Raman Lidar Measurements of Ozone During Pollution Events

Karoline R. Mulik and C. Russell Philbrick
The Pennsylvania State University
Department of Electrical Engineering
University Park, PA 16802 USA
krm124@psu.edu and crp3@psu.edu

ABSTRACT

Lidar measurements have proven to be very useful during investigations of atmospheric pollution episodes. Measurements were made during the NARSTO-North East Oxidant and Particle Study (NE-OPS) project in an urban environment using the Penn State Lidar Atmospheric Profile Sensor (LAPS) to investigate conditions for meteorological control of the ground level concentrations and population exposure to ozone and aerosol/particulate matter. LAPS has the capability of measuring ozone, water vapor, temperature, optical backscatter, and extinction by utilizing Raman scatter techniques. The analysis of the return scatter in photon counts, in combination with data processing techniques provides useful information of both the horizontal and vertical structure of the atmosphere during a period of time. Lidar measurements during the campaign have for the first time shown the important transport of aged pollution chemistry depicted in time sequence plots. The focus of this paper will be the ozone measurements obtained by the LAPS instrument and how they compare with other ozone measurements.

1. Introduction

The LAPS instrument obtains vertical profiles of atmospheric constituents by measuring several wavelengths of Raman scattered signals through use of multi-channel photon counting detection. These measurements describe the dynamics of the atmosphere and provide information about atmospheric constituents. During pollution episodes lidar measurements have shown the importance of vertical mixing, horizontal transport, and overnight storage of precursor and pollutant matter in the residual boundary layer. Vertical profiles of the atmosphere obtained from the LAPS lidar have proven to be very useful in describing the dynamics of the atmosphere, as well as determining the distribution of chemical species and concentrations of pollutants, such as ozone, in different layers of the atmosphere [1].

The LAPS lidar data can be processed during a period of time to provide time sequence plots of atmospheric elements. These plots depict both the horizontal and vertical structure of the atmosphere during a period of time. This is important because the concentration of pollutants can change with altitude, and ground measurements alone are not enough to describe the boundary layer [1,2]. Measurements were made in an urban environment, where there exists a combination of local sources, as well as contributions from long-range transport of distant sources.

2. Method of Measurement

LAPS uses a 1064 nm Nd:YAG laser beam that is sent through two frequency doubling harmonic crystals for transmission at wavelengths of 532 nm (2nd harmonic) and 266 nm (4th harmonic). The Raman scattered radiation by molecules in the atmosphere then provides the principal signals. LAPS detects return signals at eight different wavelengths and has the ability to obtain measurements during the day and night [3,4]. Vibrational Raman scatter is used to measure water vapor content, ozone, and optical extinction. Temperature profiles are measured using rotational Raman scatter.

The concentration of the water vapor is determined from the mixing ratio by taking the ratio of signals proportional to the water vapor number density to the number density of ambient nitrogen by using the 1st Stokes vibrational Raman shifted wavelengths of water over nitrogen. The equation used for this calculation is given as [5]:

$$W(z) = K * \frac{S_{H2O}(z)}{S_{N2}(z)}$$

where

S_{H2O} - received signal from the vibrational Raman shift of H_2O at 660 and 295 nm

S_{N2} - received signal from the vibrational Raman shift of N_2 at 607 and 284 nm

K - calibration constant

The constant K is determined by the ratio of sensitivities of the channels and the Raman cross-section or by fitting to radiosonde data.

Ozone is measured using a DIAL (DIfferential Absorption Lidar) analysis of the Raman shift of N_2 (285 nm) and O_2 (276 nm), which occur on the steep side of the Hartley absorption band of ozone [6]. Vertical profiles of ozone are calculated using the ratio of the O_2 signal over the N_2 signal, which is shown in the following equation [5]:

$$\frac{P_{O2}(z)}{P_{N2}(z)} = k_{system} * \exp\left[-\int_0^z [\alpha_m(\lambda_{O2},z') - \alpha_m(\lambda_{N2},z')]dz'\right]$$
$$* \exp\left[-\int_0^z [\alpha_{O3}(\lambda_{O2},z') - \alpha_{O3}(\lambda_{N2},z')]dz'\right]$$

where,

$\alpha_m(\lambda_x,z)$ is the attenuation due to molecular scattering at wavelength λ_x,

$\alpha_{O3}(\lambda_x,z)$ is the attenuation due to ozone absorption at wavelength λ_x.

The number density of ozone in a scattered volume is calculated by differentiating the integrated ozone number density corrected for molecular scattering and is shown in the following equation [1]:

$$[O_3(z)] = \frac{d}{dz}\left[\ln\left(\frac{P_{O2}(z)}{P_{N2}(z)}\frac{1}{k_{System}}\right) * \frac{1}{(\sigma_{N2} - \sigma_{O2})} + \frac{(\sigma_{O2} - \sigma_{N2})}{(\sigma_{N2} - \sigma_{O2})}K(z)\right]$$

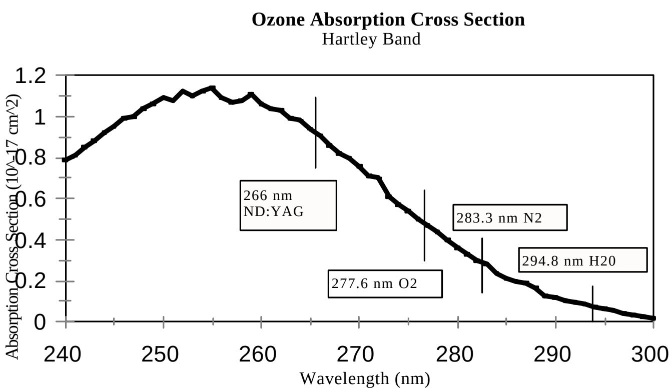

FIG. 1. Hartley absorption band of ozone with the wavelengths for LAPS transmission and measurement indicated.

During the summer months, air pollution events occur which are associated with extremely high levels of tropospheric ozone. Ozone in the lower atmosphere is formed primarily through chemical reactions, but transport of ozone precursor material from outside regions is also a large contributor. Lidar measurements from LAPS time sequence profiles of the concentration of ozone in the lower atmosphere can be used to investigate the evolution of air pollution episodes.

3. Experimental Results

Measurements made during the 1998 NE-OPS pilot study and the 1999 NE-OPS intensive campaign conducted in Philadelphia, PA are used as examples of the capabilities of lidar to investigate air quality. An urban area was chosen because frequent occurrences of poor air quality result from a number of local sources, as well as transport from distant sources. Measurements were also taken during the summer when ozone concentration tends to exceed air quality standards. A pilot study was conducted in during a two-week period in August 1998. Time sequence plots of the lidar data are smoothed for thirty minutes using five-minute time steps. A time sequence plot of water vapor during a pollution episode with the same smoothing interval is shown in Figure 2. A plume containing ozone precursors mixed downward into the rising boundary layer (BL), which produced a sudden rise in ozone concentration at the surface at about 2 PM local time (18:00 UTC). The time sequence plot in Figure 2 provides information on the exact timing of the mixing. The plot begins at 09:00 UTC, which is just before sunrise and before the start convective mixing and ends at 19:00 UTC, about two hours after the plume and convective boundary layer mixed. Figure 3 shows the ozone concentration measured by LAPS during the same period. The sudden increase of ozone is shown around 2 PM local, when the mixing occurred.

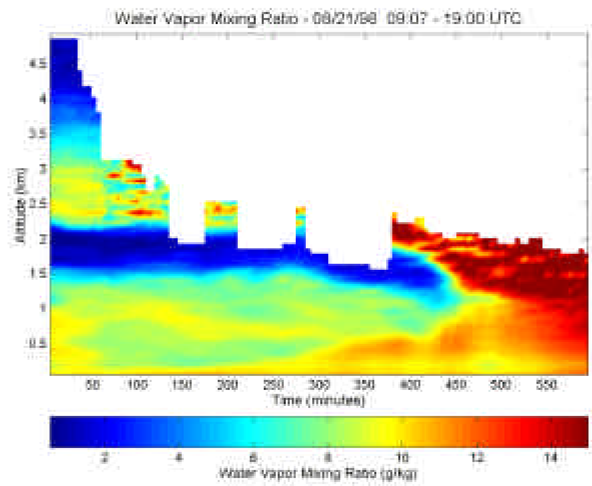

FIG. 2. LAPS time sequence vertical water vapor profile on 08/21/98 shows aloft plume mixing down into rising BL.

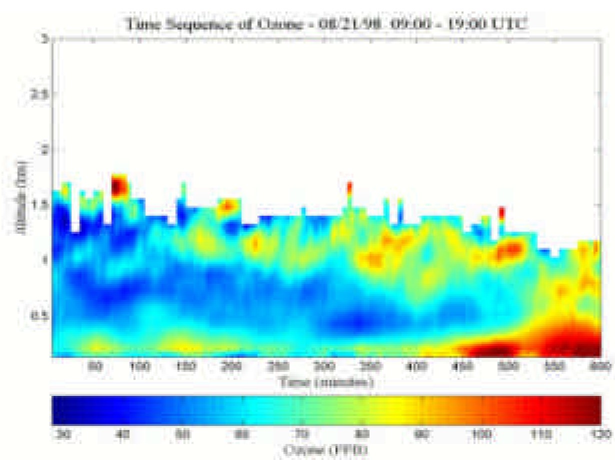

FIG. 3. LAPS time sequence vertical ozone profile on 08/21/98 shows sudden rise of ozone when plume mixed downward into the BL at around 2 PM local time (18:00 UTC).

Extinction during the pollution event was also measured by LAPS and shows an increase in extinction during the mixing of the plume and boundary layer. This is shown in Figure 4. Figure 5 displays the measured ozone from the LAPS lidar in comparison with the measured ozone from a University of Maryland aircraft. The figure shows strong correlation between the lidar and aircraft measurements, especially at the lower altitudes.

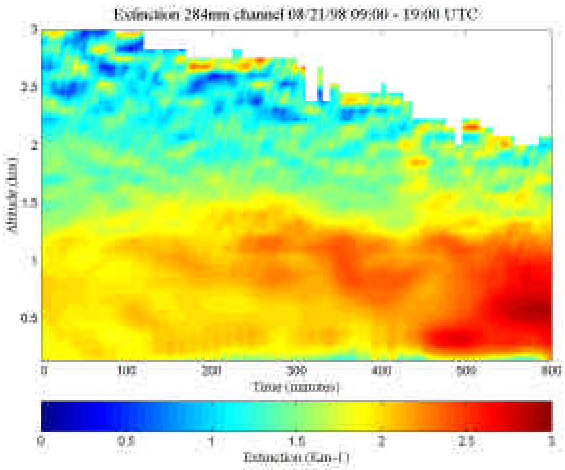

FIG. 4. LAPS time sequence vertical extinction profile at 284 nm on 08/21/98 shows a strong increase of extinction during the mixing of the plume with the BL.

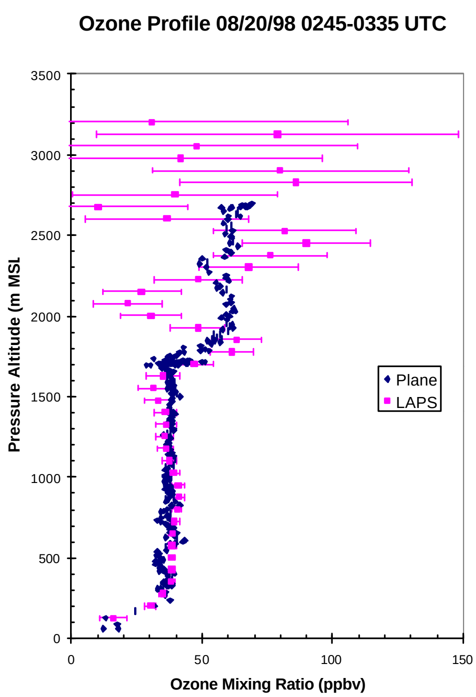

FIG. 5. Comparison of Ozone Measurements during the 1998 NE-OPS Pilot Study from the PSU LAPS Lidar Instrument and the UMd Aircraft (aircraft profile courtesy of Dr. Bruce Doddridge).

Measurements were also taken during the 1999 NE-OPS campaign, which was also performed in Philadelphia, PA. This campaign had a two-month duration starting in June and ending in August. During this campaign, eight pollution episodes were monitored, all of which resulted in measurements of high ozone concentrations. The LAPS instrument was operated continuously for periods of one day to several days during these measurement intensive periods. An example of high ozone that occurred from 03 July 99 to 05 July 99, when temperatures reached 100 degrees Fahrenheit during the daytime in shown in Figure 6. This figure depicts the high ozone during that episode in a time sequence plot starting at 23:35 UTC on 03 July and ending at 03:35 UTC on 04 July. This corresponds to the evening moving into nighttime, where the ozone begins tapering off due to no sunlight, cooler temperatures, and wind flow, which gradually removed the ozone from the region during the night. Also, note that the 4 to 6 PM local time period exhibited the scavenging of ozone by NO_X produced by work traffic on the nearby interstate highway.

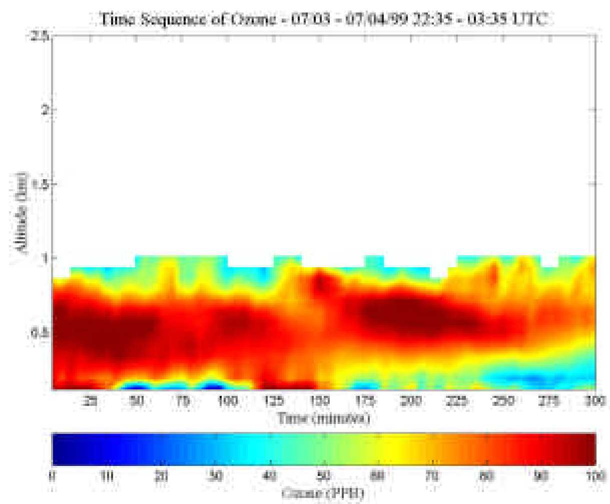

FIG. 6. LAPS time sequence vertical ozone profile on 07/04/99 shows high levels of ozone, which begins tapering off during the night.

4. Conclusions

The LAPS instrument is a multi-wavelength Raman lidar that has the capability of measuring backscatter, extinction, water vapor mixing ratio, temperature, and ozone. Measurements of ozone are obtained using a Raman/DIAL technique of the ratio of O_2 and N_2 on the steep side of the Hartley band of ozone absorption. Time sequence vertical profiles of ozone were shown from the NE-OPS pilot study and campaign during consecutive years. These measurements are important because they provide useful information about ozone concentrations and dynamics of the atmosphere, which could contribute to these concentrations. The transport of ozone precursor material could be seen for the first time using the lidar measurements as a time sequence. Comparisons of the ozone measurements with aircraft ozone measurements made during the NARSTO-NE-OPS campaign correlated well. The Raman lidar measurements are a strong tool in understanding the meteorological conditions and aerosol content during investigations of pollution episodes.

5. Acknowledgements

This work is supported by the US EPA grant titled Investigations of Factors Determining the Occurrence of Ozone and Fine Particles in Northeastern USA, grant number R826373. The efforts of Mr. George Allen of Harvard University School of Public Health, Drs. Russell Dickerson, Bruce Doddridge, and William Ryan of University of Maryland, Dr. Richard Clark of Millersville University, Dr. S.T. Rao of NY State Dept. of Environmental Conservation, Mr. Ted Erdman of EPA Region 3, Drs. Sharon LeDuc, Daewon Byun, and Francis Binkowski of USEPA, Dr. D. Lysak, Tom Petach, Guankun Li, Ginnipal Chadha, Ed Novitsky, James Carbo, Gregg O'Marr, and Steven Esposito have contributed much to the success of this project.

REFERENCES

1. Mulik, K.R., G. Li, G.S. Chadha, and C.R. Philbrick, "Evolution of Air Pollution Events Determined from Raman Lidar", *Proceedings of the A&WMA Specialty Conference and Exhibition, PM2000: Particulate Matter and Health*, Charleston,South Carolina, pp. 4ASP2: 11-13, January 24-28, 2000.
2. Saxeena, Pradeep and Glen Cass, "Designing Atmospheric Experiments to Enable Estimation of Source-Receptor Relationships for Fine Particles", *Proceedings of the PM Measurements Research Workshop*, EPA Report No. 4, Chapel Hill, North Carolina, pp. 19-26, July 22-23, 1998.
3. Philbrick, C.R., "Raman Lidar Measurements of Atmospheric Properties", Atmospheric Propagation and Remote Sensing III, SPIE Vol. 2222, 922-931, 1994.
4. Philbrick, C.R., "Raman Lidar Capability to Measure Tropospheric Properties", *Proceedings of the Nineteenth International Laser Radar Conference*, NASA Langley Research Center, Hampton, VA, NASA Conf. Publ. 207671, pp. 289-292, July 1998.
5. Esposito, Steven T., "Applications and Analysis of Raman Lidar Techniques for Measurements of Ozone and Water Vapor in the Troposphere", Master of Science Thesis for Penn State University, Department of Electrical Engineering, May, 1999.
6. Esposito, Steven T. and C. Russell Philbrick, "Raman/DIAL Technique for Ozone Measurements", *Proceedings of the Nineteenth International Laser Radar Conference*, NASA Langley Research Center, Hampton, VA, NASA Conf. Publ. 207671, pp. 407 - 410, July 1998.