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PHOENIX, ARIZONA, REVISITED: INDICATIONS OF AEROSOL EFFECTS ON O_3, NO_2, UV-B, AND NO_3

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1. INTRODUCTION

Fine particulate matter and tropospheric ozone levels are of concern because of their potential for health impacts, as well as their radiative effects. Both ozone and PM-2.5 standards are being exceeded in many urban and regional areas where transport and background levels can appreciably affect observed concentrations. Anthropogenic nitrogen oxides and other primary pollutant species can interact with natural organics to form secondary aerosol products via synthesis of nitric acid and its subsequent reaction with ammonia to yield ammonium nitrate. In addition, natural organics and lower-reactivity organic compounds, particularly aromatic species and monoterpenes, can generate secondary organic aerosols, both of which contribute 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 generate significant regional levels of ozone (O_3) and other oxidants, such as peroxyacyl nitrates.

Peroxyacyl nitrates ($R\text{-}C{=}O\text{-}O\text{-}O\text{-}NO_2$; PANs) are key species in determining the apparent age of the background air that might be affecting an urban air parcel (Gaffney *et al.,* 1989; 1993; 1997). The most common member of the family is peroxyacetyl nitrate (PAN; $R{=}CH_3\text{-}$), which 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 ($R\text{-}C{=}O\text{-}O\text{-}O$). The PANs are produced by the oxidation reactions of organics, particularly reactions of aldehyde oxidation products with OH radical during daytime, photochemically active periods. The reaction of nitrate radical (NO_3) via abstraction with aldehydes has been proposed by a number of researchers (Gaffney *et al.,* 1989) as a nighttime mechanism for formation of PANs.

Locally generated urban plumes can interact with regional-scale air pollutants and reactive natural organic hydrocarbons, such as isoprene and monoterpene emissions from vegetation, in daytime chemistry driven by photochemistry and in nighttime chemistry driven by nitrate and ozone reactions. Such interactions can lead to oxidant and aerosol production. At night the formation of nitrate radical is coupled directly to ozone and nitrogen dioxide chemistry, because the source of nitrate radical at low concentrations is

$$NO_2 + O_3 \rightarrow NO_3 + O_2 . \qquad [1]$$

Aerosols can also affect the photochemistry by scattering actinic radiation, absorbing it, or both, as was reported recently for smoke from brush fires in Florida that resulted in a reduction of UV-B radiation (Kaye *et al.,* 1999). In addition, recent work in nonurban areas has indicated that aerosols can have a significant effect on ultraviolet radiation and resulting photochemistry, leading to ozone formation (Reuder and Schwander, 1999).

Evaluation of the urban and regional interactions of NO_2, PANs, O_3, and NO_3 requires high-frequency measurements of these species, plus light intensity and temperature. Identification of regional and background levels and assessment of locally versus regionally driven chemistry and meteorology further requires the measurements to be made over a reasonable time period. We previously reported preliminary results for the Phoenix, Arizona, air quality study of the U.S. Department of Energy's Atmospheric Chemistry Program (ACP; Gaffney et al., 1999). In that work, approximately four weeks of 1-min time-resolved data for NO_2, PANs, O_3, UV-B, and temperature were measured at a site near Usery Mountain, located above the nearby urban Phoenix air basin, in May-June 1998.

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Gas-phase measurements included real-time NO_2, NO_x, O_3, PAN, UV-B, temperature, olefins, and nitric acid. Size-fractionated aerosol samples were also collected at the site. Aerosol sample were examined for optical properties and for natural radionuclides as a means of estimating the lifetimes of fine aerosols. Reported here are further analyses of the data set, with a focus on the aerosol results, the effect of interaction with smoke from Mexican brush fires on Phoenix O_3 backgrounds and UV-B levels, and the formation of nighttime plumes of NO_2 (up to 50 ppb) observed at Usery Pass. The last observation is discussed with regard to the consequences for high nitrate radical production rates on the edges of the Phoenix urban plume and the subsequent downwind chemistry of aerosol and oxidant formation on regional scales.

2. EXPERIMENTAL METHODS

The field site chosen for this part of the Phoenix air quality study is located near Usery Mountain, just outside Mesa, Arizona. The site is at a saddleback between two hills overlooking the Phoenix air basin. Instrumentation was housed inside an air-conditioned building. Air samples were monitored continuously by use of an air pump that drew air from a tower approximately 10 m from a sample inlet manifold. All sample inlet materials were Teflon^{Tm} or stainless steel. The sample inlet was approximately 4 m above the ground on a tower. Ozone measurements were made via ultraviolet absorption (Dasibi Model AH-8000). Outside temperature was measured with a thermocouple (K-type). Ultraviolet-B radiation measurements from 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 measurement of broadband ultraviolet radiation (290-320 nm). A modified NO_x analyzer (Monitor Labs 8840) was used in an attempt to estimate levels of nitric acid and reactive olefins. Modifications involved changing the red filter to a blue-green filter in one channel, as well as using a nylon filter and a timer circuit to look at total nitrogen oxides less nitric acid. These data were obtained at a 10-s frequency and stored by using LabTech Notebook software and a 486 Pentium^{TM} personal computer. Data were stored to floppy discs and to a SparQ^{TM} drive (1.0 GB, Syquest) for further analysis.

A luminol-based chemiluminescence detection system with fast capillary gas chromatography was used to measure NO_2 and PANs. This method has been described in detail elsewhere (Gaffney *et al.,* 1999). Data were obtained at 1-min intervals and stored on a laptop computer using Peak 96 (Hewlett-Packard).

Data were processed with personal computers and Excel (Microsoft). All data are 1-min averages except for NO_2 and PANs, which were sampled at 1-min intervals. For these studies, a 2-cm^3 sampling loop was used, and 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 (5% O_2 in He) flow rate 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 O_3, CO, and NO_x were taken simultaneously at this site by the Arizona Department of Environmental Quality (ADEQ). The results were supplied for comparison with the high-resolution data reported here.

3. RESULTS AND DISCUSSION

The concentrations of NO_2 and O_3, as well as UV-B data taken during this study, are shown graphically in Figures 1-4. Nighttime and daytime high temperatures during this period ranged from 15°C to 38.5°C, respectively.

Our NO_2 data and the ADEQ data for NO_x were found to be in excellent agreement, as were the Argonne and ADEQ O_3 data sets. Both the Argonne and ADEQ data captured a nighttime plume of pollutants that typically traversed the Usery site at midnight. This behavior was strong during the period of sampling. Figure 1 is a comparison of the O_3 and NO_2 profiles during the sampling period. The arrows mark periods during the evening hours when the nocturnal planetary boundary layer meteorology led to the titration of O_3 by locally emitted NO. This nighttime titration in the boundary layer results in the production of NO_2 by the following reaction:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad [2]$$

Thus, reaction 2 leads to a reduction of O_3 in the nocturnal boundary layer with the concurrent production of NO_2.

The winds during this time were typically from the north (Coulter, 1998). Thus, the pollution observed during these nighttime plume events at the Usery field site is from the Phoenix air basin. Also of interest is that the PAN values observed during this study were generally below 1 ppb, consistent with high daytime temperatures typically above 35°C. During the periods of highest NO_2 concentration (during the midnight plumes), PAN values were typically below 0.1 ppb. Ratios of PAN/NO_2 were typically below 1.0, consistent with the high-temperature environment of Phoenix during the entire sampling period.

The strong anti-correlation between O_3 and NO_2 is consistent with reaction 2 being followed by transport of the NO_2-enriched, O_3-depleted plume over the Usery Pass sampling site.

In Figure 2, ADEQ data for CO are compared to the NO_2 profiles. Arrows mark periods when the NO_2 plumes were measured and CO levels were shown to correlate. These results indicate that the NO_2 plumes were associated with CO emissions, suggesting that mobile sources in the Valley of the Sun contributed to of the observed phenomenon. Early in the sampling period, CO levels were very low on Julian Day (JD) 141. Background levels of CO increased from JD 149 to JD 160, as did O_3 (see Figure 1), indicating that long-range transport of material from southern California was occurring. PAN levels were also observed to be higher, consistent with an older air parcel.

The period of low CO on JD 141 was accompanied by a significant amount of smoke aerosol transported to Phoenix from Mexican brush fires in progress at this time. Figure 3 compares O_3 and UV-B measurements taken at the Usery Pass site that clearly demonstrate the decrease in UV-B and O_3 accompanying this smoke event. Similar observations in rural Germany were attributed to aerosols (Reuder and Schwander, 1999), and a decrease in UV-B was observed over Florida during wild fires (Kaye *et al.*, 1999). Observed NO_2 levels in the range of 1-6 ppb during this period were more typical of a fairly well mixed air mass transported over a long range (JD 156-JD 160; Figure 2).

These results strongly indicate that smoke aerosols can substantially reduce UV-B radiation and hence reduce photochemical production of O_3. This observation is consistent with findings for a nonurban region (Reuder and Schwander, 1999). The observation also indicates that aerosols can play an important role in the actinic radiative balance of the atmosphere, leading to lower O_3 levels. Visibility was strongly reduced during our study, although the conditions were not cloudy. The reduced visibility was probably due to carbonaceous soot aerosols (black carbonaceous soot), which are known to be both a strong light absorber and a light scatterer.

Our data clearly indicate that background ozone levels at the Usery field site vary with time. At this time of year, the Phoenix O_3 background can apparently range from a low of 35 ppb to a high of 55 ppb. Regional long-range transport of O_3 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. The observed plumes of NO_2 pose an interesting problem for the potential downwind formation of O_3 over the nearby forested sites, particularly when plumes of NO_2 in the 20- to 50-ppb range were observed during a number of these episodes.

The observation of NO_2 plumes has other consequences. Nitrate radical formed by reaction 1 is in equilibrium with N_2O_5 by the following reaction with NO_2:

$$NO_2 + NO_3 \leftrightarrow N_2O_5 \qquad [3]$$

Reaction 3 is very rapid. In an environment with high humidity or high aerosol loadings, reactions of N_2O_5 can lead to rapid loss of NO_3 and aerosol nitrate formation. Thus, the absolute levels of NO_3 in this environment will likely be lower than the formation rates calculated by using reaction 2 would indicate. Note, however, that the Phoenix aerosol loadings measured at the Usery Mountain site with cascade impactors and a sampling time of one week were typically in the range of 7-10 $\mu g\ m^{-3}$. In addition, relative humidity levels in Phoenix are typically very low, and thus the production rates for NO_3 serve as a first-order estimate of the maximum levels for nighttime events.

Although NO_3 photolyzes rapidly during the daytime (Finlayson-Pitts and Pitts, 1986), it is a very reactive oxidant capable of initiating important nighttime chemistry. Figure 4 Is a comparison of UV-B data and NO_3 production rates based on reaction 1 and calculated on a 1-min basis from our O_3 and NO_2 data sets. These production rates do not take into account loss or storage reactions like reaction 3. The calculations do suggest the potential of NO_3 to participate in nighttime chemical reactions, when the UV-B levels are low. These periods are denoted by arrows in Figure 4. Note that NO_3 production is far from constant. Indeed, as noted by the arrows in the figure, high levels of NO_3 are produced on the edges of the nocturnal plumes, where the O_3 and NO_2 mix. In these same areas, NO_3 could form N_2O_5 or react with natural hydrocarbons like isoprene or monoterpenes. In both cases, the resulting products would probably be nitric acid and organic species that would contribute to fine-aerosol loading during regional transport out of the area.

The data sets obtained in our Phoenix study clearly indicate the importance of the interaction of regional background chemistry and urban plume chemistry for the overall air quality of the region. We will need to consider coupled mixing phenomena like nocturnal boundary layer processes and plumes transported over long distances to devise urban control strategies that will be effective both locally and regionally.

4. ACKNOWLEDGMENTS

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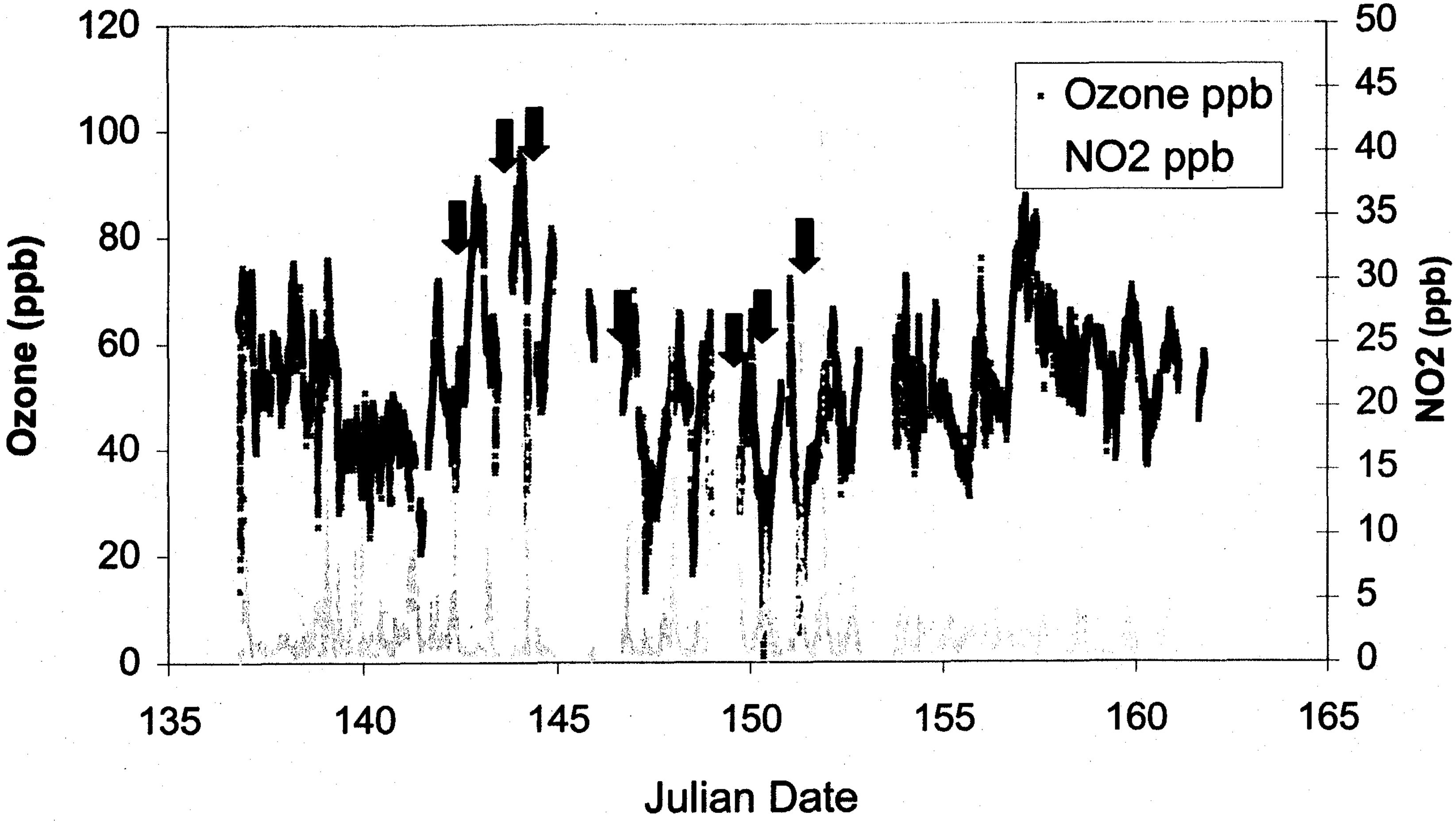

Figure 1. Comparison of ozone and nitrogen dioxide data for Usery Pass during this study. Arrows indicate time periods where the meteorology led to nocturnal boundary layer NO titration of ozone.

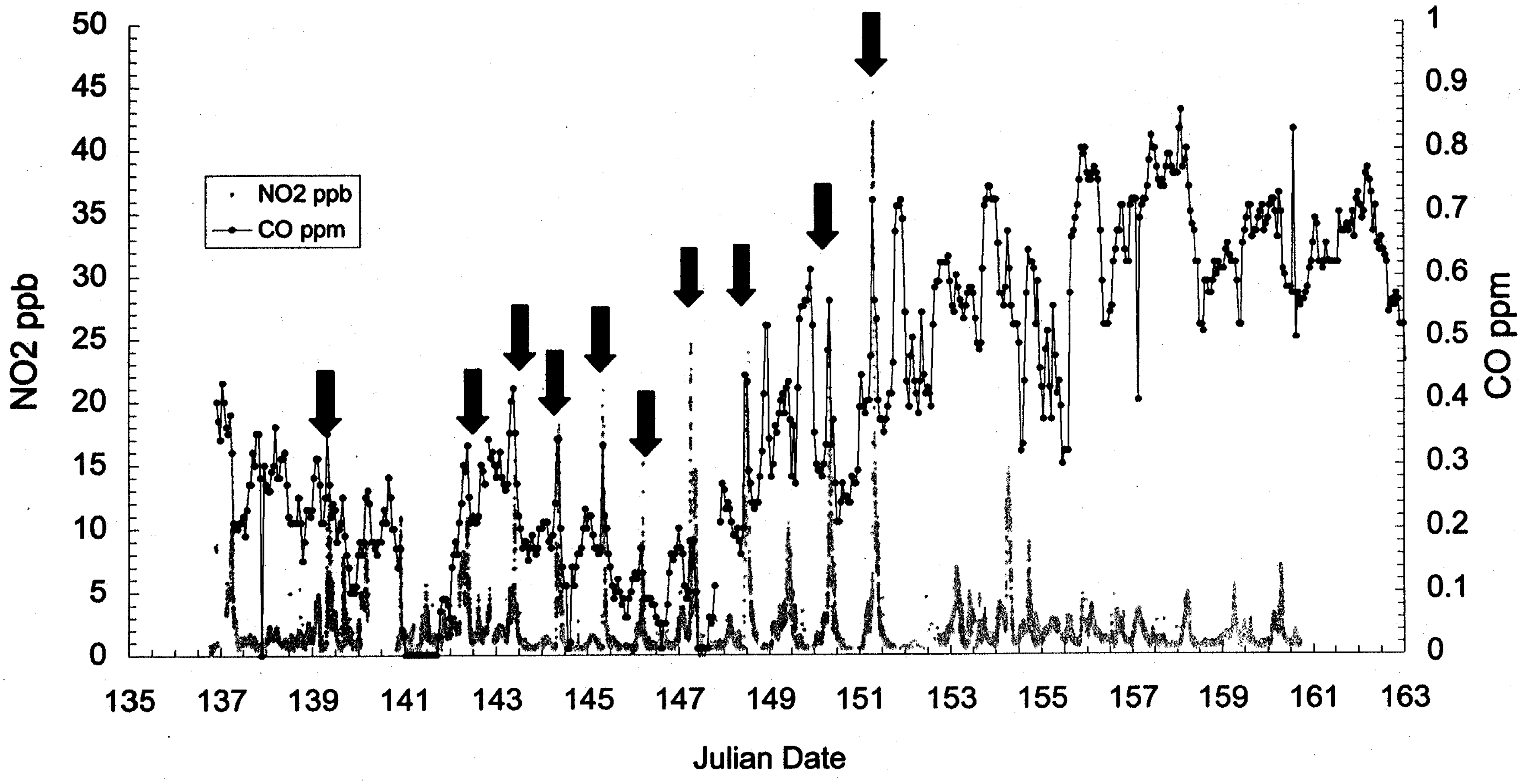

Figure 2. Comparison of nitrogen dioxide and ADEQ CO profiles for Usery Pass site. Arrows show time periods when both nitrogen dioxide and CO peaks were correlated, indicating local sources.

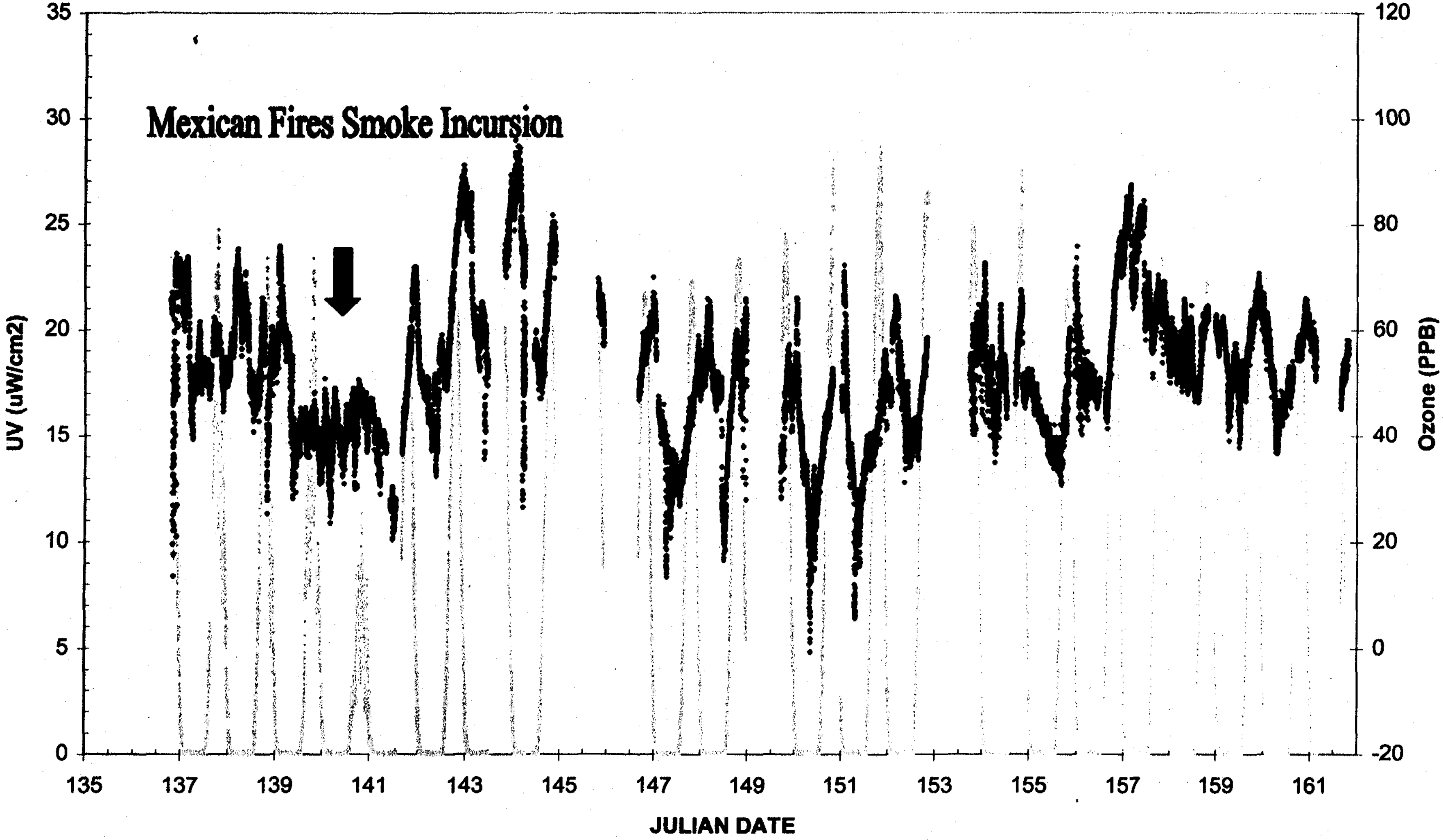

Figure 3. Ozone and UV-B comparison showing approx. 50% reduction in UV-B and 15 ppb ozone during the Mexican fires smoke incursion. Arrow denotes time period of smoke event in Phoenix.

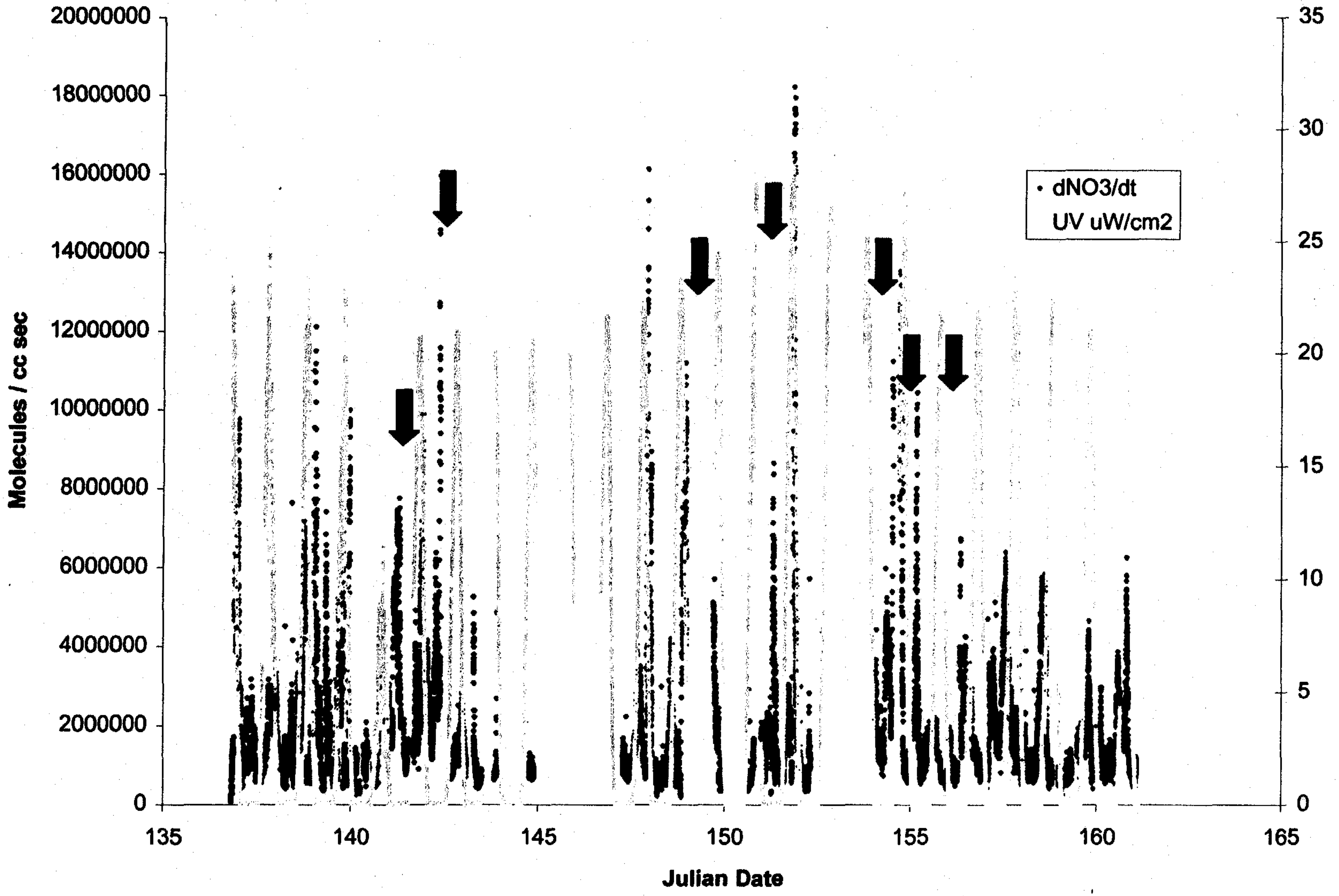

Figure 4. Comparison of UV-B data with calculated nitrate radical production rates. Note that nitrate radical is rapidly photolyzed. Arrows indicate periods of high nitrate radical and low UV-B are when it will act as an oxidant.