

APPENDIX D

ELEVATED PLUME RESEARCH PLAN

D. ELEVATED PLUME RESEARCH PLAN

Study Objective

An integrated assessment of ozone formation in central California is being performed under the Central California Ozone Study (CCOS). The objective of the work proposed in this report is to estimate the impact of power plant emissions on formation ozone in central California. An important aspect of this study is to link the ground based air quality monitoring network of the CCOS with aircraft based measurements of ozone and ozone precursors in and around power plant plumes.

The data collected will be used in an analysis of the physical and chemical processes occurring in the plume that contribute to ozone formation over central California. The issues to be resolved include evaluating the effect of transport and mixing processes on ozone formation in and around power plant plumes, the impact of power plant emissions on the relative importance of VOCs and NO_x emissions in limiting ozone production in central California and the evaluation of air quality models and their parameterizations of the power plant plumes (such as plume in grid).

Specifically the following four questions will be addressed in this study.

1. What are the rates of ozone formation and NO_x conversion in power plant plumes?
2. What are the characteristics of dilution and mixing downwind of a plume for different conditions of atmospheric stability?
3. What is the effect of plume-in-grid parameterizations (PiG) on model predictions and do PiGs allow better fitting of the observations?
4. How well do alternative model treatments of power plant plumes perform?
5. Can the data serve as a basis for future plume model or parameterization development?

Scientific Background

The most significant emissions from power plants are nitrogen oxides (NO_x = NO + NO₂) and particles from an air quality perspective. The nitrogen oxide emissions are important because they lead to the formation of ozone when they react photochemically with volatile organic compounds (VOC) emitted from biological and anthropogenic sources.

Initially the power plant plume contains nitric oxide, CO₂, CO and little VOC. The combustion in power plants is extremely efficient so they emit little VOC but the high temperatures that contribute to the efficient combustion lead to the production of NO_x. Under these conditions there is no real production of ozone; ozone mixing ratios are controlled by the ozone/NO_x photochemical stationary state. In the absence of VOC reactions (1) and (3) control the concentrations of ozone and NO_x and their concentrations are described by equation (4).



$$[O_3] = J[NO_2] / k[NO] \quad (4)$$

where $O(^3P)$ are ground state oxygen atoms, $h\nu$ represents ultraviolet radiation, M is either a nitrogen or oxygen molecule, $[O_3]$, $[NO_2]$ and $[NO]$ are the mixing ratios of ozone, NO_2 and NO , respectively, and J is the photolysis rate parameter of NO_2 and k is the rate constant for the reaction of O_3 with NO .

If there is no CO or VOC there is no formation of ozone because reactions 1 through 3 only recycle O_3 . To produce ozone the power plant plume must be diluted and mixed with VOC containing air. Biogenic sources located along the trajectory of the plume may be one important source of VOC to the plume. Another important source of VOC and other ozone precursors, such as CO and PAN , is mixing with urban plumes.

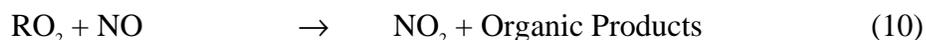
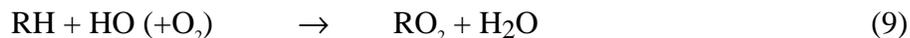
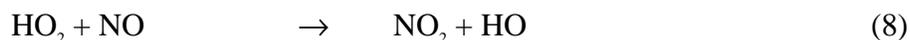
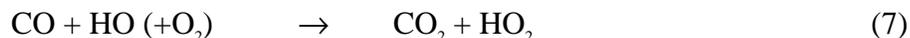
Ozone is produced through reactions that cycle NO back to NO_2 as the plume mixes with VOC containing air. The process begins with the photolysis of ozone that produces an excited oxygen atom, $O(^1D)$.



A fraction of the $O(^1D)$ reacts with water to produce hydroxyl radicals (HO).



Hydroxyl radicals react with CO and VOC (represented structurally as RH below) to produce peroxy radicals (HO_2 or RO_2). Peroxy radicals react with NO to convert it back to NO_2 which photolyzes to produce additional O_3 .



The organic products of reaction (10) may react with HO or photolyze to produce more ozone if there is sufficient NO_x (Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986).

The ozone formation chain reactions are terminated under high NO_x conditions when HO reacts with NO_2 to form nitric acid.



The chemistry of O₃ formation is a highly nonlinear process (i.e. Dodge, 1984; Liu et al., 1987; Lin et al., 1988). Figure 1 is a three dimensional plot of ozone concentrations produced from the given initial concentrations of NO₂ and VOC. The catalytic production efficiency of NO_x is defined as the ratio of the rate at which NO molecules are converted to NO₂ to the total rate of the NO_x loss through conversion of NO_x to nitric acid, organic nitrates or its loss through deposition (Liu et al., 1987; Lin et al., 1988; Hov, 1989). The O₃ production efficiency is inversely related to the NO_x concentration for most atmospheric conditions. The O₃ production efficiency varies over a wide range of values because in the continental boundary layer, NO_x concentrations vary over a range of three orders of magnitude but it is relatively independent of the VOC concentrations, Figure 2. For these reasons the formation of ozone in a plume depends on the characteristics of its dilution and the flights must be used to determine these characteristics.

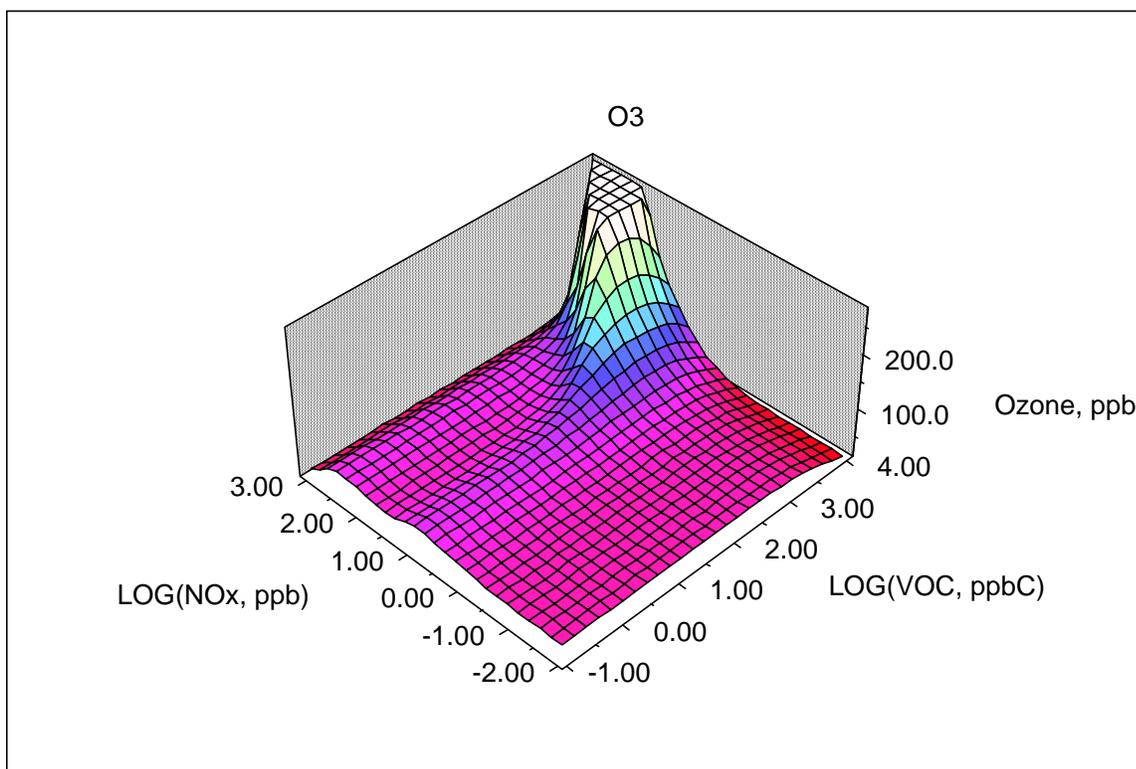


Figure 1. Typical ozone isopleth. The maximum ozone concentrations have been removed to allow the structure at lower NO_x and VOC concentrations to be seen.

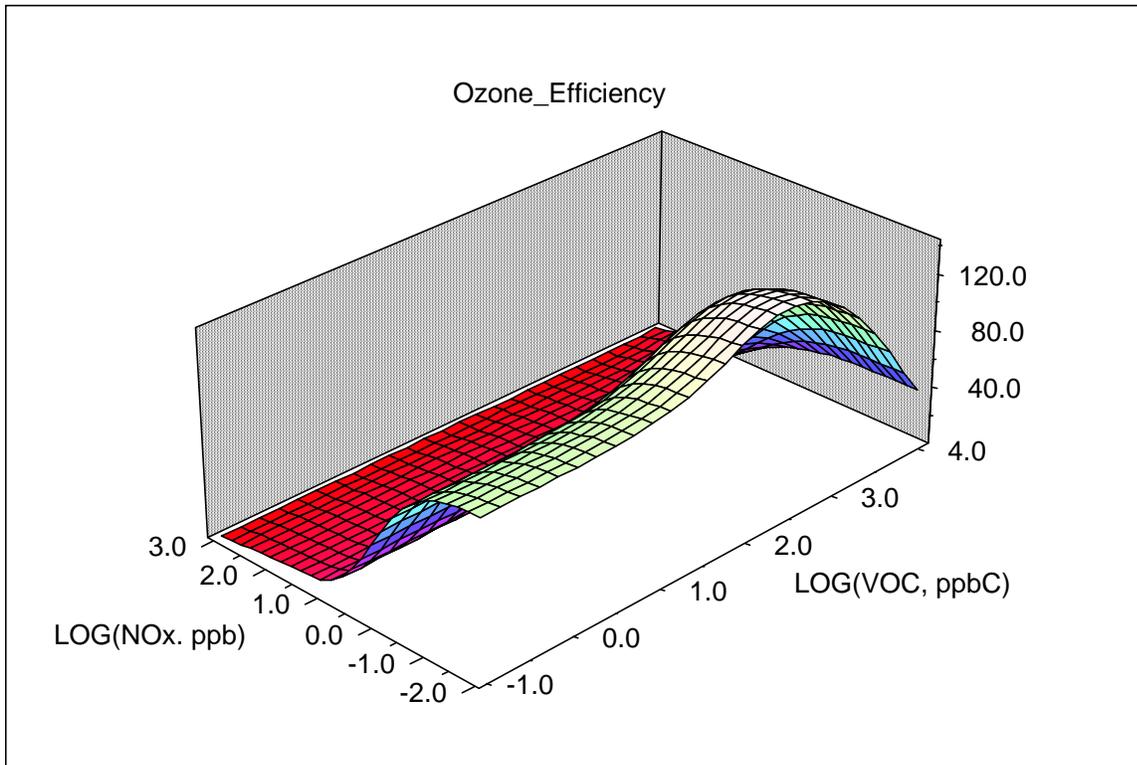


Figure 2. Ozone efficiency in terms of moles of ozone produced per moles of NO_x converted to NO_y.

Reflecting the knowledge that ozone production in elevated point source plumes containing high concentrations of NO_x should be quite different than when plume contents are diluted into typical grid cell volumes --because of vastly different VOC/NO_x ratios, some air quality models use a plume-in-grid (PiG) approach. In this approach, a gaussian-shaped plume is generally simulated in a Lagrangian reference frame that moves with the local wind vector, superimposed on the Eulerian reference frame of the host grid model. After a period of time, the contents of the plume are released into the grid cell or cells the plume occupies at the time of release, determined usually by the relative sizes of the plume and grid cell. Confining the plume for this period of time is thought to be a better way of simulating the plume chemistry and dispersion than immediately diluting the plume contents into a grid cell volume upon emission. Some drawbacks in the way this approach is currently implemented in air quality models are that:

- The schemes used to simulate plume dispersion are based on time-averaged plumes rather than instantaneous plumes and thus are overly dispersive with respect to simulating the chemistry accurately.
- The effect of turbulence on chemistry is usually not simulated.
- The effect of wind shear on plume separation is not simulated

These drawbacks are sufficient to compromise the realism of these simpler PiG approaches.

Under EPRI sponsorship a more advanced approach has been developed. It relies on a Lagrangian puff dispersion model (SCIPUFF -- Second order Closure Integrated PUFF model) that uses a second order closure treatment of turbulent mixing. This gives it the ability to simulate instantaneous concentrations of plume constituents. It also can accommodate wind shear by separating puffs and can merge puffs when they converge. The version of SCIPUFF that includes chemistry is called SCICHEM and can be used as a stand-alone reactive plume model. Its parameterization of turbulent chemistry makes simulations more realistic than simpler approaches, particularly within the first few kilometers downwind of the smokestack, where plume confinement and turbulent chemistry have the greatest effect on local as well as overall ozone production. SCICHEM has been evaluated favorably against the extensive plume data acquired using the TVA instrumented helicopter during the 1995 Nashville/Middle Tennessee Ozone Study.

In an environment where the plume encounters concentration gradients in the background air caused by heterogeneous sources and sinks, plume chemical evolution is best handled by embedding SCICHEM in a gridded Eulerian air quality model. With this arrangement, the Eulerian model supplies SCICHEM with time-and-space-varying background concentrations and SCICHEM supplies the Eulerian model with a more realistic sub-grid-scale treatment of plume chemistry and dispersion. Based on early results, the outcome is less ozone produced per unit of NO_x emitted from elevated point sources than if the plume NO_x is dispersed more rapidly, consistent with plume observations during the Nashville study

The first implementation of SCICHEM in a PiG was using MAQSIP as the host model. This marriage of models is referred to as MAQSIP-APT -- for Advanced Plume Treatment. SCICHEM has been implemented into MAQSIP as a flexibly interfaced module so that it should be relatively straightforward to implement it in any other modeling system. In fact, EPRI is currently implementing SCICHEM into Models-3/CMAQ. SCICHEM could be embedded in whichever model(s) is (are) selected by the Technical Committee.

If any PiG treatment is to be used to model elevated point sources in the central California domain, the temporal and spatial evolution of one or more such plumes must be sufficiently characterized to form an accurate conceptual model of plume evolution as well as provide an observational data set against which to evaluate the PiG model. Without such data, it would be very difficult to demonstrate whether any differences seen among different plume treatments are real and if they exert a real and significant impact on ozone production from elevated point source NO_x emissions. A good candidate for such a study would be the Pittsburg electric generating station. A second candidate is the electric generating station at Moss Landing.

Measurement Plan

Our approach relies on the use of the Tennessee Valley Authority Bell 205 helicopter, Figure 3. The low speed and high maneuverability of a helicopter makes it an ideal platform for this study. The Tennessee Valley Authority Bell 205 helicopter is equipped with instrumentation for the measurement of ozone, carbon monoxide, sulfur dioxide, nitric oxide, nitrogen dioxide, total nitrogen oxides (NO_y), NO_y^{*} (NO_y - HNO₃), canister measurements for VOC, aerosol particle size and distribution and meteorological parameters. It will be used to characterize the VOC concentrations at selected locations in the background air. A detailed list of the instrumentation is given in Table 1.

This aircraft would make a series of plume transects at successively greater distances from the stack, timed to sample approximately the same air parcel in a quasi-Lagrangian experiment. A series of transects will be made under a variety of meteorological conditions.



Figure 3. Bell 205 Helicopter: TVA Environmental Research Center

**Table 1. Flight characteristics and instrumentation of Bell 205 Helicopter:
TVA Environmental Research Center**

Endurance	2 hrs	Payload	500 kg
Ceiling	2.5 km	Research Speed	40-50 m/s
Aircraft Instrument Package for the TVA Bell 205 Helicopter			
Parameter	Time Resolution	Method	Det. Limit
Ozone (O ₃)	1 s	NO Chemiluminescence	2 ppb
Carbon Monoxide (CO)		NDIR or HgO reduction	
Sulfur Dioxide (SO ₂)	5 s	UV Pulsed Fluorescence	0.5 ppb
Nitric Oxide (NO)	1 s	NO/O ₃ Chemiluminescence	1 ppb
Nitrogen Dioxide (NO ₂)	5 s	Photolysis, NO/O ₃ Chem.	1 ppb
Total Nitrogen Oxides (NO _y)	1 s	Au Converter, NO/O ₃ Chem.	1 ppb
NO _y *	1 s	NO _y detection + Nylasorb Filter	1 ppb
Canister VOCs	1 min	Canister Sampling, GC/FID	
bscat	5 s	Nephelometer	< 10 ⁻⁶ m ⁻¹
Aerosol Size Distribution	1 s	PCASP	(0.17 - 3µm)
Particle Composition	variable	Filter Pack, IC analysis	
Particle Composition by Size	variable	Anderson Cascade Impactor	
Air Temperature	5 s	Platinum Thermistor	
Dewpoint	5 s	Capacitance Sensor	
Altitude	5 s	Barometric	
Position	5 s	GPS	
Air Speed	5 s	Pitot- Static Pressure	2 m/s
Heading	5 s	Flux Gate Compass	0.5 deg.

The instrumentation given in Table 1 was used in flights made for the Southern Oxidant Study (SOS). The minimum research speed of 40 m/s must be maintained to avoid contamination problems associated with emissions from the helicopter and the downwash of its propeller. Although the 1999 SOS Field Study Science Plan for Nashville indicated that particle measurements, CO, CO₂ and SO₂ could be used as tracers of opportunity for power plant plumes it appears that these tracers are not feasible because of their low concentrations in the power plant plumes of central California. However, high measurements of CO might be used to identify those urban plumes that may mix with the power plant plumes.

It would be highly desirable if a filter radiometer for the measurement of the photolysis rate parameter of NO₂ (J_{NO_2}) could be added to the instrumentation. Measurement of J_{NO_2} would allow a more direct calculation of the ozone - NO_x photostationary state as described above. Without this measurement J_{NO_2} must be calculated from a radiative transfer model. Given that ozone formation occurs only during the daytime, safety considerations and the limited budget the plume measurement flights should be restricted to the daylight hours.

The O₃ and NO_x measurements should be sufficient to track the plume. A SODAR in the vicinity of the power plant stack or aircraft based LIDAR system or the release of tracers is highly desirable for a complete study. Since a LIDAR system will be expensive for the CCOS study a radar/RASS profiler will be located in the vicinity of the power plant stacks selected for study to ensure that the local 3D winds are well defined for accurate model simulation during the crucial early stages of plume dispersion. The radar/RASS profiler will be moved as necessary for the measurements planned for the power plants at Moss Landing and at Pittsburgh.

It may be possible that the measurement of aerosols by the TVA helicopter will allow some evaluation of the plume in grid models for their ability to describe aerosols but aerosol concentrations may be too low in the plumes measured by CCOS.

It is crucial that the helicopter measure background concentrations to evaluate the plume in grid model. Karamchandani and Seigneur (1999) have shown that indicates that the measurement of background concentrations of O₃, VOC, and PAN are crucial for the correct representation of the formation of nitrate and sulfates inside power plant plumes. They are also important to simulate ozone formation inside power plant plumes and for the evaluation of the host grid model.

Another reason to measure the background O₃ and NO_x is that the formation of ozone in the plume has been characterized by the quantity “excess ozone”. Excess ozone is defined as the difference between the ambient ozone and the ozone within the plume (Luria et al., 1999). Therefore it will be necessary to sample the air upwind of the power plant stack and to sample the air surrounding the plume.

Both horizontal flight paths made at constant altitude and “vertical” plume characterization flights are needed to characterize the plume. Figure 4. The horizontal flights start with measurements made upwind of the stack. Next the aircraft flies across the plume as close to the stack as possible within the limits imposed by safety. The aircraft flies out of the plume and then returns to fly through the plume at a greater distance than the first path. This flight path is continued as long as a plume can be identified by NO_x and aerosol measurements.

The flight strategy is similar for the “vertical” plume flights. The flights should begin upwind of the stack. Next the aircraft should fly down as near as possible to the stack and through the plume. When the aircraft reaches the bottom of its trajectory it should fly upward through the plume. As with the horizontal flights this flight path is continued as long as a plume can be identified by NO_x and aerosol measurements.

During the 1995 SOS Nashville study of power plant plume study it was possible to follow the plume for about 5 to 6 hours or between 50 and 100 kilometers downwind of the stack (Luria et al., 1999). The power plants that affect central California have NO_x photostationary state as described above. Without this measurement J_{NO_2} must be ca emission rates that are about a factor of 10 lower than those around Nashville. These lower emission rates will reduce the distance over which the plumes can be tracked. However, since lower NO_x concentrations may lead to greater ozone production efficiencies enhanced ozone mixing ratios might be observed relatively nearer the stack for the central California power plant plumes.

Luria et al. (1999) also showed the importance of making measurements of VOC during the plume measurements. About 8 measurements were made during each flight. One of the VOC canister samples should be collected upwind of the stack, 6 should be made within the plume and 1 sample should be collected outside the stack but downwind of the stack.

The flights need to be coordinated with the ground-based CCOS air quality monitoring stations. One of the most important uses of the stations will be to provide the meteorological conditions to help determine the aircraft flight plans. The meteorological conditions and the air quality measurements provided by the ground stations will be extremely important for the interpretation of the aircraft measurements. While it is clear that measurements should be made during episodes of high ozone measurements should also be made during periods of average or low ozone. A valid model must be able to predict both peak and average ozone concentrations.

The power plant plumes to be investigated in California include those from Pittsburgh and the Moss Landing. The Pittsburgh, CA, power plant plume has the advantage in that it often interacts strongly with the urban plume from the San Francisco Bay area and it would be expected to have a significant impact on air quality. Observations of Pittsburgh plume would allow its contributions to formation of ozone in the urban plume to be evaluated. On the other hand since the Pittsburgh power plant plume is in a much more polluted area it would be harder to follow.

Figure 5 shows estimated NO_x concentrations for the plume from the Pittsburgh electric power generating station. The NO_x concentrations were calculated from a simple dispersion model. Assuming an ambient background NO_x concentration of 15 ppb it should be possible to follow the plume for at least 15 km under the most stable conditions. The calculation suggests that 20 to 30 km will be more typical.

Alternatively the Moss Landing power plant would be easier to follow because it is in proximity to the coast with cleaner and more stable air conditions. However given its location the plume will contribute less to ozone formation in central California than the Pittsburgh plume. Given the choice between Pittsburgh and the Moss Landing more flight hours should be devoted to the Pittsburgh power plant plume.

To get a more complete description of the effect of meteorological conditions on the plume it will be necessary to make some flights during the morning hours when the mixing height is low and rising. To capture the effect of the plume on the photochemistry of ozone formation it will be necessary to make flights during the afternoon. A reasonable split between the morning and afternoon flight hours would be a ratio of one to two.

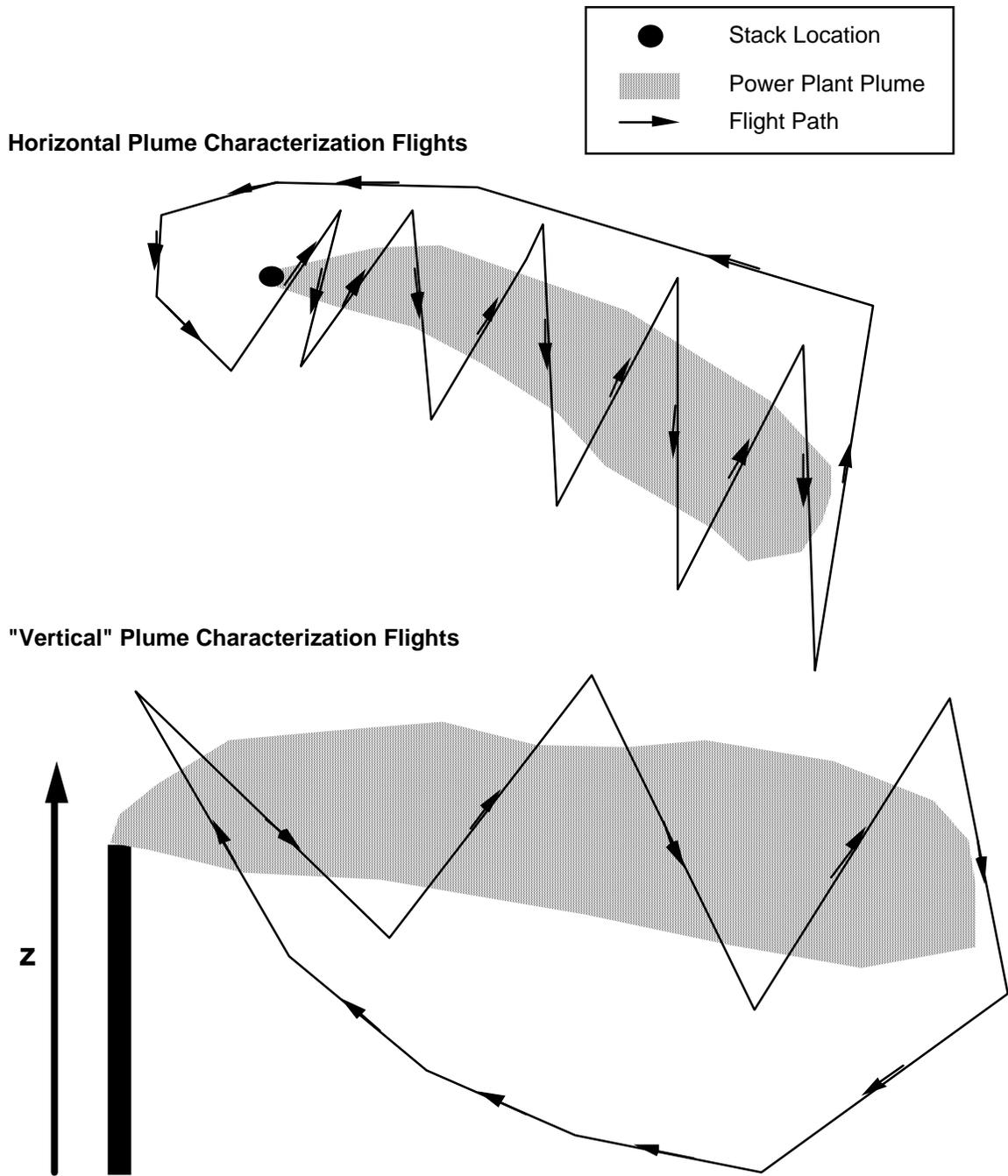


Figure 4. Proposed flight plans for plume measurement experiments.

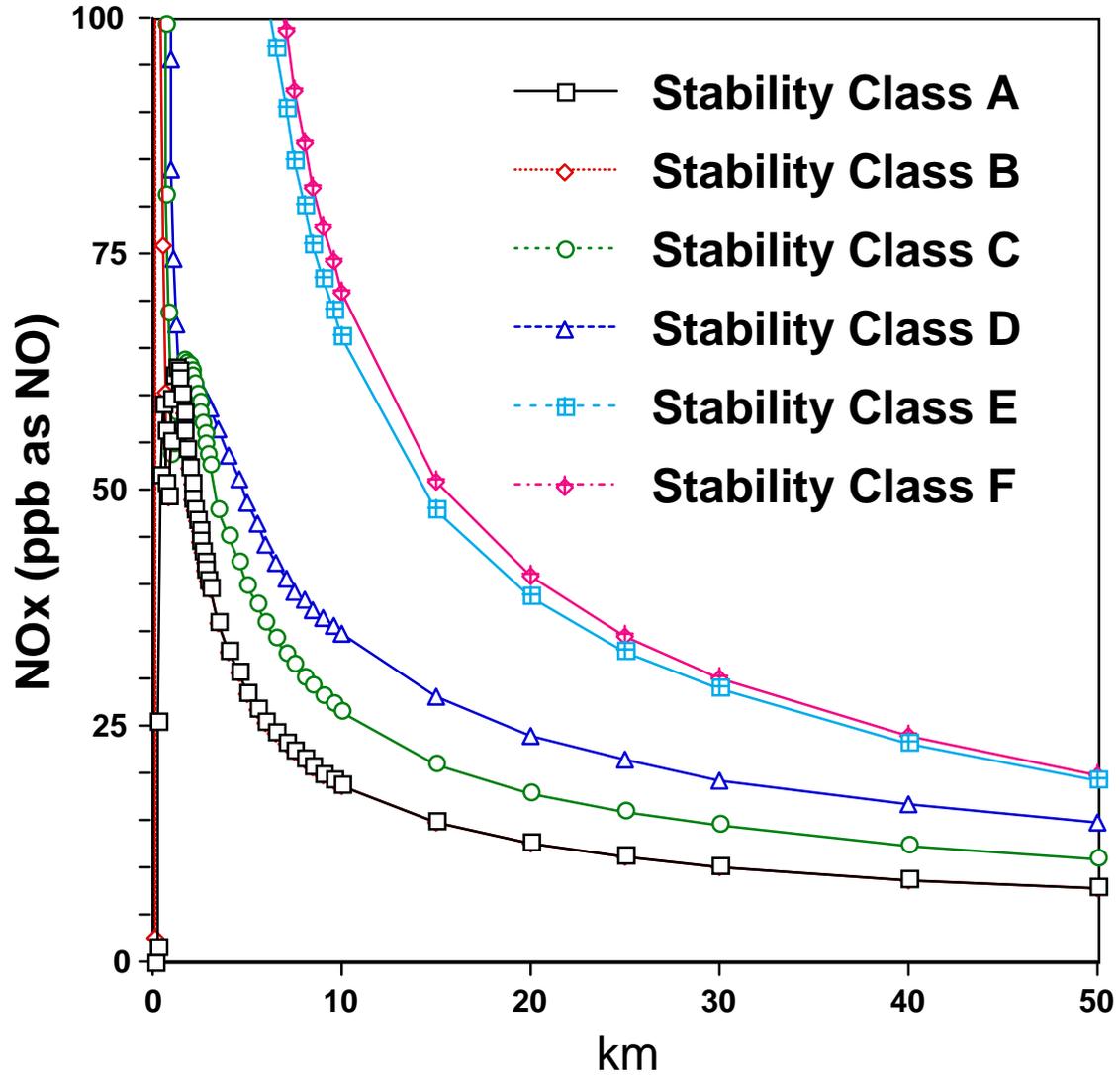


Figure 5. Estimated NO_x concentrations for the plume from the Pittsburgh electric power generating station. The NO_x concentrations were calculated from a simple dispersion model.

Data Analysis and Model Evaluation

Models use plume-in-grid to represent the chemistry and dispersion of large point source plumes. Typically the individual sub-grid scale plumes are simulated in a Lagrangian mode. The plumes are assumed to have a Gaussian distribution that can be treated analytically and these plumes may extend 10 to 20 km from the point source. The chemistry is often simplified to account only for the high NO_x concentrations found within the plumes and the effect of NO_x on ozone concentrations while ignoring VOC chemistry. The plumes disperse and undergo chemical reaction until the spatial extent of the plume and the pollutant concentrations reach levels that can be adequately represented within a 3-d model grid. The size of the plumes relative to the size of the grid cell is one criteria while another criteria is the age of the plume for terminating the plume and mixing its contents in to the regular grid.

It is not clear that the treatment of plumes by state-of-the-art models is adequate. Aircraft measurements of NO_x, ozone and VOC concentrations made in plumes are required to test the validity of the treatment of plume dispersion and chemistry and the procedures for terminating the plume in to the regular model grid by plume-in-grid parameterizations.

Model simulations are required to compare with the measurements to evaluate the models. The reliability of model outputs is assessed through operational and diagnostic evaluations and application of alternative diagnostic tools. Operational evaluations consist of comparing concentration estimates from the model to ambient measurements. The key question in an operational model evaluation is to determine the extent of agreement between simulated and measured concentrations of ozone and its precursors? The measured and simulated ozone and its precursor concentrations should agree in their spatial extent and in their timing. Typical statistics for model evaluation: the comparisons of predicted and observed 1-hr observed ozone concentrations, comparison of 90th percentile concentrations, mean bias (ppb) and mean normalized bias (%) and the mean error (ppb) and mean normalized error (%) (Lurmann et al., 1998).

Diagnostic evaluations are required to determine if the model is estimating ozone concentrations for the right reasons. The emissions, chemistry and transport are assessed to determine if these are treated correctly within the model. The emissions may be assessed through process analysis and mass balance analysis. The chemistry may be assessed through the measurement of predicted secondary chemical products. The transport might be evaluated through comparisons of the spatial and vertical distributions of ozone and its precursors. This broad task also involves reconciliation of data analysis and observation-based results with modeling results. It includes the evaluation of modeling uncertainties, processes, and the assumptions, and their effect on observed differences among model results, measurements, and data analysis results. A key finding of a diagnostic evaluation should be to determine the physical and chemical reasons for the concentration differences between those predicted by models and the measurements. It would also be highly desirable if the likely model bias induced by a model's deficiencies could be identified.

Particular attention needs to be devoted to the Lagrangian puff dispersion models, SCIPUFF and SCICHEM, that were developed under EPRI sponsorship. These models rely on a second order closure treatment of turbulent mixing and are expected to provide more realistic simulations than simpler approaches. The improvement may be greatest nearest the stack. It will be important to

compare the evaluation of SCICHEM with CCOS data to its evaluation made with data from the 1995 Nashville/Middle Tennessee Ozone Study.

References

- Dickerson, The Impact of Aerosols on Solar Ultraviolet Radiation and Photochemical Smog" Science. Vol. 278, 1997.
- Hov \emptyset ., Changes in tropospheric ozone: A simple model experiment. In: Bojkov RD and Fabian P (eds) *Ozone in the Atmosphere, Proceedings of the Quadrennial Ozone Symposium 1988 and Tropospheric Ozone Workshop*. Deepak, Hampton, Virginia, pp 557-560, 1989.
- Karamchandani and Seigneur, Simulation of Sulfate and Nitrate Chemistry in Power Plant Plumes. *Journal of the A&WMA* 49, 175-181, 1999.
- Lin X, Trainer M, Liu SC On the nonlinearity of the tropospheric ozone production. *Journal Geophysical Research* 93:15879-15888, 1988.
- Liu SC, Trainer M, Fehsenfeld FC, Parrish DD, Williams EJ, Fahey DW, Hübler G, Murphy PC Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *Journal Geophysical Research* 92:4191-4207, 1987.
- Lurmann, F.W. and N. Kumar, R. Londergan, G. Moore, Evaluation of the UAM-V Model Performance in the Northeast Region for OTAG Episodes, Ozone Transport Assessment Group, 1998.