

Ozone production efficiency and loss of NO_x in power plant plumes: Photochemical model and interpretation of measurements in Tennessee

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Abstract: A model for photochemical evolution in power plants has been developed and used in combination with measurements to investigate ozone production efficiency (OPE) per NO_x and the rate of photochemical removal of NO_x. The model is a two-dimensional (2-D) Lagrangian model with 1 km horizontal resolution and vertical resolution ranging from 25 m to 300 m, nested within a larger 3-D regional model. These results are compared with measured O₃, NO_x, and SO₂ along aircraft transects through power plant plumes (Ryerson *et al.*, 1998). Measured flux of NO_x and SO₂ in plume transects is 33%-50% lower than plume emission rates, suggesting that a fraction of plume emissions remained above the top of the convective mixed layer. The measured loss rate of SO₂ is greater than expected from photochemistry and surface deposition, suggesting the possibility of cumulus venting of the boundary layer. If model parameters are adjusted to reflect this hypothesized transport of plume air above the boundary layer, then the model NO_x removal rate agrees with measurements. OPE is derived from measured fluxes of O₃, NO_x and SO₂ in the plume. The resulting OPE (1.2-2.5) is somewhat higher than the previous estimate by Ryerson *et al.* OPE in models is slightly higher than measurements (2-3). Higher OPE (3-4) is predicted for power plant plumes 18 hours downwind of the emission source. OPE for these far downwind plumes is comparable to OPE for other emission sources of NO_x. OPE and NO_x lifetime are both correlated with plume NO_x concentrations. Model results suggest that OPE inferred from statistical correlations between O₃ and tracers such as SO₂ underestimate the true OPE in situations where the correlation between O₃ and SO₂ is nonlinear.

1. Introduction

Generation of electricity from coal and gas-fired power plants accounts for approximately 33% of the anthropogenic source of oxides of nitrogen (NO_x equal to NO+NO₂) in the United States, and a similar percentage elsewhere. Power plant NO_x emissions are believed to make a significant contribution to region-wide ozone formation and transport in eastern North America. The U.S. Environmental Protection Agency (EPA) has recently proposed major reductions in power plant NO_x emissions, with the intent of reducing O₃.

The process of ozone formation in power plants differs in many respects from the more familiar photochemistry of urban and rural environments. Individual power plants often emit NO_x at a higher rate than the summed NO_x emissions from all sources in major metropolitan areas. Such high point-source emissions generate narrow plumes with extremely high NO_x concentrations. In contrast with most urban sources, power plants typically emit relatively small amounts of volatile organic compounds (VOC), and VOC/NO_x ratios in power plant plumes are typically lower than in urban plumes by a factor of 10 or more. There have been many investigations of power plant plume chemistry over the past 25 years [Miller *et al.*, 1978, White *et al.*, 1983, Gillani and Pleim, 1996], but there is generally less information about rates of ozone formation in power plant plumes than about ozone formation rates in urban and rural areas.

Ryerson *et al.* [1998] used a series of aircraft-based measurements of O₃, NO_x, and SO₂ in power plants in Tennessee during meteorological conditions favorable to ozone formation, and used them to derive rates of ozone formation and loss of NO_x. They found that the ozone production efficiency (OPE) per NO_x associated with large power plants was much lower than OPE in urban areas or in small point sources (OPE equal to 1 in large power plant plumes, OPE equal to 3-7 in urban areas or smaller point-source plumes). They also derived a removal rate of NO_x (0.2 hour⁻¹) that is likely to be much higher than the oxidizing capacity within large power plant plumes. It is unclear whether this low rate of ozone formation and high rate of NO_x removal is consistent with the current understanding of O₃-NO_x-VOC chemistry and plume dynamics, or whether it should be interpreted as evidence for an additional unknown mechanism for removal of NO_x. The low ozone production efficiency observed by Ryerson *et al.* also might be interpreted as evidence that proposed reductions in power plant NO_x would have only a modest effect on ozone formation rates.

Significant insight can be gained if the measurements reported by Ryerson *et al.* [1998] are compared with results of photochemical models for ozone formation in power plants. Model-measurement comparisons can address the following issues: (1) Does the low OPE and rapid loss of NO_x reported by Ryerson *et al.* provide evidence for an additional, unknown sink of NO_x in power plant plumes? (2) Are there errors in the observation-based approaches for determining OPE used by Ryerson *et al.* and others [St. John *et al.*, 1998; Nunnermacker *et al.*, this issue] that can be identified by using photochemical models? (3) Is the low OPE reported by Ryerson *et al.* a general feature of large power plants, or is higher OPE expected for

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conditions with different meteorology, different biogenic VOC emissions, or greater downwind distance?

The current study describes the development of a dynamical/photochemical model for the evolution of power plant plumes and its application to the data set from Ryerson et al. The model is a two-dimensional (2-D) Lagrangian model with 1 km horizontal resolution (crosswise through the power plant) and 25-300 m vertical resolution. This Lagrangian model has been embedded in a larger three-dimensional (3-D) Eulerian model for urban and regional-scale photochemistry and transport [Sillman et al., 1998].

Results suggest that there is an unknown removal process affecting both SO₂ and NO_x in the power plants measured by Ryerson et al. [1998]. Since the unknown removal process has similar magnitude for both species, it is more likely to be explained by dynamics rather than unknown chemistry. Reinterpretation of measurements results in a measurement-based OPE (equal to 1.2-2.5) that is higher than reported by Ryerson et al. (OPE equal to 1) and slightly lower than model predictions (model OPE equal to 2-3). Model results suggest that OPE in power plant plumes should be greater at greater downwind distances (12-18 hours downwind), due to greater horizontal dispersion of NO_x. Model results also predict that OPE for power plants at far downwind distances is only slightly lower than OPE for NO_x from urban sources. The issue of dynamical versus photochemical removal can represent a significant uncertainty when OPE is inferred from a series of measurements in power plant transects. There are also potential errors in OPE derived from correlations between O₃ and SO₂, due to nonlinear chemistry.

2. Description of the Event and Measurements

The study focuses on July 7, 1998. This day was characterized by moderate temperatures (maximum 30°C) and wind speeds (3 m s⁻¹ at the surface) [McNider et al., 1998] and sunny conditions. A cold front had passed through Tennessee on July 6, and in its aftermath winds were from the NW. Although unreported for this event, conditions following the passage of cold fronts are often characterized by fair weather cumulus. Measured O₃ in the region were lower than average during the month-long Middle Tennessee Ozone Study. This day was selected because the winds generated well-defined power plant plumes which could be monitored over long downwind distances.

The region of the study included Nashville, a metropolitan area of roughly 1 million residents. Two major coal-fired power plants are located in the region: Cumberland (Tennessee), located 80 km WNW of Nashville, and Paradise (Kentucky), 140 km NNW of Nashville. Each of these power plants has estimated NO_x emission rates of 5-8x10²⁵ mol s⁻¹, which is much higher than NO_x emitted from the Nashville metropolitan area (2x10²⁵ mol s⁻¹, estimates from EPA, [1993] and Ryerson et al., [1998]). The Paradise plant also emits significant quantities of SO₂ (7x10²⁵ mol s⁻¹), while the Cumberland plant emitted much less SO₂ in 1995 (0.7x10²⁵ mol s⁻¹). There are also two smaller power plants in the vicinity: Johnsonville, located 120 km west of Nashville; and Gallatin, located 35 km NW of Nashville. NO_x emissions from these plants (2x10²⁵ mol s⁻¹ for Gallatin) are comparable to emissions from Nashville and much lower than emissions from Cumberland and Paradise. However, these plants also have high SO₂ emissions (8x10²⁵ mol s⁻¹ for Gallatin).

The measurements used in this study were published in the work of Ryerson et al. [1998] and are described in detail there.

A series of aircraft transects were flown through the plumes from the Cumberland, Paradise, and Johnsonville power plants at downwind distances ranging from 15 to 180 km, and at times extending from noon to 1700 local standard time (LT). The measurements included here were at altitude 500-600 m above the surface. Results of individual plume transects are identified by the transect air parcel age (downwind travel time) which are reported by Ryerson et al. [1998, Table 1]. Reference to this table and the transect map [Ryerson et al., 1998, Figure 2]) should provide more precise information about the plume transects reported here.

Ryerson et al. [1998] estimate that the mixed layer height during the event was 1400 m +/-100 m, based on vertical gradients in potential temperature, humidity, wind speed and direction, and chemical data measured by aircraft. McNider et al. [1998] derived a higher mixed layer height (1800 m) based on rawinsonde temperature profiles, but this estimate was less precise than the estimate of Ryerson et al. Ryerson et al. also reported that wind speeds in the mixed layer were 5 m s⁻¹ +/- 1 m s⁻¹, significantly higher than the surface wind speed reported by McNider et al.

3. Simulation Methods

Representation of power plant plumes requires greater horizontal and vertical resolution than is usually found in 3-D Eulerian models for urban and regional-scale photochemistry. Previous studies have found errors in models that lack adequate resolution [Kumar and Russell, 1996]. Model horizontal resolution has obvious importance because power plant plumes are characterized by sharp horizontal gradients in species concentrations over short distances [e.g. Gillani and Pleim, 1996]. Vertical resolution is especially important because plume chemistry is influenced by emission of relatively short-lived biogenic VOC, primarily isoprene. Isoprene concentrations have been found to decrease sharply with height, even within a well-mixed boundary layer [Andronache et al., 1994; Guenther et al., 1996a, b].

In this study, power plant plumes are represented by a 2-D Lagrangian model, representing a vertical "slice" through the plume perpendicular to the wind direction. The Lagrangian reference frame moves downwind following the movement of the plume center, and air throughout the vertical slice is assumed to be advected downwind at the same speed. Horizontal resolution across the plume is 1 km with domain width 60 km. The model represents the mixed layer and extends to an altitude of 2100 m. It includes 16 vertical layers with resolution ranging from 25 m over the lower 100 m of the atmosphere up to 300 m at the top of the model domain.

This type of model formulation explicitly ignores wind shear, although it is expected that wind speed and direction both vary with altitude. The effect of wind shear and turbulent diffusion are both represented through a horizontal eddy diffusion coefficient in accordance with standard K theory. The value of the horizontal eddy diffusion coefficient is from Gifford [1982]. In this representation the rate of diffusion is assumed to increase with downwind distance, as estimated by Gifford. Although this type of representation is imprecise in terms of fluid dynamics, it is expected to be adequate for representing species distributions and chemistry within a power plant plume. It will be shown below that the cross-plume species profiles compare well with measured profiles in aircraft transects.

Vertical mixing within the convective mixed layer is adapted from *Pleim and Chang* [1992]. Pleim and Chang represent mixing by assuming direct upward transport from the lower model layer to all higher layers contained within the region of convective mixing and mass-conserving downward transport from each layer to the next-lower layer. This mimics the transport associated with rising thermals in the convective mixed layer and represents a significant improvement over normal eddy diffusion. The method of Pleim and Chang has been used to represent convective mixing between 50 m and the top of the daytime mixed layer. Transport between the ground and 50 m is calculated from eddy diffusion coefficients with values that increase linearly from zero at 0 m to 25 m² s⁻¹ at 50 m. This representation generates the expected slower transport from near the surface and insures that the near-surface model layers will have higher concentrations of directly emitted species, especially isoprene, as reported by *Andronache et al.* [1994] *Guenther et al.* [1996a, b]. At nighttime and above the mixed layer, vertical transport is represented through standard vertical eddy diffusion coefficients. A diffusion rate of 0.5 m² s⁻¹ is assumed for stable regions of the atmosphere, including the region above the daytime convective mixed layer and most of the model domain at nighttime. Near-surface vertical transport at nighttime is represented by eddy diffusion rates of 0.5 m² s⁻¹ at 25 m, increasing to 4 m² s⁻¹ at 100 m and decreasing to 0.5 m² s⁻¹ at 300 m and higher, where the higher rate at 100 m is due to turbulence generated by friction and the synoptic wind in the stable boundary layer. Between 1800 and 2300 local time the boundary layer is assumed to be neutrally stable with eddy diffusion coefficients decreasing linearly from 5 m² s⁻¹ at 100-200 m to 0.5 m² s⁻¹ at the top of the former convective mixed layer. These values were derived from exercises with the model of [*Yamartino et al.*, 1992] for summertime conditions (II. Westberg, Washington State University, private communication, 1999) and are similar to representations used elsewhere and compared with measurements [*Stull*, 1988; *Plummer et al.*, 1996; *Guenther et al.*, 1996a, b].

Surface emission rates are derived from the EPA [1993] and biogenic emissions inventory system (BEIS2) [*Geron et al.*, 1994] inventories based on the assumed trajectory of the Lagrangian "slice." The assumed emission rates are varied based on location, including both cross-plume variations and downwind progression of the plume, and also reflect time-of-day variations in emission of anthropogenic and biogenic species. Emission from the power plant is entered into the 800-1000 m vertical layer of the model at the start of each Lagrangian simulation, with rates from *Ryerson et al.* [1998] in the initial scenario. (Some model scenarios include modified emission rates, described in section 4.) This initial representation of a vertically confined plume is typical following plume rise in a stable atmosphere [*Miller*, 1978; *Seinfeld and Pandis*, 1998]. If the plume is initially contained within the convective mixed layer, this initially confined plume will be mixed vertically as part of the regular model vertical transport.

A 3-D regional simulation for the event is used to establish initial and boundary conditions for the 2-D Lagrangian model. The 3-D model is described elsewhere [*Sillman et al.*, 1998]. Chemistry and dry deposition rates in the 2-D model are identical to the 3-D model. A brief summary will be presented here. The model uses a photochemical mechanism based on *Lurmann et al.* [1986] with numerous updates, including updated reaction rates [*DeMore et al.*, 1994], and chemistry of isoprene and related species based on *Paulson and Seinfeld* [1992]. The model also

includes updated RO₂-HO₂ reaction rates and additional RO₂-RO₂ reactions recommended by *Kirchner and Stockwell* [1996]. The reaction rates for organic peroxides with OH were updated based on recommendations from *Stockwell et al.* [1997]. Other minor modifications are described by *Sillman et al.* [1998]. Meteorology in the 3-D model is from the Rapid Update Cycle (RUC) model [*Benjamin et al.*, 1994].

Dry deposition velocities during the daytime are SO₂, O₃, and NO₂, 0.6 cm s⁻¹; NO, 0.1 cm s⁻¹; peroxyacetyl nitrate (PAN), 0.25 cm s⁻¹; H₂O₂ and HNO₃, 5 cm s⁻¹; and organic peroxides, 1.2 cm s⁻¹. Deposition velocities at nighttime are equal to half these values. The high deposition velocity for H₂O₂ and HNO₃ is based on results from *Sillman et al.* [1998] and *Hall and Claiborn* [1997]. The deposition velocity for SO₂ is consistent with *Wesley* [1989] and *Meyers et al.* [1998] and other estimates for deposition rates over eastern forests and grasslands. Since SO₂ deposition varies greatly based on local ecology, land use, and the presence or absence of wet surfaces, this value should be recognized as uncertain. Results from *Wesley* [1989] and *Meyers et al.* [1998] suggest that the size of this uncertainty is +/- 0.5 cm s⁻¹.

4. Model Application and Scenarios

Model applications have been developed for conditions on July 7, 1995, in Tennessee. The 2-D Lagrangian component is used to represent the Cumberland and Paradise power plant plumes along downwind trajectories with initialization at various times of day. For purposes of comparison, additional calculations were done with the 2-D Lagrangian component representing the plume from the smaller Gallatin power plant and the chemical evolution of the plume generated by the Nashville metropolitan area.

The initial model scenario uses power plant emission rates, wind speeds, and mixing layer heights reported by *Ryerson et al.* [1998] for the Lagrangian component. The regional model uses emissions and meteorology from EPA, BEIS2, and RUC as described above.

The initial scenario results in fluxes of primary species (NO_x and SO₂) that are significantly larger than the fluxes derived from measured plume transects, even in transects located 1-3 hours downwind from the plume. This result is described in detail in the following section and also was reported by *Ryerson et al.* [1998]. While it is possible that this model-measurement discrepancy is the result of erroneous or unknown model chemistry, it is also possible that the discrepancy results from nonchemical errors in the model. Possible other sources of error include the following:

4.1 Emission Rates

Ryerson et al. [1998] estimated that the uncertainty in emission estimates was +/-20%. The observed flux of NO_x and SO₂ in transects close to the plume sources were 33%-50% lower than the emitted flux. Although this discrepancy is larger than the estimated uncertainty in emission estimates, the possibility of erroneous emission rates should be considered as a possible explanation for the low observed fluxes.

4.2 Rise and Entrainment in the Mixed Plume Layer

The standard representation of the dynamics of plumes directly after emission assumes that the hot exhaust rises until it

reaches a fixed altitude [e.g. *Seinfeld and Pandis*, 1998]. Since plume evolution is a diffusive process it is possible that the initial plume rise results in plume emissions being distributed over a wider range of altitudes. In this case some of the emitted plume could remain above the top of the mixed layer. *Ryerson et al.* [1998] reported evidence that some plume emissions during the measured event remained above the top of the mixing layer.

4.3 Venting of the Mixed Layer

Fair-weather cumulus clouds have been found to export air out of the boundary layer and inject boundary layer air at higher elevations [e.g., *Greenhut et al.*, 1984; *Stull*, 1985; *Ching et al.*, 1988; *Cotton et al.*, 1995; *Flossman and Wobrock*, 1996]. There is evidence that cloud venting can lead to elevated plumes of polluted air at higher elevations and a corresponding reduction in pollutant concentrations within the boundary layer (see section 9). It is not known whether fair-weather cumulus was present during the event, but there is anecdotal evidence (T.B. Ryerson, private communication, 1999), and meteorological conditions during the event were generally conducive to the formation of fair-weather cumulus.

A modified model scenario was developed based on the hypothesis that a combination of emission errors, uncertain plume rise/entrainment, and cloud venting were responsible for much of the model-measurement discrepancy in the initial scenario. The modified scenario includes modified emission rates and assumed mixing between the mixed layer and the top of the model domain, reflecting the impact of cloud venting. The modified emissions and rate of cloud venting were established to insure that the model agreed with the measured NO_x flux in the earliest plume transects (1 hour downwind for Cumberland, 2.6 hours downwind for Paradise) and that the model agreed with measured SO₂ fluxes for all plume transects. In effect, the modified scenario uses the earliest measured plume transects in order to establish NO_x and SO₂ emission rate into the boundary layer (rather than estimates from emission inventories or plant operators), and uses measured SO₂ fluxes in downwind transects to establish the dynamical loss due to cloud venting. It implicitly assumes that SO₂ chemistry and deposition in the model is correct.

The modified scenario includes the following adjustments. For Cumberland the initial emission estimate is reduced by 33% for both NO_x and SO₂. For Paradise the initial emission estimate is reduced by 50% for NO_x and 33% for SO₂. For both Cumberland and Paradise it is assumed that air is exported from the top of the boundary layer to above the model domain between the hours of 1100 and 1800 LT, at a rate equal to 0.031 m s⁻¹ (equivalent to 0.08 hour⁻¹ for the entire mixed layer) and replaced by subsiding air at the same rate.

Care must be taken in evaluating the results of the modified scenario in comparison with measurements since the parameters of the modified scenario have been modified to insure good agreement. In the modified scenario the photochemical loss rate of NO_x and rate of production of O₃ are still calculated entirely through model internal processes. Horizontal dispersion of species is also calculated internally. The satisfactory performance of this scenario in comparison with measured NO_x and O₃ is not sufficient to demonstrate that model plume photochemistry is correct, but it is sufficient to establish the scenario assumptions as a plausible hypothesis to explain the measurements. This is discussed in greater detail in the discussion below.

5. Results

5.1 Plume Transects

Figure 1 shows model and measured NO_x, SO₂, and O₃ for selected horizontal plume transects at 7.1 and 9.3 hours downwind. The measured plume transects show a well-defined maximum for primary emissions (NO_x and SO₂). Despite the simplicity of calculated horizontal dispersion in the model, the pattern and extent of horizontal dispersion in the model is similar to the measured horizontal profiles. Results for SO₂ in the modified simulation show good agreement with measured horizontal profiles. The parameters of the modified simulation have been modified to insure agreement with measured SO₂, but the similarity of model and measured horizontal profiles provides some validation for the calculation of horizontal diffusion in the model.

The plume transect patterns can obviously be interpreted as representing a plume from an individual source (presumably the Cumberland or Paradise power plant) superimposed on a relatively uniform background. This interpretation is consistent with the analysis of *Ryerson et al.* [1998]. Transect measurements at distances between 20 and 40 km of the plume center (where the center is defined by peak SO₂) show near-uniform concentrations, though with significant scatter. This scatter is especially important for SO₂ in the Cumberland plume where the range of measured background values (0.5 ppb) has magnitude similar to the amount of excess SO₂ in the plume center (1-1.5 ppb).

Model and measured values for SO₂ and NO_x show obvious maxima at the plume center. O₃ shows a more complex pattern with maxima sometimes occurring on the sides of the plume and a relative minimum in the plume center. This reflects a well-known pattern of photochemical evolution within plumes [e.g., see *Gillani and Pleim*, 1996]. Photochemical removal of NO_x and production both occur more rapidly and efficiently at the sides of the plume, where NO_x concentrations are elevated but lower than in the plume center. In general, NO_x concentrations in an initially emitted plume are first diluted through dispersion. Photochemical processes become increasingly significant after NO_x concentrations have first been lowered through dispersion. This pattern of dynamics and photochemistry provides a basis for interpreting the behavior of the plume.

Following *Ryerson et al.* [1998] and his antecedents, subsequent results will all be reported in terms of model and measured net excess flux associated with the plume during each transect. Net flux is calculated as in the work of *Ryerson et al.*:

$$\text{net flux} = v \cos \alpha \int_0^z n(z) dz \int_{-y}^y (X_m(y) - X_{m0}) dy \quad (1)$$

where v is the wind speed (assumed to be constant and uniform); α is the angle between the aircraft track and the direction normal to the wind direction (automatically zero in the model); $n(z)$ is density as a function of altitude z , and is integrated to the top of the mixed layer; $X_m(y)$ is the species mixing ratio at horizontal distance y from the plume center, and X_{m0} is the background mixing ratio, assumed equal to average mixing ratio at 20-30 km horizontal distance from the plume center. This calculation assumes that mixing ratios measured along aircraft transects are constant between the ground and the top of the mixed layer, an assumption that is consistent with the broader set of measurements. Measured flux values and uncertainties are taken

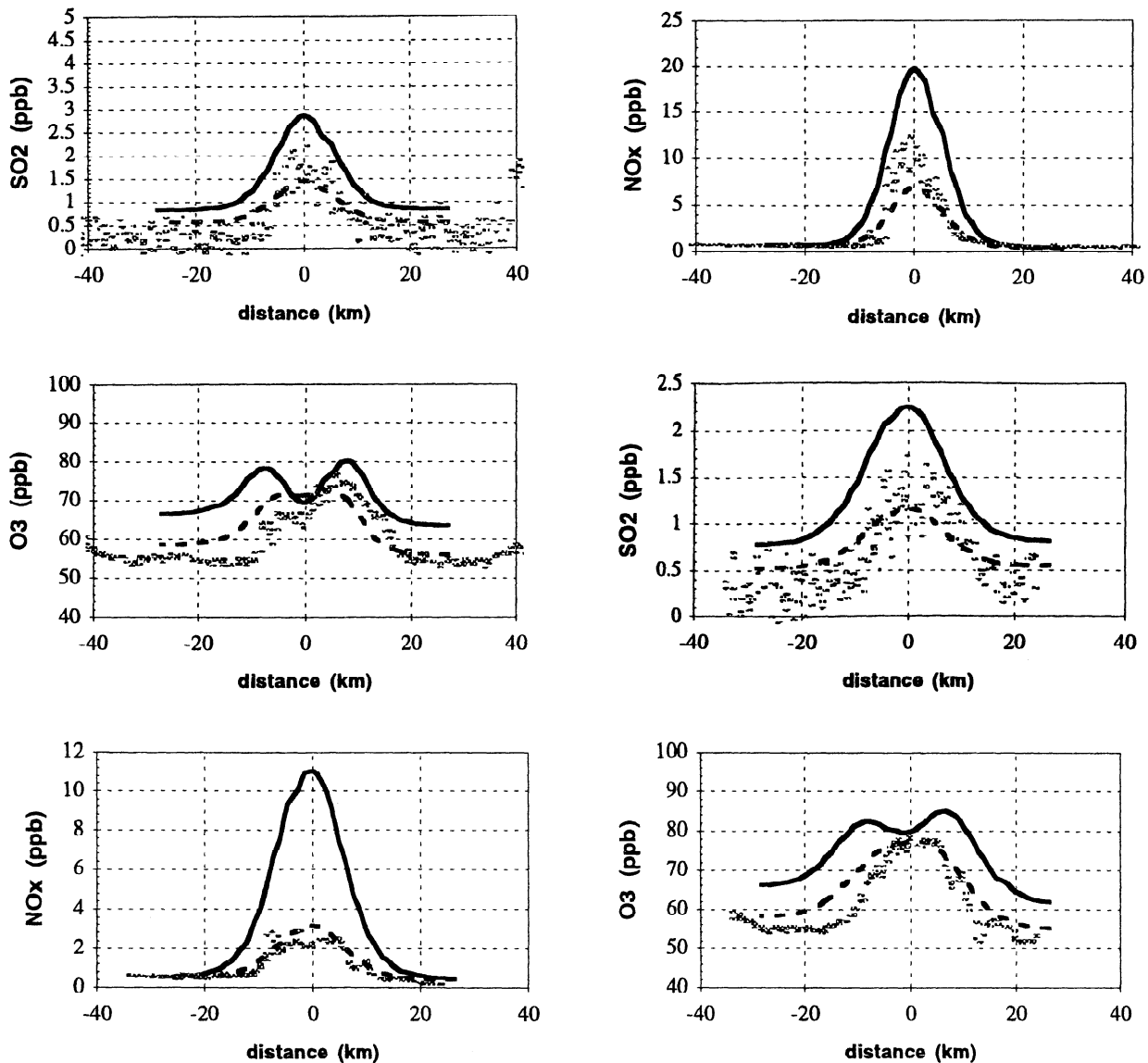


Figure 1. Model and measured SO₂, NO_x and O₃ (ppb) versus distance from the plume center (km) along aircraft transects through the Cumberland power plant plume at 7.1 and 9.3 hours downwind from the plume source at 1600-1700 LT, July 7, 1995. The solid line represents the initial model scenario, the dashed line represents the modified model scenario, and points represent measurements. Figures (a-c) represent SO₂, NO_x, and O₃ respectively in the transect 7.1 hours downwind. (d-f) At 9.3 hours downwind.

directly from Ryerson *et al.* [1998]. The uncertainties in wind speed reported by Ryerson *et al.* have also been used to derive an uncertainty associated with plume age (downwind travel time) in each transect. Model flux values are calculated similarly. Model net flux determined in this manner can also be tested by comparing the model background (X_{m0}) with the equivalent mixing ratio when the model is repeated with the plume taken out. Little difference was found.

Figures 2-4 show the model and measured net flux of SO₂, NO_x, and O₃ in the plume transects as a function of downwind distance, expressed as estimated travel time from the plume source. The results in Figures 2-4 represent values during the afternoon at various downwind distances and do not represent the photochemical evolution of an individual plume as it moves downwind. The time of day of the model plume transects was chosen to match the time of the measured transects of Ryerson *et*

al. and varies from 1300 local standard time (LT) for the plumes closest to the emission source to 1800 LT for far downwind plumes. Thus model values for downwind travel times corresponding to measurements represent results that are directly comparable to the measured values. The model results for far downwind distances (15-18 hours) are not comparable to any measurements and show predictions for net flux at 1800 from a plume emitted at night (2400-0300) and transported downwind. The other model results and measured transects all represent plumes that were emitted in the morning (0600-1200).

The results show that the initial model scenario overpredicts flux of primary pollutants (NO_x and SO₂) in all the plume transects. The model-measurement discrepancy is larger as a fraction of the measured flux at greater downwind distances, especially for NO_x. In the first Cumberland transect the model overestimates NO_x flux by almost a factor of 2 in comparison

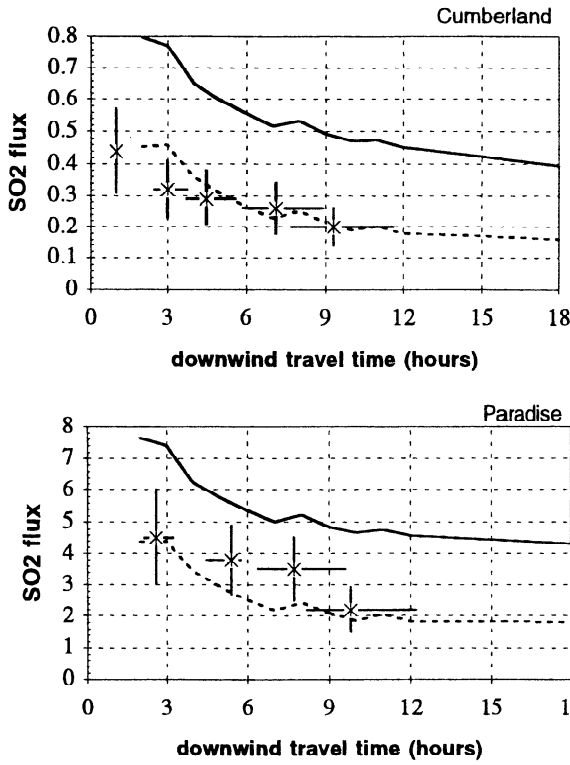


Figure 2. Net excess flux of SO₂ (10^{25} mol s⁻¹) in the (a) Cumberland and (b) Paradise power plant plume transects versus downwind travel time. The crosses with error bars represent measurements from Ryerson *et al.* [1998], the solid line represents the initial model scenario, and the dashed line represents the modified scenario. Time of day in the model transects corresponds with the time of measurements (13-1700 LT). The far downwind transects are all at 1800 LT.

with measurements, but in the last downwind transect the model overestimates NO_x flux by a factor of 6. The initial scenario also underpredicts O₃ during the first 6 hours of plume evolution. These discrepancies suggest that this model scenario has less active chemistry than implied by measurements. Most of the model-measurement error is eliminated in the modified scenario. The modified scenario automatically agrees with measured SO₂ flux, but model values for NO_x and O₃ are also reasonable. The model still overestimates NO_x (by a factor of 2) and O₃ (by 40%) during the final Cumberland transect. However this underestimate is small relative to the range of measured NO_x flux throughout the Cumberland plume.

5.2 NO_x Removal Rates

The removal rate of NO_x can be examined in greater detail by examining the ratio NO_x/SO₂ in model and measured transects [e.g. Ryerson *et al.*, 1998]. Because SO₂ has a relatively long lifetime (30 hours in the model) changes in NO_x/SO₂ during plume evolution are largely due to loss processes for NO_x (although downwind emissions can also affect this ratio). Differences between model and measured NO_x/SO₂ can also be used to identify model-measurement differences relating to NO_x removal rates.

Results (Figure 5) show that the initial model scenario agrees with measured NO_x/SO₂ in the Cumberland transects near the plume source, but overestimates NO_x/SO₂ during downwind

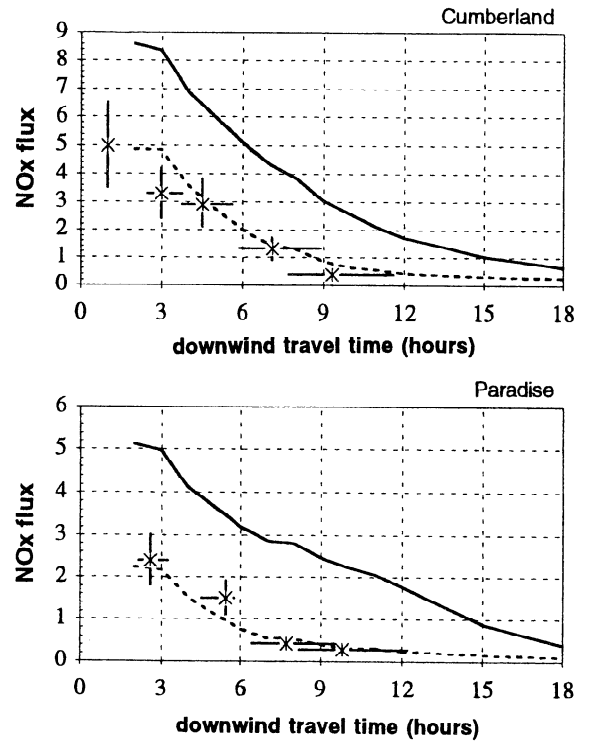


Figure 3. Net excess flux of NO_x (10^{25} mol s⁻¹) in the (a) Cumberland and (b) Paradise power plant plume transects versus downwind travel time (as in Figure 2). The crosses with error bars represent measurements from Ryerson *et al.* [1998], the solid line represents the initial model scenario, and the dashed line represents the modified scenario.

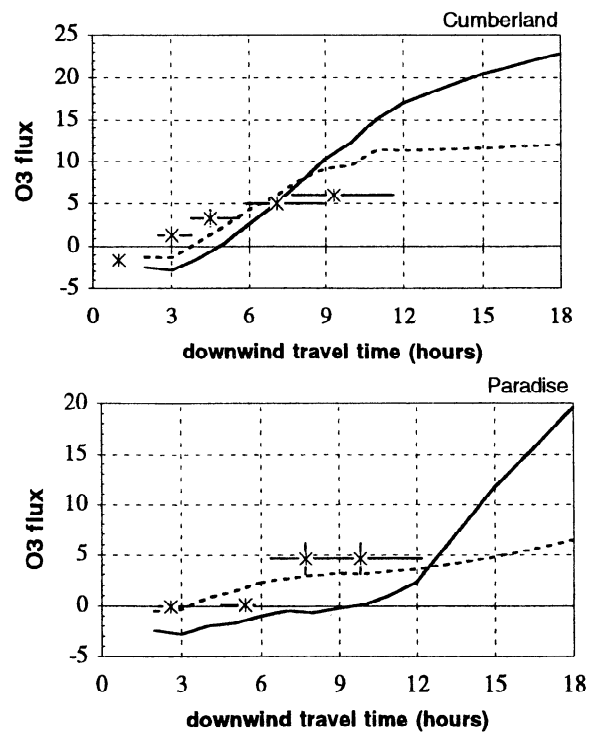


Figure 4. Net excess flux of O₃ (10^{25} mol s⁻¹) in the (a) Cumberland and (b) Paradise power plant plume transects versus downwind travel time (as in Figure 2). The crosses with error bars represent measurements from Ryerson *et al.* [1998], the solid line represents the initial model scenario, and the dashed line represents the modified scenario.

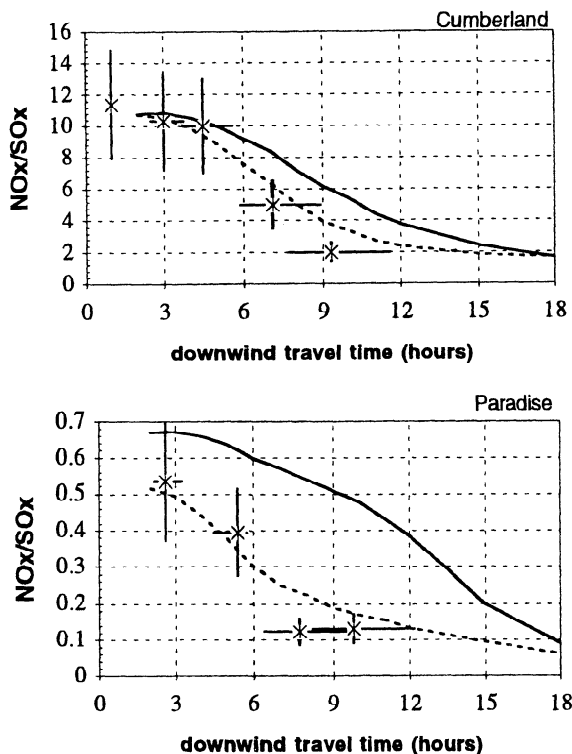


Figure 5. Net excess flux of NO_x divided by net excess flux of SO₂ in the (a) Cumberland and (b) Paradise power plant plume transects versus downwind travel time (as in Figure 2). The crosses with error bars represent measurements from Ryerson et al. [1998], the solid line represents the initial model scenario, and the dashed line represents the modified scenario.

transects. In the Paradise plume transects the initial model scenario overestimates NO_x/SO₂ by a factor of two or more in all transects, including transects relatively near the plume source. This consistent overestimate provides the basis for adjusting the NO_x/SO₂ emissions ratio in the modified scenario. The modified scenarios show much better agreement. There is still a significant underestimate for NO_x/SO₂ during one Cumberland transect (at 9.3 hours downwind) and during one Paradise transect (at 7.7 hours downwind).

The NO_x/SO₂ comparison also illustrates that models with higher NO_x (c.g. the original versus modified scenario) also have lower NO_x removal rates. This is a familiar result [e.g. Liu et al., 1987], but it has added significance in power plant plume studies. If a model initially overestimates the NO_x content of a plume (due to erroneous emissions or dispersion), the resulting model-measurement discrepancy propagates downwind and becomes larger since initial NO_x overestimate also causes an underestimate in NO_x removal rates. Evaluation of model NO_x removal rates is therefore especially sensitive to the accuracy of emission estimates and plume dispersion.

Figures 6 and 7 show the calculated photochemical lifetime of NO_x in plumes at various downwind distances. A distinction must be made between the lifetime at a specific hour (the "instantaneous" lifetime, Figure 6) and the cumulative lifetime over the duration of the plume up to the specified downwind distance (Figure 7). The instantaneous lifetime represents the average NO_x concentration along a plume transect divided by the average instantaneous removal rate along the transect. The cumulative lifetime is based on summed NO_x removal over the

history of the plume and is calculated as follows:

$$\frac{1}{\text{lifetime}} = \frac{1}{t} \ln \left(\frac{\int_0^z \int_{-y}^y (\text{NO}_x(y, z, t) - \text{NO}_{x0}(y, z, t)) dy dz}{\int_0^z \int_{-y}^y (\text{NO}_{c0}(y, z, t) - \text{NO}_{c0}(y, z, t)) dy dz} \right) \quad (2)$$

Where NO_x(*y, z, t*) represents the model NO_x concentration at distance *y* from the plume center, altitude *z* (integrated from the ground to the top of the convective mixed layer) and downwind travel time *t*. NO_{x0}(*y, z, t*) represents the equivalent NO_x concentration in a model with zero plume emissions, and NO_{c0}(*y, z, t*) and NO_{c0}(*y, z, t*) represent the equivalent concentrations of a counter species for NO_x. The counter species in the model is emitted at a rate equal to the rate of model NO_x emissions and is transported along with all other model species, but with no deposition and no photochemical sources and sinks. The cumulative lifetime would be associated with the ratio NO_x/NO_v if there was no loss of NO_y and no significant source of NO_x other than the power plant. The cumulative lifetime is especially important because it is often estimated from measured NO_x/SO₂ and NO_x/NO_y in plumes and is thus directly comparable to measurement-based estimates.

Figure 6 shows results for Cumberland, the smaller Gallatin plume, and the Nashville urban plume. As expected, NO_x lifetime decreases with downwind distance. NO_x lifetime also is shorter in the modified Cumberland scenario (with lower NO_x emissions), shorter still in the smaller Gallatin plume, and shortest (2 hours) in the Nashville urban plume. The lifetime estimates for the Gallatin and Nashville plumes are comparable

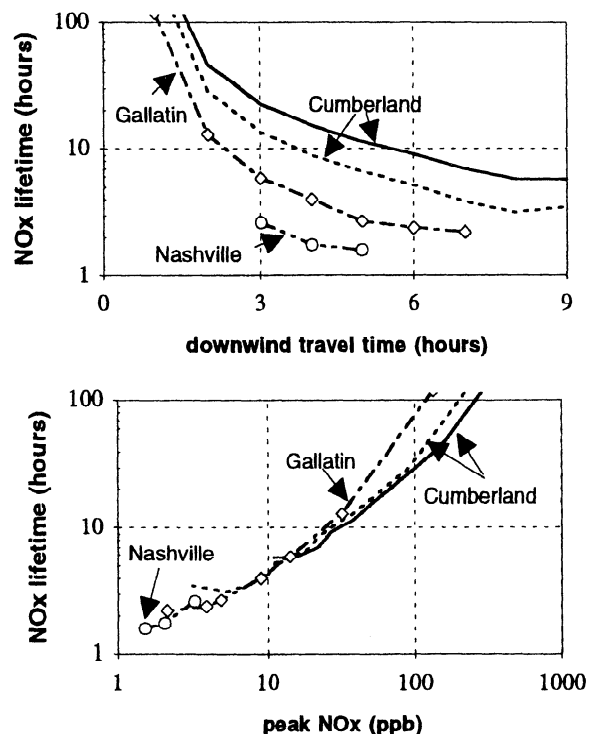


Figure 6. Model instantaneous NO_x lifetime (hours), calculated as the average NO_x concentration along model transects divided by the average removal rate at a specified time. Instantaneous lifetime is plotted against (a) downwind travel time (hours) of the plume transect, as in Figure 2, and (b) peak NO_x concentration (ppb) in the model plume.

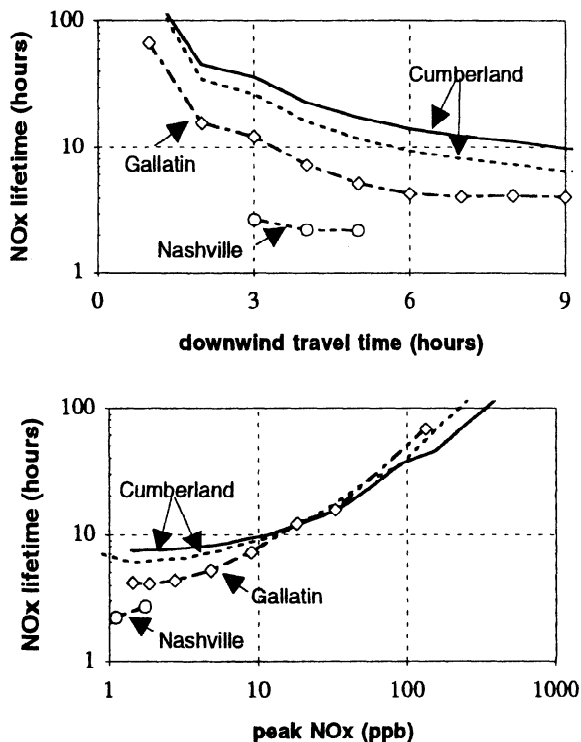


Figure 7. Model cumulative NO_x lifetime (hours), calculated based on summed NO_x removal over the history of the plume up to the specified travel time as in Equation (2). Cumulative lifetime is plotted against (a) downwind travel time (hours) of the plume transect, as in Figure 2, and (b) peak NO_x concentration (ppb) in the model plume.

with measurement-based estimates by *Nunnermacker et al.* [1998, this issue]. Figures 6 and 7 also show that the calculated NO_x lifetime in all plume transects correlates closely with peak NO_x in the plume transect, despite many physical differences between the Cumberland, Gallatin, and Nashville plumes.

The cumulative lifetime for the final Cumberland transect in the initial model scenario (10 hours) is significantly higher than the measurement-based photochemical lifetime reported by *Ryerson et al.* [1998] (5.6 hours). The lifetime in the modified scenario (6.4 hours) is much closer to the estimate by *Ryerson et al.*

6. Ozone Production Efficiency per NO_x

The net ozone production efficiency per NO_x (referred to throughout as OPE) will be defined here as the ratio of the net rate of photochemical production of O₃ divided by the NO_x removal rate through photochemistry and deposition. As was the case with NO_x lifetime, the results shown here represent the cumulative value over the plume history and throughout the horizontal transect rather than the instantaneous value. The cumulative value is favored because it can be used more readily to estimate the amount of downwind transport of O₃ and contribution to global-scale photochemistry for a given NO_x emission rate, and because the average lifetime can be related to measured quantities such as O₃/(NO_y-NO_x) [e.g., *Trainer et al.*, 1993]. The OPE presented here refers only to ozone production and NO_x removal within the convective mixed layer and does not include ozone or NO_x that has been vented above the mixed layer.

OPE in models is determined as follows:

$$OPE = \frac{\int_{0-y}^z \int_{0-y}^y (O_3(y, z, t) - O_{30}(y, z, t)) dy dz}{\int_{0-y}^z \int_{0-y}^y [(NO_c(y, z, t) - NO_x(y, z, t)) - (NO_{c0}(y, z, t) - NO_{x0}(y, z, t))] dy dz} \quad (3)$$

Parameters are defined as in equation (2). In this calculation, O₃, NO_x, and the NO_x counter species (NO_c) must all be integrated over the same area and subject to the same dynamical losses. This insures that venting of ozone and NO_x does not bias the calculation of OPE within the mixed layer.

Methods of estimation of OPE from measurements are less precise than the model-based OPE calculation and require certain assumptions about plume photochemistry. *Ryerson et al.* [1998] estimated OPE as the ratio of O₃ flux in plume transects (determined as described above) divided by the NO_x emission rate. However, the results shown above suggest that the NO_x content of the Cumberland and Gallatin plumes is significantly lower than the estimated NO_x emission rate. If this lower NO_x content is attributed either to errors in the emission rate or to

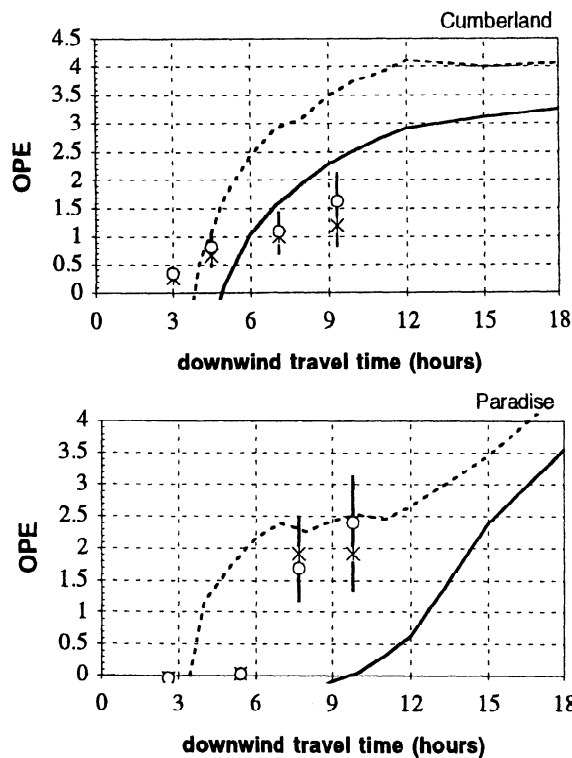


Figure 8. Cumulative ozone production efficiency (OPE) along measured and model transects of the (a) Cumberland and (b) Paradise power plant plumes, plotted versus downwind travel time (hours). The crosses with error bars represent OPE calculated from measured O₃ and NO_x fluxes (equation (4)) without adjusting for loss due to cloud venting. The circles with error bars represent OPE calculated from measured fluxes with adjustment for cloud venting based on measured SO₂ flux (equation (5)). Model OPE is calculated as in equation (3) for the initial scenario (solid line) and modified scenario (dashed line).

dynamics (including export of NO_x above the boundary layer), then the initial estimate by *Ryerson et al.* will underestimate OPE. Here, the source of NO_x in the downwind plume is derived from the measured net flux of NO_x during the earliest plume transect rather than the estimated NO_x emission rate. The resulting measurement-based OPE is as follows:

$$\text{OPE}(t) = \frac{F_{\text{O}_3}(t)}{r(t)F_{\text{NO}_x}(t_1) - F_{\text{NO}_x}(t)} \quad (4)$$

$F_{\text{O}_3}(t)$ and $F_{\text{NO}_x}(t)$ represent the measured net flux of O₃ and NO_x at time t (equation (1)), and $F_{\text{NO}_x}(t_1)$ represents measured net flux during the earliest plume transect. This results in a significantly higher OPE than is found by *Ryerson et al.* [1998], especially for the Paradise plume. The factor $r(t)$ represents an adjustment that accounts for hypothesized dynamical losses (e.g., through cloud venting) in the plume as it travels downwind from the first transect (t_1) to the time of the OPE estimate (t). In the initial estimate for OPE it is assumed there are no dynamical losses ($r(t)=1$). A second estimate has been calculated in which dynamical losses are estimated from the measured SO₂ flux. In this estimate it is assumed that the removal rate for SO₂ through deposition and photochemistry is equal to the model value, and any remaining loss of SO₂ (inferred from measured fluxes) is due to dynamics. The resulting modified estimate uses Equation (4) with the dynamic adjustment factor $r(t)$ calculated as follows:

$$r(t) = \frac{F_{\text{SO}_2}(t) M_{\text{SO}_2}(t_1)}{F_{\text{SO}_2}(t_1) M_{\text{SO}_2}(t)} \quad (5)$$

where $M_{\text{SO}_2}(t)$ represents net flux at time t in the initial model scenario with zero dynamical losses. OPE from measurements will be estimated both with and without assumed dynamic losses. Additional uncertainties associated with each estimate are adopted from *Ryerson et al.* [1998].

Figure 8 shows the resulting OPE from the two model scenarios and the two measurement-based estimates. The measurement-based estimates for OPE in the downwind transects are significantly higher than the estimates by *Ryerson et al.* [1998] (1.3-1.7 for Cumberland versus 0.8 in *Ryerson et al.*, 1.9-2.4 for Paradise versus 1.0 of *Ryerson et al.*). Model OPE in the modified scenario generally agrees with the measurement-based estimates for Paradise. However, the model OPE significantly overestimates OPE in the downwind Cumberland plume, especially in the modified scenario (model OPE equal to 3.5). This model-measurement discrepancy for Cumberland is especially noteworthy because it did not appear so clearly in the previous comparisons with measured concentrations or fluxes. Referring to Figures 3-5, it can be seen that the model overestimates the flux of O₃ in the final downwind Cumberland transect, overestimates the flux of NO_x and overestimates the NO_x/SO₂ ratio. These individual discrepancies produce a larger model-measurement discrepancy for OPE. Because the model showed better agreement in direct comparisons with measurements (Figure 1), it might be argued that the model-measurement discrepancy in the downwind Cumberland plume occurs because uncertainties in the measurement-derived OPE are larger than estimated. The initial model scenario for Cumberland has lower OPE and shows better agreement with measured OPE, but the improved OPE versus measurements only occurs because the scenario overestimates NO_x. A model

scenario for Cumberland with low OPE can also be produced if it is assumed that biogenic emissions are much lower than estimated (see Figure 11, below).

As was the case for NO_x removal, OPE in models is closely associated with NO_x content, and lower NO_x leads to higher OPE [*Liu et al.*, 1987]. OPE in Figure 8 is much lower in the initial model scenarios than in the modified scenarios (with lower initial NO_x and cloud venting), especially for the Paradise plume. Figure 9 shows model and measured OPE in comparison with peak NO_x in each plume transect. When presented in this manner, model OPE shows less sensitivity to assumed emission rates for plume NO_x or downwind biogenics. The difference between model and measured OPE in the final Cumberland transect is especially obvious and cannot be corrected by changed model parameters. The other measured transects all show better agreement with model values.

It is also possible to derive estimates for OPE from the measured correlation between O₃ and SO₂, where SO₂ is regarded as a tracer for power plant NO_x emissions [*Ryerson et al.*, 1998; *Nummermacker et al.*, 1998, this issue]. A comparison between modeled and measured correlations between O₃ and SO₂ also provides an additional basis for model evaluation. Figure 10 shows comparisons between model results and measurements for O₃ versus SO₂ during plume transects. Visually, there is good agreement between measured values and results from the modified model scenario, but the linear least squares coefficient (derived from a fit of the data to the linear equation [O₃] = $\alpha_0 + \alpha_1[\text{SO}_2]$) is significantly higher in the modified model scenario than in measurements (see Table 1). The nonlinear pattern noted by *Ryerson et al.* [1998] is especially apparent in the model results.

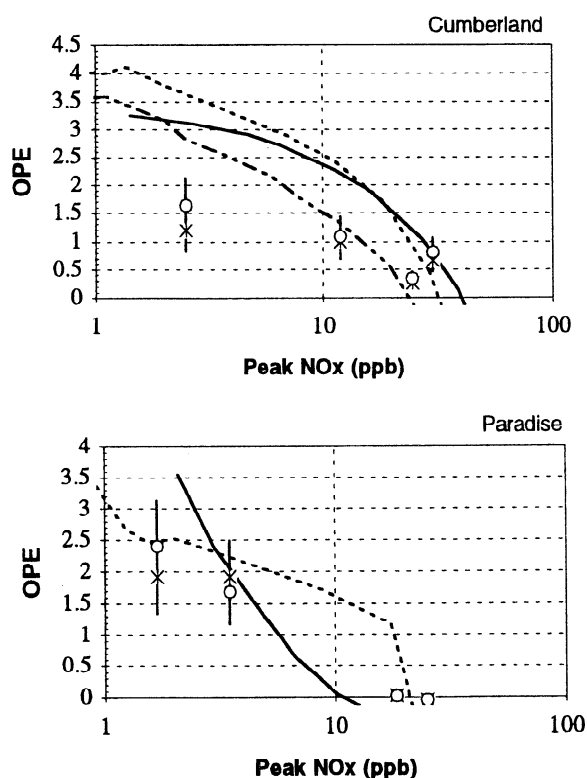


Figure 9. Cumulative ozone production efficiency (OPE) along measured and model transects of the (a) Cumberland and (b) Paradise power plant plumes, as in Figure 8, plotted versus measured and model peak NO_x (ppb) in the transect.

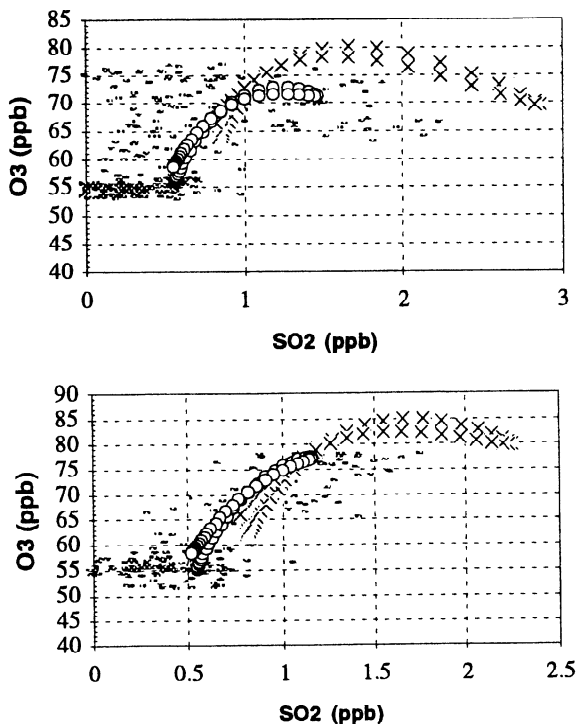


Figure 10. Measured and model O₃ versus SO₂ (ppb) along Cumberland transects (a) 7.1 hours downwind and (b) 9.3 hours downwind of the plume source as in Figure 1. The crosses represent the initial model scenario, circles represent the modified scenario, and points represent measurements.

As was the case with ozone fluxes, there are two different ways to estimate OPE from the measured O₃-SO₂ slope, depending on whether removal of SO₂ along the plume trajectory is assumed to be due to deposition and photochemistry (affecting only SO₂) or to dynamics (affecting O₃ and NO_x as well). Estimated OPE is determined through the following equation:

$$OPE(t) = S(t) \frac{F_{SO_2}(t)}{r(t)F_{NO_x}(t_1) - F_{NO_x}(t)} \quad (6)$$

where $S(t)$ represents the O₃-SO₂ slope. In the initial estimate it is assumed that there are no dynamical losses and $r(t)=1$. In the second estimate dynamic losses are inferred from the measured SO₂ flux as described above, and $r(t)$ is equal to the value in equation (5). This method differs significantly from that of Ryerson *et al.* [1998].

Table 2 shows a comparison of estimated OPE for plume transects from the different methods. The model results in Table 2 include estimates for OPE derived from model O₃ and NO_x fluxes and O₃-SO₂ slopes along with the true OPE derived from equation 3. This comparison between estimated and true OPE in models provides a basis for evaluating the accuracy of measurement-based OPE estimates. The flux-based methods underestimate OPE by 10%-30% in comparison with the true model value, presumably because the background region to the side of the plume contains some O₃ that was produced from plume NO_x. For the modified model scenario (which assumes dynamical losses) the proper comparison between estimated and true model OPE must include dynamical losses in the estimation.

Omission of dynamical losses would lower the estimated OPE by an additional 30%. The OPE estimates derived from O₃-SO₂ slopes in models underestimate the true OPE by amounts ranging from 15% to a factor of 3. This underestimate is directly associated with the nonlinearity of the O₃-SO₂ correlation and is especially bad in model plume transects that contain a large amount of unreacted NO_x. The largest error in OPE estimated from the O₃-SO₂ slope occurs for a model transect (illustrated in Figure 1) that has peak O₃ at the sides of the plume rather than in the plume center.

Figure 11 shows a comparison between model OPE in simulations for Cumberland with model OPE for the smaller Gallatin plume and for the Nashville urban plume. OPE is also shown for Cumberland with 75% lower biogenic emissions. Several features of this comparison are noteworthy. The range of predicted OPE for Nashville (4-5) and Gallatin (3-4) are both in general agreement with other recent measurement- and model-based estimates for OPE [Gilliani *et al.*, 1998a; Nunnermacker *et al.*, 1998, this issue; St. John *et al.*, 1998, Sillman *et al.*, 1998]. Predicted OPE for these plumes is much higher than for the Cumberland plume for downwind travel times of 6 hours or less. However, the difference in OPE between Nashville, Gallatin, and the Cumberland plume becomes much smaller at greater distances downwind. For downwind travel time of 18 hours an OPE value close to 4 is predicted for all three plumes. The model scenario for Cumberland with reduced biogenic emissions (possibly relevant to power plants with similar emission rates in less forested regions) has very low OPE, but even in this case OPE is expected to increase at far downwind distances to a level (2.6) that is not much lower than the predicted OPE for the plumes from Nashville and Gallatin. This far downwind, OPE is important because it represents the probable impact of power plant NO_x emissions on O₃ at downwind locations during multiday events. It also represents the probable impact of power plant NO_x on O₃ at the global scale.

The relatively modest impact of biogenic VOC on the final OPE associated with plume export can be understood in terms of dynamic and photochemical processes within the plume. Large power plants generate extremely high NO_x concentrations close to the plume source. These high- NO_x conditions are associated with very low OPE, but they also have a very slow rate of photochemical removal of NO_x (see Figures 6 and 7). Consequently, in the early stages the plume evolution is characterized by dilution rather than by photochemical removal of NO_x or production of O₃. As NO_x concentrations are lowered by diffusion, especially at the sides of the plume, the relative rate of photochemical removal of NO_x increases, and the OPE also increases. Thus photochemical removal of NO_x is delayed until the plume NO_x concentration has been lowered to the point where

Table 1. Linear Least Squares Estimates for O₃-SO₂ Correlations

	7.1 Hours Downwind			9.3 Hours Downwind		
	α ₀	α ₁	r ²	α ₀	α ₁	r ²
Measurements	59	7.6	0.34	52	16.2	0.67
Initial model scenario	65	3.8	0.51	59	12.2	0.38
Modified model scenario	49	18.4	0.54	40	34.5	0.45

Intercept (α₀), slope (α₁) and correlation coefficient (r²) for O₃ as a function of SO₂ (through the linear least squares fit to [O₃]=α₀+α₁[SO₂]) from measurements and model results for the Cumberland plume transects shown in Figure 10.

Table 2. Comparison of OPE Derived From Fluxes and From O₃-SO₂ Slopes With True OPE

	7.1 Hours Downwind			9.3 Hours Downwind		
	Measured	Initial Model Scenario	Modified Model Scenario	Measured	Initial Model Scenario	Modified Model Scenario
<i>Fluxes in First Model Transect</i>						
NO _x	5.0	8.6	4.9	5.0	8.6	4.9
SO ₂	0.43	0.8	0.45	0.43	0.80	0.45
<i>Fluxes in Downwind Transects</i>						
NO _x	1.3	4.3	1.5	0.40	3.0	0.85
SO ₂	0.26	0.51	0.23	0.20	0.49	0.21
O ₃	5.0	4.8	5.7	6.0	10.3	9.2
<i>Estimated OPE From Fluxes</i>						
Without dynamical loss	1.4	1.1	1.7	1.3	1.8	2.3
With dynamical loss	1.5	1.1	2.4	1.8	1.8	3.2
<i>Estimated OPE From O₃-SO₂ Slopes</i>						
Without dynamical loss	0.5	0.5	1.2	0.7	1.1	1.8
With dynamical loss	0.7	0.4	1.7	1.4	1.1	3.0
<i>True Model OPE</i>						
	x	1.6	2.9	x	2.3	3.4

OPE is estimated from net excess flux of O₃, SO₂ and NO_x (equation (4)) using measured and model flux, with or without the adjustment for dynamical losses described in the text (equation (5)). OPE is estimated from O₃-SO₂ slopes (equation (6)) in measurements or in models, with or without the adjustment for dynamical losses. True OPE is derived from equation (3) for models only. The table shows estimated OPE from measurements and model scenarios for two Cumberland transects (7.1 and 9.3 hours downwind), along with measured and model fluxes (10²⁵ mol s⁻¹) used in the calculation. O₃-SO₂ slopes are shown in Table 1.

ozone is produced efficiently. Emission of biogenic and other VOC obviously influences this process, causing higher OPE than would otherwise occur for a given NO_x concentration. However, biogenic VOC also increase the removal rate of NO_x, with the result that NO_x removal occurs at higher NO_x concentrations than would have otherwise occur. Higher NO_x concentrations are associated with lower OPE, an affect which buffers the tendency toward higher OPE due to biogenic VOC. Increased biogenic VOC causes the plume chemistry to progress more rapidly, resulting in higher maximum O₃ at smaller downwind distances. It also causes an increase in cumulative OPE for the plant, but this effect is relatively minor.

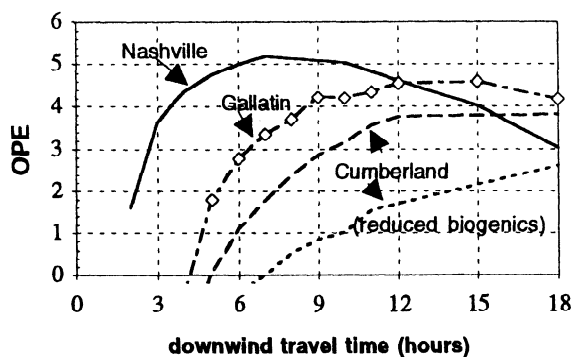


Figure 11. Ozone production efficiency (OPE) along model plume transects versus downwind travel time (hours), as in Figure 8. The dashed line represents the modified model scenario for Cumberland. The dotted line represents the same scenario with biogenic emissions reduced by 75%. The line-diamond line represents the Gallatin plume, and the solid line represents the Nashville urban plume.

It must also be understood that the predicted increase in OPE at far downwind distances is dependent on model assumptions. The increase in OPE occurs because the power plant has been allowed to diffuse overnight, so that ozone-producing photochemistry during the daytime occurs at lower NO_x concentrations. The diffusion process for power plant plumes at nighttime is uncertain, and it is possible that nighttime plumes during stable atmospheric conditions undergo little horizontal diffusion. If the diffusion rate were slower, then the resulting OPE would be less.

7. Discussion

It is obvious that the initial model scenario contains large discrepancies in comparison with measurements. The model overpredicts NO_x and SO₂ throughout the simulated power plant plumes. The NO_x lifetime is too long. Ozone production efficiencies are too low in the Paradise plume and too high in Cumberland. The modified scenario shows much better agreement with measurements, although it must be kept in mind that conditions for the scenario were adjusted to assure agreement with the measured flux of SO₂ in all plume transects and with the measured flux of NO_x in the first transect. The horizontal distribution of NO_x and SO₂ in plume transects, the NO_x removal rate and OPE all compare reasonably well with measurements in the modified scenario, although the model significantly overpredicts NO_x and overpredicts OPE along the last Cumberland transect.

There are two plausible interpretations of these results: (1) the discrepancies between the initial model scenario and measurements might be due to unknown photochemical processes; or (2) the discrepancies might be due to a combination of erroneous emissions and dynamical loss processes in the

plume, as hypothesized in the modified model scenario. It is also possible that the differences between models and measurements are due to errors or uncertainties in the measurements, although the size of the discrepancy for the initial model scenario in comparison with estimated measurement uncertainties suggests that this explanation is unlikely.

If it is assumed that the source of error is unknown photochemistry, then the assumptions of the modified model scenario should be interpreted as representative of the major features of the unknown chemistry. There would need to be rapid removal of both NO_x and SO₂ close to the plume source, accounting for the 33% underprediction for both NO_x and SO_x in the initial Cumberland plume transect and the 50% underprediction for NO_x in the first Paradise transect. This rapid removal of NO_x and SO₂ would be confined to the early stages of the plume and would likely be related to the high aerosol content in the concentrated plumes. In addition there would need to be a photochemical sink of 8% per hour for both NO_x and SO₂ as the plume moves downwind. These NO_x and SO₂ sinks would not be accompanied by additional production of O₃. It might be hypothesized that the observed loss of SO₂ is due to dry deposition. The loss rate of SO₂ in the model scenario with cloud venting could also be produced by dry deposition of SO₂, but this would require a deposition rate (3.7 cm s⁻¹) much higher than most estimates [Weseley, 1989; Meyers *et al.*, 1998]. This interpretation (dry deposition and unknown photochemical removal) would suggest that OPE in power plant plumes is much lower than predicted in models and lower than recent estimates for OPE in urban plumes and plumes from smaller power plants.

It might be hypothesized that the observed loss of SO₂ is due to dry deposition. The loss of SO₂ in the model scenario with cloud venting could also be produced in models without cloud venting if the dry deposition rate for SO₂ were higher, but this would require a deposition rate (3.7 cm s⁻¹ as opposed to 0.6 cm s⁻¹ in the model standard scenario) much higher than most estimates [Weseley, 1989; Meyers *et al.*, 1998]. This interpretation would suggest that OPE in power plant plumes is much lower than predicted in models and also much lower than recent estimates for OPE in urban plumes and plumes from smaller power plants.

The alternative explanation, favored here, attributes the error in the model base case to a combination of erroneous emission rates in the power plants and loss of primary species through vertical dynamics. The dynamical processes could include diffusion during the initial plume rise, with the result that not all plume contents become entrained in the daytime convective mixed layer during the event. The simultaneous underestimate of flux of both primary species (SO₂ and NO_x) suggests lost through dynamical rather than photochemical processes.

The 33% underestimate of primary species in the early plume transects is strongly suggestive of errors in emission rates or dynamics associated with plume rise. It is unlikely that an unknown photochemical sink would result in rapid initial loss of NO_x and SO₂ and a much slower loss rate farther downwind. There is also observational evidence for export of plume emissions above the top of the daytime convective mixed layer [Ryerson *et al.*, 1998].

There is less evidence in support of the hypothesized removal of mixed layer species due to vertical export. The estimated 8%-per-hour removal rate was obtained by matching model SO₂ flux to measured flux for a small number of transects. However the difference in SO₂ with and without this assumed removal process still lies within the estimated range of measurement uncertainty.

The data are also too sparse to determine whether the missing removal process for SO₂ and NO_x is linear. A linear removal process would be more consistent with dynamics than with the highly nonlinear chemistry illustrated in Figure 6. Even if the hypothesized cloud venting did not occur, the rate of photochemical removal in the modified model scenario (equivalent to a 6 hour NO_x lifetime in the downwind Cumberland plume) explains most of the observed loss of NO_x in the plume. When the 8%-per-hour removal due to cloud venting is included in the measurement-based calculation of OPE, the calculated OPE is increased by 30% (See Figure 8). The previous analysis by Ryerson *et al.* [1998] included loss of NO_x from cloud venting in their measurement-based estimate of NO_x lifetime but not for OPE.

Model- and measurement-based investigations of cloud venting have concluded that convective clouds can transport air out of the boundary layer and inject it in the free troposphere at rates of 30% per hour or higher [Cotton *et al.*, 1995; Flossman and Wobrock, 1996]. Updraft speeds of 4 m s⁻¹ and area-averaged transport speeds of 0.3 m s⁻¹ have been measured [Greenhut *et al.*, 1984]. Although many of these studies were based on relatively well-developed clouds, venting of the boundary layer by fair-weather cumulus has also been reported [Stull, 1985; Ching *et al.*, 1988] (see summary of Cotton, *et al.* [1995]). Ching *et al.* [1988] reported injection of O₃ associated with power plant plumes above the boundary layer due to cloud venting, during an event with post cold front meteorology similar to the meteorological event studied here. Thus hypothesized rate of cloud venting (0.031 m s⁻¹) is easily within the range of possible venting rates from fair weather cumulus.

The possibility of cloud venting may also provide an explanation for other data sets with rapid loss of NO_x and NO_y. Gillani [1998b] and Nunnermacker [this issue] have suggested the possibility of rapid deposition of NO_y species (7 cm s⁻¹ or higher) to explain loss of NO_y in power plants. This removal rate may be unrealistically high for dry deposition. It is possible that these high removal estimates are due in part to cloud venting.

Although the modified scenario shows generally satisfactory results in comparison with measurements, there are still some model-measurement discrepancies that hint at unknown processes. The measured NO_x/SO₂ in the earliest Paradise plume transect (2.6 hours downwind) is 30% lower than both the model value and the emissions ratio. This discrepancy can only be explained through an erroneous emissions ratio or unknown photochemical removal of NO_x. No such discrepancy appears in the Cumberland plume (which also had much lower SO₂). The NO_x content of the final Cumberland transect is significantly lower than model values, even in the modified scenario. OPE derived from measured fluxes in this transect is also significantly lower than model OPE. This combination of overpredicted NO_x and overpredicted OPE in the model for this transect is especially hard to explain because higher NO_x is usually associated with lower OPE. The poor model performance for this transect can only be explained by assuming that the sampled plume during this transect had lower initial NO_x than the other transects, or by postulating an unknown NO_x sink.

8. Conclusions

The model calculations and reinterpretation of measurements presented here are intended to gain insight on two questions: the rate of removal of NO_x from large power plant plumes and the ozone production efficiency (OPE) per NO_x. Results were also

used to evaluate the accuracy of measurement-based methods to derive OPE. The results confirm many of the original findings from Ryerson *et al.* [1998], but there are some significant differences and modifications.

Results of the modeling exercise show that the NO_x and SO₂ content of power plant plumes during this event were lower than the plume emission rates by 33% or more. This has been interpreted as evidence that a portion of power plant emissions are exported above the top of the daytime convective mixed layer during the event, or as evidence for errors in the estimated emission rate. The SO₂ content within the power plant also decreases as the plume moves downwind at a rate more rapid than can be explained by chemistry and deposition. This has been interpreted as evidence for venting of the mixed layer through cumulus convection. These interpretations have a significant impact on estimates for OPE. If emission errors and vertical export are accepted as the probable cause for the model-measurement discrepancies in the initial plume transects, then there is no strong evidence for an unknown photochemical sink for NO_x.

OPE has been determined from measured net flux of excess O₃ and NO_x in the power plant reported by Ryerson *et al.* [1998]. The resulting OPE (1.2-2.5) is somewhat higher than the estimate by Ryerson *et al.* The model predicts slightly higher OPE (2-3) than the value inferred from measurements. OPE in the model is also consistent with other estimates for power plants [Nunnemacker *et al.*, this issue; Gillani *et al.*, 1998a] and with recent estimates for OPE in urban plumes [Sillman *et al.*, 1998; Nunnemacker *et al.*, 1998; St. John *et al.*, 1998]. These recent estimates for OPE in polluted environments are significantly lower than older estimates [e.g., Trainer *et al.*, 1993; Olszyna *et al.*, 1994] for reasons discussed by Sillman *et al.* [1998].

Model results also predict that OPE in large power plant plumes is much higher at far downwind distances (15-18 hours downwind) than at shorter downwind distances. At distances of 6-9 hours downwind, OPE in large power plant plumes is predicted to be lower than OPE in plumes from small power plants or in urban plumes by 50% or more. However, at 15-18 hours downwind the OPE in large power plants is predicted to be comparable to OPE from other NO_x emission sources. This far downwind OPE may be more relevant for evaluating the impact of power plants during multiday regional pollution episodes or their impact on global-scale O₃. The higher downwind OPE is predicted because the plumes were assumed to undergo horizontal dispersion even at night.

Several results pertaining to methods for estimating OPE are noteworthy. OPE estimates were derived from net excess flux of O₃, NO_x, and SO₂ in the model, following the same method that would be used to derive OPE from measurements. These estimates compared reasonably well with the correct model OPE, though they tended to underestimate OPE by 10%-30%. OPE estimates were also derived from the statistically derived slope between O₃ and a tracer (SO₂) in the model, along with corrections for photochemical loss of SO₂. This method was found to significantly underestimate OPE in comparison with the correct model value. Statistical correlations between O₃ and other species as tracers (NO_y, CO) have been widely used to infer OPE [e.g., Chin *et al.*, 1994; Sillman *et al.*, 1998]. The problem with this method identified here appears to be a special problem of power plant plumes and occurs because the correlation between O₃ and SO₂ in these plumes is nonlinear. The OPE derived from net flux of O₃ and NO_x in models and in

measurements provides a useful way to evaluate model performance.

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