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INTERACTIONS BETWEEN SUMMER STORMS AND PHOTOCHEMICAL AIR QUALITY IN SW INDIANA

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INTRODUCTION

Acidic precipitation, although not now considered a major threat to ecosystems in the Midwestern United States, remains an important measure of environmental quality. The identification of the sources of railfall acidity need to take into account the gaseous and particulate atmospheric environment, the type of storm event and its duration, the synoptic conditions surrounding the storm, and the trajectory of the storm prior to its activity over the site of interest. Nitrogen compounds in precipitation are generally not the primary sources of precipitation acidity in the eastern half of the United States, but previous work has indicated that 80% of the summer concentrations of nitrate are associated with hydrogen ion concentrations (Grant, 1988). Since nitric acid is derived from oxidation reactions involving nitrogenous aerosols and gasses, particulate and gaseous air quality are directly linked to precipitation acidity.

The gaseous nitrogen species present in the atmosphere are almost all highly reactive and have temperature sensitive kinetics, resulting in short atmospheric residence times. The residence time for NO_2 and NO is probably between 6 to 10 hours during the summer (Singh, 1987). Therefore, during the summer the gaseous concentrations of NO_2 and NO measured from the day prior to the time of the precipitation may represent the levels in the formation of nitric acid within the storm and consequently the nitrate ion in the precipitation. This relationship would be confused by local sources of NO. A relationship between NO_2 and NO and precipitation NO_3^- may also be masked by gaseous NO_3, HNO_3, N_2O_5, and HO_2NO_2 and particulate NO_3 that may be important in the formation of aqueous NO_3^- and gaseous HNO_3 (Singh, 1987). In addition, there could be non-chemical advective processes that may change atmospheric concentrations due to wind direction, turbulent mixing, and diffusion.

The nitrogen oxides in combination with sunlight and reactive non-methane hydrocarbons control the concentrations of ozone. The high levels of ozone near the earth's surface that occur during the day is indicative of the UV environment and the NO emission and NO_2 formed during the night. In this paper, NO_x equals NO + NO_2. The relationships between the concentrations of ozone, nitric oxide, and nitrogen dioxide and wind direction, amount of precipitation, type of storm producing precipitation, and the nitrate ion in the precipitation are discussed in this paper. PAN and non-methane hydrocarbons, although known to be important in the formation of ozone, were not considered due to lack of measurements.

MATERIALS AND METHODS

Measurements of hourly ozone, nitric oxide, and nitrogen dioxide concentrations as well as wind direction were made at the Southwest Purdue Agricultural

TABLE 1. Characteristics of the growing season mean daily air quality.

Specie	1986		1987		Combined	
	Mean[1]	% Capture[2]	Mean	% Capture	Mean	% Capture
NO_X	14.9	71	15.3	80	15.1	76
NO_2	11.0	66	11.5	68	11.2	67
NO	3.9	66	3.8	68	3.9	67
NO_2/NO	4.9	66	5.5	68	5.2	67
O_3	34.0	96	36.6	91	35.5	94

[1] Concentrations in ppb.

[2] Calculated as percent from # days with > 50% of the hours measured/total number of days in period.

Center by the Indiana Department of Environmental Management (IDEM) as part of the air quality network. The ozone concentration was determined by chemiluminescence. The nitrogen oxides were estimated by chemiluminescence using a CSI model 1600. It was assumed that the peroxyacetyl nitrate (PAN) and gaseous HNO_3, also measured by the analyzer, was significantly less than the nitrogen oxides at this rural site. Nitrogen dioxide was determined by reduction of the nitrogen oxides to nitric oxide. Quality assurance and control of the analyzers was maintained by the IDEM. Wind direction was measured at 7 m (4 m above a trailer).

Aerosols were collected using an Andersen five stage impactor located at a farm near Decker, Indiana, located 20 km from the Southwest Purdue Agricultural Center. Aerosol collections were made for 24 hour periods at a flow rate of 9440 cm^3s^{-1}, resulting in a sample volume of 1835 m^3. The sampler was mounted at a height of 7 m with a rectangular gabled roof over the intake resulting in an upper size limit for the sampler of approximately 30 μm (Hidy, 1984). The sampler had four stages of Whatman 41 filters which separated the aerosol into the size classes with effective cutoff diameters of 7, 3.3, 2, and 1.1 μm, and a last (backup) stage that had an effective cutoff diameter of approximately 0.05 μm. Aerosol samples were collected every three and four days (alternating) from 11 September 1985 to 4 December 1985 and every seven days from then until 23 September 1987 by PSI Energy. All filters were quality-assured before and after exposure and catalogued by the IDEM. Quality assurance involved the repeated weighing of desiccated filters for constancy.

The water-soluble nitrate concentation of the particle fractions was determined using standards of 5 and 10 ppm NO_3 and methods according to Grant and McFee (1989). Positive artifacts of nitrate are found on cellulose filters similar to the first four stages (Appel, *et al.,* 1979), probably resulting in overestimates of the true nitrate aerosol. Smaller positive artifacts have also been found for nitrate on quartz fiber filters like the backup filter (Spicer and Schumacher, 1977); however, other studies suggest substantial losses, if significant fractions of the particulate are in the form of ammonium nitrate (Forrest, *et al.,* 1980). Since much of the nitrate is expected to be present in submicron sizes, the estimates of the nitrate particulate concentration represent at best a lower limit estimate of nitrate particulates.

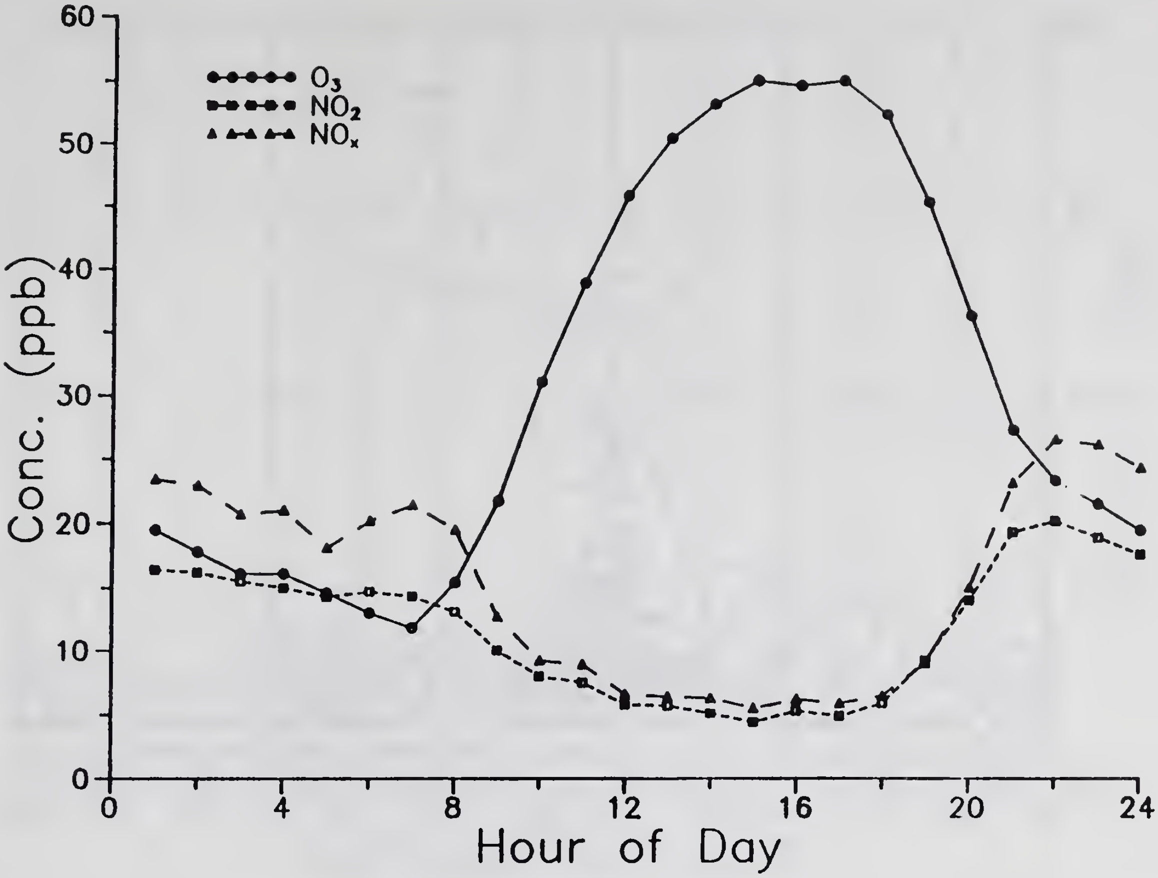

FIGURE 1. Hourly mean concentrations of O_3, NO_2, and NO for the 1986 growing season. O_3, NO_2, and NO are indicated by the solid, dashed, and dotted lines respectively. Note the increased NO levels around morning rush hour (8 AM EST) and in the nightime.

Wet deposition of nitrate in the precipitation was determined as part of the National Atmospheric Deposition Program (NADP) weekly wet deposition collections. Quality control and assurance were maintained by the NADP Central Analytical Laboratory (Schroeder, *et al.,* 1986).

Each day of valid particle and gas concentration was classified as to whether precipitation occurred, how much precipitation occurred, and what kind of storm produced the precipitation. The precipitation days were identified by the occurrence of measurable precipitation at the Vincennes NADP weighting bucket raingauge. The type of storm producing the precipitation was determined by evaluating the synoptic National Weather Service daily weather maps. The storms were classified into air mass and frontal type storm precipitation. Air mass storms primarily occurred in the cyclone warm sector. Frontal storms included stationary, cold, and warm front storms.

RESULTS

The mean daily ozone, nitrogen dioxide, and nitric oxide concentrations were approximately the same for the 1986 and 1987 growing seasons (Table 1). During both seasons, the missing nitrogen compound measurements occurred mostly during the month of July.

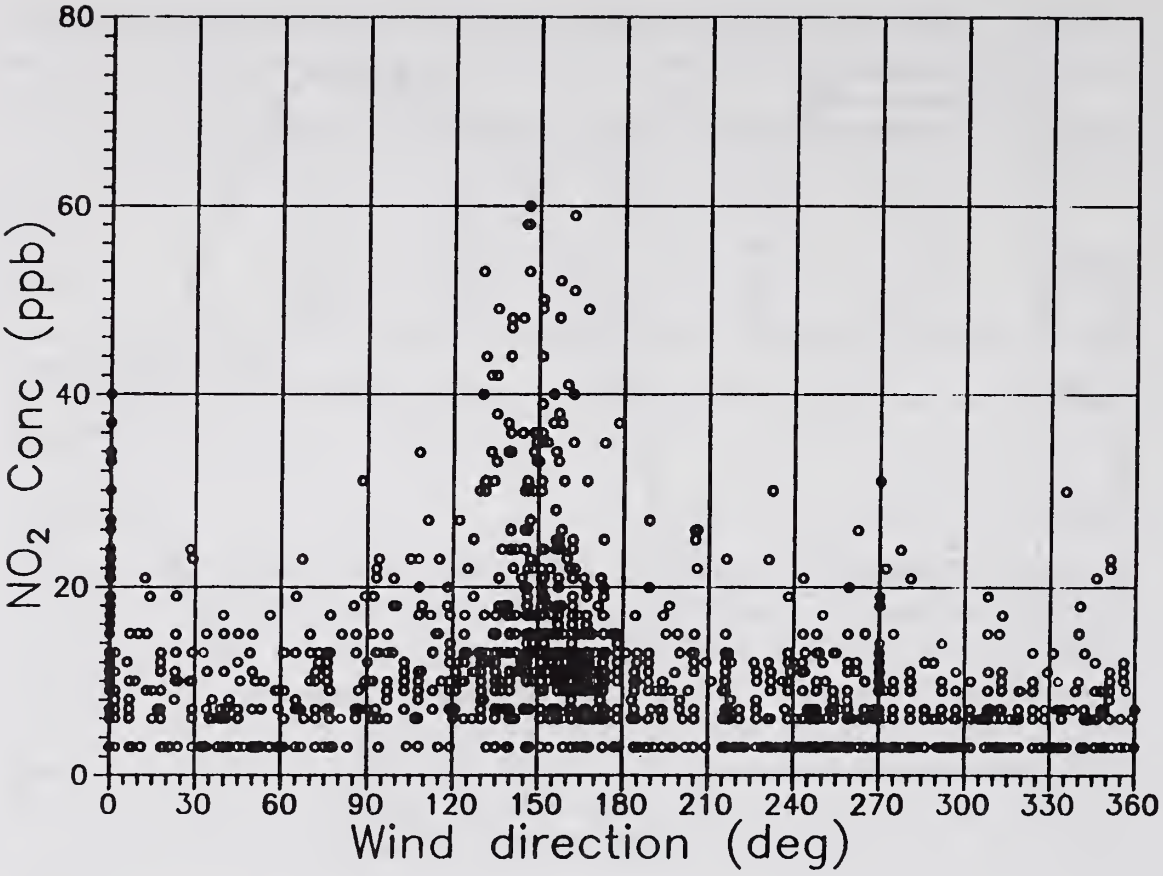

FIGURE 2. Influence of wind direction on the [NO_2] concentration at 7 m.

TABLE 2. Statistical test of the influence of precipitation on air quality specie concentrations.

Specie	Concentration Change	T	Prob > T	n
NO_x	−2.7[1]	−3.06	0.004	44
NO_2	−1.9[1]	−3.50	0.01	55
O_3	−0.8[2]	−0.63	0.53	62

[1] Mean daily concentration on day of precipitation less that on prior day.
[2] Mean daily concentration on day after precipitation less that on day of precipitation.

The hourly mean [NO], [NO_2], and [O_3] for the study period followed the expected diurnal pattern (Figure 1). The nitrogen oxides are high during the night and low during the day, while ozone is high during the day and low at night. The local peaks of [NO] at 700 h and possibly 2200 h may be influenced by local traffic emissions, when the surface boundary layer of the atmosphere is stable. The diurnal variation of [O_3] was largely due to the deposition of O_3 from the nocturnal boundary layer during the night and the mixing of the upper and convective boundary layer during the day (Shepson, *et al.,* 1992). The ratio of [NO_2] to [NO] provides an indication of the rapidly formed steady state relationship with [O_3] and is typically about 5. Results for the combined seasons fit this average condition well (Table 1).

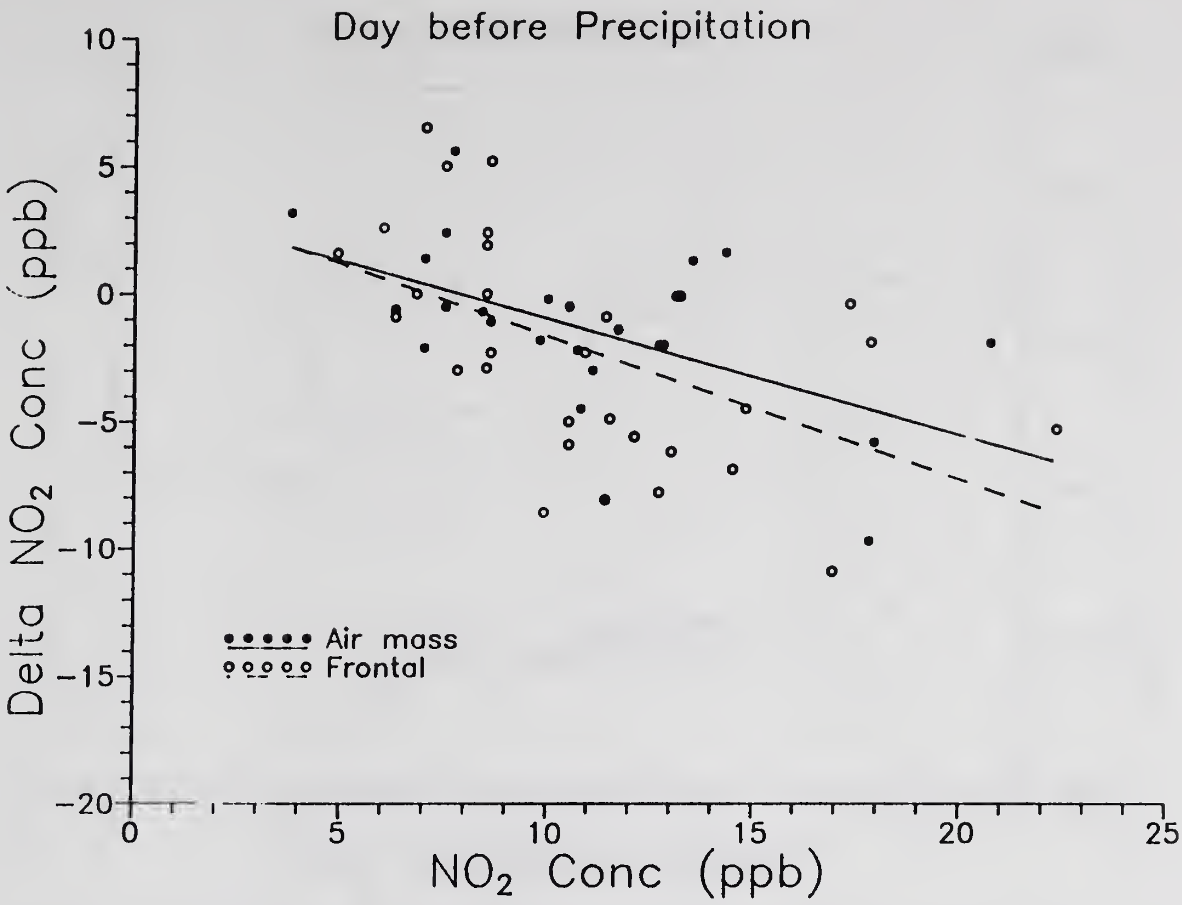

FIGURE 3. The change in [NO_2] due to precipitation vs. the precipitation day [NO_2]. The closed circle and solid line represent the daily values for days in which the storms were within air masses and the corresponding linear regression respectively. The open circle and dashed line represent the daily values for days in which the storms were due to frontal passages and the corresponding linear regression reprectively. Note that the change is greatest when the [NO_2] is above the seasonal mean of 11 ppb.

Of the 244 days of the study, 63 days had precipitation occurring. Of those days, 59% of the days were wet due to frontal storms, and 41% of the days were wet due to air mass convection storms. During the study period, 12 valid samples with NADP nitrate chemistry were collected.

Wind direction averaged 200 deg (North 0 degrees) for the combined two seasons with the mean direction during days of frontal and air mass type precipitation being 211 deg and 170 deg. The variation in the hourly mean [NO_x] and [NO_2] (e.g., Figure 2) over the study period varied with wind direction, while that of [O_3] did not. The highest hourly mean [NO_x] and [NO_2] occurred when the wind was bearing between 160 and 180 degrees. This corresponds to the direction of a major source of [NO_x] approximately 30 km from the sample site. This also corresponds with the mean direction of the air mass type storm typically derived during the summer from unstable moist maritime airmass air originating in the Gulf of Mexico or the Atlantic Ocean.

The occurrence of precipitation caused a 17% reduction in the [NO_2] and a 18% reduction in [NO_x] from the prior day mean (Tables 1 and 2). The change in [NO_2]

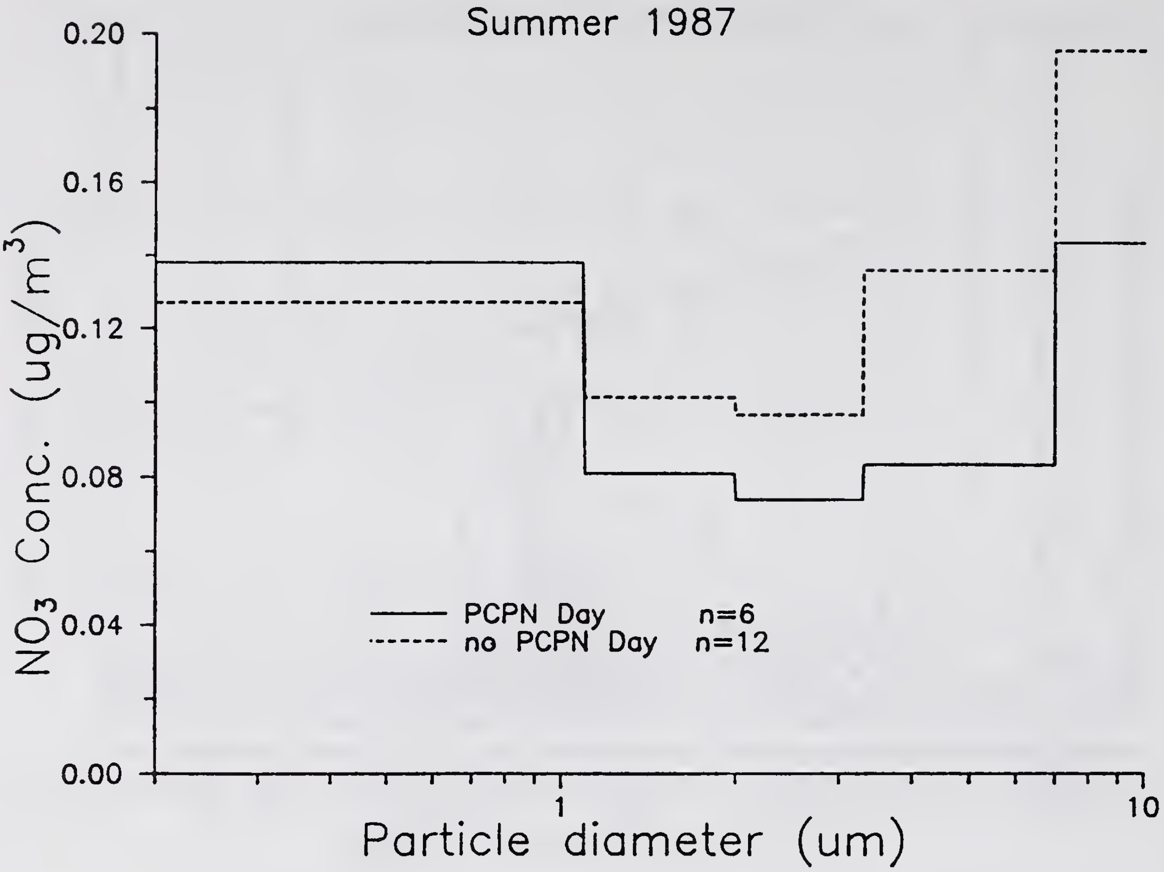

FIGURE 4. The influence of precipitation on the particulate [NO_3^-] distribution. The solid line represents the mean concentration distribution for particulate collections on days of precipitation. The dashed line represents the mean concentration distribution for particulate collections made on days during the study period in which no precipitation occurred.

and [NO_x] was greater for frontal storms than for air mass storms with a decrease of 2.2 ppb [NO_2] and 3.0 ppb [NO_x] with the frontal storm precipitation and a decrease of 1.4 ppb [NO_2] and 2.4 ppb [NO_x] with the air mass storm precipitation. The differences in magnitude and level of probable difference are probably due to the confounding of the [NO_2] and [NO_x] with the change in wind direction associated with passage of the front. Most frontal storms were cold fronts, resulting in a shift in the wind to the west and away from the bearings of the highest hourly means [NO_2] (presumably a major local source of the gas). Since the air mass storm differences also corresponded with continued southerly air flow, the influence of the local [NO_x] source should be continuous throughout the period of day before, day of, and day after precipitation. Thus, the changes [NO_2] and [NO_x] associated with air mass storm precipitation days probably better represent the storm effects on [NO_2] and [NO_x] levels in the near surface atmosphere. Results show that the change in [NO_2] was greater when the [NO_2] on the day before precipitation was higher, with distinct decreases in [NO_2] occurring when the [NO_2] on the day before precipitation was higher than the mean growing season concentration (Figure 3). This relationship was found for both air mass convective and frontal storms but again was more evident for frontal storm precipitation days. Therefore, shifts in the wind direction, affecting the influence of local sources

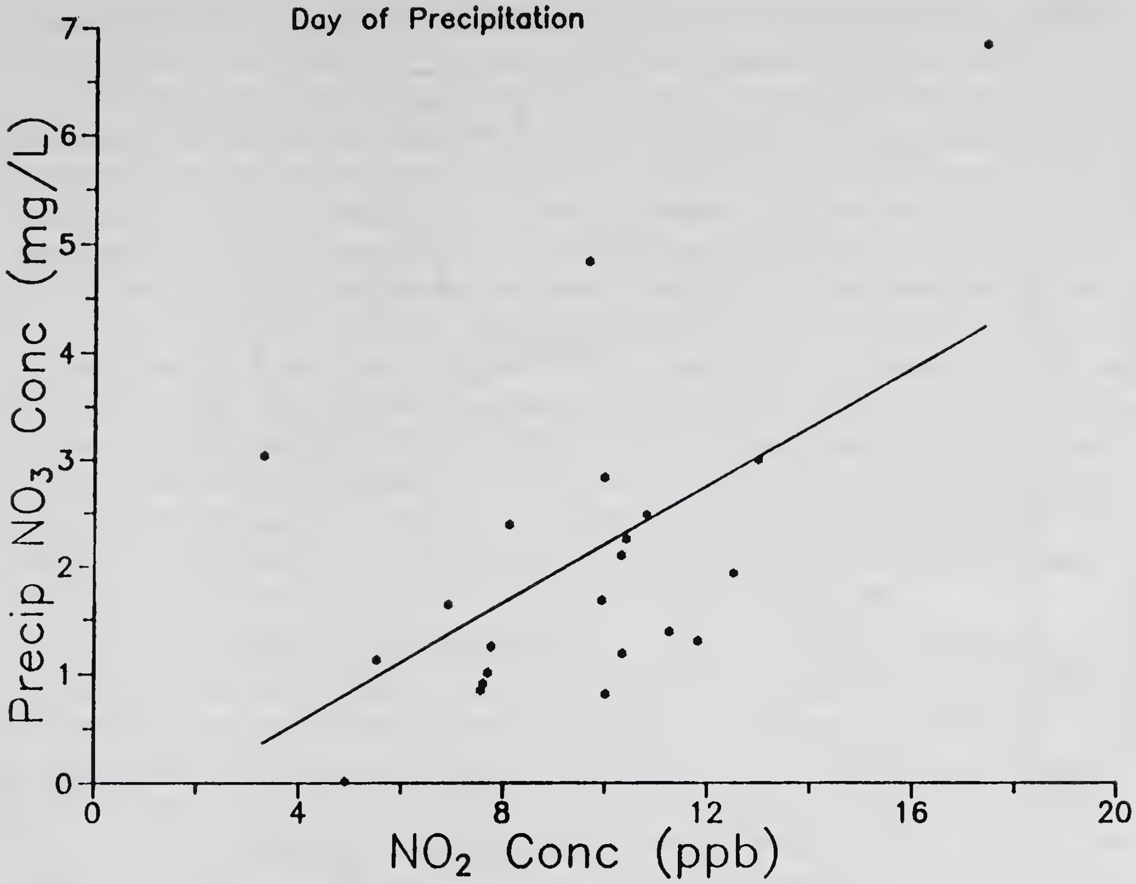

FIGURE 5. The relationship of [NO_2] reductions associated with precipitation to precipitation [NO_3^-].

of the [NO_x] influence the strength of precipitation influence but do not account for most of the changes in [NO_2] associated with the precipitation.

The change in [NO_2] due to precipitation amount indicates that there is no trend in increased [NO_2] reductions with increased precipitation. Considering only air mass convective storms, the range in the change in [NO_2] does tend to decrease with increased precipitation, but this may solely be the small sample size. The range in the change in [NO_2] in frontal storms shows much less decrease with increasing precipitation.

Although there were significant decreases in the mean [NO_2] and [NO_x] with the receipt of precipitation (Figure 3), these decreases did not carry over into the subsequent day after the precipitation. Daily mean concentrations of [NO_2] and [NO_x] for the day before and the day after precipitation were not significantly different. Thus, while a storm reduces the concentrations, it is only reduced for the day of precipitation.

The reduction in the mean [NO_2] may be due to chemical oxidation reactions on the surface of the aerosols and precipitation droplets or vertical convection of the gas to the free troposphere through the updraft of the storm cell (Dickerson, *et al.*, 1987). Scavenging of NO_2 by the precipitation is negligible due to its low

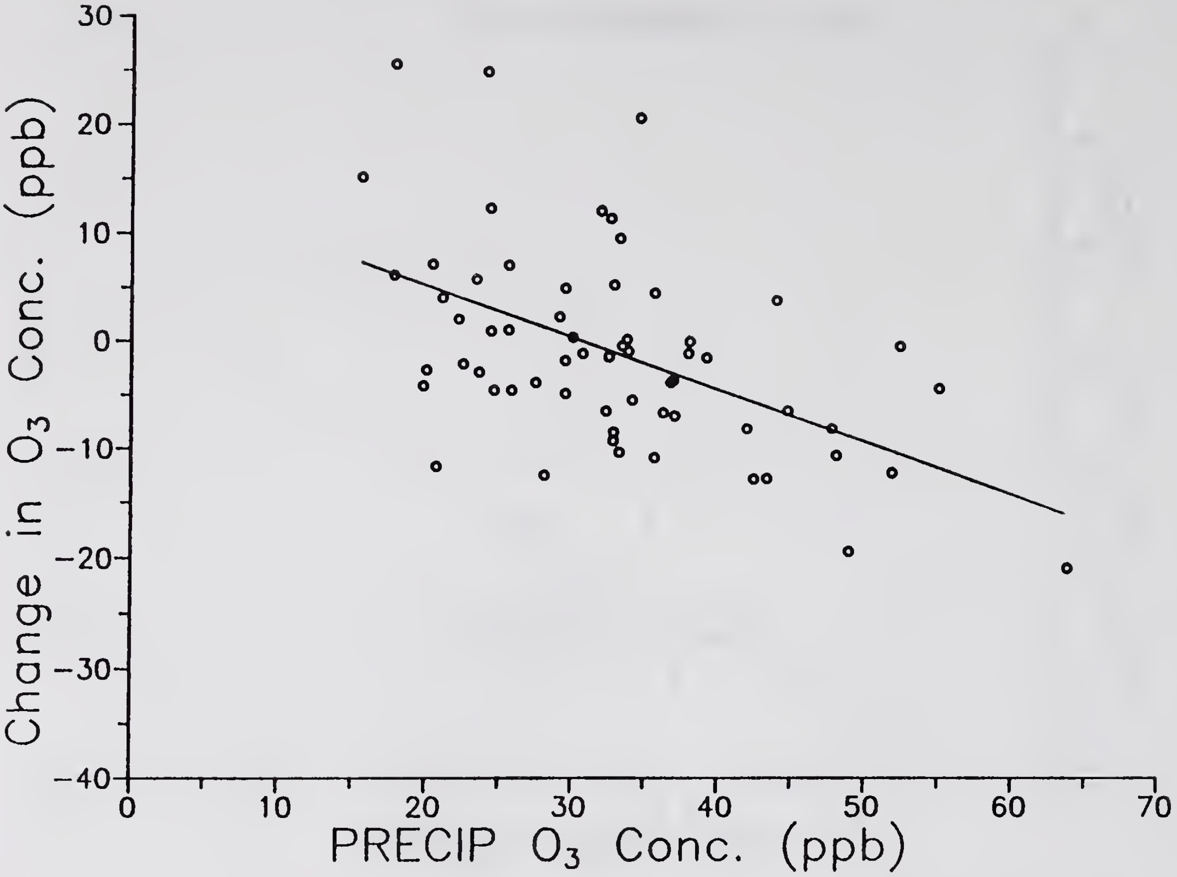

FIGURE 6. Effect of precipitation on [O_3]. Note that the precipitation does not influence the daily mean [O_3] until the [O_3] exceeds the seasonal mean of 35 ppb.

solubility in water (Pierson, *et al.*, 1987). Reductions in NO_2 through oxidation to HNO_3 during the daytime with subsequent scavenging of the HNO_3 by precipitation is possible since the solubility of HNO_3 in water is high, but no information on the [HNO_3] was available at the study site. Noting that the [NO_2] reduction due to storm activity seems to make a step change at about 10 ppb (Figure 3), and the seasonal mean [NO_2] is 11 ppb (Table 1), it appears that the storm activity vents [NO_2] to the free troposphere through the vertical convection updrafts of storm cells.

Comparing the precipitation [NO_3] to the reduction in [NO_2] shows that while the [NO_2] is lower during the day of precipitation, it does not significantly influence the composition of the precipitation. A regression of the precipitation nitrate concentration by the change in [NO_2] (Figure 5) yielded an r^2 of 0.12, while nitrate deposition on in [NO_2] yielded an r^2 of only 0.06. Similar lack of correlation was found in comparing the wet concentration and deposition of NO_3 to the mean [NO_2] during the day of precipitation. These results suggest that gaseous HNO_3 and particulate NO_3^- (and other nitrogenous compounds) are major contributors to the precipitation [NO_3^-], and not gaseous NO_2. Furthermore, the lack of correlation between precipitation NO_3^- and reductions in [NO_2] corresponding to days of precipitation indicates that the [NO_2] reductions are probably primarily due to vertical convection.

Scavenging of particulate nitrate ($[NO_3^-]_p$) by the precipitation is expected, as rainout is an efficient scavenger of the aerosol (Stewart, *et al.*, 1990). For the summer of 1987, 18 aerosol collections were made with 33% collected during days of precipitation. the mean $[NO_3^-]_p$ present in the atmosphere of dry days was 0.21 mg m^{-3} while that in the atmosphere of the wet days was 0.15 mg m^{-3}. The 29% decrease in concentration between the non-precipitation and precipitation days was significant at the 0.20 level. The distribution of the $[NO_3^-]_p$ (Figure 4) showed that the smallest size fraction (< 1.1 μm diameter) was greater for the days of precipitation than for days without precipitation, while all other size fractions showed greater $[NO_3^-]_p$ for the days without precipitation than with precipitation. The only significantly different $[NO_3^-]_p$ size fractions were those particles $\geqslant 7$ μm and those $\geqslant 2$ μm and < 3 μm. The smalller $[NO_3^-]_p$ present in the larger fractions during days of precipitation are consistent with that expected after scavenging processes. Remembering the artifact problems, the larger size fractions of the collections have potential for substantial positive artifacts, while the last stage has the potential for negative artifacts. Therefore, due to the limited sampling of the particulates and the probable nitrate artifacts on the filters used, no conclusions as to the magnitude of the scavenging can be made.

As a result of the observed reduction in $[NO_2]$ on the day of precipitation, it may be expected that since O_3 is produced from NO_2, the $[O_3]$ on the day following the precipitation would also be reduced. While a reduction was indicated (Table 2), the reduction was not significant at even the 0.20 level using a students t-test. The $[O_3]$ apparently is not locally derived but is probably largely advected into the area. Reductions in O_3 associated with the occurance of precipitation was only evident when the $[O_3]$ was greater than the seasonal mean of 35 ppb (Figure 6). This 35 ppb level corresponds to the two growing season mean $[O_3]$ (Table 1). Mean daily ozone levels above the mean probably represent locally produced O_3 that is in addition to that advected across the region. As with the $[NO_2]$, storm activity probably vents the elevated (above regional average) $[O_3]$ to the free troposphere through the vertical convection updrafts of the storm cells.

CONCLUSIONS

Near surface hourly mean $[NO_2]$ is influenced by the direction of the wind. Winds coming from the southeast to south sector had higher $[NO_2]$ than the rest of the bearings, indicating a local source of NO and NO_2 to the Vincennes site. The high levels, however, were not always evident and were partly influenced by the time of day with night-time southerly winds producing higher levels than daytime southerly winds. The near surface hourly mean $[O_3]$ was not related to wind direction, in support of the contention that the majority of the O_3 is being advected into the area and not produced locally.

A significant reduction in daily mean $[NO_2]$ occurred on the day of precipitation. This indicates a local source of NO. The $[NO_2]$ reduction did not correspond to higher precipitation concentrations or depositions of $[NO_3^-]$. Therefore, (1) the NO_3^- in precipitation was probably due to the oxidation of unmeasured gaseous NO_3, HNO_3, N_2O_5, and organic nitrogen compounds in the troposphere and/or the washout of particulate NO_3^- and HNO_3, and (2) the $[NO_2]$ reductions were probably due to vertical convection within the storm system of the locally-produced NO_2 from the surface to the free troposphere.

Precipitation did not significantly influence the daily mean $[O_3]$. This would be expected, if the mean daily O_3 was a result of advection and not local production. Some evidence exists to indicate that high levels (above mean ambient regional levels) O_3 represent locally produced O_3, with some reductions in $[O_3]$ probably also due to vertical convection of the gas within the storm system from the surface to the free troposphere.

Evidence tends to support the hypothesis that the precipitation acts to 'cleanse' the atmosphere of NO_2 for at least a short time through the physical process of vertical convection of elevated concentrations of pollutants from lower troposphere to the free troposphre. There is, however, no evidence that the precipitation NO_3^- is directly related to the chemical oxidation of ambient $[NO_2]$. Trends and tendencies found in this study may be significant when the time of storm precipitation is taken into account and shorter term mean concentrations are considered to establish influences of the precipitation. Additional work also needs to be done to determine the other nitrogenous compounds (HNO_3, PAN, and others) in the atmosphere over Vincennes, and their relationship to the nitrate ion content of the precipitation.

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