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ON THE MECHANISMS OF HIGH OZONE OCCURRENCE AT A RURAL SITE

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1. INTRODUCTION

Long distance transport plays a paramount role in occurrence of high surface ozone concentration in addition to *in situ* photochemistry, vertical mixing and deposition. Numerical modeling studies widely support that high ozone at rural sites is caused by nocturnal long distance transport and daytime mixing down processes (Banta et al. 1998). Surface ozone and meteorological observations have been extensively analyzed to associate high surface concentration with synoptic circulation (Lyons and Cole 1976; Chung 1977; Wolff et al. 1980; Pont and Fontan 2000). Alternatively, surface ozone precursors, SO_2, HNO_3 and NO_x, were also examined to show that aloft pollutants are the main source for the elevated pollution at the surface at rural locations (Kleinman at al. 1994). Upper air ozone data, however, is sorely lacking. Few aircraft measurements illustrated the large scale transport and downward propagation of aloft ozone (Blumenthal et al. 1974; Kleinman et al. 1996; Zhang and Rao 1999). Therefore, the intent of this paper is to use a time series of observed ozone vertical distribution to identify the role of long range transport in high surface ozone occurrence.

We analyzed the ozone data at four altitudes during the summers of 1995-1999 at the Auburn TV tower in North Carolina. An index was defined to classify ozone episodes into different groups. Backward trajectories prior to each episode are performed at three heights in an attempt to associate each episodic category with a certain flow patterns. Last, a scale analysis was carried out to extract the component containing fluctuations longer than one day from the raw data in an effort to determine the influence of transport processes at different elevations.

2. DATA AND METHODOLOGY

The multi-elevation ozone data at the Auburn-TV tower, North Carolina, was measured by the Ambient Monitoring Section, Division of Air Quality, North Carolina State Department of Environmental and Natural Resources. The site information and measurement techniques can be found in the reports by Davis et al. (2000). Ozone concentration was measured hourly at 2.4 m, 233 m, and 433 m from June 1 through August 31 in 1995 and at 2.4 m, 78 m, 128 m, and 433 m during the summers of 1996-1999.

The Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT4) model (Draxler 1997) was applied to calculate backward trajectories for identifying the characteristics in the transport processes linked to different episode types. The three dimensional wind field as computed from the output of National Meteorological Center's Nested Grid Model (NGM) or ETA Data Assimilation System (EDAS), whichever is available. The forecast fields were available on 180 km grid at 10 vertical layers with the lowest level approximately 200 m above ground. The domain covers most of North America. We calculated three day backward trajectories starting at 17 GMT on the first day of each episode.

Time series of ozone observations consist of components of varying time scales (Hogrefe et al. 2000). The most dominating periodicities are the diurnal cycle (24 hours), synoptic (2-21 days) and long-term (periods greater than 21 days) fluctuations in surface ozone observation. The synoptic scale is often associated with long range transport. In order to extract this component from the raw hourly ozone data, we used the Kolmogrov-Zurbenko (KZ) filter (Zurbenko 1986) to separate the time scales. Prior to analysis, a three-point moving average was applied to remove the high frequency component. A log-transform was necessary to stabilize the variance in the data set (Milionis and Davies 1994). Thus, the results presented later are in log-scale. If long range transport is truly the chief component in causing high surface ozone at rural locations, positive anomalies in the synoptic scale forcing should be expected before/during episodes.

An index, ozone anomaly, is defined to classify ozone episodes. Ozone anomaly is calculated by subtracting the diurnal cycle composite from the raw data. It is then applied for ozone episode classification.

3. RESULTS AND DISCUSSION

3.1 Ozone Anomaly and Classification of Ozone Episodes

Compared to the surface, ozone at higher altitudes shows the same level of daily maxima while the nocturnal concentration does not reduce to the same low level due to the absence of losses by surface deposition. The absolute values of aloft ozone hardly suggest the existence of a reservoir. As an alternative strategy, ozone anomalies at higher altitudes were examined. In this analysis, we found a distinct feature that distinguishes episodic ozone days from non-episodic conditions. On days of surface ozone greater than 80 ppb, nearly 80% of daily maximum anomaly at 433 m reaches 20 ppb or more. The time of the anomaly peak varies largely, ranging from the previous evening to later during the day.

An episode is defined as daily maximum surface ozone greater than 80ppb persistent over at least two consecutive days. Forty two episodes are found during the summers of 1995–1999. They are classified into three groups, large phase lag (>7 hours), small phase lag (>0 and ≤7 hours) and no phase lag (≤0). Here, phase lag is the time difference between the surface ozone maximum and the daily maximum anomaly at 433 m reaching 20 ppb or greater on the first day of an episode. We need to point out that, the criteria, 7 hours, is selected based on the estimated inversion layer breaking time prior to the occurrence of the surface daily maximum ozone concentrations (typically 1400 EST). This way, in the case of large (small) phase lag, the aloft ozone pool occurs before (after) the inversion layer breaks. 27% of the episodes show that an anomaly ≥20 ppb at 433 m occurs more than 7 hours earlier than the surface ozone maximum (typically around 1400 EST) on the first day of an episode, and 49% 0-7 hours. It means that aloft ozone increases hours before the onset of an episode. Berman et al. (1999) found a nighttime mixing depth averaged 250 m over both land and water in the northeastern US. Thus, we consider the level of 433 m to be in the residual layer. At a rural site with low local emissions, such nocturnal or early morning increases can be interpreted as a result of transport process. Thus, it is important to identify the features in the flow patterns for different episode types.

3.3 Trajectories

Three days trajectories were run for the three episode categories defined as above when input data was available. Figure 1 shows the three day backward trajectories at 200m, 400m, and 800m starting at 1700 GMT on the first day of each episode.

Compared to the other categories, the eleven episodes with large phase lag show two features. First, they show vertically coherent direction at all three levels except for the 200 m altitude where sometimes the trajectories are restrained to the Appalachian leeside. Second, they originate in Minnesota, Ohio Valley, the southern States and the mid-Atlantic urban corridor region where emissions are concentrated. In this case, it is speculated that a meteorological condition favorable for ozone formation is prevailing on a large scale, and thus high ozone is formed on route to the site. As a consequent, an ozone pool exists aloft along with high ozone precursor concentrations when arriving at the site. As mixing process develops, downward propagation triggers an episode. This episode type shows significant phase lag.

The nine episodes with small phase lag show two distinct directions, westerly and northerly. Only one single trajectory is southerly along the coastline. In this case, the aloft ozone pool appears after the morning inversion layer breaks. One of the possibilities could be that the meteorological condition favorable for ozone formation does not cover the region which the transport routes span over or occurs after abundant ozone precursors have arrived at the site. Thus, ozone precursors are transported to the site in the residual layer at night and start forming ozone after sunrise followed by mixing down a few hours later, which incurs a small phase lag.

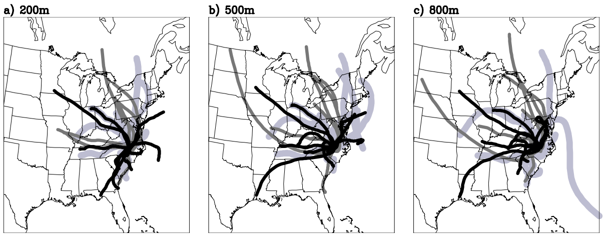

Fig.1 Three days backward trajectories starting at 17 GMT on the first day of each episode at a) 200 m, b) 500 m and c) 800 m. The lightest gray is for the episodes with no phase lag, gray small phase lag and black large phase lag.

In the twelve episodes with no phase lag, mostly either the trajectories dwelled in the vicinity of the monitoring site or they came afar but differed in direction at all levels. Directionally diversified trajectories at different altitudes lead to varying air quality in the vertical. Perhaps high ozone is formed at the surface first while vigorously mixed up. Thus, no phase lag or delayed peaks aloft features this category. As an exception, three trajectories show consistent directions at all three levels, one from Canada, one from the Midwest and the other through Tennessee.

The link between transport processes and high surface ozone is complicated, and additional analysis is needed to gain a more complete understanding of this link than the one achieved by trajectory analysis alone. For an individual episode, the synoptic system should be examined. For instance, anti-cyclones frequently prevail during episodes in the northeastern US. Nevertheless, the position of the monitoring site in this anti-cyclone system may result in different development of ozone formation (Chung 1977).

3.4 Scale Analysis

As opposed to the conspicuous diurnal oscillation at the surface (Fig. 2a), ozone at 433 m suggests flat diurnal variation, remaining 50 ppb before 0900 EST and rising to 70 ppb around 1200 EST with small variation thereafter. The large vertical gradient begins to reduce at 0600 EST and nearly disappears in three hours. This indicates that surface ozone increases through the processes of photochemistry and vertical mixing with the upper air.

The ozone data at the surface and 433 m are decomposed into diurnal, synoptic and long term components. Since the data is only available in summer, we will focus on the diurnal and synoptic terms. Only the 1999 summer segment is displayed in Figure 2b and c. The episodes are marked using horizontal arrows. The diurnalcomponent reflects processes such as turbulence, photochemical perturbation caused by the daily variability in emission, fluctuations caused by daytime photochemical production and nighttime removal processes, and the diurnal evolution of the boundary layer height. Therefore, as expected, the surface diurnal component is much stronger than that at 433m (Fig. 2b).

Episodic days find stronger oscillation in diurnal component. This is consistent with the better mixed planetary boundary layer owing to more violent turbulence, or lower mixing heights due to subsidence and faster photochemistry in response to high temperature and stronger solar flux. The synoptic component, on the time scale of more than one day, is often associated with long range transport. The surface synoptic term contributes much less energy to the over all variance than the diurnal term, whereas at 433 m, the synoptic term contributes more energy than the diurnal component. It implies that the synoptic term is the dominating contributor to upper air ozone. Positive synoptic term most frequently occurs on episodic days, indicating the possibility of enhanced long range transport processes during those days. The resulting excessive ozone aloft could be one of the main sources to the high surface ozone. Localized spectral analysis is needed in the future to quantify such a potential link.

4. SUMMARY

During the summers of 1995-1999, we identified 41 episodes. Among them, seven have large phase lag, twenty small phase lag and the rest no phase lag. The backward trajectories show that the large phase lag group is associated with a deeper transport system originated from the regions with concentrated emissions. For the other two groups, more diversified trajectories are found. The spectral analysis shows distinct differences in the diurnal and synoptic scales embedded in the surface and aloft ozone. In aloft ozone, the synoptic component dominates over the diurnal, and its positive fluctuation occurs during episodic days. It implies the possibility of enhanced long range transport processes in upper air, which is possibly linked to the high surface ozone at the time. It needs further observational data analyses and numerical modeling to obtain a better understanding for the ozone/transport linkage.

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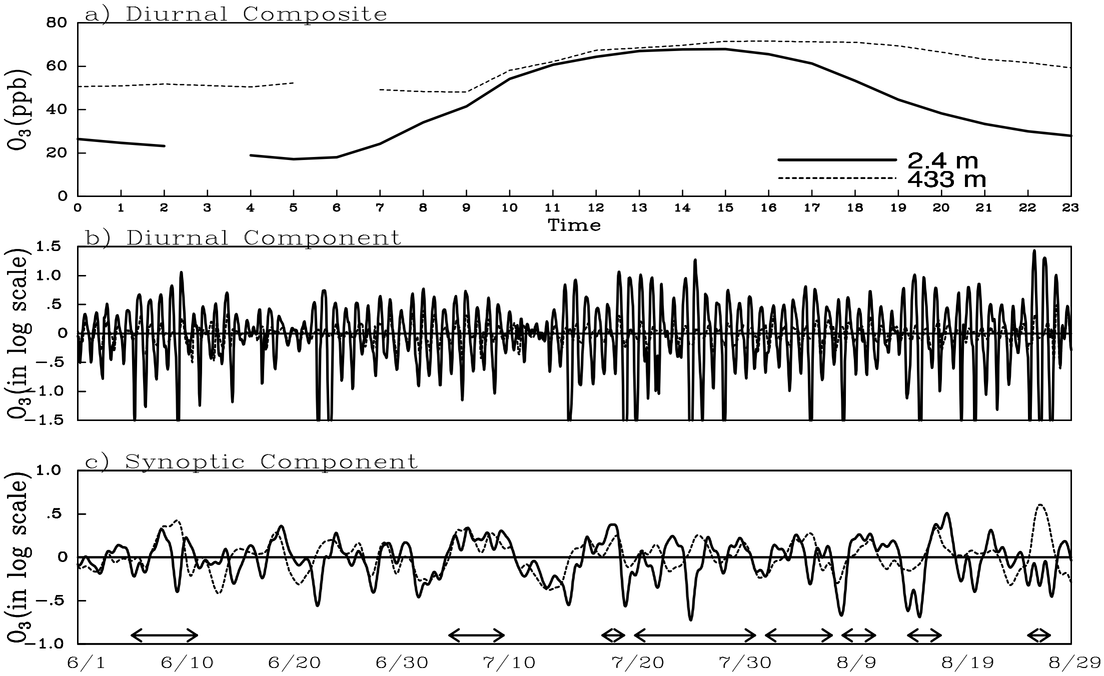

Fig. 2 Time series of a) diurnal composite, b) diurnal component, and c) synoptic component embedded in the raw ozone data at 2.4 m (solid) and 433 m (dotted) during the period of June 1 to August 30, 1999.