2.1 A STUDY ON VERTICAL DISTRIBUTION OF OZONE IN THE PBL OF THE PHOENIX VALLEY

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1. INTRODUCTION

In general, ozone concentrations increase with height above the ground. During the nighttime, in particular, the ozone concentrations decreas sharply from the top of the surface inversion layer to the ground and displays an almost constant concentration within the residual layer (Nue *et al.*,1994; Teichmann *et al.*, 1997; Gusten *et al.*, 1998). Previous studies (Neu *et al.*, 1994; Aneja *et al.*, 2000) show a strong correlation between nighttime and early morning ozone concentrations in the residual layer and the maximum ground level concentration in the following afternoon.

The spatial and temporal distribution of ozone concentration within the planetary boundary layer is a collusion of meteorological and chemical processes. The atmospheric structure over complex terrain is known to complicate air pollution dispersion and its prediction. Therefore, a better understanding of atmospheric processes over complex terrain and their influence on the level of air pollutants need to be carefully studied to understand air quality issues of metropolitan areas located in complex terrain. Phoenix is one of the metropolitan cities located in complex terrain of the southwest plagued by air pollution problems.

Therefore, in the present study, an effort is made to understand micro-metrological process in complex terrain and their effects on the distribution of air pollutants. In particular, we are interested in nocturnal high-ozone episodes and their relation to the nocturnal turbulent characteristics as well as the urban heat island phenomenon. Multi-layered structure induced by complex terrain features and its influence on local ozone concentration within the PBL are also investigated. State-of-the-art numerical models were also employed to examine meteorological and chemical processes influencing the distribution of ozone concentrations.

2. DESCRIPTION OF THE FIELD CAMPAIGN

A field experiment was conducted in the summer of 2001, from 11 June to 30 June 2001, at the Arizona

State Fairgrounds, which are located in the downtown Phoenix area. This was a part of the DOE's Phoenix 2001 Sunrise experiment. The experiment aimed at characterizing ozone, ozone precursors, other pollutants and their dependence on the evolving atmospheric boundary layer structure. The effects of the storage of ozone in the residual layer aloft on ground level ozone concentrations were also of interest. In order to measure the vertical structure of the lower atmosphere. two tethered balloons (Atmospheric Research Inc. TSB-9), each carrying meteorological tethersondes (TMT-5A-SP), were used to measure the air temperature, relative humidity, pressure, wind speed and wind direction. One balloon carried 5 tether sondes and the other was traversed simultaneously carrying one meteorological sonde and an ozone monitor (2B Technologies Inc). The meteorological instruments measuring the mean and turbulent components of the atmospheric flow were located on a 14 m mast. The instruments consisted of anemometersultrasonic fast-response two thermometers, two cup-anemometers, two thermistors, a pyranometer and a pyrgeometer.

3. RESULTS

During the field campaign, nocturnal high-ozone concentrations were frequently observed. The ratio of NO to NO₂ was relatively low during the nocturnal ozone episodes. The opposite was true for the low ozone case. This indicates that the air masses containing high ozone are relatively "aged" compared to nocturnal ozone free air masses containing newly emitted NO. With the sudden increase of ground-level nocturnal ozone, sharp increases of downward vertical momentum flux and r.m.s. vertical velocity fluctuation were observed. At the same time, there was an increase in ground level wind speed. These indicate that a nocturnal overturning process transports the air mass in the residual layer to the ground. Interestingly, a positive heat flux and a sudden decrease of air temperature were observed during the overturning period. This event could be attributed to the urban heat island effect that intermittently releases convective thermals into the overlying stratified layer.

Vertical profiles of ozone and meteorological variables were made regularly during the morning hours. The multi layered structure, probably induced by complex terrain (Fernando *et al.*, 2001), and the formation of the convective boundary layer were well

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captured by the measurements. The vertical distribution of ozone concentration matched well with the meteorological structure of the PBL. For example, the effects of low level jets, vertical mixing, and the local circulation pattern on ozone concentration were evident.

Figure 1 shows the formation of convective boundary layer. Two layers - the convective boundary layer at the lower level and the remnant of the residual layer at the upper level - were observed at 0806 LST. The well-defined layered structure of ozone in consonance with meteorological structure was also observed. A relatively ozone free lower laver was a result of nighttime titration, and ozone rich upper layer was a remnant of the previous night's residual layer. Twenty-three minutes later (0829 LST), the convective layer developed up to 350 m agl. The ozone concentration around 300 m agl decreased significantly. This is because the ground based convection brought NO_x to the upper level, titrating ozone at a rate higher than that produced by the photochemistry: note the abundance of NOx and relatively weak solar radiation in the morning which contribute to this observation.

Two numerical models – Mesoscale Meteorological model (MM5) and the recently released US EPA's photochemical model, Models-3/CMAQ were employed for the post-facto prediction of ozone. The simulations



Figure 1. The vertical profiles of potential temperature and water vapor mixing ratio (a, c), and ozone concentration (b, d). (a), (b) correspond to 0806 LST, and (c), (d) correspond to 0829 LST 25 June 2001.

showed the relative contribution of each process (e.g. photochemical reactions, emissions, vertical and horizontal transports) to the resultant concentration of ozone and other pollutants. Within the Phoenix valley, during the daytime, photochemical reactions lowered ozone concentration while vertical transports increased ozone concentration within 10 m agl. Contrarily, ozone was produced by chemical reactions and flushed away by the vertical transports at upper levels (around 300m agl).

4. CONCLUSION

The vertical and temporal structure of ozone concentration in the Phoenix valley was investigated using measurements taken during a field campaign conducted during 11 June - 30 June 2001. Numerical models were also employed to investigate the role of meteorology and chemical reactions on ozone concentration. Frequently observed nocturnal highozone episodes during the field campaign was explained by the overturning of the nocturnal boundary layer, which was delineated by the variation of vertical turbulent fluxes and mean variables. The observed vertical structure of ozone was well explained by invoking meteorological processes - e.g. low level jet, the formation of convective boundary layer and the local mountain/valley circulation pattern. The interpretation was supported by the numerical simulations.

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