OXIDES OF NITROGEN SPECIES MEASUREMENTS AND ANALYSIS IN THE CENTRAL PIEDMONT OF NORTH CAROLINA, U.S.A.

DEUG-SOO KIM[1] and VINEY P. ANEJA[2]

[1]Department of Environmental Engineering
Kunsan National University, Kunsan, Chonbuk 573-360, Korea

[2]Department of Marine, Earth and Atmospheric Sciences
North Carolina State University, Raleigh, N.C. 27695-8208, U.S.A.

ABSTRACT The quantitative knowledge of $NO_y (= NO_x + HNO_3 + PAN + NO_3 + N_2O_5 + HNO_2 + NO_3^- +$ organic nitrates + ...)distribution is essential in tropospheric chemistry, especially that related to understandings the processes leading to ozone production. Ambient concentrations of NO, NO_2, HNO_3 and PAN as well as total NO_y were measured during June and early July 1992 at a rural site(Candor,NC), in the central Piedmont region of NC. NO_y, NO_2 and NO showed diurnal variations with maxima in the morning. Products of photochemical oxidants, $(NO_y - NO_x)$, such as HNO_3 and PAN, as well as ozone showed diurnal variation with maxima in the afternoon and minima at night. NO_x was the major species to total NO_y (45%). NO concentrations appeared to be nearly constant whether the prevailing winds were from continental areas or from oceanic areas. Linear regression of O_3 with $(NO_y-NO_x)/NO_y$ (i.e. percent NO_x converted to the photochemical products of NO_y) yielded $[O_3] = 25.8 [NO_y-NO_x]/[NO_y] + 27$, $(r^2 = 0.58)$. The regression intercept is interpreted as the ozone back ground (intercept = 27 ppbv) and the slope suggests that 8.6 molecules of ozone are formed per molecule of NO_x oxidized products (when the average NO_y concentration, about 3 ppbv at the site, is used).

1. INTRODUCTION

Recent experiments and model calculations (Williams and Feshenfeld, 1991; Ridley and Robinson, 1992) indicate that oxides of nitrogen, NO_x ($= NO + NO_2$), play an important role in the tropospheric chemistry. They participate not only in the acidification of precipitation but also in the formation of tropospheric ozone. Mainly NO_x reacts with ozone (O_3) and radicals, e.g. hydroxyl radical (OH) and hydroperoxyl radical (HO_2) in the atmosphere. Throughout these reactions, the concentration of NO_x plays an important role in the distribution of O_3 and the radical balance in the atmosphere. Peroxy radicals are responsible for much of the oxidation of NO to NO_2. In the lower troposphere, ozone is formed as a by-product of the photooxidation of hydrocarbons while NO_x acts as a catalyst. Thus, the characterization of the levels of NO_x is essential to the understanding of tropospheric photochemistry.

In this paper, the partitioning of the major nitrogen species to total NO_y and the balance between the primary nitrogen species, NO_x, and total reactive nitrogen were investigated at a rural site near Candor, NC which is located in the central Piedmont of North Carolina. These observational results are important because the regional distribution of NO_y within the rural South is almost completely unknown. The temporal variation in the composition of NO_y is also examined and compared to that reported for other measurement sites. Additionally, an observational based analysis is performed to explore the relationship between the composition of NO_y with both photochemistry and meteorology. Because the site is indicative of a typical rural setting throughout much of the Southeast United States (being colocated to a NDDN site designated as rural), it is hoped that the analysis and discussion of the NO_y measurements made at the site may shed light on the regional characteristics of reactive nitrogen species in the Southeast United States.

EXPERIMENTAL

Air Quality group of North Carolina State University operates an enhanced chemistry site in the central Piedmont region of North Carolina (35.26 °N, 79.84 °W, ~170 m MSL). Number of species, i.e. NO, total NO_y, SO_2, CO, O_3, particulates, and meteorological data are measured year round. From June 6, 1992 to July 7, 1992 an intensive measurement period was operated where NO_2, PAN, H_2O_2, HNO_3, and speciated NMHC's were also monitored. The sampling site is in an open field (area ~ 1200 m^2) which was previously used to grow soybeans (~ 10 years ago) and is surrounded by mixed

deciduous and coniferous forest. The site is located on the eastern border of the Uwharrie National Forest. Four large urban areas of North Carolina are within a 160 km radius of the sampling site. These sources of anthropogenic pollution, Raleigh-Durham, Greensboro, and Winston-Salem as well and the junction between two busy interstate highways, I-40 and I-85, are situated to the north and northeast of the site and were upwind approximately 35% of the sampling period. Charlotte is nearly due west of the site and is relatively close but was upwind only approximately 10% of the sampling period. When the prevailing wind direction is from the west, north, or northeast the site can be impacted by the more polluted air masses emanating from or crossing over these urban areas.

RESULTS AND DISCUSSION

Figure 1 illustrates the composite diurnal profiles of nitrogen species and O_3 for the entire measurement period. Total NO_y and NO_2 show consistent maxima in the early morning hours between 06:00 and 09:00 EST with the average time of morning maximum being 07:00 EST. The mechanism most likely to be responsible for the morning peaks of the pollutants is regional transport of polluted air masses which often reached the site overnight. At sunrise, when increased solar insolation triggers the breakup of the low NBL a period of downward mixing bring the relatively undepleted polluted air mass aloft to the surface.

The diurnal profile of NO_2 reached a minimum during the early afternoon when solar insolation was at its peak. Daytime NO_2 is thought to be depleted mainly for HNO_3 formation; PAN and other higher order nitrates. Increase of daytime mixing height also causes a decrease in NO_2 concentration. The NO_2 mixing ratio then gradually increases throughout the night until the rapid early morning rise to the daily maximum. This slow nighttime buildup occurs regularly in our data set and is not typically accompanied by an increase of SO_2 or CO and is thus not thought to be related to transport.

An alternative hypothesis for the nighttime buildup of NO_2 is that the increase is due to natural emissions of nitrogen species from the local soils is investigated. A dynamic flux chamber experiment to measure nitrogen compound flux was conducted on several different days during the measurement period (Kim et al., 1994). The results of the experiment, however, show that while there was no appreciable nighttime flux of NO_2 from the soil which could explain the buildup of NO_2 at night; that frequently there was a significant level of NO flux from the soil at night, typically about 2.4 $ngNm^{-2}s^{-1}$ of NO flux. No evidence of a buildup of NO during the night was found in the data set, however. It seems, then, that a chemical mechanism may be converting the NO emitted from the soil during the night into NO_2, i.e. oxidation of NO by ozone. Levels of O_3 overnight are typically near 30 ppbv and are sufficient to immediately titrate any NO from the soil to NO_2. Rough calculation of a rate of increases in NO_2 from the soil emission using a typical NO emission rate of site was about 0.1 ppbv/hr when the height of NBL was assumed 100 m. The rate of increase in NO_2 is quite consistente to the observed increase rate of NO_2 during nighttime period. This would suggest that the soil emission and the persistance of O_3 overnight at the site may facilitate the conversion of NO to NO_2 and effectively increase the background concentration of NO_2 at the site.

NO shows a morning maximum between 07:00 and 09:00 EST. The time of the NO peak is sometimes the same as the NO_y, NO_2 and SO_2 peak but typically follows the NO_2 peak by one to two hours. For this reason, the existence of a morning maximum of NO mixing ratio is considered to be the combination of three seperate mechanisms. The first is the same mechanism that brings NO_2 to the site; medium range transport from one of the regional urban areas followed by downward mixing during the breakup of the nocturnal boundary layer. A second possible mechanism is the regeneration of NO from NO_2 after the onset of NO_2 photolysis in the morning. To test this second hypothesized mechanism, the regeneration of NO from NO_2, a simple calculation based on photostationary state equilibrium (PSS) between NO_2, O_3, and NO was made. The resulting mixing ratio of NO is ~0.5 ppbv, a mixing ratio that is very comparable to that observed in the morning NO profile (Figure 1). A third possible

contributing factor to the morning NO peak is found in the data from the flux experiment (Kim et al., 1994). A morning increase in NO flux rates is found approximately 30% of the time in the experiment results. This natural injection of NO into the site environment could be responsible for a portion of the morning NO peak. Thus the diurnal behavior of NO is thought to be a combination of direct transport of NO_x from regional pollution sources, the regeneration of NO by the early moring near-PSS conditions, and possibly natural emission of NO from the soil.

Figure 2 shows a plot of O_3 against $(NO_y-NO_x)/NO_y$. This plot shows the relationship between O_3 and the degree of conversion of NO_x to reservoir species of NO_y, i.e. (NO_y-NO_x). The slope of the plot indicates the amount of O_3 production for a given amount of NO_x conversion in the air mass. O_3 increases as photochemical conversion rate of NO_x increases. A linear regression of O_3 and $(NO_y-NO_x)/NO_y$ is $[O_3] = 25.8 * (NO_y-NO_x)/NO_y + 27, R = 0.76)$. Applying ~3 ppbv of average NO_y concentration at the site, the slope of regression suggests that 8.6 molecules of O_3 are formed for every molecule of NO_x conversion to NO_y and intercept is interpreted as 27 ppbv of ozone background. Similar statistical relationship between ozone and photochemical productions of nitrogen species have been reported, resulting from northeastern rural continental sites measurements (Trainer et al., 1993). Ozone concentration is expected to be low in young air masses because in the troposphere O_3 is mainly formed by the same photochemical processes that lead to the conversion of NO_x into reservoir species such as PAN and HNO_3. Thus, as the ratio increases, indicating a more aged air mass and more complete photochemical conversion of NO_x to reservoir species of NO_y, the concentration of O_3 also increases. In a very old air mass with the value of the $(NO_y-NO_x)/NO_y$ ratio approaching unity the O_3 should continue to increase while the reservoir NO_y species begin to decrease due to their shorter lifetimes.

RATIONAL AND CONCLUSIONS

In conclusion, while this study has shed some light on the behavior of reactive odd-nitrogen compounds in the southeast U.S., it is clear that more comprehensive research into the role of naturally produced nitrogen species and its characteristics and the behavior of photochemical oxidants is needed to enhance our understanding of the chemical climatology of the southeast U.S.. Such knowledge will be required if an accurate chemical model to research atmospheric chemistry in this area or region is to be developed. The understanding gained from field research and future chemical models developed based on data collected in field research are of great importance to the formation of basic pollution control policy in the southeast U.S..

REFERENCES

Kim, D.S, Aneja V.P. and Robarge W.P (1994) Characterization of nitrogen oxide fluxes from soil of a fallow field in the Central Piedmont of North Carolina. Atmospheric Environment, 28, 1126-1137.

Ridley, B. A. and Robinson E. (1992) The Mauna Loa Observatory Photochemistry Experiment, J. Geophys. Res., 97, 10285-10290.

Train M. et al. (1993) Correlation of ozone with NOy in photochemically aged air, J. Geophys. Res., 98, 2917 - 2925.

Williams, E. J. and Fehsenfeld F.C. (1991) Measurement of soil nitrogen oxide emissions at three north American ecosystem, J. Geophys. Res., 96, 1033 -1042.
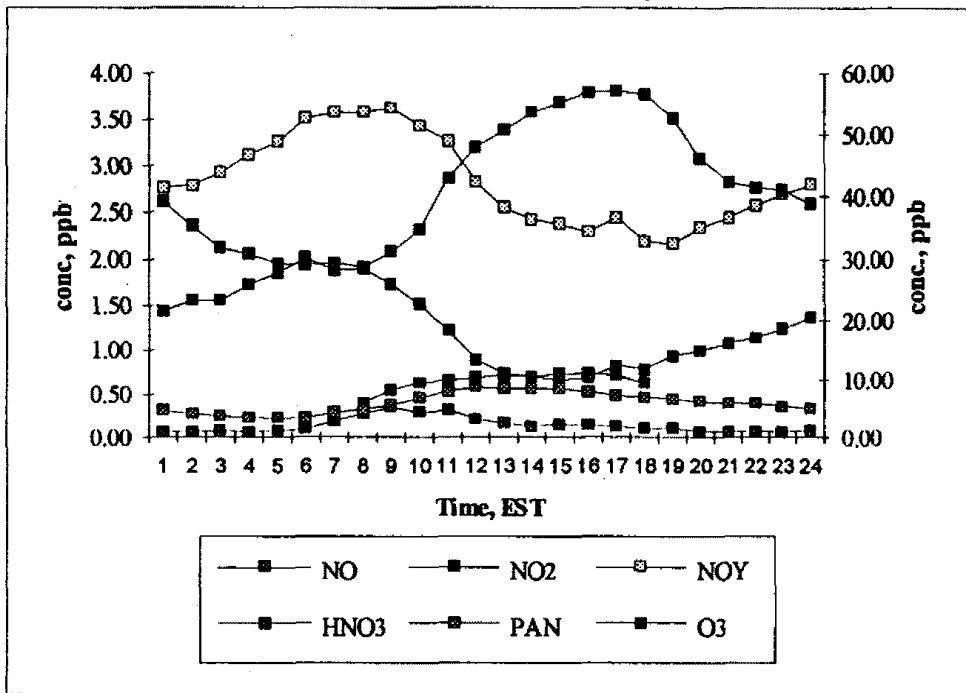
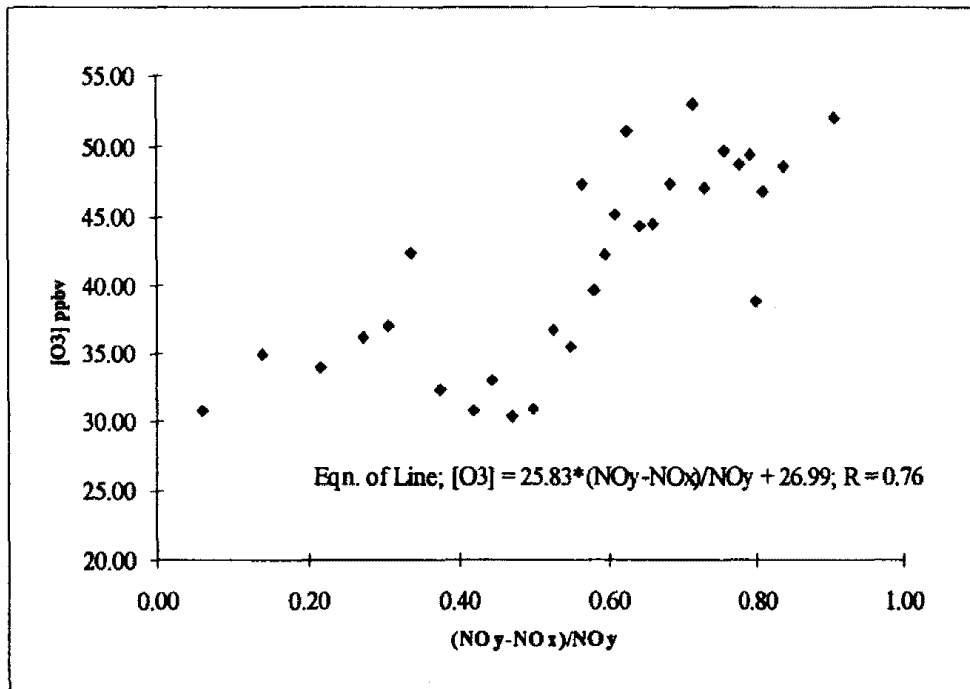Figure 1. Composite diurnal profiles of nitrogen species and ozone

Eqn. of Line; [O3] = 25.83*(NOy-NOx)/NOy + 26.99; R = 0.76

Figure 2. Variation of O3 versus the ratio (NOy-NOx)/NOy.