

**AIRCRAFT MEASUREMENTS OF  
POWER PLANT PLUMES DURING  
CENTRAL CALIFORNIA OZONE STUDY  
AND THEIR USE FOR THE  
EVALUATION OF THE SCICHEM MODEL**

**PIER COLLABORATIVE REPORT**

**EPRI**



Arnold Schwarzenegger, *Governor*

March 2006  
CEC-500-2006-036



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# **Aircraft Measurements of Power Plant Plumes During CCOS and Their Use for the Evaluation of the SCICHEM Model**

**1007633**

Final Report, March 2003

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This report describes research jointly sponsored by EPRI and the California Energy Commission.

The report is a corporate document that should be cited in the literature in the following manner:

*Aircraft Measurements of Power Plant Plumes During CCOS and Their Use for the Evaluation of the SCICHEM Model*, EPRI, Palo Alto, CA, California Energy Commission, Sacramento, CA: 2003. 1007633.



# REPORT SUMMARY

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This report describes aircraft measurements of power plant plumes during the Central California Ozone Study (CCOS) in July and August 2002 and use of those measurements to evaluate the Second-order Closure Integrated puff model (SCIPUFF) with CHEMistry (SCICHEM).

## Background

CCOS is one component of the Central California Air Quality Studies (CCAQS) program. It consists of a field program, data analysis, emission inventory development, and modeling. The California Air Resources Board (ARB) and local air quality management districts plan to use CCOS results to prepare for demonstrating attainment for the ozone (O<sub>3</sub>) standard in central California areas that are currently in non-attainment. As part of the study, the Tennessee Valley Authority (TVA) conducted aircraft measurements of two power plant plumes in late July and early August 2000.

## Objectives

- To characterize formation of ozone and other secondary pollutants in power plant plumes and their potential contribution to air pollution in the San Joaquin Valley (SJV).
- To evaluate a state-of-the-science reactive plume model, SCICHEM, using data from the TVA aircraft measurements of two power plant plumes.

## Approach

The two power plants whose plumes were sampled were the Pittsburg power plant in the Sacramento River delta and the Moss Landing power plant on the Pacific Coast near Monterey. A total of eight flight missions were made in which the plumes of Moss Landing (3 missions) and Pittsburg power plants (5 missions) were sampled. In addition, one mission (Flight 7) was flown as an intercomparison flight alongside a UC Davis aircraft. All or parts of four of the nine flights were made under conditions where the plumes could be identified as distinct from the background for a significant distance from the plant (20-60 km) along with more detailed observations. The SCICHEM reactive plume model was evaluated using plume measurements from this study. The Community Multiscale Air Quality (CMAQ) model was run to provide background concentrations for SCICHEM.

## **Results**

This report gives a brief description of SCICHEM and includes the previous performance evaluation of a prior version of the model with helicopter plume measurements made in the southeastern United States. Also detailed in the report are this project's experimental setup and flight synopses. Plume  $\text{NO}_y$  chemistry and ozone chemistry using the observational data are provided along with the modeling approach, results, and project conclusions.

## **EPRI Perspective**

The results of the Pittsburg and Moss Landing plume aircraft measurements study were significantly different than what TVA investigators have found in studies in the mid-south region of the United States. Specifically, the power plants at Moss Landing and Pittsburg produced no detectable excess ozone during most flights during downwind transport up to the point at which the plume could no longer be distinguished from the background. The SCICHEM model was unable to predict plume observations of  $\text{O}_3$ ,  $\text{NO}_y$ , and other species in most cases. It is likely that a large part of the discrepancies that were found in this study between the SCICHEM results and the plume measurements can be attributed to two factors: (1) errors in the model inputs and (2) corruption of plume measurements themselves due to incorporation of emissions from other sources into the plumes during their transport. The meteorology and emission inputs used in project calculations are preliminary and are believed to have large uncertainties and errors. Some improvement in model performance is expected when more accurate meteorological and emissions inputs are available later from the modeling component of the CCOS program.

## **Keywords**

SCICHEM model

Power plant plumes

Plume measurements

Central California ozone study

Ozone

## ACKNOWLEDGMENTS

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We would like to thank the California Air Resources Board (ARB) for providing access to data files for the CMAQ simulations conducted in this study to develop background concentrations for the plume model calculations. ARB also provided stack and emissions information for the two power plants simulated in this study. The building information for the plume downwash calculations was obtained from the California Energy Commission for a previous study.

TVA authors acknowledge the assistance of TVA staff Solomon Bairai and Lynn Humes and summer intern David Branscomb, and of the pilots from Twin Otter, Inc. in the collection and processing of the aircraft data. We are grateful for the assistance of the staff of the Monterey Airplane Co. for their friendly assistance in aircraft operations. We also thank the California Air Resources Board (especially Saffet Tanrikulu), the California Energy Commission (Guido Franco) for supporting both the experimental and data analysis portions of this work.



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# 1

## INTRODUCTION

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The Central California Ozone Study (CCOS) is one of the components of the Central California Air Quality Studies (CCAQS) program. It consists of a field program, data analysis, emission inventory development and modeling. The entire effort is expected to be completed by 2005. The California Air Resources Board (ARB) and local air quality management districts plan to use the CCOS results to prepare the demonstration of attainment for the ozone (O<sub>3</sub>) standard for areas in central California that are currently in non-attainment.

The CCOS field program was conducted during the summer of 2000. As part of the study, the Tennessee Valley Authority (TVA) conducted aircraft measurements of two power plant plumes in late July and early August 2000. The purpose of these measurements was to characterize the formation of ozone and other secondary pollutants in the power plant plumes and their potential contribution to air pollution in the San Joaquin Valley (SJV). The two power plants whose plumes were sampled were the Pittsburg power plant, located in the Sacramento River delta, and the Moss Landing power plant, located on the Pacific Coast near Monterey.

A total of eight flight missions were made in which the plumes of Moss Landing (3 missions) or Pittsburg power plants (5 missions) were sampled. In addition, one mission (Flight 7) was flown as an intercomparison flight alongside a UC Davis aircraft. All or parts of four of the nine flights were made under conditions that the plumes could be identified as distinct from the background for a significant distance from the plant (20-60 km), and were further examined in detail: Flight 3 (7/31/00), Pittsburg plant, AM and PM segments; Flight 4 (8/1/00), Moss Landing plant, AM and PM segments; Flight 8 (8/9/00), Pittsburg plant, AM segment only; and Flight 9 (8/11/00), Pittsburg plant, PM segment only.

Another objective of the study described in this report was to evaluate a state-of-the-science reactive plume model, SCICHEM, using data from the TVA aircraft measurements of the two power plant plumes. Section 2 provides a brief description of SCICHEM, including the previous performance evaluation of a prior version of the model with helicopter plume measurements conducted in the southeastern United States. The experimental setup and synopses of flights are provided in Section 3. Plume NO<sub>y</sub> chemistry and ozone chemistry using the observational data are described in Section 4. The modeling approach and results are described in Section 5. Section 6 summarizes the study and presents our conclusions.



# 2

## THE REACTIVE PLUME MODEL

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The reactive plume model used in this study is the Second-order Closure Integrated puff model (SCIPUFF) with Chemistry (SCICHEM). Plume transport and dispersion are simulated with SCIPUFF, a model that uses a second-order closure approach to solve the turbulent diffusion equations. SCIPUFF was originally developed and tested by Titan/ARAP under EPRI sponsorship as part of the Plume Model Validation and Development (PMV&D) project (Sykes et al., 1988). SCIPUFF was further developed under Defense Nuclear Agency (DNA) sponsorship to include a number of improvements, both in the description of the physical phenomena and also in the efficiency of the numerical computation. With additional funding from EPRI and the Defense Nuclear Agency (DNA), a capability to describe the evolving chemical composition of a dispersing scalar was included in SCIPUFF. This allows a general chemical reaction scheme to be specified, with an arbitrary number of species. This reactive version of the model is referred to as SCICHEM.

In SCIPUFF, the plume is represented by a collection of three-dimensional puffs that are advected and dispersed according to the local characteristics (wind speed and direction, turbulence) of the atmosphere. Thus, plume dispersion is not constrained by any geometric function but instead reflects the non-stationary non-homogeneous nature of atmospheric processes. A second-order turbulence closure scheme is used to parameterize turbulent diffusion, providing a direct connection between measurable velocity statistics and the predicted dispersion rates.

Each puff has a Gaussian representation of the concentrations of emitted inert species. The overall plume, however, can have any spatial distribution of these concentrations, since it consists of a multitude of puffs that are independently affected by the transport and dispersion characteristics of the atmosphere. SCIPUFF can simulate the effect of wind shear since individual puffs will evolve according to their respective locations in an inhomogeneous velocity field and since the full Gaussian spatial moment tensor is used, rather than just the diagonal moments. As puffs grow larger, they may encompass a volume that cannot be considered homogenous in terms of the meteorological variables. A puff splitting algorithm accounts for such conditions by dividing puffs that have become too large into more smaller puffs. Conversely, puffs may overlap significantly, thereby leading to an excessive computational burden. A puff merging algorithm allows individual puffs that are similar in size and location and, therefore, are affected by the same (or very similar) micro-scale meteorology, to combine into a single puff. Also, the effects of buoyancy on plume rise and initial dispersion are simulated by solving the conservation equations for mass, heat, and momentum.

The chemical reactions within the puffs are simulated using a general framework that allows any chemical kinetic mechanism to be treated. The user enters the chemical reactions and their associated rate parameters, and SCICHEM sets the corresponding system of ordinary differential equations (ODE) to be solved. Chemical species concentrations in the puffs are treated as perturbations from the background concentrations. The formulation of nonlinear chemical kinetics within the puff framework has been described by Sykes et al. (1997). The effect of turbulence on chemical kinetics can be simulated explicitly (the user selects the reactions for which the turbulent kinetic term is simulated).

The puff chemistry can also be simulated using a staged chemical kinetic mechanism where the number of reactions treated increases as the puff mixes with background air (Karamchandani et al., 1998). This multistage approach offers reasonable accuracy (within 10%) with increased computational speed.

Karamchandani et al. (2000) conducted an evaluation of an early version of SCICHEM using helicopter power plant plume measurements from the 1995 Southern Oxidants Study (SOS) Nashville/Middle Tennessee Ozone Study. The model was applied for 6 days in June and July of 1995 and the model's ability to estimate physical and chemical plume characteristics, such as plume width and reactive species concentrations, was evaluated using the helicopter measurements. The model performed well in comparison with plume measurements for isolated plume cases with a good characterization of the meteorology and background chemistry. The agreement with observations for other cases (interacting plumes from different power plants, interaction between power plant plumes and urban plumes, complex meteorology) was mixed, with good agreement for total nitrogen oxides ( $\text{NO}_y$ ), but poor agreement for secondary species, such as  $\text{O}_3$ .

Gupta et al. (2001) performed a comparative evaluation of SCICHEM with CALPUFF, the modeling system endorsed by EPA as a refined tool for modeling the long-range transport and dispersion of emissions from one or a few sources to assess their impacts on visibility in Class I areas. The models were applied for the Nashville region to evaluate their ability to simulate the measured chemistry of the Cumberland power plant plume during July 1999. While both models tended to underpredict observed concentrations, the underpredictions in CALPUFF were more pronounced than in SCICHEM and CALPUFF was found to oxidize NO more rapidly than SCICHEM since it does not account for  $\text{O}_3$  depletion in the plume during the early plume stages (Gupta et al., 2001).

SCICHEM has been incorporated into two grid-based models, MAQSIP and the U.S. EPA Models-3/CMAQ, to develop a Plume-in-Grid (PiG) model that can be used to treat the subgrid scale effects, associated with  $\text{NO}_x$  emissions from large elevated point sources, on  $\text{O}_3$  formation. The version implemented in CMAQ is referred to as CMAQ-APT (Advanced Plume Treatment) and its development and application are described by Karamchandani et al. (2002).

Under EPRI sponsorship, several improvements to SCICHEM have been incorporated since the model was evaluated by Karamchandani et al. (2000). These include the incorporation of modules for aerosol thermodynamics and aqueous-phase chemistry (Santos et al., 1999; 2000) and the incorporation of a state-of-the-science module for treating the effects of building

downwash on plume rise and dispersion of stack emissions. The aerosol thermodynamic module is based on SCAPE2, originally developed by Meng et al. (1995). SCAPE2 simulates the equilibrium phase distribution of sulfuric acid, sulfate, nitric acid, nitrate, ammonia, ammonium, sodium, potassium, calcium, magnesium, chloride, hydrochloric acid, carbonate and carbon dioxide. The aqueous-phase chemistry module incorporated in SCICHEM is based on the model developed by Strader et al. (1998). This model includes 17 gas-aqueous equilibrium reactions, 17 aqueous equilibrium reactions, and 99 aqueous kinetic reactions among 18 gas-phase species and 28 aqueous-phase species.

The building downwash treatment is based on the Plume Rise Model Enhancements (PRIME) model (Schulman et al., 2000). PRIME incorporates the two fundamental features associated with building downwash: enhanced plume dispersion coefficients due to the turbulent wake, and reduced plume rise caused by a combination of the descending streamlines into the lee of the building and the increased entrainment in the wake. PRIME has been incorporated into the U.S. EPA regulatory model, ISC3. It has been tested against data from field studies and wind tunnels.

In addition to the above improvements, EPRI has recently sponsored a beta-testing study in which two independent organizations, not associated with the development of the model, have tested both a stand-alone version of SCICHEM and the PiG version of SCICHEM (CMAQ-APT). This beta testing has resulted in additional modifications and improvements to the model. Most of these modifications were incorporated in the version of SCICHEM used in the study described in this report.



# 3

## EXPERIMENTAL SETUP AND FLIGHT SYNOPSES

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### 3.1 Aircraft Measurement Systems

The aircraft measurement system used for the plume measurements in CCOS is described in Table 3-1. The filter system was used for the  $\text{NO}_Y^*$  measurements except during the last 2 flights (Flights 8 and 9) when a NaCl-impregnated annular denuder was used. The CO instrument appeared to function properly early in flights but during the warm afternoon periods did not produce interpretable data.

**Table 3-1**  
**Instrument Systems used Aboard the TVA-rented Twin Otter Aircraft during CCOS 2000 Experiments**

Parameter	Time Resolution	Method	Det. Limit
$\text{O}_3$	1s	NO Chemiluminescence	2 ppb
CO	5s	NDIR	ND
NO	1s	NO/ $\text{O}_3$ Chemiluminescence	1ppb
$\text{NO}_2$	5s	Photolysis NO/ $\text{O}_3$ Chem.	1ppb
$\text{NO}_Y$	1s	Au Converter. NO/ $\text{O}_3$ Chem.	1ppb
$\text{NO}_Y^*$	1s	$\text{NO}_Y^+$ nylon Filter or Annular denuder	1ppb
$\text{SO}_2$	5s	UV Pulsed Fluorescence	0.5 ppb
Light scattering	5s	TSI 3- $\lambda$ Nephelometer	about 2 $\text{Mm}^{-1}$
Canister VOCs	1 min grab	Canister Sampling, GC/FID	Variable
Temperature	5s	Platinum Thermistor	
Dew Point	5s	Capacitance Sensor	
Altitude	5s	Barometric Pressure	
Position	5s	GPS	
Air Speed	5s	Pitot-Static System	2m/s
Heading	5s	Flux gate compass	0.5 deg

### **3.2 Other Experimental Data**

Air samples were collected for hydrocarbon analysis using 6-L canisters during TVA Flights 3-9. These samples were collected on board using an automated procedure in which the evaluated canisters were filled to 45 psi three consecutive times to flush the canister, then capped at 45 psi for later analysis. The sampling lines were continuously flushed with ambient air during flights (even when not sampling) to minimize contamination. Analyses were performed for hydrocarbons and selected oxygenated species by Dr. Rei Rasmussen and staff at Biospheric Research Corp. and the data later provided to TVA for incorporation into TVA's database.

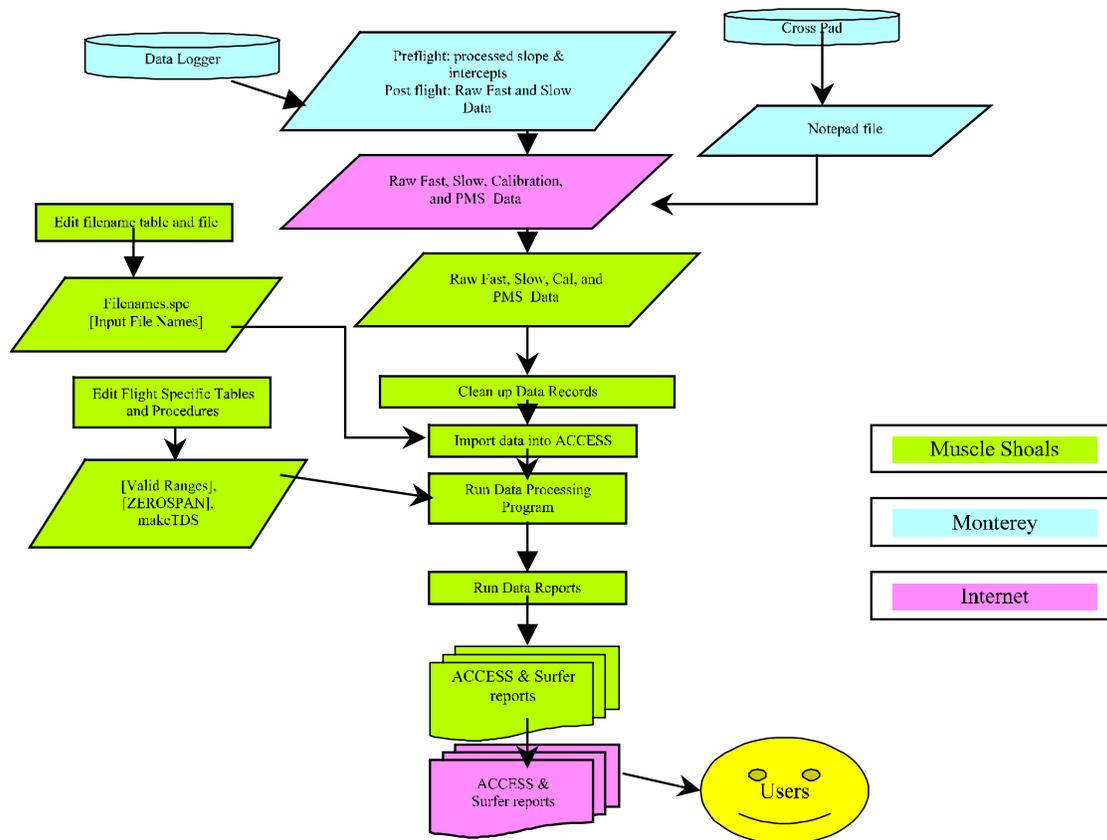
Air samples were collected into Tedlar bags on board during Flights 4-9, using procedures provided by Dr. Kochy Fung of AtmAA, Inc. These samples were post-processed in the field by pulling the air sample in the bag through DNPH-impregnated cartridges. The cartridges were then forwarded to AtmAA, Inc., for analysis of carbonyl species. The data were later provided to TVA for incorporation into TVA's database.

### **3.3 Data Processing**

Data were processed after each flight according to the scheme in Figure 3-1. The data logger file from each individual flight was combined with preflight slope and intercept data for each instrument to produce raw fast (1-s) and slow (5-s) data files to which the Cross Pad notepad file has been added. The combined files were then placed on a restricted Internet site. The combined file was then downloaded by the data processing person in Muscle Shoals who cleaned up the files, imported them into Access and ran the data processing program to generate actual chemical species concentration tables for that day's flight. This includes the time-delay and smoothing routines which provide synchronous data files for all species. Data reports were then generated from the Access files to provide cross-plume plots of species and Surfer representations of the concentration fields of measured and derived variables for that flight. The Access files and data reports were then returned to the restricted Internet site for viewing by the staff in Monterey, usually by the time decisions regarding go or no-go for a flight on the following day were made (usually 0700-0900 hr).

### **3.4 Flight Synopses**

A total of eight flight missions were made in which the plumes of Moss Landing (3 missions) or Pittsburg power plants (5 missions) were sampled. In addition, one mission (Flight 7) was flown as an intercomparison flight alongside one of the UC Davis aircraft, piloted by J. Carroll. All or parts of four of the nine flights were made under conditions that the plumes could be identified as distinct from the background for a significant distance from the plant (20-60 km), and were further examined in detail: Flight 3 (7/31/2000), Pittsburg plant, AM and PM segments; Flight 4 (8/1/2000), Moss Landing plant, AM and PM segments; Flight 8 (8/9/2000), Pittsburg plant, AM segment only; and Flight 9 (8/11/2000), Pittsburg plant, PM segment only. A map showing the location of the Moss Landing (ML) and Pittsburg (PI), CA, power plants is shown as Figure 3-2.



**Figure 3-1**  
**CCOS 2000 Data Processing Overview**

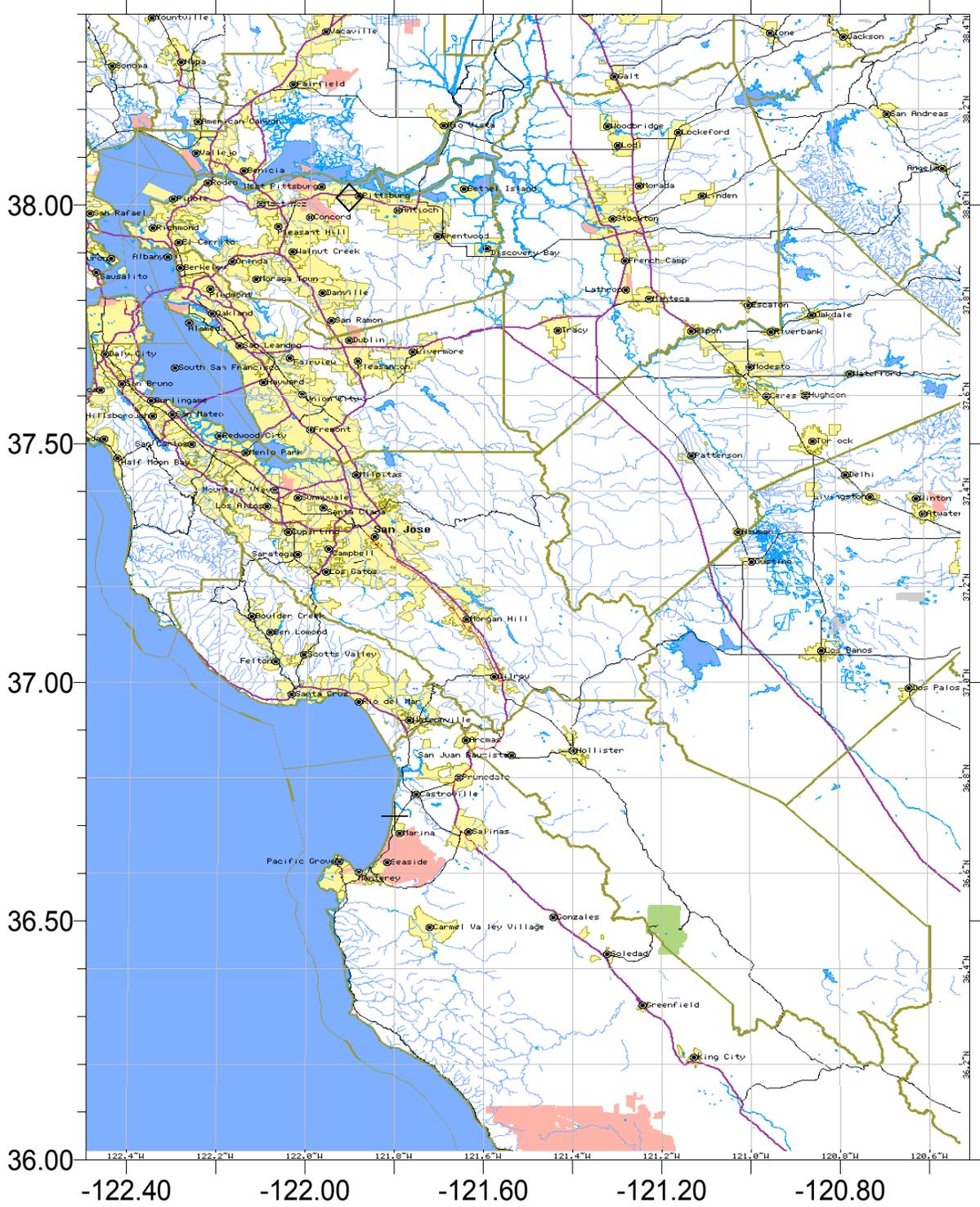
### 3.4.1 Flight 3, AM

July 31, 2000, Pittsburg power plant, conducted late morning to early afternoon (PST). The plume was detected up to 40 km from the stack. Ozone was depleted in the plume and recovered up to the levels in the background (about 70 ppbv). Plume oxidation of  $\text{NO}_x$  to  $\text{NO}_z$  can be detected, as evidenced by the increase in the plume excess chemical age ( $\text{NO}_z/\text{NO}_y$ ) to about 0.5 as the plume mixed to become indistinguishable from background air.

VOC levels were variable, with alkenes averaging about 2 ppbC early in the plume. The last AM sample, taken near the I-5 intersection with the Hetchy aqueduct, appeared to be contaminated with natural gas components (23.5 ppbC non-methane alkanes; 12.7 ppbC alkenes, mostly  $\text{C}_2\text{-C}_4$ ). No carbonyl samples were taken.

### 3.4.2 Flight 3, PM

July 31, 2000, Pittsburg power plant, conducted mid- to late afternoon. The plume was detected up to 45 km from the stack. There is a clear indication that background ozone was titrated near the source, but recovered to form up to 10 ppbv of excess ozone in the wings. Chemical age in the center of the plume recovered to about 0.5 by the time that the plume mixed to become indistinguishable from background air.



**Figure 3-2**  
**Map of the CCOS Operations Area for TVA Flights**  
◊ = Pittsburg Power Plant, + = Moss Landing Power Plant

An urban plume from the San Francisco Bay area was clearly observed to the south and west of the power plant plume. Sampling was conducted in portions of this plume which was (in flight) mistaken at times for the power plant plume. Ozone concentrations during the afternoon flight were about 90 ppbv in the background and increased up to about 150 ppbv as the urban plume was transported out of the immediate Bay area. During this transport, the chemical age gradually increased to  $>0.7$ . The highest ozone readings (Surfer plot-indicated levels  $>130$  ppbv) were observed in the areas immediately in the South Bay around San Jose/Fremont, a smaller area west of Morgan Hill, and a larger area in the hills east of the Gilroy/Hollister area.

During the PM flight, three canister samples were taken in the power plant plume at distances of approximately 3 km, 25 km, and 55 km from the Pittsburg stack near the locations of Antioch, Lake Del Valle, and Coe State Park, respectively. These samples were analyzed for VOCs. The samples all contain modestly significant amounts of isoprene (0.8 to 2.6 ppbC). The Antioch sample contains much larger amounts of lower alkanes and MTBE, suggestive of gasoline vapors. The third sample (over Coe SP) contained little in the way of alkenes other than isoprene. The reactivity of the HC samples taken in Flight 3 (PM), coupled with the modest transport speeds, may explain the fact that this was the only flight at Pittsburg with any indication of power plant plume formation of excess ozone ( $\leq 10$  ppbv). No carbonyl samples were taken during Flight 3 (AM or PM).

### **3.4.3 Flight 4, AM**

August 1, 2000, Moss Landing power plant plume, conducted in mid- to late morning (0940-1140 hr PDT). During the AM flight, the plume traveled almost due south, passing just east of Monterey, and towards, but not reaching the Big Sur Coast before the plume was not distinguishable from the background (about 25 km from the stack). The extent of initial titration of  $O_3$  in the plume was difficult to determine, possibly due to difficulties in traversing the narrow plume near the stack, but plume transport could be easily followed using the  $NO_Y$  data. Chemical age increased gradually up to background air levels ( $>0.7$ ), but there was no net  $O_3$  formed in the plume. Apparently high ozone production efficiencies (average ratio of excess  $O_3$  to excess  $NO_Y$ ) were calculated for areas outside the plume itself, unrelated to the point source emissions (see discussion below).

In the plume near Moss Landing to over Marina, VOC levels were low, HCHO was about 4 ppbv and no isoprene was detected. During the next traverse east of the airport, alkenes were a little higher and a trace of isoprene (0.5 ppbC) was detected. The next sample, taken in the hills south of Carmel Valley, contained an elevated HCHO level (6.2 ppbv) and one of the highest isoprene levels (5.8 ppbC) observed in the study although other alkene levels were lower. The final AM VOC sample taken at 5000 ft over the ocean west of Carmel contained no detectable isoprene and very low levels of other VOCs except aromatics. These data are consistent with low hydrocarbon reactivity in the plume until it was about dispersed into the background at a location with elevated biogenic VOCs.

#### **3.4.4 Flight 4, PM**

August 1, 2000, Moss Landing power plant plume, conducted in the mid-afternoon (1500-1725 PDT). The wind direction at plume release was out of the NW (300°) near the coast, and the plume drifted past Salinas and into the hills along the Salinas Valley. Part of the plume was advected to the SSE along and up the Valley, and was tracked for almost 60 km. The plume traveled over Hwy 101 and traffic emissions therefrom may have been mixed with the Moss Landing plume in air sampled during the last several traverses. For the first 60 km of transit, the power plant plume was the major emission source, as indicated by the uniformly increasing chemical age of the plume. A fresh source (possibly mobile source emissions from Hwy 101) had a strong impact on “plume” levels from 60 km to 100 km downwind. This is indicated by a marked increase in NO and the ratio  $\text{NO}_x/\text{NO}_y$ , and a decrease in  $\text{O}_3$  and the ratio  $\text{NITR}/\text{NO}_y$ .

It is possible that up to 10 ppbv of excess ozone was formed in the power plant plume. This was most noticeable on traverses between Chualar and Gonzales in which an  $\text{NO}_y$  plume is observed coincident with elevated  $\text{NO}_z$  and NITR levels, and with a broad ozone peak (possibly with “wings”). As noted above, additional sources of  $\text{NO}_x$  appear to be introduced South and East of Gonzales which obscure any additional power plant plume chemistry.

Interestingly, no detectable levels of isoprene were found in any of the afternoon flight samples. Formaldehyde levels were about 6 ppbv in both bag samples taken in the PM. In general, alkene levels were a small fraction of observed VOCS (<10% of observed ppbC) for samples taken near the plant. One sample with significantly higher lower alkane and benzene levels was taken about 7 km SE of central Salinas (possible gasoline vapors?).

#### **3.4.5 Flight 8, AM**

August 9, 2000, Pittsburg power plant plume, conducted in the late morning. The power plant plume was detected up to 25 km downwind, traveling toward the east in the direction of the Stockton-Modesto area. Ozone in the background air was quite low, in the range of 20-30 ppbv, with titration in the fresh plume lowering ozone to 10-20 ppbv. There was little  $\text{NO}_z$  formation in this AM plume, and the chemical age had increased only to the order of 0.2 maximum by the time the plume became indistinguishable from background air. We postulate that the relatively low temperatures and the low background reactivity and ozone levels slowed any photochemical conversion to near zero.

Is this hypothesis supported by the VOC and carbonyl data? The formaldehyde levels were near 4 ppbv, the alkene levels were moderate (of the order of 3 ppbC), isoprene levels were detectable but less than 0.5 ppbC (except for one sample taken over the hills about 10 mi SW of Brentwood, E. of Mt. Diablo), and the temperatures were relatively low (<26°C). This flight appears to have been conducted in a plume advected into relatively clean marine layer air. The influence from the Bay Area plume was minimal, which may explain the absence of plume-excess ozone formation.

### **3.4.6 Flight 9, PM**

August 11, 2000, Pittsburg power plant plume, conducted in the mid-afternoon. The plume was detected up to 25 km downwind but disappeared before reaching the Tracy area. Ozone was titrated in the plume, and the ozone deficit was clearly coincident with the NO<sub>Y</sub> plume. No excess formation of ozone in the plume was observed. The evolution of the NO<sub>Y</sub> chemistry demonstrated that it was the power plant plume that was being sampled and the chemical age in the plume increased to ~0.5 before it disappeared.

Alkenes levels were low (<2 ppbC) and no isoprene was found in the plume, except for one sample taken in the foothills about 3-4 km south of Pittsburg. HCHO levels were also low (2.5-4.5 ppbv) throughout the flight.



# 4

## OBSERVATIONAL ANALYSIS OF PLUME NO<sub>y</sub> CHEMISTRY AND OZONE PRODUCTION

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We begin our discussion of the data analysis of the plume measurements with a brief description of the aircraft plume measurements conducted during CCOS, followed by sections on the observed NO<sub>y</sub> chemistry and ozone production efficiencies in the Pittsburg and Moss Landing plumes.

### 4.1 CCOS Plume Measurements

As described in Section 3.4, the TVA-rented Twin Otter aircraft flew a total of eight flight missions to sample the Pittsburg (5 missions) and Moss Landing (3 missions) plumes. In addition, one mission was flown as an intercomparison flight alongside a UC Davis aircraft. Of these flights, there were four in which the plumes could be identified as distinct from the background for a significant distance from the plant (20-60 km), and were further examined in detail by TVA data analysts. Of these four flights, only two were conducted during the period that CMAQ data files were available to develop the SCICHEM inputs (see Section 5.1). These include Flight 3, which was conducted on July 31, 2000, and sampled the Pittsburg (PI) plume during the morning and afternoon; and Flight 4, which was conducted on August 1, 2000, and sampled the Moss Landing (ML) plume during the morning and afternoon. See the synopses for Flights 3 and 4 in Section 3.4 for experimental details for these flight days.

The morning segment of Flight 3 was conducted during the late morning to early afternoon period. Six traverses of the Pittsburg plume were conducted in this segment, at downwind distances ranging from 4 to 26 km from the source. Six traverses were also conducted during the afternoon segment of Flight 3, from mid to late afternoon, at downwind distances ranging from 4 to 38 km of the Pittsburg power plant. An urban plume from the San Francisco Bay area was clearly observed to the south and west of the power plant plume. Sampling was conducted in portions of this plume, which was (in flight) mistaken at times for the power plant plume.

For the Moss Landing plume measurements on August 1, the morning segment of Flight 4 was conducted during mid- to late-morning, with 6 traverses of the plume at downwind distances ranging from 4 km to 32 km. The afternoon segment, conducted in mid-afternoon, included 14 plume traverses at downwind distances ranging from 4 km to 75 km.

The plume measurements from many of the Moss Landing afternoon traverses are not suitable for comparison with model results because they are likely to be contaminated by emissions from sources that were not explicitly simulated with the plume model. For example, for traverses 214009 and 214109, the plumes are fresh with much higher NO<sub>y</sub> concentrations than expected

and are further south and west of where they are expected to be based on other data, and may be due to local sources. During the next traverse, 214010, the aircraft was turning and proceeding to the next downwind distance (based on bearing and GPS distance from the source) when it encountered a somewhat bifurcated Moss Landing plume. Thus, the downwind distance was changing and the observed plume width is not valid. For traverses 214013 to 214018, there are varying amounts of fresh emissions (presumably from transportation and mobile sources) incorporated into the Moss Landing plume as it passes up the Salinas Valley, and it is no longer possible to distinguish between the contributions of the Moss Landing emissions and the fresh emissions from transportation sources along the plume path in and southeast of Salinas.

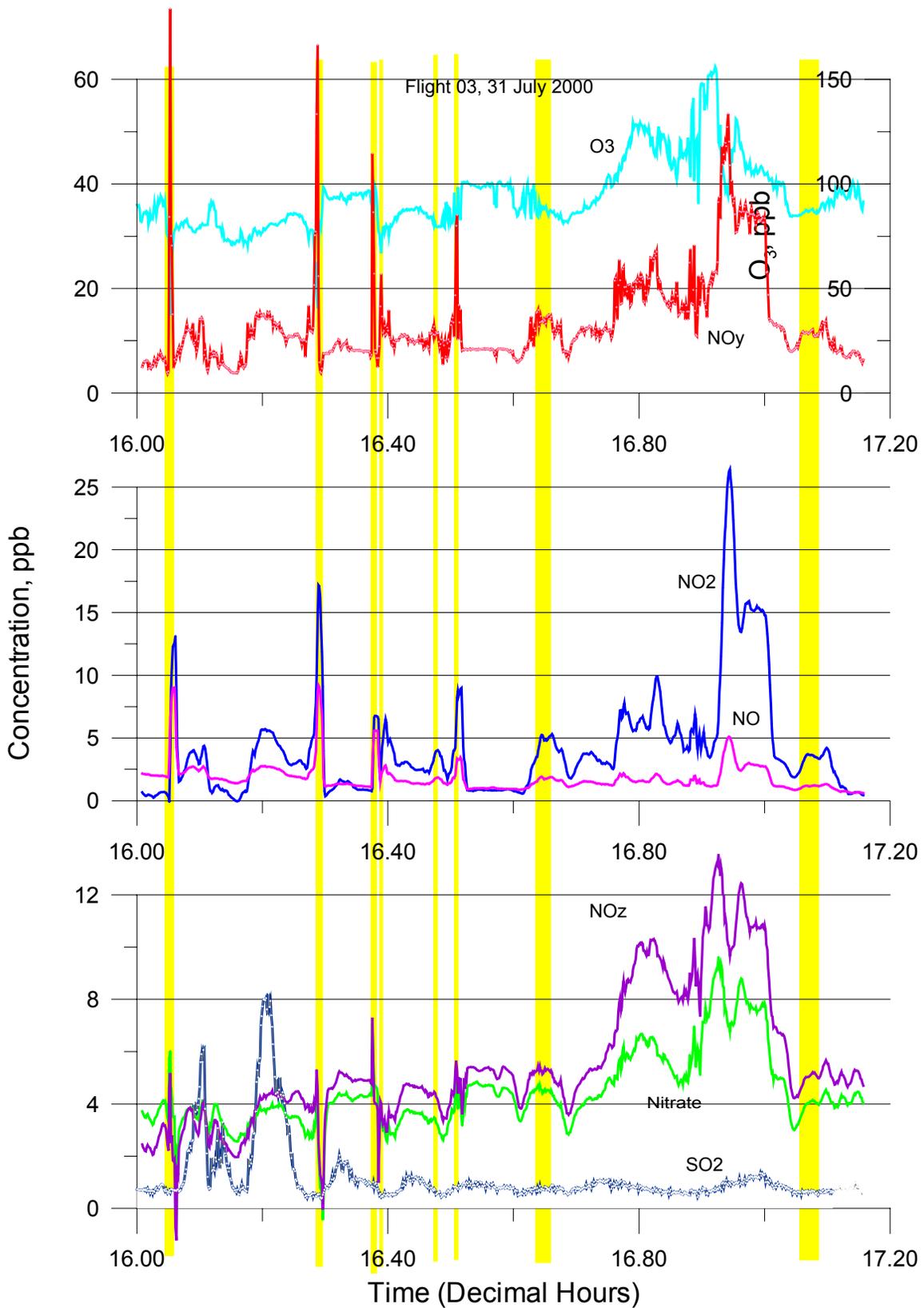
## 4.2 Plume NO<sub>y</sub> Chemistry

For the flights examined in detail, rates of formation and removal of all of the nitrogen oxide species were calculated relative to the sum of all species (NO<sub>y</sub>). The method consists of calculating the average ratios of various nitrogen oxide species to that of NO<sub>y</sub> at each traverse distance (see Table 4-1) using the plume identifications for that flight. In Figure 4-1 we show the plume identifications for the PM portion of Flight 3 in the Pittsburg power plant plume. Recall that all of the traverses were conducted along an arc at a constant distance from the release point (the stack). The mean winds were used to calculate a travel time since release. The concentration ratios were then plotted vs. travel time on a semilog plot (see Figure 4-2 for an example from the PM portion of Flight 3). Positive slopes indicate net formation of the species; negative slopes indicate net loss; *r*<sup>2</sup> values (in parentheses) are the variances of the data from a linear fit of the semi log plot. The slope of the plot is then listed in Table 4-2 as the loss rate (or formation rate) in units of hr<sup>-1</sup>. This assumes that the net formation or loss of the species is pseudo first order with time, whether by reaction or deposition. Plotting the ratios corrects for the fact that NO<sub>y</sub> is not strictly speaking a conserved “species”. Indeed NO<sub>y</sub> is believed to be deposited as NO<sub>z</sub> species (nitrate, nitric acid and possibly other species) at rates significant relative to the transport of the (detectable) plume (Gillani et al., 1998b; Imhoff et al., 2001).

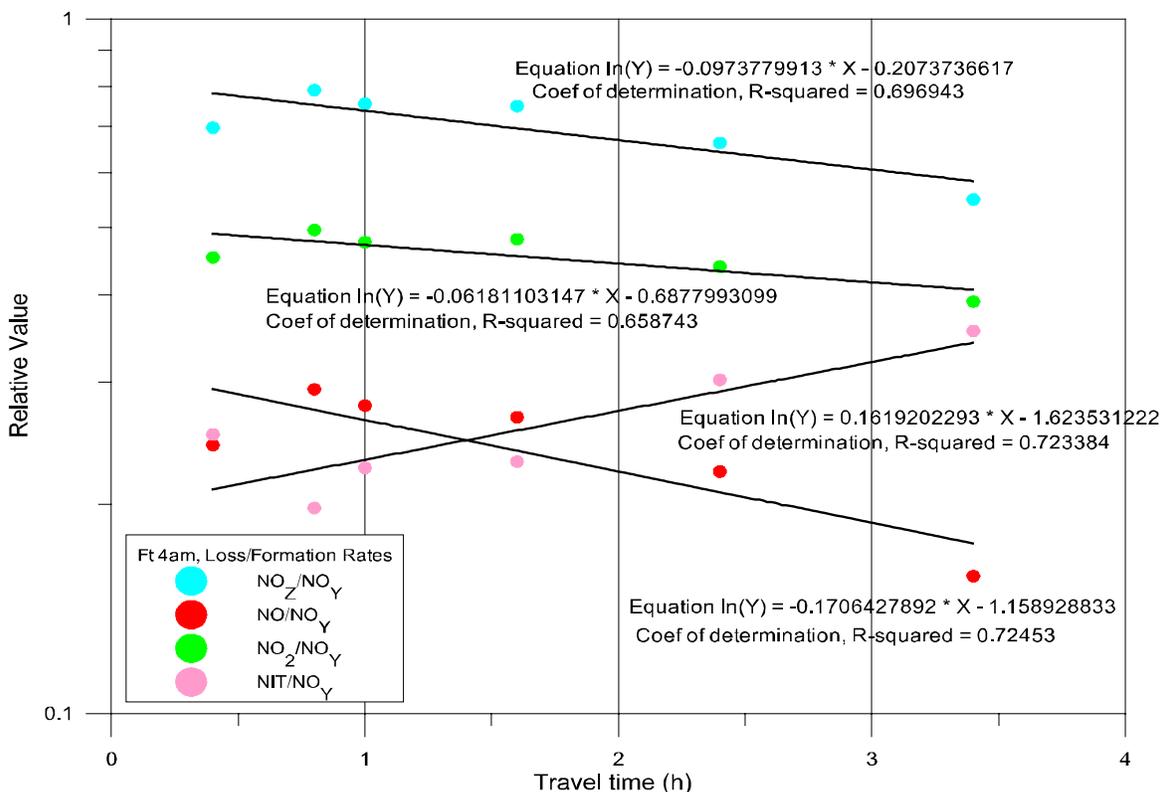
**Table 4-1**  
**Plume-Excess Ratios of Nitrogen Oxide Species to NO<sub>y</sub> for the PM Portion of Flight 3,**  
**Pittsburg Power Plant, July 31, 2000**

Pass #	Distance (nm)	Traverse Time, hr	NO/NO <sub>y</sub>	NO <sub>2</sub> /NO <sub>y</sub>	NO <sub>x</sub> /NO <sub>y</sub>	NO <sub>z</sub> /NO <sub>y</sub>	NIT/NO <sub>y</sub>
1	2	0.14	0.410	0.556	0.967	0.033	ND
2 <sup>a</sup>	5	0.36	0.261	0.644	0.905	0.118	ND
3 <sup>a</sup>	7	0.50	0.290	0.658	0.929	0.173	0.050
4 <sup>a</sup>	10	0.71	0.162	0.453	0.778	0.105	0.124
5 <sup>a</sup>	15	1.07	0.104	0.636	0.822	0.133	0.181
6 <sup>a</sup>	20	1.43	0.094	0.640	0.734	0.148	0.160

<sup>a</sup> Sum of NO<sub>x</sub>/NO<sub>y</sub> and NO<sub>z</sub>/NO<sub>y</sub> ratios may not equal one due to background uncertainties and measurement errors.



**Figure 4-1**  
**Plume Identifications for the PM Portion of Flight 3, 7/31/00**



18 April, 2001

**Figure 4-2**  
**Loss (Formation) Rate Plots for NO<sub>y</sub> Species for the AM Portion of Flight 4 in the Moss Landing Power Plant Plume, August 1**

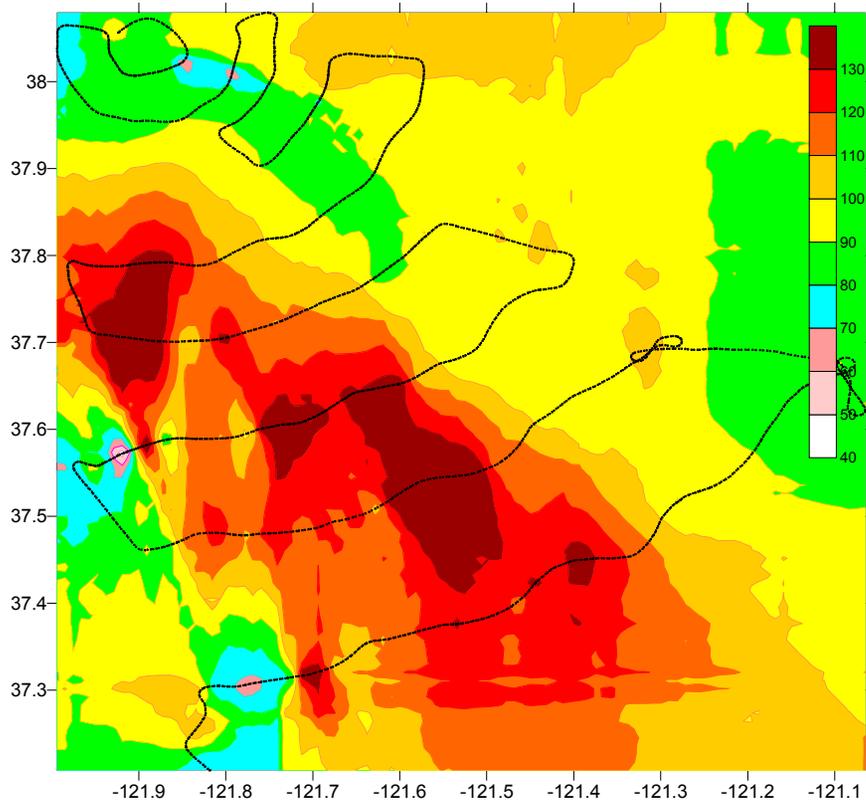
The highest NO<sub>x</sub> oxidation ratios were observed on the afternoon segments of Flights 3 and 4. Significant net O<sub>3</sub> production was not observed in the ML and PI plumes for any of the California flights. Small amounts of excess ozone (<10 ppbv) were formed during the PM segments of Flights 3 and 4 (see Figure 4-3 which gives the flight path and the Surfer representation of ozone levels during the PM portion of Flight 3, and Figure 4-4 which shows the cross-plume traverse data for ozone, NO<sub>y</sub> species and SO<sub>2</sub> for the traverse at 19 km downwind). During all flights listed in Table 4-2, rapid NO<sub>x</sub> oxidation to chemical ages exceeding 0.5 and rapid formation of NO<sub>z</sub> species–nitrate (p-NO<sub>3</sub> + HNO<sub>3</sub>(g)) was observed, except for Flight 4, AM. This suggests that under the conditions that the Moss Landing and Pittsburg plumes were sampled during the CCOS study, the chain termination process usually overwhelmed the chain propagation process. This led to NO<sub>x</sub> -to-nitrate or nitric acid formation, but no significant net photochemical production of ozone occurred in the plumes.

**Table 4-2**  
**CCOS Conversion Rates Summary**

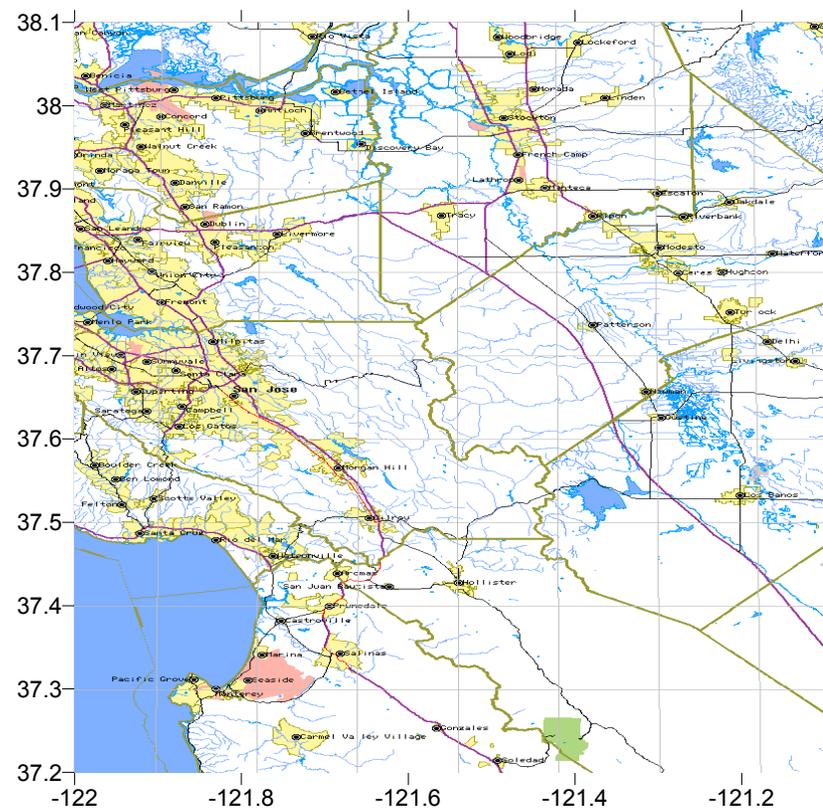
Flight/Date	Start/End Times	PP	Wind Speed/ Direction, m/s, °	Max Dist, km	$T_{\text{max}}$ , °C	Chemical Age (end)	$\text{NO}$ Loss Rate, $\text{h}^{-1}$ ( $r^2$ )	$\text{NO}_2$ Loss Rate, $\text{h}^{-1}$ ( $r^2$ )	$\text{NO}_x$ Loss Rate ( $\text{h}^{-1}$ ) ( $r^2$ )	$\text{NO}_z$ Form Rate ( $\text{h}^{-1}$ ) ( $r^2$ )	NIT Form Rate ( $\text{h}^{-1}$ ) ( $r^2$ )
3-AM 7/31/00	1110-1350	PI	4.5/340	65	33	0.55±0.1	-0.29 (0.67)	-0.27 (0.60)	-0.27 (0.65)	0.47 (0.55)	0.49 (0.54)
3-PM 7/31/00	1600-1750	PI	7/320	61	37	0.44±0.1	-1.0 (0.94)	-0.32 (0.76)	-0.48 (0.92)	2.9 (0.60)	2.0 (0.36)
4-AM 8/1/00	0950-1140	ML	2.5/360	43	32	0.45±0.1	-0.17 (0.72)	-0.06 (0.66)	-0.10 (0.70)	0.19 (0.63)	0.16 (0.72)
4-PM 8/1/00	1500-1725	ML	11/300	122	36	0.60±0.1	-0.70 (0.68)	-0.06 (0.05)	-0.36 (0.53)	0.77 (0.57)	0.56 (0.53)
8-AM 8/9/00	1000-1248	PI	3/280	76	23	0.15±0.1	-0.09 (0.92)	0.02 (0.42)	-0.03 (0.88)	0.32 (0.88)	0.06 (0.30)
9-PM 8/11/00	1515-1700	PI	3.5/300	45	32	0.40±0.1	-0.49 (0.81)	0.07 (0.18)	-0.15 (0.66)	0.35 (0.77)	0.31 (0.30)

Times in PDT; PI=Pittsburg, ML=Moss Landing; Max Dist = maximum distance at which power plant plume was detected; chemical age at last plume traverse with cross-plume variability; rates are first order rates ( $\text{h}^{-1}$ ) from log ratios vs. time plots, with  $r^2$  uncertainties in slope in parentheses; - indicates loss rate of species, + indicates formation rate of species.

Flight 3N PM Ozone, ppb



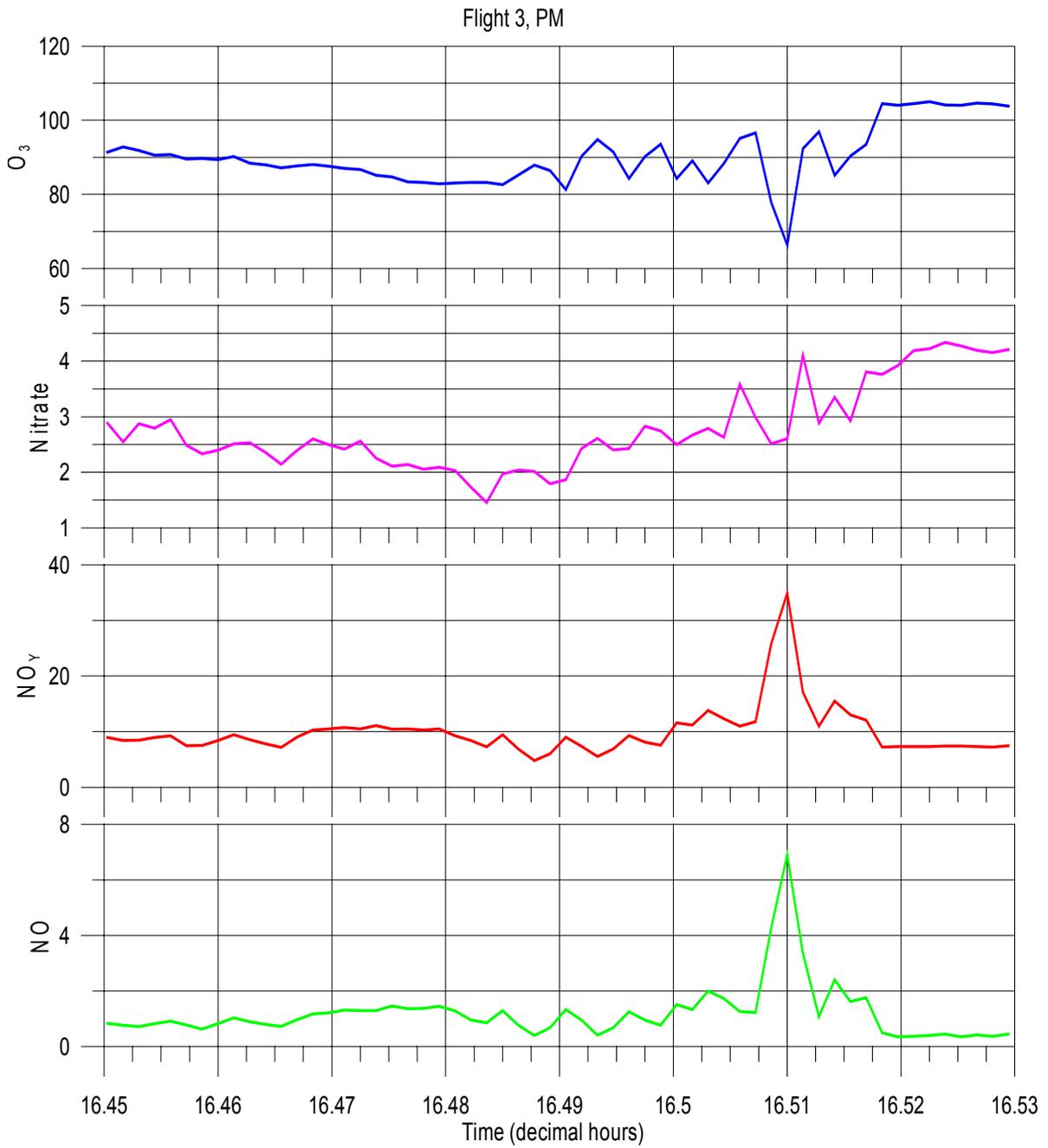
(a)



(b)

**Figure 4-3**

**(a). Surfer Plot of Ozone Concentrations Color Coded in ppbv, Generated from Flight 3-PM Data in the Pittsburg Power Plant Plume. Line is Flight Path of Aircraft, and Power Plant is Located at Approximately 38.0°N/121.9°W. (b). Map of Region in which the Flight was Conducted (July 31, 2000).**



**Figure 4-4**  
**Cross-Plume Data for  $\text{O}_3$  and  $\text{NO}_y$  Species for the Traverse at 19 km Downwind on the PM Portion of Flight 3, 7/31/00**

### 4.3 Plume Ozone Production

Ozone production efficiencies were calculated for each flight by calculating the average ratio of excess O<sub>3</sub> to excess NO<sub>y</sub> for each cross-plume traverse. Table 4-3 shows the OPE calculations for two periods, one for the PM portion of Flight 3 in which a small amount of excess ozone (ca. 10 ppbv maximum) was observed during two of the traverses, and one for Flight 9, PM portion, in which no excess ozone formation was observed. OPEs were calculated for each of the individual traverses as follows: an average ozone concentration in the background air on either side of the plume was selected and subtracted from the ozone values for each of the 5-s data points in the plume. An average plume excess NO<sub>y</sub> for each traverse was calculated in an analogous fashion, and the ratio of plume excess ozone to plume excess NO<sub>y</sub> determined. This ratio represents the molar ratio of plume ozone formed to NO<sub>y</sub> emitted by the point source. Typically, the ratio is negative in the portion of the plume until average ozone recovers from ambient O<sub>3</sub>-plume NO “titration” up to the background ozone level. If no excess ozone is formed from in-plume chemistry, this ratio does not exceed zero. The point at which the ratio approaches an asymptotic “final value” represents the best estimate of the ozone production efficiency. This is shown for Flight 3, PM in Figure 4-5.

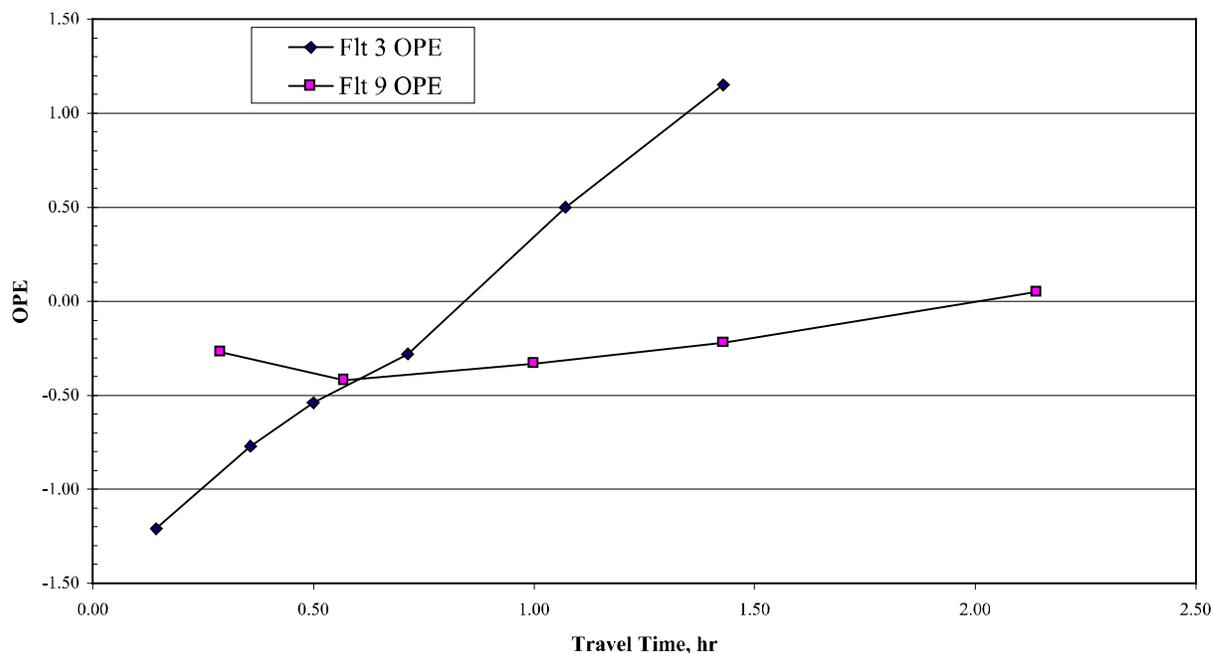
**Table 4-3**  
**OPE Calculations from Pittsburg Power Plant Plume**

**(a) Flight 3, PM Portion**

Pass #	Distance (nm)	Travel Time, hr	Ozone (Plume-Bkgd)	NO <sub>y</sub> (Plume-Bkgd)	OPE
1	2	0.143	-21.53	17.85	-1.21
2	5	0.357	-17.13	22.25	-0.77
3	7	0.500	-4.51	8.39	-0.54
4	10	0.714	-2.39	8.48	-0.28
5	15	1.071	2.64	5.32	0.50
6	20	1.429	1.36	1.19	1.15

**(b) Flight 9, PM Portion**

Pass #	Distance (nm)	Travel Time, hr	Ozone (Plume-Bkgd)	NO <sub>y</sub> (Plume-Bkgd)	OPE
1 to 3	2	0.29	-2.4	8.9	-0.27
4 to 6	4	0.57	-10.3	24.6	-0.42
7,8	7	1.00	-5.6	17.1	-0.33
9,10	10	1.43	-4.8	22.2	-0.22
11,12	15	2.14	0.9	18.5	0.05



**Figure 4-5**  
**Ozone Production Efficiency vs. Travel Time CCOS 2000 Flights 3-PM and 9-PM**

Some investigators (Gillani et al., 2002) refer to this quantity as the yield, since it reflects, if corrected for in-plume depositional losses, the ratio of the amount of net ozone formed to the amount of  $\text{NO}_x$  emitted (both in molar or mixing ratio units). The ratio of excess ozone to excess  $\text{NO}_z$  in the plume is then defined as the ozone production efficiency (OPE). Clearly, it will be necessary to specify which quantity is the most appropriate parameter to use in comparing observations with model simulations.

Overall then, no excess formation of ozone in the plumes was observed on CCOS flights reported herein ( $\text{OPE} \leq 0$ ), except in a limited area during Flight 3, PM and Flight 4, PM, as described above. The calculated OPE for Flight 3, PM was  $1 \pm 1$ , and the OPE for Flight 4, PM could not be reliably estimated due to instrument precision limitations. Little or no excess production of ozone would be anticipated in the case that the plume ratios of  $\text{NO}_x$  to VOCs were relatively large and/or that the speciated VOCs present included very little reactive species such as anthropogenic alkenes or biogenic emissions such as isoprene.

Alkene levels varied widely from sample to sample and day to day (Table 4-4). However, reactive hydrocarbons such as alkenes were present in low amounts except for a few cases for which samples were taken in areas expected to have significant isoprene emissions (foothills and ridges of the Coastal mountains) or which were contaminated by local sources (gasoline or natural gas). Modestly significant amounts of formaldehyde and acetaldehyde were observed, with respect to potential reactivity towards ozone formation (see also Table 4-4). It is somewhat puzzling why there was very little or no ozone formation in the power plant plumes compared to the amounts formed in urban plumes and in power plant plumes in the Southeast USA (Gillani et al., 1998a).

**Table 4-4**  
**VOC and Formaldehyde Concentrations**

Flight No. (Date)	Source	Alkenes, ppbC		Formaldehyde, ppbv	
		Range	Mean (N)	Range	Mean (N)
3-AM (7/31/00)	PI	0.9-3.0	2.0 (2)	No data	No data
3-AM (7/31/00) [outlier]	PI	Not applicable	12.7 (1)	No data	No data
3-PM (7/31/00)	PI	2.2-5.9	4.0 (3)	No data	No data
4-AM (8/1/00)	ML	1.0-6.0	1.9 (6)	4.9-6.2	5.5 (2)
4-PM (8/1/00)	ML	1.1-9.1	3.0 (6)	5.7-6.1	5.9 (2)
8-AM (8/9/00)	PI	1.5-3.6	2.5 (5)	3.8-4.5	4.1 (4)
9-PM (8/11/00)	PI	0.2-1.8	0.9 (5)	1.6-4.3	3.0 (4)

# 5

## SCICHEM SIMULATIONS

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In this section we discuss the CMAQ simulations that were used to develop the SCICHEM inputs, and the development of the SCICHEM input files from the CMAQ three-dimensional files.

For the simulations described here, we used the latest stand-alone version of SCICHEM, version 1.502, with inputs from a three-dimensional grid model, the EPA Community Multiscale Air Quality (CMAQ) model. We selected the option for calculating building downwash effects with the embedded PRIME module. We did not use the optional inorganic aerosol equilibrium and aqueous-phase chemistry modules because of the lack of input data for these modules as well as insufficient observations to evaluate these components.

### 5.1 Development of SCICHEM Inputs

SCICHEM requires the following inputs:

- Meteorological data
- Air quality data, i.e., ambient (background) concentrations of chemical species
- Terrain data
- Source characteristics and emission rates

The model can use either observed or gridded (e.g., from simulations with other models) meteorological and air quality data. Both options have their respective advantages and disadvantages. Gridded outputs from model simulations provide three-dimensional temporally varying fields that cannot be obtained from observations. On the other hand, if the grid model estimates do not agree well with available observations, then using these gridded fields is likely to introduce errors in the SCICHEM simulation.

For the study described here, we selected the option of using input and output files from a three-dimensional grid model to develop hourly three-dimensional SCICHEM meteorological and background concentration inputs. Specifically, we used CMAQ data files, for the period July 30 to August 3, 2000, to develop the relevant SCICHEM input files. The California Air Resources Board provided the CMAQ meteorology input data files for this purpose. The initial and boundary condition files for the CMAQ simulation were prepared by AER using profiles provided by ARB.

In addition, ARB provided pre-merged SAQM-format area, biogenic, mobile and point source emission files that were processed at AER to develop the CMAQ 3-D emission files. ARB also provided the information necessary to identify the Pittsburg and Moss Landing power plants in the SAQM point source input file. This information was used to develop the SCICHEM emissions input file, as well as to exclude these sources in the 3-D emissions file developed for the CMAQ simulation. Table 5-1 summarizes the total NO<sub>x</sub> and VOC emissions in the domain from the various source types for July 30 (representing Sunday emissions) and July 31 and August 1 (representing week-day emissions) and also shows the Pittsburg and Moss Landing emissions for comparison.

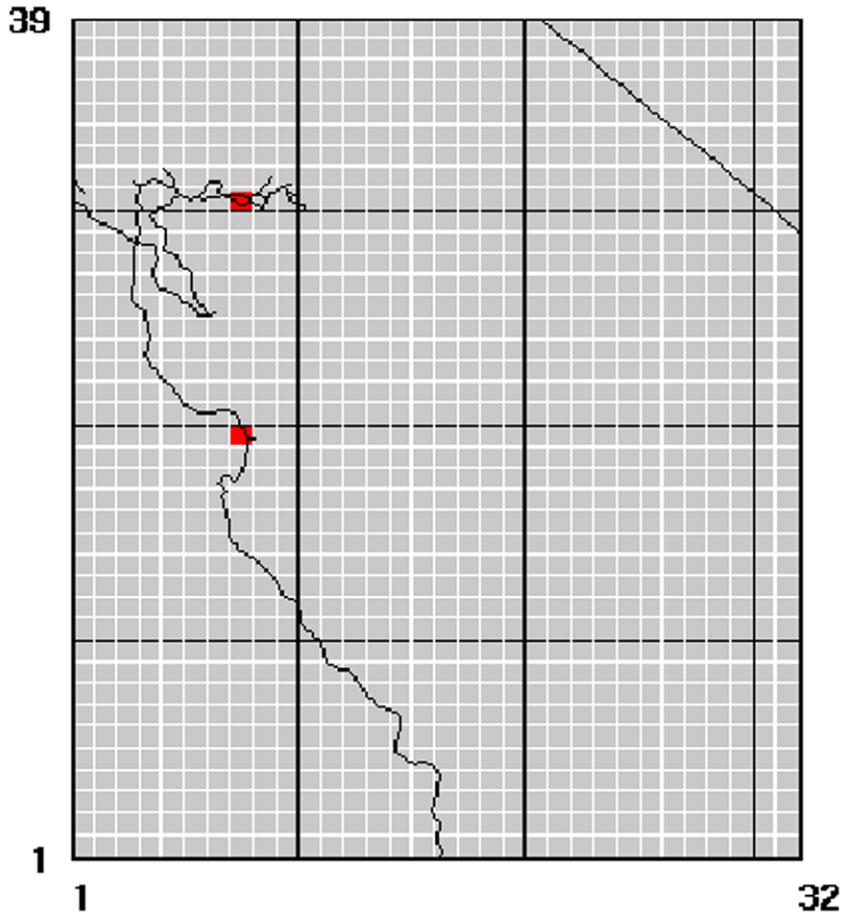
**Table 5-1**  
**Domain – Total VOC and NO<sub>x</sub> Emissions (in metric tons per day)**

Source Type	NO <sub>x</sub> Emissions*		VOC Emissions	
	July 30	July 31 & August 1	July 30	July 31 & August 1
Area sources	640	640	800	820
Biogenic sources	0	0	1040	1200
Mobile sources	530	680	460	590
Point sources	170	65	180	98
Pittsburg	3.1	6	< 0.1	< 0.1
Moss Landing	3.6	4.6	0.3	0.3

\* as NO<sub>2</sub>

We conducted a CMAQ simulation for the above period for the modeling domain shown in Figure 5-1. The domain consists of 32 by 39 grid cells in the horizontal (with a grid resolution of 12 km on a Lambert conformal projection) and 15 layers in the vertical. The vertical structure of the CMAQ grid is presented in Table 5-2. As noted above, the emissions from the two point sources that were to be explicitly simulated with SCICHEM in our study were excluded from the CMAQ simulations. The first day of simulation (July 30) was used as a spin-up day and the CMAQ results for July 31 and August 1 were used for the SCICHEM simulations.

Processors were developed to read the CMAQ input meteorology files and output concentration files to create the hourly three-dimensional SCICHEM meteorology and background concentration input files. The emissions information for the 2 point sources of interest was processed to develop the SCICHEM emission files. We also used building information data for the 2 point sources, available from a previous study conducted for the San Joaquin Valleywide Air Pollution Study Agency (Karamchandani and Vijayaraghavan, 2001), for the PRIME building downwash calculations.



**Figure 5-1**  
**Models-3/CMAQ Modeling Domain for the CCOS Simulation (the Locations of the Pittsburgh and Moss Landing Power Plants are Highlighted)**

We understand from the ARB that the provided CMAQ meteorology files and SAQM emission files are preliminary – the meteorological files were created without the use of Four Dimensional Data Assimilation (FDDA) and the emissions inventory is not the final SIP inventory. We also understand that the CMAQ model performance with these inputs is poor (Saffet Tanrikulu, private communication, 2002). Efforts are underway at ARB to develop more accurate fields for the next cycle of model evaluation with the CCOS and CRPAQS databases, but these improved data sets were not available in time for our study. In addition to anomalies in some of the plume measurements, these flaws in the input data sets may explain many of the discrepancies found between model estimates and observed plume measurements, as described in the following section.

**Table 5-2  
Models-3/CMAQ Grid Layers for the CCOS Simulation**

Layer Number	$\sigma$ -p	Approximate Layer Top (m agl)
15	0.00	14680
14	0.156	10064
13	0.326	6941
12	0.464	5038
11	0.600	3487
10	0.740	2119
9	0.814	1468
8	0.866	1035
7	0.902	746
6	0.918	621
5	0.934	496
4	0.950	374
3	0.966	253
2	0.980	148
1	0.992	59
0	1.000	0

## 5.2 Results

### 5.2.1 Pittsburg Plume Traverses

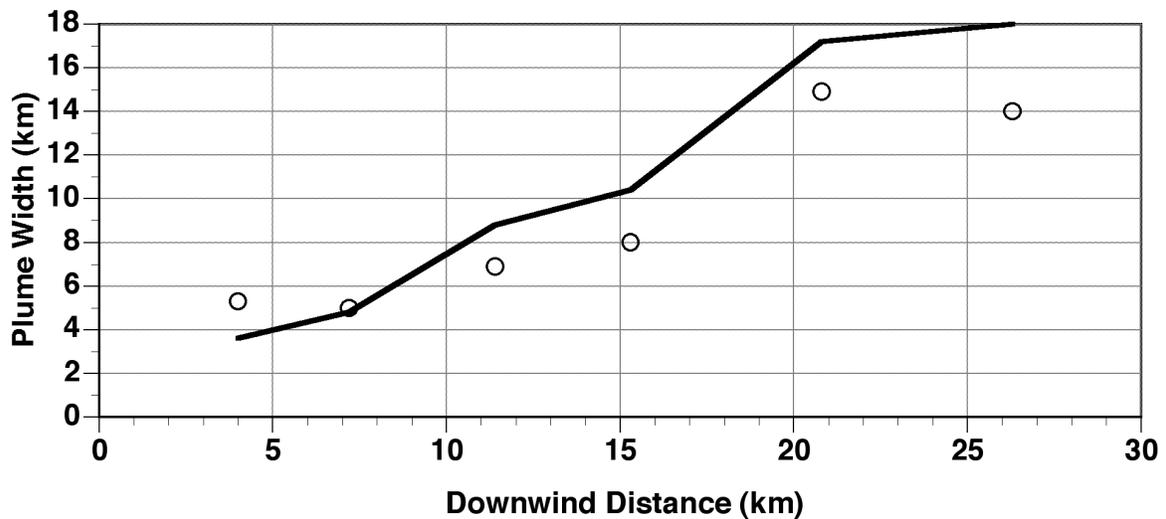
The six morning Pittsburg traverses (see Section 4.1) were conducted from 11:15 a.m. PDT to 12:00 p.m. PDT on July 31, 2000. Table 5-3 shows the average distance from the source of each traverse as well as the measured width of the plume and the general direction of the measured plume with respect to the source. For comparison, the simulated plume widths and directions at each downwind distance are also shown in the table. We calculated the simulated plume widths as the extent of the plume containing 95% of the plume mass (represented by an inert tracer species emitted at the source).

**Table 5-3**  
**Plume Directions and Widths for Pittsburg Morning Traverses, July 31**

Traverse ID	Downwind Distance (km)	Plume Direction*		Plume Width (km)	
		Observed	Simulated	Observed	Simulated
213001	4	SE	S	5.3	3.6
213002	7.2	SE	S	5.0	4.8
213003	11.4	SE	SSW	6.9	8.8
213004	15.3	ESE	SSW	8.0	10.4
213005	20.8	SE	SSW	14.9	17.2
213006	26.3	ESE	SSW	14.0	18.0

\* with respect to source

Table 5-3 shows that there are large differences between the simulated and measured directions of travel of the Pittsburg plume during the morning traverses. The observations indicate that the plume is traveling to the southeast or east-southeast of the Pittsburg source, while the simulated plume goes to the south or south-southwest of the source. This discrepancy between the observed and simulated plume directions also appears for the afternoon Pittsburg traverses as well as for the Moss Landing traverses, as discussed later. Although the differences between the measured and simulated plume widths are smaller (Figure 5-2), the simulated plume widths increase with downwind distance while the observed plume widths show similar but less consistent behavior.



**Figure 5-2**  
**Variation of Measured (Circles) and Simulated (Solid Line) Plume Widths with Downwind Distance for Pittsburg Morning Traverses**

Because of the differences between the observed and simulated plume directions, we did not sample the simulated plume at the observed locations for comparison purposes. Instead, we aligned the centerlines of the observed and simulated plumes and then sampled at the same cross-plume distances as the observed plume. Furthermore, we sampled the simulated plume at a number of elevations between the surface and about 1 km to find the closest match between the observed and simulated peak excess (above background values) NO<sub>y</sub> concentrations.

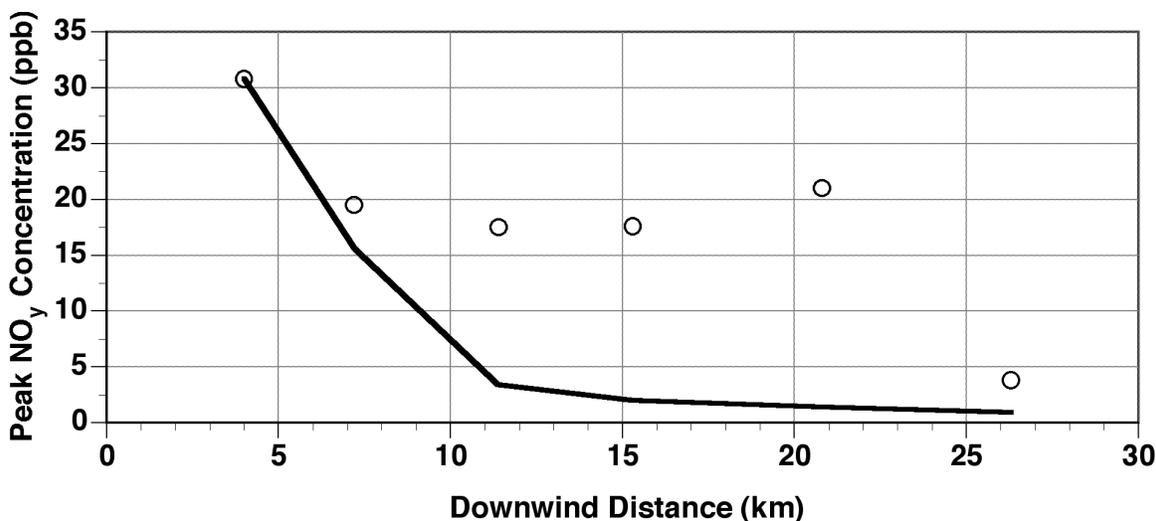
Table 5-4 presents a comparison of the observed and simulated peak excess (i.e., over background) NO<sub>y</sub> concentrations for the Pittsburg morning traverses. For the first morning traverse, 213001, at a downwind distance of 4 km, the maximum simulated peak excess NO<sub>y</sub> concentration at an altitude of 300 m MSL is about the same as the observed peak of 31 ppb at 257 m MSL. However, the actual maximum simulated peak for traverse 213001 is about 51 ppb at 100 m MSL. For all the other morning traverses, the maximum simulated peaks at all altitudes are lower than the observed peaks. These differences between the observed and simulated peaks increase with downwind distance from the source. Figure 5-3 shows the observed and simulated peaks as a function of downwind distance. As seen in the figure, the estimated peak plume NO<sub>y</sub> excess concentration decreases steadily with downwind distance, showing the effect of dispersion, while the observed peak concentration decreases initially but then remains fairly constant or increases with downwind distance. The observations may have been affected by interception of other NO<sub>y</sub> sources, specifically the Antioch point source plume, during traverses 214003 through 214005.

**Table 5-4**  
**Peak Plume Excess NO<sub>y</sub> Concentrations for Pittsburg Morning Traverses, July 31, 2000**

Traverse ID	Peak Excess NO <sub>y</sub> Concentration (ppb)		Number of Peaks in Traverse	
	Observed	Simulated	Observed	Simulated
213001	30.8	30.8 <sup>a</sup>	Single	Single
213002	19.5	15.7 <sup>b</sup>	Single	Single
213003	17.5	3.4 <sup>b</sup>	Multiple	Single
213004	17.6	2.0 <sup>b</sup>	Multiple	Single
213005	21.0	1.4 <sup>b</sup>	Multiple	Single
213006	3.8	0.9 <sup>b</sup>	Multiple	Single

<sup>a</sup> at 300 m MSL; observed peak at 257 m MSL; maximum simulated peak = 51 ppb at 100 m MSL

<sup>b</sup> maximum at all altitudes between surface and 1 km MSL



**Figure 5-3**  
**Variation of Measured (Circles) and Simulated (Solid Line) Peak Plume Centerline Excess NO<sub>y</sub> Concentrations with Downwind Distance for Pittsburg Morning Traverses**

As shown in Table 5-4, in 4 of the six morning Pittsburg morning traverses, at downwind distances greater than 10 km, multiple NO<sub>y</sub> peaks are observed, suggesting that the aircraft may have sampled multiple plumes. On the other hand, the simulations show only a single peak for the Pittsburg plume.

Figure 5-4 shows the observed and simulated cross-plume excess concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub> for the first Pittsburg morning traverse, 213001, at about 4 km downwind of Pittsburg. Figure 5-5 shows the corresponding plume excess concentrations for NO<sub>y</sub> and O<sub>3</sub>. As mentioned previously, we have aligned the simulated plume centerline with the observed plume centerline even though they do not occur at the same location. Also, the observed cross-plume profiles are at an average altitude of 257 m MSL, while the SCICHEM estimates are for an altitude of 300 m MSL. We see from Figures 5-4 and 5-5 that, for this traverse, there is good agreement between the observed and simulated cross-plume concentrations for all the species.

The comparisons of observed and estimated excess cross-plume concentrations for the second Pittsburg morning traverse (213002), at about 7 km downwind of Pittsburg, are shown in Figure 5-6 for NO, NO<sub>2</sub>, and NO<sub>x</sub>, and in Figure 5-7 for NO<sub>y</sub> and O<sub>3</sub>. The observed cross-plume profiles are at an average altitude of 334 m MSL, while the SCICHEM estimates are for an altitude of 140 m MSL. The estimated cross-plume concentration profiles compare reasonably well with the measured values, although the comparison is not as good as it is for traverse 213001.

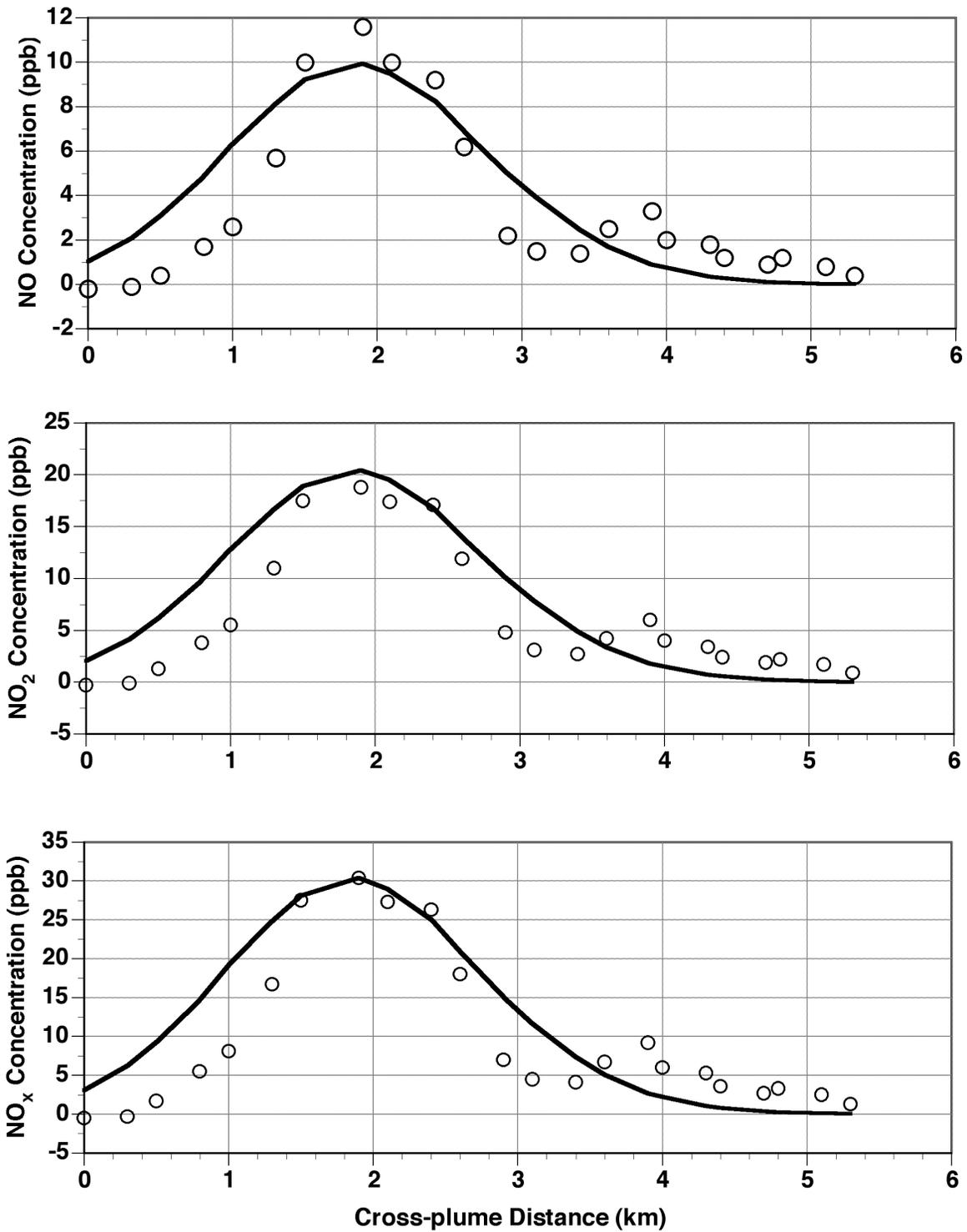
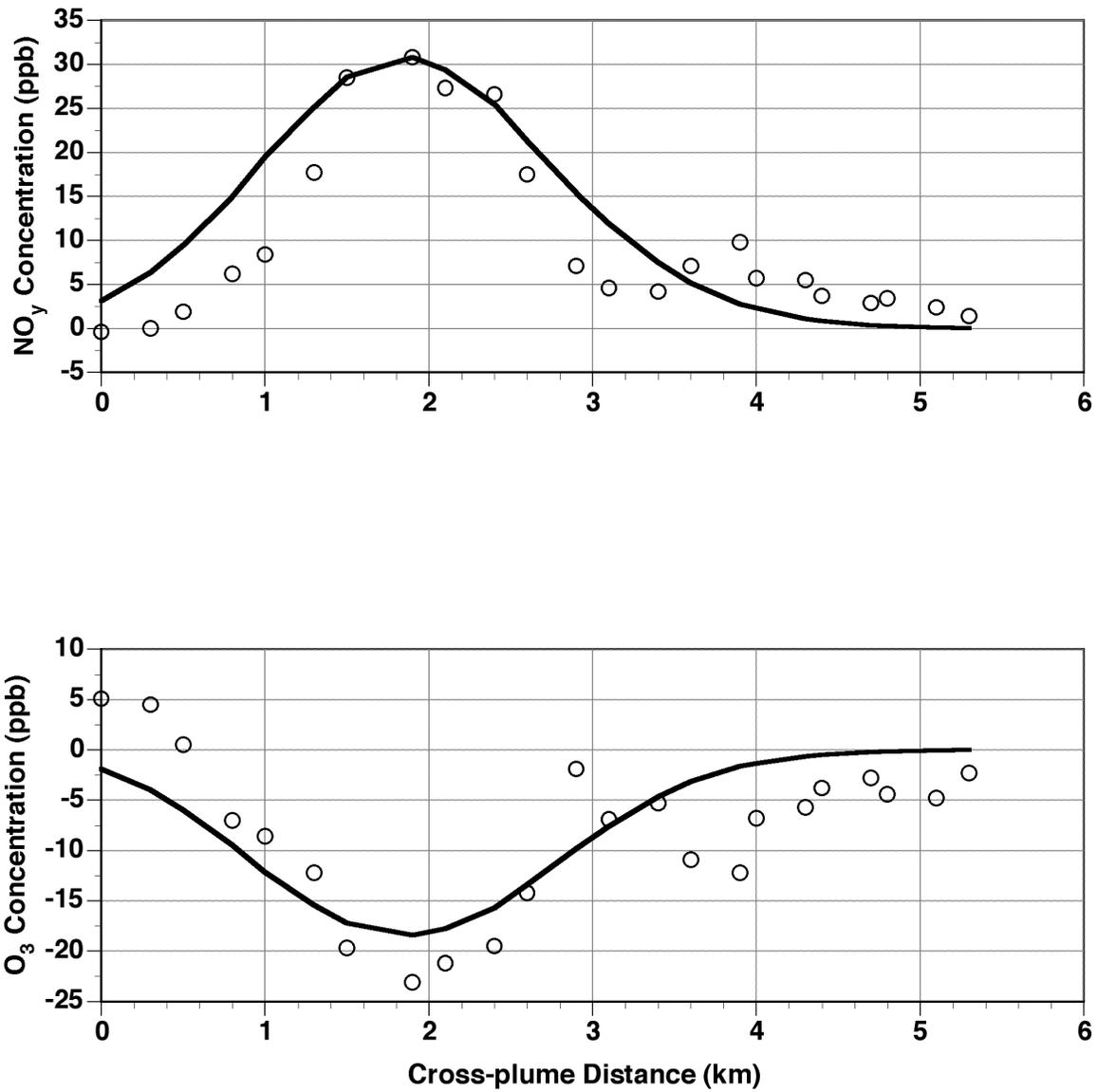


Figure 5-4  
 Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume  
 Concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> for Pittsburg Morning Traverse 213001  
 (4 km Downwind) on July 31, 2000



**Figure 5-5**  
**Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume**  
**Concentrations of NO<sub>y</sub> and O<sub>3</sub> for Pittsburg Morning Traverse 213001**  
**(4 km Downwind) on July 31, 2000**

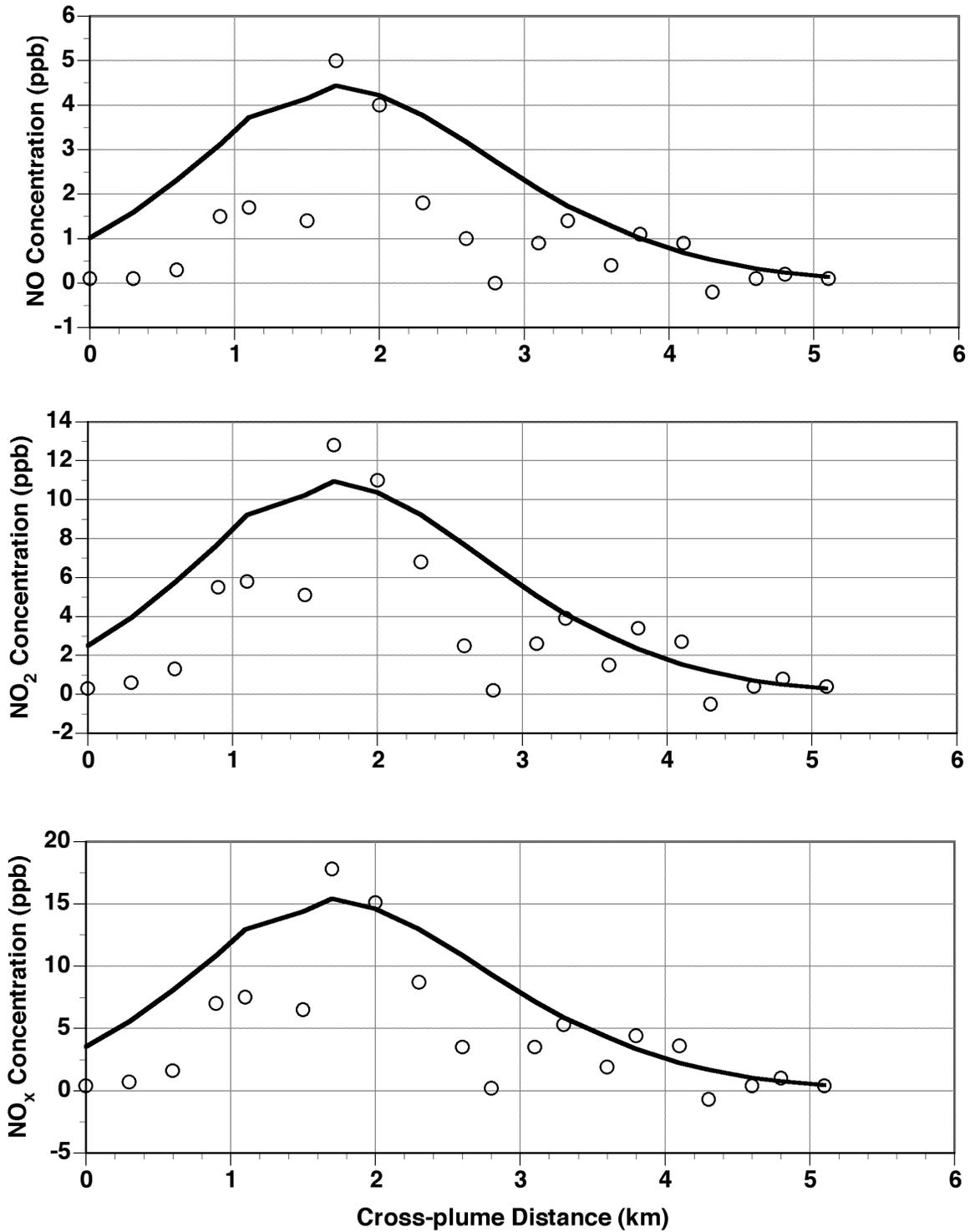
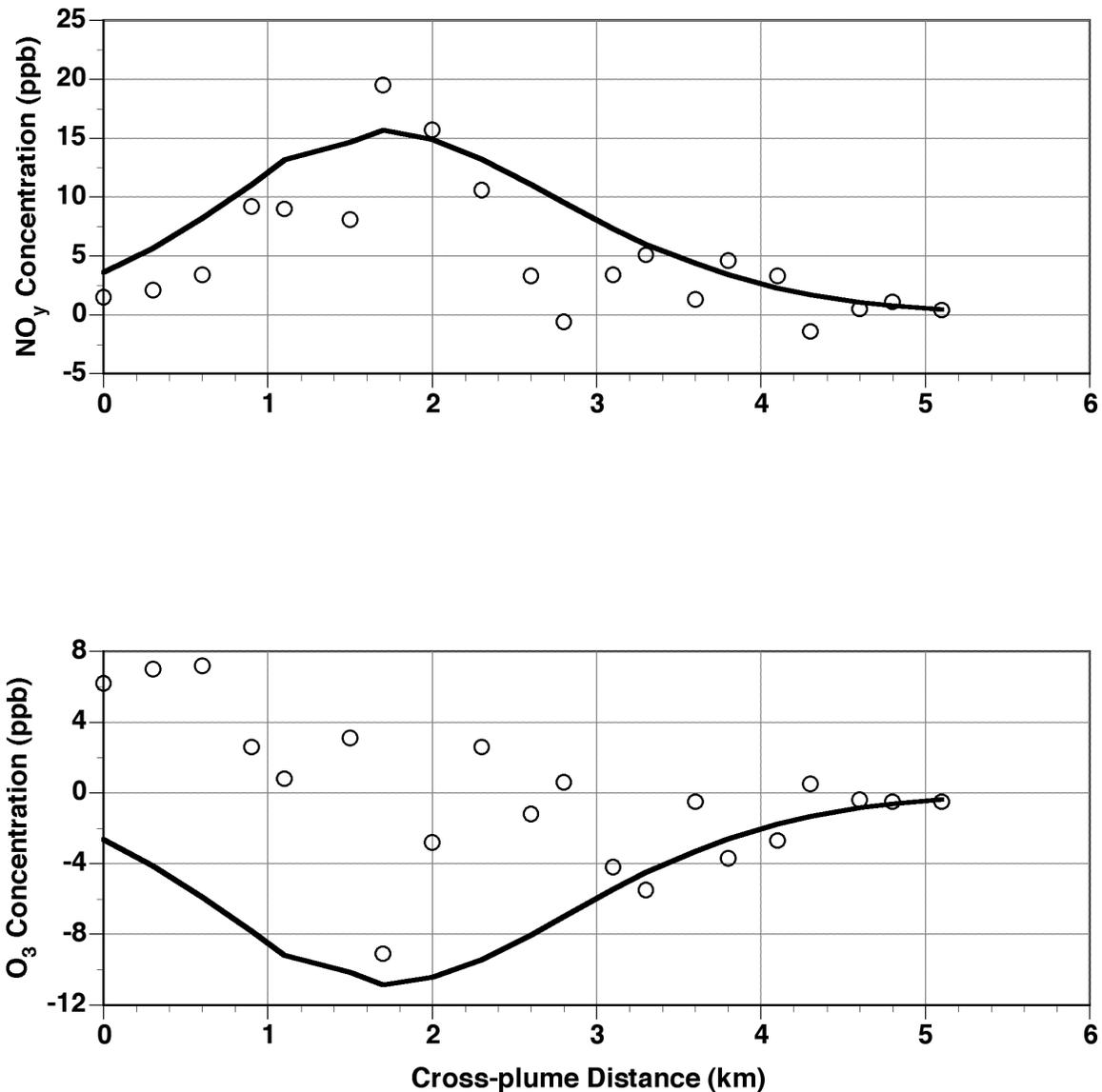


Figure 5-6  
 Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume  
 Concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> for Pittsburg Morning Traverse 213002  
 (7 km Downwind) on July 31, 2000



**Figure 5-7**  
**Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume**  
**Concentrations of NO<sub>y</sub> and O<sub>3</sub> for Pittsburgh Morning Traverse 213002**  
**(7 km Downwind) on July 31, 2000**

We do not show the cross-plume concentration profiles for the remaining Pittsburgh morning traverses since the measured and estimated peaks are in poor agreement for these traverses, as shown in Table 5-4 and Figure 5-3. For these traverses, at downwind distances larger than about 10 km, the modeled plume is well-mixed vertically, and the estimated plume excess NO<sub>y</sub> concentrations are 4 to 10 times lower than the measured values. These differences may be partly due to the errors in the model input fields. However, there may be other explanations for the poor performance at the larger downwind distances. For example, as mentioned previously, the measured peak concentrations do not appear to show a consistent variation with downwind distance, and the multiple peaks in the traverses at the larger downwind distances suggest that the aircraft may have encountered plumes from other sources for some of the traverses.

We next discuss results for the 6 afternoon Pittsburg traverses, conducted from about 4:00 p.m. PDT to about 5:06 p.m. PDT on July 31, 2000. For all the afternoon Pittsburg traverses, there is generally poor comparison between the modeled and measured plume variables, as shown in Tables 5-5 and 5-6. The modeled plume is well-mixed vertically and also shows significant horizontal spread with low peak  $\text{NO}_Y$  concentrations, while the observed plume shows large  $\text{NO}_Y$  peaks with smaller horizontal dispersion. Table 5-5 compares the general plume directions and widths for the observed and simulated plumes. While there is better agreement in the general flow directions as compared to the morning traverses, the plume widths are significantly different at downwind distances larger than 4 km. Furthermore, as in the case of the morning traverses, the simulated plume widths increase with downwind distance while the observed plume widths show less consistent behavior. Table 5-6 shows that, even at a downwind distance of only 4 km, the simulated peak excess  $\text{NO}_Y$  concentration is a factor of 5 lower than the measured peak, even though the measured and simulated plume widths are comparable at this downwind distance. For the 5<sup>th</sup> afternoon traverse, 213015, at a downwind distance of 28 km, the simulated and measured peak excess  $\text{NO}_Y$  concentrations are comparable, but Figure 5-8 shows that the cross-plume variability in the measured plume is not reproduced in the much wider simulated plume.

**Table 5-5  
Plume Directions and Widths for Pittsburg Afternoon Traverses, July 31, 2000**

Traverse ID	Downwind Distance (km)	Plume Direction*		Plume Width (km)	
		Observed	Simulated	Observed	Simulated
213011	4.4	ESE	SE	3.1	4.0
213012	9.7	ESE	SE	5.4	8.4
213013	13.6	ESE	SE	5.5	12.4
213014	19.1	ESE	SE	5.1	15.2
213015	28.1	ESE	SE	8.0	17.6
213016	37.7	ESE	SE	6.8	18.0

\* with respect to source

Following the approach used in Section 4 above, we calculated the rates of formation and removal of all of the simulated nitrogen oxide species ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_X$ ,  $\text{NO}_Z$  and  $\text{HNO}_3$ ) relative to the sum of all simulated nitrogen species ( $\text{NO}_Y$ ). The method consists of calculating the ratios of the average plume excess concentrations of various nitrogen oxide species to that of  $\text{NO}_Y$  at each traverse distance. The mean wind speeds are used to calculate a travel time since release. For our calculation, we used the same mean wind speeds used in Section 4. Then, a regression analysis is performed to describe the change in the concentration ratio as a function of travel time for each species. The slope of the best-fit line provides the rate of formation or removal of that species.

**Table 5-6**  
**Peak Plume Excess NO<sub>y</sub> Concentrations for Pittsburg Afternoon Traverses, July 31, 2000**

Traverse ID	Peak Excess NO <sub>y</sub> Concentration (ppb)		Number of Peaks in Traverse	
	Observed	Simulated	Observed	Simulated
213011	60.4	12.1*	Single	Single
213012	60.8	6.3*	Single	Single
213013	44.8	4.4*	Single	Single
213014	27.5	4.0*	Single	Single
213015	7.8	5.5*	Multiple	Single
213016	4.2	4.1*	Multiple	Single

\* maximum at all altitudes between surface and 1 km MSL

Table 5-7 compares the measured and simulated conversion rates for the Pittsburg plume on July 31, 2000 for the morning traverses. The NO loss rates in both the measured and simulated plumes are comparable. However, in the simulated plume, the ratio NO<sub>2</sub>/NO<sub>y</sub> initially increases as the plume NO is converted to NO<sub>2</sub>, followed by a gradual decrease as the NO<sub>2</sub> is converted to NO<sub>z</sub>. Thus, the slope of the best-fit NO<sub>2</sub>/NO<sub>y</sub> line is slightly positive for the simulations, but the measurements show a negative slope (i.e., loss rate). The overall simulated NO<sub>x</sub> loss rate for the morning traverses is about a factor of 4 smaller than the measured NO<sub>x</sub> loss rate. To complete the comparison, Table 5-7 also shows the formation rates of the NO<sub>x</sub> products, NO<sub>z</sub> and HNO<sub>3</sub>. Note that these numbers are not as meaningful as the calculated NO<sub>x</sub> loss rates, which can be construed as a true measure of the plume oxidation rates. The simulated NO<sub>z</sub> and HNO<sub>3</sub> formation rates are almost a factor of 3 larger the measured NO<sub>z</sub> and NIT formation rates. However, the simulated NO<sub>z</sub> and HNO<sub>3</sub> values are small so that even small increases in the NO<sub>z</sub>/NO<sub>y</sub> and HNO<sub>3</sub>/NO<sub>y</sub> concentration ratios due to NO<sub>x</sub> oxidation will result in large formation rates.

Table 5-8 compares the measured and simulated conversion rates for the afternoon Pittsburg traverses on July 31, 2000. As in the case of the morning traverses, the simulated and measured values of the NO loss rates are comparable. Furthermore, the afternoon NO loss rates are considerably higher as compared to the morning loss rates. We also see a significant increase in the simulated NO<sub>2</sub> loss rate in the afternoon, while the measured rate increases slightly. The simulated NO<sub>2</sub> loss rate is within a factor of 1.5 of the measured NO<sub>2</sub> loss rate. The overall NO<sub>x</sub> afternoon loss rates for both the simulated and measured plumes are also in good agreement.

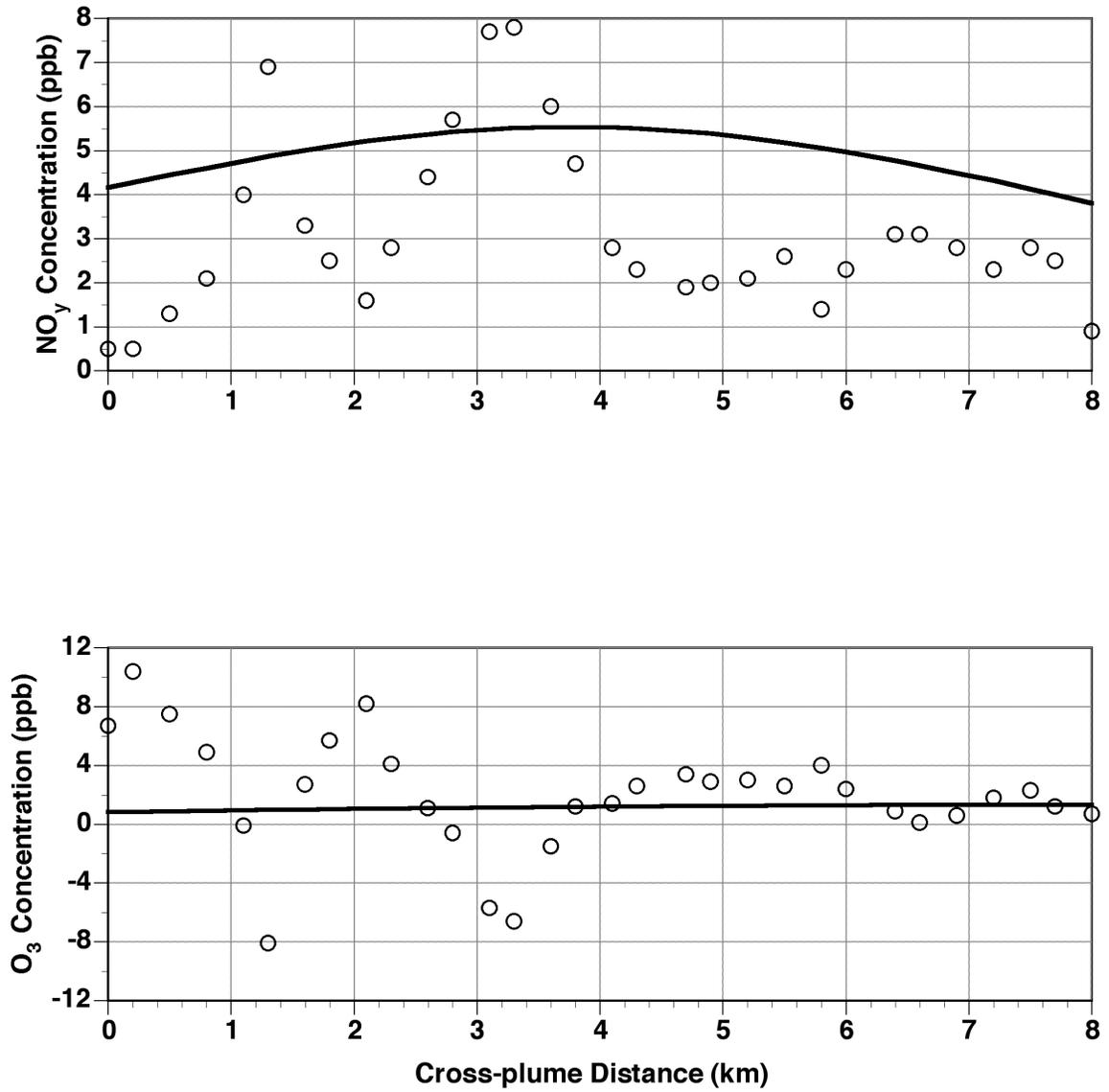


Figure 5-8  
Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume  
Concentrations of NO<sub>y</sub> and O<sub>3</sub> for Pittsburg Afternoon Traverse 213015  
(28 km Downwind) on July 31, 2000

**Table 5-7**  
**Plume Nitrogen Species Conversion Rate Summary<sup>a</sup> for Pittsburg Morning Traverses,**  
**July 31, 2000**

Species	Conversion Rate, h <sup>-1</sup> (r <sup>2</sup> )	
	Observed	Simulated
NO	-0.29 (0.67)	-0.29 (0.87)
NO <sub>2</sub>	-0.27 (0.60)	0.02 (0.08)
NO <sub>x</sub>	-0.27 (0.65)	-0.07 (0.94)
NO <sub>z</sub>	0.47 (0.55)	1.41 (0.98)
NIT <sup>b</sup>	0.49 (0.54)	1.44 (0.93)

<sup>a</sup> rates are first order rates (h<sup>-1</sup>) from log ratios vs. time regression analysis, with correlation information (r<sup>2</sup>) in parentheses

<sup>b</sup> measured NIT is compared to simulated HNO<sub>3</sub>

**Table 5-8**  
**Plume Nitrogen Species Conversion Rate Summary<sup>a</sup> for Pittsburg Afternoon Traverses,**  
**July 31, 2000**

Species	Conversion Rate, h <sup>-1</sup> (r <sup>2</sup> )	
	Observed	Simulated
NO	-1.00 (0.67)	-0.70 (0.92)
NO <sub>2</sub>	-0.32 (0.76)	-0.46 (0.95)
NO <sub>x</sub>	-0.48 (0.92)	-0.50 (0.95)
NO <sub>z</sub>	2.90 (0.60)	1.40 (0.75)
NIT <sup>b</sup>	2.00 (0.36)	1.37 (0.74)

<sup>a</sup> rates are first order rates (h<sup>-1</sup>) from log ratios vs. time regression analysis, with correlation information (r<sup>2</sup>) in parentheses

<sup>b</sup> measured NIT is compared to simulated HNO<sub>3</sub>

### 5.2.2 Moss Landing Plume Traverses

The six morning Moss Landing traverses (see Section 3) were conducted from about 9:55 a.m. PDT to 10:51 a.m. PDT on August 1, 2000. Table 5-9 shows the average distance from the source of each morning traverse as well as the measured and simulated widths of the plume and the general directions of the measured and simulated plumes with respect to the source.

**Table 5-9**  
**Plume Directions and Widths for Moss Landing Morning Traverses, August 1, 2000**

Traverse ID	Downwind Distance (km)	Plume Direction*		Plume Width (km)	
		Observed	Simulated	Observed	Simulated
214001	4.3	SSW	W	4.9	1.0
214002	7.8	S	W	12.5	2.0
214003	9.7	SSW	WSW	10.9	4.0
214004	15.1	S	WSW	12.7	10.0
214005	22.7	S	WSW	10.4	6.4
214006	31.9	SSW	W	4.7	12.8

\* with respect to source

As in the case of the Pittsburg traverses, the observed and simulated plumes travel in different directions, with the observed plume traveling to the south or south-southwest of the Moss Landing source, and the simulated plume traveling to the west or west-southwest of the source. The differences in observed and simulated plume widths are larger than the differences for the Pittsburg morning traverses, suggesting that additional local sources in the Monterey area may have been present in the Moss Landing plume.

Table 5-10 compares the observed and simulated peak excess  $\text{NO}_Y$  concentrations for the Moss Landing morning traverses. Table 5-10 also shows that multiple  $\text{NO}_Y$  peaks are observed across the plume for many of the traverses, while the model simulates only one peak at the plume centerline.

The results for the peak  $\text{NO}_Y$  excess concentrations for the Moss Landing morning traverses are qualitatively similar to those for the Pittsburg morning traverses. For the first morning traverse, 214001, at a downwind distance of 4 km, the maximum simulated peak excess  $\text{NO}_Y$  concentration (altitude not available in observation database) is about the same as the observed peak of 11 ppb at 227 m MSL. However, the actual maximum simulated peak for traverse 214001 is about 29 ppb at 400 m MSL, indicating that the aircraft may have missed the most concentrated part of the plume on this traverse. For all the other morning traverses, the maximum simulated peaks at all altitudes are lower than the observed peaks. These differences between the observed and simulated peaks increase with downwind distance from the source.

**Table 5-10**  
**Peak Plume Excess NO<sub>y</sub> Concentrations for Moss Landing Morning Traverses,**  
**August 1, 2000**

Traverse ID	Peak Excess NO <sub>y</sub> Concentration (ppb)		Number of Peaks in Traverse	
	Observed	Simulated	Observed	Simulated
214001	11.2	11.2 <sup>a</sup>	Single	Single
214002	48.9	17.2 <sup>b</sup>	Multiple	Single
214003	37.2	16.0 <sup>b</sup>	Multiple	Single
214004	31.4	11.4 <sup>b</sup>	Multiple	Single
214005	17.6	6.7 <sup>b</sup>	Multiple	Single
214006	10.8	7.8 <sup>b</sup>	Multiple	Single

<sup>a</sup> at 227 m MSL; altitude of observed peak missing; maximum simulated peak = 29 ppb at 400 m MSL

<sup>b</sup> maximum at all altitudes between surface and 1 km MSL

Figure 5-9 shows the observed and simulated cross-plume excess concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub> for the first Moss Landing morning traverse, 214001, at about 4 km downwind of Moss Landing. Figure 5-10 shows the corresponding plume excess concentrations for NO<sub>y</sub> and O<sub>3</sub>. As in the case of the Pittsburg traverses, we have aligned the simulated plume centerline with the observed plume centerline even though they do not occur at the same location. Also, the altitude of the observed cross-plume profiles for this traverse is not available. For the simulated cross-plume profiles in Figures 5-9 and 5-10, we selected an altitude at which the simulated peak excess NO<sub>y</sub> plume concentration was comparable to the observed peak. As shown in Figures 5-9 and 5-10, the observed cross-plume variabilities in the concentrations of the various species are in good agreement with simulated values. However, while the simulated NO<sub>y</sub> and NO<sub>x</sub> peaks match the observed values (because of our selection of the altitude for the simulated values), the simulated peak NO and NO<sub>2</sub> concentrations and the plume centerline O<sub>3</sub> deficits are different from those measured. The simulated plume appears to be more reactive than the measured plume during the early plume stages.

As is clear from Table 5-10, the measured peak excess NO<sub>y</sub> concentrations in the plume are significantly higher than the simulated values for most of the remaining morning traverses. Like the case of the Pittsburg morning traverses, the modeled plume is well-mixed vertically at downwind distances larger than about 10 km. For the last morning traverse, 214006, the measured and simulated peak excess NO<sub>y</sub> values are comparable, but the simulated plume is more than a factor of two wider than the observed plume, and the O<sub>3</sub> deficit at the plume centerline is less than 2 ppb in the simulations and almost 20 ppb in the observations.

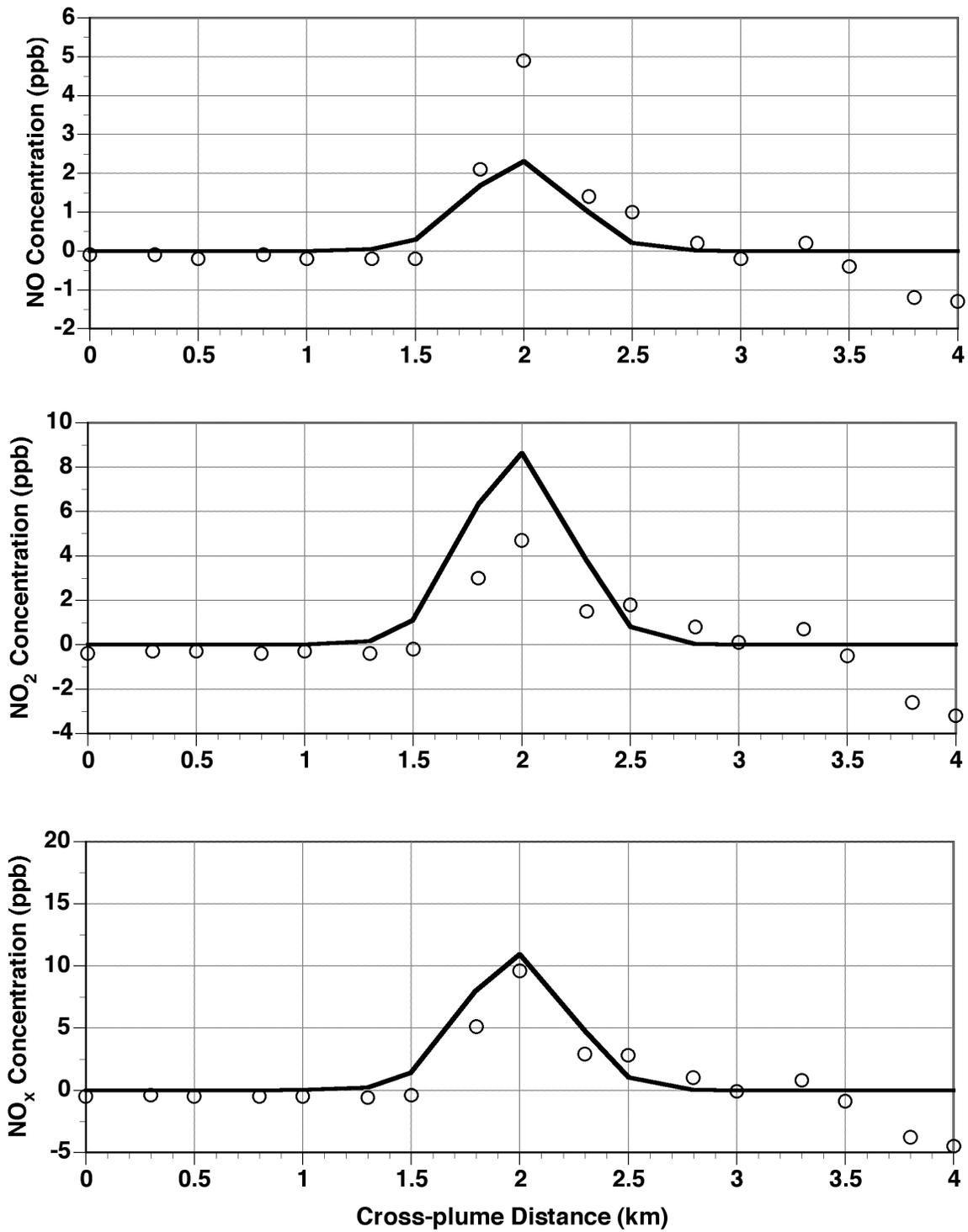
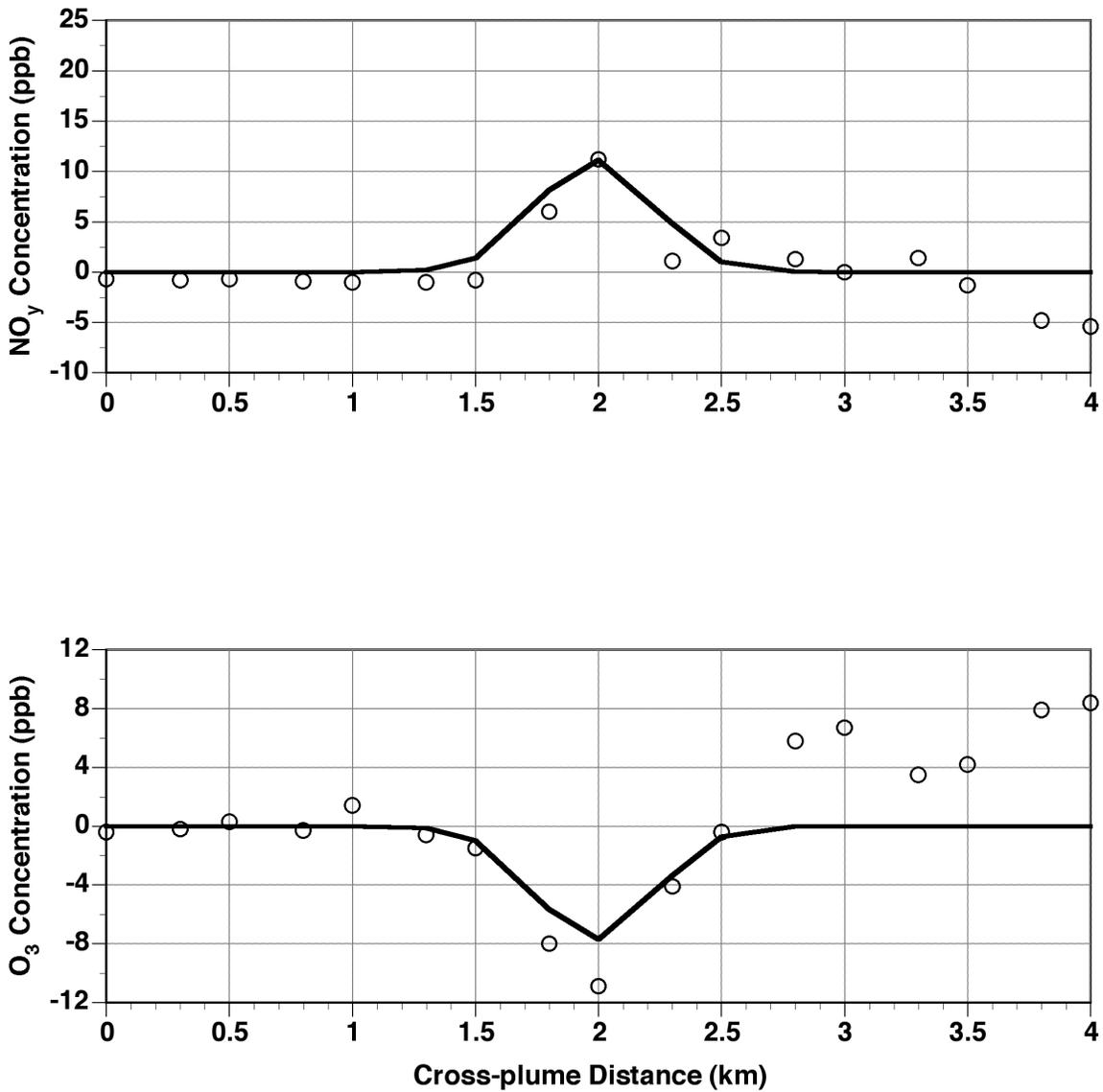


Figure 5-9  
 Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume  
 Concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> for Moss Landing Morning Traverse 214001  
 (4 km Downwind) on August 1, 2000



**Figure 5-10**  
**Comparison of SCICHEM (Solid Line) with Measured (Circles) Cross-Plume**  
**Concentrations of NO<sub>y</sub> and O<sub>3</sub> for Moss Landing Morning Traverse 214001**  
**(4 km Downwind) on August 1, 2000**

The 14 Moss Landing afternoon traverses commenced at about 2:57 p.m. PDT, with the last traverse starting at 4:42 p.m. PDT. Two of the traverses, 214109 and 214110, were made at about the same downwind distances as traverses 214009 and 214010, respectively.

For all the afternoon Moss Landing traverses, there is generally poor agreement between modeled and measured plume variables, as shown in Tables 5-11 and 5-12.

**Table 5-11**  
**Plume Directions and Widths for Moss Landing Afternoon Traverses, August 1, 2000**

Traverse ID	Downwind Distance (km)	Plume Direction*		Plume Width (km)	
		Observed	Simulated	Observed	Simulated
214007	4.2	SSE	ENE	4.3	4.8
214008	8.0	SSE	ENE	6.3	12.8
214009	13.5	S	E	3.3	16.0
214109	13.6	SSE	E	2.4	16.0
214010	17.7	SE	E	1.3	14.8
214110	19.1	SE	E	13.2	14.8
214011	24.5	SE	E	7.2	16.0
214012	30.0	SE	E	8.1	17.2
214013	36.0	SE	E	7.3	17.2
214014	43.1	SE	E	10.9	18.4
214015	50.6	SE	ESE	8.4	18.8
214016	58.0	SE	ESE	8.6	18.8
214017	67.6	SE	ESE	4.0	18.0
214018	74.6	SE	ESE	5.5	18.0

\* with respect to source

These results are similar in nature to the results for the Pittsburg afternoon traverses: the modeled plume is well-mixed vertically within a few km of the source, and also shows significant horizontal spread with low peak  $\text{NO}_Y$  concentrations. In contrast, the observed plume is quite narrow for most of the afternoon traverses with very large peak  $\text{NO}_Y$  concentrations. However, both the measured peak  $\text{NO}_Y$  concentrations and the measured plume width vary inconsistently with downwind distance. In particular, the peak measured  $\text{NO}_Y$  concentrations in traverses 214009 and 214109, at a downwind distance of about 13.5 km, are more than a factor of 20 higher than the simulated peaks, and more than a factor of 2 larger than the measured peak  $\text{NO}_Y$  concentration in traverse 214008, at a downwind distance of 8 km. Furthermore, for traverses 214010 and 214110, which were made at approximately the same downwind distances (17.7 km and 19.1 km, respectively), the measured plume widths are different by a factor of 10, while the simulated plume widths are identical.

**Table 5-12**  
**Peak Plume Excess NO<sub>y</sub> Concentrations for Moss Landing Afternoon Traverses,**  
**August 1, 2000**

Traverse ID	Peak Excess NO <sub>y</sub> Concentration (ppb)		Number of Peaks in Traverse	
	Observed	Simulated*	Observed	Simulated
214007	174.8	60.0	Single	Single
214008	72.2	11.1	Single	Single
214009	175.6	7.0	Single	Single
214109	173.8	6.9	Single	Single
214010	21.4	5.8	Multiple	Single
214110	36.8	5.8	Multiple	Single
214011	46.7	4.4	Multiple	Single
214012	6.5	2.7	Multiple	Single
214013	44.2	1.8	Multiple	Single
214014	53.6	1.1	Multiple	Single
214015	44.6	0.6	Multiple	Single
214016	19.2	0.3	Multiple	Single
214017	8.0	0.2	Multiple	Single
214018	9.9	0.1	Multiple	Single

\* maximum at all altitudes between surface and 1 km MSL

As discussed in Section 4.1, the measurements from several of the afternoon traverses are likely not suitable for plume model evaluation. For most of traverses, the Moss Landing plume seems to be impacted from local sources, making it impossible to distinguish between the contributions of the Moss Landing emissions and the fresh local emissions. Therefore, it is difficult to draw any conclusions from comparison between the measured and simulated plume concentrations for this application.

Table 5-13 compares the conversion rates, calculated from the measured and simulated average plume excess concentrations of nitrogen species, for the Moss Landing morning traverses on August 1, 2000. The NO, NO<sub>2</sub> and NO<sub>x</sub> loss rates in both the measured and simulated plumes are comparable. In contrast, Table 5-14 shows that, for the Moss Landing afternoon traverses, the simulated NO loss rate is comparable to the measured rate, but both the simulated NO<sub>2</sub> and NO<sub>x</sub> loss rates are higher than those calculated from the measured plume variables, suggesting that the plume NO<sub>x</sub> is being converted to NO<sub>z</sub> at a higher rate in the simulated plume than in the measurements. These differences may be related to the issues with some of the Moss Landing afternoon traverses noted earlier.

**Table 5-13**  
**Plume Nitrogen Species Conversion Rate Summary<sup>a</sup> for Moss Landing Morning Traverses, August 1, 2000**

Species	Conversion Rate, h <sup>-1</sup> (r <sup>2</sup> )	
	Observed	Simulated
NO	-0.17 (0.72)	-0.12 (0.96)
NO <sub>2</sub>	-0.06 (0.66)	-0.07 (0.72)
NO <sub>x</sub>	-0.10 (0.70)	-0.08 (0.87)
NO <sub>z</sub>	0.19 (0.63)	0.83 (0.96)
NIT <sup>c</sup>	0.16 (0.72)	0.75 (0.94)

<sup>a</sup> rates are first order rates (h<sup>-1</sup>) from log ratios vs. time regression analysis, with correlation information (r<sup>2</sup>) in parentheses

<sup>b</sup> measured NIT is compared to simulated HNO<sub>3</sub>

**Table 5-14**  
**Plume Nitrogen Species Conversion Rate Summary<sup>a</sup> for Moss Landing Afternoon Traverses, August 1, 2000**

Species	Conversion Rate, h <sup>-1</sup> (r <sup>2</sup> )	
	Observed	Simulated
NO	-0.70 (0.68)	-0.77 (0.84)
NO <sub>2</sub>	-0.06 (0.05)	-0.56 (0.96)
NO <sub>x</sub>	-0.36 (0.53)	-0.59 (0.96)
NO <sub>z</sub>	0.77 (0.57)	1.12 (0.59)
NIT <sup>c</sup>	0.56 (0.53)	1.08 (0.51)

<sup>a</sup> rates are first order rates (h<sup>-1</sup>) from log ratios vs. time regression analysis, with correlation information (r<sup>2</sup>) in parentheses

<sup>b</sup> measured NIT is compared to simulated HNO<sub>3</sub>

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## SUMMARY AND CONCLUSIONS

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The results of the Pittsburg and Moss Landing plume aircraft measurements study were significantly different than what the TVA investigators have found in studies in the mid-south region of the USA. Specifically, the power plants at Moss Landing and Pittsburg produced no detectable excess ozone during most flights during downwind transport up to the point at which the plume could no longer be distinguished from the background. The  $\text{NO}_x$  emission rates for these plants are several times smaller than for the large coal-fired plants which were sampled in the mid-south, but even so, the ozone production efficiencies were greater than zero for the afternoon portions of only two flights, one each at Moss Landing and Pittsburg. Even for those two flights (Flights 3 and 4 on 31 July and 1 August, 2000, respectively), the ozone production was miniscule compared to that observed in the greater Bay Area urban plume on one of the flight days. The operating hypothesis, supported by the VOC data (but not fully by the carbonyl data) remains that the VOC reactivity in the marine layer diluting the plume was relatively low and resulted primarily in termination reactions leading to  $\text{NO}_z$  (nitric acid and organic and inorganic nitrates) formation but not leading to any net ozone production in most cases.

The results from the evaluation of SCICHEM with CCOS 2000 aircraft plume measurements show that, with the provided inputs, the model does not explain the observed plume data at downwind distances larger than about 10 km. The model performance is better for the morning plume traverses than for the afternoon traverses. The SCICHEM plume is more widely dispersed, and hence more dilute, than the measured plume. In addition, the model results show that, at the larger downwind distances, the modeled plume is vertically well-mixed to 1 km and above, particularly for the afternoon traverses. While there are insufficient data to determine the vertical distributions for the observed plume, some of the discrepancies between model estimates and measurements may also be associated with errors in the boundary layer and vertical diffusion inputs to SCICHEM.

There are many possible explanations for the poor performance for the model. Some of the errors could be explained to model limitations. However, the previous performance evaluation of SCICHEM with the TVA helicopter measurements of the Cumberland plume (Karamchandani et al., 2000) showed a significantly better performance than that obtained here. As mentioned above, the Pittsburg and Moss Landing power plants have significantly lower  $\text{NO}_x$  emissions than Cumberland and part of the poor comparison of model estimates with plume measurements in the current study can be attributed to the difficulties in measuring relatively modest point source plumes in the presence of a relatively large and variable background.

In their recent detailed evaluation of the stand-alone and Plume-in-Grid versions of SCICHEM, Mathur et al. (2002) noted enhanced plume dispersion in SCICHEM at large downwind distances. However, their simulations used the large-scale variability (LSV) option, which is

intended to account for mesoscale or synoptic scale variability in the wind field (meandering). This option is recommended for downwind distances larger than 50 to 100 km. In the simulations performed here for the Pittsburg and Moss Landing plumes, we did not use the LSV option, so the enhanced plume dispersion (as compared to the measurements) noted here cannot be explained to the choice of this option.

Thus, it is more likely that a large part of the discrepancies that were found in this study between the SCICHEM results and the plume measurements can be attributed to errors in the model inputs, as well as to errors in the plume measurements themselves due to incorporation of emissions from other sources into the plumes during their transport. The meteorology and emission inputs used in our calculations are preliminary and are believed to have large uncertainties and errors (S. Tanrikulu, ARB, private communication, 2002). For most of the traverses simulated, the modeled plume was traveling in a different direction from the observed plume, showing that there are errors in the input wind fields. In addition, the plume measurements are not always consistent. Both the observed plume widths and plume centerline concentrations of the conserved species  $\text{NO}_Y$  (neglecting the effect of dry deposition) do not show a consistent variation with downwind distance. For many of the traverses, multiple peaks of  $\text{NO}_Y$  and  $\text{NO}_X$  are measured, suggesting that multiple plumes were sampled. As discussed in the data analysis section of this document (Section 4), the measurements indicate some interference with urban plumes and mobile source  $\text{NO}_X$  emissions during the afternoon traverses for both the Pittsburg and Moss Landing plumes.

We expect some improvement in model performance when more accurate meteorological and emissions inputs are available later from the modeling component of the CCOS program. However, we still expect some discrepancies between the model and the plume measurements because of the issues with the plume measurements noted previously. Nevertheless, it would be useful to repeat the model simulations with the more accurate meteorological and emissions inputs, and to confine the comparison of model predictions with observations to the Moss Landing and Pittsburg plume traverses that are not affected by interference from other plumes. This will provide a better understanding of the performance of SCICHEM and possible improvements that could be made to the model.

# 7

## REFERENCES

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1. Gillani, N.V., M. Luria, J.F. Meagher, R.J. Valente, R.E. Imhoff, and R.L. Tanner (1998a). Relative production of ozone and nitrates in urban and rural power plant plumes, *J. Geophys. Res.* **103**, 22,593-22,615.
2. Gillani, N.V., M. Luria, R.J. Valente, R.L. Tanner, R.E. Imhoff, and J.F. Meagher (1998b). Loss rate of  $\text{NO}_Y$  from a power plant plume based on aircraft measurements, *J. Geophys. Res.* **103**, 22,585-22,592.
3. Gillani, N.V., Y. Wu, and R.E. Imhoff (2002). Relative production of ozone and nitrates in urban and rural power plant plumes: II. Detailed case study of ozone production efficiency and  $\text{NO}_Y$  loss rate in a rural plume based on aircraft data analysis and reactive plume modeling, *J. Geophys. Res.*, submitted.
4. Gupta, M., N. Kumar, P. Karamchandani and S.-Y. Wu, 2001. Intercomparison of SCICHEM and CALPUF models using Cumberland plume data, *Guideline on Air Quality Models: A New Beginning*, Air and Waste Management Association International Symposium, April 4-6, Newport, RI.
5. Imhoff, R.E., M. Luria, R.J. Valente, and R.L. Tanner (2001).  $\text{NO}_Y$  removal from the Cumberland power plant plume, *Atmos. Environ.* **35**, 179-183.
6. Karamchandani, P., A. Koo and C. Seigneur, 1998. A reduced gas-phase kinetic mechanism for atmospheric plume chemistry, *Environ. Sci. Technol.*, **32**, 1709-1720.
7. Karamchandani, P. and C. Seigneur, 1999. Simulation of sulfate and nitrate chemistry in power plant plumes, *J. Air Waste Manage. Assoc.*, **49**, 175-181.
8. Karamchandani, P., L. Santos, I. Sykes, Y. Zhang, C. Tonne and C. Seigneur, 2000. Development and evaluation of a state-of-the-science reactive plume model, *Environ. Sci. Technol.*, **34**, 870-880.
9. Karamchandani, P. and K. Vijayaraghavan, 2001. *Planning Studies for Power Plant Plume Measurements During CCOS 2000*, AER Report CP073-01-1, prepared for San Joaquin Valleywide Air Pollution Study Agency, Sacramento, CA, February.
10. Karamchandani, P., C. Seigneur, K. Vijayaraghavan and S.-Y. Wu, 2002. Development and application of a state-of-the-science plume-in-grid model, *J. Geophys. Res.*, in press.

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References

11. Mathur, R., S. Arunachalam, Z. Adelman, K. Alapaty, A. Hanna, G. Yarwood, C. Emery, S. Lau and G. Wilson, 2002. *Review, Testing and Evaluation of SCICHEM and CMAQ-APT*. Draft Technical Report prepared for EPRI, Palo Alto, CA, November.
12. Meng, Z., J.H. Seinfeld, P. Saxena and Y.P. Kim, 1995. Atmospheric gas-aerosol equilibrium, IV: Thermodynamics of carbonates, *Aerosol Sci. Technol.*, **23**, 131-154.
13. Santos, L., R.I. Sykes, P. Karamchandani, C. Seigneur, F. Lurmann and R. Arndt, 1999. *Second-order Closure Puff Model with Aqueous-Phase Chemistry and Aerosols*, Report for EPRI, Palo Alto, CA.
14. Santos, L., R.I. Sykes, P. Karamchandani, C. Seigneur, F. Lurmann, R. Arndt and N. Kumar, 2000. Second-order Closure Integrated Puff (SCIPUFF) model with gas and aqueous phase chemistry and aerosols. In: *Preprints of the 11<sup>th</sup> Joint Conference on the Applications of Air Pollution Meteorology with the A&WMA*, pp. 138-143.
15. Schulman, L.L., D.G. Strimaitis and J.S. Scire, 2000. Development and evaluation of the PRIME plume rise and building downwash model, *J. Air Waste Manage. Assoc.*, **50**, 378-390.
16. Strader, R., C. Gurciullo, S. Pandis, N. Kumar and F.W. Lurmann, 1998. *Development of Gas-phase Chemistry, Secondary Organic Aerosol, and Aqueous-phase Chemistry Modules for PM Modeling*. Report prepared for Coordinating Research Council, Atlanta, GA., by Carnegie Mellon University, Pittsburgh, PA and Sonoma Technology, Inc., Petaluma, CA, STI-997510-1822-FR, October.
17. Sykes, R.I., W.S. Lewellen, S.F. Parker and D.S. Henn, 1988. *A Hierarchy of Dynamic Plume Models Incorporating Uncertainty, Volume 4: Second-order Closure Integrated Puff*, EPRI EA-6095 Volume 4, Project 1616-28, EPRI, Palo Alto, CA.
18. Sykes, R.I., L.P. Santos, C. Seigneur and P. Karamchandani, 1997. A New Model for Simulating Stack Plume Dispersion and Chemistry, *90<sup>th</sup> Air and Waste Management Association Annual Meeting*, June 8-13, 1997, Toronto, Ontario, Canada.