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TECHNICAL MEMORANDUM

To: The NETAC Technical Advisory Committee
From: Susan Kemball-Cook, Piti Piyachaturawat and Greg Yarwood
Date: October 23, 2007
Subject: Analysis of VOC Measurements at Longview CAMS 19 During 2006

Introduction

At the end of 2007 ozone season, the 8-hour ozone design value at the Longview Continuous Air Monitoring Station (CAMS 19) is expected to be 84 ppb, which is just in compliance with the 8-hour National Ambient Air Quality Standard. It is important to understand the mechanisms of ozone formation leading to exceedances at the Longview monitor. Ozone is formed by chemical reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC) in the presence of sunlight. Previous NETAC studies (Stoeckenius and Yarwood, 2004) have shown NO_x control to be the most effective strategy for reducing local ozone production because biogenic VOCs are abundant in Northeast Texas and are not controllable. Nevertheless, identifying the composition of VOCs present at Longview can suggest possible origins of these ozone precursors and improve our conceptual understanding of ozone formation in Northeast Texas. During the summer of 2006, VOC canister samples were collected at the CAMS 19 site near Longview. In this technical memorandum, we present an analysis of the VOC data set derived from these samples.

Data

During August and September of 2006, VOC monitoring was conducted in Northeast Texas at the CAMS 19 site operated by the Texas Commission on Environmental Quality and located at Gregg County Airport. A total of 38 air samples were collected over 2-hour periods on 8 separate days at the CAMS 19 site by Air Quality Solutions, Inc. (AQSI). Samples were sent to Analysis Inc. in Austin to be analyzed for VOC composition. The general procedures outlined in the "Compendium Method TO-14A Determination Of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography" (USEPA, 1999) were followed during this analysis.

Data collection was focused on high ozone days. 34 out of the 38 samples were taken on seven Ozone Action Days, which are days when ozone concentrations close to or exceeding the NAAQS were forecast to occur in the Longview area. Although high 1-hour ozone concentrations were measured on several of the sampling days, August 17 was the only day on

which the CAMS 19 monitor recorded an exceedance of the 8-hour ozone standard. A summary of the sampling periods and daily high 1-hour ozone concentrations is given in Table 1. Samples were taken at different times during each day in order to resolve the diurnal variation of VOCs.

Table 1. Sampling days and times for VOC analysis of samples collected at Longview (CAMS 19) during Summer, 2006. Table 5 of AQSI (2006).

| Sampling Date | Sampling Periods | Ozone Action Day | Maximum Daily 1-Hour Average Ozone at CAMS 19 (ppb) |
|---------------------|--|------------------|---|
| 8/16/2006 Wednesday | 3-5pm, 5-7pm, 7-9pm | yes | 76 |
| 8/17/2006 Thursday | 1-3pm, 5-7pm | yes | 103 |
| 8/18/2006 Friday | 7-9am, 9-11am, 1-3pm, 3-5pm, 5-7pm, 7-9pm | yes | 81 |
| 8/24/2006 Thursday | 12-2pm, 2-4pm, 6-8pm, 8-10pm | no | 94 |
| 9/01/2006 Friday | 7-9am, 9-11am, 1-3pm, 3-5pm, 5-7pm | yes | 100 |
| 9/02/2006 Saturday | 7-9am, 9-11am, 11am-1pm, 1-3pm 3-5pm, 5-7pm, 7-9pm | yes | 80 |
| 9/09/2006 Saturday | 7-9am, 9-11am, 11am-1pm, 1-3pm 3-5pm, 5-7pm, 7-9pm | yes | 86 |
| 9/14/2006 Thursday | 7-9am, 9-11am, 11am-1pm, 1-3pm | yes | 79 |

Results

Analysis of VOC Concentrations

The VOC data from each day were analyzed to determine which VOC species appeared most frequently at CAMS 19 and which species had the highest concentrations. Table 2 shows a summary of the 38 VOC samples taken at CAMS 19 during the summer of 2006. The most frequently detected VOCs were alkanes. Also detected frequently were benzene, isoprene, propylene, and toluene. Ethylene does not appear in Table 2 because it was reported as zero in every sample which is unlikely and suggests some problem in the analysis for ethylene. Isoprene is primarily biogenic in origin, and is an important component of the emission inventory in Northeast Texas.

Table 2. Most commonly occurring VOCs in 38 samples collected at Longview (CAMS 19) on 8 days between 8/16/2006 and 9/14/2006.

| Compound Name | Maximum Concentration (ppbC) | All Samples | | | Samples when Compound was among Top Five | |
|-----------------|------------------------------|-------------|-------------------|---------------|--|-------------------|
| | | Frequency | Avg. Conc. (ppbC) | Median (ppbC) | Frequency | Avg. Conc. (ppbC) |
| ethane | 122 | 38 | 41.6 | 27.9 | 38 | 41.6 |
| propane | 73.1 | 38 | 21.9 | 14.6 | 38 | 21.9 |
| n-butane | 60.6 | 38 | 11.1 | 6.93 | 37 | 11.3 |
| isobutane | 28.9 | 38 | 8.84 | 5.64 | 32 | 10.0 |
| isopentane | 23.6 | 33 | 5.72 | 2.19 | 18 | 9.63 |
| isoprene | 4.18 | 36 | 1.61 | 1.32 | 12 | 2.82 |
| benzene | 13.1 | 38 | 5.04 | 2.41 | 5 | 7.37 |
| n-pentane | 8.08 | 37 | 3.70 | 2.63 | 3 | 5.60 |
| propylene | 2.84 | 38 | 0.669 | 0.317 | 3 | 2.00 |
| 2-methylpentane | 0.960 | 38 | 3.57 | 1.90 | 2 | 0.738 |
| toluene | 15.4 | 38 | 4.23 | 1.45 | 2 | 12.6 |

Because alkanes were the most frequently detected compounds, time series of alkane concentrations were plotted to determine whether the alkane concentrations were correlated with one another. These time series are shown in Figure 1, and suggest that the alkanes do vary together. To quantify the relationship among the alkane concentration time series, a regression analysis was performed. Figure 2 shows the correlation between the concentrations of ethane and n-butane with propane. In Figure 2, each point represents one sample. The points approximate a straight line, and there is an excellent correlation between ethane and propane (0.97) and between n-butane and propane (0.99). Similar results were obtained for other alkanes (e.g. pentane, hexane) detected at CAMS 19. The fact that the alkanes are so well-correlated implies a common source. Light alkanes such as ethane, propane, and n-butane are constituents of natural gas, strongly suggesting that natural gas production is the source of these alkanes, as reported previously by Katzenstein et al., (2003).

Comparison with Katzenstein et al. (2003) VOC Data

We now compare VOC data from CAMS 19 with concentrations measured in an observational study of hydrocarbon pollution in Texas and surrounding states (Katzenstein et al., 2003). Katzenstein et al. sampled surface level air in a gridded pattern across Texas, Oklahoma, Louisiana, Arkansas, Missouri, Kansas, New Mexico as well as in parts of Colorado, Mississippi and Arizona during September, 2001 and April-May, 2002. They analyzed the air samples for non-methane hydrocarbons, and found enhanced levels of light alkanes associated with natural gas production throughout the region. They found a good correlation between locations of enhanced alkane concentrations and locations of natural gas production and identified Northeast Texas as a “hot spot” for air concentrations of light alkanes. Katzenstein et al. (2003) calculated regional averages of concentrations of light alkanes, and we compare their ratios of ethane/propane and n-butane/propane concentrations with those measured at Longview (Table 3).

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The ratios measured at Longview are within ~30% of the Katzenstein et al. (2003) values for ethane/propane, and within ~20% for n-butane/propane. Katzenstein et al. (2003) report correlation coefficients of 0.91 for ethane and propane concentrations and 0.84 for ethane and n-butane concentrations; the corresponding values for the Longview VOC data are 0.97 and 0.98, respectively. Because the Katzenstein et al. (2003) values are regional averages, we do not expect exact correspondence with the values measured at Longview, but the reasonable agreement provides a measure of confidence in the VOC data measured at CAMS 19 and lends support to the hypothesis that natural gas is the primary source of alkanes measured at Longview.

Table 3. Ratios of the average concentrations of ethane, n-butane, and propane in 38 samples collected at Longview and 346 samples collected at rural locations in the southwestern U.S. by Katzenstein et al. (2003).

| Species Ratio | Longview CAMS 19 (This study) | Texas and Surrounding States (Katzenstein et al., 2003) |
|------------------|----------------------------------|--|
| ethane/propane | 1.8 | 1.2 |
| n-butane/propane | 0.45 | 0.54 |

Importance of Several VOC Categories

VOC species were categorized into four main categories: (1) natural gas (i.e. alkanes with less than 8 carbon atoms), (2) highly reactive VOCs (excluding biogenics) (3) biogenic species, and (4) other species. For each sample taken during August-September 2006, the total VOC concentration was plotted along with the breakdown into the 4 groups described above. Figure 3 shows the VOC concentration time series, and indicates on each bar the percentage of the sample total comprised by the natural gas constituents.

Figure 3 shows that VOC species associated with natural gas production are the most abundant type of VOC measured at CAMS 19 during this time period. The total concentrations of the species in the natural gas group represent the bulk of the measured VOC concentrations in each sample (> 60% of the total concentration averaged over all samples). HRVOC species and biogenic species contribute significantly less in terms of the total VOC concentration in these samples. However, biogenic VOCs and HRVOCs have a much greater potential to cause ozone formation than do the alkanes.

Ozone Forming Potential

VOCs have differing tendencies to form ozone. For example, two of the frequently detected VOCs identified in Table 2 (isoprene and propylene) are so-called “highly-reactive VOCs” (HRVOCs) because they have a strong tendency to form ozone quickly. Carter (1994) developed a ranking system for ozone forming potential of VOCs called the maximum incremental reactivity (MIR) scale. We used the MIR scale to compare the ozone forming potential of VOCs detected at Longview.

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The VOC concentrations shown in Figure 3 are multiplied by their respective MIR weighting factors in Figures 4 and 5 which show ozone forming potential. The ozone potential is an estimate of the maximum ozone that the VOCs might form under “ideal” conditions. Figures 4 and 5 display the same information; the only difference between them is that Figure 4 displays time on the horizontal axis, consistent with Figure 3, while in Figure 5, the samples are arranged according to time of day, with morning hours on the left and evening hours on the right.

Figures 4 and 5 show that while alkanes consistent with the signature of natural gas were present at Longview throughout the sampling period, their ozone forming potential and their contribution to the total sample ozone forming potential vary greatly. The ozone forming potential of the natural gas VOC component is at a maximum in the morning, and diminishes as the day goes on. This is due to the daily rise of the mixed layer as the earth’s surface heats up. As the surface heats up, the depth of the mixed layer increases, and pollutants are diluted through a greater depth of the atmosphere; this reduces their concentration. This diurnal cycle in the alkane concentrations is also apparent in Figure 1. The ozone forming potential for the Other VOC category is also greater at night than during the day.

The biogenic VOC isoprene has high ozone forming potential and makes up a larger fraction of the sample total ozone forming potential later in the day. This is because biogenic emissions increase with sunlight and increasing temperature. The biogenic contribution is generally the least important of the four categories in the early morning samples. The air samples collected at CAMS 19 for this study will tend to under-represent the regional contribution of biogenic emissions because (1) CAMS 19 is located on an airfield that is cleared of trees, and (2) many of these air samples were collected in the morning.

The influence of the HRVOCs was variable. Note that the contribution of HRVOCs is likely under-represented in these data because the method systematically failed to detect ethylene which is expected to be the most common HRVOC. There is no clear diurnal cycle in HRVOC contribution contrary to biogenics and alkanes. Some HRVOCs are always present at Longview and, although their absolute concentrations were relatively small (Figure 3), their occasional importance in ozone formation is made clear in Figures 4 and 5. For example, in the 1700-1900 sample taken on August 16, HRVOCs make up less than 5% of the total VOC concentration but account for 48% of the ozone forming potential. Given the variability in HRVOC ozone potential shown in Figures 4 and 5, and the episodic nature of this emissions category, it seems likely that the intermittent sampling performed in this study may not fully characterize the impact of HRVOCs.

Average incremental reactivity (MIR) factors were calculated for each VOC category as shown in Table 4. The average MIR for each category approximates its tendency to form ozone. Natural gas is the largest contributor to the average VOC concentration as well as the ozone forming potential, despite having the lowest incremental reactivity (0.38). The Other VOC category also had a low incremental reactivity (0.81) and was comparable to HRVOCs and biogenics in terms of its ozone forming potential. The incremental reactivities of the HRVOC and biogenic

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categories were several times higher than those of natural gas and Other VOCs so that, although their concentrations were low, their ozone forming potential was comparable to that of the Other VOCs.

Table 4. Average incremental reactivity (MIR) factors for VOC categories at CAMS 19.

| | Natural Gas | HRVOCs | Biogenic | Other VOC |
|-------------------------------|--------------------|---------------|-----------------|------------------|
| Average VOC (ppbC) | 113 | 2.32 | 1.61 | 11.4 |
| Average potential ozone (ppb) | 43.2 | 11.9 | 7.44 | 9.25 |
| Average MIR factor (ppb/ppbC) | 0.38 | 5.1 | 4.6 | 0.81 |

Conclusions

VOC samples collected at CAMS 19 in August-September, 2006 have been analyzed to identify what categories of VOCs are present and their potentials to form ozone. It is important to remember that other NETAC studies (Stoeckenius and Yarwood, 2004) have shown that local ozone production in Northeast Texas is limited by the availability of NO_x. The simple “ozone forming potentials” calculated above will not be realized in the atmosphere when there is insufficient NO_x to support ozone formation. The results of this analysis of VOC data do not necessarily point to effective ozone control strategies.

Light alkanes (with less than 8 carbon atoms) consistent with composition of natural gas are the most frequently detected VOCs at Longview. They are present in all samples, and the individual VOC species are well-correlated, suggesting a common source such as oil and gas production. VOC species associated with oil and gas production have low tendency to form ozone, but they are a constant presence at CAMS 19, and their concentrations are large enough that they could make a significant contribution to ozone formation.

The contribution of biogenic emissions to ozone forming potential was relatively small at CAMS 19, but the airfield monitoring site likely under-represents the regional contribution of biogenic emissions in Northeast Texas, which is heavily wooded. The biogenic contribution to potential ozone reaches a maximum in the afternoon because of warm temperatures and sunlight. Biogenic emissions are highly reactive and have a strong tendency to form ozone when they are present.

The influence of highly reactive anthropogenic VOCs (HRVOCs) is variable, as shown by Figure 4. HRVOC emissions have a strong tendency to form ozone when they are present. The major source of HRVOCs near CAMS19 is expected to be the Eastman complex (owned by Eastman, Westlake and Flint Hills) whose influence on CAMS 19 depends on the wind direction and HRVOC emission rates. It is possible that the limited sampling performed in this study may not fully characterize the impact of HRVOCs at CAMS 19. In addition, this data set under-represents the importance of HRVOCs because ethylene was not detected by the analysis method.

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Future Work

During the months of August and September, 2007, near-continuous VOC monitoring was performed at CAMS 19 using a new technology. VOCs were analyzed using photo-acoustic spectroscopy (PAS) every 5-10 minutes, 24 hours a day, providing a nearly continuous record of non-methane hydrocarbon concentrations speciated to several broad classes. This data will be analyzed to assess the variability of highly reactive VOCs at Longview, and will be compared with the 2006 data set.

References

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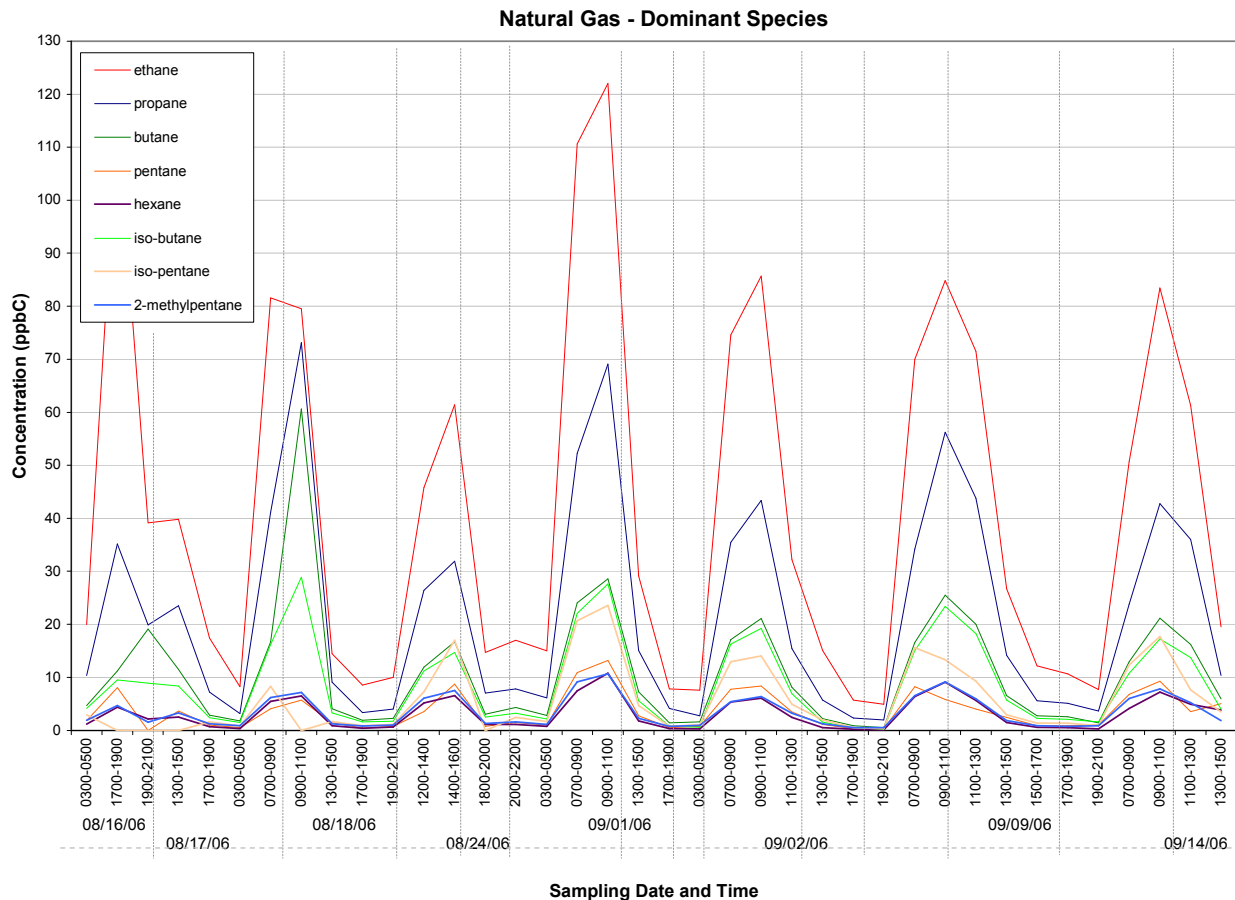


Figure 1. Time series of species that are the dominant components of natural gas from VOC samples collected at Longview (CAMS 19) during August-September, 2006.



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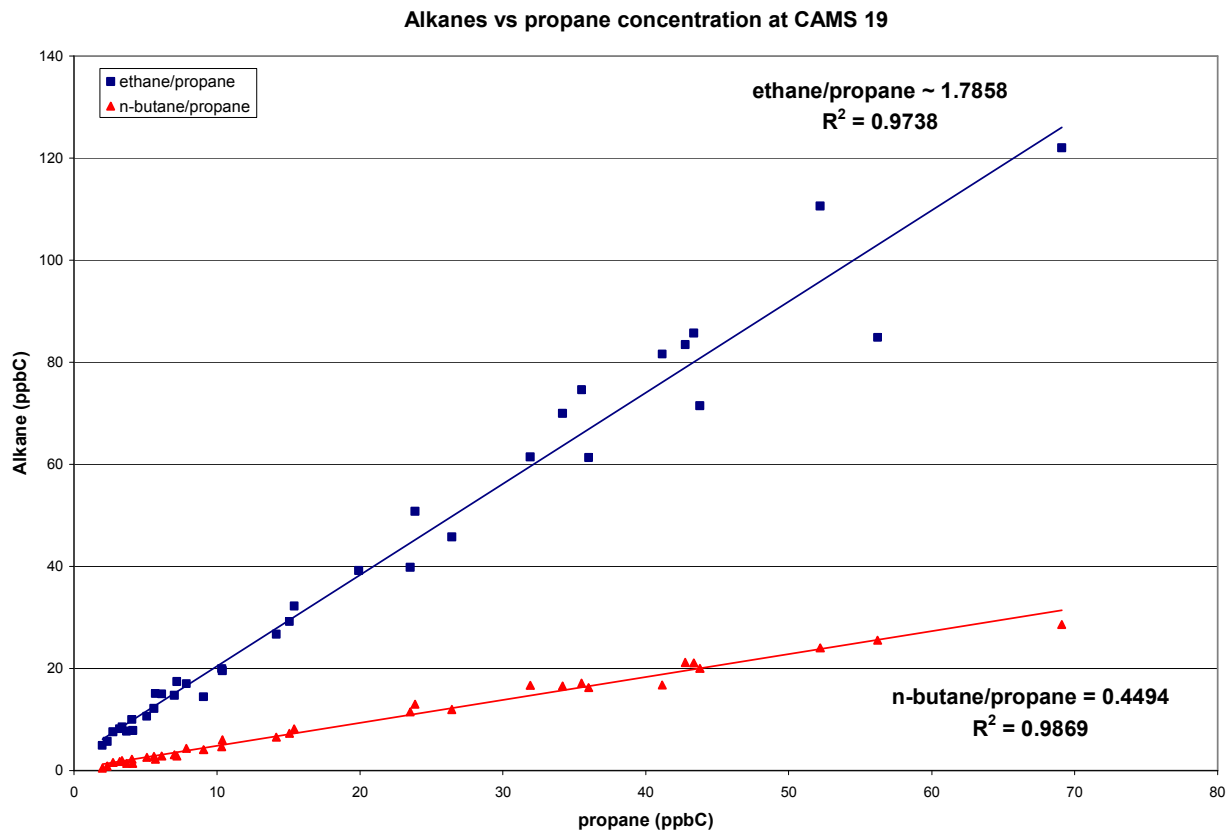


Figure 2. Ratio of ethane/propane and n-butane/propane from VOC samples collected at Longview (CAMS 19) during August-September, 2006.

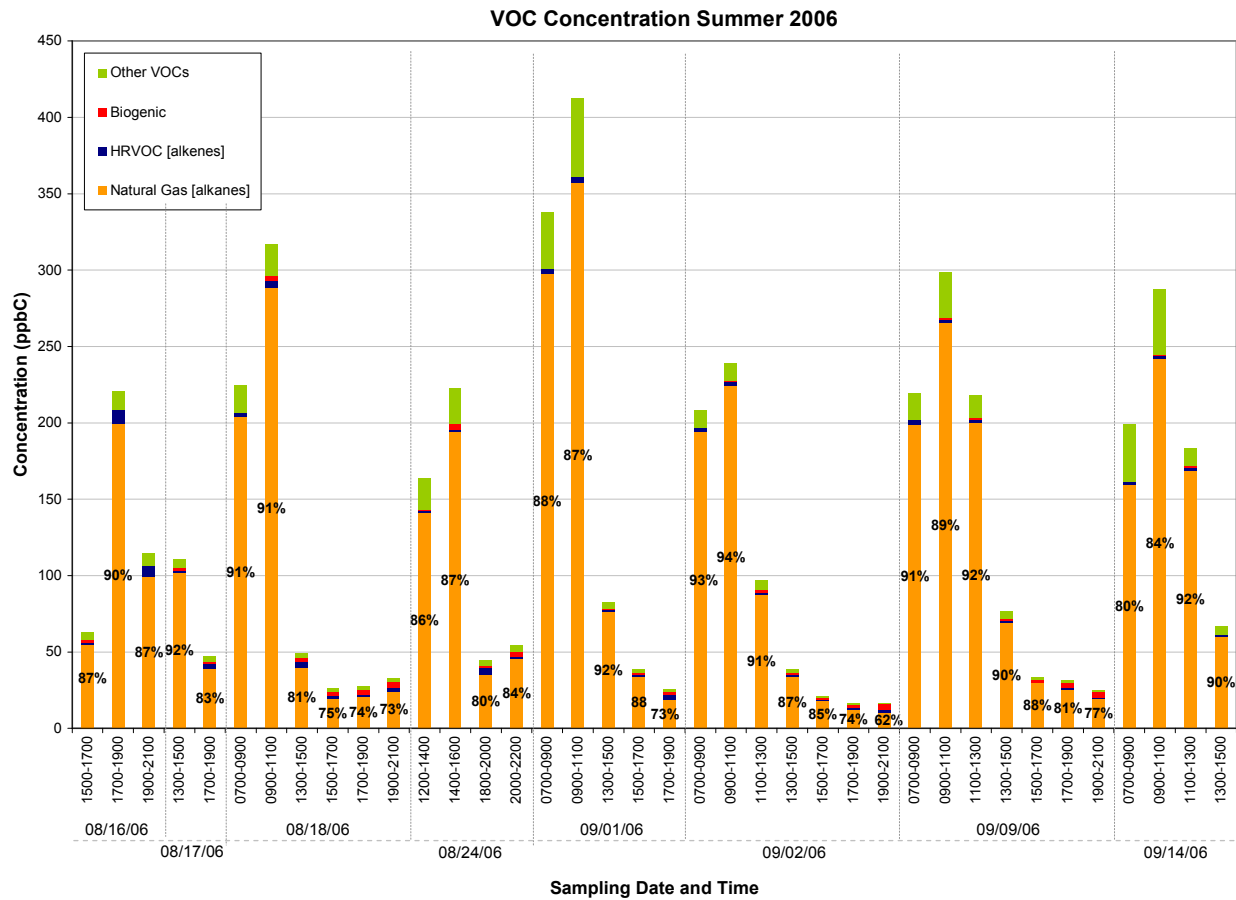


Figure 3. Total VOC concentration of VOC species in each category from samples collected at Longview (CAMS 19) during August-September, 2006. Percentages show contribution to total concentration from constituents of natural gas.



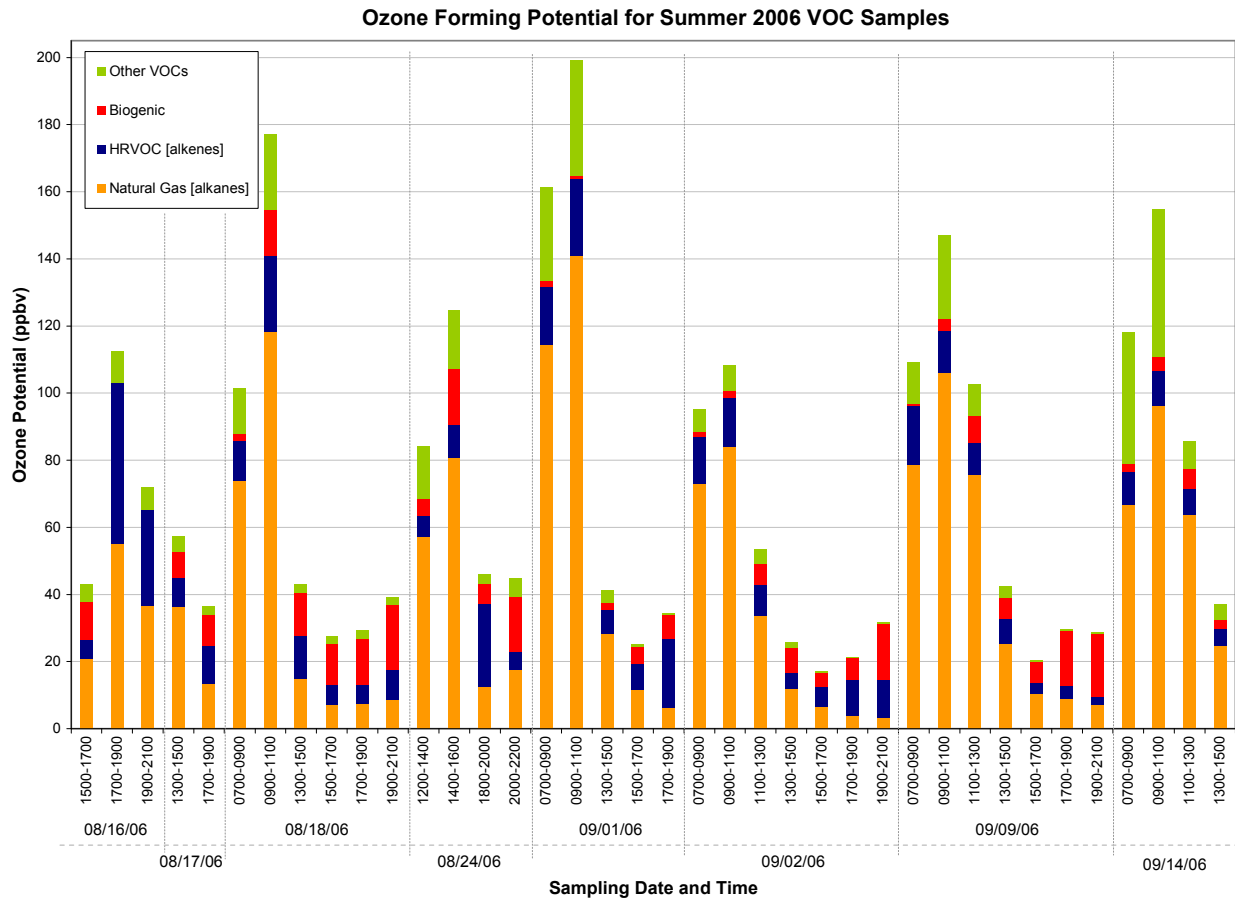


Figure 4. Ozone formation potential of VOC species of each group for samples collected at Longview (CAMS 19) during Summer 2006.

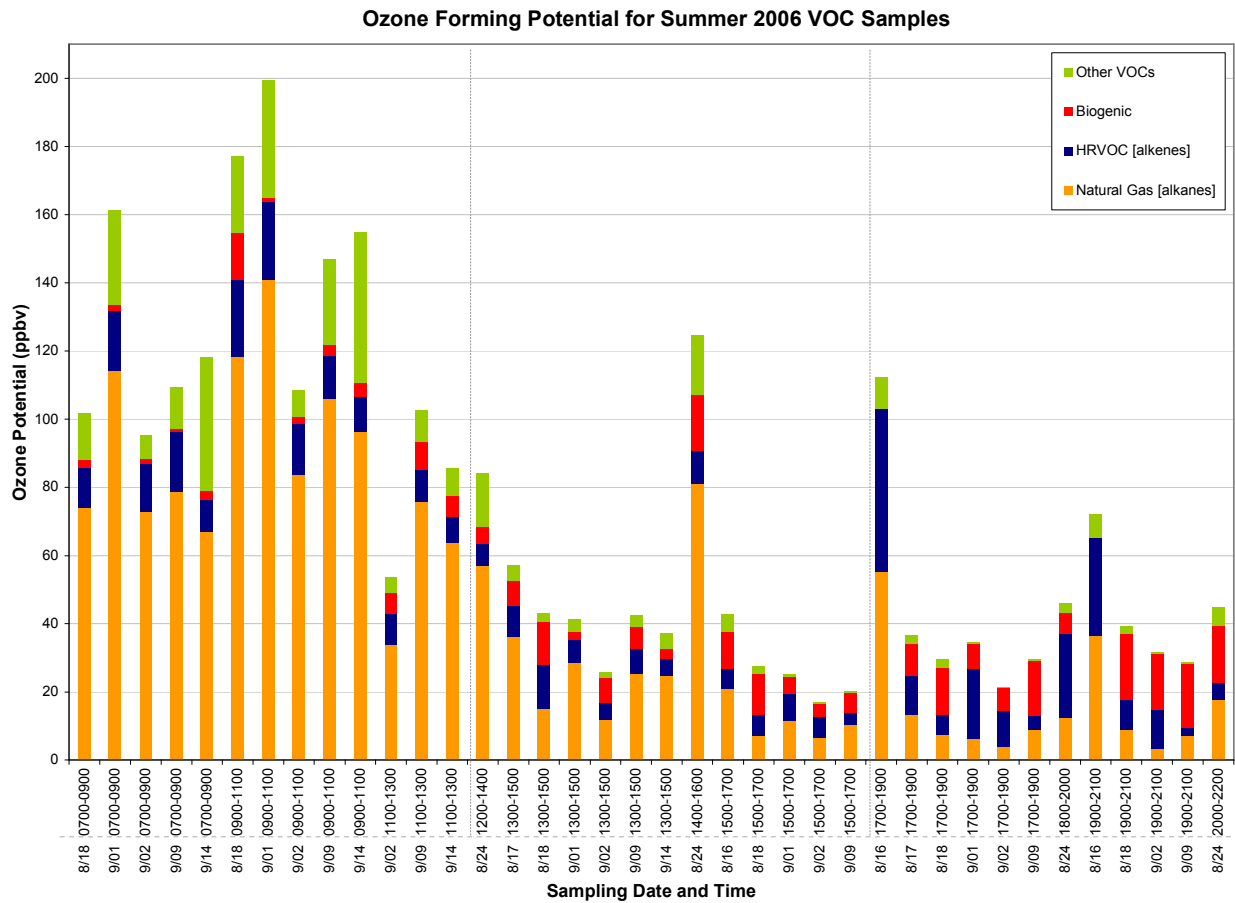


Figure 5. As in Figure 4, except that the samples are arranged by time of day, with morning samples on the left, afternoon samples in the middle and evening samples on the right.