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Regional-Scale Influences on Urban Air Quality: A Field Study in Phoenix, Arizona

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2.1 REGIONAL-SCALE INFLUENCES ON URBAN AIR QUALITY: A FIELD STUDY IN PHOENIX, ARIZONA

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1. INTRODUCTION

Regional air quality can play an important role in determining whether urban ozone or PM-2.5 standards are exceeded. Background levels of nitrogen oxide species (NO_x) and their interactions with natural organics can generate secondary aerosol products via formation of nitric acid and its subsequent reaction with ammonia to form ammonium nitrate. Natural organics and reactive anthropogenic organic compounds, particularly aromatic species and monoterpenes, can also lead to the formation of secondary organic aerosols, contributing to the formation of PM-2.5. Long-range transport and chemical transformation of hydrocarbons and NO_x via both photochemical reactions and nighttime chemistry can yield significant regional levels of ozone and other oxidants, such as peroxyacyl nitrates (R-C=O-O-O-NO_2; PANs).

The PANs are key species in determining the apparent age of an air parcel (Gaffney *et al.*, 1989, 1993, 1997). The most common member of the family is peroxyacetyl nitrate (R=CH3-; PAN), which typically accounts for more than 85% of the PANs found in an urban or rural site. The PANs are in equilibrium with NO_2. Peroxyacyl radicals (R-C=O-O-O) are typically produced by the photooxidation reactions of organics, particularly those of aldehyde oxidation products with OH radical during the daytime (photochemically active) periods. Proposed mechanisms for nighttime formation of PANs (Gaffney *et al.*, 1989) include abstraction reactions of nitrate radical (NO_3) and the initiation of OH chemistry by olefin-ozone reactions.

Locally generated urban plumes can interact with regional-scale air pollutants, as well as locally generated natural organic hydrocarbons such as isoprene and monoterpene emissions from vegetation, in photochemically driven daytime chemistry and nighttime chemistry driven by nitrate and ozone. The formation of nitrate radical is coupled directly to ozone and NO_2 chemistry, because the source of nitrate radical at low concentrations is

$$NO_2 + O_3 \rightarrow NO_3 . \qquad [1]$$

Evaluation of these urban and regional interactions of NO_2, PANs, ozone, and nitrate radical requires fairly rapid measurements of these species and of light intensity and temperature. The measurements are required over a reasonable time period to determine regional background levels and to distinguish local versus regional chemistry and meteorology. As part of the recent Phoenix Air Quality Study of the Department of Energy's Atmospheric Chemistry Program, approximately four weeks of 1-min time-resolved data for NO_2, PANs, ozone, ultraviolet-B radiation (uv-B), and temperature were obtained in May-June 1998 at a site near Usery Mountain, above the nearby urban Phoenix air basin.

Gas-phase measurements included real-time NO_2, NO_x, ozone, PAN, uv-B, temperature, olefins, and nitric acid determinations. Size-fractionated aerosol samples were also collected and examined for optical properties and for natural radionuclides as a means of estimating the lifetimes of fine aerosols. Presented here are data for ozone, NO_2, total NO_x, PAN, uv-B, and temperature. The observations are discussed in terms of regional-scale and urban-scale chemical interactions and also in terms of the local boundary layer meteorology as it affects the daytime and nighttime levels of oxidants and fine aerosols.

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2. EXPERIMENTAL METHODS

The field site chosen for this part of the Phoenix study was located near Usery Mountain, just outside Mesa, Arizona. The site lies on a saddle between two hills overlooking the Phoenix air basin. Instrumentation was housed in an air-conditioned building. Air samples were monitored continuously by using an air pump that drew air from a nearby tower, located approximately 10 m from a sample inlet manifold. All sampling inlet materials were Teflon™ or stainless steel.

The sample inlet was attached to a tower, approximately 4 m above the ground. Ozone measurements were made by ultraviolet absorption (Dasibi Model AH-8000). Outside temperature was measured with a thermocouple (K-type). Ultraviolet-B radiation measurements, made with a Richardson-Berger radiometer (Solar Light Co.), were used to assess the effective photochemical light intensity at the site during the study. This radiometer allows direct continuous measurements of broad-band ultraviolet radiation (290-320 nm). A modified nitrogen oxides analyzer (Monitor Labs 8840) was used to estimate nitric acid and reactive olefin levels. Modifications involved replacing the red filter with a blue-green filter in one channel and using a nylon filter and a timer circuit to determine total nitrogen oxides less nitric acid. The data, obtained at 10-s frequency, were stored by using LabTech Notebook software and a 486 Pentium™ personal computer. Data were stored to floppy discs and to a SparQ™ drive (1.0 GB; Syquest) for further analysis.

A luminol-based chemiluminescence system with fast capillary gas chromatography was used to determine NO_2 and PANs. This method has been described in detail elsewhere (Gaffney *et al.*, 1998). Data obtained at 1-min intervals were stored on a laptop computer with Peak 96 (Hewlett-Packard) software.

Data were processed by using IBM-compatible personal computers and Excel (Microsoft) software. All data are 1-min averages, except for NO_2 and PANs, which were sampled at 1-min intervals.

A 2-cm^3 sampling loop was used. Samples were injected into a 3-m DB-1 capillary column for separation of the PANs and NO_2. Retention times for NO_2 and PAN at a carrier gas flow (5% O_2 in He) of 45 cm^3/min were 0.15 and 0.35 min, respectively. Calibration standards were made by dilution of a 100-ppb NO_2 certified gas standard and by using the wet chemical synthesis of PAN and diffusion tubes with n-tridecane as a low-volatility solvent (Gaffney *et al.*, 1984).

Hourly averaged data on ozone, CO, and NO_x were taken at this site during the study period by the Arizona Department of Environmental Quality. These data were supplied for comparison with the high-resolution data reported here.

3. RESULTS AND DISCUSSION

The concentrations of NO_2, PAN, and ozone and uv-B data determined during this study are shown graphically in Figs. 1-4. Temperatures during the study period ranged from 15 to 38.5°C (nighttime and daytime highs, respectively).

Comparison of the 1-min time-resolved ozone and NO_2 data with total NO_x and ozone data from the Arizona Department of Environmental Quality showed excellent agreement. Both data sets indicated that during the nighttime period, typically at midnight, a plume of pollutants passed by the Usery site. This behavior was strongly observed on Julian dates 143-152. Strong positive correlations of NO_2 and CO were observed on Julian dates 147, 148, 150, and 151, as Fig. 5 shows.

During the study period, ozone was observed to correlate negatively with the nighttime plume behavior (see Fig. 6). This observation strongly suggests that local combustion sources are producing NO in the Phoenix area during the early evening. The NO then reacts with ozone to form NO_2, leading to the negative correlation. The observation of correlated CO emissions during these events is consistent with these conclusions.

The winds during the study were typically from the north (Coulter, 1998). Thus, the pollution observed during the nighttime plume events at the Usery field site came from the Phoenix air basin. We also note that the PAN values observed during this study were generally below 1 ppb, consistent with the high daytime temperatures, typically above 35°C. The PAN measurements shown were reported only if the levels were above 0.5 ppb. The density of PAN points, therefore, is a good indication of the "photochemical ages" of the air parcels. During the periods of highest NO_2 levels (i.e., in the midnight plumes), PAN values were typically near or below 0.5 ppb. Ratios of PAN/NO_2 were observed to be typically below 1.0, consistent with the high-temperature environment of Phoenix.

Early in this study, evidence of Mexican fires was noticed in a decrease in visibility and a reduction in uv-B on Julian day 141, in regional air transported from the south-southeast. Interestingly, this regional-scale event was associated with a reduction in CO and relatively low levels of NO_2. At the end of the field sampling period, background levels of ozone and PAN were higher, possibly indicating that regionally polluted air from the west was being transported into the study area. An examination of the CO and NO_2 data for the study period supports a change in the regional air mass, because the CO levels were clearly higher, correlating with PAN increases and lower NO_2 values. This type of air chemistry is consistent with an older air mass that has undergone long-range transport.

Our data clearly indicate that background ozone values at the Usery field site vary with time. At this time of year, the Phoenix background ozone levels can apparently range from a low of 35 ppb to a high of 55 ppb. The regional long-range transport of ozone and its precursors has significant consequences for control strategies, particularly for areas like Usery Mountain and the adjacent Superstition Mountains, which are protected as public lands. Similar impacts are anticipated for transport of fine aerosols into the area.

This data set will allow us to estimate the NO_3 radical production rates in the Phoenix area for both regional and local air parcels. We are continuing to examine the data set and will be reporting the results of further analyses in light of the potential loss of NO_x through the NO_3 radical pathways, including N_2O_5 (which can also be estimated from our data set of NO_2 and O_3). The data set clearly indicates the importance of regional background ozone values in terms of the potential effectiveness of urban control strategies.

4. ACKNOWLEDGMENTS

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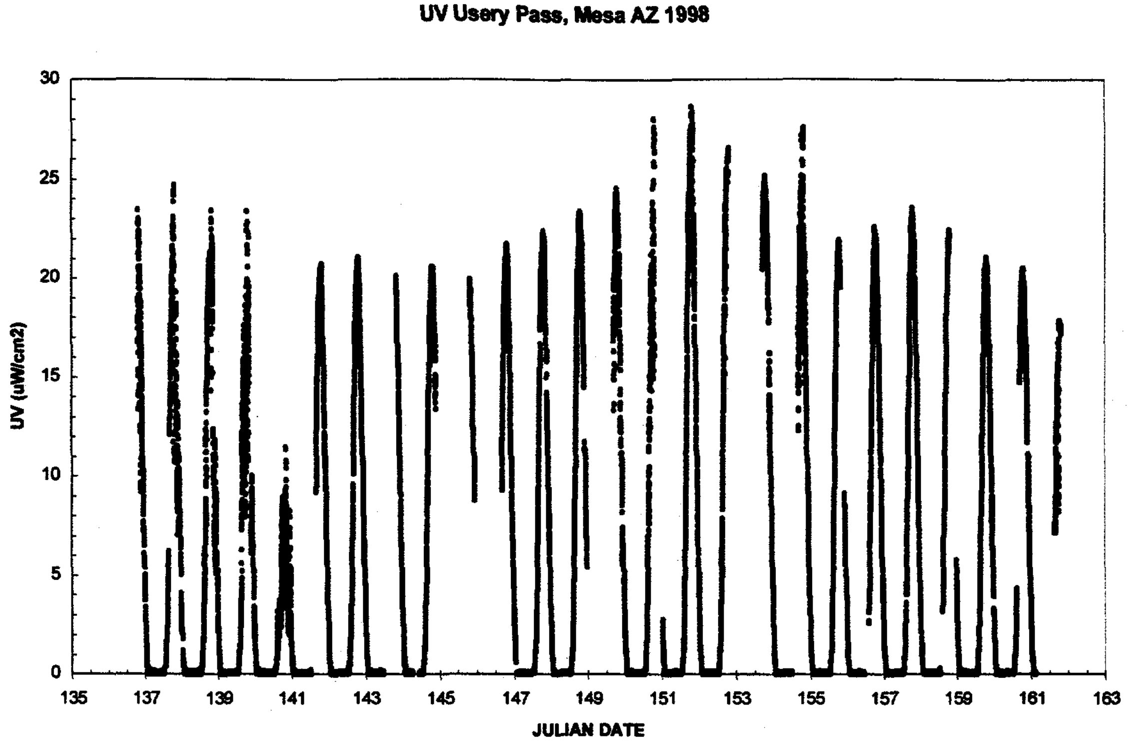

Figure 1. Ultraviolet-B measurements taken at the Usery Pass field site near Mesa, Arizona, on May 16- June 9, 1998.

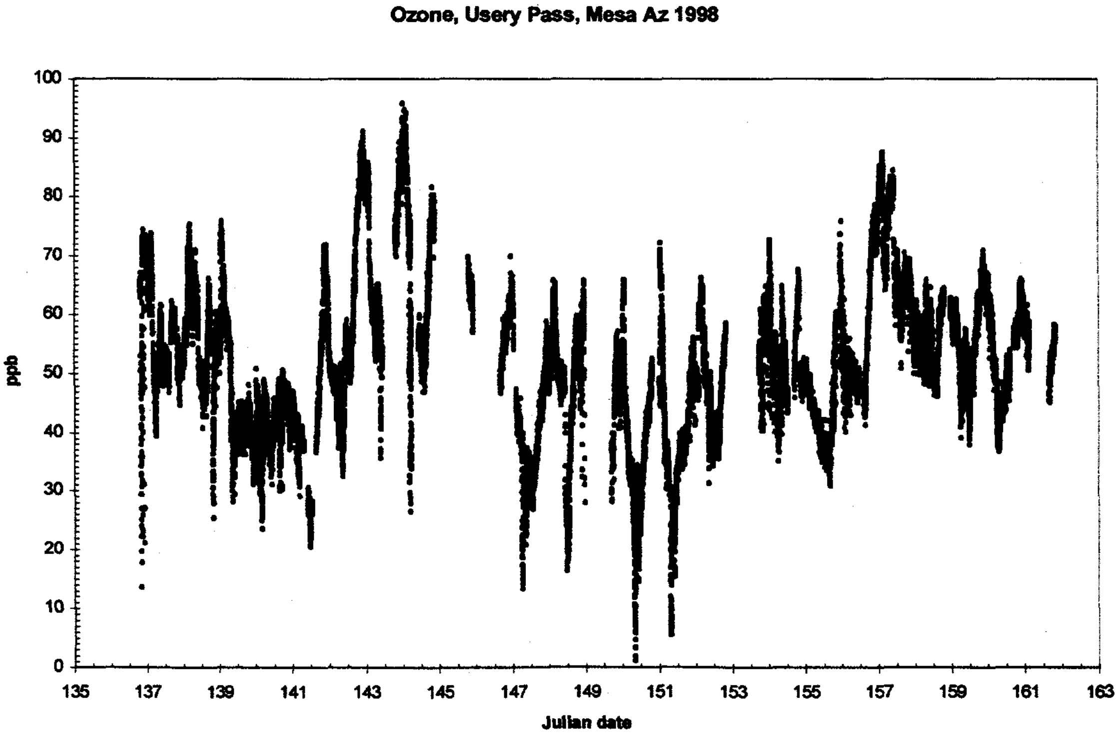

Figure 2. Ozone measurements at the Usery field site.

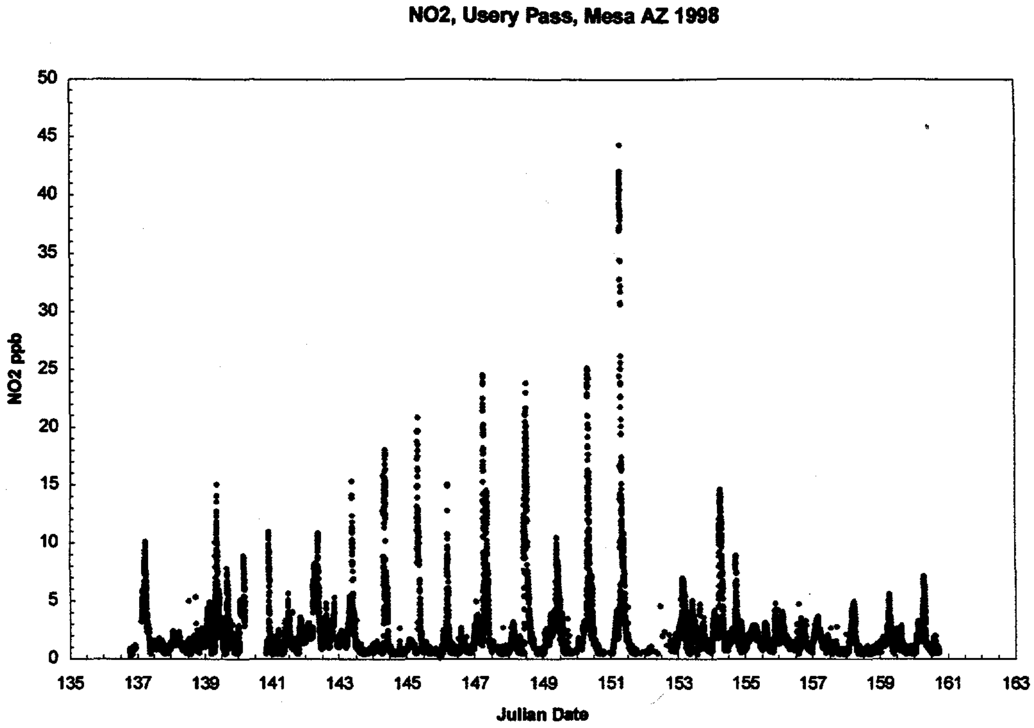

Figure 3. Nitrogen dioxide measurements at the Usery field site.

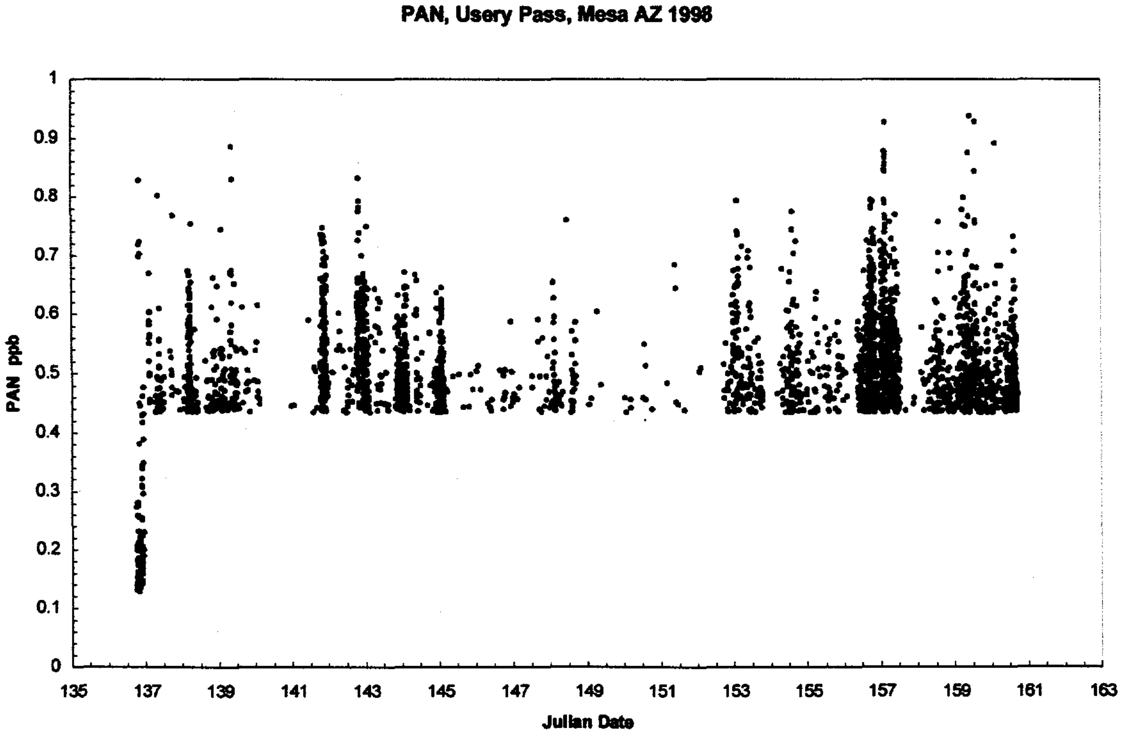

Figure 4. Peroxyacetyl nitrate measurements at the Usery field site. After Julian date 137, levels below 0.44 ppb are not shown.

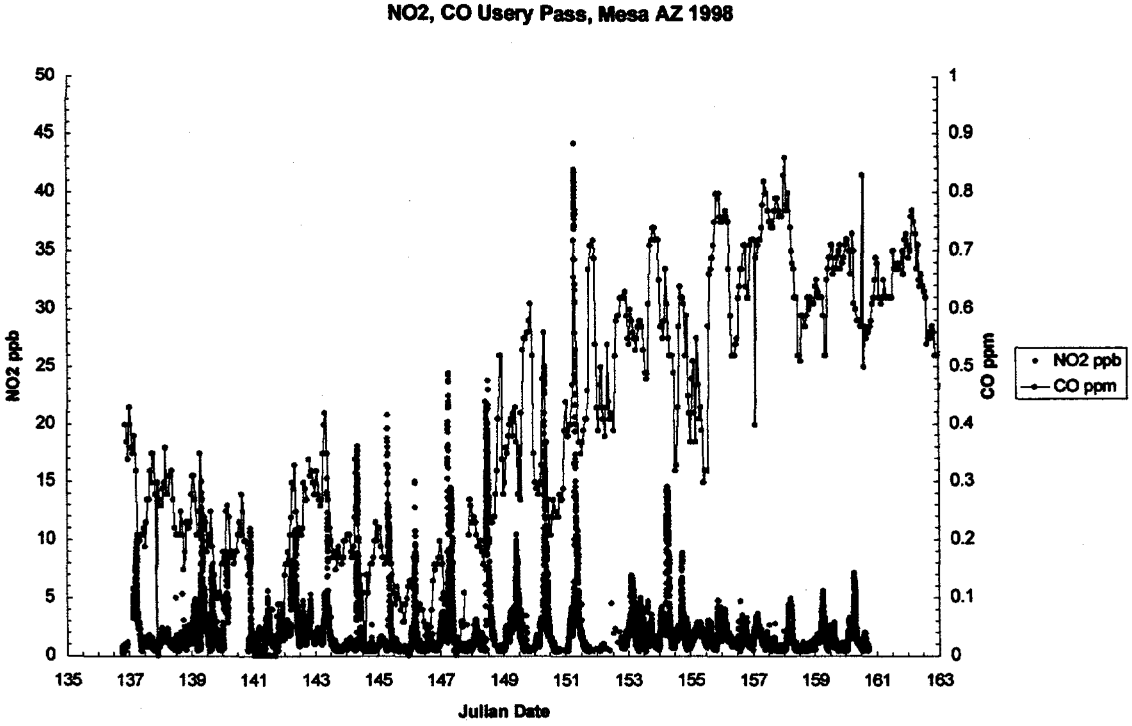

Figure 5. Comparison of nitrogen dioxide and carbon monoxide measurements at the Usery field site.

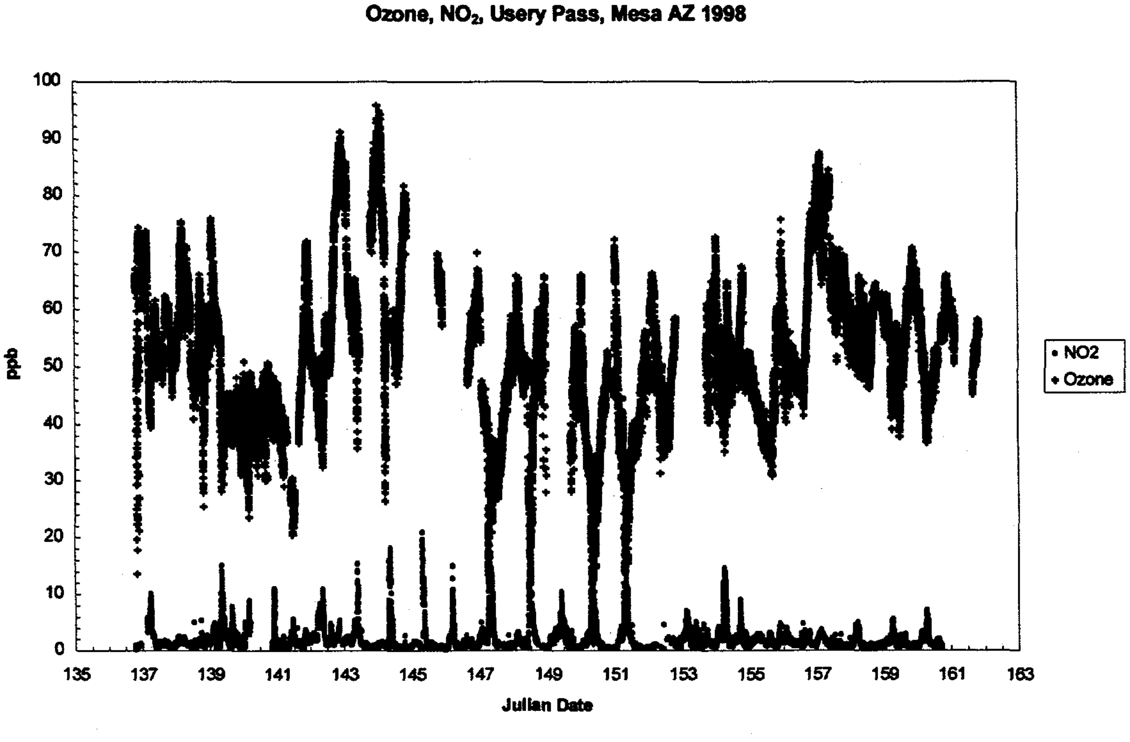

Figure 6. Comparison of ozone and nitrogen dioxide measurements at the Usery field site.