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NO_y lifetimes and O_3 production efficiencies in urban and power plant plumes: Analysis of field data

L. J. Nunnermacker, L. I. Kleinman, D. Imre, P. H. Daum, Y.-N. Lee, J. H. Lee, S. R. Springston, and L. Newman

Environmental Chemistry Division, Brookhaven National Laboratory, Upton, New York

N. Gillani

Earth System Science Laboratory, NASA-UAH Global Hydrology & Climate Center, Atmospheric Science Department, University of Alabama, Hunstville

Abstract. In an effort to describe and characterize power plant plumes in the Nashville region, emissions from a small power plant (Gallatin) and a large power plant (Paradise) were examined using data obtained on the Department of Energy G-1 airborne sampling platform. Observations made on July 3, 7, 15, 17, and 18, 1995, were compiled, and a kinetic analysis of the chemical evolution of the power plant plumes was performed. Analysis of the power plant plume data revealed a very active photochemistry, as had been determined previously for the urban plume. Ozone production efficiencies (OPE), defined as the number of molecules of O_3 formed per NO_x molecule consumed, were found to be 3 for Gallatin and 2 for Paradise. Lifetimes for NO_x (2.8 and 4.2 hours) and NO_y (7.0 and 7.7 hours) were determined for Gallatin and Paradise, respectively. These NO_x and NO_y lifetimes imply rapid loss of NO_z (NO_z is assumed to be primarily HNO_3). Lifetimes for NO_z are calculated to be 3 and 2.5 hours for Gallatin and Paradise, respectively. A sensitivity analysis indicates that the Gallatin NO_z lifetime could be as long as 5 hours, bringing it into agreement with the value determined for the Nashville urban plume. It is unlikely that the Paradise NO_z lifetime is as long as 4 hours. If NO_z loss is attributed to dry deposition, a 3 hour lifetime implies a deposition velocity greater than 10 cm s^{-1}, which is much faster than expected based on accepted theory. Possible reasons for this discrepancy are discussed.

1. Introduction

The 1995 Nashville/Middle Tennessee Southern Oxidants Study (SOS) was part of a large cooperative effort to understand the process of ozone production [*Chameides and Cowling*, 1995] so that the most effective emission control strategies (i.e., VOC versus NO_x) could be determined [*National Research Council (NRC)*, 1991; *U.S. Congress*, 1989]. Despite the fact that significant controls on volatile organic compounds have been implemented [*EPA*, 1992], during the past 14 years the Nashville/Middle Tennessee region has exceeded the National Ambient Air Quality Standard (NAAQS) of 120 parts per billion by volume (ppbv) for 1 hour [*SOS*, 1995]. It will be difficult for Nashville and its environs to stay in attainment under the new NAAQS of 80 ppbv for 8 hours [*Chameides et al.*, 1997; *Kleinman et al.*, 1998]. Several recent studies have determined that large reductions in nitrogen oxides emissions are needed to ameliorate the O_3 problem [*Trainer et al.*, 1987; *McKeen et al.*, 1991]. This is especially true, in the southeast where biogenic hydrocarbons are in abundance and impossible to control.

Coal-fired power plants are a major source of NO_x ($[NO_x] = [NO] + [NO_2]$), a precursor to O_3 formation [*Trainer et al.*, 1995]. Nashville is an area surrounded by seven large fossil fuel power plants generating at least 12.2 x 10^3 metric tons of NO_x per year for the small plants to 132 x 10^3 metric tons of NO_x per year for the larger plants [Environmental Protection Agency (*EPA*), 1993; N. Gillani, personal communication, 1998]. Depending on the prevailing meteorology, Nashville air quality may be directly impacted by the following four plants: Gallatin (35 km NE), Cumberland (80 km NW), Johnsonville (110 km W), and Paradise (130 km, NNW). Therefore, in order to determine the most effective control strategies, it is necessary to have a better understanding of the photochemistry occurring in power plant plumes.

A large fraction of the NO_x emitted in the Nashville area originates from power plant sources. Thus an important question to ask is whether the O_3 production efficiency in power plant plumes is the same as it is in the urban plume. There are reasons to believe that differences may exist, because urban and power plant plumes have very different characteristics [*Joos et al.*, 1990; *Duncan et al.*, 1995]. Chemically, for example, power plant combustion processes are finely tuned to extract energy from their fuel, and thus emit virtually no hydrocarbons that can serve as fuel for O_3 production. Hydrocarbons for O_3 production in power plant plumes must come from background biogenic hydrocarbons and anthropogenic hydrocarbons from other sources.

In order to produce O_3, power plant plumes depend on the entrainment of ambient air containing hydrocarbons. Thus the mixing process has a more important role for a point source than for a more diffuse urban plume that contains all the precursors (i.e., hydrocarbons and NO_x) necessary for O_3 production. As a plume is advected downwind from its point source, two processes occur on different timescales [*Builtjes and Talmon*, 1987]. Initially, the first process is macroscale mixing which is the turbulent mixing of the plume caused by large scale eddies. It disperses the plume effluents and mixes surrounding ambient air

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into the plume. The second process is microscale mixing which is the process of turbulent mixing on such a scale that chemical reactions take place (i.e., the reaction of NO with O_3 and subsequent O_3 formation from a power plant source) [*Gillani and Wilson*, 1980; *Vila-Guerau de Arellano et al.*, 1990; *Galmarini et al.*, 1995; *Fraigneau et al.*, 1996].

A major finding from the 1995 SOS intensive was rapid loss of NO_y from both the urban plume [*Nunnermacker et al.*, 1998] and power plant plumes [*Gillani et al.*, 1998 a,b; *St. John et al.*, 1998]. For the urban plume, rapid loss of NO_y from the air mass was observed and attributed to dry deposition of HNO_3. On average, the lifetime for NO_y in the urban plume was determined to be 6 hours [*Nunnermacker et al.*, 1998]. *Gillani et al.* [1998a] found evidence in a 1994 data set that NO_y was removed from the Cumberland plume at rate of 0.12 $hour^{-1}$, for a lifetime of NO_y of approximately 8 hours. This paper also points out that careful study of the 1995 data set for Cumberland yielded a loss rate of 0.0 ± 0.3 $hour^{-1}$, consistent with lower deposition rates of HNO_3. In addition, *St. John et al.* [1998] identified rapid loss of NO_y from the Gallatin plume but determined that no such loss was evident in the Nashville urban plume. *Ryerson et al.* [1998], have identified rapid loss of SO_2 from power plant plumes, resulting in a photochemical lifetime of 10 ± 2 hours for SO_2.

A concomitant result of the rapid loss of NO_y from the plumes is the reduction in ozone production efficiencies determined using the ratio of O_3 to NO_z. An average ozone production efficiency with respect to NO_x (OPE_x) of 3 ppbv/ppbv was determined by *St. John et al.* [1998] for Gallatin (after correcting for NO_y losses). This is quite similar to the OPE_x determined for the Nashville urban plume of 3-4 ppbv/ppbv, after correcting for depositional losses [*Nunnermacker et al.*, 1998]. On the other hand, OPE_x determined for the larger power plant plumes, such as Cumberland and Paradise, were found to be in the range of 1 to 4 [*Gillani et al.*, 1998b; *Ryerson et al.*, 1998]. Because of the importance of these issues and the unresolved differences between research groups, it is desirable to bring to bear as much evidence as possible on these topics.

In this article we extend our previous treatment of the fate of NO_x in an urban plume [*Nunnermacker et al.*, 1998] to the consideration of NO_x emissions from the Gallatin and Paradise power plants. Gallatin is a small power plant with NO_x emissions of 11 x 10^3 metric tons yr^{-1}, while Paradise is a much larger plant with emissions of 120 x 10^3 metric tons yr^{-1} [*Gillani et al.*, 1998b]. Using observations from the DOE G-1 aircraft, we determine the oxidation rate of NO_x, the deposition rate of NO_x oxidation products, and the O_3 production efficiency. In contrast to our previous study [*Nunnermacker et al.*, 1998], we require that NO_x be oxidized to products such as HNO_3 before it is susceptible to dry deposition. The loss of NO_y from a plume due to deposition is distinguished from loss due to dilution by using CO and SO_2 as conservative or quasi-conservative tracers for urban and power plant plumes, respectively. Ozone production efficiencies are corrected for NO_y loss yielding significantly lower values than given by the observed ratios of O_3 to NO_y.

2. Experiment

The main objective of the DOE G-1 aircraft was to characterize the processes responsible for elevated O_3 levels within the urban plume [*Nunnermacker et al.*, 1998; *Daum et al.*, this issue (a, b)]. As part of this activity, *Nunnermacker et al.* [1998] have reported on the chemistry of NO_x on 2 days, July 3 and 18, where the urban plume was particularly well defined. *Daum et al.* [this issue (b)] provide a model-oriented treatment of O_3 production on those days.

The DOE G-1 intercepted several power plant plumes over the course of the field experiment. Well defined plumes from the Gallatin power plant were observed on July 3, 7, 15, 17, and 18; and plumes from Paradise power plant were observed on July 7 and 17. These two plants provide an interesting contrast as the NO_x emission rate from Gallatin is one tenth that of Paradise.

A detailed description of the instrumentation used on board the DOE G-1 is given by *Nunnermacker et al.* [1998]. We briefly note that oxides of nitrogen (NO, NO_2, and NO_y) were measured using a three channel NO/O_3 chemiluminescence instrument. NO_y was converted to NO by a 350°C Mo catalyst; NO_2 was converted to NO by UV photolysis. Uncertainty in the measurement of oxides of nitrogen for 10 s averaged data is estimated to be 20 parts per trillion by volume (pptv) + 15% of the NO measurement, 20 pptv + 15% of the NO_2 concentration, and 50 pptv + 15% of the NO_y concentration. Ozone (O_3) was determined by UV absorption (Thermo Environmental Instruments (TEI), Model 49-100) and the estimated uncertainty in the O_3 concentration is 5%; CO was determined by nondispersive infrared (modified TEI, Model 48) with an estimated uncertainty of 30 ppbv + 15% of the measured CO concentration; and SO_2 was determined by pulsed fluorescence (modified TEI, Model 43S) and an uncertainty of the order of 200 pptv + 15% of the measured SO_2 concentration.

2.1. Meteorology

The plume studies presented here were conducted under conditions of light to moderate wind speeds. Wind direction was reasonably steady allowing the plumes to be tracked for up to 180 km. A brief description of the synoptic conditions on these days is given below. Additional information is given by *McNider et al.* [1998].

2.1.1. July 3, 1995. Conditions on this day were dominated by a high-pressure system located to the north of Nashville. Winds were out of the southwest at 3 to 4 m s^{-1}, pushing the Gallatin plume to the northeast.

2.1.2. July 7, 1995. A surface cold front passed through the Nashville area late on July 6. A strong high pressure region began building in western and middle Tennessee. Low-level winds were from the northwest at speeds of 4 to 6 m s^{-1}. Mid and upper levels of the atmosphere were very dry, but sufficient boundary layer moisture was present to develop scattered clouds.

2.1.3. July 15, 1995. The high-pressure ridge that dominated the weather pattern from July 10-14 weakened, and strong westerly flow aloft gradually moved to the south. Wind profiler data showed weak southeasterly to southerly flow at 2 to 3 m s^{-1}, bringing warm moist air into the region. Late afternoon thunderstorms developed over middle Tennessee as subsidence under the high continued to weaken.

2.1.4. July 17, 1995. A strong surface cold front extended southwestward from a low-pressure system over western New York to western Texas. Light northwesterly winds flowed over western and middle Tennessee at 4 to 5 m s^{-1}, ahead of the approaching front. During the afternoon, prefrontal convection again formed as the front began to move rapidly to the east over western and middle Tennessee.

2.1.5. July 18, 1995. An east-west oriented cold front moved through Tennessee during the early morning hours bringing cool dry air. Boundary layer wind speeds ranged between 4 and 6 m s^{-1}, with the top of the boundary layer at 1000 m (1000a local sounding).

2.2. Flight Tracks

Shown in Figure 1 are the flight tracks for the DOE G-1 on July 3, 7, 15, 17, and 18. On these maps the point of interception for

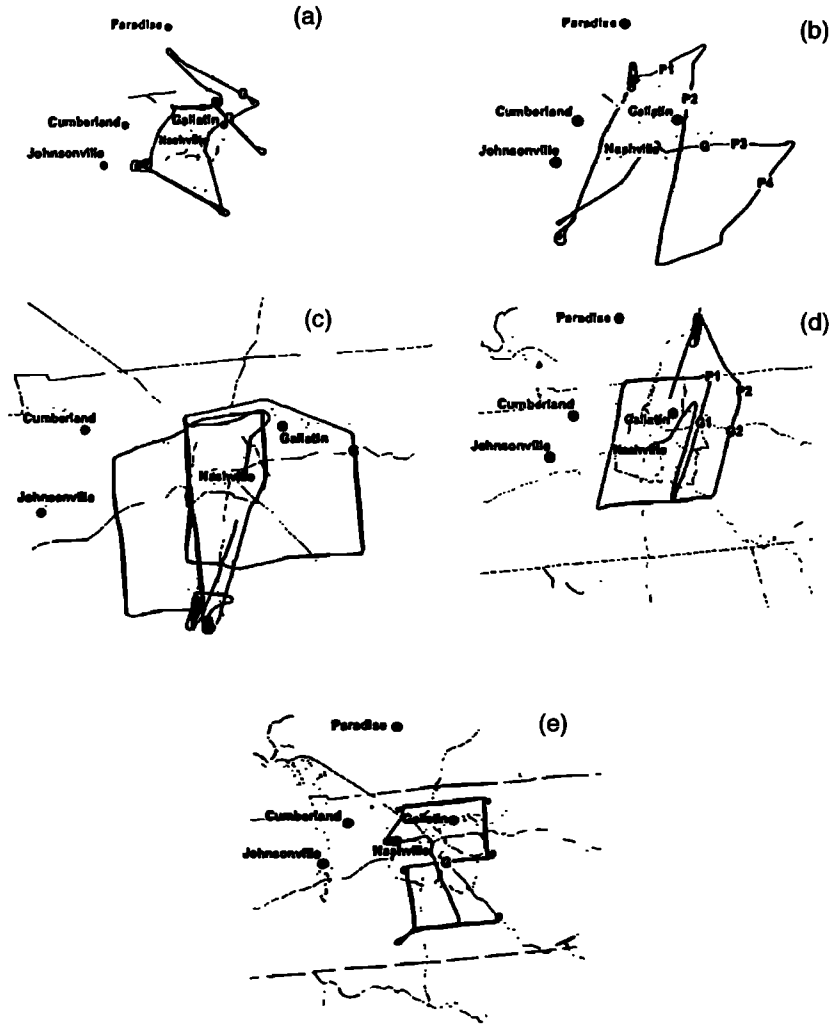

Figure 1. Flight tracks for the DOE G1 on July 3, 7, 15, 17, and 18, 1995 (a-e, respectively). The bold-faced G (Gallatin) and P (Paradise) indicate the interception points on the traverse for the power plant plumes.

the Gallatin or Paradise power plant plume is indicated by the letter G or P, respectively. Unless noted otherwise, the chemical data were obtained at approximately the same altitude (<750 m) on all of the flights. The measurements were all collected within the boundary layer (typically 1200 m), as determined by altitude profiles performed on the DOE G-1 and NOAA profiler data.

Plume age, defined as the travel time of a plume from its source to the point of observation, was determined as the distance from the Nashville urban center or power plant, divided by wind speed. Wind data (speed and direction) were obtained from the NOAA radar profilers deployed at Hendersonville (close to downtown Nashville), Youth Inc., and Dickson (50 km to the northwest of Nashville). A weighted average of the wind speeds observed at three profiler sites was used to calculate the elapsed times. On the basis of the standard deviation of this average, we estimate that the uncertainty in the determination of time is of the order of 30 to 35%.

3. Methodology and Results

In this section we use observed concentrations of NO_x, NO_y, and either CO or SO_2 as a tracer to identify the plume and to determine the oxidation rate of NO_x and the deposition rate of NO_x oxidation products. The NO_x oxidation rate is used to determine a corrected value for ozone production efficiency.

There are three processes that have to be considered. The first is oxidation of emitted NO_x to products such as HNO_3. The second is dry deposition of HNO_3. Because the deposition velocity of HNO_3 is significantly greater than for NO or NO_2, we assume that NO_x has to be oxidized before it dry deposits. The third is dilution which affects all components of NO_y. The initial conversion of emitted NO is not explicitly considered, but is implicitly taken into account by defining an oxidation rate with respect to the ambient mixture of NO and NO_2.

Our procedure is to use multiple intercepts of the plumes to determine $NO_x(t)/NO_x(0)$ and $NO_y(t)/NO_y(0)$ as a function of time. Rate constants for oxidation of NO_x and deposition of NO_z are determined by fitting the experimental points to curves whose form is dictated by the expected kinetics in the plume.

A general feature of our analysis is that we use concentration ratios of compounds measured on a plume transect, to account for the effects of dilution. These ratios are determined as the slope of a linear regression fit to the concentration of the species measured cross-plume. The ratios determined in this manner are

independent of background concentrations. Another feature of our study is that we combine data from more than one day in order to increase the range of reaction times that are considered in our analysis. Our justification for this procedure is empirical. We find that the combined data sets yield relatively smooth changes in ratios as a function of downwind distance. Variations in meteorology are not extreme. In particular, the 2 days used for the analysis of the Paradise power plant plume (July 7 and 17) had almost identical wind fields.

3.1. Urban

The urban source was treated by *Nunnermacker et al.* [1998], but without the explicit restriction that deposition only occurs for the NO_x oxidation products. We repeat parts of the analysis here because it serves as the starting point for the power plant plume calculations.

CO is used as an inert tracer of the urban plume. The ratio of CO to NO_y at the emission source is known from measurements made downtown [*Kleinman et al.*, 1998] and also from a close-in transect of the urban plume. All plume ingredients (NO_x, NO_y, and CO) will be equally affected by venting to the free troposphere and plume dispersion in the boundary layer. As we travel downwind of the city, NO_y decreases more rapidly than CO because it is also susceptible to dry deposition, causing the ratio CO/NO_y to increase. Oxidation causes NO_x to decrease more rapidly than CO. Downwind concentrations of CO, NO_x, and NO_y are given by

$$CO(t) = D(t)\,CO(0) \tag{1a}$$

$$NO_x(t) = R(t)\,D(t)\,NO_x(0) \tag{1b}$$

$$NO_y(t) = C_{NO_y}(t)\,D(t)\,NO_y(0) \tag{1c}$$

where $D(t)$ is a dispersion factor common to CO, NO_x, and NO_y; $R(t)$ is the fraction of NO_x not oxidized; and $CNO_y(t)$ is the fraction of NO_y not deposited. Combining equations 1a and 1c, yields

$$C_{NO_y}(t) = \frac{NO_y(t)}{CO(t)} \Big/ \frac{NO_y(0)}{CO(0)} \tag{2}$$

As indicated above, the ratio $[CO(t)]/[NO_y(t)]$ (and the inverse, NO_y/CO) is determined as the slope of a linear regression between CO and NO_y [*Nunnermacker et al.*, 1998, Figure 8]. C_{NO_y} (the fraction of NO_y not deposited) is thus used to describe the loss of NO_y from the plume independent of what is happening to the background. The initial ratio, $[CO(0)]/[NO_y(0)]$, has a value of 10.0 as determined from the close-in transect. Within the accuracy of the measurements this is the same as the downtown value of 9.3.

Conversion of NO_x to reaction products is determined from the initial NO_y to CO ratio and from correlations between $NO_x(t)$ and $NO_y(t)$ and between $NO_y(t)$ and $CO(t)$. It is assumed, at the point of emission, that $NO_x(0) = NO_y(0)$. If there was no dispersion, the fraction of NO_x remaining at time t would be given by $R(t)$ of equation (1b). We will call this fraction $(NO_x(t)/NO_x(0))^C$, where the superscript "C" denotes a value that has been corrected for dispersion. From equations (1) and (2) we obtain,

$$R(t) \equiv \left[\frac{NO_x(t)}{NO_x(0)}\right]^C = C_{NO_y}(t)\left(\frac{NO_x(t)}{NO_y(t)}\right) \tag{3}$$

By relying on regressions to determine ratios, all quantities in equation (3) are independent of background concentrations.

Figure 2a shows a plot of $[NO_x(t)/NO_x(0)]^C$ versus time. The solid line is a fitted curve of the form

$$\left[\frac{NO_x(t)}{NO_x(0)}\right]^C = e^{(-\alpha t)}(1-C_x)+C_x \tag{4}$$

in which α is the first-order rate constant for oxidation of NO_x. The inclusion of a constant, C_x, reflects the observation that there is a distributed NO_x source such that oxidation does not go to completion far from the source region. Equation (4) is fit to the experimental points (from equation (3)) by using a trial and error procedure to find values of α and C_x that minimizes a RMS (root mean square) difference. According to the fit in Figure 2a, the urban plume data indicates a NO_x lifetime ($1/\alpha$) with respect to oxidation of 2 hours.

If there was no dispersion, the fraction of NO_y remaining at time t would be given by $C_{NO_y}(t)$ of equation (1c). We will call this fraction $(NO_y(t)/NO_y(0))^C$, again using the notation that a superscript "C" denotes a value that has been corrected for dispersion. The time evolution of NO_y, corrected for dispersion and independent of background concentrations, is therefore given in terms of observed quantities by

$$\left(\frac{NO_y(t)}{NO_y(0)}\right)^C \equiv C_{NO_y}(t) \tag{5}$$

Data points in Figure 2b show $(NO_y(t)/NO_y(0))^C$ as a function of time as determined from multiple traverses of the urban plume. By fitting the data points in Figure 2b to a kinetic model we will determine the deposition rate for NO_z ($[NO_z] = [NO_y] - [NO_x]$).

Equation (6) gives the concentration of NO_z based on its formation from NO_x and its disappearance by deposition, which we assume obeys first order kinetics with rate constant β. It is further assumed that not all NO_z is susceptible to deposition loss. A fraction, C_Y, is taken to be a nondepositing (or slowly depositing) compound such as PAN, while the remaining fraction, $(1-C_Y)$, is taken to be a rapidly depositing species, that is, HNO_3.

$$\left(\frac{NO_z(t)}{NO_x(0)}\right)^C = \int_0^t \left(\frac{NO_x(t')}{NO_x(0)}\right)^C k(NO_x \rightarrow NO_z)\left[(1-C_y)e^{(-\beta(t-t'))}+C_y\right]dt' \tag{6}$$

Equation (6) has 3 factors in the integrand which, reading from left to right, represent (1) the fraction of NO_x molecules which survive to time t' as given by (4); (2) the rate of conversion of NO_x to NO_z at time t'; and 3) the fraction of NO_z formed at t' which survives until t. For the urban plume the oxidation rate constant is not time-dependent, and one can write an analytic expression for NO_z. An integral expression is given here because it is used for the power plant case where the oxidation rate constant increases with travel distance from the source.

The solid lines in Figure 2b have the form

$$\left(\frac{NO_y(t)}{NO_y(0)}\right)^C = \left(\frac{NO_x(t)}{NO_x(0)}\right)^C + \left(\frac{NO_z(t)}{NO_z(0)}\right)^C \tag{7}$$

where $(NO_x(t)/NO_x(0))^C$ and $(NO_z(t)/NO_x(0))^C$ are given by (4) and (6), respectively. In fitting (7) to the data points, C_x and α were fixed to the values determined from Figure 2a. A trial and error selection of parameters (β and C_Y in equation (6)) yielded a good fit for a deposition rate of NO_z (β) of 0.2 $hour^{-1}$.

An estimate of the efficiency with which NO_x is used in producing O_3 is provided by ozone production efficiency with respect to NO_x (OPE_x) [*Trainer et al.*, 1993]. Operationally, OPE_x is determined from the relation between O_3 (or $O_x = O_3 + NO_2$; O_x

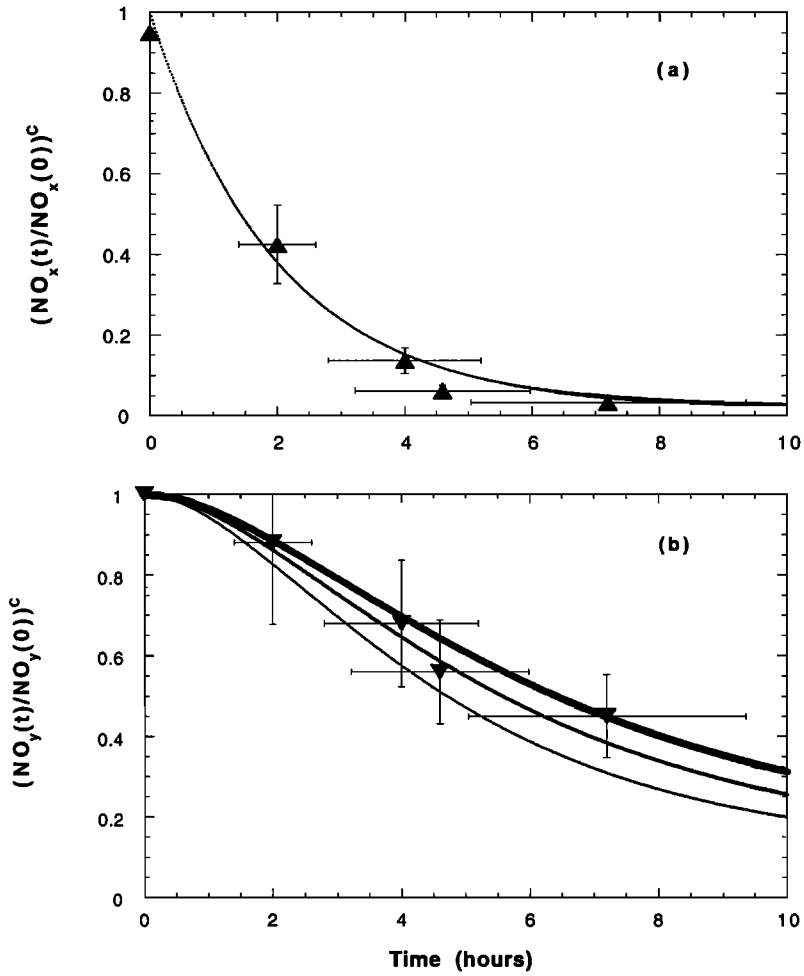

Figure 2. Nashville urban area: (a) Loss of NO_x due to reaction. Symbols are observed values from equation (3) and are corrected for dispersion. Equation (2) is used to determine CNO_y. Curve is calculated from equation (4). (b) Loss of NO_y due to deposition of NO_z. Symbols are observed values from equation (5) and are corrected for dispersion. Curves are calculated from equation (7), using equations (4) and (6). Constants for the urban plume are as follows: α = 0.5 hour^{-1}, C_x = 0.02, β = 0.2 hour^{-1}, and C_y = 0.1. Sensitivity calculations were performed with the same values of α, C_x, and C_y, but also with β = 0.25 and 0.33. The corresponding NO_z lifetimes ($1/\beta$) are 3 hours (thin line), 4 hours (medium line), and 5 hours (thick solid line). Vertical error bars represent the root-mean-square uncertainty determined for the calculated ratio based on error in the measurements of NO_x, NO_y, CO, or SO_2 and the error in the slope of the regression line used to determine each ratio. The horizontal error bars represent a 30% uncertainty in the determination of plume age based on wind speed data.

being the more conserved quantity) in a plume and NO_x oxidation products. Numerically, there is only a slight difference (i.e., 10%) if O_x is used instead of O_3 for the determination of OPE_x. One way of doing this is to determine the slope of a graph of O_x versus NO_z. However, as was inferred from Figure 2b, NO_z loss can be quite rapid and therefore the measured NO_z concentration is only a fraction of the NO_x that was consumed. If there was no deposition, the concentration of $NO_z(t)$ would be

$$NO_z(t)^* = \frac{NO_y(t)}{C_{NOy}} - NO_x(t) \qquad (8)$$

Using the corrected values for NO_z (i.e., NO_z* from equation (8)), we arrive at an OPE_x of 3-4 for the Nashville urban plume in the downwind region where maximum O_3 occurs [*Nunnermacker et al.*, 1998]. This range of values is a factor of 2 lower than would be obtained if NO_z was not corrected for losses.

3.2. Power Plants

3.2.1. Observations. Table 1 provides a summary of the traverses of the Gallatin and Paradise power plant plumes. The Gallatin data were acquired relatively close to the power plant with plume ages ranging from 0.5 to 4 hours. This range is adequate for determining an oxidation rate but is too short to determine an accurate value for the rate of NO_z loss. The Paradise data were collected farther away from the emission source, with transects ranging from 2.8 to 9.6 hours downwind. Accordingly, it provides a better description of the loss process.

Table 1 includes the ratios NO_y/SO_2 and NO_x/NO_y needed for the kinetic analysis. Figures 3 and 4 show a series of plots from the July 7 traverses of the Paradise power plant plume with travel times varying from 2.8 to 9.6 hours, as an example of the regressions that were used to generate these ratios. Several trends are apparent. As downwind travel time increases, the plumes get

Table 1. Data Summary for Power Plant Analysis

	Date	Travel time	Observed[a]		Corrected[b]	
			$[NO_y]/[SO_2]$	$[NO_x]/NO_y]$	$(NO_y(t)/NO_y(0))^{C}$ [c]	$(NO_x(t)/NO_x(0))^{C}$ [d]
Paradise	July 7, 1995	2.8	0.60	0.80	0.77	0.61
	July 7, 1995	4.6	0.51	0.61	0.61	0.37
	July 7, 1995	7.7	0.35	0.13	0.37	0.05
	July 7, 1995	9.6	0.30	0.11	0.29	0.03
	July 17, 1995	6.0	0.46	0.61	0.52	0.32
	July 17, 1995	6.5	0.40	0.38	0.44	0.17
Gallatin	July 3, 1995	0.5	0.17	0.95	0.98	0.93
	July 3, 1995	3.5	0.15	0.36	0.77	0.28
	July 7, 1995	2.3	0.18	0.48	0.97	0.46
	July 15, 1995	4.0	0.13	0.40	0.65	0.26
	July 17, 1995	2.0	0.15	0.49	0.81	0.40
	July 17, 1995	2.5	0.15	0.52	0.80	0.42
	July 18, 1995	2.0	0.17	0.72	0.92	0.67

[a] Observed ratio from slope of least squares fit to data points collected on plume traverse.
[b] Ratios corrected for plume dispersion and loss of SO_2 from deposition and oxidation.
[c] Corrected NO_y ratio = $CNO_y(t)$ which is calculated from equation (9).
[d] Corrected NO_x ratio = $CNO_y(t)$ times the observed NO_x ratio (see equation (3)).

wider as indicated by the number of data points in each plot; absolute concentrations of NO_y, NO_x, and SO_2 decrease due to dispersion and removal processes; the ratio NO_x/NO_y decreases due to loss of NO_x by oxidation; and the ratio NO_y/SO_2 decreases due to loss of NO_y by deposition. Correlation coefficients remain reasonably high (r^2 >0.9) except for NO_x/NO_y at 7.7 and 9.6 hours. At a plume age of 9.6 hours the plume is only contributing a maximum of 0.3-0.4 ppbv of NO_x above background, thus lowering the r^2 value.

3.2.2. Kinetic analysis. Our analysis of the power plant plumes parallels that of the urban plume except that SO_2 is used in place of CO as a tracer. Unlike CO, SO_2 is removed by dry deposition and by oxidation at rates which are not negligible over the timescale of the plume experiments. The oxidation rate of SO_2 is about 2% h^{-1} for a power plant plume [*Gillani*, 1978; *Forrest et al.*, 1981], an order of magnitude lower than that found for NO_2 (see below). The dry deposition velocity of SO_2 is estimated to be about 0.7 cm s^{-1} for the terrain types found near Nashville [*Sheih et al.*, 1979; *Wesley et al.*, 1985]. This translates into a 2% h^{-1} removal rate for a 1200 m boundary layer height. Summing these two processes, we arrive at an estimated removal rate of SO_2 of 4% h^{-1}.

For the power plant plumes the correction factor for NO_y loss is,

$$C_{NO_y(t)} = \frac{\dfrac{NO_y(t)}{SO_2(t)e^{0.04t}}}{\dfrac{NO_y(0)}{SO_2(0)}} \qquad (9)$$

An initial ratio of SO_2 to NO_y of 0.17 was used for Gallatin, and 0.7 was used for Paradise. These ratios were calculated based on reported plant emissions [*Ryerson et al.*, 1998], and have an associated uncertainty of ± 20% based on variations in the fuel, burners, and other parameters. The factor $e^{(0.04t(\text{hours}))}$ that accounts for SO_2 removal has a value of 1.5 at the farthest downwind traverse which corresponds to a plume age of 9.6 hours. As with other ratios, $NO_y(t)/SO_2(t)$ is determined from the slope of a linear regression of NO_y versus SO_2 for a plume transect at a given location.

Figures 5a and 6a show $(NO_x(t)/NO_x(0))^{C}$ versus time, as determined from equations (3) and (9), for the Paradise and Gallatin power plant plumes. The solid line is a curve of the form

$$\left(\frac{NO_x(t)}{NO_x(0)}\right)^{C} = e^{(-\alpha t^{n})} * (1 - C_x) + C_x \qquad (10)$$

In order to obtain a smooth fit of the data with the theoretical expression (equation (10)), the oxidation constant must increase with time. This also makes physical sense based on what is known about plume chemistry. The form used in equation (10) satisfies the objective of giving a rate constant that starts small and grows. Thus, the parameter "n," n > 1, accounts for the increase in the NO_x oxidation rate as the plume dilutes and becomes more reactive. Figures 5b and 6b show the time dependence of $(NO_y(t)/NO_y(0))^{C}$ for Paradise and Gallatin, as determined by (5) and (9). The solid line is from a kinetic model in which $(NO_x(t)/NO_x(0))^{C}$ is given by (10) and $(NO_z(t)/NO_x(0))^{C}$ is given by (6).

The curves in Figures 5 and 6 depend on five rate constants and parameters: C_x, α, n, β, and C_y. For both power plants they were determined by first finding a set of C_x, α, and n that fit the NO_x data points, then values for β and C_y that fit the NO_y data points. A fit was obtained by trial and error. Values of C_x, α, n, β, and C_Y are given in the captions to Figures 5 and 6. Because the NO_x and NO_y kinetic expressions depend on five parameters, they are fairly flexible, and it is therefore not surprising that the fitted curves agree with most of the data points to within the uncertainties shown on the graphs. Alternate sets of parameters can be found that also do a reasonable job in fitting the data points. However, the kinetic expressions start to give a noticeably poorer fit when parameters are changed by more than 1/3. An exception is the deposition rate of NO_z in the Gallatin plume where the value for β has an uncertainty greater than 1/3 because the sampling points do not cover a long enough time span to show much NO_z loss.

From the fitted curves in Figures 5b and 6b we estimate an NO_z lifetime ($1/\beta$) of 2.5 and 3 hours for Paradise and Gallatin, respectively. NO_z lifetimes up to 5 hours in the Gallatin plume are judged to be within the uncertainty of the analysis procedure as illustrated in Figure 6b. Changing the Paradise NO_z lifetime to 4

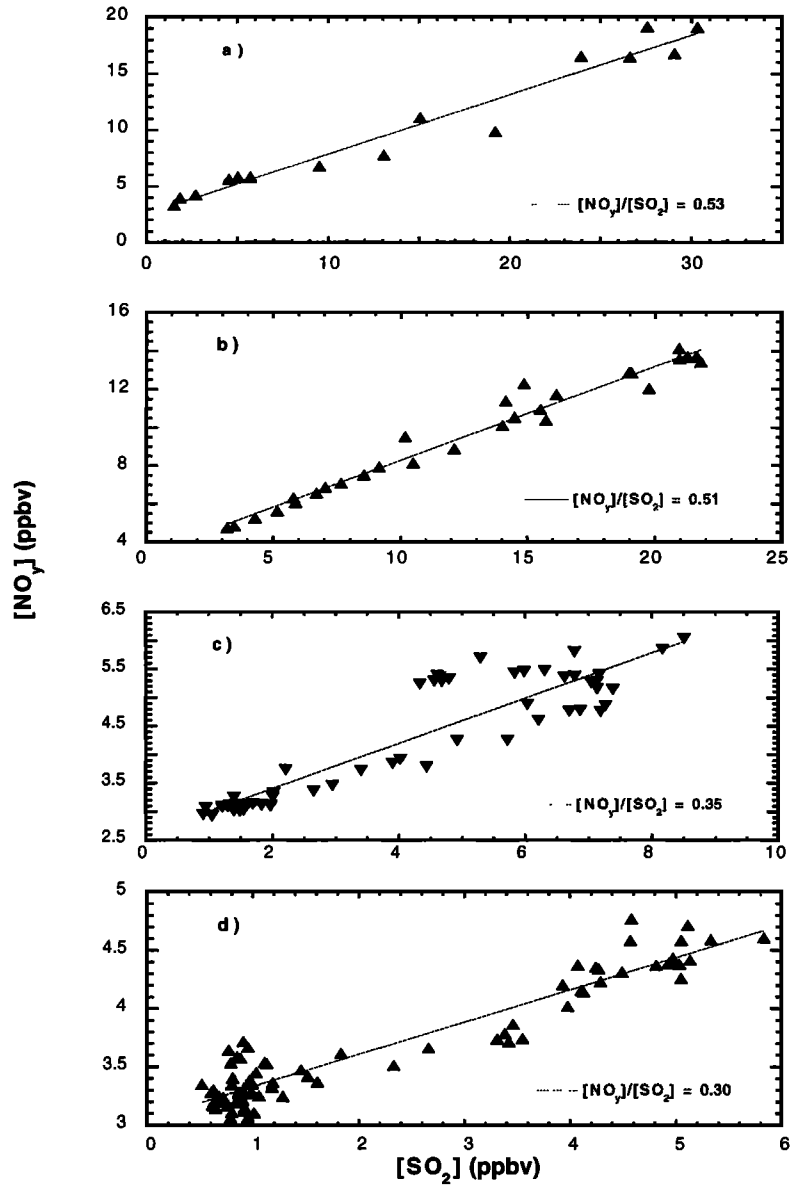

Figure 3. Paradise NO_y/SO_2 ratios at different travel times from the point of emission for July 7, 1995: (a) 2.8 hours, (b) 4.6 hours, (c) 7.7 hours, and (d) 9.6 hours.

or 5 hours, gives a poorer fit as illustrated in Figure 5b. The fit is only slightly worse for an NO_z lifetime of 2 hours. Changing the values of the other 4 parameters (C_x, α, n, and C_Y) for Paradise does not alter the conclusion that the best fit value of β gives an NO_z lifetime of only 2.5 hours.

In order to provide a qualitative picture of the nonlinear decay of NO_x and NO_y it is useful to define a phenomonological lifetime as the time needed for these substances to decay to 1/e of their original concentrations, and can be determined from Figures 5 and 6. The NO_x lifetimes are 2.8 and 4.2 hours for Gallatin and Paradise, respectively. For NO_y, the corresponding lifetimes are 7.0 and 7.7 hours. NO_y decays more slowly than NO_z because of the delay that exists in first converting NO_x to NO_z.

Results depend on the SO_2 loss rate which is only estimated. A sensitivity calculation for Paradise indicates that a zero SO_2 loss rate yields an increase in lifetimes from 4.2 to 5 hours for NO_x and 2.5 to 3.5 hours for NO_z. An SO_2 loss rate greater than 4% h^{-1} would cause the calculated lifetimes to decrease.

Figures 7a and 7b show the correlation between O_x and NO_z^* for Paradise and Gallatin. From this, we determine that OPE_x (i.e., slope of the line) has a value of 2 with an $r^2 = 0.95$ in the Paradise plume. For Gallatin an $OPE_x = 3$ with an $r^2 = 0.85$ was found. An error estimate of 45% is arrived at by adding in root-mean-square fashion a 25% error due to the uncertainties in the measurements of O_3 and the oxides of nitrogen and a 35% error due to the determination of C_{NOy}. Values as much as a factor of 2 higher would be obtained if the deposition correction was not made.

4. Discussion

Oxidation and deposition lifetimes and ozone production efficiencies for the urban and power plant plumes are summarized

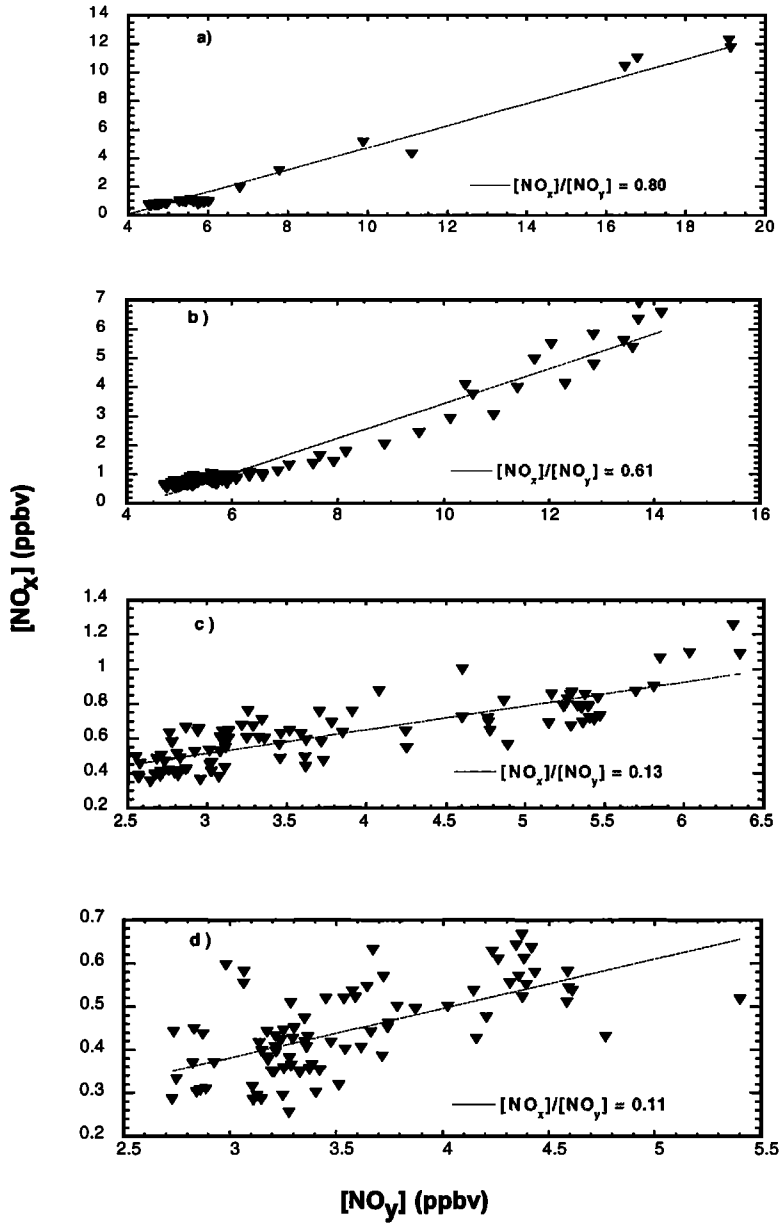

Figure 4. Paradise NO_x/NO_y ratios at different travel times from the point of emission for July 7, 1995: (a) 2.8 hours, (b) 4.6 hours, (c) 7.7 hours, and (d) 9.6 hours.

in Table 2. A physically reasonable trend is the increase in NO_x lifetimes from 2.0 hours in the urban plume to 2.8 hours in the plume of a small power plant to 4.2 hours in the plume of a large power plant. Urban and power plant plumes have very different characteristics. An urban plume contains a mixture of NO_x and reactive hydrocarbons. Except for the very early morning hours, an urban plume is sufficiently dilute that an active photochemistry can occur even in the source region. A power plant plume, in contrast, contains very high NO_x but relatively little reactive hydrocarbons, and O_3 formation cannot occur until there is dilution of the initially high NO_x and mixing with hydrocarbon containing background air. Dilution and mixing take time, which is why NO_x oxidation is slower in a power plant as compared with the urban plume and why it is slower in a large power plant as compared with a small one.

Model calculations indicate that OPE_x should be a nonlinear function of NO_x concentration. All other things being equal, OPE_x should be low at high NO_x and increase at low NO_x levels [*Lin et al.*, 1988]. In support of this prediction, OPE_x in the more concentrated Paradise plume is about a factor of 1.5 lower than in the Gallatin plume. However, the urban area and Gallatin both have an OPE_x of 3-4 even though higher NO_x levels occur in the Gallatin plume. This feature of the chemistry has been noted by *St. John et al.* [1998]. We note that the comparisons of OPE_x between sources is not altogether straightforward because processing times and hydrocarbon environments differ.

As has been noted in other studies of the Nashville plumes [*Gillani et al.*, 1998a, b; *St. John et al.*, 1998], the disappearance rate of NO_y is quite rapid. In the urban and power plant plumes considered here, the phenomonological lifetime of NO_y varies

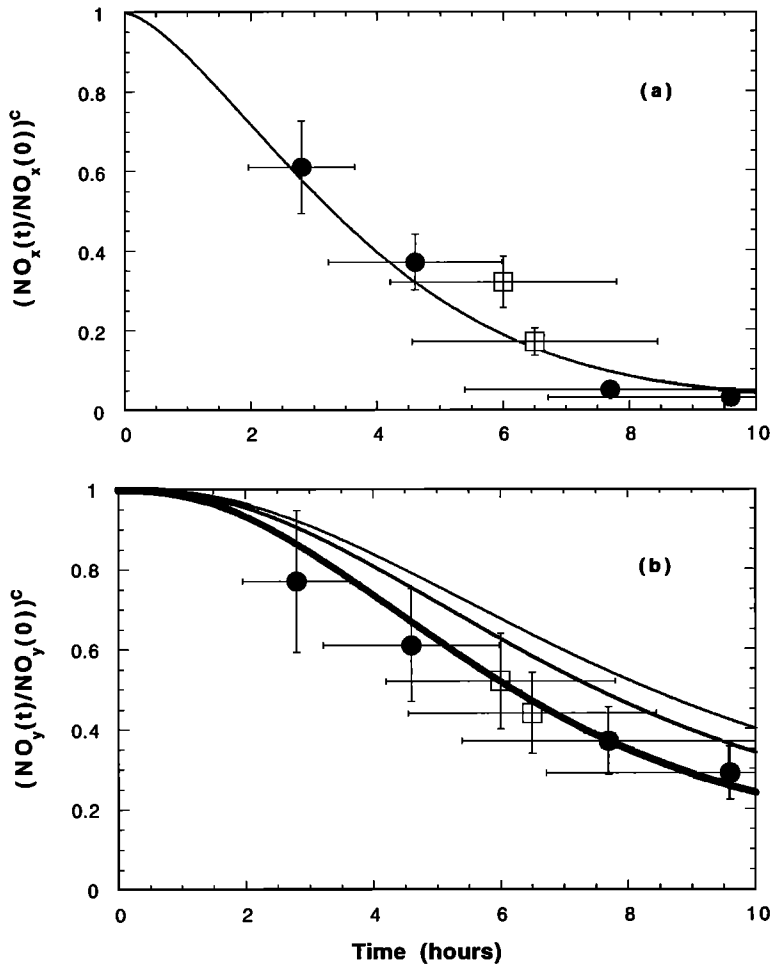

Figure 5. Paradise power plant: (a) Loss of NO_x due to reaction. Symbols are observed values from equation 3 and are corrected for dispersion. Equation (9) is used to determine CNO_y. Curve is calculated from equation 10. (b) Loss of NO_y due to deposition of NO_z. Symbols are observed values from equation (5) and are corrected for dispersion. Curves are calculated from equation (7), using equations (6) and (10). Constants determined for Paradise are as follows: $\alpha = 0.12$ hour^{-1}, $C_x = 0.02$, n = 1.5, $\beta = 0.4$ hour^{-1}, and $C_y = 0.1$. Sensitivity calculations were performed with the same values of α, C_2, and n, but also with $\beta = 0.2$ and 0.25. The corresponding NO_z lifetimes ($1/\beta$) are 3 hours (thin line), 4 hours (medium line) and 5 hours (thick line). Error bars same as in Figure 2. Symbols: solid circle, July 7, 1995; cross-hatched square, July 17.

from 7 to 9 hours. Loss of NO_z occurs with a lifetime of 2.5 to 5 hours. There is no apparent reason why the power plants and the Nashville urban area have different NO_z lifetimes. We note that, at least in the case of the Gallatin plume, the uncertainty in the analysis procedure is large enough to accommodate a 5 h NO_z lifetime, the same as in the urban plume. Also, the urban NO_y data could be fit almost equally well with an NO_z disappearance rate of about 4 hours, bringing it closer to the power plants. Although the data set and analysis procedure is only good enough to indicate a range of possible values for the NO_z loss rate, it is clear that measurements are only consistent with very rapid loss of NO_z. NO_y is seen to have a lifetime that is significantly greater than NO_z since the NO_y lifetime reflects the additional time needed to convert NO_x into a substance (i.e., HNO_3) which is susceptible to loss by deposition.

A 5 hour lifetime for NO_z corresponds to a midboundary layer dry deposition velocity of 6.7 cm s^{-1} for a 1200 m deep boundary layer (i.e., 6.7 cm s^{-1} = 1200 * 10^2 cm/ (5 hours × 3600 s h^{-1})). A 3 hour lifetime gives a deposition velocity of 11 cm s^{-1}. Even assuming that NO_z is 100% HNO_3 and that the surface resistance of HNO_3 is zero, these are higher than the normally expected deposition velocities [*Huebert and Robert*, 1985; *Hall and Claiborne*, 1997]. The discrepancy with existing measurements is actually greater than we have stated because deposition velocities are typically measured a few meters above the ground. A rapidly depositing gas will develop a vertical gradient such that an emptying of the whole of the boundary layer at a velocity of 6.7 cm s^{-1} implies a significantly higher deposition velocity near ground level.

The very high apparent NO_z deposition velocities inferred here are puzzling. We do not have an explanation, but can speculate on several sources of error in the analysis. First, there may be errors in the NO_y measurements. NO_x may be converted to an odd-N species which is not being detected as part of NO_y. This would lead to an underestimate in NO_y that would get worse farther from the source, thereby mimicking a loss process. Laboratory and field

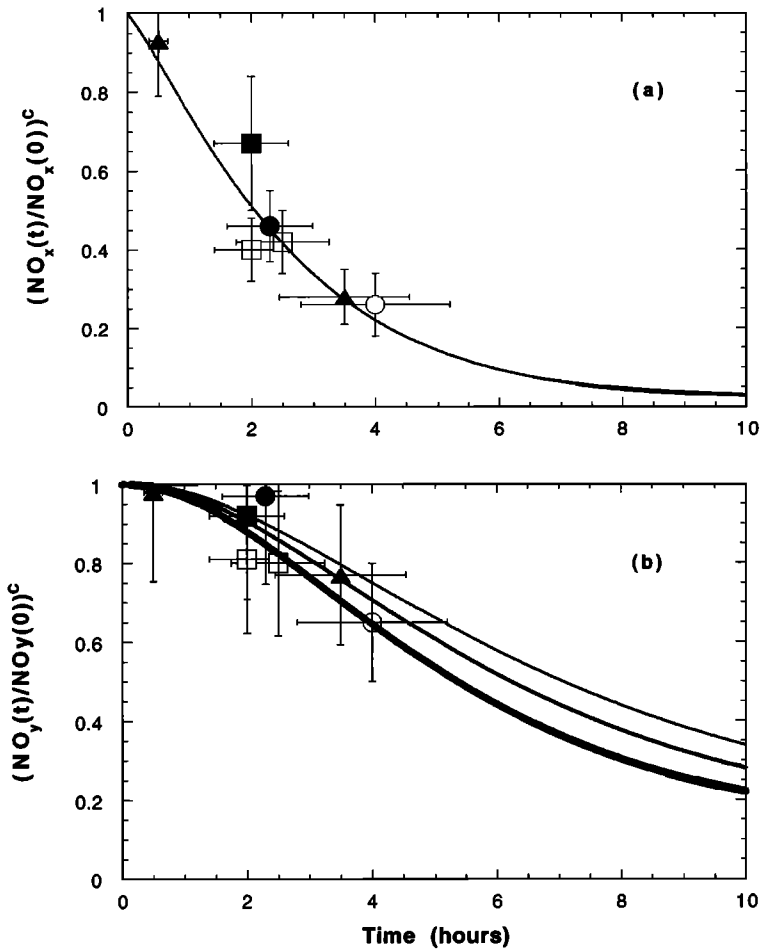

Figure 6. Gallatin power plant: (a) Loss of NO_x due to reaction. (b) Loss of NO_y due to deposition of NO_z. Calculated as in Figure 5. Constants determined for Gallatin are as follows: $\alpha = 0.3$ hour^{-1}, $C_x = 0.02$, n = 1.2, $\beta = 0.333$ hour^{-1}, and $C_y = 0.1$. Sensitivity calculations were performed with the same values of α, C_x, and n, but also with $\beta = 0.2$ and 0.25. The corresponding NO_z lifetimes ($1/\beta$) are 3 hours (thin line), 4 hours (medium line) and 5 hours (thick line). Error bars same as in Figure 2. Symbols: solid triangle, July 3; solid circle, July 7; open circle, July 15; cross-hatched square, July 17; solid square, July 18.

tests indicate that the NO_y detector, used on the DOE G-1, measures commonly occurring gaseous odd-N compounds with near 100% efficiency [*Fehsenfeld et al.*, 1987; *Nunnermacker*, 1990; *Williams et al.*, 1998]. Owing to the design of the Mo converter, it is assumed that small nitrate particles (i.e., diameter <1 μm) are converted with 100% efficiency [*Williams et al.*, 1998]. However, NO_z compounds incorporated into large aerosols (i.e., diameter >1 μm) may not be detected, due to inlet losses. Second, the effective mixing height may be less than 1200 m. Observations were done on power plant effluents that had been emitted early in the day when mixing heights were lower (i.e., not fully developed). If the mixing height was less than 1200 m, a smaller deposition velocity could account for the observed rapid disappearance of NO_y. Third, there may be systematic errors in the analysis procedure. For example, if the initial NO_x to SO_2 emission ratio for Paradise was 0.5, then a reasonable fit to the NO_y decay curve could be obtained with $\beta = 0.2$ (i.e., a 5 hour NO_z lifetime). Some combination of these factors along with a deposition velocity that is indeed high may explain these results.

5. Conclusions

The Nashville area is dominated by a very rapid photochemistry as demonstrated by the short lifetime of NO_x in both the urban and power plant plumes. The rate of oxidation for NO_x also varies from small power plant (i.e., Gallatin had a NO_x lifetime of 2.8 hours) to large power plant (i.e., Paradise had a NO_x lifetime of 4.2 hours).

Table 2. Summary of the Urban and Power Plant Plume

Plume Characteristics	Nashville	Gallatin	Paradise
NO_x lifetime (hours)	2.0	2.8	4.2
NO_y lifetime (hours)	8.7	7.0	7.7
NO_z lifetime[a] (hours)	5	3	2.5
Average OPE_x	3-4	3	2

[a] NO_z lifetime is based on the best calculated fit to NO_y loss.

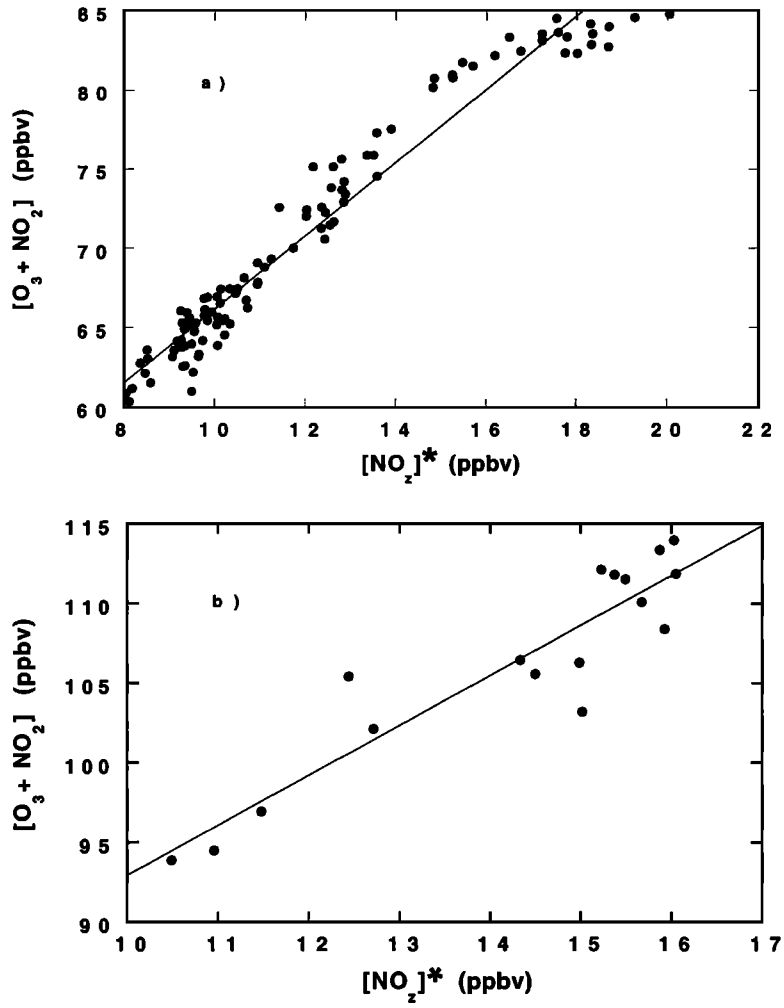

Figure 7. The ozone production efficiency (OPE_x) determined for the Gallatin and Paradise power plants: (a) An $OPE_x = 2$ was determined from the slope of the regression line for the Paradise power plant on the final transect (i.e., see Figure 1b, P4), July 7, 1995, and (b) an $OPE_x = 3$ was determined from the slope of the regression line for the Gallatin power plant on the final transect (i.e., see Figure 1c, G), July 15, 1995. Note that the NO_z concentrations were corrected for losses.

The kinetic analysis indicates NO_z lifetimes ranging from 2.5 to 3 hours for the power plants to 5 hours for the urban area. Although the uncertainties on these values are high, the data unequivocally show rapid NO_z loss. If this loss is attributed to dry deposition of HNO_3, it implies a deposition velocity of 7 to 13 cm s^{-1}. This is much faster than anticipated based on currently accepted rates of deposition for HNO_3 (1-4 cm s^{-1}). Further studies are needed to determine if other processes, such as large particle formation, are at work in the Nashville region.

Ozone production efficiency also varies depending on the size of the power plant. The larger power plant (Paradise) has a 30% lower OPE_x than the smaller power plant (Gallatin). Another important point is that despite the differences in precursor concentrations the OPE_x for the Gallatin power plant is virtually the same as that of the Nashville urban plume (3 to 4 O_3/NO_x). The lower OPE_x determined for the larger power plant (Paradise) provides important information for determining future emission control strategies.

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P. H. Daum, D. Imre, L. I. Kleinman, J. H. Lee, Y.-N. Lee, L. Newman, L. J. Nunnermacker, and S. R. Springston, Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973. (lindan@bnl.gov)

N. Gillani, Earth System Science Laboratory, Atmospheric Science Department, University of Alabama, Huntsville, AL 35806.

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