J4.4 ANALYSIS OF THE MEXICO CITY URBAN PLUME AT ALTZOMONI SITE AT 4.000 M A.S.L.

B. Rappenglück *
Department of Geoscience, University of Houston, Houston, USA

R. Steinbrecher, R. Forkel
Institute of Meteorology and Climate Research, Atmospheric Environmental Division, Forschungszentrum Karlsruhe GmbH (FZK), Garmisch-Partenkirchen, Germany

J. Allan
School of Earth, Atmospheric & Environmental Sciences, University of Manchester, United Kingdom

L. Russell
Scripps Institution of Oceanography, University of California at San Diego, La Jolla, USA

M. Grutter, D. Baumgardner
Centro de Ciencias de la Atmósfera – UNAM, Universidad Nacional Autónoma de México (UNAM), México

1. INTRODUCTION

It is well known that urbanized zones represent areas where significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. Particularly in tropical and subtropical regions, where intensive global radiation and high daytime temperatures are usually observed, many dynamic metropolitan areas exist nowadays and both their number and their size are continuously growing.

The metropolitan area of Mexico City with approximately 20 million inhabitants is not only a large area with significant releases of various anthropogenic pollutants, but being located at about 2.300 m a.s.l. these emissions are already injected at a higher altitude into the troposphere. The surrounding mountains which reach up to almost 5.500 m a.s.l. help to transport these emissions into even higher altitudes due to mountain venting.

This paper reports results from a field campaign in March 2006 performed at the Altzomoni site located at about 4.000 m a.s.l. between the two volcanoes Iztaccíhuat (5.286 m a.s.l) and Popocatépetl (5.462 m a.s.l). approximately 60 km to the southeast of Mexico City. The measurements were carried out during March 2006.

* *Corresponding author address*: Bernhard Rappenglück, Department of Geoscience, University of Houston, 4800 Calhoun Rd, Houston, TX 77204, USA; e-mail: brappenglueck@uh.edu

2. EXPERIMENTAL SETUP

The location of the measurement site Altzomoni is shown in Fig. 1:

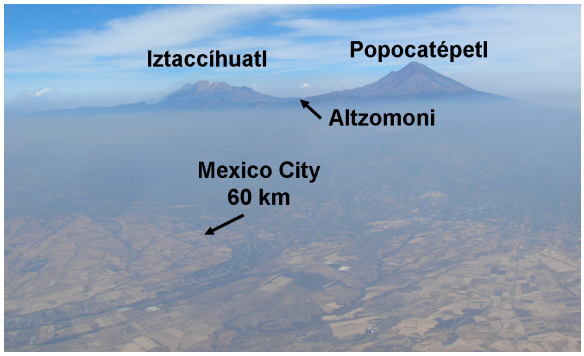

FIG. 1. Measurement site Altzomoni (picture courtesy W. Junkermann).

Among the various instrumentation continuous measurements at Altzomoni included gas chromatography using electron capture detection (GC-ECD) for measurements of peroxiacetic nitric anhydride (PAN) and peroxipropionic nitric anhydride (PPN) [University of Houston], measurements of O_3 and CO by Fourier-Transformations-IR-spectroscopy (FTIR) using a 350 m path length [Universidad Nacional Autónoma de México], speciated aerosol measurements by aerosol mass spectrometry (AMS) [University of California at San Diego/University of Manchester], ceilometer measurements [FZK], and measurements of meteorological parameters [UNAM/ FZK].

3. RESULTS AND DISCUSSION

3.1. *General observations*

Figure 2 displays a section of the Altzomoni measurements for PAN, PPN, O_3, and CO. Contrary to ozone, PAN and PPN show more distinct peaks and better reflects anthropogenic impacts on secondary pollutant formation. Under free troposphere conditions, e.g. March 19 and 20, PAN and PPN are below detection limit (about 30 and 35 pptv, respectively), while CO is around 80 ppbv and O_3 around 40 ppbv. Under the influence of the Mexico City plume, e.g. nighttime March 20/21 and daytimes on March 21 and 23) maximum values up to 2.84 ppbv for PAN and 570 pptv for PPN were observed, which are remarkably high values for almost mid-tropospheric conditions. In addition, PPN/PAN ratio increased up to 20 indicating an increasing contribution of PPN. This indicates larger impact from anthropogenic VOC sources. In these events also CO is increased, hinting to traffic related combustion processes.

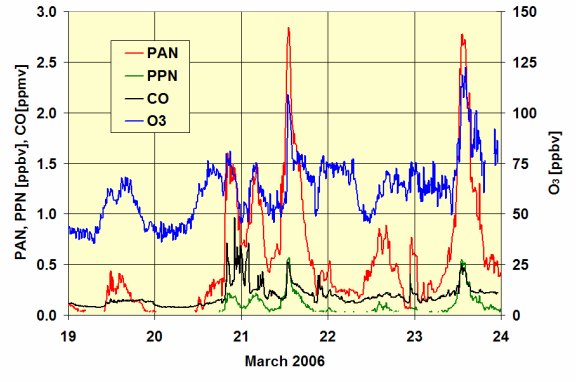

FIG. 2. Time series of PAN, PPN, O_3, and CO.

High daytime PAN peaks are usually associated with shift in wind direction from SE to NW, pointing to Mexico City. Rapid early morning increases are coinciding with increasing boundary layer, i.e. the Altzomoni site is no longer exposed to free tropospheric conditions.

3.2. *Case study: Nighttime pollution event*

During the night from March 20 to March 21, strongly enhanced values of PAN, PPN, and CO were observed (see Fig. 3). The values increased after sunset during the evening hours on March 21. Mixing

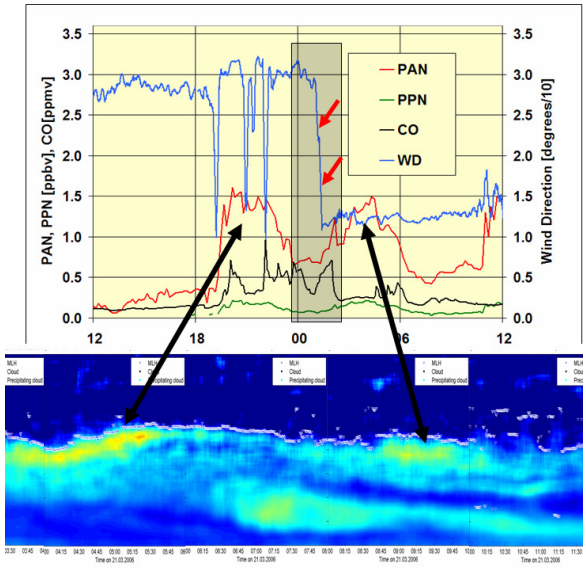

FIG. 3. Time series of PAN, PPN, CO and wind direction (above) and ceilometer (below). The ceilometer was placed down at the valley, about 1630 m lower in altitude than the Altzomoni site.

ratios decreased during the time period 12-2 am and again showed high values until 6 am. As shown in the wind direction data winds came from northwestand displayed a sudden shift sotheast around 2 am coinciding with increasing PAN and PPN values. The ceilometer data indicates high reflectivity in a layer at about 2.000 m a.g.l.. Both observations lead to the conclusion that in a thin layer decoupled from the surface a polluted air mass reached the Altzomoni site before midnight and that the same air mass returned after shift in wind direction from northwest to southeast.

3.2. *Aerosols and PANs*

The time series of total aerosol mass and PANs indicate nice correlation during the entire field campaign. Overall, also the organic aerosol fraction showe good correlation with PAN (see Figure 4). However, under distinct impact of the Mexico City plume, e.g. on March 23, the relative contribution of NO_3 and SO_4 (SO_4 not shown in Figure 4) aerosol fraction gains more importance compared to the organic aerosol. The concentration of NO_3 and SO_4 at this supposedly remote site reaches even magnitudes similar to those measured in Houston during TEXAQS-II.

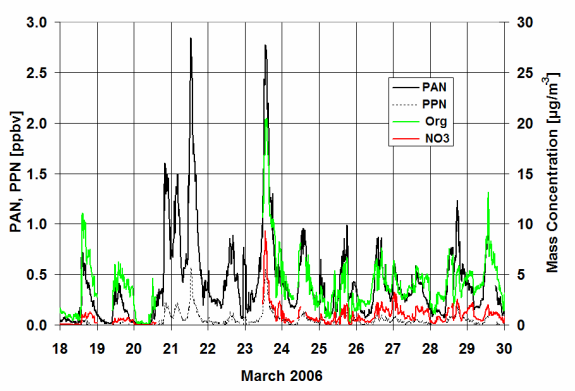

FIG. 4. Time series of PAN, PPN, organic and NO_3 aerosols.

3.3. *Lifetime estimations for PAN*

The atmospheric lifetime of PAN depends on the temperature and the NO_2/NO ratio. Low temperatures and higher NO_2/NO ratios will lead to longer lifetimes. Fig. 5 shows that ambient temperature varied between < 0 °C and 14 °C at the Altzomoni site.

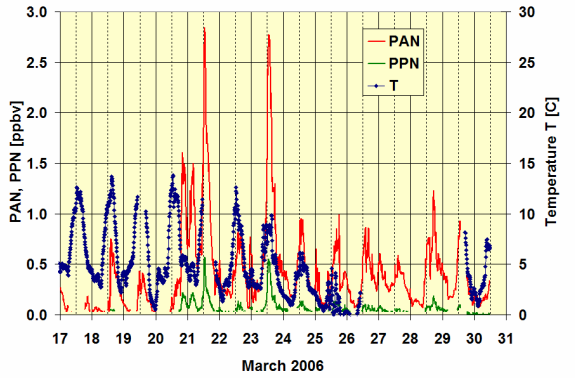

FIG. 5. Time series of PAN, PPN, and ambient temperature.

According to Perros [1994] PAN lifetimes in remote areas may be calculated using the following equation:

$$\tau_{PAN} = \frac{1}{k_1}\left(1 + \frac{k_4 k_2 [O_3]}{J_{NO_2} k_3}\right)$$

where the $[NO_2]/[NO]$ ratio has been replaced by the expression for the photostationary state of ozone:

$$[O_3] = \frac{J_{NO_2}[NO_2]}{k_5[NO]}$$

K_1 is the reaction rate for the thermal decay:

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2$$

K_2 is the reaction rate for the formation of PAN:

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2$$

K_3 and K_4 are the reaction rates for the following loss rates for NO:

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

J_{NO2} the photolysis rate of NO_2:

$$NO_2 + h\nu \rightarrow NO + O$$

J_{NO2} was estimated using STAR (System for the Transfer of Atmospheric Radiation) developed by Ruggaber et al. (1994) with updated NO_2 absorption cross sections (Sander et al., 2006). Calculations were based on profiles of temperature and relative humidity retrieved from simulation results of the mesoscale meteorology-chemistry model MCCM (Grell et al., 2000) for the considered episode. Albedo was based on grass landcover. Average continental aerosol was assumed. Aerosol optical thickness was assumed to be 0.0001 taken at 550 nm. This approximation will lead to a lower limit for PAN lifetime. As shown in Fig. 6 PAN lifetime varies between 0.5 and 68 days during times when solar radiation is available. At daytime temperatures < 5 °C daytime PAN-lifetime is between 5-10 days. These lifetimes may help PAN to act efficiently as a reservoir species for NO_2 for long range transport.

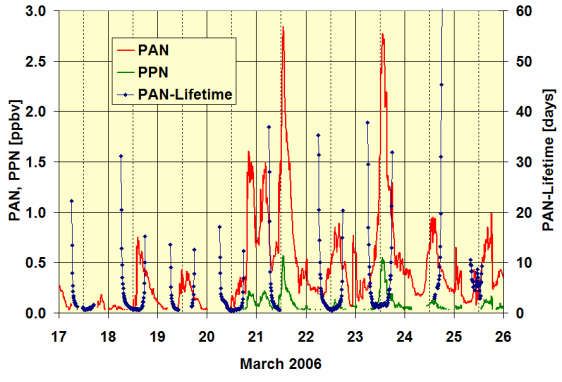

FIG. 6. Time series of PAN, PPN, and PAN lifetime.

4. Conclusion

Within the scope of the ALTZOMONI field campaign in March 2006 it was possible to sample various times the urban plume of Mexico City at a site located at about 4000 m a.s.l. and approximately 60 km to the southeast of the city. Continuous GC-ECD measurements of peroxiacetic nitric anhydride (PAN) and peroxipropionic nitric anhydride (PPN) were used to determine the pollution plume events. High PAN and PPN levels usually coincided with higher CO levels and slightly enhanced O_3 values as determined by FTIR. Aerosol Mass Spectrometer results show that, overall, organic aerosols correlate well with PANs. However, some individual PAN peaks are also accompanied by higher aerosol fractions of NO_3 and SO_4. The results indicate that polluted air masses are present at high altitudes over the Mexico City basin and may likely have a long-range effect. This is in particular true for PAN and PPN. Maximum values up to 2.84 ppbv for PAN and 570 pptv for PPN were observed, which are remarkably high values for almost mid-tropospheric conditions. Together with considerable long lifetimes at this altitude PAN may serve efficiently as a reservoir species for NO_2 and thus may likely have a long-range effect.

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