

# Hourly Measurements of VOCs by AutoGC at the New Hendersonville, TN Southern Oxidants Study Site - June 17-27, 1995

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At The New Hendersonville, TN Southern Oxidants Study Site  
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## INTRODUCTION

The North American Research Strategy for Tropospheric Ozone (NARSTO) program has sponsored the development of advanced measurement tools for monitoring organic atmospheric compounds related to the formation of tropospheric ozone. Some of these compounds are known to be emitted from anthropogenic sources, others originate from biogenic sources, and some are created by reactions in the ambient air. Many compounds are reactive so that the transport and conditioning of the air sample must be undertaken with care to avoid loss of sample integrity. New autoGC instrumentation was demonstrated over a ten day period as part of the NARSTO contribution to the summer 1995 Southern Oxidants Study (SOS) at the New Hendersonville, TN site, northeast of Nashville. This was a rural site although within a mile of a major highway and close to residential subdivisions. The site was approximately 15 miles from downtown Nashville. This presentation documents the capabilities of the new autoGC by showing some of the interesting compound variations that were observed when monitoring with hourly updates.

## EXPERIMENTAL

The autoGC system was comprised of a XonTech Model 930 sample concentrator, a XonTech Model 940 cryogenic concentrator, and a Varian STAR 3700 GC with a Saturn II ion trap. The reader is referred to the companion presentation by Daughtrey et al.<sup>1</sup> for details of the system and its operational characteristics. The system is designed to reduce the water content of air samples while retaining water-soluble compounds. This is done in three ways, first during sample concentration onto a multisorbent packing when approximately 2/3 of the water vapor breaks through the packing and then during a dry purge of the packing with He when another 50% of the water vapor is lost. Finally the sample is split during transfer to the GC column so that only 20% is analyzed. The total reduction in water is estimated as greater than 90%.

At the New Hendersonville site, sample air was channeled at a rapid rate through large diameter tubing from the top of a 30m tower. A heated secondary tubing was used to route air from the tower tube to a heated manifold equipped with a sample port leading past the inlet to the sample concentrator. A second ten day study was performed near the EPA facility in the Research Triangle Park, NC using the same secondary tubing (heated) but elevated only approximately 10 m above the ground. Some of the interesting types of observations made in the Nashville field study were made again.

## RESULTS AND DISCUSSION

As expected, the extent of diurnal variations from different compounds depended on wind direction. Generally rural areas to the north contributed a higher biogenic mixture at the site than did the area to the south and southwest in the direction of Nashville. Significant differences in concentration levels for trace VOCs were found in the Research Triangle Park, NC as compared to the New Hendersonville, TN site.

### **Isoprene, Alpha and Beta Pinene**

Some typical diurnal variations obtained for compounds generally identified as biogenic emissions were seen at the New Hendersonville site as shown in the Figures 1a&b. Figure 1a shows the typical diurnal variation of the compound isoprene over the ten day study period. The estimates of concentration are based on a calibration using a reference standard obtained from Alphagaz (Walnut Creek, CA). The patterns are well defined as repetitive, systematically varying changes with one dominant concentration peak per day occurring in the time span between noon and early evening. Similar patterns have been noted in Atlanta, Georgia<sup>2</sup>, although the peak concentrations are much more pronounced in the data from New Hendersonville. Figure 1b shows the diurnal patterns of alpha pinene, indicating a pattern of concentration that generally peaks at the same time as isoprene. Concentration levels are based on calibrations made by dynamic dilution of a 10 ppmv standard gas mix from Alphagaz. When alpha pinene is plotted versus beta pinene, as in Figure 2a, the two are shown to be linearly related, a fact that suggests that the two are driven by the same mechanism. When this experiment was repeated at the Research Triangle Park, NC, the same linear relationship was noted between the two compounds although a factor of forty increase in average concentrations was noted. This may be the result of emissions from the different types of trees in the Research Triangle as compared to Nashville. Nashville has primarily deciduous trees while the Research Triangle Park is dominated by varieties of southern pine.

### **Higher Aldehydes**

Throughout this study and in other studies in rural Alabama near Mobile and at a site in the semi-rural environment of the Research Triangle Park, NC, a number of higher molecular weight aldehydes are present and often dominate in chromatograms of samples from the ambient air. As an example of this, Figure 1c shows the apparent pronounced diurnal variations of decanal at the New Hendersonville site, with a peak in concentration at noon (central daylight saving time). Similar variations were observed for nonanal and lower molecular weight aldehydes. The variations are superimposed on what appears to be a monotonically decreasing background concentration (note trend of lowest nonzero concentration) during the course of the study. Values of concentrations, although high and easily observed on the chromatograms, are subject to unresolved uncertainties associated with the method of calibration and cannot be specified accurately at this point; the values shown are therefore shown as a percentage of the maximum. However, as with the case of alpha and beta pinene, the concentrations of decanal and nonanal are linearly related as noted in Figure 2b, and appear to be driven by the same mechanism, possibly temperature. The observation of these aldehydes in Japan as reported by Yokouchi and coworkers<sup>3</sup> and in Italy as reported by Ciccioli and coworkers<sup>4</sup> seem to confirm these observations. The same type of diurnal concentrations patterns were noted at the Research Triangle Park and nonanal and decanal concentrations were again observed to be linearly related.

The investigation of possible artifact formation of aldehydes during sample transport and conditioning must still be completed before accepting these data as what actually occurs in the ambient air. In the present case the adsorbent Tenax GR was the first adsorbent in the sample concentrator trap and must still be examined for potential artifacts due to the reaction of atmospheric compounds, most notably ozone. In previous research Helmig and Greenberg<sup>5</sup> report that n-aldehyde species observed in their ambient air sampling with Tenax and Tenax GR are unlikely to be due to adsorbent and system contaminants.

### **Benzene, Toluene, and o-Xylene**

Anthropogenic sources of the BTX (benzene, toluene, and xylene) compounds were evident in the patterns observed when plotting wind direction versus concentrations. As noted in Figure 3 for benzene, toluene and o-xylene versus wind direction, the patterns indicate pronounced common sources of the three at 220-230 degrees from north and a source of only toluene at 30-40 degrees. Traffic activity from the general direction of downtown Nashville would explain the common source of BTX. We have noted such patterns in previous field studies and have suggested their use to locate emission sources and to spot departures from toxic release inventories on a presence/absence basis<sup>6</sup>.

### **CONCLUSION**

The new type of autoGC system used in this study was highly effective in producing an essentially complete, hourly update of VOC concentrations from the ambient air. The results promise to provide a database rich in information on the prevalence and variation of both biogenic and anthropogenic compounds. While the demonstration of monitoring techniques was the main objective of this study, a brief review of the data indicates the presence of potentially important information on the prevalence of aldehydes and pinenes, and the factors affecting their diurnal variations. Due to the hourly updating of the data, abrupt changes in concentration of toluene, benzene and other compounds are immediately evident in plots of concentration versus wind direction and can be used to identify the effect of local sources on the VOC database.

### **DISCLAIMER**

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency (EPA) under contract 68-D0-0068 to ManTech Environmental Technology, Inc. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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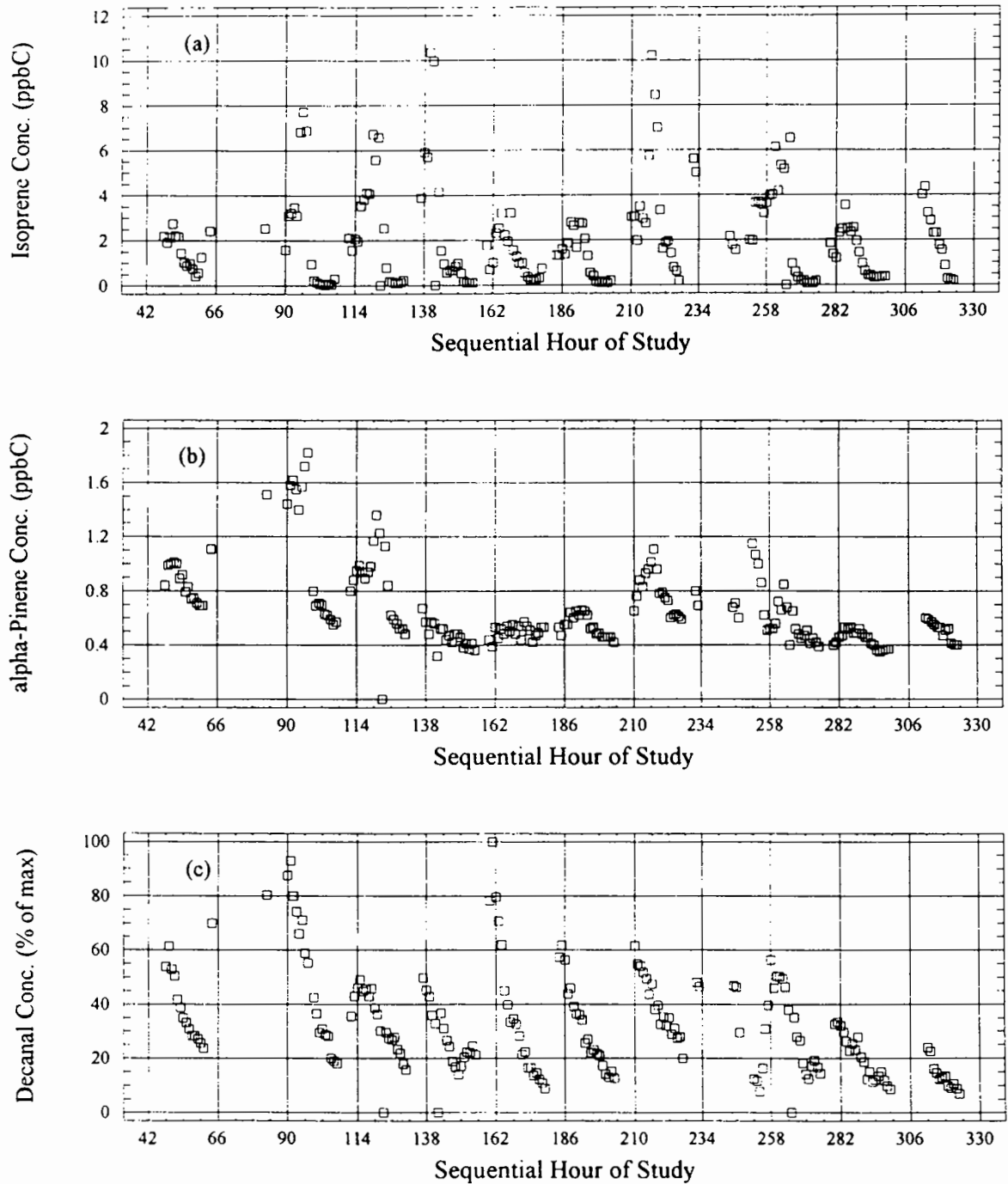


Figure 1. Plot of biogenic gas concentrations versus sequential hour of study: (a) isoprene; (b) alpha pinene; (c) decanal. Vertical lines coincide with noon hours.

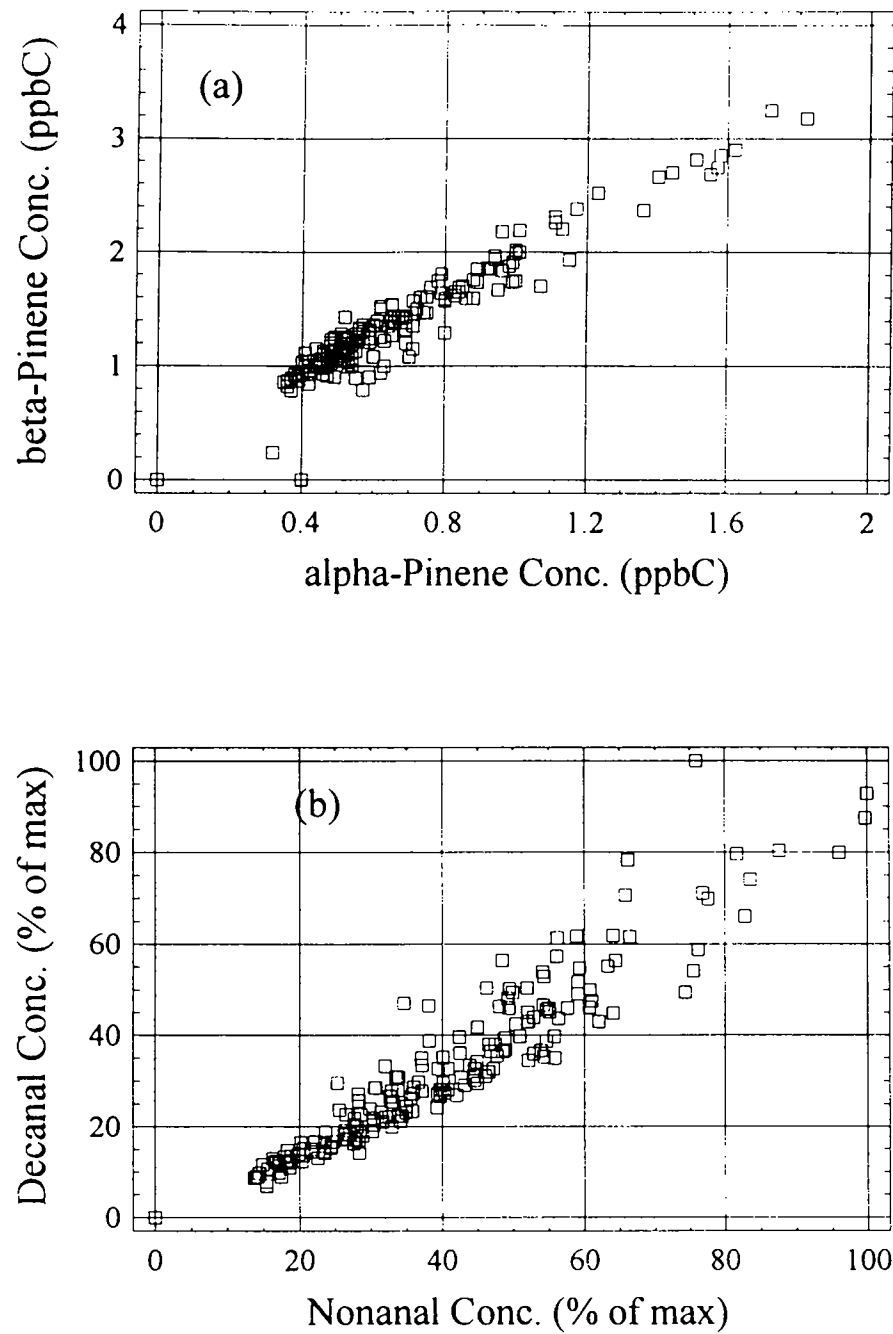


Figure 2. Plots of one biogenic trace gas versus another at the New Hendersonville site: (a) alpha versus beta pinene; (b) nonanal versus decanal.



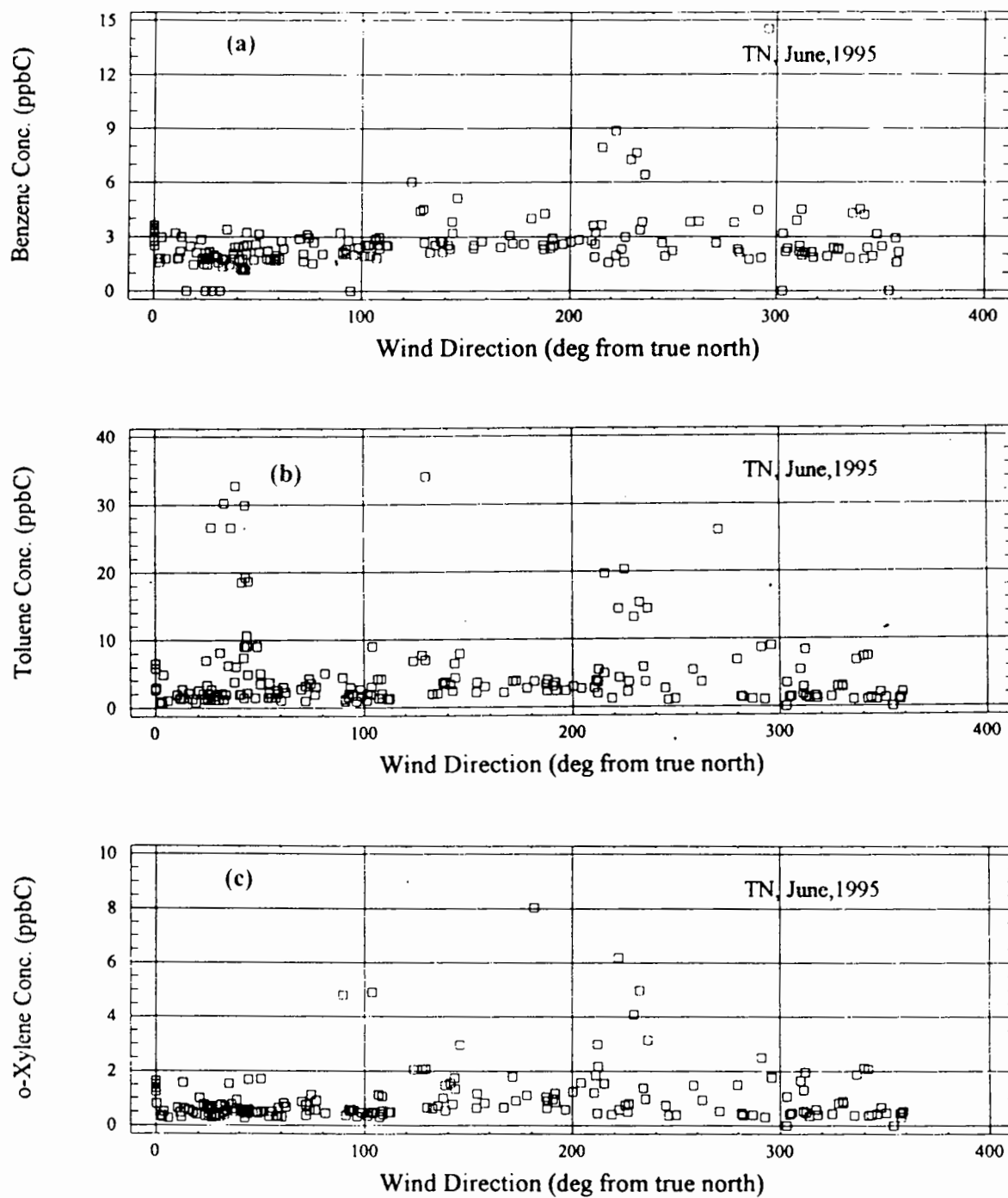
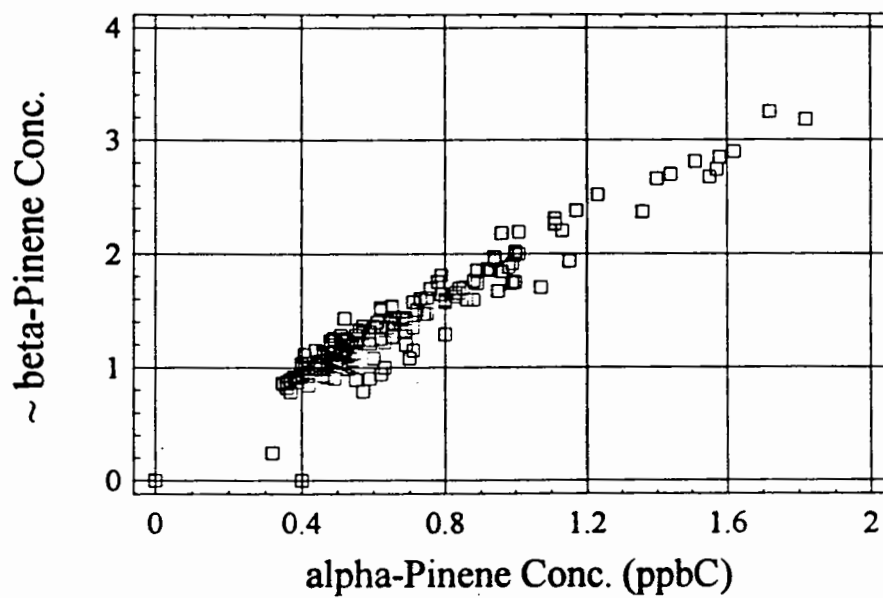


Figure 3. Plot of trace gas concentrations versus wind direction at the New Hendersonville site: (a) benzene; (b) toluene; and (c) o-xylene.



Replacement Figure 2(a) Plot of  $\alpha$ - versus  $\beta$ -pinene at the New Hendersonville Site.

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