**P1.10** AIR QUALITY MEASUREMENTS IN PHOENIX, ARIZONA

Nancy A. Marley and Jeffrey S. Gaffney*
Environmental Research Division
Argonne National Laboratory

## 1. INTRODUCTION

Peroxyacyl nitrates (R-C=O-O-O-$NO_2$; PANs) are key species in determining the apparent age of background air that might affect an urban air parcel (Gaffney et al. 1989). The most common member of the family, peroxyacetyl nitrate (PAN; R=$CH_3$-), typically accounts for approximately 85% of the PANs found in urban or rural air. The PANs are in equilibrium with nitrogen dioxide ($NO_2$) and peroxyacyl radicals (R-C=O-O-O). The PANs are produced by the oxidation reactions of organics (particularly aldehyde oxidation products) with hydroxyl radical (OH) during daytime, photochemically active periods. The reaction of nitrate radical ($NO_3$) via abstraction with aldehydes has been proposed (Gaffney et al. 1989) as a nighttime mechanism for formation of PANs. As part of our continuing studies of the formation of PANs in urban and regional-scale environments, we have been involved with field measurements in the Phoenix, Arizona, area under the Department of Energy's Atmospheric Chemistry Program.

Previously, we had taken measurements at Usery Pass, northeast of the city of Phoenix, and observed a number of interesting transport-related phenomena at the eastern end of the urban area (Gaffney et al. 2002). In studies performed in May-June of 1998, we took measurements of ultraviolet-B (UV-B) and the pollutants PAN, $NO_2$, and ozone ($O_3$), among other variables, to examine diurnal behavior. The site at Usery Pass placed the study in the outflow from the city. We found that nighttime titration of NO by $O_3$ was leading to transport over the Usery Pass site of high levels of $NO_2$, in some cases reaching 50 ppb (Gaffney et al. 2002). On the edges of these plumes, $NO_3$ production was as high as 2 x $10^7$ molecules $cm^{-3}$ $s^{-1}$. The downwind potential for the formation of PANs by the $NO_3$ process, plus photolysis in the early morning, was expected to increase downwind oxidants in the surrounding mountain regions east of the Phoenix metropolitan area.

Because Phoenix is representative of a number of western U. S. cities in arid climates, further air quality measurements were taken there during June 2001 as part of Atmospheric Chemistry Program studies in the southwestern United States. Reported here are results for a site at the western boundary of the Phoenix metropolitan area. The sampling station was at the University of Arizona's Citrus Experimental Agricultural Station in Waddell, Arizona.

**Corresponding author address:* Jeffrey S. Gaffney, Environmental Research Division, 9700 South Cass Avenue, Argonne National Laboratory, Argonne, IL 60439-4843. e-mail: gaffney@anl.gov.

## 2. MEASUREMENTS

A fast gas chromatograph system with luminol detection was used for the detection of $NO_2$ and PAN at 30-sec time resolution. This system was modified from a previous design (Gaffney et al. 1998). Details on the earlier instrument are reported in another paper presented at this meeting (Marley et al. 2003). Results shown here are 1-min averages.

Besides conventional $O_3$ instrumentation, we also deployed a reactive olefin monitor that was a modified version of an $O_3$ chemiluminescence hydrocarbon detection system described previously (Marley and Gaffney 1998). The detector was modified to use a Hamamatsu photon counting system and was calibrated to ethylene as a standard reactive olefin. The reactions of $O_3$ with olefins expected to be faster than the reaction with ethylene. The monitoring system sees isoprene and monoterpene hydrocarbons such as alpha-pinene, beta-pinene, and d-limonene that are presumed to be emitted from natural vegetation and the surrounding citrus groves. The actual signals are proportional to the reactivities of the hydrocarbons and their concentrations (Marley and Gaffney 1998).

We were interested in the natural hydrocarbon levels in this area, because sizeable citrus groves at the western end of the Phoenix metropolitan area probably contribute to the mix of reactive hydrocarbons. The monoterpenes are so reactive with $O_3$ that they are not expected to be transported but should contribute to local production of peroxy radicals. These same radicals will form PAN and $O_3$ in the presence of NO and $NO_2$.

## 4. RESULTS AND DISCUSSION

Figure 1 shows the $O_3$ levels observed during the Phoenix 2001 study at the Waddell site. The highest $O_3$ levels observed were below 70 ppb. This is in contrast to previous measurements at the eastern (downwind) site at Usery Pass, where observed $O_3$ levels were as high as 95 ppb and were over 80 ppb on a number of days.

Data obtained for $NO_2$ and PAN are shown in Figure 2 and Figure 3. The $NO_2$ levels observed were much lower than those seen at the Usery Pass site, and we found no evidence for nocturnal transport of $NO_2$.

Titration of $O_3$ by NO from morning rush hour traffic on the freeways approximately 5 mi south of the Waddell site appears in the $NO_2$ data as plumes of $NO_2$ during the early morning hours. For the most part, local production of PAN is seen as a clear diurnal variation in PAN concentrations, despite the increase in temperature throughout the day and the short anticipated lifetime of PAN.

Figure 4 shows the data collected by the reactive olefin monitor. On days 168-169 thundershowers in the foothills led to an increased signal. We believe that the diurnal signal on subsequent days is due to increased release of isoprene from the citrus groves and natural vegetation in the area. After these events the levels of reactive hydrocarbons continued to subside until previous levels were observed at the end of the sampling period.

We were curious to see whether PAN formation by reaction of $NO_3$ could be detected at night. Figure 5 shows calculated production rates for $NO_3$ at this site during the evening periods. The levels do not exceed 2 x $10^6$ molecules $cm^{-3}$ $s^{-1}$. These $NO_3$ formation rates are lower by a factor of ten than those estimated at the Usery Pass site, where NO titration of $O_3$ produced in the urban area leads to nocturnal plume production and regional transport. Like our observations of PAN at the Waddell site, these results indicate that nocturnal production of PANs is not important relative to local daytime production.

Interestingly, the baseline values observed for PAN, about 100 ppt, were essentially the same at the Waddell site and in the 1998 study, despite the very high temperatures in the area. This observation points to the importance NO and $HO_2$ in the loss of PAN. The data indicate that the $NO_2$ levels are high enough to maintain a background level of PANs in this region at 0.1 ppb.

## 5. CONCLUSIONS

The observations made at the Waddell site indicate that natural hydrocarbons from local vegetation and agricultural activities might be important in the Phoenix area and should be considered in oxidant production schemes. The potential of these species to produce OH by reaction with $O_3$ might also be important, especially in this arid environment where water vapor concentrations are very low, and $O(^1D)$ reactions to form OH are slow (Finlayson-Pitts and Pitts 2000).

The data do not indicate major transport of pollutants into the region during the study period. This result is in contrast to observations during the 1998 study at the Usery Pass site, which clearly indicated long-range transport affecting Phoenix. Beryllium-7 data for the Waddell site in 2001, reported at this meeting, are consistent with this observation (Gaffney and Marley 2003).

In combination with data on other key oxidants, the rapid measurement of $NO_2$ and PANs enables a number of chemical and transport processes to be probed. We plan to continue data analysis from this work and also intend to examine multifilter rotating shadowband data obtained at the Waddell site to evaluate aerosol levels at this upwind location.

## 6. ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Atmospheric Chemistry Program and Global Change Education Program, under contract W-31-109-Eng-38. This work was performed at Argonne National Laboratory.

## 7. REFERENCES

Finlayson-Pitts, B. J., and J. N. Pitts, Jr., 2000: *Chemistry of the Upper and Lower Atmosphere.* Academic Press, San Diego, CA.

Gaffney, J. S., and N. A. Marley, 2003: Natural radioactivity in aerosols and what it can tell us. *Preprints*, Fifth Conference on Atmospheric Chemistry, American Meteorological Society National Meeting, Long Beach, CA, on CD-ROM.

Gaffney, J. S., N. A. Marley, and E. W. Prestbo, 1989: Peroxyacyl nitrates (PANS): Their physical and chemical properties. *Handbook of Environmental Chemistry,* Volume 4/Part B (*Air Pollution*), edited by O. Hutzinger, Springer-Verlag, Berlin, 1-38, and references therein.

Gaffney, J. S., R. M. Bornick, Y.-H. Chen, and N. A. Marley, 1998: Capillary gas chromatographic analysis of nitrogen dioxide and PANs with luminol chemiluminescent detection. *Atmos. Environ.*, **32**, 1445-1454.

Gaffney, J. S., N. A. Marley, P. J. Drayton, P. V. Doskey, V. R. Kotamarthi, M. M. Cunningham, J. C. Baird, J. Dintaman and H. L. Hart, 2002: Field observations of regional and urban impacts on $NO_2$, ozone, and nitrate radical production rates in the Phoenix air basin. *Atmos. Environ.*, **36**, 825-833.

Marley, N. A., and J. S. Gaffney, 1998: A Comparison between flame ionization and ozone chemiluminescence for the detection of atmospheric hydrocarbons. *Atmospheric Environment*, **32**, 1435-1444.

Marley, N. A., J. S. Gaffney, R. L. Gunter, and W. L. Luke, 2003: New improved fast GC-luminol instrument for PAN and nitrogen dioxide measurements. *Preprints*, Fifth Conference on Atmospheric Chemistry, American Meteorological Society National Meeting, Long Beach, CA, on CD-ROM.

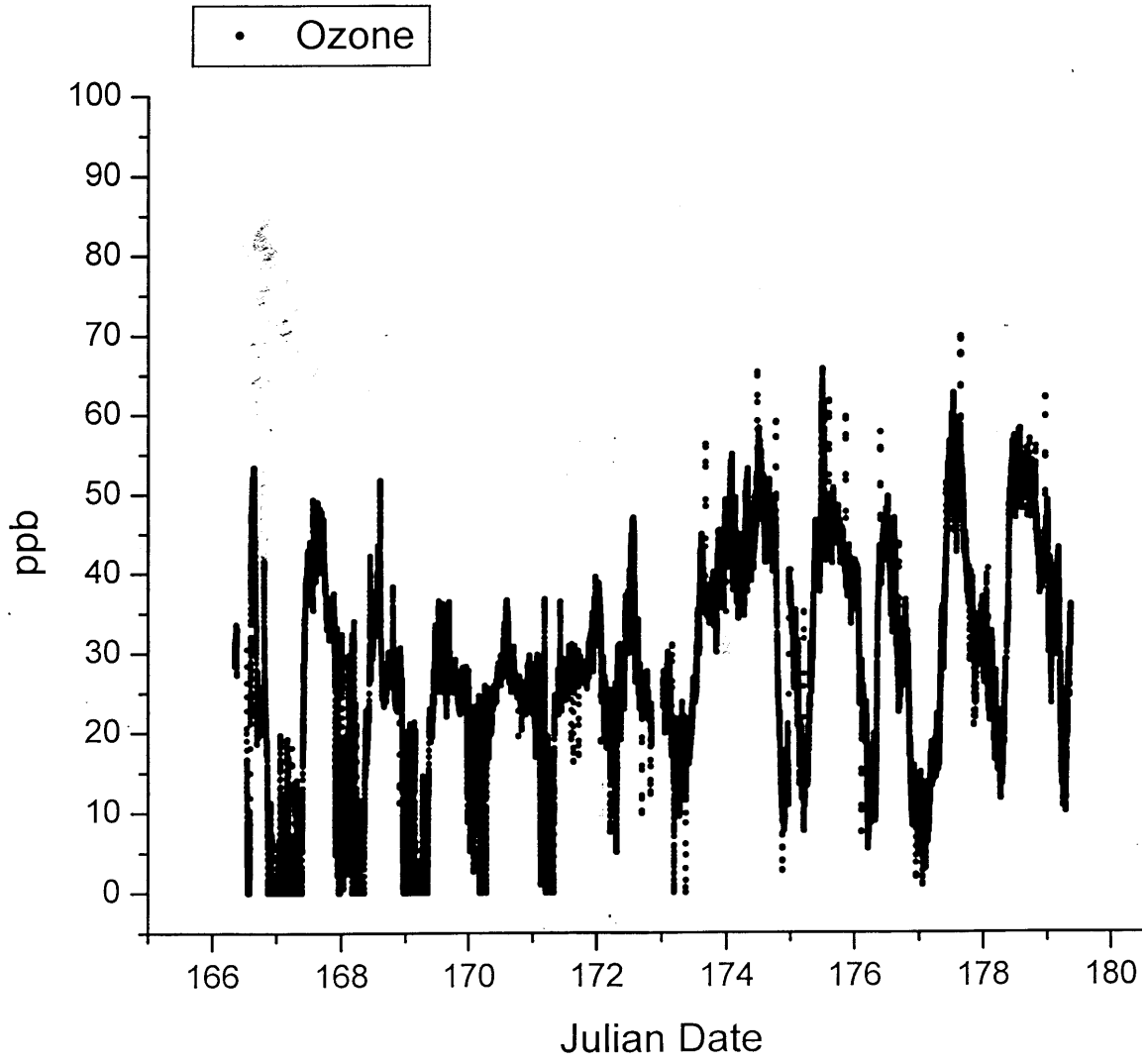


Figure 1. Ozone levels observed in the Phoenix 2001 study at the Waddell site.

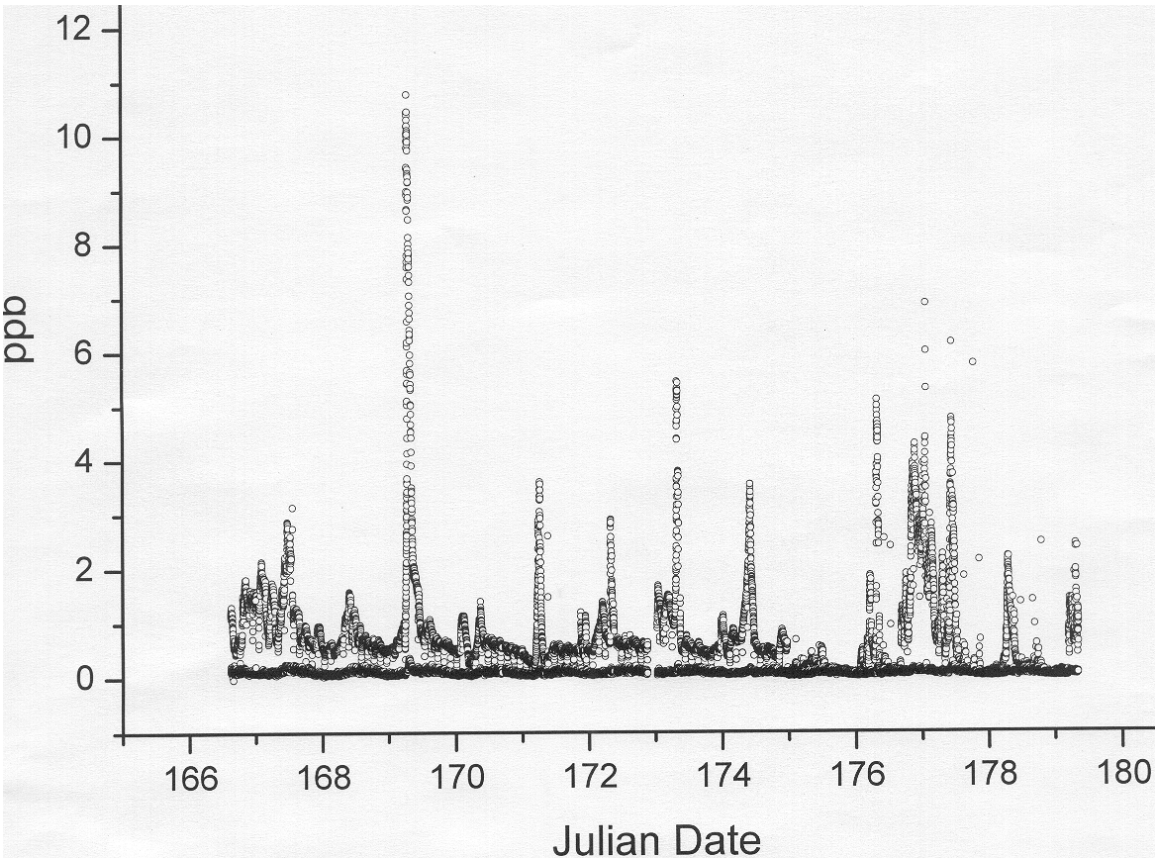


Figure 2. Nitrogen dioxide (open circles) and PAN levels (closed circles) observed at the Waddell site in 2001. Concentrations are in ppb.

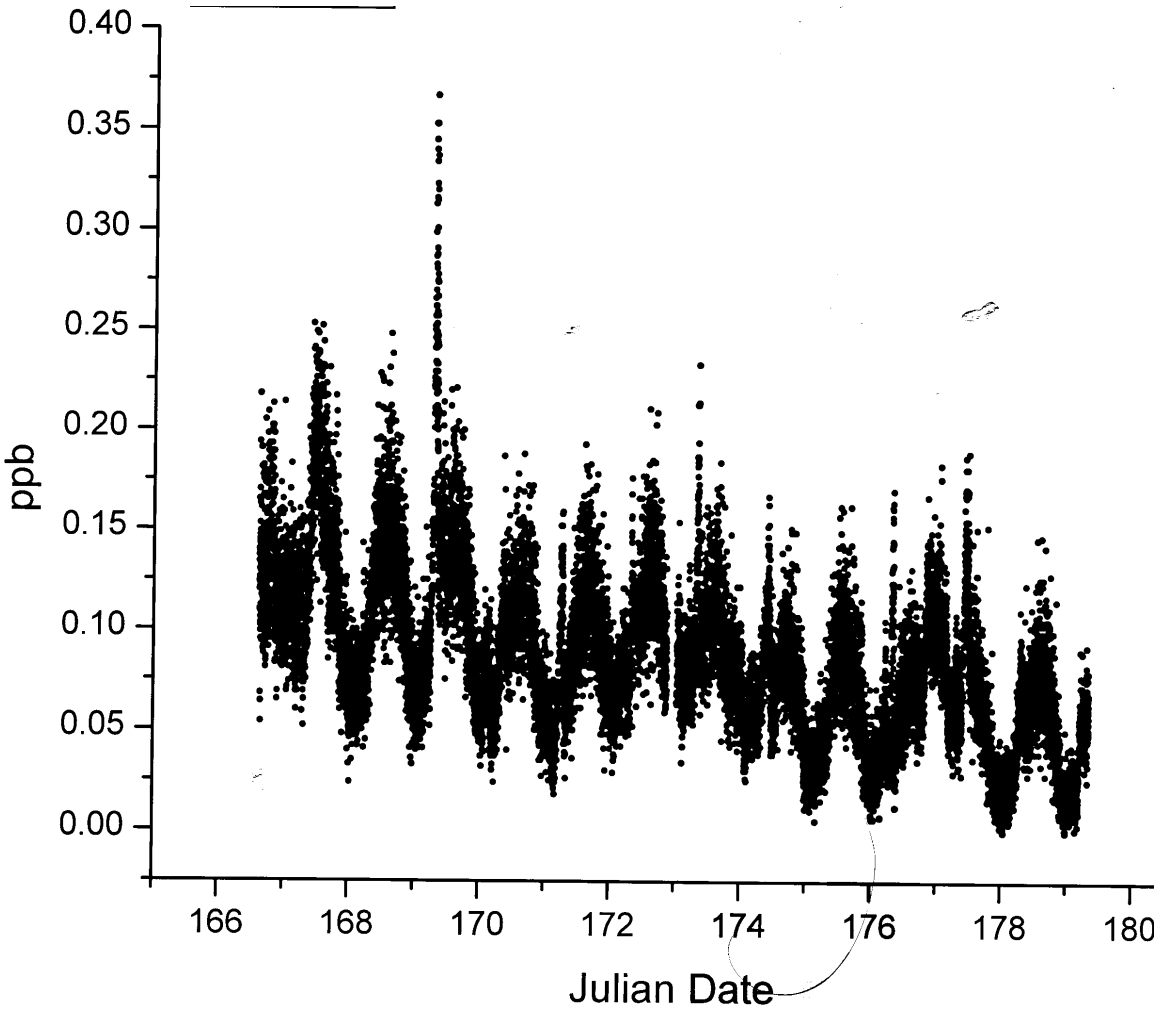


Figure 3. PAN levels measured at Waddell site in 2001, showing strong diurnal production. Detection limits for the instrumentation were approximately 0.020 ppb.

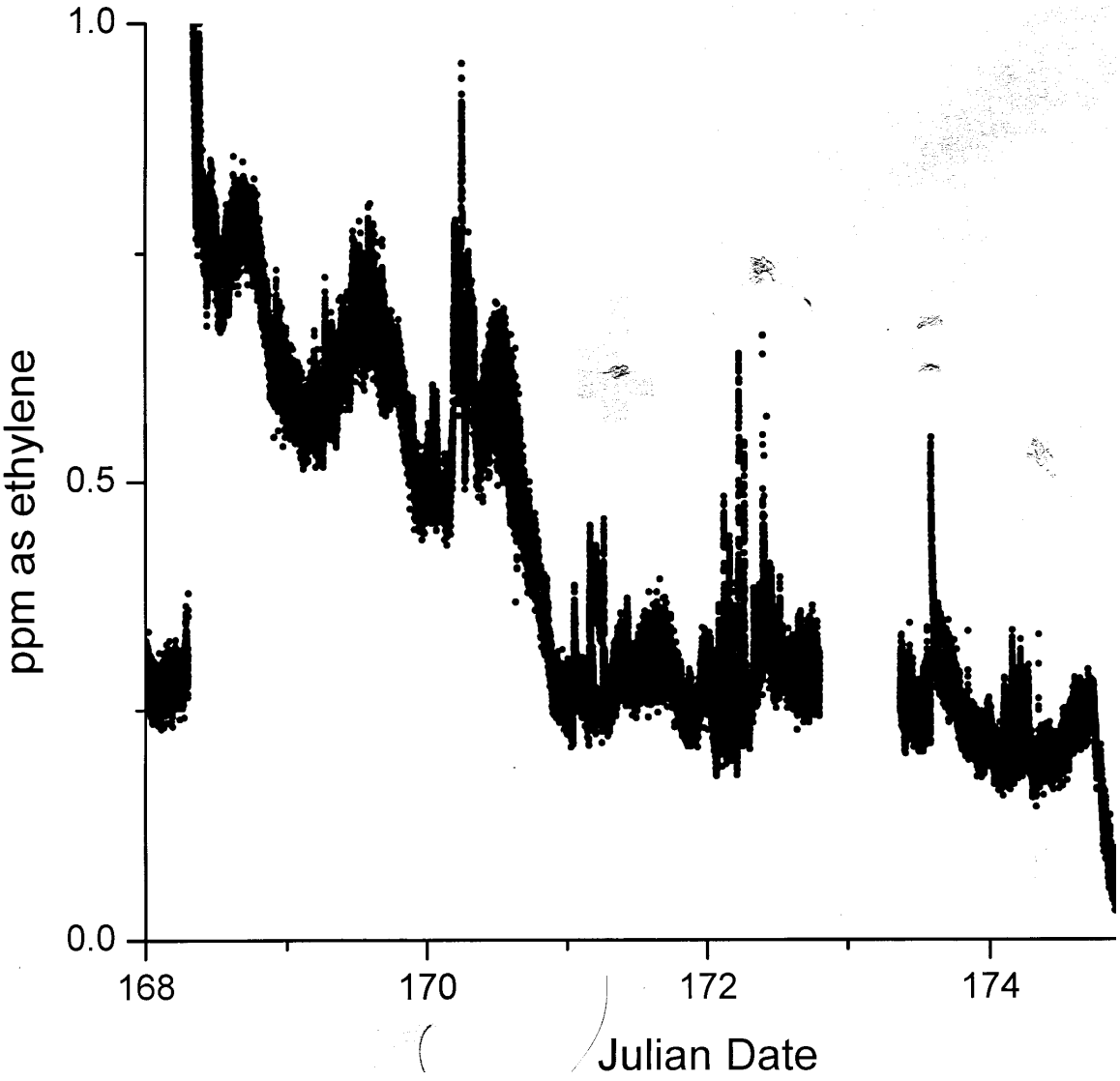


Figure 4. Reactive olefin measurements at the Waddell site in 2001. A precipitation event on Julian Date 168-169 led to higher levels of emissions. The clear diurnal signal on subsequent days was likely due to isoprene.

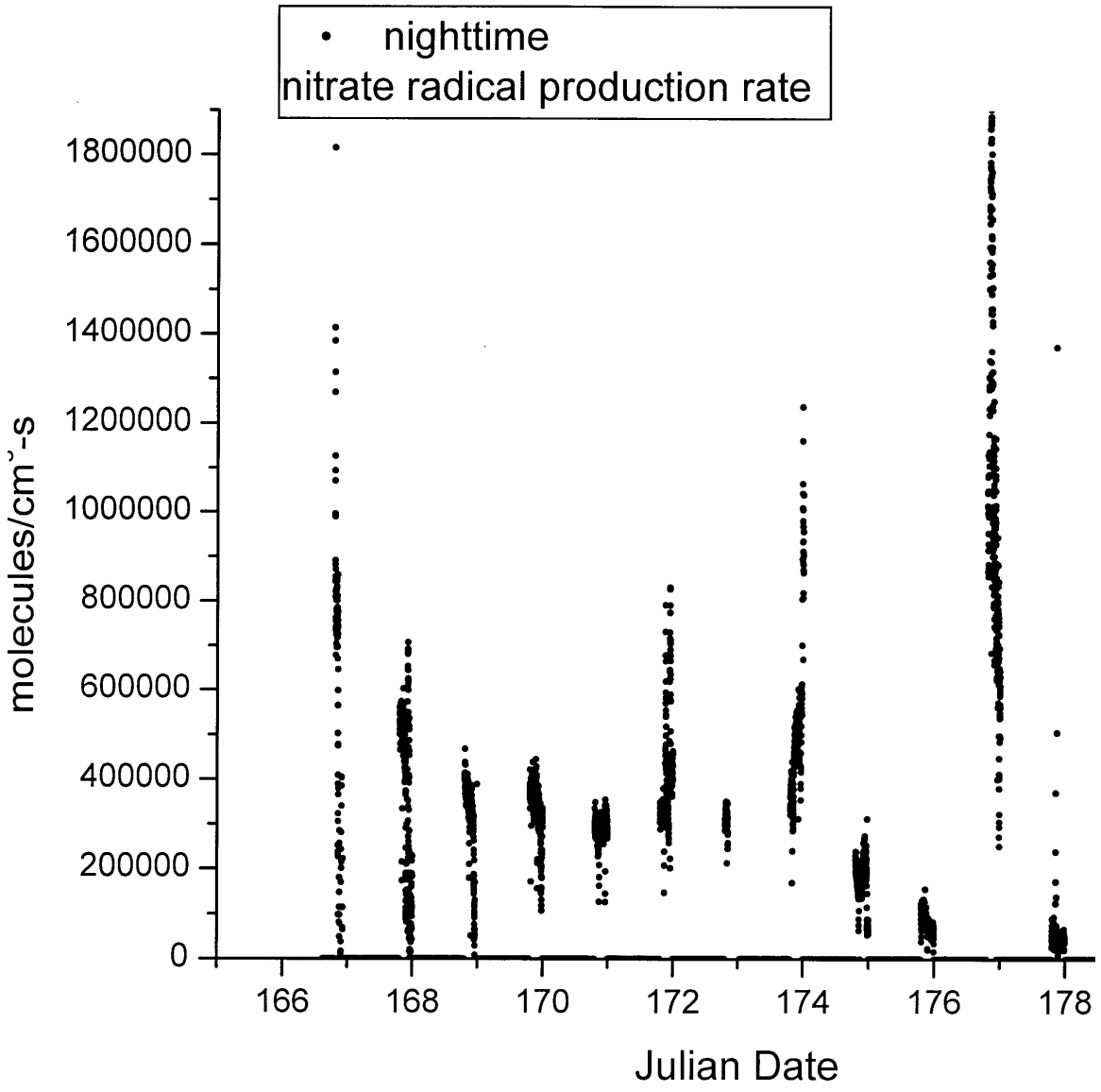


Figure 5. Nitrate radical production rates calculated from the measured $NO_2$ and $O_3$ levels at the Waddell site in 2001.