ANL/ER/CP-100179

MEASUREMENTS OF NONMETHANE HYDROCARBONS IN PHOENIX, ARIZONA*

by

P. V. Doskey and V. R. Kotamarthi
Environmental Research Division
Argonne National Laboratory
Argonne, Illinois

and

J. Rudolph
Centre for Atmospheric Chemistry
York University
North York, Ontario

RECEIVED
JAN 18 2000
OSTI

Extended Abstract for Preprint Volume and Presentation at

Symposium on Atmospheric Chemistry Issues in the 21st Century
American Meteorological Society
9-14 January 2000
Long Beach, California

---

*Work supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Environmental Sciences Division, under contract W-31-109-Eng-38.

DISCLAIMER

2.1 MEASUREMENTS OF NONMETHANE HYDROCARBONS IN PHOENIX, ARIZONA

P. V. Doskey* and V. R. Kotamarthi
Environmental Research Division
Argonne National Laboratory, Argonne, Illinois

J. Rudolph
Centre for Atmospheric Chemistry, York University
North York, Ontario

1. INTRODUCTION

Nonmethane hydrocarbons (NMHCs) are precursors to oxidant formation. They are oxidized by hydroxyl radical (OH), forming a complex mixture of peroxy radicals that oxidize NO to NO_2 without consuming ozone (O_3) and thus allow O_3 to increase in the atmospheric boundary layer. The reactivities of the NMHCs that compose biogenic and anthropogenic emissions vary greatly. For example, isoprene, which is emitted by deciduous vegetation, has an atmospheric lifetime with respect to oxidation by OH of about 20 min in polluted air ($[OH] = 10^7$ radicals cm^{-3}). The atmospheric lifetimes of 2-methylpropene, 2-methylbutane, and the xylenes, which are found in vehicle emissions, are approximately 30 min, 7 hr, and 1.5 hr, respectively.

We made measurements of the NMHCs at a surface site and aloft aboard the Battelle Gulfstream (G-1) aircraft, as part of an air quality study in the Phoenix area during May 1998. Diurnal variations in the NMHC distributions and their *propene-equivalent* concentrations are used to examine origins and reactivities of the air masses that were sampled at the surface site.

2. EXPERIMENTAL ASPECTS

Three-hour integrated samples were collected over six periods of 24 hr each in May 1998 at Usery Pass, a hilly region east of Phoenix, Arizona. Ambient air was sampled through gas chromatographic grade stainless steel tubing (3 m × 0.635 cm OD) into Summa® passivated stainless steel canisters (Scientific Instrumentation Specialists, Moscow, ID) with a Viton® diaphragm pump. The flow was controlled with a differential pressure flow controller located between the pump and canister.

The air samples were cryogenically preconcentrated with a Chemical Data Systems (CDS) 330 sample concentrator (Autoclave Inc., Oxford, PA) and were analyzed with a Hewlett-Packard 5890A high-resolution gas chromatograph (Palo Alto, CA) with a flame ionization detector (FID) by an analytic technique described in detail by Fukui and Doskey (1996). Briefly, the whole-air samples were preconcentrated at -100°C in a 15-cm section of a glass-lined stainless steel tube (0.180 cm ID) packed with 60/80 mesh porous glass beads (Unibeads 1S; Alltech Associates, Inc., Deerfield, IL). The preconcentrated samples were thermally desorbed at 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 FID was calibrated daily with a mixture of C_2-C_6 *n*-alkanes, benzene, and toluene at a level of 10 ppb each (Scott Specialty Gases, Inc., Plumsteadville, PA).

3. RESULTS AND DISCUSSION

Distributions of the NMHCs at the Usery Pass location varied diurnally and were typical of vehicle emissions that had undergone various stages of photochemical processing. The most prominent saturated hydrocarbons included ethane, propane, 2-methylpropane, *n*-butane, 2-methylbutane, *n*-pentane, 2,3-dimethylbutane, *n*-hexane, and 2,2,4-trimethylpentane. The major unsaturated hydrocarbons included ethene, acetylene, propene, 2-methylpropene, and isoprene, while the most prominent aromatics were benzene, toluene, *p*- and *m*-xylene, and *o*-xylene. All of these hydrocarbon species, with the exception of isoprene, are major constituents of vehicle emissions (Doskey et al. 1992). Isoprene is attributed to biogenic emissions from deciduous vegetation (Guenther et al. 1993).

The total NMHC levels at the Usery Pass location were typically between 40 and 140 ppbC. The lowest values were found in samples collected between 0700 and 1000 local time (LT), and the highest concentrations were observed between 0100 and 0400 LT (Fig. 1). Diurnal variations of the saturated, unsaturated, and aromatic hydrocarbons followed the same trends as did the total NMHCs (Figs. 2 and 3). Concentrations of the saturated hydrocarbons were similar to the levels of the unsaturated hydrocarbons, while the levels of the aromatic hydrocarbons were lower by approximately a factor of 3. Values of the toluene/benzene ratios between 0100 and 0400 LT were 2.0-2.6, similar to values reported for vehicle exhaust (Conner et al. 1995). NMHC distributions at this time were characteristic of vehicle emissions originating from the evening rush hour in Phoenix that had undergone some photochemical processing during transport to the Usery Pass site. Toluene/benzene ratios in samples collected before 1600 LT were between 1.0 and 1.5, typical of vehicle emissions that had been processed more extensively.

Biogenic emissions of isoprene were evident during the daylight hours. Isoprene was first detected at 0400-0700 LT; concentrations attained maximum values of about 70 pptv during the sampling period at 1300-1600 LT (Fig. 3). The temporal profile of the isoprene concentration that we observed at the Usery Pass location is similar to the profile observed by others for isoprene-emitting species of vegetation (Guenther et al. 1993). The local vegetation was considered to be the likely source of the isoprene, because air sampled near

---

Corresponding author address: Paul V. Doskey, Bldg. 203, Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439-4843; e-mail: pvdoskey@anl.gov.

shrubs at the site exhibited isoprene concentrations much greater than the levels observed in ambient air. For example, a sample collected near a shrub at 1430 LT exhibited an isoprene/*n*-pentane ratio of 56, while ambient air collected at the same time at a height of 3 m exhibited a ratio of 2. The isoprene concentration was normalized to the *n*-pentane levels because *n*-pentane is derived from anthropogenic sources and is expected to be well mixed near the surface.

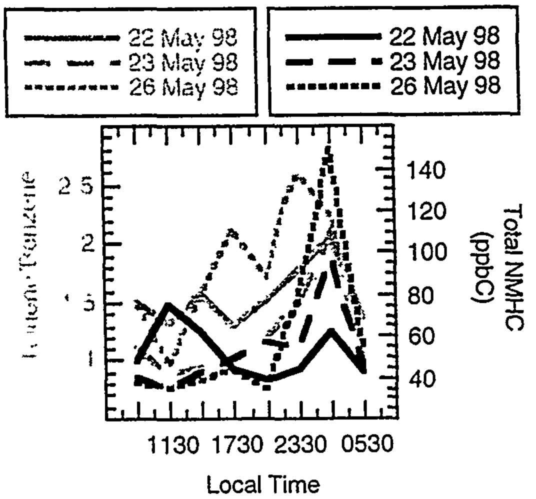

Fig. 1. Diurnal variations of the total NMHC concentrations and toluene/benzene ratios on 22, 23, and 26 May 1998 at the Usery Pass sampling site.

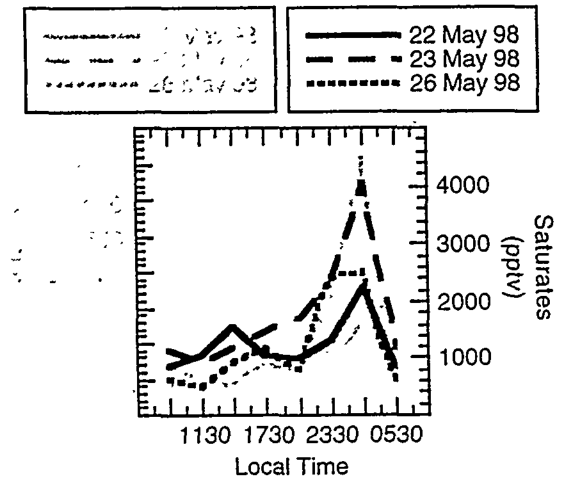

Fig. 2. Diurnal variations of the saturated and unsaturated hydrocarbon concentrations on 22, 23, and 26 May 1998 at the Usery Pass sampling site.

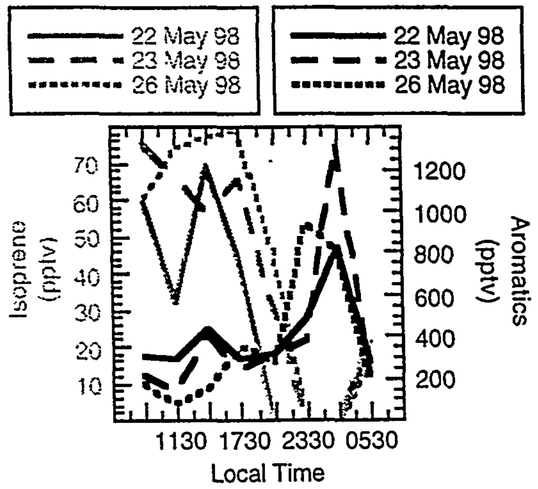

Fig. 3. Diurnal variations of the aromatic hydrocarbon and isoprene concentrations on 22, 23, and 26 May 1998 at the Usery Pass sampling site.

Haze from forest fires that originated in southern Mexico during the spring of 1998 was visible at Usery Pass on 20 May. Methyl chloride emissions from biomass burning are estimated to contribute about 20% of the global emissions (Rudolph et al. 1995). Diurnal variations of the methyl chloride concentrations for five sampling periods are compared in Fig. 4. On 20 May, methyl chloride values were 940 pptv during the sampling period at 0700-1000 LT, while values on the other days were 700-780 pptv, similar to the background values observed in continental air. The difference in concentrations observed on 20 May and the other sampling days was much greater than the diurnal variation of methyl chloride observed at this location.

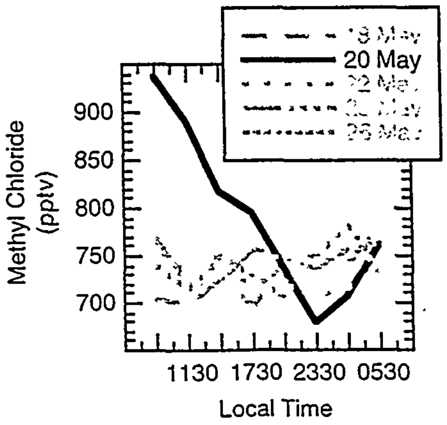

Fig. 4. Diurnal variations of the methyl chloride concentrations on 18, 20, 22, 23, and 26 May 1998 at the Usery Pass sampling site.

Propene-equivalent concentrations of the NMHCs have been used to estimate the relative contributions of hydrocarbon species to the production of O_3 (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. Values for isoprene and the saturated, unsaturated, and aromatic hydrocarbons on 22, 23, and 26 May at 1430 LT and 0230 LT are compared in Fig. 5. The propene-equivalent concentrations of the total NMHCs were greater during the early morning hours than in the afternoon. The difference was greatest for 22 May, when values at 0230 LT were greater by a factor of four than the levels at 1430 LT. The contribution of the saturated hydrocarbons to the overall reactivity during the sampling period at 0100-0400 LT was fairly constant, about 40%. In contrast, the contributions by the unsaturates and aromatics were variable. This trend is consistent with partial oxidation of the evening rush hour emissions during transport to Usery Pass. In general, the unsaturated and aromatic hydrocarbons are more reactive toward oxidation by OH than are the saturated hydrocarbons. If photochemical processing of the evening rush hour emissions occurred during transport to Usery Pass, the levels of the unsaturated and aromatic hydrocarbons would be diminished relative to levels of the saturated hydrocarbons. This is the trend we observed at 0230 LT. In contrast, the contributions of the various hydrocarbon classes to the overall reactivity at 1430 LT were similar on all three days, indicating that air sampled at this time of day is photochemically aged. Biogenic emissions of isoprene were a significant fraction of the hydrocarbon reactivity during the daylight hours; the contributions were 25-40% at 1430 LT on all three days.

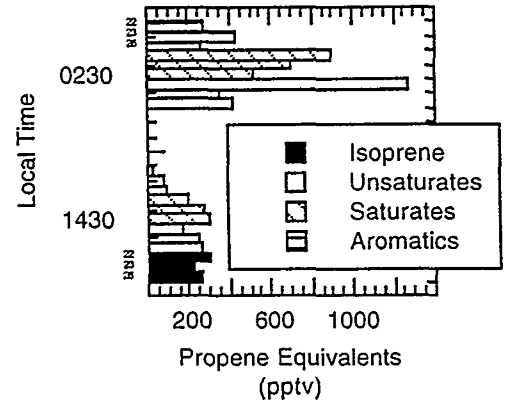

Fig. 5. Propene equivalent concentrations of isoprene, and the saturated, unsaturated, and aromatic hydrocarbons for the sampling periods at 0100-0400 LT and 1300-1600 LT on 22, 23, and 26 May 1998 at the Usery Pass sampling site.

4. CONCLUSIONS

Diurnal variations of the distributions of the NMHCs at Usery Pass were significant and were typical of vehicle emissions that had undergone various stages of photochemical processing. Concentrations of the saturated, unsaturated, and aromatic hydrocarbons reached maximum values between 0100 and 0400 LT. During this period, the toluene/benzene ratios were 2.0-2.6, characteristic of partially reacted vehicle emissions that might have originated from the evening rush hour in the Phoenix metropolitan area. Biogenic emissions of isoprene were evident during the daylight hours. Toluene/benzene ratios in samples collected before 1600 LT were usually between 1.0 and 1.5, typical of vehicle emissions that had been more extensively processed than the ambient air sampled between 0100 and 0400 LT at the site. The propene-equivalent concentrations of the hydrocarbon mixture in ambient air at 0100-0400 LT were greater than the levels at 1300-1600 LT. Isoprene contributed a significant fraction of the hydrocarbon reactivity during the daylight hours.

Acknowledgments–We thank Randy Redman of the Arizona Department of Environmental Quality for arrangements at the Usery Pass sampling location. This work was supported by the U.S. Department of Energy under contract W-31-109-Eng-38, as part of the Atmospheric Chemistry Program (ACP) of the Office of Science, Office of Biological and Environmental Research, Environmental Sciences Division.

5. REFERENCES

Chameides, W. L., F. Fehsenfeld, M. O. Rodgers, C. Cardelino, J. Martinez, D. Parrish, W. Lonneman, D. R. Lawson, R. A. Rasmussen, P. Zimmerman, J. Greenberg, P. Middleton, and T. Wang, 1992: Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.*, 97, 6037-6055.

Conner, T. L., W. A. Lonneman, and R. L. Seila, 1995: Transportation-related volatile hydrocarbon source profiles measured in Atlanta. *J. Air Waste Manage. Assoc.*, 45, 383-394.

Doskey, P. V., J. A. Porter, and P. A. Scheff, 1992: Source fingerprints for volatile non-methane hydrocarbons. *J. Air Waste Manage. Assoc.*, 42, 1437-1445.

Fukui, Y., and P. V. Doskey, 1996: An enclosure technique for measuring nonmethane organic compound emissions from grasslands. *J. Env. Qual.*, 25, 601-610.

Guenther, A. B., P. R. Zimmerman, P. C. Harley, R. K. Monson, and R. Fall, 1993: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *J. Geophys. Res.*, 98, 12,609-12,617.

Rudolph, J., A. Khedim, R. Kloppmann, and B. Bonsang, 1995: Field study of the emissions of methyl chloride and other halocarbons from biomass burning in Western Africa. *J. Atmos. Chem.*, 22, 67-80.