

NORTHEAST OXIDANT AND PARTICLE STUDY (NEOPS):
PRELIMINARY RESULTS FROM THE CENTERTON, NEW JERSEY, FIELD SITE

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1. INTRODUCTION

During the summer of 1999, the Northeast Oxidant and Particle Study (NEOPS), as part of the North American Research Strategy for Tropospheric Ozone (NARSTO), investigated the factors leading to the occurrence of increased levels of ozone and fine particles during the summer months in the northeastern United States. The primary NEOPS air sampling station was located in the city of Philadelphia, Pennsylvania, at the Baxter Water Treatment Plant on the west bank of the Delaware River, northeast of the city center. Supplemental chemistry and meteorology measurements were taken at Centerton, New Jersey, a rural site 30 miles south of Philadelphia and 25 miles north of Delaware Bay. This paper reports the preliminary atmospheric chemistry and aerosol results obtained at the rural sampling site near Centerton. In particular, the nitrogen dioxide (NO_2) and peroxyacetyl nitrate (PAN) data obtained with our second-generation luminol instrument are discussed and compared to results obtained with conventional nitrogen oxides (NO_y) measurements.

Ozone (O_3), NO_y , ultraviolet-B (UV-B), and nephelometry data were obtained at Centerton at 1-min intervals for a period of 20 days (July 24-August 12). Aerosol samples collected with cascade impactors were analyzed for ^{210}Pb , ^{210}Po , and ^{210}Bi as a means of estimating the aerosol residence times.

Data on NO_2 and PAN were obtained at 1-min intervals by using a new, second-generation fast gas chromatography (GC) system with luminol detection. Measurements of these species at time intervals shorter than 1 min have been difficult in the past. The rapid analysis time allowed for the determination of nighttime nitrate radical (NO_3) production rates, as well as PAN/ O_3 and PAN/ NO_2 concentration ratios. An important intermediate in the photochemical production of O_3 , PAN acts as a reservoir for NO_2

(Singh, 1987; Finlayson-Pitts and Pitts, 2000). Its stability at low temperatures, low reactivity with OH radical, photochemical stability, and low aqueous solubility give PAN a longer atmospheric lifetime than other reactive nitrogen species; therefore, it is a key species in determining the apparent age of a background air parcel when measured simultaneously with NO_2 (Gaffney et al., 1989, 1993, 1998). Results will be discussed in terms of local and regional production and transport of ozone.

2. SECOND-GENERATION LUMINOL SYSTEM

The peroxyacyl nitrates are typically monitored by using GC with electron capture detection (see reviews by Gaffney et al., 1989; Roberts, 1990). However, this approach is affected by significant responses due to oxygen and water vapor, and time resolution faster than about 4 min is difficult to achieve. Typically measurements are obtained at 15- to 30-min resolution (for example, see Gaffney et al., 1999).

We have demonstrated that fast capillary GC coupled with luminol detection can accomplish direct measurement of NO_2 and PAN simultaneously in less than 1 min. The first-generation fast GC-luminol detection system for NO_2 and PAN was described in detail previously (Gaffney et al., 1998). We modified the first instrument by replacing the Unisearch (Scintrex) LMA-3 luminol detection system with a reaction cell and a Hamamatsu photon counting detection module (HC-135), which is computer controlled with Q-Basic software. A smaller peristaltic pump and mass flow controllers were added to maintain flow rates in the system. The second-generation instrument is now capable of 30-sec time resolution. Calibration standards for PAN were made by using diffusion tubes containing PAN synthesized by the wet chemical method (Gaffney et al., 1984). Field calibrations were accomplished with commercially available NO_2 gas standards.

3. OTHER INSTRUMENTATION

Ozone measurements were taken by using UV absorption (Dasibi Model AH-8000). The UV-B radiation measurements, used to assess the effective photochemical light intensity, were taken with a Robertson-Berger radiometer (Solar Light Co.). This radiometer allows direct continuous measurement of

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broadband UV radiation (290-320 nm). Outside temperature was measured with a K-type thermocouple. Measurements of NO and NO_y were obtained with a chemiluminescent nitrogen oxide analyzer (Monitor Labs 8840). The aerosol scattering extinction coefficient (b_{scat}) was measured by nephelometry (MRI Model 1567).

Aerosol samples were collected by using a nine-stage cascade impactor (Graseby-Anderson Model 20-800) at a flow rate of 0.028 m³/min (1 scf/min) with sample collection times of approximately 6 days. Samples were collected on Teflon membranes in stages 1-8 and on a glass membrane filter in the final stage. To evaluate the aerosol atmospheric residence times, ²¹⁰Pb, ²¹⁰Bi, and ²¹⁰Po were determined on the samples as a function of aerosol size (Marley et al., 2000).

4. RESULTS

The O₃ measurements obtained at Centerton are shown in Figure 1. The maximum O₃ levels were observed on Julian day 205 (July 24), the first day of monitoring. The daytime maximum ozone concentrations for all days exceeded 80 ppb, with 10 days \geq 100 ppb.

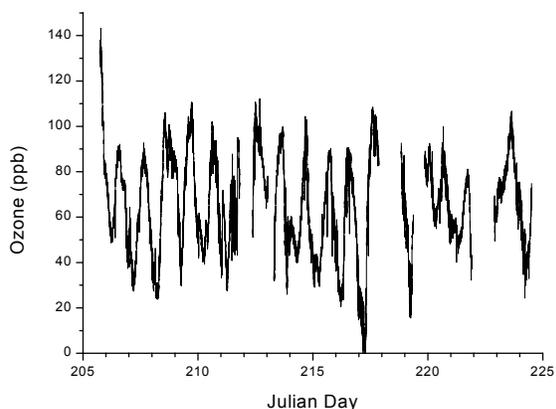


Figure 1. Ozone concentrations (ppb) at Centerton on July 24-August 12, 1999.

Measurements of the nitrogen oxides (NO and NO_y) obtained with the conventional chemiluminescence analyzer are shown in Figure 2.

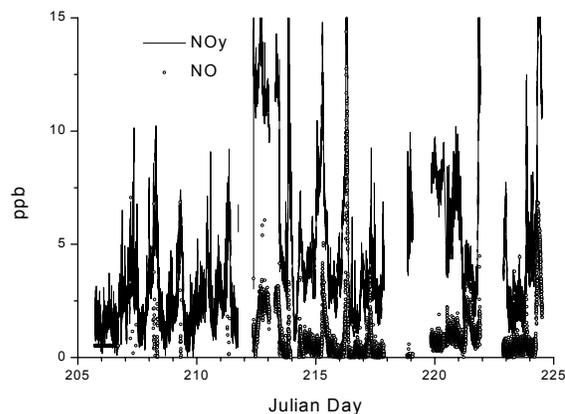


Figure 2. Measurements of NO and NO_y (ppb) at Centerton on July 30-August 11, 1999.

On a number of mornings with very calm conditions, we observed a rapid rise in NO levels at sunrise, accompanied by a decrease in O₃ in the shallow boundary layer due to titration by the NO, and concurrent production of NO₂ (see Figure 3) by reaction [1]:



This is the expected response for deposition of nitrogen oxides (HNO₃, NO₂, etc.) to soil surfaces, followed by heterogeneous production of HONO at night and its rapid photolysis at daybreak to produce NO. Because deposition of nitrogen oxides to surfaces is known to lead to the formation of HONO in indoor air and in urban centers (Finlayson-Pitts and Pitts, 2000), we propose that similar chemistries are occurring in rural soils. Very rapid NO production associated with the photolysis of HONO would be a reasonable explanation for the observed rapid increase in NO at daybreak.

The potential for HONO to be the source of NO has some interesting implications for soil chemistry, the early morning boundary layer, or both, depending on whether HONO is on the soil surface or in the air. This is because photolysis leads to production of OH, a very strong oxidizing agent. Clearly, better radiation measurements and direct measurement of HONO to assess this process and its importance in rural O₃ and oxidant production would be of interest.

The results of PAN and NO₂ measurements obtained with the second-generation GC/luminol instrument are shown in Figure 3. These results agree well with the NO_y data presented in Figure 2. Differences in the sum of NO₂ + PAN concentrations and total NO_y minus NO are probably due to HNO₃ or nitrate aerosol.

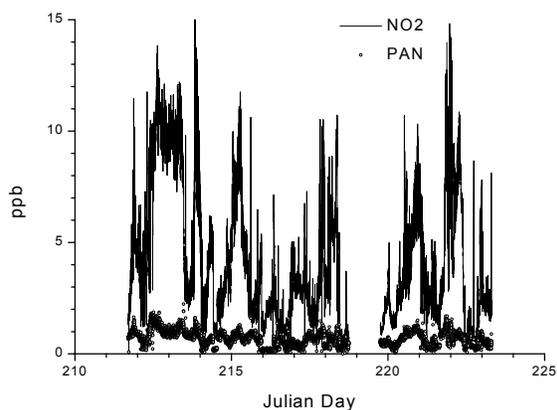
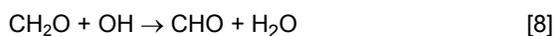
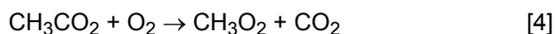
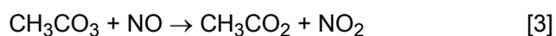


Figure 3. PAN and NO₂ concentrations (ppb) at Centerton on July 30-August 11, 1999.

The PAN levels measured at the Centerton site were quite high, exceeding 1 ppb on most days, even though daytime temperatures reached 30-40°C. Because PAN is in thermal equilibrium with NO₂ and the peroxyacetyl radical (CH₃CO₃), at higher temperatures PAN can undergo unimolecular decomposition back to these species via reaction [2]:



Loss of PAN can then occur if the peroxyacetyl radical undergoes further reaction before back-reacting with NO₂ to reform PAN. The important reactions for this loss of the peroxyacetyl radical are with NO and HO₂, the former being dominant when NO is abundant. This reaction in turn forms NO₂ and more peroxy radicals, which can form more NO₂ from NO. Thus, the following reactions show that the reaction of peroxyacetyl radical in the presence of NO can lead to significant NO₂ formation:



During daytime photochemical oxidation of organic species leads to formation of peroxyacetyl radical via OH reactions. During nighttime PAN decomposes thermally, leading to the formation of NO₂ in the presence of NO. The PAN/NO₂ ratio then should show a strong diurnal variation, with higher values during the day and lower values at night, when the loss of PAN leads to NO₂ formation.

The ratio of PAN/NO₂ concentrations is plotted in Figure 4 along with the ambient temperature, and the ratio for PAN/O₃ is shown in Figure 5.

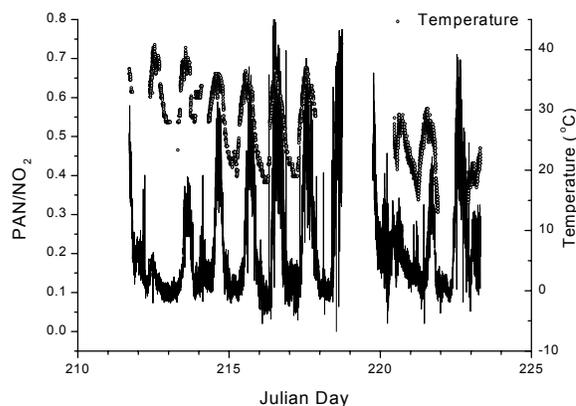


Figure 4. The ratio of PAN/NO₂ concentrations and ambient temperature (°C) at Centerton on July 30-August 11, 1999.

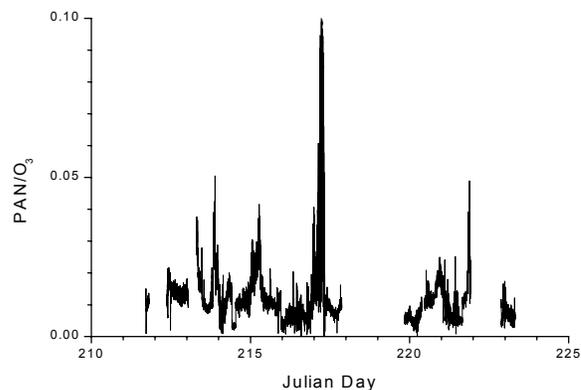


Figure 5. The ratio of PAN/O₃ concentrations at Centerton on July 30-August 11, 1999.

The PAN/O₃ ratio also shows some diurnal variation that is due to the formation of O₃ from the reaction of

peroxy radical with NO. The ratios for PAN in the Centerton site are lower than ratios seen in many areas, except for Julian day 217, perhaps because the

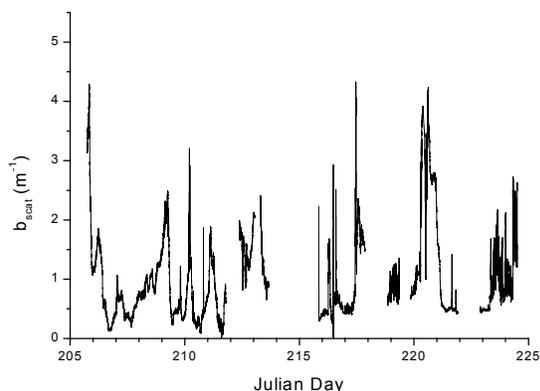


Figure 6. Aerosol scattering extinction coefficient, b_{scat} (m^{-1}) obtained at Centerton on July 24-August 12, 1999.

Table 1. Aerosol residence times calculated from the $^{210}\text{Po}/^{210}\text{Pb}$ ratios for samples collected at Centerton.

Date in 1999	D (μm)	$^{210}\text{Po}/^{210}\text{Pb}$	Age (days)
7/24-7/30	9.2	0.112	32
	5.8	0.139	39
	4.2	0.142	40
	3.1	0.107	31
	2.0	0.177	50
	1.05	0.156	44
	0.62	0.125	35
	0.43	0.101	29
	0.1	0.132	37
7/30-8/6	9.2	0.131	37
	5.8	0.095	27
	4.2	0.144	41
	3.1	0.159	45
	2.0	0.106	30
	1.05	0.156	44
	0.62	0.094	27
	0.43	0.085	25
	0.1	0.069	20
8/6-8/12	9.2	-	-
	5.8	0.156	44
	4.2	0.137	39
	3.1	0.125	35
	2.0	0.129	36
	1.05	0.133	37
	0.62	0.110	31
	0.43	0.136	39
	0.1	0.138	39

titration of ozone by NO is much faster than the thermal decomposition of PAN. This fact leads to less O_3 relative to the PAN levels and higher observed values for PAN/ O_3 .

The aerosol scattering extinction coefficient is shown in Figure 6, and aerosol residence times as determined by the $^{210}\text{Po}/^{210}\text{Pb}$ ratio (Marley et al., 2000) are shown in Table 1. The residence times for the samples collected at Centerton range from 20 to 50 days, with an average of 36 days. The period of high aerosol loading around Julian day 220 (August 8) corresponds with an average aerosol age of 36 days.

The UV-B radiation measurements used to assess the effective photochemical light intensity are shown in Figure 7. Aerosols can affect photochemistry by scattering and/or absorbing actinic radiation. This effect was recently reported for smoke events in Phoenix, Arizona (Gaffney et al., 2001). The high particulate levels on day 220 are accompanied by decreased UV-B radiation, indicating a reduction in effective photochemical light intensity and therefore a reduction in overall photochemistry and lower levels of O_3 , PAN, and NO_2 .

Urban plumes can interact with regional-scale pollutants and reactive natural organic hydrocarbons, such as isoprene and monoterpenes, in both photochemically driven daytime chemistry and NO_3 - and O_3 -driven nighttime chemistry. These reactions can lead to both oxidant and aerosol production. At night the formation of NO_3 is coupled to O_3 and NO_2 chemistry by reaction [11].

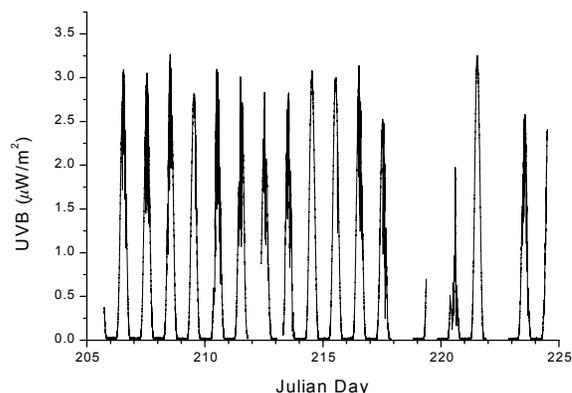


Figure 7. Broadband UV-B radiation (290-320 nm) at Centerton on July 24-August 12, 1999.



Although NO_3 photolyzes rapidly during the daytime, it is a very reactive oxidant that can initiate important nighttime chemistry. Production rates for NO_3 can be calculated from the NO_2 , O_3 , and temperature data, along with reaction rates published by others (Atkinson et al., 1997), via Equation [12]:

$$d[\text{NO}_3]/dt = k[\text{NO}_2][\text{O}_3] \quad [12]$$

Results of this calculation are shown in Figure 8. The highest NO_3 production rate, for Julian day 220, corresponds to the period of high aerosol loading.

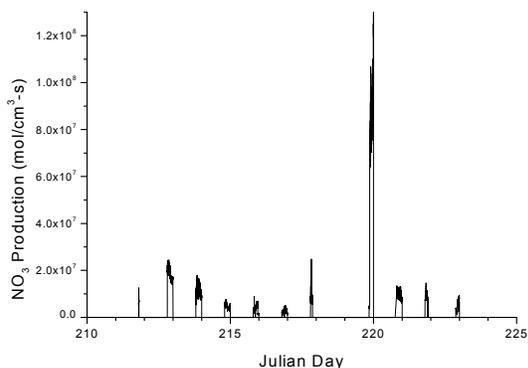


Figure 8. Nighttime NO_3 (molecules/ $\text{cm}^3 \cdot \text{s}$) production rates, neglecting loss mechanisms, calculated from equation [12] for July 30-August 11, 1999, at Centerton.

4. CONCLUSIONS

This work demonstrated that the second-generation fast GC/luminol detection system for monitoring NO_2 and PAN can be run for reasonably long periods in ground-based field sites. The rapid measurements of NO_2 and PAN made possible with the new instrumentation enable calculation of NO_2/PAN and O_3/PAN ratios, as well as NO_3 production rates.

Rapid measurements of NO and UV-B radiation suggest that HONO produced on soils is photolyzed in the early morning to generate a rapid burst of NO. The potential for HONO to be the source of NO has some interesting implications for soil chemistry, the early morning boundary layer, or both, depending on whether HONO is on the soil surface or in the air. This is because photolysis leads to production of OH, a very strong oxidizing agent. Clearly, better radiation measurements and direct measurement of HONO to assess this process and its importance in rural ozone and oxidant production would be of interest.

The PAN/ NO_2 ratio shows very strong diurnal variation at this site, consistent with photochemical generation of PAN with subsequent production of NO_2 by the reaction of PAN with NO at night. These results indicate that PAN decomposition during hot summer evenings can be an important source of peroxy radicals and formaldehyde. The NO_2 formed from this nighttime chemistry can also be involved in nitrate radical

reactions that should be considered in the chemical oxidations.

6. ACKNOWLEDGMENTS

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