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1. INTRODUCTION

Nonmethane hydrocarbons (NMHCs) are precursors to oxidant formation. They are oxidized by hydroxyl radical (OH) to form a complex mixture of peroxy radicals that oxidize NO to NO₂ without consuming ozone (O₃) and thus allow O₃ to increase in the atmospheric boundary layer. The composition, concentrations, and reactivities of the NMHCs that compose biogenic and anthropogenic emissions vary greatly. Thus, for a particular urban area, the strength of the emissions from these various sources will have a substantial effect on the regional production of oxidants.

We made measurements of the NMHCs at tall building sites in Nashville (Polk Building), Houston (Williams Tower), and Phoenix (Bank One Building), as part of three multiagency air quality studies during the summers of 1999, 2000, and 2001, respectively. Diurnal variations in the NMHC distributions and their propene-equivalent concentrations are used to examine the origins and reactivities of the air masses sampled at the tall building sites in the 1999 and 2000 studies.

2. EXPERIMENTAL ASPECTS

The sampling strategy consisted of sample collection over 5-min intervals every 2 hr between 0700 and 1900 local time (LT) and every 3 hr between 1900 and 0700 LT. An automated sampler (Doskey and Bialk 2001) was used to collect samples in Summa[®] passivated stainless steel canisters from elevations of 100 m, 253 m, and 139 m in Nashville, Houston, and Phoenix, respectively. The sampler consisted of a Neuberger Viton[®] diaphragm pump; a 2-position, 3-port valve; a 10-port multiposition valve (VICI, Houston, TX); and a digital valve sequence programmer (VICI, Houston, TX). All connecting tubing and fittings were Silcosteel[®] coated (Restek, Bellefonte, PA).

The air samples were analyzed with two analytic systems consisting of panel-mounted sample preconcentration units and Hewlett-Packard (HP 5890) high-resolution gas chromatographs with flame ionization detectors (FIDs). The analytic systems are described in detail by Doskey and Bialk (2001). Briefly, the whole-air samples were preconcentrated at -185°C in a 16-cm section of Silcosteel[®] tubing (0.216 cm ID) packed with 9 cm of fused silica wool (Alltech Associates, Inc., Deerfield, IL). The analytes were thermally desorbed at approximately 100°C for 2 min and were transferred to either (1) a 60-m × 0.32-mm-ID

fused-silica capillary column coated with a 1-μm-thick film of polydimethylsiloxane (DB-1; J&W Scientific, Folsom, CA) or (2) a 30-m × 0.53-mm-ID porous-layer open tubular column coated with alumina (GS-Alumina; J&W Scientific, Folsom, CA). The FIDs were calibrated daily with a mixture of C₂-C₆ *n*-alkanes, benzene, and toluene at a level of 10 ppb each (Scott Specialty Gases, Inc., Plumsteadville, PA). The C₂ and C₃-C₁₂ hydrocarbons were resolved on the GS-Alumina and DB-1 columns, respectively (Fukui and Doskey, 1996). The comparability of the two analytic systems was verified by quantifying the C₃ and C₄ hydrocarbons in the same air sample on both analytic systems.

3. RESULTS AND DISCUSSION

3.1 Nashville Data from July 1999

The focus of the Nashville data set will be on samples collected on the 5th and 6th of July 1999, when ozone concentrations attained levels of approximately 100 ppbv at the Polk Building site. The NMHC distribution at 1100 LT was typical of vehicle emissions (Fig. 1). High concentrations of acetylene, *n*-butane,

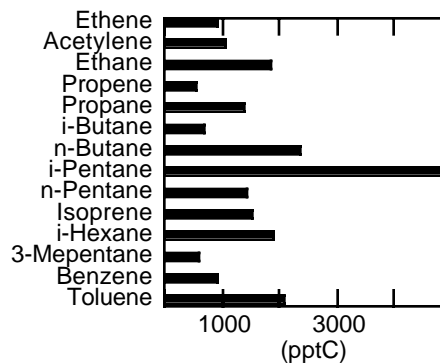


Fig. 1. Distribution of NMHC concentrations at 1100 LT on 5 July 1999 in Nashville.

i-pentane, and toluene were characteristic of vehicle emissions (Doskey et al. 1992; Conner et al. 1995). Mixing ratios of the NMHCs exhibited a strong diurnal pattern (Fig. 2). The highest NMHC concentrations were observed between 2200 and 0400 LT. Toluene/benzene, xylene/benzene, and *i*-pentane/*n*-butane ratios were greatest at night and in the early morning hours and were typical of mobile emissions (Fig. 3). Values of the ratios decreased during the daylight hours, indicating that the hydrocarbon mixture was being processed photochemically. The temporal profile of the mixing ratios during the night and early morning hours is

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produced by recent emission of hydrocarbons into a developing nocturnal boundary layer. At 0400 LT mixing ratios decreased dramatically, indicating that the rooftop site was above the nocturnal boundary layer.

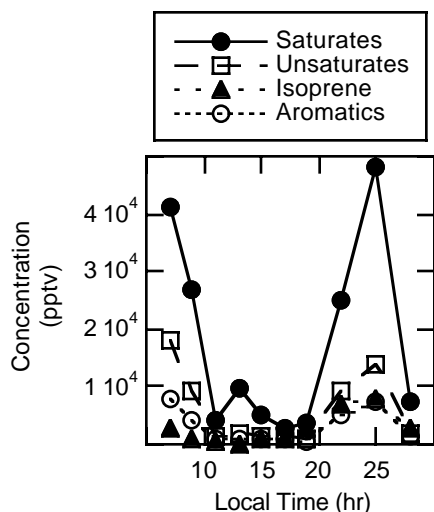


Fig. 2. Diurnal variations of NMHC concentrations on 5-6 July 1999 in Nashville.

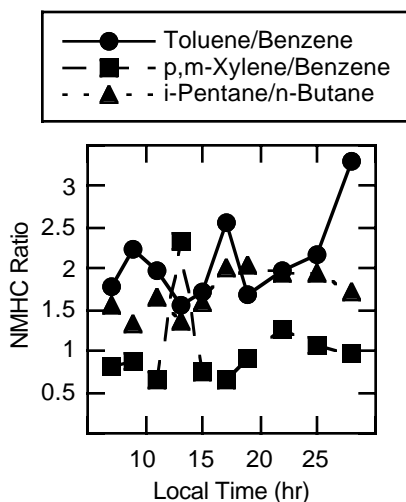


Fig. 3. Diurnal variations of NMHC ratios on 5-6 July 1999 in Nashville.

Isoprene levels attained a maximum of about 8000 pptv at 0100 LT. Back trajectories show the origin of the air to the south, in high-isoprene source regions located in Alabama. Chemical trajectory modeling calculations suggest that the measured isoprene values are attainable in metropolitan Nashville during the early morning hours if the air parcel trajectories have low NO_x (≤ 2 ppb) and moderate O_3 (~ 40 ppb). High O_3 (> 80 ppb)

and high NO_x (~ 10 ppb) in the air parcel will produce less than 200 pptv of isoprene.

Propene-equivalent concentrations of the NMHCs have been used to estimate the relative contributions of hydrocarbon species to the production of ozone (e.g., Chameides et al. 1992). The propene-equivalent concentration is calculated by multiplying the concentration of each NMHC by the ratio of its OH rate constant to the OH rate constant for propene. The reactivity values of the hydrocarbon mixture in ambient air during the night and early morning hours were greater than the levels during the day (Fig. 4). Isoprene contributed approximately 50% of the hydrocarbon reactivity during this period. These observations indicate very little photochemical processing of the hydrocarbon mixture, which probably originated from vehicle emissions during the evening rush hour in Nashville along with biogenic emissions transported to the metropolitan area.

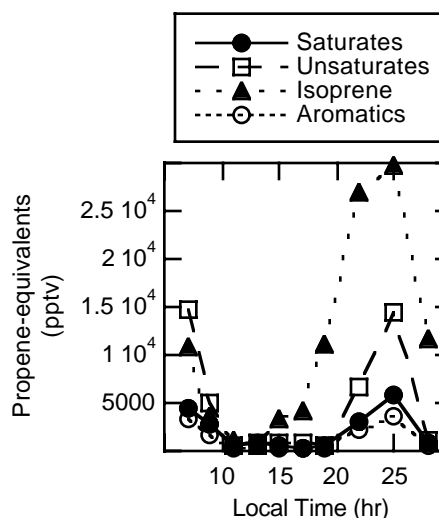


Fig. 4. Diurnal variations of propene-equivalent concentrations of NMHCs on 5-6 July 1999 in Nashville.

3.2 Houston Data from September 2000

The focus of the Houston data set will be on samples collected on the 6th and 7th of September, when ozone concentrations attained levels of approximately 120 ppbv at the Williams Tower site. The NMHC distribution at 1100 LT on the 6th was somewhat different than the distribution in Nashville (Fig. 5; compare to Fig. 1). Levels of many of the NMHCs were greater by a factor of two in Houston. However, the concentrations of ethane and propane were greater by nearly a factor of four, and the NMHC distribution was typical of emissions from petroleum refinery flares. Although isoprene levels were similar to those observed in Nashville, the temporal variation at the Williams Tower site and a site located in an industrial section of Houston suggest that an anthropogenic source of isoprene is likely. Mixing ratios of the NMHCs exhibited a strong diurnal pattern (Fig. 6). The highest

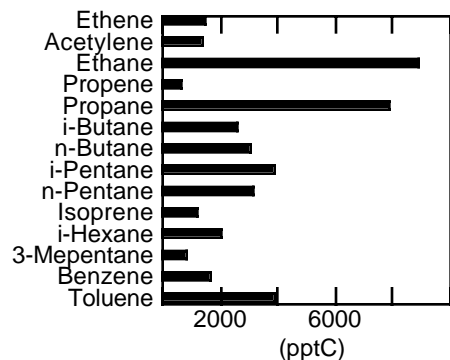


Fig. 5. Distribution of NMHC concentrations at 1100 LT on 6-7 September 2000 in Houston.

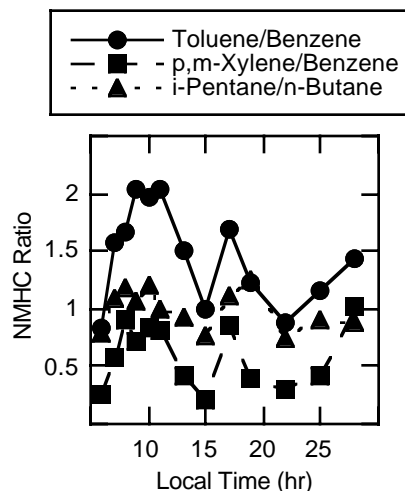


Fig. 7. Diurnal variations of NMHC ratios on 6-7 September 2000 in Houston.

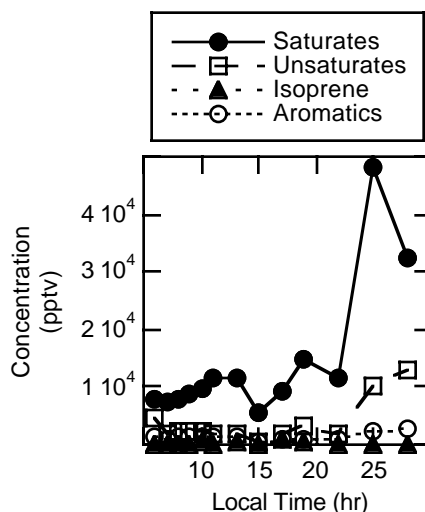


Fig. 6. Diurnal variations of NMHC concentrations on 6-7 September 2000 in Houston.

concentrations were observed between 2200 LT and 0100 LT. The levels of all hydrocarbons increased dramatically during this period, but the largest increases were observed for the saturated hydrocarbons. In particular, propane increased in concentration by more than a factor of seven. Hydrocarbon ratios exhibited a decline during the day, characteristic of photochemical processing (Fig. 7). The propene-equivalent concentrations of the saturated and unsaturated hydrocarbons during the daylight hours are similar, indicating photochemical processing of the unsaturates (Fig. 8). Late at night and during the early morning hours the unsaturates, particularly ethene and propene, contributed much of the potential reactivity. Isoprene contributions were greatest at 1300 and 1700 LT.

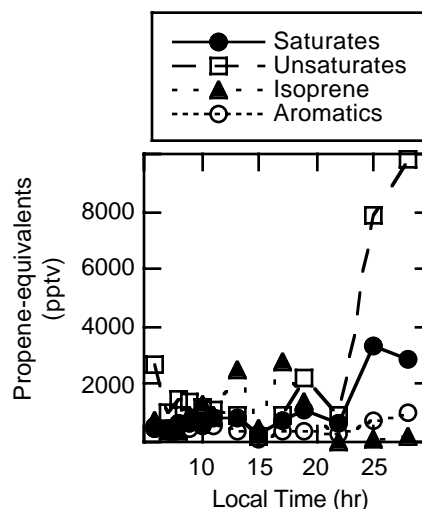


Fig. 8. Diurnal variations of propene-equivalent concentrations of NMHCs on 6-7 September 2000 in Houston.

4. CONCLUSIONS

Distributions of NMHCs in Nashville and Houston exhibited contributions from vehicle emissions. However, the origin of isoprene in metropolitan Nashville during the early morning hours was traced to long-range transport of air from forested regions to the south. For Houston, contributions of light NMHCs from refinery emissions appeared to make a significant contribution to the atmospheric burden. For both urban areas, unsaturated hydrocarbons that accumulated in the late evening and early morning hours were a major source of potential reactivity. In Nashville, the unsaturated

hydrocarbons originated from vehicle and biogenic (isoprene) emissions. In Houston, the unsaturated hydrocarbons in greatest abundance were ethene and propene that originated from the many industries in the metropolitan area.

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