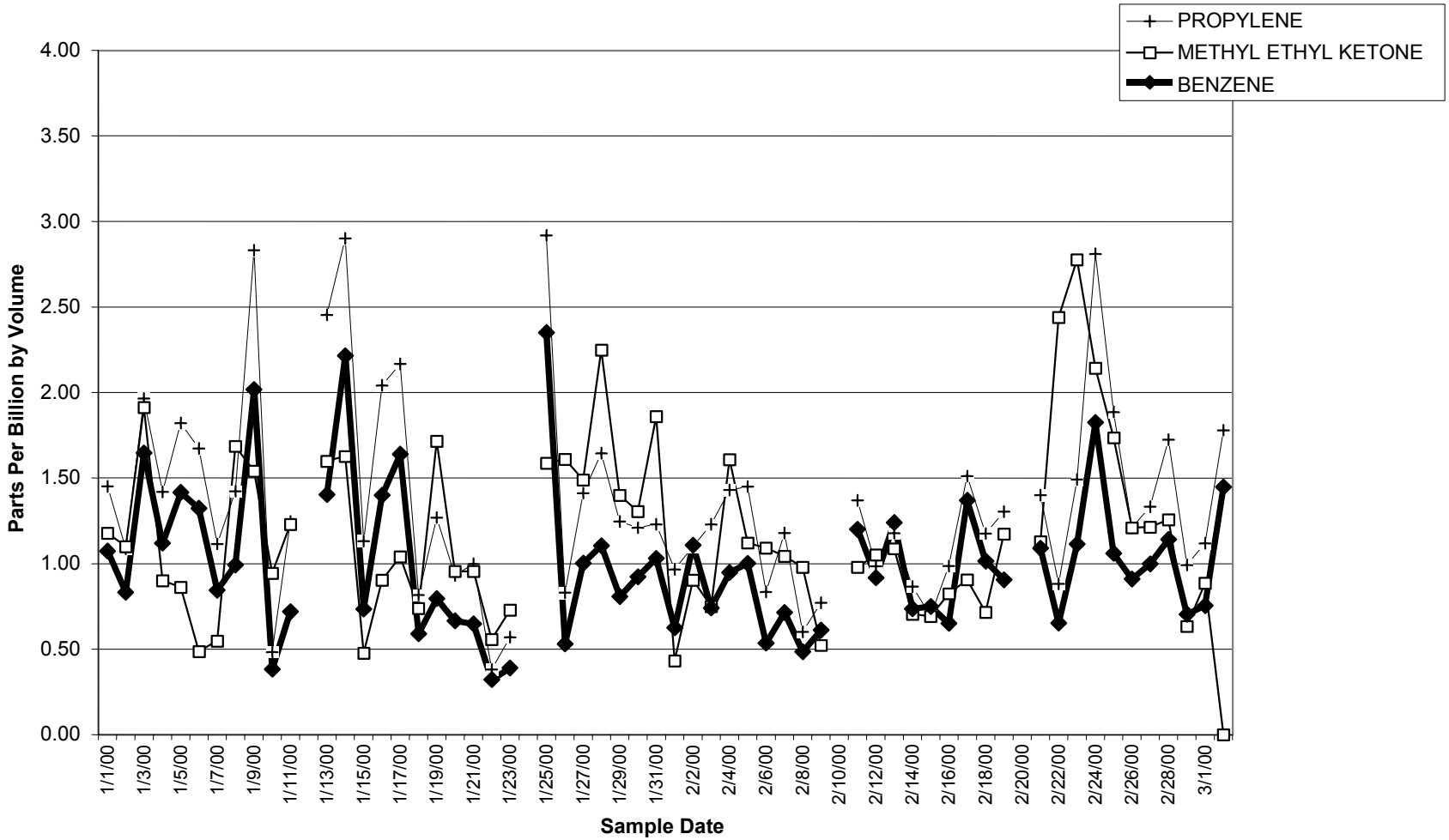



**Figure 3.9**

## Compounds As Groups

For the purpose of analysis, some of the compounds were graphed in groups. Figure 3.2 shows that the two largest-concentration VOCs, acetylene and toluene, frequently trend up and downwards simultaneously. Figures 3.4 through 3.10 graph various chlorofluorocarbons that are expected to have common sources. Dichlorodifluoro-methane trends closely with chloromethane. Trichlorofluoromethane often follows trends for methylene chloride. 1,1,1-trichloroethane and carbon tetrachloride show similar trends. Tetrachloroethylene is rarely detected, but sometimes peaks along with trichloroethylene. Trichlorotrifluoroethane remains consistently low, and does not follow the pattern for methylene chloride. 1,1,1-trichloroethane and carbon tetrachloride remain low for much of the time, but track each other closely. The two trimethylbenzene isomers mirror each other, although 1,3,5 is always lower than the 1,2,4 isomer. O-xylene levels are mid-way between those of the trimethylbenzene isomers.

The next graph (Figure 3.11) is a plot of benzene, toluene, ethyl-benzene, xylenes, and styrene. These compounds are emitted by sources such as motor vehicles, gasoline stations and oil refineries. This year-long graph shows that they trend up and down together.

**Figure 3.4 - Dichlorodifluoromethane Versus Chloromethane**

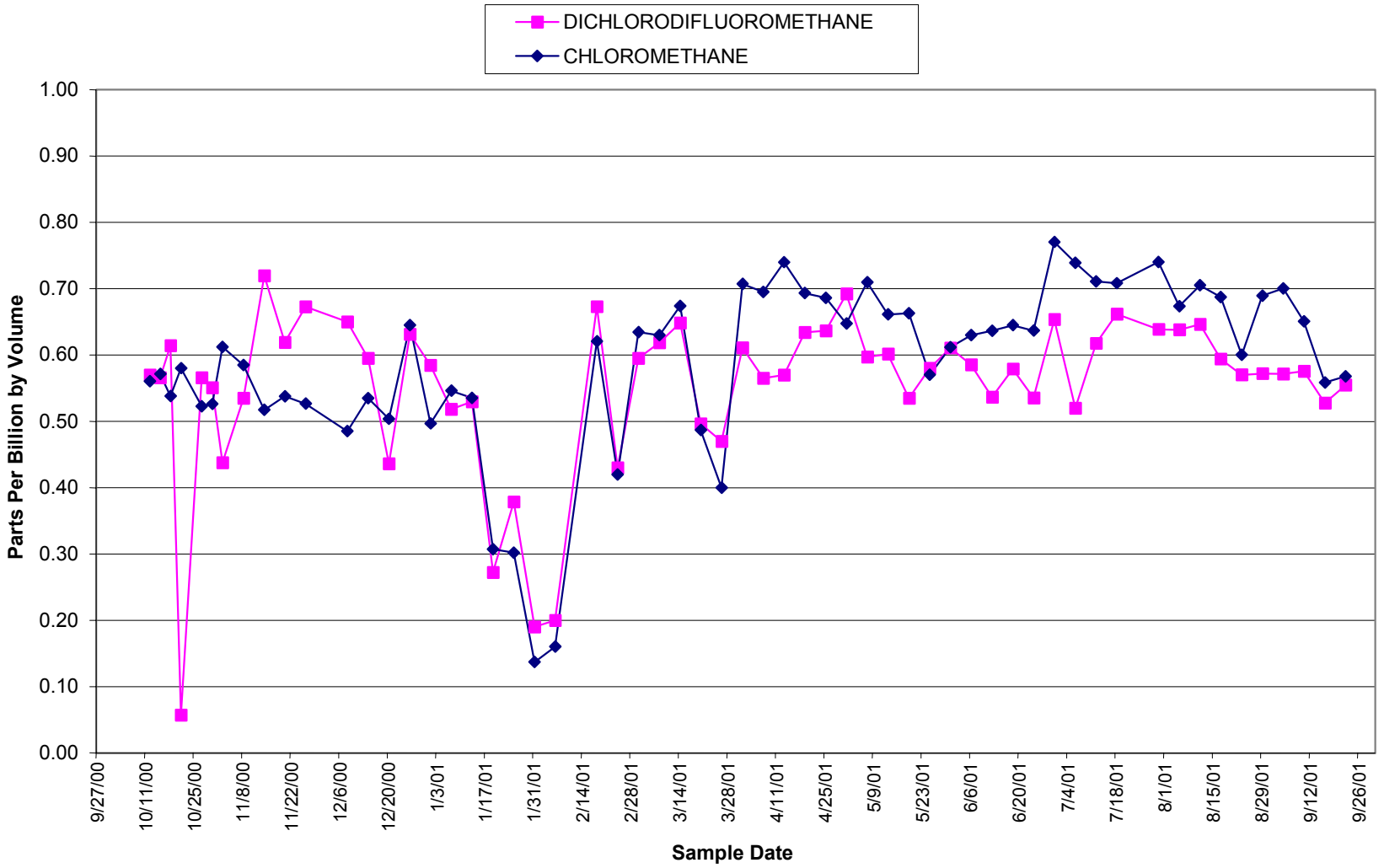


**Figure 3.5 - Trichlorofluoromethane Versus Methylene Chloride**

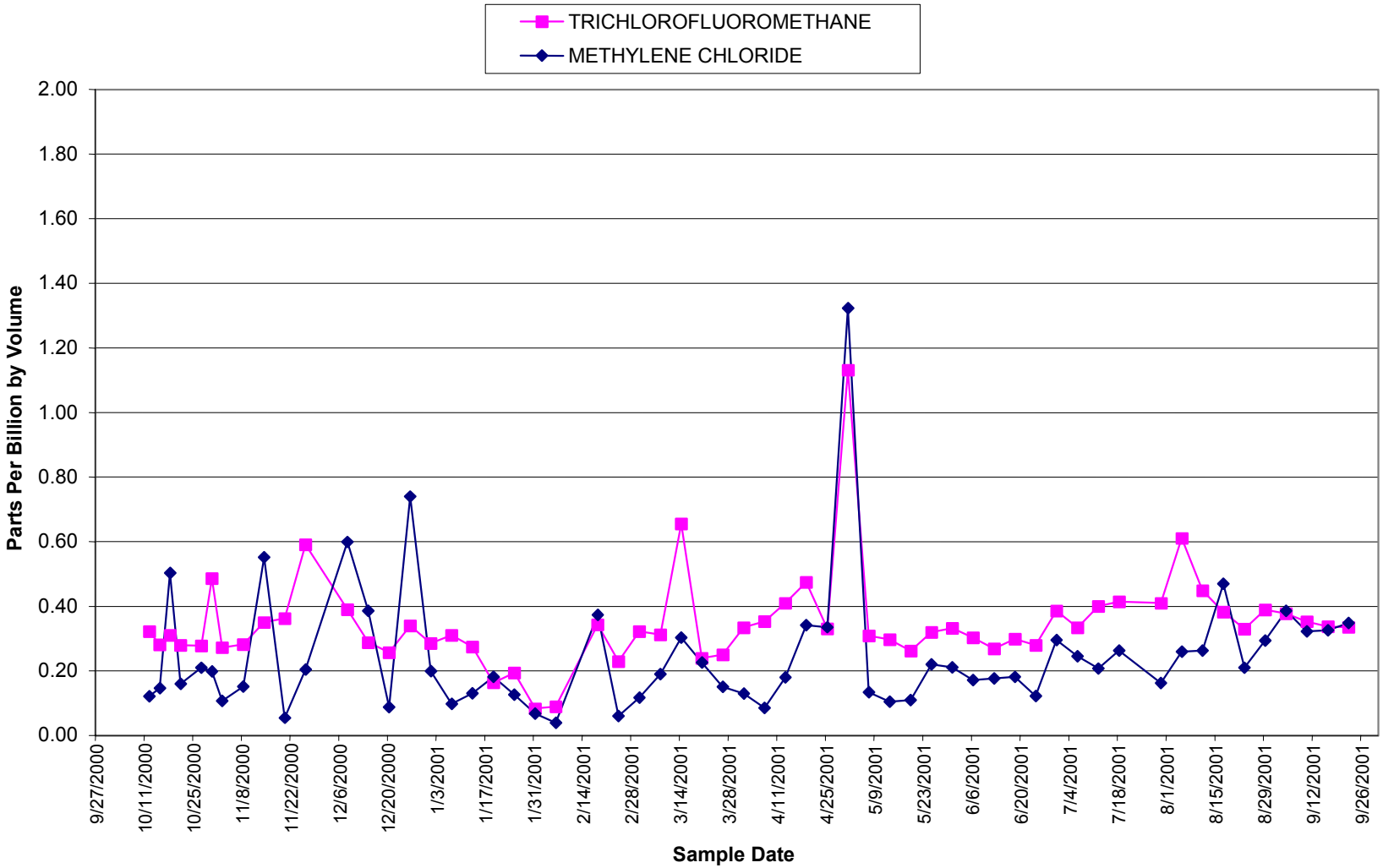


**Figure 3.6 – 1,1,1-Trichloroethene Versus Carbon Tetrachloride**

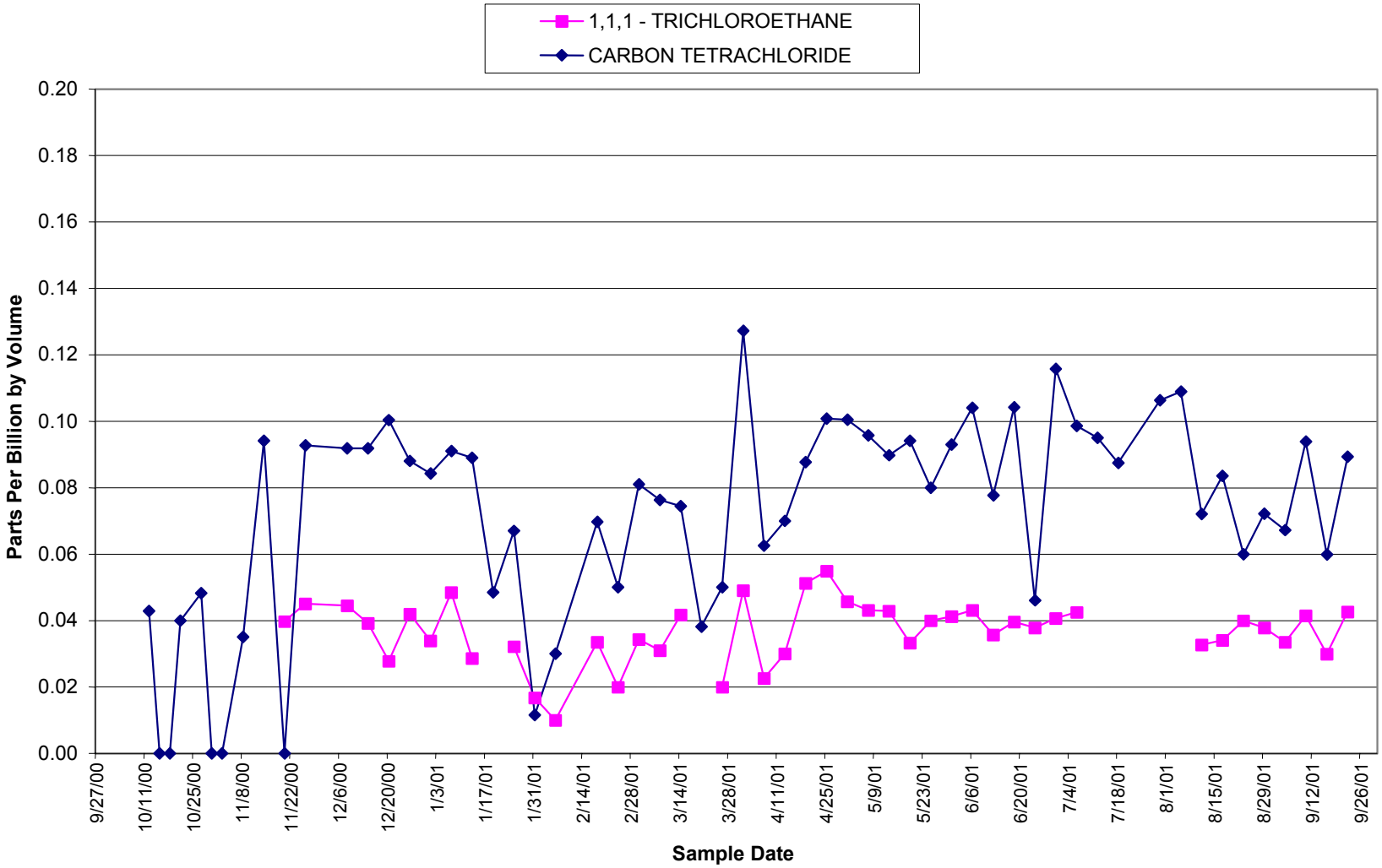


**Figure 3.7 - Trichloroethylene Versus Tetrachloroethylene**

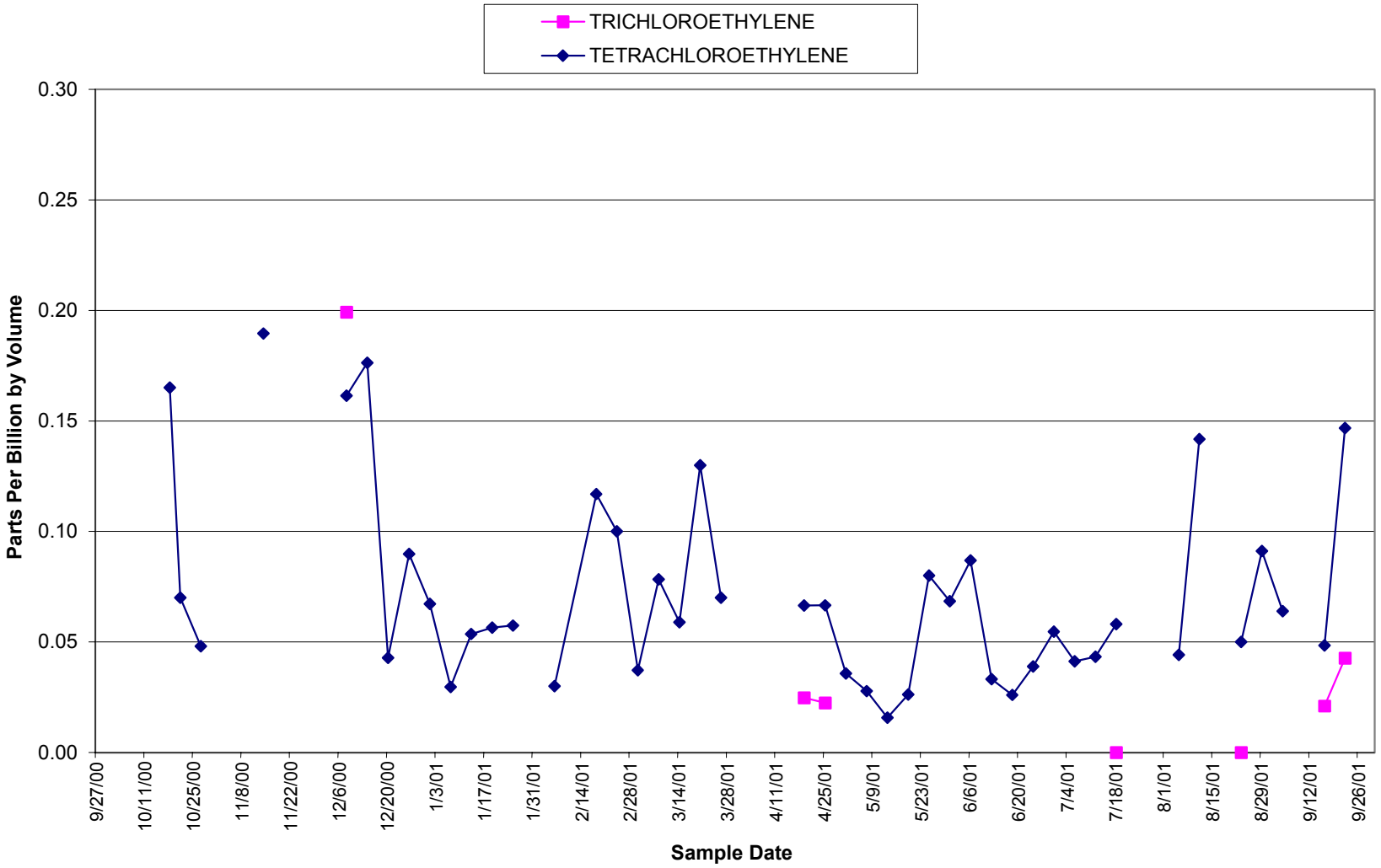


**Figure 3.8 - Methylene Chloride Versus Trichlorotrifluoroethane**

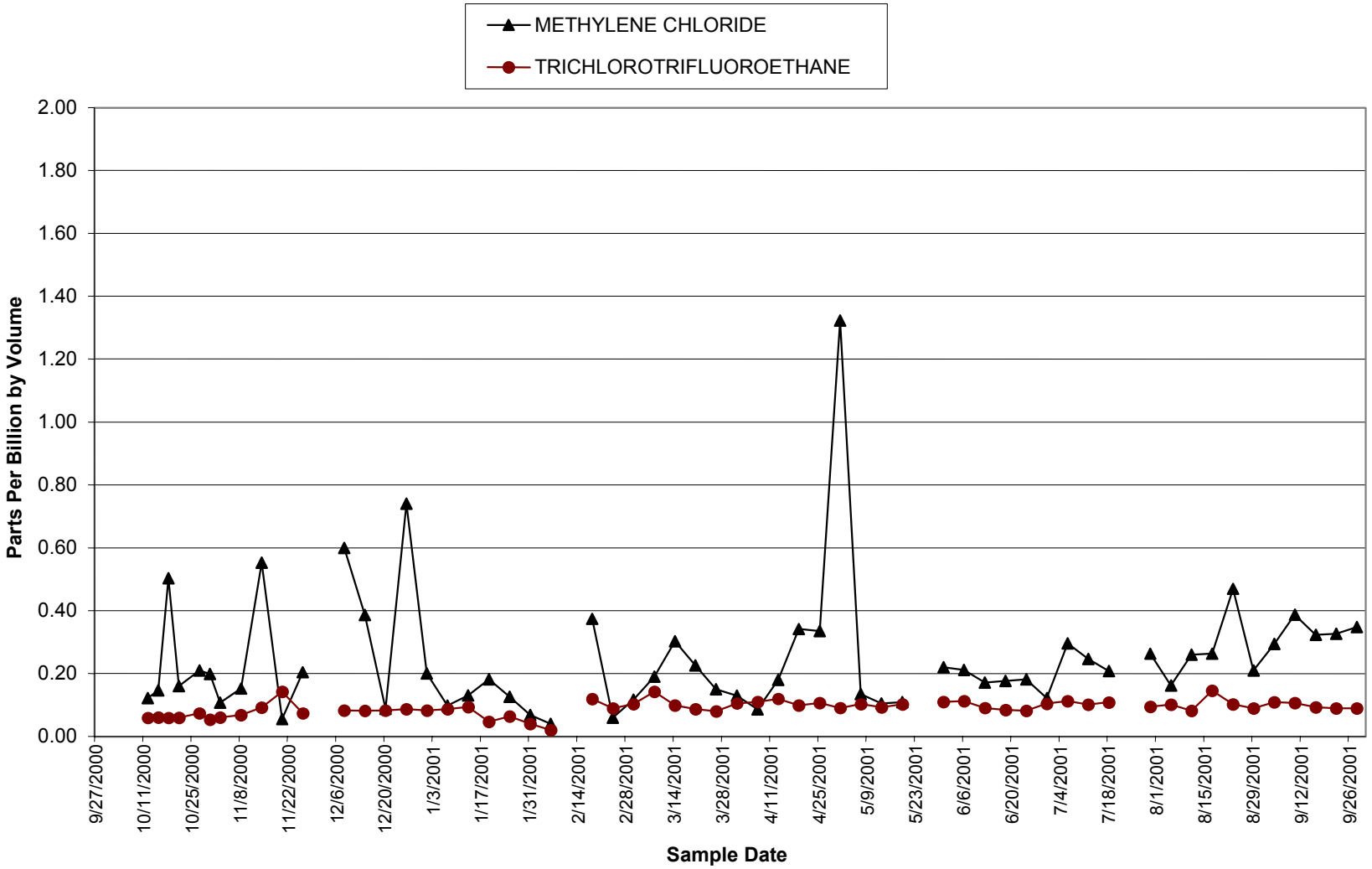


**Figure 3.9 - 1,1,1 - Trichloroethane Versus Carbon Tetrachloride**

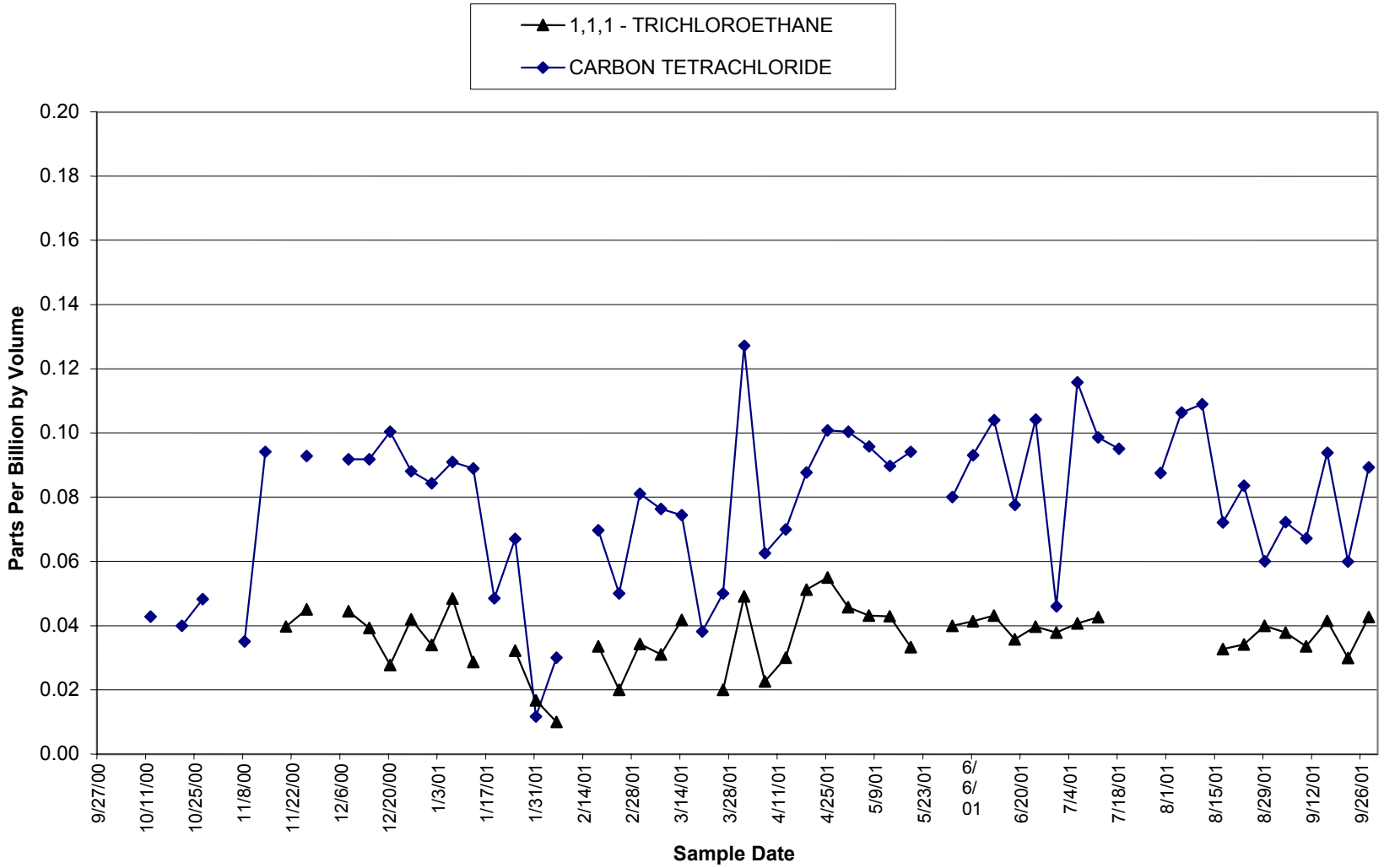


**Figure 3.10 - Trimethylbenzene Isomers Versus o-Xylene**

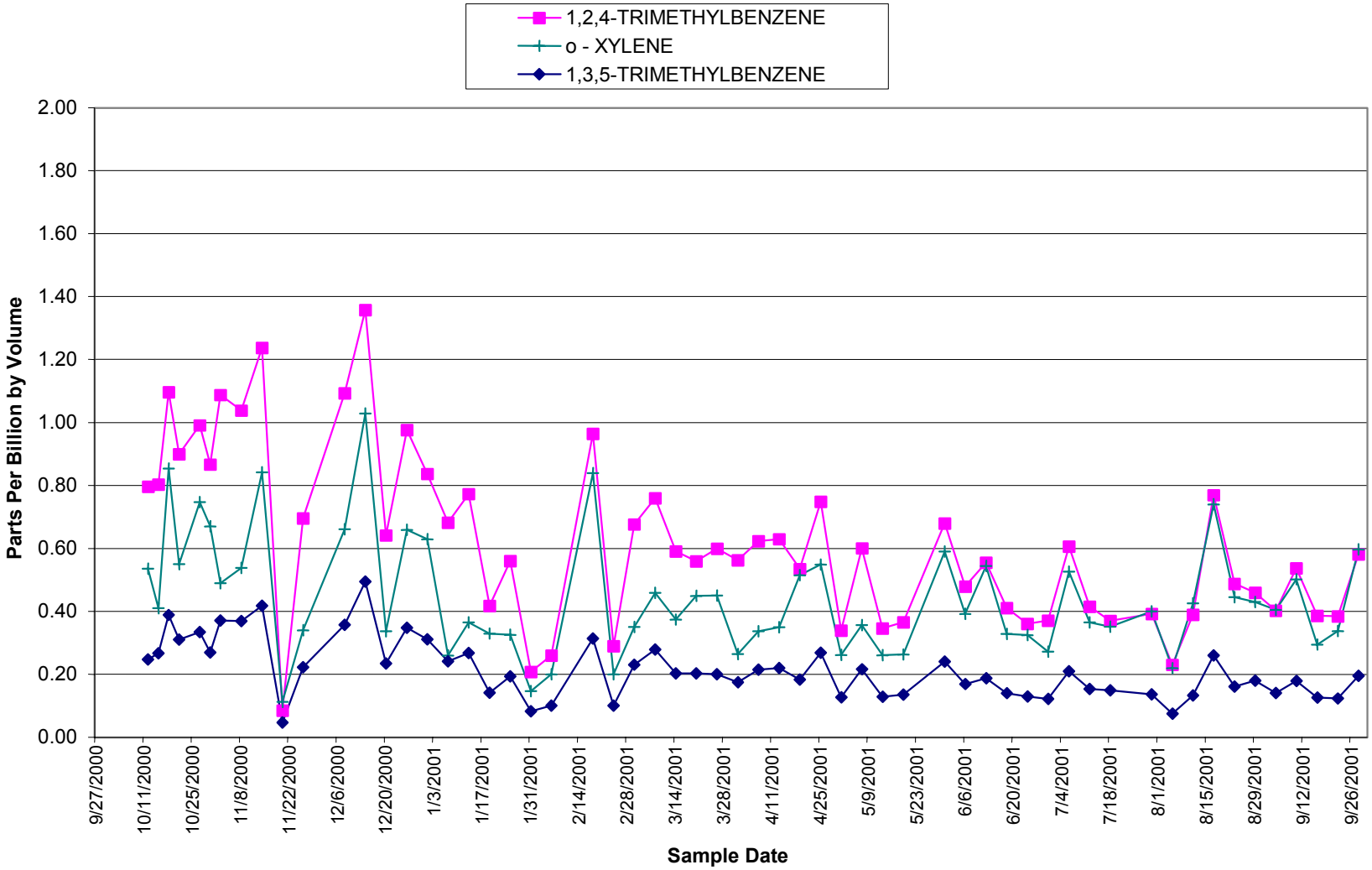
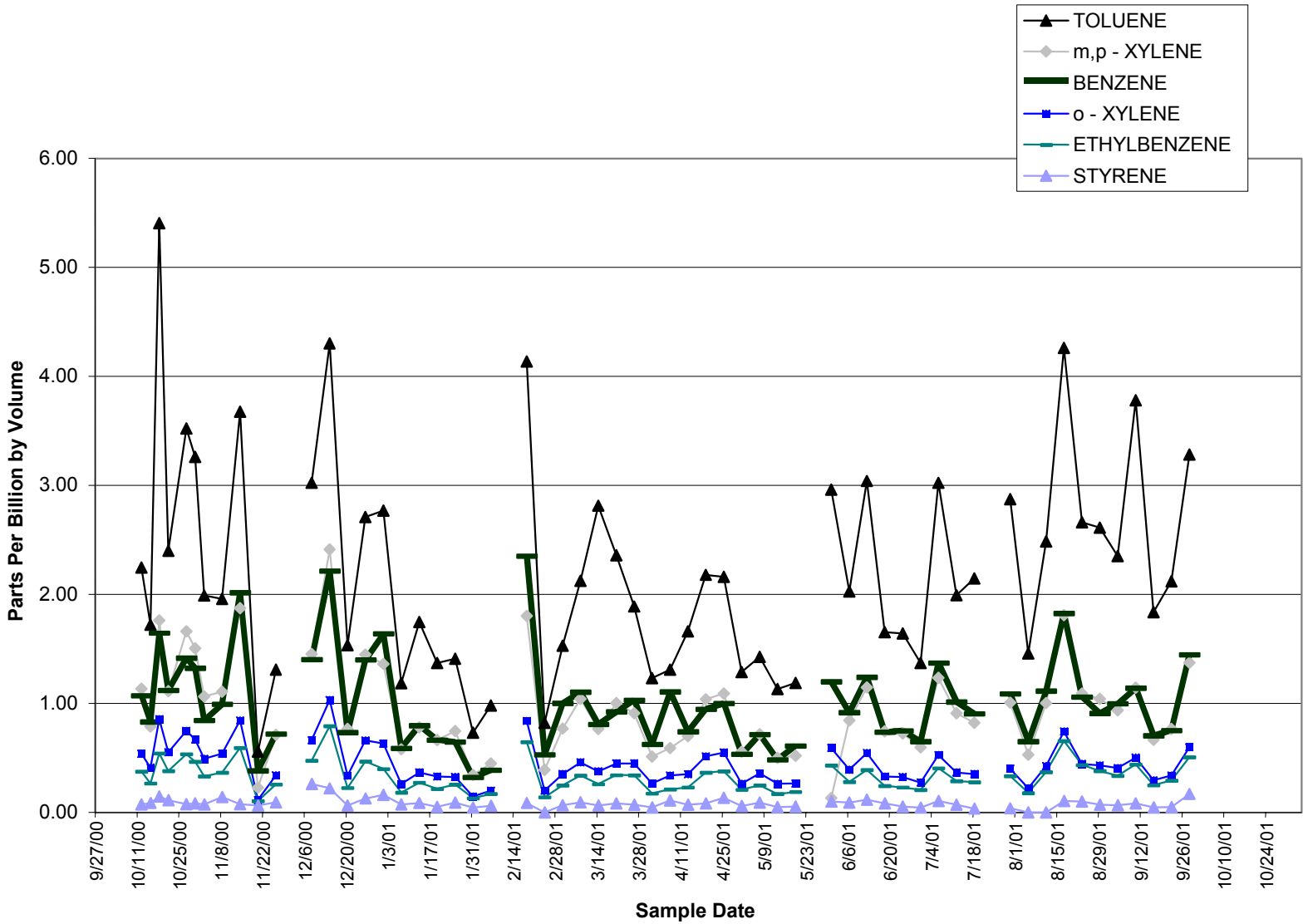


**Figure 3.11 - BTEX Compounds**



## Correlation Coefficients Between Compounds – Volatile Organic Compounds

A correlation coefficient analysis was conducted for the volatile organic compounds. To simplify the calculations, only VOCs detected in over 75% of the air samples were analyzed for correlation to other compounds. Results (Table 3.6) show that acetylene and propylene, the largest concentration compounds, are correlated strongly to the benzene-toluene-ethylbenzene-xylene (BTEX) group. The chlorofluorocarbons are not correlated to the BTEX suite, but show some correlation to one another. This is expected, because air emissions of different compound groups likely come from different sources.

**Table 3.6 - Correlation Coefficients For VOCs Detected In Over 75% of the Samples**

| | Acetylene | Propylene | Dichlorodi-Fluoromethane | Chloromethane | 1,3-Butadiene |
|---|---|---|---|---|---|
| **Acetylene** | 1.00 | | | | |
| **Propylene** | **0.83** | 1.00 | | | |
| **Dichlorodifluoromethane** | 0.26 | 0.39 | 1.00 | | |
| **Chloromethane** | -0.08 | 0.16 | 0.65 | 1.00 | |
| **1,3-Butadiene** | 0.73 | **0.77** | 0.13 | -0.09 | 1.00 |
| **Trichlorofluoromethane** | 0.01 | 0.11 | 0.56 | 0.47 | -0.07 |
| **Methylene Chloride** | 0.28 | 0.40 | 0.41 | 0.20 | 0.23 |
| **Trichlorotrifluoroethane** | -0.01 | 0.19 | 0.61 | 0.68 | -0.03 |
| **Methyl Ethyl Ketone** | 0.22 | 0.44 | 0.34 | 0.14 | 0.21 |
| **Benzene** | **0.83** | **0.94** | 0.37 | 0.17 | **0.76** |
| **Carbon Tetrachloride** | 0.06 | 0.13 | 0.64 | 0.61 | -0.09 |
| **Toluene** | 0.61 | **0.84** | 0.35 | 0.20 | 0.69 |
| **N-Octane** | **0.78** | **0.82** | 0.26 | -0.04 | 0.61 |
| **Tetrachloroethylene** | 0.63 | **0.78** | 0.23 | -0.14 | 0.54 |
| **Ethylbenzene** | 0.73 | **0.93** | 0.31 | 0.12 | **0.77** |
| **M,P-Xylene** | **0.75** | **0.90** | 0.28 | 0.10 | 0.74 |
| **Styrene** | 0.51 | 0.61 | 0.16 | -0.04 | 0.67 |
| **O-Xylene** | **0.79** | **0.91** | 0.29 | 0.09 | **0.78** |
| **1,3,5-Trimethylbenzene** | **0.76** | **0.74** | 0.15 | 0.00 | 0.66 |
| **1,2,4-Trimethylbenzene** | **0.76** | **0.75** | 0.16 | 0.00 | 0.66 |

**Bold = Correlation Greater Than + 0.75**

**Correlation Coefficients For VOCs Detected In Over 75% of the Samples**

| | Trichloro-fluoromethane | Methylene Chloride | Trichlorotri-Fluoroethane | Methyl Ethyl Ketone | Benzene | Carbon Tetrachloride |
|---|---|---|---|---|---|---|
| **Acetylene** | | | | | | |
| **Propylene** | | | | | | |
| **Dichlorodifluoromethane** | | | | | | |
| **Chloromethane** | | | | | | |
| **1,3-Butadiene** | | | | | | |
| **Trichlorofluoromethane** | 1.00 | | | | | |
| **Methylene Chloride** | 0.68 | 1.00 | | | | |
| **Trichlorotrifluoroethane** | 0.29 | 0.09 | 1.00 | | | |
| **Methyl Ethyl Ketone** | 0.23 | 0.18 | 0.25 | 1.00 | | |
| **Benzene** | 0.05 | 0.33 | 0.16 | 0.37 | 1.00 | |
| **Carbon Tetrachloride** | 0.42 | 0.28 | 0.47 | 0.06 | 0.14 | 1.00 |
| **Toluene** | 0.12 | 0.38 | 0.09 | 0.36 | **0.88** | 0.12 |
| **N-Octane** | -0.02 | 0.37 | -0.08 | 0.30 | **0.83** | 0.08 |
| **Tetrachloroethylene** | -0.04 | 0.33 | 0.08 | 0.49 | **0.76** | -0.03 |
| **Ethylbenzene** | 0.06 | 0.38 | 0.07 | 0.38 | **0.94** | 0.06 |
| **M,P-Xylene** | 0.04 | 0.36 | -0.02 | 0.33 | **0.90** | 0.08 |
| **Styrene** | -0.02 | 0.28 | -0.05 | 0.41 | 0.58 | 0.13 |
| **O-Xylene** | 0.02 | 0.35 | -0.01 | 0.31 | **0.94** | 0.07 |
| **1,3,5-Trimethylbenzene** | -0.07 | 0.22 | -0.13 | 0.17 | 0.73 | 0.02 |
| **1,2,4-Trimethylbenzene** | -0.05 | 0.22 | -0.15 | 0.17 | 0.73 | 0.02 |

**Bold = Correlation Greater Than + 0.75**

**Table 3.6, continued.**

**Correlation Coefficients For VOCs Detected In Over 75% of the Samples**

| | Toluene | N-Octane | Tetrachloro-Ethylene | Ethylbenzene | M,P-Xylene | Styrene |
|---|---|---|---|---|---|---|
| **Acetylene** | | | | | | |
| **Propylene** | | | | | | |
| **Dichlorodifluoromethane** | | | | | | |
| **Chloromethane** | | | | | | |
| **1,3-Butadiene** | | | | | | |
| **Trichlorofluoromethane** | | | | | | |
| **Methylene Chloride** | | | | | | |
| **Trichlorotrifluoroethane** | | | | | | |
| **Methyl Ethyl Ketone** | | | | | | |
| **Benzene** | | | | | | |
| **Carbon Tetrachloride** | | | | | | |
| **Toluene** | 1.00 | | | | | |
| **N-Octane** | **0.77** | 1.00 | | | | |
| **Tetrachloroethylene** | 0.72 | 0.74 | 1.00 | | | |
| **Ethylbenzene** | **0.92** | **0.84** | **0.78** | 1.00 | | |
| **M,P-Xylene** | **0.86** | **0.85** | 0.74 | **0.93** | 1.00 | |
| **Styrene** | 0.50 | 0.55 | 0.67 | 0.61 | 0.59 | 1.00 |
| **O-Xylene** | **0.90** | **0.89** | **0.78** | **0.97** | **0.93** | 0.65 |
| **1,3,5-Trimethylbenzene** | 0.62 | **0.78** | 0.67 | 0.73 | **0.76** | 0.66 |
| **1,2,4-Trimethylbenzene** | 0.63 | **0.79** | 0.69 | 0.74 | **0.77** | 0.64 |

**Bold = Correlation Greater Than + 0.75**

**Table 3.6, continued.**

**Correlation Coefficients For VOCs Detected In Over 75% of the Samples**

| | O - Xylene | 1,3,5-Trimethyl-Benzene | 1,2,4-Trimethyl-Benzene |
|---|---|---|---|
| **Acetylene** | | | |
| **Propylene** | | | |
| **Dichlorodifluoromethane** | | | |
| **Chloromethane** | | | |
| **1,3-Butadiene** | | | |
| **Trichlorofluoromethane** | | | |
| **Methylene Chloride** | | | |
| **Trichlorotrifluoroethane** | | | |
| **Methyl Ethyl Ketone** | | | |
| **Benzene** | | | |
| **Carbon Tetrachloride** | | | |
| **Toluene** | | | |
| **N-Octane** | | | |
| **Tetrachloroethylene** | | | |
| **Ethylbenzene** | | | |
| **M,P-Xylene** | | | |
| **Styrene** | | | |
| **O-Xylene** | 1.00 | | |
| **1,3,5-Trimethylbenzene** | **0.84** | 1.00 | |
| **1,2,4-Trimethylbenzene** | **0.84** | **0.99** | 1.00 |

**Bold = Correlation Greater Than + 0.75**

**Table 3.6, completed**.

## Precision of Sample Results – Volatile Organic Compounds

Periodically throughout the year, a second canister was sampled simultaneously with the main sample. These additional samples, known as duplicates, were collected in order to assess the precision (repeatability) of the canister sampling method. On the duplicate sampling dates, the laboratory also conducted a test of the precision of the analytical process by injecting two samples of each canister's air into the gas chromatograph/mass spectrometer. These samples are known as the laboratory replicates. Thus, this project collected two types of precision data – duplicate data, which assesses both sampling and analysis procedures, and replicate data, which assesses laboratory analytical method repeatability. Detailed information regarding precision and accuracy results is presented in the appendix to this report, which is available as a separate document.

## Field Blanks – Volatile Organic Compounds

The volatile organic compound sampling method involves sampling in stainless steel canisters with specially-treated interior surfaces. The canisters are re-used. After a full canister is analyzed, it is pumped out repeatedly to a high vacuum. This procedure cleans it for the next use. Periodically, one canister from each cleaning batch is tested to make sure the method is performing adequately. The test canister is filled with ultra-pure air, and then analyzed. If it shows no contamination, the batch is released for use. If contamination is found, the entire batch is sent through the cleaning process for a second time. The canisters arrive in the field closed, and under 20 to 30 inches of vacuum. Therefore, field blanks are not used in this method. The canisters are "blanked" at the laboratory prior to shipping to the field.

## Compounds of Significance: Sources and Health Effects

Of the fifty-eight volatile organic compounds sampled, six showed annual mean concentrations greater than 1 part per billion (ppb) in Denver air. These are: acetonitrile, acetylene, benzene, methyl ethyl ketone, propylene, and toluene. Four of the compounds whose annual means were less than 1 ppb, 1,3-butadiene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene, had concentrations that were above the EPA concern level for cancer health effects. Acrylonitrile results show a cancer risk greater than one in a million, but results use a single value as the "annual mean" concentration, because all other daily values were below the detection limit. Information regarding the nature, sources, and potential health effects of each of these compounds (except acrylonitrile) is given below. Levels observed in Denver are also compared to national EPA "benchmark" concentrations, which are used to evaluate whether areas are meeting national EPA goals for reducing concentrations of hazardous air pollutants. However, unlike national ambient air quality standards governing pollutants such as carbon monoxide or ozone, these EPA "benchmark" values do not have the force of law or regulation. They are simply levels at which EPA believes these pollutants may begin to cause health effects on sensitive members of the population.

### Acetonitrile

Acetonitrile is a volatile organic compound with the formula $CH_3CN$. In the atmosphere, it exists as a gas. Acetonitrile is used in the chemical industry for making acrylic fibers, nitrile rubber, perfumes and pharmaceuticals. (CARB Fact Sheet on Acetonitrile). It is often used as a solvent.

Emissions from automobiles and manufacturing operations are the main atmospheric sources of acetonitrile. The California Air Resources Board indicates that coating, engraving, and allied services are the main stationary sources of the compound in California (CARB Fact Sheet on Acetonitrile).

Acetonitrile, also known as methyl cyanide, is metabolized to hydrogen cyanide in the human body (EPA OPPT Chemical Fact Sheet on Acetonitrile). Thus, health reactions to an exposure to acetonitrile may be delayed. Acetonitrile is an irritant to the skin, eyes, and lungs. Very high exposures can affect the nervous system, leading to drooling, nausea, vomiting, confusion, headache, and convulsions. Levels greater than 500 ppm can cause death (New Jersey Hazardous Substance Fact Sheet on Acetonitrile). Studies have indicated that acetonitrile can cause birth defects in animals, but generally only at levels where the mother is experiencing obvious symptoms. It is not known whether acetonitrile can cause cancer. Due to a lack of studies in this area EPA considers it not classifiable as to carcinogenic status.

EPA's OPPT chemical fact sheet on acetonitrile cites air concentration information in the Hazardous Substance Data Bank (HSDB). According to this source, levels in rural and urban US areas range from 2 to 7 ppb. The maximum observed in this study, 5.5 ppb for a 24-hour average, fits right within this range. Unfortunately, EPA has not developed cancer "benchmark" levels for this compound. However, EPA indicates a noncancer "reference concentration" of 60 ug/m3 (36 ppb) acetonitrile in air. This reference concentration is described by EPA as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime." In other words, levels below 36 ppb are believed to keep one "safe" from health effects other than cancer, even over a life-long exposure. Yet this 36 ppb "safe" level estimate has an uncertainty factor of 10, indicating that health effects could occur at levels ten times lower (3.6 ppb). Thus, the levels of acetonitrile seen in Denver and urban US air could be cause for concern. However, acetonitrile was only detected in 9% of the downtown Denver samples .

## Acetylene

Acetylene is a hydrocarbon compound with the formula $C_2H_2$. It exists in the atmosphere as a colorless and odorless gas. It is used in the production of organic chemicals such as vinyl chloride, vinyl acetate, and acrylates (Kirk-Othmer, Vol. 1, p 240). Another common use is in welding torches used to cut or solder metals.

Acetylene is emitted into the atmosphere from engines (CARB Fact Sheet on Acetylene) and from wood burning. (EPA CHIEF, Residential Wood Stove Chapter). As acetylene is produced by the thermal cracking of hydrocarbons (NIOSH Criteria Document on acetylene), petroleum refineries are another source.

Acetylene is an asphyxiant that can decrease the amount of available oxygen. Thus, the health effects of exposure to large concentrations of this compound involve oxygen deprivation and include headache, dizziness, lightheadedness, unconsciousness, and death. These concerns generally apply to workers using acetylene-powered welding torches in confined spaces. In outdoor air, acetylene is at much lower concentrations. According to the National Institute for Occupational Safety and Health, acetylene is not believed to have any toxic health effects beyond its asphyxiant properties. In fact, during the early twentieth century acetylene was used as an anesthetic for surgical patients. (NIOSH Criteria Document on Acetylene). Acetylene has not been investigated for carcinogenic effects, or ability to cause birth defects (New Jersey Hazardous Substance Fact Sheet on Acetylene).

The EPA AIRS system lists data from the state of California. Annual concentrations of acetylene in California typically range from 1 to 5.5 ppbv. The annual mean of the Denver CAMP data is 3.75 ppbv, within the California range.

The EPA national air toxics analysis effort has not developed any recommended benchmark values for acetylene. The Air Pollution Control Division does not believe that the maximum value of 15 ppb observed in Denver air during this study has any health significance.

## Benzene

Benzene is a hydrocarbon compound with the formula $C_6H_6$. It exists in the atmosphere as a colorless gas with a sweet odor. It is used in chemical manufacturing of medicines, detergents, explosives, shoes, dyes, leather, resins, paints, plastics and inks (CARB Fact Sheet on Benzene). It is also present in gasoline.

The largest sources of benzene in ambient air are automobiles, service stations, refineries, and chemical plants. Burning of vegetative matter in forest fires and woodstoves is also a source. In ambient air, benzene reacts with hydroxyl (OH) radicals within a few hours. This chemical transformation prevents the build-up of large concentrations in outdoor air.

From a toxicological standpoint, benzene is a serious concern. Unlike many of the compounds discussed here, benzene is a proven human carcinogen. It damages the blood-forming capacity of the body, leading to anemia or leukemia. Like the other volatile organic compounds, breathing large amounts can cause lightheadedness, headache, vomiting, convulsions, coma and death. Experiments with laboratory animals suggest that benzene exposure may be associated with numerous cancers. It may cause bone marrow damage and bone formation problems for a developing fetus (ATSDR Toxicological Profile for Benzene). It also irritates the skin and eyes, exerting a drying effect.

ATSDR cites national 1984 to 1986 data from 300 cities, which indicate an average benzene level of 1.8 ppb for urban and suburban areas (ATSDR Toxicological Profile for Benzene). The Denver mean of 1 ppb observed in this study is somewhat lower. This may reflect recent national progress in reducing benzene emissions from motor vehicle fuel. The Denver levels may be assessed by comparing them to national EPA “benchmark” values for benzene.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Tables 3.7 and 3.8 summarize the EPA benchmarks available for benzene. This compound has benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks for a 24 –hour period have yet to be developed.

Table 3.7 compares the annual mean values of this compound to the EPA " risk factor" for developing cancer. Columns two and three of Table 3.7 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 3.7 gives the cancer risk factor associated with breathing average concentrations of 1 ug/m3 of benzene during a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, cancer risk from benzene is twenty-five times higher than the EPA goal.

Table 3.8 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.8 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For benzene the risk is well below 1.0.

**Table 3.7 - Benzene Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 (1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **Benzene** | **1.00** | **3.19** | **0.0000078** | **2.49E-05** |

**Table 3.8 - Benzene Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Benzene** | **1.00** | **3.19** | **30** | **0.106** |

## 1,3-Butadiene

1,3-Butadiene is a hydrocarbon compound with the formula $C_4H_6$. It exists in the atmosphere as a colorless gas with an odor similar to gasoline. It is used in making rubber and plastics. The most important use is in tire production. It is also used in the production of chemicals such as 1,4-hexadiene (NIOSH Current Intelligence Bulletin 41).

According to the California Air Resources Board, most emissions of 1,3-butadiene come from combustion of fuels in diesel and gas-powered motor vehicles. Other sources that they list include petroleum refining, tire wear, residential wood heating, and forest fires. Rubber and chemical production plants also have emissions.

1,3-Butadiene is of concern toxicologically because it is a probable carcinogen that also has adverse effects on reproduction and fetal development. Exposure to high concentrations can cause irritation and central nervous system effects such as eye irritation, cough, sore throat, headache, drowsiness, nausea, unconsciousness, and death. Rats and mice exposed to this compound in laboratory tests developed multiple cancers within single individuals. The animals had damaged testes and ovaries, and offspring of the animals had skeletal problems.

ATSDR estimates that urban and suburban areas have an average concentration of 0.3 ppb 1,3-butadiene, while rural areas have 0.1 ppb (ATSDR Toxicological Profile for 1,3-Butadiene). The annual average at CAMP, 0.2 ppb, is within this range. The significance of the Denver concentrations can be assessed by comparing them to national EPA "benchmark" values for 1,3-butadiene.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Tables 3.9 and 3.10 summarize the EPA benchmarks available for 1,3-butadiene. This compound has benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks for a 24-hour period have yet to be developed.

Table 3.9 compares the annual mean values of this compound to the EPA " risk factor" for developing cancer. Columns two and three of Table 3.9 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 3.9 gives the cancer risk concentration associated with breathing an average concentration of 1 ug/m3 benzene over a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, cancer risk from 1,3-butadiene is 11 times higher than the EPA goal.

Table 3.10 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.10 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that

this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For 1,3-butadiene the risk is well below 1.0.

**Table 3.9 - 1,3-Butadiene Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 (1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **1,3-Butadiene** | **0.17** | **0.38** | **0.00003** | **1.13E-05** |

**Table 3.10 - 1.3-Butadiene Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **1,3-Butadiene** | **0.17** | **0.38** | **2** | **0.188** |

## Carbon Tetrachloride

Carbon tetrachloride, also known as tetrachloromethane or methane tetrachloride, is a chlorinated hydrocarbon with the formula $CCl_4$. It exists in the atmosphere as a gas and it has a sweet odor. The primary uses of carbon tetrachloride were as a dry cleaning solvent, a grain fumigant, as a refrigerant, and as an aerosol propellant. Carbon tetrachloride has a long atmospheric half-life; it can travel to the higher reaches of the atmosphere and damage the earth's ozone layer. Due to its toxicity and ozone-damaging qualities, most uses of carbon tetrachloride have been banned. It is still in use in industrial settings for producing refrigerants.

Carbon tetrachloride is emitted to the air from industrial sources and from petroleum refineries (California Air Resources Board Toxic Air Contaminant Identification List Summary for Carbon Tetrachloride). There are no natural sources of carbon tetrachloride; it is produced by man (ATSDR Toxicological Profile for Carbon Tetrachloride).

As is true for many of the chlorinated hydrocarbons, breathing large concentrations of carbon tetrachloride has central nervous system effects including lightheadedness, coma, convulsions, double vision, intoxication, and death. It can also cause vomiting. In animal studies, it had effects on the liver and kidney. Male rats exposed to carbon tetrachloride had lower sperm production. Female rats exposed to it had stunted offspring with birth defects. Carbon tetrachloride has been associated with liver and kidney cancer in animals, but EPA considers it a Class B2 Carcinogen (probable human carcinogen).

The California Air Resources Board has monitored carbon tetrachloride at a number of locations, and found a mean value of 0.078 ppb (California Air Resources Board Toxic Air Contaminant Identification List Summary for Carbon Tetrachloride). The 0.08 ppb mean observed in this Denver study is at the same level. The significance of the Denver concentrations can be assessed by comparing them to national EPA "benchmark" values for carbon tetrachloride.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here,

one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Table 3.11 compares the annual mean values of this compound to the EPA " risk factor" for developing cancer. Columns two and three of Table 3.11 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 3.11 gives the cancer risk concentration associated with breathing an average concentration of 1 ug/m3 carbon tetrachloride over a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, cancer risk from carbon tetrachloride is seven times higher than the EPA goal.

Table 3.12 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.12 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For carbon tetrachloride the risk is well below 1.0.

**Table 3.11 – Carbon Tetrachloride Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 (1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **Carbon Tetrachloride** | **0.08** | **0.50** | **0.000015** | **7.55E-06** |

**Table 3.12 – Carbon Tetrachloride Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Carbon Tetrachloride** | **0.08** | **0.50** | **40** | **0.013** |

## 1,4-Dichlorobenzene

1,4-Dichlorobenzene, also known as para-dichlorobenzene, is a chlorinated hydrocarbon with the formula $C_6H_4Cl_2$. It exists in the atmosphere as a gas and it has a mothball-like odor. The primary uses of 1,4-dichlorobenzene are for mothballs, insecticide, or as a dry solid room/trash bin/toilet deodorant.

Most emissions of 1,4-dichlorobenzene in air come from its household uses as an insecticide and deodorant, or from factories that produce these household products. Industrial operations producing polyphenylene sulfide may also emit it, as 1,4-dichlorobenzene is used in the production process. There are

no natural sources of 1,4-dichlorobenzene; it is produced by man (ATSDR Toxicological Profile for 1,4-Dichlorobenzene).

As is true for many of the chlorinated hydrocarbons, breathing large concentrations of 1,4-dichlorobenzene has central nervous system effects including lightheadedness, coma, convulsions, double vision, intoxication, and death. It also can cause vomiting. In animal studies, it had effects on the liver and kidney. 1,4-dichlorobenzene also effects the blood, leading to anemia and possibly, leukemia. (New Jersey Hazardous Substance Fact Sheet for 1,4-Dichlorobenzene). 1,4-dichlorobenzene has been associated with liver and kidney cancer in animals, but EPA considers it a Class C Carcinogen (possible human carcinogen).

The Environmental Protection Agency has monitored 1,4-dichlorobenzene at a number of locations, and found a mean value of 0.17 ppb during 1976 – 1986 (California Air Resources Board Toxic Air Contaminant Identification List Summary for 1,4-Dichlorobenzene). The 0.03 ppb mean observed in this Denver study is significantly lower. The significance of the Denver concentrations can be assessed by comparing them to national EPA "benchmark" values for 1,4-dichlorobenzene.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Table 3.13 compares the annual mean values of this compound to the EPA " risk factor" for developing cancer. Columns two and three of Table 3.13 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 3.13 gives the cancer risk concentration associated with breathing an average concentration of 1 ug/m3 1,4-dichlorobenzene over a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, cancer risk from 1,4-dichlorobenzene is two times higher than the EPA goal.

Table 3.14 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.14 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For 1,4-dichlorobenzene the risk is well below 1.0.

**Table 3.13 – 1,4-Dichlorobenzene Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 (1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| 1,4-Dichlorobenzene | 0.03 | 0.18 | 0.000011 | 1.98E-06 |

**Table 3.14 – 1,4-Dichlorobenzene Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| 1,4-Dichlorobenzene | 0.03 | 0.18 | 800 | 0.000 |

## Methyl Ethyl Ketone

Methyl Ethyl Ketone is a hydrocarbon compound with the formula $C_4H_8O$. In the atmosphere, it is a colorless gas with a sweet odor. Methyl Ethyl Ketone is commonly used as a solvent in glues, paints, plastics, printing inks, and cleaning solutions.

The California Air Resources Board states that the primary sources of this chemical in that state are motor vehicle exhaust, wood processing, wood furniture manufacturing operations, and footwear manufacturers (CARB Air Toxics Profile for Methyl Ethyl Ketone). CARB states that the half-life of this chemical in air is 9 to 13 days. Therefore, it can be transported into an area from other places.

Like other volatile organic compounds measured in this study, methyl ethyl ketone has irritant and central nervous system effects. Methyl ethyl ketone can irritate the eyes, skin, and throat. Effects on the brain include headache, dizziness, and blurred vision. It also causes nausea (New Jersey Hazardous Substance Fact Sheet on Methyl Ethyl Ketone). There is not enough information to determine whether this compound is carcinogenic. Animal testing indicates that high exposures to the mother may be associated with birth defects in the offspring.

In 1996 the average concentration for methyl ethyl ketone within the California Air Resources Board air monitoring network was 0.11 ppb (CARB Air Toxics Profile for Methyl Ethyl Ketone). This compares to a mean concentration of 1.18 ppb for the year of monitoring at CAMP. The significance of the Denver concentrations can be assessed by comparing them to national EPA "benchmark" values for methyl ethy1 ketone.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Table 3.15 summarizes the EPA benchmark available for methyl ethyl ketone. This compound has a benchmark for "chronic", but "cancer" and 24-hour "acute" benchmarks have yet to be developed.

Table 3.15 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.15 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For methyl ethyl ketone the risk is well below 1.0.

**Table 3.15 - Methyl Ethyl Ketone Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Methyl Ethyl Ketone** | **1.18** | **3.48** | **1000** | **0.003** |

## Propylene

Propylene, also known as propene, is a hydrocarbon compound with the formula $C_3H_6$. As a gas, it has a slight odor and is colorless. Propylene is used in the manufacture of chemicals, resins, and plastics.

Propylene is emitted into the air from paper mills, petroleum refining, oil and gas extraction, and motor vehicle exhaust (CARB Air Toxics Profile on Propene). CARB lists an atmospheric half-life of 9 to 13 hours. Thus, propylene is unlikely to be transported for long distances. CARB states that it reacts with OH radicals to form formaldehyde, acetaldehyde, and other compounds.

Propylene is an explosive compound that decreases the amount of available oxygen. These asphyxiant and explosive properties are mainly a concern to workers using propylene in confined spaces. In high concentrations, propylene may cause dizziness, unconsciousness, and death. Propylene is also an irritant to the eyes and lungs. It may also create heart and liver damage. It is not known whether propylene can damage a developing fetus. The cancer-causing potential of this compound is unknown, because there has not been adequate research.

The EPA AIRS system lists data from the state of California. Annual concentrations of propylene in California typically range from 0.3 to 1.7 ppbv. The annual mean of the Denver CAMP data is 1.36 ppbv, within the California range.

Unfortunately, there are no EPA propylene "benchmark" estimates for cancer, acute non-cancer, or chronic non-cancer health effects.

## Tetrachloroethylene

Tetrachloroethylene, also known as perchloroethylene, is a chlorinated hydrocarbon with the formula $C_2Cl_4$. It exists in the atmosphere as a gas. It has a "chloroform-like" odor (NIOSH Pocket Guide to Chemical Hazards, Tetrachloroethylene). The primary uses of tetrachloroethylene are as a dry cleaning solvent, a metal cleaning solvent, or for chemical production. Tetrachloroethylene is used in paints, inks,

aerosols, glues, polishes, silicones and rubber products (CARB Fact Sheet on Tetrachloroethylene and OPPT Chemical Fact Sheet on Tetrachloroethylene).

Most emissions of tetrachloroethylene come from degreasing, dry cleaning, or chemical production facilities. There are microorganisms that can produce tetrachloroethylene (ATSDR Toxicological Profile For Tetrachloroethyelene).

As is true for many of the chlorinated hydrocarbons, breathing large concentrations of tetrachloroethylene has central nervous system effects including lightheadedness, coma, convulsions, double vision, intoxication, and death. It also can cause vomiting. In animal studies, it had effects on the liver and kidney. It also is an irritant to eyes, lungs, and skin. Some animal studies suggest that tetrachloroethylene exposure may lead to leukemia (NIOSH Registry of Toxic Effects of Chemical Substances Information for Tetrachloroethylene). Tetrachloroethylene has been associated with liver and kidney cancer in animals, but EPA considers it a Class B2 or C Carcinogen (probable or possible human carcinogen).

The California Air Resources Board has monitored tetrachloroethylene at a number of locations within their state, and found a mean value of 0.019 ppb during 1996 (California Air Resources Board Toxic Air Contaminant Identification List Summary for Tetrachloroethylene). The 0.07 ppb mean observed in this Denver study is significantly higher. As seen in Table 3.17, the chronic hazard index for this chemical is low. However, the cancer risk in air is almost three times higher than the EPA goal of one in a million.

**Table 3.16 – Tetrachloroethylene Annual Mean Versus Cancer Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Cancer Risk Per ug/m3 (1/(ug/m3)) | Cancer Risk In Ambient Air |
|---|---|---|---|---|
| **Tetrachloroethylene** | **0.07** | **0.47** | **0.0000059** | **2.80E-06** |

**Table 3.17 – Tetrachloroethylene Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Tetrachloroethylene** | **0.07** | **0.47** | **270** | **0.002** |

## Toluene

Toluene is a hydrocarbon compound with the formula $C_7H_8$. It exists in the atmosphere as a gas with an odor similar to that of benzene. Toluene has a number of industrial uses. It is used in high-octane gasoline. Toluene is employed in production processes for paints, resins, glues, and rubber. The printing, plastics, and furniture industries frequently use toluene.

Automotive-related activities are one of the largest sources of toluene in the atmosphere. Toluene is emitted from automobile exhaust, and from gasoline stations and refineries. Toluene is a component of wood smoke. Furniture manufacturers emit toluene, due to its use in paints and coatings. Forest fires are a natural source of toluene emissions.

Toluene is of great concern toxicologically. It is an irritant, has central nervous system effects (both temporary and permanent), and can damage a developing fetus. As an irritant, it causes stinging eyes, coughing, and skin irritation. Toluene can affect the brain. Individuals with exposures to large amounts have experienced slower reflexes, memory loss, hearing loss, and difficulty concentrating. Headache, dizziness, unconsciousness and death may result from exposure to large concentrations. Nausea and appetite loss may also occur. Mothers who abused toluene as an inhalant had children with brain dysfunction, attention deficits, craniofacial problems, and limb abnormalities. However, the CARB Air Toxics Profile on toluene, which discusses these problems in offspring, notes that the mothers also had exposure to other chemicals. Toluene can cause problems in the liver and kidneys. Due to an inadequate number of studies, it is not known whether toluene can cause cancer.

ATSDR indicates that toluene occurs in polluted air at levels of 0.3 to 7.98 ppb (ATSDR Toxicological Profile on Toluene). Thus, the Denver mean level of 2.2 ppb observed in the year of monitoring at CAMP is right within a typical US range. The ATSDR Toxicological Profile on Toluene indicates that children living in central urban core areas with large amounts of traffic had 56% more toluene detected in their blood than children living in rural areas. The significance of the Denver levels can be assessed by comparing them to EPA "benchmark" concentrations for this compound.

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found on the following EPA web page:

http://www.epa.gov/ttn/atw/toxsource/summary.html

Table 3.18 summarizes the EPA benchmark available for toluene. This compound has a benchmark for "chronic", but "cancer" and 24-hour "acute" benchmarks have yet to be developed.

Table 3.18 compares the annual mean value of this compound to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.18 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For toluene the risk is well below 1.0.

**Table 3.18 - Toluene Annual Mean Versus Non-Cancer Chronic Risk**

| Compound | Annual Mean ppbv | Annual Mean ug/m3 | Non-cancer Chronic ug/m3 | Non-cancer Chronic Hazard Index |
|---|---|---|---|---|
| **Toluene** | **2.22** | **8.37** | **400** | **0.021** |

# Health Implications – Volatile Organic Compounds

EPA has developed "benchmarks" for a number of volatile organic compounds. For completeness, two tables comparing compounds measured in this study with EPA "benchmark" values were developed. These tables include the compounds discussed previously, as well as hazardous air pollutants occurring at lower concentrations, which were not discussed previously.

Tables 3.19 and 3.20 summarize the EPA benchmarks available for volatile organic compounds. As seen from the tables, not all of the compounds measured have benchmark values. These compounds have benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks for a 24 hour averaging period have yet to be developed.

Table 3.19 compares the annual mean values of these compounds to the EPA "risk factor" for developing cancer. Columns two and three of Table 3.19 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 3.19 gives the cancer risk factor associated with breathing an average concentration of 1 ug/m3 of each pollutant over a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, p-dichlorobenzene, and acrylonitrile exceed the risk goals. However, the acrylonitrile risk is quite sensitive to the method used to calculate the annual mean. For this study, only samples above detection limit were averaged in to the annual mean for the compound. Thus for acrylonitrile, the one sample measured above detection limits determined the annual mean concentration.

Table 3.20 compares the annual mean values of these compounds to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 3.20 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For all compounds, the risk is well below 1.0.

**Notes for Tables 3.19 and 3.20:**

**Acrylonitrile annual mean is based on a single detection.**

All compounds listed in the reference, even those having "no factor", are listed here.

**ND = Compound not detected during the study.**

m,p – xylene and o-xylene mixed xylenes Reference Concentration taken from EPA IRIS database, Feb 21, 2003 update.

Methyl Isobutyl Ketone Reference Concentration taken from EPA IRIS database, April 25, 2003 update.

**Table 3.19 - Annual Mean Versus Cancer Risk for VOCs**

| Annual Mean Versus Cancer Risk | | | | |
|---|---|---|---|---|
| **Compound** | **Annual Mean ppbv** | **Annual Mean ug/m3** | **Cancer Risk Per ug/m3 (1/(ug/m3))** | **Cancer Risk In Ambient Air** |
| | | | | |
| **Chloromethane** | **0.59** | **1.22** | **No Factor** | |
| **Vinyl Chloride** | **ND** | **ND** | **0.0000088** | |
| **1,3-Butadiene** | **0.17** | **0.38** | **0.00003** | **1.13E-05** |
| **Bromomethane** | **ND** | **ND** | | |
| **1,1-Dichloroethene** | **ND** | **ND** | | |
| **Methylene Chloride** | **0.25** | **0.87** | **0.00000047** | **4.08E-07** |
| **1,1-Dichloroethane** | **ND** | **ND** | **0.0000016** | |
| **Methyl Tert-Butyl Ether** | **ND** | **ND** | **No Factor** | |
| **Methyl Ethyl Ketone** | **1.18** | **3.48** | **No Factor** | |
| **Chloroform** | **0.05** | **0.24** | **No Factor** | |
| **1,2-Dichloroethane** | **ND** | **ND** | **0.000026** | |
| **1,1,1-Trichloroethane** | **0.04** | **0.22** | **No Factor** | |
| **Benzene** | **1** | **3.19** | **0.0000078** | **2.49E-05** |
| **Carbon Tetrachloride** | **0.08** | **0.50** | **0.000015** | **7.55E-06** |
| **1,2-Dichloropropane** | **ND** | **ND** | **0.000019** | |
| **Ethyl Acrylate** | **ND** | **ND** | **0.000014** | |
| **Trichloroethylene** | **0.06** | **0.32** | **0.000002** | **6.45E-07** |
| **Methyl Methacrylate** | **ND** | **ND** | **No Factor** | |
| **Trans-1,3-Dichloropropene** | **ND** | **ND** | **0.000004** | |
| **1,1,2-Trichloroethane** | **ND** | **ND** | **0.000016** | |
| **Toluene** | **2.22** | **8.37** | **No Factor** | |
| **1,2-Dibromoethane** | **ND** | **ND** | **0.00022** | |
| **Tetrachloroethylene** | **0.07** | **0.47** | **0.0000059** | **2.80E-06** |
| **Chlorobenzene** | **ND** | **ND** | **No Factor** | |
| **Ethyl Benzene** | **0.33** | **1.43** | **No Factor** | |
| **M,P-Xylene** | **0.95** | **4.12** | **No Factor** | |
| **Bromoform** | **ND** | **ND** | **0.0000011** | |
| **Styrene** | **0.09** | **0.38** | **No Factor** | |
| **1,1,2,2-Tetrachloroethane** | **ND** | **ND** | **0.000058** | |
| **O-Xylene** | **0.44** | **1.91** | **No Factor** | |
| **P-Dichlorobenzene** | **0.03** | **0.18** | **0.000011** | **1.98E-06** |
| **1,2,4-Trichlorobenzene** | **ND** | **ND** | **No Factor** | |
| **Hexachloro-1,3-Butadiene** | **ND** | **ND** | **0.000022** | |
| **Acrylonitrile** | **0.27** | **0.59** | **0.000068** | **3.98E-05** |
| **Acetonitrile** | **2.49** | **4.18** | **No Factor** | |
| **Chloroprene** | **ND** | **ND** | **No Factor** | |
| **Methyl Isobutyl Ketone** | **0.19** | **0.78** | **No Factor** | |

**Table 3.20 - Annual Mean Versus Non-Cancer Chronic Risk for VOCs**

| Annual Mean Versus Non-Cancer Chronic Risk | | | | |
|---|---|---|---|---|
| **Compound** | **Annual Mean ppbv** | **Annual Mean ug/m3** | **Noncancer Chronic ug/m3** | **Noncancer Chronic Hazard Index** |
| | | | | |
| **Chloromethane** | **0.59** | **1.22** | **90** | **0.014** |
| **Vinyl Chloride** | **ND** | **ND** | **100** | |
| **1,3-Butadiene** | **0.17** | **0.38** | **2** | **0.188** |
| **Bromomethane** | **ND** | **ND** | **5** | |
| **1,1-Dichloroethene** | **ND** | **ND** | **200** | |
| **Methylene Chloride** | **0.25** | **0.87** | **1000** | **0.001** |
| **1,1-Dichloroethane** | **ND** | **ND** | **500** | |
| **Methyl Tert-Butyl Ether** | **ND** | **ND** | **3000** | |
| **Methyl Ethyl Ketone** | **1.18** | **3.48** | **1000** | **0.003** |
| **Chloroform** | **0.05** | **0.24** | **98** | **0.002** |
| **1,2-Dichloroethane** | **ND** | **ND** | **2400** | |
| **1,1,1-Trichloroethane** | **0.04** | **0.22** | **1000** | **0.000** |
| **Benzene** | **1** | **3.19** | **30** | **0.106** |
| **Carbon Tetrachloride** | **0.08** | **0.50** | **40** | **0.013** |
| **1,2-Dichloropropane** | **ND** | **ND** | **4** | |
| **Ethyl Acrylate** | **ND** | **ND** | **No Factor** | |
| **Trichloroethylene** | **0.06** | **0.32** | **600** | **0.001** |
| **Methyl Methacrylate** | **ND** | **ND** | **700** | |
| **Trans-1,3-Dichloropropene** | **ND** | **ND** | **20** | |
| **1,1,2-Trichloroethane** | **ND** | **ND** | **400** | |
| **Toluene** | **2.22** | **8.37** | **400** | **0.021** |
| **1,2-Dibromoethane** | **ND** | **ND** | **0.8** | |
| **Tetrachloroethylene** | **0.07** | **0.47** | **270** | **0.002** |
| **Chlorobenzene** | **ND** | **ND** | **1000** | |
| **Ethyl Benzene** | **0.33** | **1.43** | **1000** | **0.001** |
| **M,P-Xylene** | **0.95** | **4.12** | **100** | **0.041** |
| **Bromoform** | **ND** | **ND** | **No Factor** | |
| **Styrene** | **0.09** | **0.38** | **1000** | **0.000** |
| **1,1,2,2-Tetrachloroethane** | **ND** | **ND** | **No Factor** | |
| **O-Xylene** | **0.44** | **1.91** | **100** | **0.019** |
| **P-Dichlorobenzene** | **0.03** | **0.18** | **800** | **0.000** |
| **1,2,4-Trichlorobenzene** | **ND** | **ND** | **200** | |
| **Hexachloro-1,3-Butadiene** | **ND** | **ND** | **90** | |
| **Acetonitrile** | **2.49** | **4.18** | **60** | **0.070** |
| **Chloroprene** | **ND** | **ND** | **7** | |
| **Methyl Isobutyl Ketone** | **0.19** | **0.78** | **80** | **0.010** |

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# Section 4 - Speciated Non-Methane Organic Compounds at CAMP Station

## October 2000 to September 2001

# Summary Statistics – Speciated Non-Methane Organic Compounds

## Minimum, Maximum, Mean – All Samples

Speciated non-methane organic compound (SNMOC) data collected at the downtown CAMP station from October 2000 through September 2001 are presented in this section of the Air Toxics Monitoring Report. For the year-long period, speciated non-methane organic compounds were sampled on a one-in-six day basis, for a total of 63 samples attempted. Of these, the laboratory successfully processed 57, for a percentage data recovery rate exceeding 90%. (See Table 4.1).

Table 4.2 summarizes the annual minimum, maximum, and mean concentrations for each of the 78 speciated non-methane organic compounds (SNMOCs) measured during the study. Results show that ethylene, acetylene, ethane, propylene, propane, isobutane, n-butane, isopentane, n-pentane, 2-methyl-pentane, n-hexane, benzene and toluene were the compounds with the highest concentrations in ambient air. These compounds all had sample mean levels at one ppb or greater, and were detected in 100% of the canister samples taken. In fact, the majority of the SNMOCs were detected consistently. Of the 78 compounds sampled, 62 were present more than 90% of the time.

**Table 4.1 - Percentage Data Recovery For SNMOC Samples**

| Sample Days Scheduled | Samples Recovered | Percentage Recovered |
|---|---|---|
| 63 | 57 | 90.5 |

**Table 4.2 - Annual minimum, maximum, and mean concentrations for each of the 78 speciated non-methane organic compounds**

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage Of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| Ethylene | 1.92 | 17.73 | 5.41 | 0 | 0 | 100 |
| Acetylene | 1.43 | 15.57 | 4.25 | 0 | 0 | 100 |
| Ethane | 3.74 | 61.15 | 13.22 | 0 | 0 | 100 |
| Propylene | 0.58 | 3.79 | 1.59 | 0 | 0 | 100 |
| Propane | 2.01 | 24.10 | 6.55 | 0 | 0 | 100 |
| Propyne | 0.10 | 0.10 | 0.10 | 56 | 98 | 2 |
| Isobutane | 0.57 | 6.75 | 1.92 | 0 | 0 | 100 |
| Isobutene/1-Butene | 0.14 | 0.98 | 0.37 | 0 | 0 | 100 |
| 1,3-Butadiene | 0.04 | 0.55 | 0.18 | 0 | 0 | 100 |
| n-Butane | 1.49 | 14.34 | 4.28 | 0 | 0 | 100 |
| trans-2-Butene | 0.09 | 0.66 | 0.25 | 0 | 0 | 100 |
| cis-2-Butene | 0.11 | 0.59 | 0.25 | 0 | 0 | 100 |
| 3-Methyl-1-butene | 0.03 | 0.22 | 0.06 | 21 | 37 | 63 |
| Isopentane | 1.58 | 11.50 | 5.52 | 0 | 0 | 100 |
| 1-Pentene | 0.07 | 0.33 | 0.17 | 0 | 0 | 100 |
| 2-Methyl-1-butene | 0.04 | 0.47 | 0.19 | 1 | 2 | 98 |
| n-Pentane | 0.56 | 9.13 | 3.15 | 0 | 0 | 100 |
| Isoprene | 0.07 | 0.41 | 0.18 | 1 | 2 | 98 |
| trans-2-Pentene | 0.09 | 0.51 | 0.24 | 0 | 0 | 100 |
| cis-2-Pentene | 0.08 | 0.30 | 0.15 | 0 | 0 | 100 |
| 2-Methyl-2-butene | 0.06 | 0.65 | 0.24 | 0 | 0 | 100 |

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage Of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| 2,2-Dimethylbutane | 0.10 | 0.44 | 0.23 | 0 | 0 | 100 |
| Cyclopentene | 0.05 | 0.35 | 0.17 | 25 | 44 | 56 |
| 4-Methyl-1-pentene | 0.03 | 0.03 | 0.03 | 55 | 96 | 4 |
| Cyclopentane | 0.09 | 0.61 | 0.25 | 0 | 0 | 100 |
| 2,3-Dimethylbutane | 0.14 | 0.75 | 0.34 | 0 | 0 | 100 |
| 2-Methylpentane | 0.28 | 3.15 | 1.28 | 0 | 0 | 100 |
| 3-Methylpentane | 0.23 | 1.93 | 0.79 | 0 | 0 | 100 |
| 2-Methyl-1-pentene | 0.02 | 0.09 | 0.04 | 23 | 40 | 60 |
| 1-Hexene | 0.05 | 0.23 | 0.14 | 0 | 0 | 100 |
| 2-Ethyl-1-butene | | | | 57 | 100 | 0 |
| n-Hexane | 0.24 | 3.09 | 1.18 | 0 | 0 | 100 |
| trans-2-Hexene | 0.02 | 0.11 | 0.07 | 52 | 91 | 9 |
| cis-2-Hexene | 0.02 | 0.14 | 0.05 | 34 | 60 | 40 |
| Methylcyclopentane | 0.14 | 1.36 | 0.53 | 0 | 0 | 100 |
| 2,4-Dimethylpentane | 0.08 | 0.40 | 0.18 | 0 | 0 | 100 |
| Benzene | 0.35 | 2.34 | 1.00 | 0 | 0 | 100 |
| Cyclohexane | 0.11 | 1.98 | 0.40 | 0 | 0 | 100 |
| 2-Methylhexane | 0.07 | 0.82 | 0.33 | 0 | 0 | 100 |
| 2,3-Dimethylpentane | 0.11 | 0.53 | 0.24 | 0 | 0 | 100 |
| 3-Methylhexane | 0.09 | 1.00 | 0.37 | 0 | 0 | 100 |
| 1-Heptene | 0.03 | 0.27 | 0.10 | 7 | 12 | 88 |
| 2,2,4-Trimethylpentane | 0.12 | 3.70 | 0.37 | 0 | 0 | 100 |
| n-Heptane | 0.08 | 1.05 | 0.38 | 0 | 0 | 100 |
| Methylcyclohexane | 0.08 | 0.95 | 0.40 | 0 | 0 | 100 |
| 2,2,3-Trimethylpentane | 0.02 | 0.29 | 0.08 | 0 | 0 | 100 |

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage Of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| 2,3,4-Trimethylpentane | 0.05 | 0.27 | 0.11 | 0 | 0 | 100 |
| Toluene | 0.53 | 5.71 | 1.85 | 0 | 0 | 100 |
| 2-Methylheptane | 0.04 | 0.33 | 0.11 | 0 | 0 | 100 |
| 3-Methylheptane | 0.04 | 0.34 | 0.10 | 0 | 0 | 100 |
| 1-Octene | 0.01 | 0.06 | 0.03 | 16 | 28 | 72 |
| n-Octane | 0.06 | 0.43 | 0.16 | 0 | 0 | 100 |
| Ethylbenzene | 0.08 | 0.63 | 0.26 | 0 | 0 | 100 |
| m-Xylene/p-Xylene | 0.25 | 2.09 | 0.83 | 0 | 0 | 100 |
| Styrene | 0.04 | 0.56 | 0.18 | 0 | 0 | 100 |
| o-Xylene | 0.09 | 0.83 | 0.33 | 0 | 0 | 100 |
| 1-Nonene | 0.02 | 0.09 | 0.04 | 1 | 2 | 98 |
| n-Nonane | 0.03 | 0.31 | 0.12 | 0 | 0 | 100 |
| Isopropylbenzene | 0.02 | 0.08 | 0.04 | 1 | 2 | 98 |
| a-Pinene | 0.01 | 0.28 | 0.13 | 1 | 2 | 98 |
| n-Propylbenzene | 0.04 | 0.19 | 0.10 | 0 | 0 | 100 |
| m-Ethyltoluene | 0.07 | 0.65 | 0.31 | 0 | 0 | 100 |
| p-Ethyltoluene | 0.05 | 0.34 | 0.16 | 0 | 0 | 100 |
| 1,3,5-Trimethylbenzene | 0.02 | 0.46 | 0.21 | 0 | 0 | 100 |
| o-Ethyltoluene | 0.03 | 0.37 | 0.18 | 1 | 2 | 98 |
| b-Pinene | 0.01 | 0.13 | 0.05 | 13 | 23 | 77 |
| 1,2,4-Trimethylbenzene | 0.06 | 1.09 | 0.53 | 0 | 0 | 100 |
| 1-Decene | 0.42 | 0.42 | 0.42 | 56 | 98 | 2 |
| n-Decane | 0.04 | 0.56 | 0.20 | 0 | 0 | 100 |
| 1,2,3-Trimethylbenzene | 0.02 | 0.29 | 0.13 | 0 | 0 | 100 |
| m-Diethylbenzene | 0.02 | 0.11 | 0.05 | 2 | 4 | 96 |

| | Summary Statistics (PPB) | | | Count of Non-Detects | | Percentage Of Samples In Which Compound Was Detected |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Number | Percentage | |
| p-Diethylbenzene | 0.02 | 0.06 | 0.03 | 0 | 0 | 100 |
| 1-Undecene | 0.01 | 0.11 | 0.02 | 34 | 60 | 40 |
| n-Undecane | 0.06 | 0.90 | 0.20 | 0 | 0 | 100 |
| 1-Dodecene | 0.01 | 0.22 | 0.03 | 30 | 53 | 47 |
| n-Dodecane | 0.02 | 0.36 | 0.08 | 0 | 0 | 100 |
| 1-Tridecene | | 0.23 | 0.12 | 55 | 96 | 4 |
| n-Tridecane | 0.01 | 0.36 | 0.04 | 33 | 58 | 42 |

**Table 4.2, completed.**

## Percentage of Samples For Which Compound Was Detected

Table 4.2 shows the percentage of the samples in which each SNMOC was detected. Sixty-two of the compounds were detected in over 90% of the samples. These compounds are listed in Table 4.3. In contrast, only one SNMOC (2-ethyl-1-butene) was never detected at all during the study. The six compounds detected in fewer than ten percent of the samples are listed in Table 4.4.

**Table 4.3 - Compounds Detected in Over 90% of the SNMOC Samples Taken At CAMP**

| | | |
|---|---|---|
| **Ethylene** | **2,3-Dimethylbutane** | **Ethylbenzene** |
| **Acetylene** | **2-Methylpentane** | **M-Xylene/P-Xylene** |
| **Ethane** | **3-Methylpentane** | **Styrene** |
| **Propylene** | **1-Hexene** | **o-Xylene** |
| **Propane** | **n-Hexane** | **1-Nonene** |
| **Isobutane** | **Methylcyclopentane** | **n-Nonane** |
| **Isobutene/ 1-Butene** | **2.4-Dimethylpentane** | **Isopropylbenzene** |
| **1,3 -Butadiene** | **Benzene** | **a-Pinene** |
| **n-Butane** | **Cyclohexane** | **n-Propylbenzene** |
| **Trans-2-Butene** | **2-Methylhexane** | **m-Ethyltoluene** |
| **Cis-2-Butene** | **2,3-Dimethylpentane** | **p-Ethyltoluene** |
| **Isopentane** | **3-Methylhexane** | **1,3,5-Trimethylbenzene** |
| **1-Pentene** | **2,2,4-Trimethylpentane** | **o-Ethyltoluene** |
| **2-Methyl-1-Butene** | **n-Heptane** | **1,2,4-Trimethylbenzene** |
| **n-Pentane** | **Methylcyclohexane** | **n-Decane** |
| **Isoprene** | **2,2,3-Trimethylpentane** | **1,2,3-Trimethylbenzene** |
| **Trans-2-Pentene** | **2,3,4-Trimethylpentane** | **m-Diethylbenzene** |
| **Cis-2-Pentene** | **Toluene** | **p-Diethylbenzene** |
| **2-Methyl-2-Butene** | **2-Methylheptane** | **n-Undecane** |
| **2,2-Dimethylbutane** | **3-Methylheptane** | **n-Dodecane** |
| **Cyclopentane** | **n-Octane** | |

**Table 4.4 - Compounds Detected In Fewer Than 10% of the SNMOC Samples Taken At CAMP**

| |
|---|
| **Propyne** |
| **4-Methyl-1-Pentene** |
| **2-Ethyl-1-Butene** |
| **Trans-2-Hexene** |
| **1-Decene** |
| **1-Tridecene** |

## Weekend Vs. Weekday Results

For the year of SNMOC data, an analysis of weekday versus weekend levels was conducted. Table 4.5 gives summary statistics for minimum, maximum, and mean of the weekday samples versus the same statistics for the weekend samples. Figure 4.1 is a graph of these results. For almost all SNMOCs, the weekday and weekend results are fairly close. Interestingly, some SNMOCs were significantly higher during the weekend periods. These are ethane, propane, n-butane, 1-decene, 1-undecene, 1-dodecene, 1-tridecene and 1-tridecane.

## Graphs – Speciated Non-Methane Organic Compounds

### Individual Compounds

The most prevalent compounds detected during the study are graphed in Figures 4.2 through 4.6. The figures are grouped by the maximum y-axis value on each graph, with an attempt to keep related compounds together. For example, the compounds detected at the highest concentration were ethane, ethylene, and acetylene, which are graphed with 100 ppbv as the maximum value on the y-axis. The next two groups of compounds, graphing at 25 ppbv on the y-axis, include propane, isobutane, n-butane, isopentane, n-pentane, and 2-methylpentane. Benzene and toluene are graphed at a 10 ppbv scale. Propylene, 1,3-butadiene and n-hexane are graphed at a 5 ppbv scale. 1,3-butadiene occurs at a very low level, but is graphed because this concentration is toxicologically significant. (See Section on "Health Implications – Speciated Non-Methane Organic Compounds").

### Compounds As Groups

Figures 4.7 and 4.8 show some of the largest-concentration SNMOCs graphed on a 100 ppbv scale. The graphs show that these compounds follow consistent trends, with relative relationships that remain stable over time. The lower-concentration SNMOC graphs (Figures 4.9 through 4.10), also suggest that the relationships between the various compounds remain stable over time. These similar ratios of concentration across the entire year imply a common source for these compounds.

**Table 4.5 – Weekend Vs. Weekday Statistics for the SNMOCs**

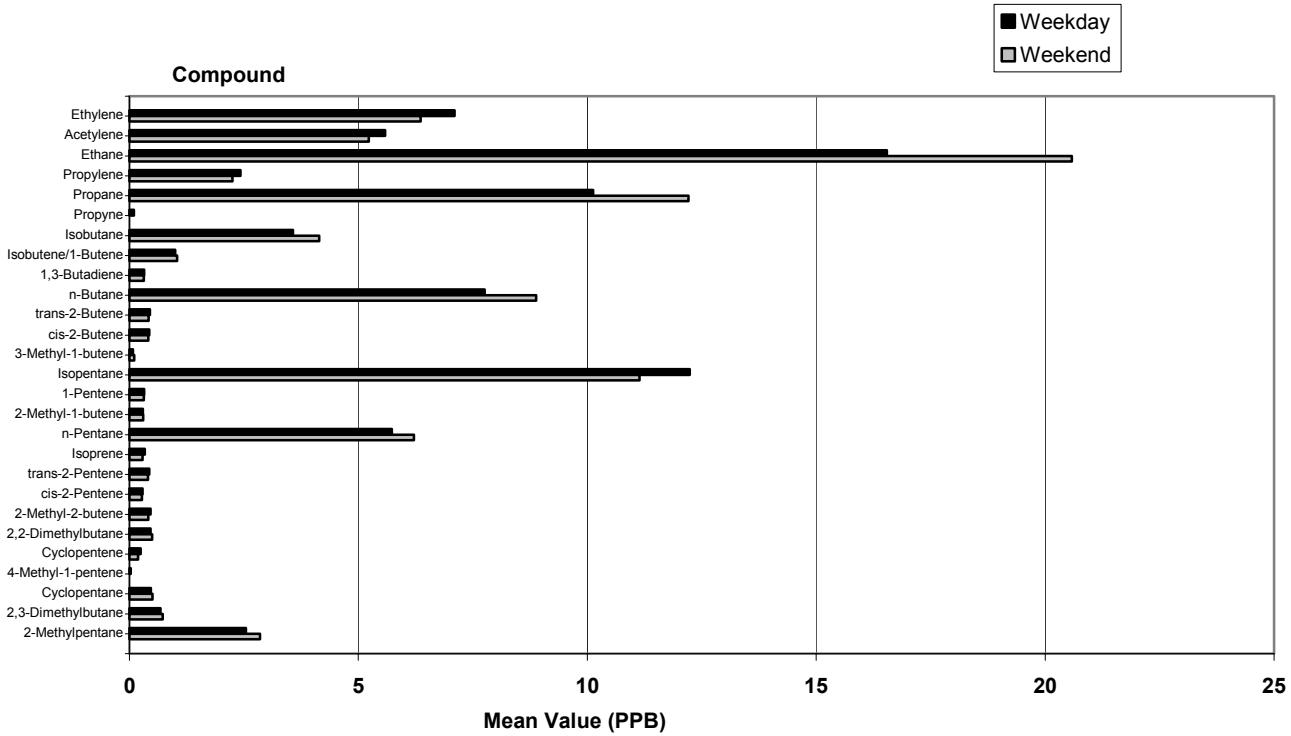
| | Summary Statistics WEEKDAY (PPB) | | | Summary Statistics WEEKEND (PPB) | | |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean | Minimum | Maximum | Mean |
| Ethylene | 2.00 | 23.85 | 7.10 | 1.92 | 35.47 | 6.36 |
| Acetylene | 1.82 | 22.55 | 5.58 | 1.43 | 31.14 | 5.23 |
| Ethane | 3.74 | 89.06 | 16.55 | 4.49 | 122.31 | 20.58 |
| Propylene | 0.58 | 7.89 | 2.43 | 0.73 | 11.07 | 2.25 |
| Propane | 2.31 | 69.11 | 10.13 | 2.01 | 72.30 | 12.21 |
| Propyne | 0.10 | 0.10 | 0.10 | | | |
| Isobutane | 0.57 | 24.00 | 3.57 | 0.59 | 27.00 | 4.14 |
| Isobutene/1-Butene | 0.20 | 4.52 | 1.00 | 0.20 | 6.76 | 1.04 |
| 1,3-Butadiene | 0.04 | 1.36 | 0.32 | 0.06 | 1.93 | 0.31 |
| n-Butane | 2.00 | 47.97 | 7.76 | 1.49 | 57.35 | 8.89 |
| trans-2-Butene | 0.13 | 1.53 | 0.45 | 0.10 | 2.65 | 0.42 |
| cis-2-Butene | | 1.34 | 0.43 | 0.13 | 2.37 | 0.41 |
| 3-Methyl-1-butene | 0.03 | 0.27 | 0.08 | 0.03 | 0.52 | 0.10 |
| Isopentane | 1.62 | 49.57 | 12.24 | 1.58 | 70.12 | 11.14 |
| 1-Pentene | 0.09 | 1.21 | 0.32 | 0.10 | 1.66 | 0.31 |
| 2-Methyl-1-butene | 0.08 | 0.75 | 0.29 | 0.06 | 1.63 | 0.30 |
| n-Pentane | 0.56 | 27.74 | 5.73 | 1.46 | 39.50 | 6.21 |
| Isoprene | 0.07 | 1.22 | 0.33 | 0.08 | 1.34 | 0.29 |
| trans-2-Pentene | 0.10 | 1.54 | 0.44 | 0.11 | 2.37 | 0.40 |
| cis-2-Pentene | 0.08 | 0.90 | 0.28 | 0.08 | 1.40 | 0.27 |
| 2-Methyl-2-butene | 0.08 | 2.14 | 0.46 | 0.08 | 2.61 | 0.41 |
| 2,2-Dimethylbutane | 0.12 | 1.76 | 0.46 | 0.16 | 2.62 | 0.50 |
| Cyclopentene | 0.10 | 1.49 | 0.24 | 0.05 | 0.69 | 0.19 |
| 4-Methyl-1-pentene | 0.03 | 0.03 | 0.03 | | | |
| Cyclopentane | 0.09 | 2.03 | 0.47 | 0.13 | 3.04 | 0.51 |
| 2,3-Dimethylbutane | 0.14 | 2.68 | 0.68 | 0.19 | 4.47 | 0.73 |
| 2-Methylpentane | 0.28 | 11.78 | 2.54 | 0.64 | 18.92 | 2.85 |
| 3-Methylpentane | 0.23 | 7.22 | 1.61 | 0.40 | 11.55 | 1.74 |
| 2-Methyl-1-pentene | 0.02 | 0.30 | 0.07 | 0.03 | 0.50 | 0.14 |

| | Summary Statistics WEEKDAY (PPB) | | | Summary Statistics WEEKEND (PPB) | | |
|---|---|---|---|---|---|---|
| | **Minimum** | **Maximum** | **Mean** | **Minimum** | **Maximum** | **Mean** |
| | | | | | | |
| 1-Hexene | **0.05** | **1.24** | **0.31** | **0.08** | **1.38** | **0.32** |
| 2-Ethyl-1-butene | | | | | | |
| n-Hexane | **0.24** | | **2.51** | **0.52** | **18.52** | **2.76** |
| trans-2-Hexene | **0.02** | **0.11** | **0.07** | **0.10** | **0.10** | **0.10** |
| cis-2-Hexene | **0.02** | **0.82** | **0.08** | **0.03** | **0.06** | **0.04** |
| Methylcyclopentane | **0.14** | **5.31** | **1.12** | **0.24** | **8.17** | **1.23** |
| 2,4-Dimethylpentane | **0.10** | | **0.40** | **0.11** | **2.37** | **0.41** |
| Benzene | **0.39** | **11.40** | **2.18** | **0.43** | **13.79** | **2.23** |
| Cyclohexane | **0.11** | **2.86** | **0.77** | **0.16** | **5.21** | **0.77** |
| 2-Methylhexane | **0.07** | **3.98** | **0.83** | **0.15** | **5.74** | **0.84** |
| 2,3-Dimethylpentane | **0.12** | **2.27** | **0.54** | **0.14** | **3.17** | **0.55** |
| 3-Methylhexane | **0.09** | **4.74** | **0.82** | **0.14** | **7.00** | **0.90** |
| 1-Heptene | **0.03** | | **0.28** | **0.04** | **1.88** | **0.30** |
| 2,2,4-Trimethylpentane | **0.16** | **4.49** | **0.88** | **0.18** | **4.48** | **0.73** |
| n-Heptane | **0.08** | **5.11** | **0.92** | **0.15** | **6.30** | **1.00** |
| Methylcyclohexane | **0.08** | **4.86** | **0.98** | **0.18** | **6.64** | **1.19** |
| 2,2,3-Trimethylpentane | **0.02** | **1.21** | **0.20** | **0.04** | **1.26** | **0.20** |
| 2,3,4-Trimethylpentane | **0.07** | **1.19** | **0.28** | **0.06** | **1.62** | **0.27** |
| Toluene | **0.53** | **18.84** | **4.55** | **0.77** | **25.56** | **4.17** |
| 2-Methylheptane | **0.05** | **1.65** | **0.28** | **0.04** | **1.57** | **0.29** |
| 3-Methylheptane | **0.05** | **1.79** | **0.28** | **0.04** | **1.68** | **0.28** |
| 1-Octene | **0.01** | **0.47** | **0.09** | **0.02** | **0.40** | **0.11** |
| n-Octane | **0.06** | **3.32** | **0.46** | **0.06** | **2.51** | **0.45** |
| Ethylbenzene | **0.08** | **3.10** | **0.71** | **0.11** | **4.04** | **0.67** |
| m-Xylene/p-Xylene | **0.25** | **10.68** | **2.25** | **0.35** | **12.51** | **2.09** |
| Styrene | **0.04** | **2.24** | **0.47** | **0.13** | **1.88** | **0.45** |
| o-Xylene | **0.09** | **4.22** | **0.90** | **0.15** | **5.00** | **0.86** |
| 1-Nonene | **0.02** | **0.65** | **0.13** | **0.02** | **0.68** | **0.13** |
| n-Nonane | **0.03** | **1.47** | **0.34** | **0.05** | **1.71** | **0.38** |
| Isopropylbenzene | **0.02** | **0.46** | **0.11** | **0.02** | **0.45** | **0.12** |
| a-Pinene | **0.02** | | **0.34** | **0.10** | **1.49** | **0.41** |
| n-Propylbenzene | **0.04** | **1.19** | **0.29** | **0.05** | **1.43** | **0.30** |

| | Summary Statistics WEEKDAY (PPB) | | | Summary Statistics WEEKEND (PPB) | | |
|---|---|---|---|---|---|---|
| | **Minimum** | **Maximum** | **Mean** | **Minimum** | **Maximum** | **Mean** |
| | | | | | | |
| m-Ethyltoluene | **0.07** | **4.09** | **0.94** | **0.15** | **4.42** | **0.97** |
| p-Ethyltoluene | **0.05** | **1.94** | **0.47** | **0.08** | **2.21** | **0.50** |
| 1,3,5-Trimethylbenzene | **0.02** | **2.73** | **0.63** | **0.09** | **2.68** | **0.66** |
| o-Ethyltoluene | **0.03** | **2.36** | **0.53** | **0.07** | **2.57** | **0.59** |
| b-Pinene | **0.02** | **0.89** | **0.18** | **0.01** | **0.90** | **0.16** |
| 1,2,4-Trimethylbenzene | **0.06** | **6.93** | **1.56** | **0.24** | **6.74** | **1.67** |
| 1-Decene | | | | **0.42** | **0.42** | **0.42** |
| n-Decane | **0.04** | **2.50** | **0.60** | **0.08** | **3.00** | **0.66** |
| 1,2,3-Trimethylbenzene | **0.02** | **2.22** | **0.38** | **0.05** | **1.68** | **0.42** |
| m-Diethylbenzene | **0.03** | **0.62** | **0.14** | **0.02** | **0.51** | **0.14** |
| p-Diethylbenzene | **0.02** | **0.40** | **0.09** | **0.02** | **0.47** | **0.10** |
| 1-Undecene | **0.01** | **0.37** | **0.06** | **0.02** | **1.26** | **0.38** |
| n-Undecane | **0.06** | **3.96** | **0.67** | **0.06** | **4.58** | **0.77** |
| 1-Dodecene | **0.01** | **0.86** | **0.11** | **0.01** | **2.64** | **0.41** |
| n-Dodecane | **0.02** | **1.85** | **0.27** | **0.03** | **4.18** | **0.43** |
| 1-Tridecene | **0.11** | **0.11** | **0.11** | **2.94** | **2.94** | **2.94** |
| n-Tridecane | **0.01** | **0.36** | **0.09** | **0.01** | **3.60** | **0.63** |

**Table 4.5, completed.**

## Figure 4.1 - Weekday Vs. Weekend Mean For SNMOCs At CAMP



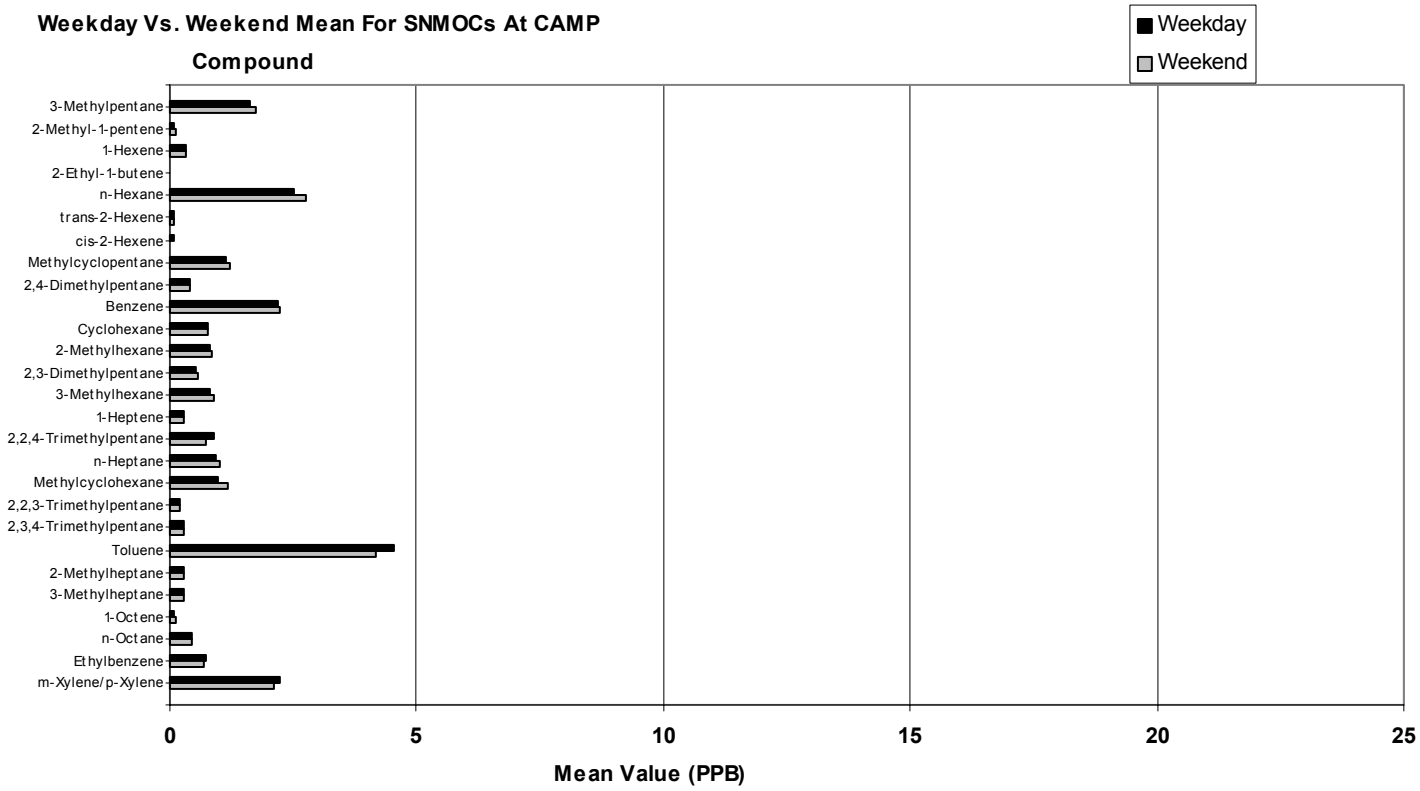



**Figure 4.1 continued.**

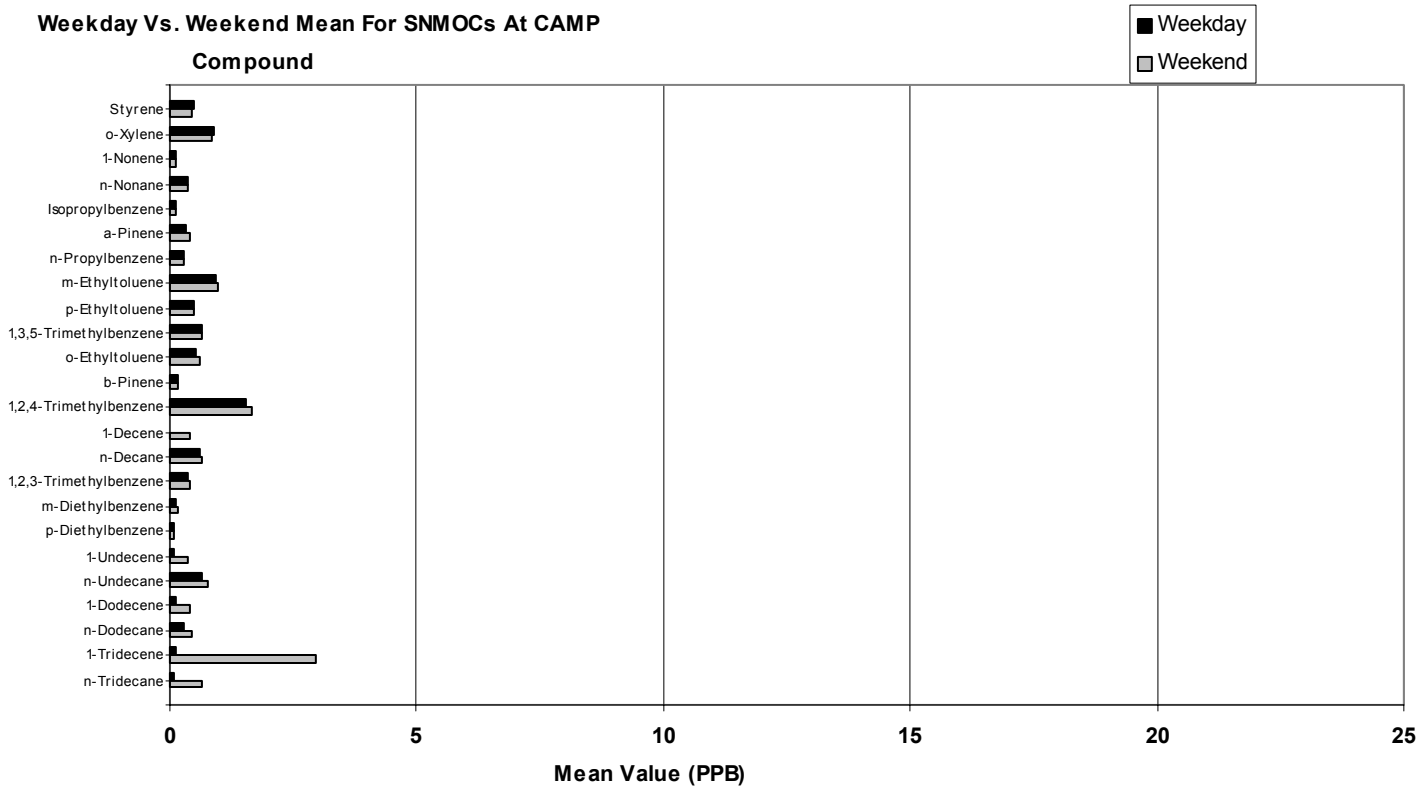



**Figure 4.1 completed.**

**Figure 4.2 - Ethane, Ethylene, and Acetylene**

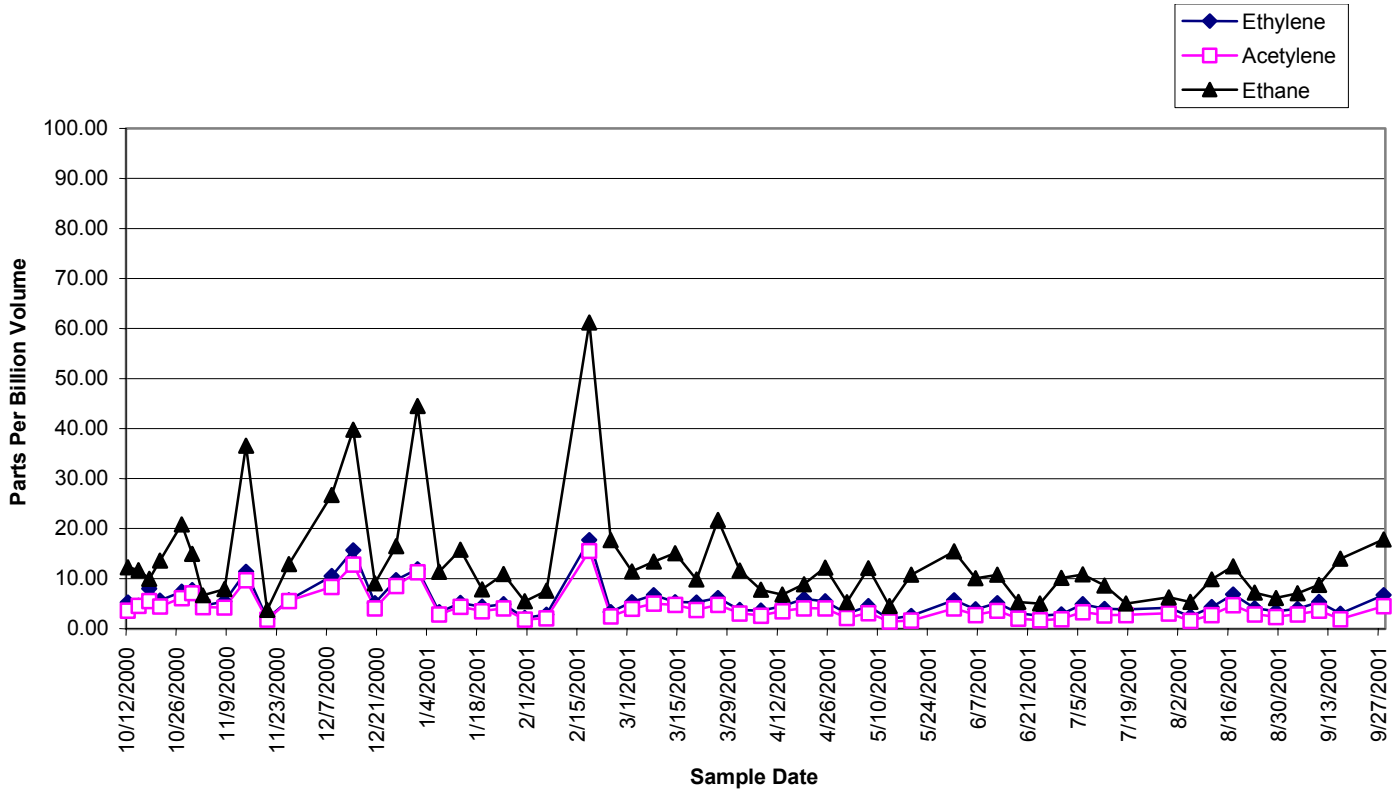


**Figure 4.3 – Propane, Isobutane, and n-Butane**

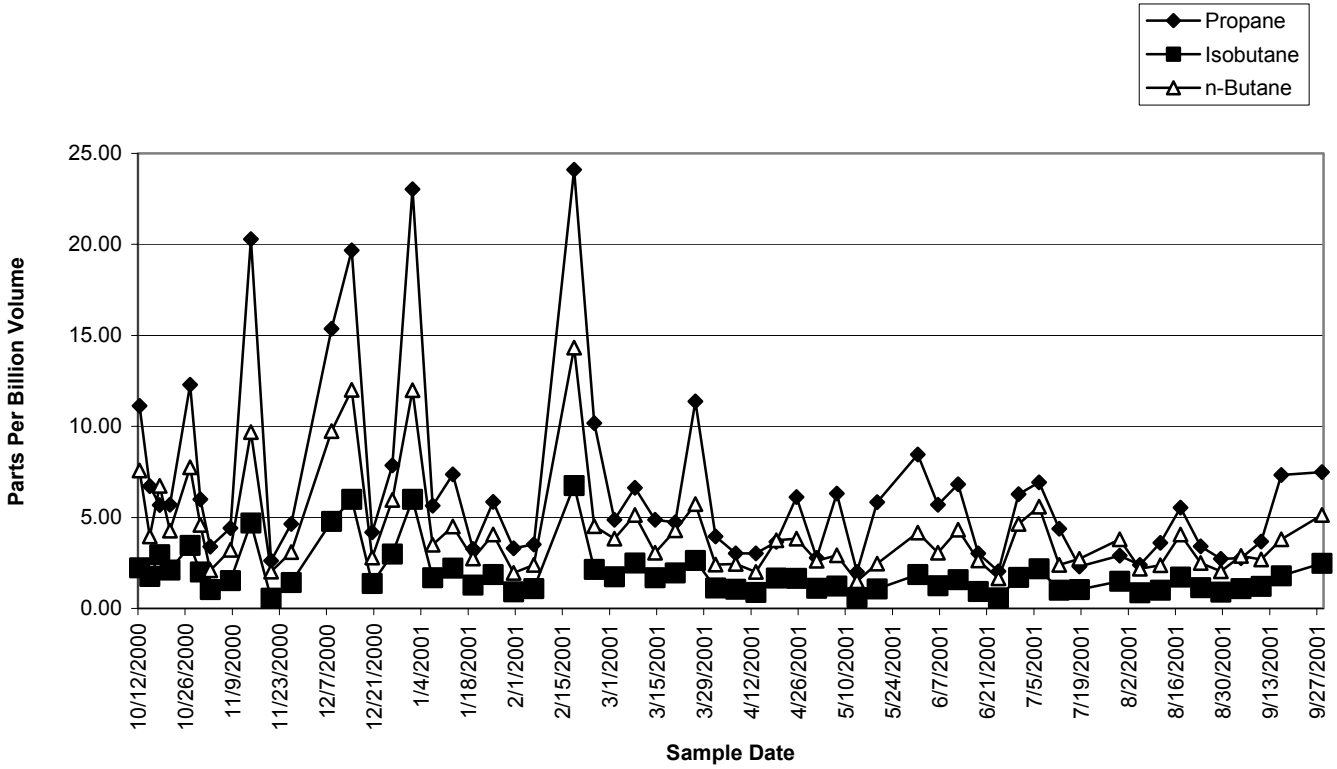


**Figure 4.4 - Isopentane, n-Pentane, and 2-Methylpentane**

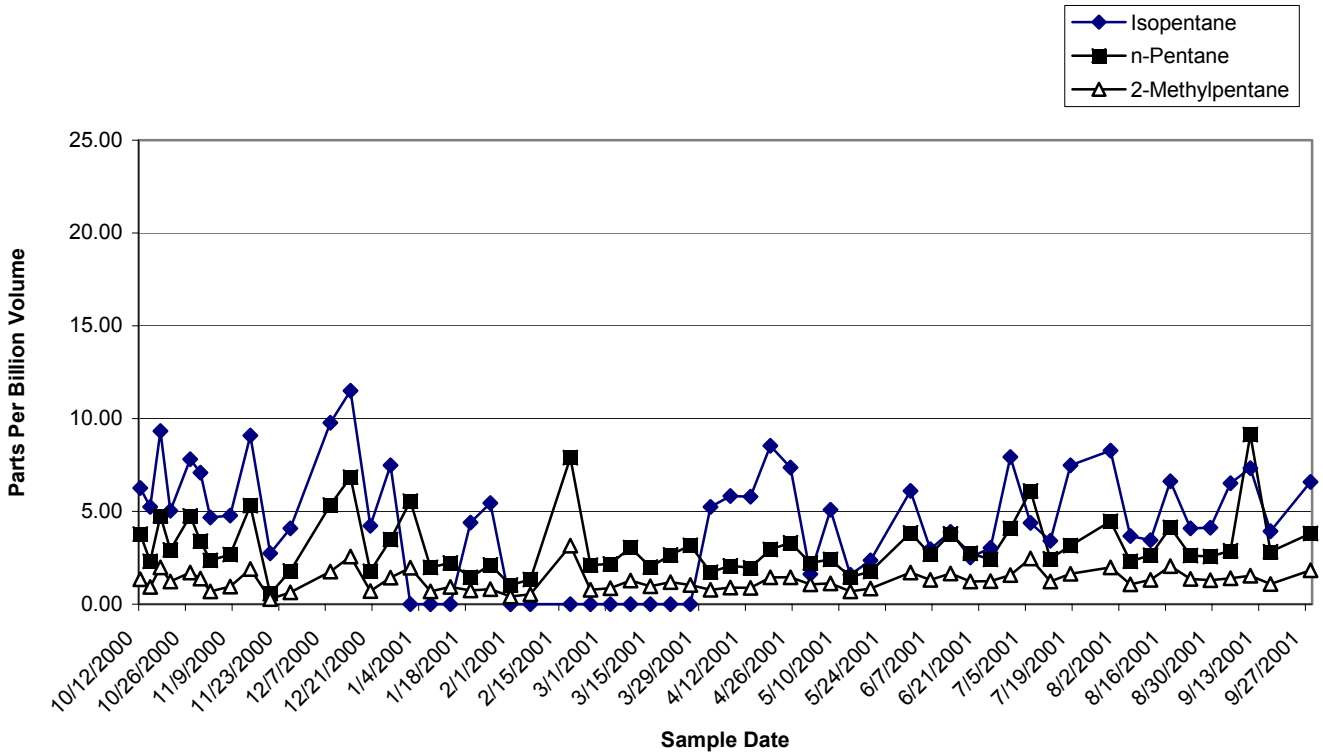


**Figure 4.5 – Benzene and Toluene**

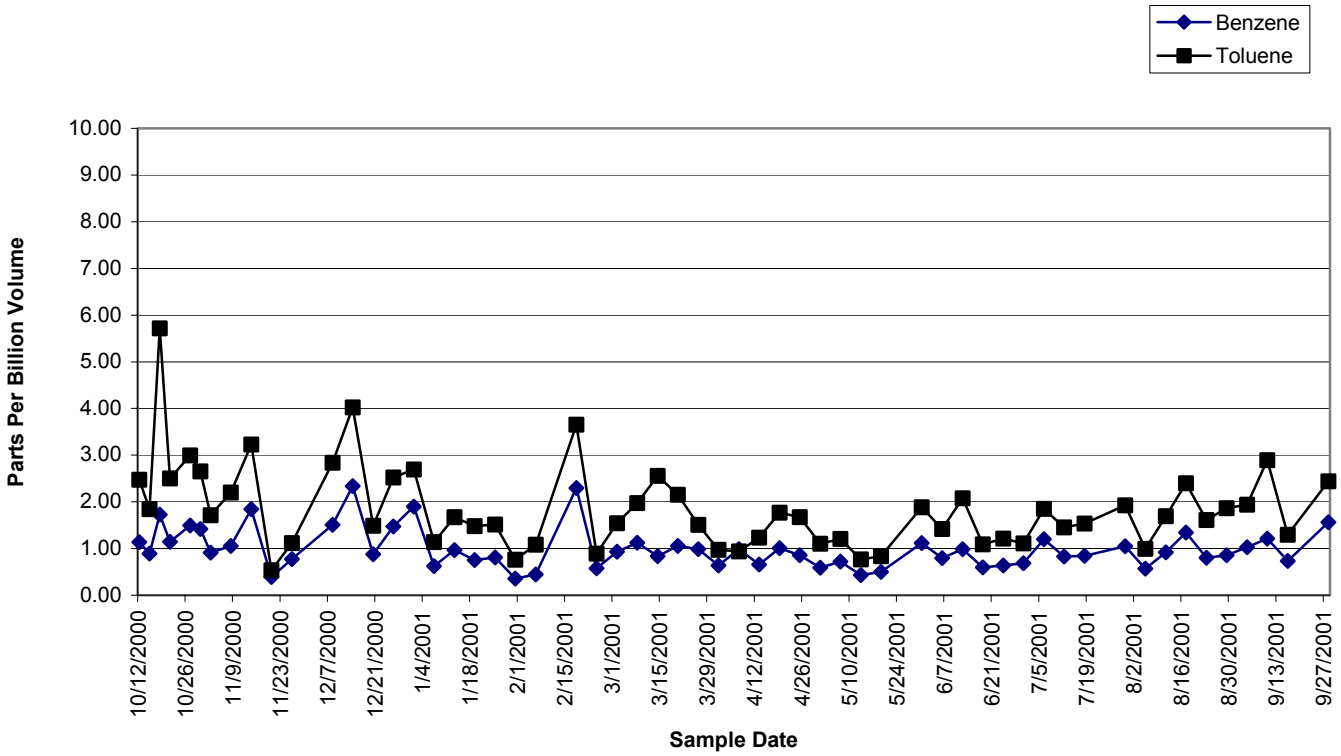


**Figure 4.6 – Propylene, 1,3-Butadiene and n-Hexane**

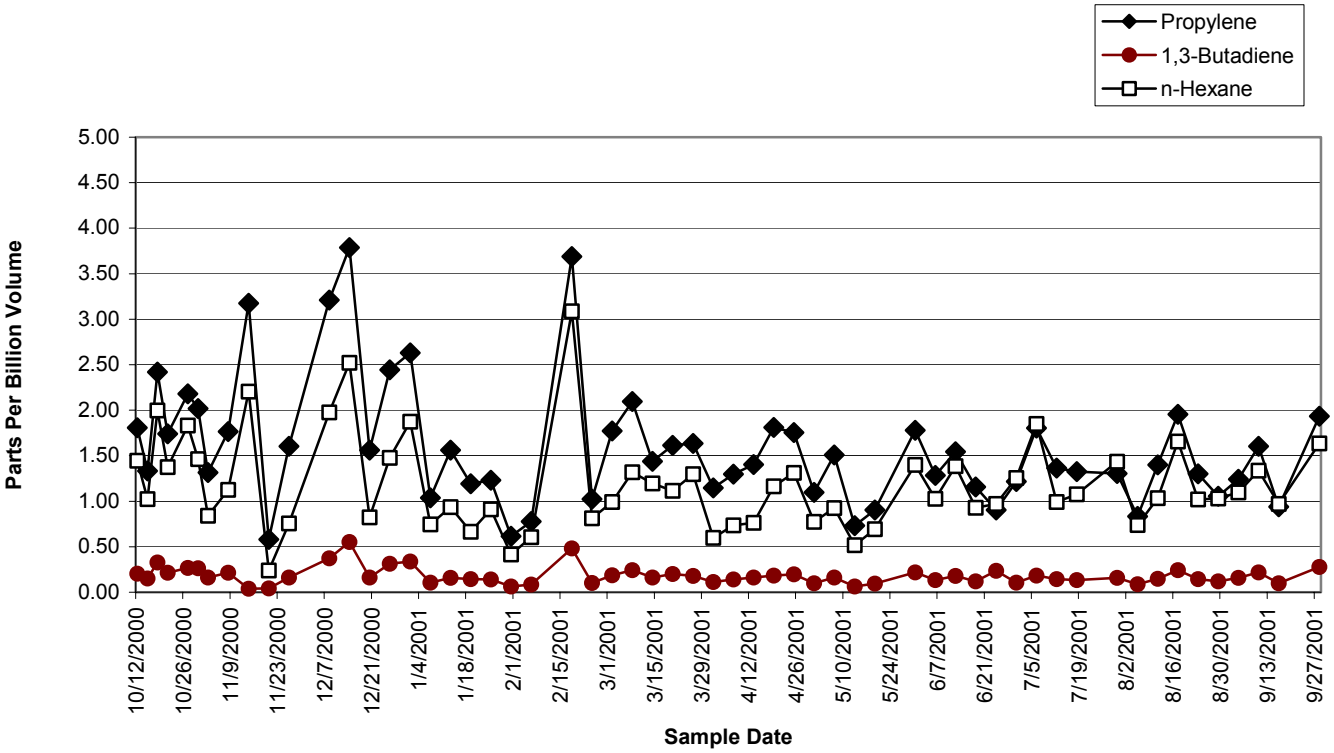


**Figure 4.7 – Largest Concentration SNMOCs At CAMP**

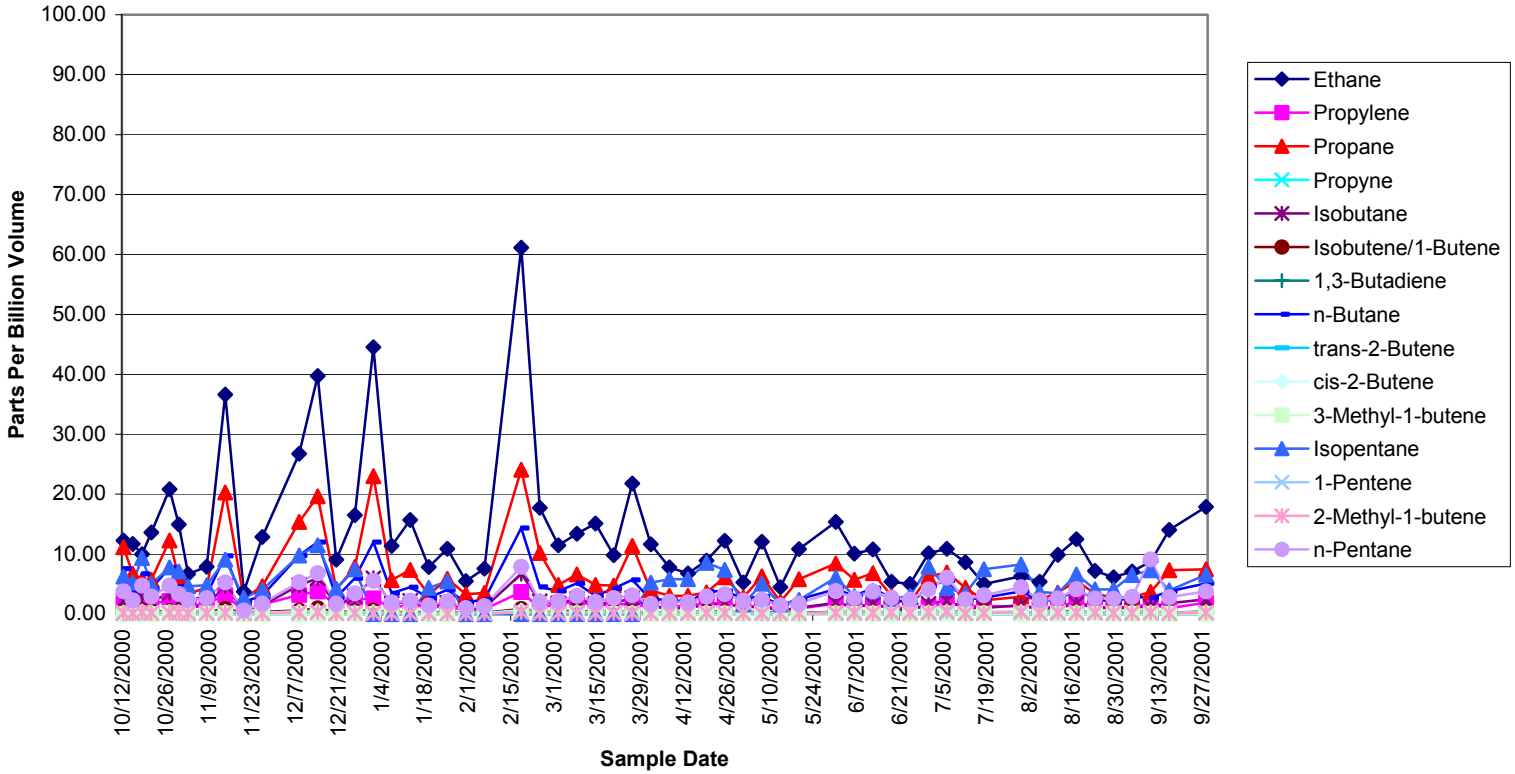


**Figure 4.8 – Largest Concentration SNMOCs At CAMP (2)**

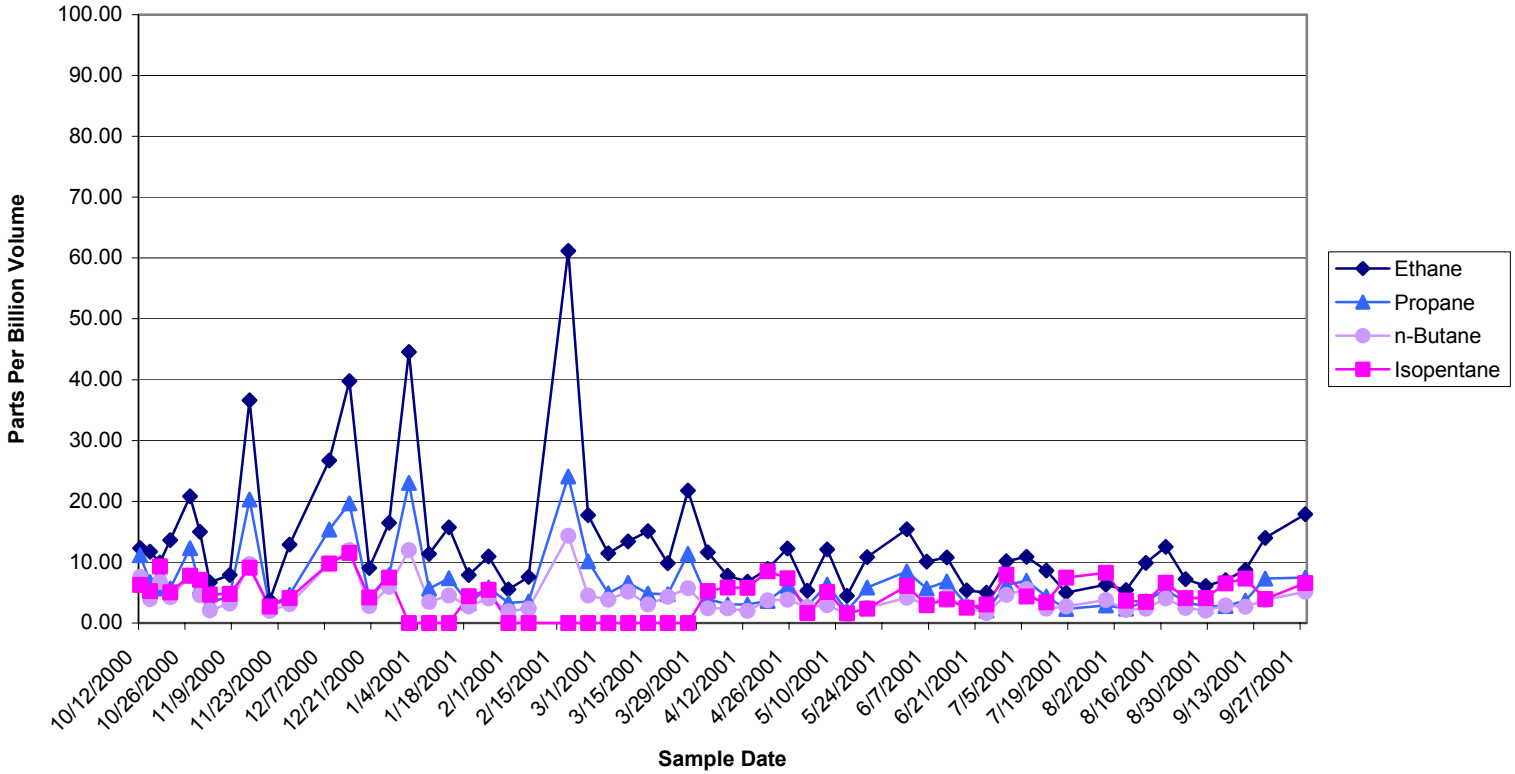


**Figure 4.9 – Higher - Concentration SNMOCs At CAMP**

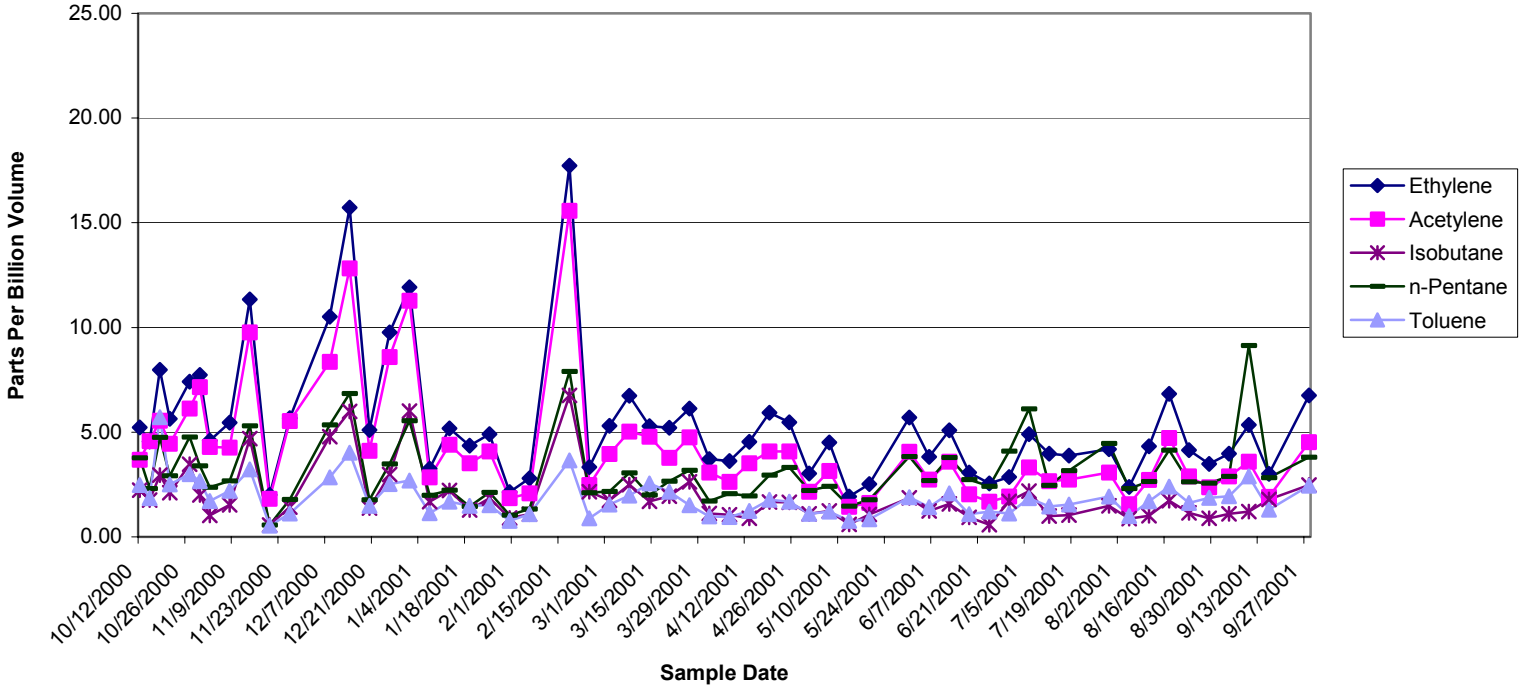
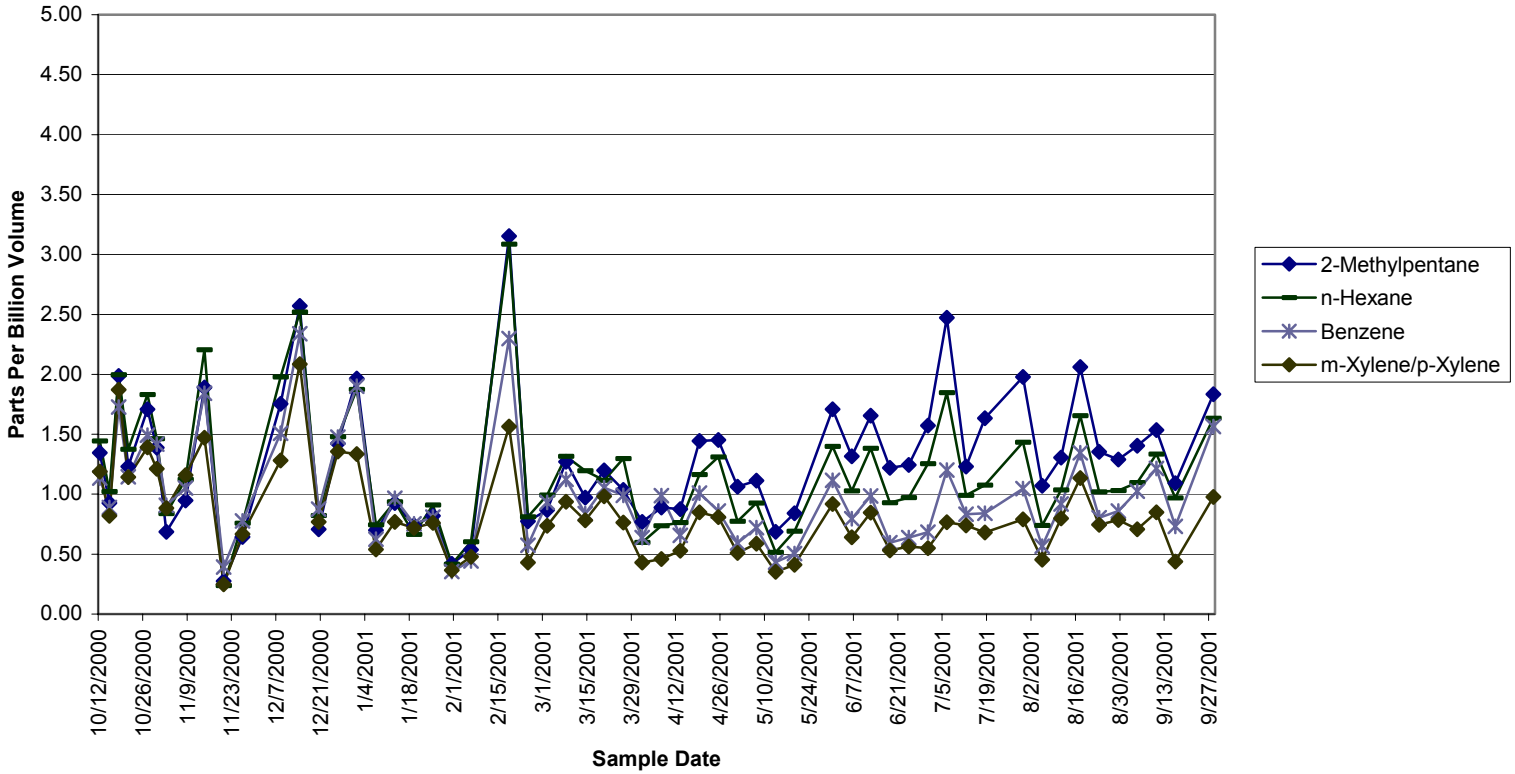


**Figure 4.10 – High - Concentration SNMOCs At CAMP**



## Correlation Coefficients Between Compounds – Speciated Non-Methane Organic Compounds

A correlation coefficient analysis was conducted for the speciated non-methane organic compounds. To simplify the calculations, only SNMOCs measured at one or more twenty-four hour levels greater than 1 ppbv were included. Results (Table 4.6) show that there is strong inter-correlation between these compounds. This inter-correlation suggests a common source for these emissions.

**Table 4.6 - Correlation Coefficients for SNMOCs**

| | Ethylene | Acetylene | Ethane | Propylene | Propane | Isobutane |
|---|---|---|---|---|---|---|
| **Ethylene** | 1.0000 | | | | | |
| **Acetylene** | **0.9851** | 1.0000 | | | | |
| **Ethane** | **0.9010** | **0.9132** | 1.0000 | | | |
| **Propylene** | **0.9653** | **0.9257** | **0.8223** | 1.0000 | | |
| **Propane** | **0.8560** | **0.8614** | **0.9602** | **0.8150** | 1.0000 | |
| **Isobutane** | **0.9359** | **0.9303** | **0.9476** | **0.9027** | **0.9544** | 1.0000 |
| **Isobutene/1-Butene** | **0.9362** | **0.8903** | **0.8001** | **0.9645** | **0.7879** | **0.8745** |
| **n-Butane** | **0.9131** | **0.8997** | **0.9232** | **0.8929** | **0.9533** | **0.9844** |
| **Isopentane** | **0.7703** | 0.7266 | 0.6393 | **0.7876** | 0.6079 | 0.7463 |
| **n-Pentane** | 0.7084 | 0.6435 | 0.6244 | 0.7369 | 0.6314 | 0.6855 |
| **2-Methylpentane** | 0.7239 | 0.6436 | 0.6282 | **0.7541** | 0.6117 | 0.6870 |
| **3-Methylpentane** | **0.8397** | **0.7703** | 0.7182 | **0.8724** | 0.7097 | **0.7951** |
| **n-Hexane** | **0.8868** | **0.8292** | **0.7916** | **0.9119** | **0.7863** | **0.8608** |
| **Methylcyclopentane** | **0.9028** | **0.8431** | **0.7967** | **0.9206** | **0.7863** | **0.8673** |
| **Benzene** | **0.9349** | **0.8931** | **0.7943** | **0.9422** | **0.7768** | **0.8758** |
| **Cyclohexane** | 0.3456 | 0.3424 | 0.2438 | 0.3797 | 0.2934 | 0.2923 |
| **2-Methylhexane** | **0.9283** | **0.8703** | **0.8127** | **0.9440** | **0.7980** | **0.8918** |
| **3-Methylhexane** | **0.8687** | **0.8049** | 0.7391 | **0.8835** | 0.7164 | **0.8024** |
| **2,2,4-Trimethylpentane** | 0.1614 | 0.1193 | 0.1107 | 0.2244 | 0.2333 | 0.1726 |
| **n-Heptane** | **0.9217** | **0.8884** | **0.8111** | **0.9386** | **0.8337** | **0.9118** |
| **Methylcyclohexane** | **0.9015** | **0.8908** | **0.8075** | **0.9240** | **0.8199** | **0.8964** |
| **Toluene** | **0.7617** | 0.7048 | 0.5510 | **0.8006** | 0.5520 | 0.6908 |
| **m-Xylene/p-Xylene** | **0.8656** | **0.8215** | 0.6509 | **0.8994** | 0.6685 | **0.7884** |
| **1,2,4-Trimethylbenzene** | 0.7293 | 0.7176 | 0.5444 | **0.7913** | 0.5748 | 0.6744 |

**Bolded if correlation > 0.75**

| | Isobutene/1-Butene | n-Butane | Isopentane | n-Pentane | 2-Methylpentane | 3-Methylpentane | n-Hexane |
|---|---|---|---|---|---|---|---|
| **Ethylene** | | | | | | | |
| **Acetylene** | | | | | | | |
| **Ethane** | | | | | | | |
| **Propylene** | | | | | | | |
| **Propane** | | | | | | | |
| **Isobutane** | | | | | | | |
| **Isobutene/1-Butene** | 1.0000 | | | | | | |
| **n-Butane** | **0.8653** | 1.0000 | | | | | |
| **Isopentane** | 0.7372 | 0.7419 | 1.0000 | | | | |
| **n-Pentane** | 0.7197 | 0.7142 | 0.6571 | 1.0000 | | | |
| **2-Methylpentane** | **0.7511** | 0.7261 | 0.6461 | **0.8602** | 1.0000 | | |
| **3-Methylpentane** | **0.8606** | **0.8247** | **0.7502** | **0.8701** | **0.9684** | 1.0000 | |
| **n-Hexane** | **0.8939** | **0.8829** | **0.7675** | **0.8590** | **0.9223** | **0.9816** | 1.0000 |
| **Methylcyclopentane** | **0.9046** | **0.8834** | **0.7792** | **0.8635** | **0.9305** | **0.9869** | **0.9924** |
| **Benzene** | **0.9265** | **0.8727** | **0.7922** | **0.7949** | **0.8187** | **0.9142** | **0.9363** |
| **Cyclohexane** | 0.3468 | 0.3193 | 0.2096 | 0.2983 | 0.2266 | 0.3235 | 0.3678 |
| **2-Methylhexane** | **0.9254** | **0.8911** | **0.8024** | **0.8232** | **0.8611** | **0.9385** | **0.9645** |
| **3-Methylhexane** | **0.8710** | **0.8137** | 0.6926 | **0.8433** | **0.8933** | **0.9444** | **0.9379** |
| **2,2,4-Trimethylpentane** | 0.1928 | 0.3043 | 0.1834 | 0.2362 | 0.2216 | 0.2514 | 0.2665 |
| **n-Heptane** | **0.9354** | **0.9101** | 0.7480 | **0.7710** | **0.7603** | **0.8794** | **0.9269** |
| **Methylcyclohexane** | **0.8845** | **0.8863** | 0.7057 | 0.6563 | 0.6285 | **0.7777** | **0.8543** |
| **Toluene** | **0.8097** | 0.6990 | 0.7128 | 0.7135 | 0.7048 | **0.8094** | **0.8389** |
| **m-Xylene/p-Xylene** | **0.8862** | **0.7918** | 0.7332 | 0.6793 | 0.7074 | **0.8358** | **0.8680** |
| **1,2,4-Trimethylbenzene** | 0.7429 | 0.6532 | 0.6432 | 0.4561 | 0.4291 | 0.5887 | 0.6611 |

**Bolded if correlation > 0.75**

**Table 4.6, continued**

| | Methylcyclo-pentane | Benzene | Cyclohexane | 2-Methylhexane | 3-Methylhexane | 2,2,4-Trimethylpentane | n-Heptane |
|---|---|---|---|---|---|---|---|
| **Ethylene** | | | | | | | |
| **Acetylene** | | | | | | | |
| **Ethane** | | | | | | | |
| **Propylene** | | | | | | | |
| **Propane** | | | | | | | |
| **Isobutane** | | | | | | | |
| **Isobutene/1-Butene** | | | | | | | |
| **n-Butane** | | | | | | | |
| **Isopentane** | | | | | | | |
| **n-Pentane** | | | | | | | |
| **2-Methylpentane** | | | | | | | |
| **3-Methylpentane** | | | | | | | |
| **n-Hexane** | | | | | | | |
| **Methylcyclopentane** | 1.0000 | | | | | | |
| **Benzene** | **0.9490** | 1.0000 | | | | | |
| **Cyclohexane** | 0.3399 | 0.3955 | 1.0000 | | | | |
| **2-Methylhexane** | **0.9696** | **0.9527** | 0.3184 | 1.0000 | | | |
| **3-Methylhexane** | **0.9572** | **0.9339** | 0.3517 | **0.9302** | 1.0000 | | |
| **2,2,4-Trimethylpentane** | 0.2499 | 0.2379 | 0.3349 | 0.2235 | 0.2435 | 1.0000 | |
| **n-Heptane** | **0.9293** | **0.9565** | 0.4305 | **0.9358** | **0.8969** | 0.2547 | 1.0000 |
| **Methylcyclohexane** | **0.8431** | **0.8879** | 0.5315 | **0.8648** | **0.7989** | 0.2394 | **0.9431** |
| **Toluene** | **0.8317** | **0.8700** | 0.4063 | **0.8230** | **0.8108** | 0.2684 | **0.8706** |
| **m-Xylene/p-Xylene** | **0.8720** | **0.9273** | 0.4818 | **0.8763** | **0.8452** | 0.3002 | **0.9363** |
| **1,2,4-Trimethylbenzene** | 0.6478 | 0.7408 | 0.5893 | 0.6821 | 0.6010 | 0.2170 | **0.7830** |

**Bolded if correlation > 0.75**

**Table 4.6, continued**

| | Methylcyclohexane | Toluene | m-Xylene/p-Xylene | 1,2,4-Trimethylbenzene |
|---|---|---|---|---|
| **Ethylene** | | | | |
| **Acetylene** | | | | |
| **Ethane** | | | | |
| **Propylene** | | | | |
| **Propane** | | | | |
| **Isobutane** | | | | |
| **Isobutene/1-Butene** | | | | |
| **n-Butane** | | | | |
| **Isopentane** | | | | |
| **n-Pentane** | | | | |
| **2-Methylpentane** | | | | |
| **3-Methylpentane** | | | | |
| **n-Hexane** | | | | |
| **Methylcyclopentane** | | | | |
| **Benzene** | | | | |
| **Cyclohexane** | | | | |
| **2-Methylhexane** | | | | |
| **3-Methylhexane** | | | | |
| **2,2,4-Trimethylpentane** | | | | |
| **n-Heptane** | | | | |
| **Methylcyclohexane** | 1.0000 | | | |
| **Toluene** | **0.7990** | 1.0000 | | |
| **m-Xylene/p-Xylene** | **0.8908** | **0.9343** | 1.0000 | |
| **1,2,4-Trimethylbenzene** | **0.8907** | **0.7503** | **0.8528** | 1.0000 |

**Bolded if correlation > 0.75**

**Table 4.6, completed**

## Precision of Sample Results – Speciated Non-Methane Organic Compounds

Periodically throughout the year, a second canister was sampled simultaneously with the main sample. These additional samples, known as duplicates, were collected in order to assess the precision (repeatability) of the canister sampling method. On the duplicate sampling dates, the laboratory also conducted a test of the precision of the analytical process by injecting two samples of each canister's air into the gas chromatograph / mass spectrometer. These samples are known as laboratory replicates. Thus, this project collected two types of precision data – duplicate data, which assesses both sampling and analysis procedures, and replicate data, which assesses laboratory analytical method repeatability.

## Field Blanks – Speciated Non-Methane Organic Compounds

The speciated non-methane organic compound sampling method involves sampling with stainless steel canisters with specially-treated interior surfaces. The canisters are re-used. After a full canister is analyzed, it is pumped out repeatedly to a high vacuum. This procedure cleans it for the next use. Periodically, one canister from each cleaning batch is tested to make sure the method is performing adequately. The test canister is filled with ultra-pure air, and then analyzed. If it shows no contamination, the batch is released for use. If contamination is found, the entire batch is sent through the cleaning process for a second time. The canisters arrive in the field closed, and under 20 to 30 inches of vacuum. Therefore, field blanks are not used in this method. The canisters are "blanked" at the laboratory prior to shipping to the field.

## Inter-Method Variation For Same Compounds

Both the VOC and the SNMOC laboratory analytical methods use the same canisters of air for analysis. In addition, twelve compounds are measured by both these methods. Thus, it is possible to compare concentration data for certain compounds, as measured by the VOC method versus as measured by the SNMOC method. These results are presented in the Appendix to this report, which is issued as a separate document. In general, results are generally just outside the +/- 30 % confidence limit interval usually cited for precision of replicate and duplicate samples. An exception is styrene, for which the precision limits are wide, because of its extremely low concentration in ambient air (frequently less than 0.15 ppbv). In general, the two methods show very good precision for the same compounds.

# Compounds of Significance: Sources and Health Effects

Of the seventy-eight speciated non-methane organic compounds measured in this study, thirteen showed an annual mean greater than one part per billion (ppb) in Denver air. These are: acetylene, benzene, toluene, propylene, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, 2-methylpentane, and ethylene. Acetylene, benzene, toluene, and propylene were discussed in the chapter on volatile organic compounds. (The laboratory results discussed in this chapter measure these same compounds, from the same air canisters, that the VOC method does. The laboratory analytical procedures differ, but results match those of the other method closely. Therefore, it would be repetitive to discuss levels of these four compounds in this chapter). The remaining nine compounds will be discussed below. It should be noted that eight of these compounds are alkanes, compounds composed of chains of hydrogen and carbon atoms, where all the chemical bonds are single. The remaining compound, ethylene, is an alkene, a compound composed of hydrogen and carbon atoms, of which at least one has a double chemical bond. As the alkane compounds are closely related, they will be discussed in order of increasing complexity, as follows: ethane ($C_2H_6$), propane ($C_3H_8$), n-butane and isobutane isomers ($C_4H_{10}$), n-pentane and isopentane isomers ($C_5H_{12}$), n-hexane and its isomer 2-methylpentane ($C_6H_{14}$). The alkene, ethylene ($C_2H_4$), is discussed last.

## Ethane

Ethane is a hydrocarbon compound with the formula $C_2H_6$. It exists in the atmosphere as an odorless, colorless gas. It is used for fuel, for chemical production, and as a refrigerant (NJ Hazardous Substance Fact Sheet on Ethane). The largest source of ethane in ambient air is the combustion of automotive fuel.

Ethane is explosive in high concentrations. It is also an asphyxiant, which can reduce the available amount of oxygen if its concentration builds up in confined spaces. Exposure to concentrated amounts can cause headache, dizziness, lightheadedness, and death (NJ Hazardous Substance Fact Sheet on Ethane). It is not known whether ethane exposure can cause cancer. Ethane has not been researched sufficiently to determine whether it affects reproduction or causes birth defects in children of exposed individuals.

The EPA AIRS database lists ethane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of ethane at California locations typically ranged from 2 to 12 ppbv. For the year of CAMP results, the mean ethane concentration was 13.2 ppbv, just above the higher end of the California range.

The Environmental Protection Agency has not established any recommended “benchmark” value for ethane. Thus the cancer and health effect risk from concentrations observed in this study cannot be estimated. Due to its formation from automotive fuel combustion, ethane is common in outdoor US air and public exposure occurs nationwide.

## Propane

Propane is a hydrocarbon compound with the formula $C_3H_8$. It exists in the atmosphere as an odorless, colorless gas. It is used for home heating, automotive and industrial fuel, for chemical production, and as a refrigerant (NJ Hazardous Substance Fact Sheet on Propane). The largest source of propane in ambient air is the combustion of automotive fuel.

Like ethane, propane is explosive in high concentrations. It can reduce the available amount of oxygen if its concentration builds up in confined spaces. Health effects are similar to ethane, in that exposure to concentrated amounts can cause headache, dizziness, lightheadedness, and death (NJ Hazardous Substance Fact Sheet on Propane). It is not known whether propane exposure can cause cancer.

Propane has not been researched sufficiently to determine whether it affects reproduction or causes birth defects in children of exposed individuals.

The EPA AIRS database lists propane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of ethane at California locations typically ranged from 2 to 8.7 ppbv. For the year of CAMP results, the mean ethane concentration was 6.55 ppbv, in the middle of the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for propane. Thus the cancer and health effect risk from concentrations observed in this study cannot be estimated. Due to its presence in automotive fuel, propane is common in outdoor US air and public exposure occurs nationwide.

## n-Butane

n-Butane ("normal" butane) is a straight-chain hydrocarbon compound with the formula $C_4H_{10}$. It exists in the atmosphere as an odorless, colorless gas. It is used for fuel, for chemical production of solvents, rubber and plastics, and as a aerosol propellant in cigarette lighters (NJ Hazardous Substance Fact Sheet on n-Butane). The largest source of n-butane in ambient air is the combustion of automotive fuel.

Like the simpler alkanes discussed previously, n-butane is explosive in high concentrations. It can reduce the available amount of oxygen if its concentration builds up in confined spaces. Health effects are similar to other alkanes, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness, and death (NJ Hazardous Substance Fact Sheet on n-Butane). However, n-Butane also has irritant properties, and can cause narcotic effects on the central nervous system. These include irritability, hallucinations, and depression (Occupational Safety and Health Guideline for n-Butane). It is not known whether n-butane exposure can cause cancer. There is little research on whether n-butane affects reproduction or is linked to birth defects in children.

The EPA AIRS database lists n-butane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of n-butane at California locations typically ranged from 0.8 to 4.5 ppbv. For the year of CAMP results, the mean n-butane concentration was 4.28 ppbv, at the higher end of the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for n-butane. Thus the cancer and health effect risk from concentrations observed in this study cannot be estimated. Like the other alkanes, public exposure to n-butane in outdoor air occurs throughout the United States.

## Isobutane

Isobutane is an isomer of n-butane. It has the same number of carbon and hydrogen atoms as n-butane (formula $C_4H_{10}$), but they are arranged differently. While n-butane is a straight-chain hydrocarbon compound, isobutane is "branched", with some atoms at an angle to the main axis. Thus, the chemical properties of isobutane differ somewhat from those of n-butane. Isobutane exists in the atmosphere as an odorless, colorless gas. It is used for fuel, for chemical production of rubber , and as a aerosol propellant. It is also a refrigerant (NJ Hazardous Substance Fact Sheet on Isobutane). The largest source of isobutane in ambient air is the combustion of automotive fuel.

Like n-butane, isobutane is explosive in high concentrations. It can reduce the available amount of oxygen if its concentration builds up in confined spaces. Health effects are similar n-butane, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness, and death (NJ Hazardous Substance Fact Sheet on Isobutane). It also has irritant properties, and can cause narcotic effects on the central nervous system. Unlike n-butane, isobutane can affect the heart, causing an irregular beat. It is not known whether isobutane exposure can cause cancer. There is little research on whether it

affects reproduction or is linked to birth defects in children.

The EPA AIRS database lists isobutane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of isobutane at California locations typically ranged from 0.3 to 2.5 ppbv. For the year of CAMP results, the mean isobutane concentration was 1.92 ppbv, at the higher end of the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for isobutane. Thus the cancer and health effect risks from concentrations observed in downtown Denver cannot be estimated. Public exposure to isobutane in outdoor air occurs throughout the nation.

## n-Pentane

n-Pentane is a straight-chain hydrocarbon with the formula $C_5H_{12}$. n-Pentane exists in the atmosphere as a colorless gas. It is used as a fuel additive, for chemical production of paints, solvents, pesticides, paint removers, dye intermediates and insecticides. It is used as a blowing agent for foam, and in the production of synthetic rubber. n-Pentane is used as a laboratory solvent, and is present in lighter fluid. n-Pentane is used in the production of ice, as well (Occupational Health Guideline for Pentane). The largest source of n-pentane in ambient air is the combustion of automotive fuel.

Like other alkanes, pentane is explosive in high concentrations. It can reduce the available amount of oxygen in confined spaces. Health effects are similar to other alkanes, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness, and death (NJ Hazardous Substance Fact Sheet on n-Pentane). It also causes irritation of eyes, skin and lungs. It can cause narcotic effects on the central nervous system. Repeated exposures can damage nerves in the arms and legs, leading to numbness and weakness. It is not known whether n-pentane exposure can cause cancer. There is little research on whether it affects reproduction or is linked to birth defects in children.

The EPA AIRS database lists n-pentane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of n-pentane at California locations typically ranged from 0.4 to 2.8 ppbv. For the year of CAMP results, the mean n-pentane concentration was 3.15 ppbv, slightly above the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for n-pentane. Cancer and health effect risks from concentrations observed in downtown Denver cannot be estimated. Public exposure to n-pentane in outdoor air occurs in all urban areas.

## Isopentane

Isopentane is an isomer of n-pentane. It has the same number of carbon and hydrogen atoms as n-pentane (formula $C_5H_{12}$), but they are arranged differently. While n-pentane is a straight-chain hydro-carbon compound, isopentane is "branched", with some atoms at an angle to the main axis. Thus, the chemical properties of isopentane differ somewhat from those of n-pentane. Isopentane exists in the atmosphere as a colorless gas. It is used as a fuel additive, for chemical production of chlorinated compounds , and as a blowing agent for polystyrene. It is also a solvent (NJ Hazardous Substance Fact Sheet on Isopentane). The largest source of isopentane in ambient air is the combustion of automotive fuel.

Like n-pentane, isopentane is explosive in high concentrations. Health effects are similar to other alkanes, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness, and death (NJ Hazardous Substance Fact Sheet on Isopentane). It also causes irritation of eyes, skin and lungs. It can affect the heart, leading to an irregular beat (NIOSH International Chemical Safety Card for Isopentane). It is not known whether isopentane exposure is associated with cancer. There is little information on whether it affects reproduction or is connected to birth defects in children.

The EPA AIRS database lists isopentane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of isopentane at California locations typically ranged from 1 to 6 ppbv. For the year of CAMP results, the mean isopentane concentration was 5.52 ppbv, at the higher end of the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for isopentane. Cancer and health effect risks from concentrations observed in ambient air cannot be estimated. Public exposure to isopentane in outdoor air occurs in all areas with significant vehicular traffic.

## n-Hexane

n-Hexane is a straight-chain hydrocarbon with the formula $C_6H_{14}$. n-Hexane exists in the atmosphere as a colorless gas. It is a constituent of petroleum fuels. Its main use is in the food processing industry, for extracting vegetable oils from crops. It is also used as a solvent in the chemical laboratory. n-Hexane is present in glues such as "rubber cement", and in "white-out" fluid used to paint over typing errors. It is used in rubber manufacturing, and printers employ it as a cleaning solvent (ATSDR Toxicological Profile for n-Hexane). The largest source of n-hexane in ambient air is the combustion of automotive fuel.

Like other alkanes, n-hexane is explosive in high concentrations. Health effects are similar to n-pentane, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness, and death (NJ Hazardous Substance Fact Sheet on n-Hexane). It also causes irritation of eyes, skin and lungs. It can cause narcotic effects on the central nervous system. Repeated exposures can damage nerves in the arms and legs, leading to numbness and weakness. It is not known whether n-hexane exposure can cause cancer. There is little research on whether it affects reproduction, but exposed male rats showed damage to sperm-producing structures. Rats and mice exposed to high levels before birth showed reduced growth (CARB Fact Sheet on Hexane). There is insufficient research on whether n-hexane can cause birth defects in children.

The California Air Resources Board cites Environmental Protection Agency measurements indicating that 3.6 ppb is a typical level of n-hexane in urban air (CARB Fact Sheet on Hexane). For these Denver results, the annual mean was 1.2 ppb, a bit lower than the US average. However, this average is based on data collected from 1968 to 1987. Automotive air pollution emissions have decreased significantly in more recent years.

The Environmental Protection Agency has established a recommended "benchmark" non-cancer chronic value for n-hexane of 0.2 mg/m3 (57 ppb) in air. This reference concentration is described by EPA as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime." In other words, levels below 57 ppb are believed to keep one "safe" from health effects other than cancer, even over a life-long exposure. Yet this 57 ppb "safe" level estimate has an uncertainty factor of 10, indicating that health effects could occur at levels ten times lower (5.7 ppb). Thus, the highest concentration observed in this study, 3 ppb for a 24-hour period, is probably below any cause for concern. Cancer risks from concentrations observed in downtown Denver cannot be estimated. Public exposure to n-hexane in outdoor air occurs in all urban areas.

## 2-Methylpentane

2-Methylpentane is an isomer of hexane with the formula $C_6H_{14}$. 2-Methylpentane exists in the atmosphere as a colorless gas. It is a constituent of petroleum fuels. Search of the EPA site and other worldwide web resources did not yield information about the use of this compound. However, the largest source of 2-methylpentane in ambient air is the combustion of automotive fuel.

Like other alkanes, 2-methylpentane is explosive in high concentrations. Health effects are similar to n-pentane, in that exposure to concentrated amounts can cause headache, dizziness, light-headedness,

and death. It also causes irritation of eyes, skin and lungs. It can cause narcotic effects on the central nervous system (NIOSH Pocket Guide To Chemical Hazards Fact Sheet on 2-Methylpentane). It is not known whether exposure can cause cancer. There is little research on whether it affects reproduction. There is insufficient research on whether 2-methylpentane exposure can cause birth defects in children.

The EPA AIRS database lists 2-methylpentane data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of 2-methylpentane at California locations typically ranged from 1.2 to 1.7 ppbv. For the year of CAMP results, the mean 2-methylpentane concentration was 1.28 ppbv, within the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for this compound. Cancer and health effect risks from concentrations observed in ambient air cannot be estimated. Public exposure to 2-methylpentane in outdoor air occurs in all areas with significant vehicular traffic.

## Ethylene

Ethylene is a hydrocarbon compound with the formula $C_2H_4$. It exists in the atmosphere as an odorless, colorless gas. It is used for welding, for chemical production, and as a refrigerant. It is used to produce mustard gas and ethylene oxide (NJ Hazardous Substance Fact Sheet on Ethylene). The largest source of ethylene in ambient air is the combustion of automotive fuel.

Ethylene is explosive in high concentrations. It is also an asphyxiant, which can reduce the available amount of oxygen if its concentration builds up in confined spaces. Exposure to concentrated amounts can cause headache, dizziness, lightheadedness, and death (NJ Fact Sheet on Ethylene). It is believed that ethylene does not cause cancer. Ethylene has not been researched sufficiently to determine whether it affects reproduction or causes birth defects in children of exposed individuals.

The EPA AIRS database lists ethylene data collected in the state of California for the years 2001 and 2002. Annual mean concentrations of ethane at California locations typically ranged from 1 to 7 ppbv. For the year of CAMP results, the mean ethylene concentration was 5.41 ppbv, at the higher end of the California range.

The Environmental Protection Agency has not established any recommended "benchmark" value for ethylene. Thus the cancer and health effect risk from concentrations observed in this study cannot be estimated. Due to its formation from automotive fuel combustion, ethylene is common in outdoor US air and public exposure occurs nationwide.

## Health Implications – Speciated Non-Methane Organic Compounds

As part of its national air toxics analysis effort, EPA has developed recommended benchmark concentrations for various hazardous air pollutants. For each hazardous air pollutant the EPA has tried to develop an "acute" benchmark, as well as "chronic" and "cancer risk" benchmarks. The acute benchmark value represents a value that an individual may be exposed to for a short period of time, without risk of health effects. The period of time may vary for each pollutant, but for the purposes of the analysis here, one compares the highest twenty-four hour daily value observed over the year with the "acute" benchmark. The "chronic" and "cancer risk" benchmarks represent concentrations to which an individual may be exposed over a lifetime without a large risk of incurring health effects. For the purposes of the analysis here, one compares the annual mean to the "chronic" and "cancer risk" benchmarks.

The benchmarks for the hazardous air pollutants may be found in the following reference:

EPA Urban Air Toxics Web Site. Web Address: http://www.epa.gov/ttn/atw/toxsource/summary.html

Tables 4.7 and 4.8 summarize the EPA benchmarks available for speciated non-methane organic compounds. As seen from the tables, only a few of the compounds measured have benchmark values. These compounds have benchmarks for long-exposure period health effects (cancer and chronic), but "acute" benchmarks for 24 hour long periods have yet to be developed.

Table 4.7 compares the annual mean values of these compounds to the EPA " risk factor" for developing cancer. Columns two and three of Table 4.7 give the annual mean of the compound, as measured in parts per billion volume and then converted to micrograms per cubic meter (ug/m3). Column four of Table 4.7 gives the cancer risk associated with breathing 1 ug/m3 of the respective compound over a lifetime. Column five, Cancer Risk in Ambient Air, relates annual concentrations observed at the CAMP station to the risk of contracting cancer. EPA's goal is for the risk in column five to be 1 X 10-6 or less. Thus, only 1,3-butadiene and benzene exceed the risk goals.

Table 4.8 compares the annual mean values of these compounds to the EPA "Hazard Index" value for the risk of chronic (non-cancer) health effects. Column four, Non-cancer Chronic, of Table 4.8 gives the value at which EPA believes chronic health effects to the population will not occur. Column five is a ratio of the annual mean (column 3) to the Non-cancer chronic value in column four. EPA's goal is that this "Hazard Index" be less than 1.0. (That is, the annual concentration should be less than the Non-cancer chronic value for the pollutant). For all compounds with "benchmarks" the risk is well below 1.0. However, it should be noted that "benchmark" values are not available for most of the SNMOCs measured.

**Table 4.7 - Annual Mean Versus Cancer Risk for SNMOCs**

| Annual Mean Versus Cancer Risk | | | | |
|---|---|---|---|---|
| **Compound** | **Annual Mean ppbv** | **Annual Mean ug/m3** | **Cancer Risk Per ug/m3 (1/ug/m3)** | **Cancer Risk In Ambient Air** |
| | | | | |
| **1,3-Butadiene** | **0.18** | **0.40** | **0.00003** | **1.19E-05** |
| **Benzene** | **1.00** | **3.19** | **0.0000078** | **2.49E-05** |
| **Toluene** | **1.85** | **6.97** | **No Factor** | |
| **Ethyl Benzene** | **0.26** | **1.13** | **No Factor** | |
| **M-Xylene/P-Xylene** | **0.83** | **3.60** | **No Factor** | |
| **Styrene** | **0.18** | **0.77** | **No Factor** | |
| **0-Xylene** | **0.33** | **1.43** | **No Factor** | |
| **n-Hexane** | **1.18** | **4.16** | **No Factor** | |

**Table 4.8 - Annual Mean Versus Non-Cancer Chronic Risk for SNMOCs**

| Annual Mean Versus Non-Cancer Chronic Risk | | | | |
|---|---|---|---|---|
| **Compound** | **Annual Mean ppbv** | **Annual Mean ug/m3** | **Noncancer Chronic ug/m3** | **Noncancer Chronic Hazard Index** |
| | | | | |
| **1,3-Butadiene** | **0.18** | **0.40** | **2** | **0.199** |
| **Benzene** | **1.00** | **3.19** | **30** | **0.106** |
| **Toluene** | **1.85** | **6.97** | **400** | **0.017** |
| **Ethyl Benzene** | **0.26** | **1.13** | **1000** | **0.001** |
| **M-Xylene/P-Xylene** | **0.83** | **3.60** | **100** | **0.041** |
| **Styrene** | **0.18** | **0.77** | **1000** | **0.001** |
| **0-Xylene** | **0.33** | **1.43** | **100** | **0.019** |
| **n-Hexane** | **1.18** | **4.16** | **200** | **0.021** |

## References for Speciated Non-Methane Organic Compounds


***Agency For Toxic Substances and Disease Registry.*** (ATSDR) "Toxicological Profiles" for Various Compounds. Web Address: http://www.atsdr.cdc.gov/toxprofiles/

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***California Air Resources Board.*** (CARB)
Web Address: http://www.arb.ca.gov/toxics/cattable.htm

Hexane, dated September 1997.

***United States Environmental Protection Agency.*** (EPA) Integrated Risk Information System. Toxicological Reviews Of Various Substances.
Web Address: **http://www.epa.gov/iris/toxreviews/index.html**

***United States Environmental Protection Agency. (EPA).*** Technology Transfer Network Air Toxics Website. "Dose-Response Assessment for Assessing Health Risks Associated With Exposure To Hazardous Air Pollutants", Table 1, December 2, 2002.
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***United States Environmental Protection Agency***. (EPA). Technology Transfer Network Air Toxics Website. Health Effects Worksheets for Various Substances.
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***National Institute for Occupational Safety and Health.*** (NIOSH) International Chemical Safety Cards.

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Propane. Dated 1999. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng0319.html

Butane. Dated 1998. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng0232.html

Pentane. Dated 2000. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng0534.html

Isopentane. Dated 2002. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng1153.html

n-Hexane. Dated 2000. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng0279.html

2-Methylpentane. Dated 2002. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng1262.html

Ethylene. Dated 1998. Web Address: http://www.cdc.gov/niosh/ipcsneng/neng0475.html

***National Institute for Occupational Safety and Health.*** (NIOSH) Occupational Safety and Health Guideline for n-Butane. Dated 1992. Web Address: http://www.cdc.gov/niosh/pdfs/0068.pdf

***National Institute for Occupational Safety and Health.*** (NIOSH) Occupational Health Guideline for Pentane. Dated September 1978. Web Address: http://www.cdc.gov/niosh/pdfs/0486.pdf

***National Institute for Occupational Safety and Health.*** (NIOSH) Pocket Guide to Chemical Hazards.

Propane. Web Address: http://www.cdc.gov/niosh/npg/npgd0524.html
n-Butane. Web Address: http://www.cdc.gov/niosh/npg/npgd0068.html
Isobutane. Web Address: http://www.cdc.gov/niosh/npg/npgd0350.html
n-Pentane. Web Address: http://www.cdc.gov/niosh/npg/npgd0486.html
n-Hexane. Web Address: http://www.cdc.gov/niosh/npg/npgd0322.html
Hexane Isomers (Excluding n-Hexane).
Web Address: http://www.cdc.gov/niosh/npg/npgd0323.html

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Web Address: http://www.cdc.gov/niosh/rtecs/kh39fbc0.html

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Butane, dated July 2000.
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Pentane, dated July 2000.
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Web Address: http://www.cdc.gov/niosh/rtecs/mn8d8678.html

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***New Jersey Department of Health and Senior Services.*** "Hazardous Substance Fact Sheets" for Various Substances. Web Address:
**http://www.state.nj.us/health/eoh/rtkweb/rtkhsfs.htm**

Ethane, dated January 1997.
Propane, dated January 1997.
Butane, dated August 1998.
Isobutane, dated March 1999.
Pentane, dated February 2000.
Isopentane, dated June 1999.
n-Hexane, dated April 1997.
Ethylene, dated June 1996.

***Occupational Safety and Health Administration.*** (OSHA) "Chemical Sampling Information" for Various Substances. Web Address:
http://www.osha.gov/dts/chemicalsampling/toc

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n-Butane, dated August 1993.

***Occupational Safety and Health Administration.*** (OSHA) "OSHA Comments from the January 19, 1989 Final Rule on Air Contaminants Project". (Rule remanded by court and not currently in force).

n-Hexane. Web Address: http://www.cdc.gov/niosh/pel88/110-54.html

# Section 5 - Conclusion

# Conclusion

This report analyzes one year of urban air toxics data taken at the CAMP station in downtown Denver, Colorado from October 2000 to September 2001. Carbonyls, volatile organic compounds, and speciated non-methane organic compounds were all sampled. For carbonyls, twelve compounds were sampled. Formaldehyde, acetone, and acetaldehyde were the most prevalent. The other nine compounds occurred at levels at least one order of magnitude below the top three. Average levels observed during weekdays were greater than the weekend average concentrations. The top eight aldehydes trended together. All compounds except isovaleraldehyde showed strong correlation to formaldehyde. Isovaleraldehyde and 2,5-dimethylbenzaldehyde were detected in fewer than 35% of the samples. The other carbonyls were all detected in 90% of the samples. Only formaldehyde and acetaldehyde have EPA toxicity "benchmarks", but both these compounds were above their cancer risk benchmarks, indicating cancer risk from these compounds to be greater than one-in-a-million. Formaldehyde risk is about 100 times above the EPA-recommended level. Acetaldehyde risk is about 10 times the EPA-recommended level. Formaldehyde and acetaldehyde were below their EPA benchmarks for chronic health effects, suggesting that non-cancer risks from these compounds are not a concern. The carbonyl method had good repeatability, as shown by duplicate and replicate samples analyzed.

Fifty-eight volatile organic compounds (VOCs) were analyzed from sample canisters. Twenty-nine of these VOCs were never measured at detectable levels. In contrast, nineteen other VOCs were present in Denver air, at measurable levels, in over 90% of the samples. Average levels observed during weekdays were greater than the weekend average concentrations. Statistical correlations between concentrations of individual compounds were not that strong, but acetylene and propylene showed the strongest correlations to other compounds. Thirty-seven of the compounds measured had estimated EPA "benchmark" concentrations. 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene occur at levels believed to represent a greater than one-in-a-million risk of cancer. The single measurable value of acrylonitrile would be above the EPA one-in-a million guideline, if it occurred as an annual mean. None of the compounds had levels greater than the EPA "benchmarks" for non-cancer chronic health risk. The VOC method had good repeatability, as shown by duplicate and replicate samples analyzed.

Seventy-eight speciated non-methane organic compounds (SNMOCs) were analyzed from sample canisters. Sixty-two of the compounds were present in Denver air, at measurable levels, in over 90% of the samples. Six of the compounds were never measured at detectable levels. In general, the average weekday concentration was greater than the average weekend concentration, but some compounds were exceptions to this rule. In contrast to the VOCs, statistical correlations of individual compounds were strong. Only eight of the SNMOCs had EPA-recommended toxicity "benchmarks". Seven of these were among the compounds that were also measured by the VOC method. As with the VOC compounds, 1,3-butadiene and benzene occur at levels believed to represent a greater than one-in-a-million risk of cancer. All eight of these compounds were well below the EPA non-cancer risk "benchmarks". The SNMOC method had good repeatability, as shown by duplicate and replicate samples analyzed. A side-by-side analysis of twelve compounds measured from the same canisters by both the VOC and SNMOC laboratory methods showed that the two analytical techniques yield consistent results.

The majority of the compounds detected in Denver air can be related to automobile emissions. The strong inter-correlations between the carbonyl compounds suggest a common source. The SNMOC compounds were also strongly inter-correlated. Many of the compounds measured do not have EPA-recommended toxicity "benchmarks". Of those that do, formaldehyde, acetaldehyde, 1,3-butadiene, benzene, carbon tetrachloride, tetrachloroethylene, and p-dichlorobenzene are present in Denver air at levels that may create health concerns.