

**Plume Study to Characterize Fine Particulate
Emissions and Secondary Particle Formation
at a Large Coal-Fired Power Plant
(Cumberland Visible Emissions Study Phase II)**

**Final Report
Prepared for EPRI and DOE's Federal Energy Technology Center**

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I. INTRODUCTION

The fate of emissions of SO₂ and NO_x from point sources such as power plants has long been of concern because of the role these emissions play in the production of fine particulate sulfate and nitrate, and because NO_x emissions may control the production of secondary, tropospheric ozone in most non-urban areas of North America. Significant SO₂ emissions reductions, mandated by CAAA legislation, have taken place over the last decade from power plants, including those in the Southeastern U.S. These reductions have been attained principally through the use of stack gas scrubbers or switching to fuel supplies with lower sulfur content. The extent of sulfate aerosol formation in these scrubbed power plant plumes, for example, in TVA's Cumberland fossil plant (CUF) in north-central Tennessee, has been reduced to the point at which primary sulfate emissions may now be comparable in mass and volume to secondary sulfate aerosol formation within the identifiable plume (Imhoff et al., 2000). Secondary nitrate particles formed in scrubbed plumes with comparatively high NO_x emissions could now become more important contributors to fine particulate mass.

In this project, referred to herein as the Cumberland Visible Emissions Study, the plume of the CUF plant was sampled during the summers of 1998 and 1999, and the data collected were used to evaluate formation rates of ozone and the total mass, size distributions, and chemical composition of fine particles in-plume. The determination of plume particle formation and growth rates from the particulate measurements was an opportunistic objective designed to evaluate whether the installation of FGD scrubbers at CUF in late 1994 to remove SO₂ resulted in a proportional reduction in secondary sulfate production in the CUF plume. In other words, has the secondary sulfate formation rate in the plume remained unchanged with a 95% reduction in the SO₂ emission rate? The data are also being used to evaluate recently developed EPRI and EPA plume particle models.

Data were also acquired on concentrations of gaseous species in the CUF plume. These data are refining our knowledge of what factors most influence the fate of plume NO_x and determine the efficiency of ozone formation in the plumes of large stationary sources. Advantage was taken of planned installation of NO_x control technology in one unit of the CUF plant in late 1998 to help elucidate how ozone production efficiencies might change with NO_x emissions changes. This study also identified the potential for changes in primary and secondary PM_{2.5} nitrate and nitric acid formation in-plume as a result of these NO_x emissions reductions.

In summary, this study has examined the emissions from, and in-plume processes of, a coal-fired unit (CUF) before and after the installation of low-NO_x burners on one of the two CUF units, to determine the extent to which this modification (and the previous addition of FGD scrubbers in 1994) have significantly affected the nature of primary emissions and the extent of secondary gaseous and particle formation processes.

II. OBJECTIVES

◆ *To understand plume visibility and [plume] contributions to particle formation relevant to regional haze by characterizing the particle formation and optics in a plume as a function of distance.*

◆ *To quantify the reliability of a plume model for simulating particle formation and optics.*

Five major hypotheses were advanced and addressed based on these objectives and through analysis of data from this project:

◇ the proportion of the NO_x emitted that is converted to $\text{PM}_{2.5}$ nitrate particles is low (compared to nitric acid and organic nitrates) during the peak ozone season;

◇ primary emissions of fine particles from units equipped with high-efficiency SO_2 scrubbers make only minor contributions to ambient $\text{PM}_{2.5}$ levels;

◇ secondary sulfate formation in-plume under cloud-free, summertime conditions should decrease proportionately to SO_2 emissions reductions in the absence of changes in NO_x emissions;

◇ reductions in NO_x emissions may change (and possibly increase) SO_2 oxidation rates; and

◇ large sources with high NO_x concentrations generate ozone less efficiently than smaller NO_x emitters because of enhanced nitric acid and/or nitrate formation; reducing NO_x could increase the average in-plume ozone production efficiency in some cases.

III. EXPERIMENTAL PROGRAM

Measurement Methods. The plume from the TVA Cumberland Power Plant, located in north-central Tennessee, was sampled by the Atmospheric Sciences (now the Air, Land, and Water Sciences) Department (AL&WS) of the Tennessee Valley Authority (TVA) during the summers of 1998 and 1999, using an instrumentation package operated aboard a Bell 205 helicopter. Table 1 describes the components of that package. The gas analyzers included a Thermo Environmental Instruments Inc. (TEII, Franklin, MA) Model 43S SO_2 analyzer, several other TEII Model 42 and 42S TEII analyzers that were modified to measure NO , NO_2 , NO_y , and NO_y^* (NO_y with an inlet nylon filter to remove nitric acid and particulate nitrate), and also ozone. Other species' concentrations were derived by summing or differencing nitrogen oxide instrumental signals: $\text{NO}_x = \text{NO} + \text{NO}_2$, nitrate = $\text{NO}_y - \text{NO}_y^*$, $\text{NO}_z = \text{NO}_y - \text{NO}_x$.

The Model 43S SO_2 pulsed fluorescence analyzer used in this project proved to be significantly more sensitive than the previous used Model 43A, and it was a critical factor in more accurately measuring the rates of particle formation in, and NO_z loss from the CUF plume, as described below. Also critical to the success of the project was the use of a fast, continuous particle-measuring system, the PMS Model PCASP-100X particle-counting active scattering probe (a laser-based, particle size spectrometer), and an on-board nephelometer used to continuously measure particle light scattering. The PCASP-100X proved to be capable of measuring particle number density in the range of 0.1 and 3

Table 1

MANUFACTURER AND MODEL	PARAMETER	RANGE
Particle Measuring Systems model PCASP particle size instrument	number of particles per optical particle size bin*	0.09 - 3.0 microns
3-wavelength Nephelometer, TSI Model 3550	light scattering of blue, green and red λ	0.1 - 100 $\times 10^{-4} \text{ m}^{-1}$
Filter Sampler*	Sulfate, nitrate, H^+ and ammonium in particles	1 - 200 nmole/m ³
Thermo Electron Model 42C Nitrogen Oxides Analyzer	NO_y ($\text{NO} + \text{NO}_2 +$ other odd nitrogen species) gas concentration	Two ranges: 0.5 - 10 ppm (near-plume) & 0-0.5 ppm (far plume & bkgd.)
Thermo Electron Model 42C Nitrogen Oxides Analyzer	NO_y^* [$\text{NO}_y - (\text{HNO}_3 +$ particulate nitrate)] gas concentration	Two ranges: 0.5 - 10 ppm (near-plume) & 0-0.5 ppm (far plume & bkgd.)
Thermo Electron Model 42S Nitrogen Oxides Analyzer with upstream photolytic cell	NO_2 gas concentration	0 - 200 ppbv
Thermo Electron Model 42S Nitrogen Oxides Analyzer.	NO gas concentration	0 - 200 ppbv
Thermo Electron Model 42S Analyzer modified for fast response O_3 measurement	O_3 gas concentration	0 - 200 ppbv
Thermo Electron Model 43C Sulfur Dioxide Analyzer.	SO_2 gas concentration	0 - 1000 ppbv
Licor Model X	CO_2 gas concentration	0-500 ppm
Apollo Loran-C and GPS systems	Position (latitude and longitude) of helicopter	+/- 100 meters
	Temperature and Relative Humidity	0-50 °C and 0-100 % RH, respectively
Thermo Environmental Instruments, Inc. Multi-gas Calibration System, Model 146.	calibration gases for O_3 , NO_2 , and NO .	<u>GAS</u> <u>SPAN</u> <u>CONC</u> O_3 120 ppbv NO_2 120 ppbv NO 7.3 ppmv
Canister sampler for VOCs	C_1 - C_{10} VOCs	

*Integrative sampler with no recordable electronic outputs.

microns in 15 size bins at a scan rate of 1 Hz. Other continuous instruments measured location, pressure (altitude), temperature and humidity. Further details regarding the

airborne instruments and their performance are given in publications based on the Nashville 1995 field study (Valente et al., 1998; Tanner et al., 1998).

HiVol sampling on quartz filters and (in 1999 only) cascade impactor sampling on greased foil plates were also conducted from the helicopter platform. Sampling was conducted using gently curved, externally mounted 1.9 cm OD (1.6 cm ID) copper inlets. Sampling was conducted using two HiVol samplers, one for background air and one for plume air. Separate, composite samples were collected by integrating over all traverses at each plume distance on that sampling day. An automated solenoid was used to alternate between samplers, used pre-programmed NO_y concentration thresholds to indicate when the aircraft was in the plume, and to trigger the solenoid switches.

For the flights in 1999, a Y-tube was added to the HiVol inlet to allow for simultaneous sampling by a seven-stage cascade impactor operating at ~60 Lpm as well as the HiVol sampler with quartz filters. HiVol filter samples collected for 30 min from background air (≥ about 12 m³ in volume), and for 10 min from plume air (≥ about 4 m³) were sufficient to give quantifiable amounts of extractable soluble ions (SO₄²⁻, NO₃⁻, and NH₄⁺) for analysis by ion chromatography or automated colorimetry, as appropriate. In general, the amounts of soluble ions collected with the cascade impactor were not sufficient for quantitation.

Sampling Methods. A total of 8 sampling flights were conducted during August, 1998; during the latter four flights the CUF plume was successfully sampled, and these missions are summarized in Table 2. Due to instrumentation difficulties and the fact that meteorological conditions were generally not conducive to sampling an isolated CUF plume, analysis of 1998 plume data has focused on flight 8, conducted August 25, 1998.

Table 2 CUF 98 Flights (last four)

Flight No.	Date	HiVol Sample No.	Sample Type/ Downwind Location
6	08-23-98	Q98235-BK	In-flight bkgd.
		Q98235-P1	19 km
		Q98235-P2	54 km
7	08-24-98	Q98236-BK	In-flight bkgd.
		Q98236-P1	39 km
		Q98236-P2	102 km
8	08-25-98	Q98237-BK	In-flight bkgd.
		Q98237-P1	19 km
		Q98237-P2	56 km
		Q98237-P3	111 km
9	08-26-98	Q98238-BK	In-flight bkgd.
		Q98238-P1	28 km
		Q98238-P2	74 km

A total of 9 flights were conducted in 1999 (see Table 3), 7 flights in the CUF plume and two missions in the urban Nashville area. Of the seven CUF flights, three flights were selected for detailed analysis: flight 6 on 6 July, flight 8 on 08 July, and flight 10 on 13

Table 3 SOS Nashville 99 CUF Flights (last 3 plume flights)

Flight No.	Date	HiVol Sample No.	Sample Type/ Downwind Location
6	07-06-99	HV0706-BK1	In-flight bkgd.
	“	HV0706-P1	10 km
	“	HV0706-P2	27 km
	“	HV0706-P3	56 km
	“	No HiVol sample	80 km
8	07-13-99	HV0713-BK1	In-flight bkgd.
	“	HV0713-P1	14 km
	“	HV0713-P2	35 km
	“	HV0713-P3	63 km
10	07-15-99	HV0715-BK1	In-flight bkgd.
	“	HV0715-P1	14.5 km
	“	HV0715-P2	55 km
	“	HV0715-P3	95 km

July, 1999. All of the flights analyzed were conducted with the normal range of NO_x emission rates (about 12 tons/hr NO_x in 1998 and 9-12 tons/hr in 1999), with the exception of flight 6, during which NO_x emissions were about ½ the 1998 rate due to an unscheduled outage in CUF Unit 2. (Unit 2 had NO_x-reduction controls installed prior to the 1999 field study, Unit 1 did not, and was operating normally during the 6 July 1999 plume flight.)

A radar profiler was set up on the grounds of the CUF plant by University of Alabama at Huntsville personnel during both the 1998 and 1999 study periods. The profiler had remote downloading capability, hence data taken at the site were available in near real-time (within about 2 h), remotely. Profiler data were used, among other purposes, to make decisions concerning whether the winds were in an acceptable range of direction and velocity to accomplish the mission. The data were then archived for use in data analyses, specifically for determining in-plume travel times.

Transition was made during the course of the 1998-99 flights from a protocol incorporating linear traverses of plumes along a given direction vector normal to the wind direction to an approach in which, through the use of a GPS, a constant distance from the plume release point was maintained during individual traverses. The latter approach is preferred because the sampled plume air has then experienced a uniform travel time in all parts of the plume.

On flight days, the instrument package went through a series of calibrations and other tests in the early AM using a standard checklist, and any problems which would interfere with the acquisition of a full, validatable data set were identified and repaired if possible. In-flight zeros were taken during all flights.

Data Acquisition Procedures. Final data for four plume chemistry flights in 1998 and 5 flights (plume and urban flights) in 1999 are available in Access data files. During the course of the CUF studies, several advances were made in acquisition, processing, and rapid reduction of the data from the airborne instrument package. We describe and justify in detail the process by which a time-delay and smoothing procedure was applied to the data so that direct comparison of gaseous species concentrations with 5-s time resolution could be achieved.

The convolution process. One of the major problems in airborne sampling of power plant plumes is the relatively slow time constant of the measuring instruments. Most of the gas analyzers that are currently used for sampling from aircraft were originally designed to be operated at a surface site using an average measuring cycle of several minutes. When sampling a power plant plume from an even slow aircraft, such as the TVA Bell 205, the desired response time of the instruments is of the order of a few seconds, which is easy to attain for some instruments and difficult for others. The result of these limitations is that the recorded trace of any given parameter is somewhat delayed and deformed compared to the true profile. Although the mathematical relationship between the 'real' and the observed traces can be defined, and the 'real' trace can be uniquely reconstructed using a deconvolution transform, the noise in the measurement is greatly magnified.

Since our objective was to examine ratios between various parameters, specifically NO_y species, CO and ozone when examining plume ozone formation processes, and SO_2 and NO_y when examining differential loss processes involving NO_y species in the plume, an alternative method was developed. The concept was to mathematically degrade the response time for the fast response analyzers to the same level as that of the slowest response analyzer. By following this procedure, the signals are synchronized and therefore the concentration ratios at any given location are the same as for the 'true' instantaneous ratios between these parameters. This, of course, is at the cost of coarser spatial resolution.

Based on these considerations, a detailed procedure was introduced to time-delay and smooth the data for the gas-phase instruments. For analyses of ozone formation processes, time delay functions were applied to ozone, NO, NO_2 , NO_y , NO_y^* , and (when available) CO data to correspond to the slowest instrument in the grouping, NO_2 , which has a residence time in the system of about 8 s since sample flow must pass through the photolytic cell. This time delay/smoothing (tds) procedure was necessary to be able to look at ozone-forming plume chemistry across plume traverses during which second-to-second changes in concentrations were observed. The result was a data set with synchronized concentrations for each parameter on a 1-sec basis. The 1-s data were then averaged to 5-s to compile the final data set used for analysis. The SO_2 instrument has a

significantly longer response time, however, and the above procedure was not appropriate for calculating synchronized ratios of, e.g., NO_y-to-SO₂. A second tds program with longer delays and more extended smoothing functions was applied separately to the SO₂, NO_y and ozone data for the purpose of comparing SO₂ and NO_y data, specifically in comparing their cross-plume averaged ratios to the ratios of species being emitted from the CUF stack. This was accomplished as follows.

The NO_y analyzer had a shorter response time than the SO₂ instrument and therefore its output was the subject of the transformation. Following the method described by Luria et al. (1974) the data were transformed by using the convolution integral that in our case has the form of:

$$\text{NO}_y'(t') = \int_0^{t'} \text{NO}_y(t) P(t'-t) dt \quad (1)$$

where NO_y(t') is the signal at time t', NO_y(t) is the signal from the NO_y instrument and P(t'-t) is the delay function of the system. Assuming that the delay function of the system is a first-order (or pseudo first-order) decay, then it can be expressed as

$$P(t'-t) = A e^{-(t'-t)/\tau} \quad (2)$$

where A is a proportionality constant. Equation 3 can be rewritten as

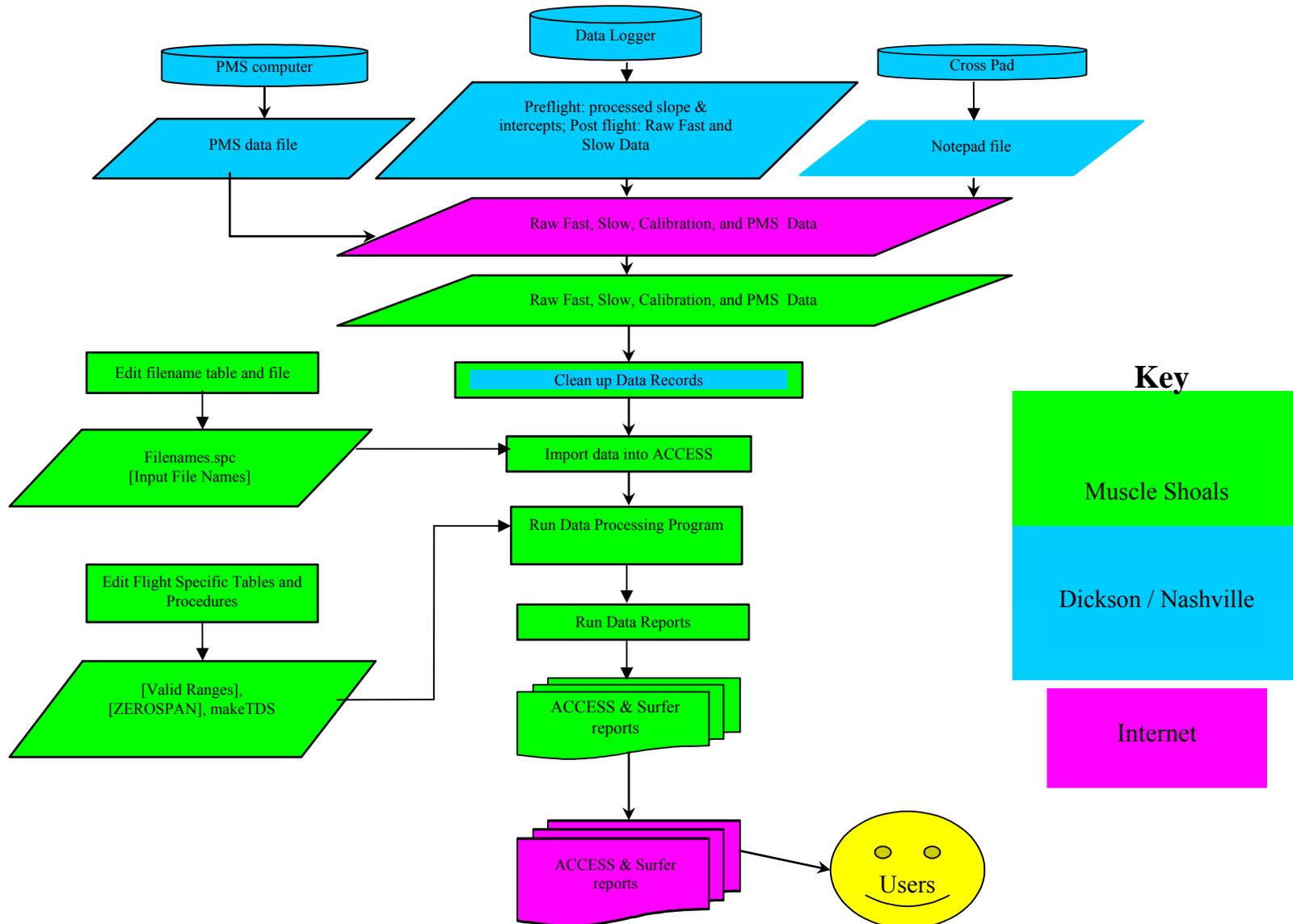
$$\text{NO}_y'(t') = A e^{-t'/\tau} \sum_{t'-4\tau}^{t'} [\text{NO}_y(t-t_1) e^{t'/\tau}] \quad (3)$$

where t₁ is the lag time. For the purpose of determining the response function, A was set to a value other than one so that the integral NO_y' equaled the integral SO₂ for a close-in plume pass (near the stack under conditions where most of the NO_y was present as NO_x). With the aid of a spreadsheet program, the value of NO_y' at any given point (t') was calculated for a series of given values of τ, using all of the preceding NO_y data points within the same plume traverse. Then, the spreadsheet program searched for the τ value that provided the smallest deviation between the calculated NO_y' and the measured SO₂ signal for the entire plume traverse. To calculate the transformed NO_y signal the proportion factor, A, is set to one after fitting the response function. The basic requirement that the integrated values of NO_y and of NO_y' across the entire plume were conserved was met. In other words, no NO_y molecules were added or removed in the process, only their specific location was changed. The results of this procedure for a specific plume traverse is presented in Figure 3 of Appendix D, which shows the original and transformed NO_y data as well as the corresponding SO₂ data for a plume traverse taken on 25 August 1998, 24 km downwind of the Cumberland Power Plant.

Data processing flow. The data processing flowchart used in the Nashville 99 field study is shown in Figure 1. The chart is color-coded to show which operations were conducted at the experimental headquarters at the Dickson Municipal Airport in Dickson, TN, near Nashville (blue boxes), which at TVA's Environmental Research Center (ERC) in Muscle Shoals, AL (green boxes), and products which were available on the Internet (magenta boxes). Three types of files were acquired during flights: Campbell datalogger

PC208 files, PMS computer files acquired by an on-board PC, and Cross Pad notebook files compiled by on-board flight operators.

Figure 1. Nashville 99 Data Processing Overview



The in-flight datalogger files were combined with preflight calibration (slope/intercept) data, and all file types combined into a set of “raw” database files available at an Internet site. These “raw” database files were downloaded by staff in Muscle Shoals, where they were cleaned up and imported into an ACCESS (Office 97) database along with a filename table (filenames.spc input table). The data processing program was then run after incorporating flight-specific look up tables, which included valid ranges, zero/span data, and flight-specific time delay-smoothing (tds) parameters.

After data processing, data reports were obtained which included ACCESS tables and Surfer plots of color-coded ozone, SO₂, and NO_y concentration distributions. These reports were archived on the Muscle Shoals ascommon (LAN) server, then placed on the Internet site so that they could be viewed by flight operators in Dickson and/or staff in Nashville. Barring significant problems in processing, these products were available by the morning following a flight and could be used in developing flight plans for that day.

IV. RESULTS

The results from the CUF Visible Emissions Study are presented in terms of tests of the hypotheses outline in the Objectives section above. As noted there, these hypotheses relate to the emission of primary particles into the FGD-scrubbed plume before and after NO_x reduction equipment was installed at the plant, the rates and extent of formation of secondary sulfate in the scrubbed plume, the formation of nitric acid and nitrate in the plume before and after NO_x-reduction, the relationship of ozone production in the plume to NO_x emission rates, and the importance of considering losses of NO_x product species in determining the extent of net ozone formation.

◆ *Tests of hypothesis one: the extent of PM_{2.5} nitrate formation (vis-à-vis nitric acid) in the plume*

This hypothesis can be addressed using two of the subsets of data from the CUF 98 and Nashville 99 missions. HiVol sampling was conducted on quartz filters, and following filter extraction, data were obtained for sulfate, nitrate and ammonium for several missions. One integrated sample was obtained at each sampling distance in the plume. Continuous data were also obtained for “nitrate” (particulate nitrate + nitric acid) from the difference between the TEII NO_y and NO_y* signals. Comparison of the average (NO_y-NO_y*) “nitrate” levels with those obtained from the HiVol samples (particulate nitrate only) allows us to estimate how much of the excess inorganic nitrate in the plume is nitric acid vis-à-vis particulate nitrate, and whether that fraction changes with down-wind distance. The HiVol filter data is shown in Table 4 for 1998 and 1999 data; only data from filter samples collected from ≥ about 4 m³ of air are shown.

We note that particulate nitrate is relative stable on quartz filters (compared to, e.g., Teflon filters) since the pressure drop is quite low and thus pressure-induced change in the nitrate-nitric acid equilibrium are likely to be modest. Nitric acid is unlikely to penetrate the copper inlet tube given the unavoidable turbulence in the inlet air stream,

but we cannot exclude the possibility that some nitric acid vapor reaches the quartz filters. Although previous experience with high temperature-pretreated tissue quartz filters suggests that retention of nitric acid by adsorption on the quartz in HiVol applications is minimal (Tanner et al., 1989), it is possible that up to 0.5 $\mu\text{g}/\text{m}^3$ of

Table 4. Summary of Helicopter HiVol Sampler Data for Nashville 99

Sample Date	Sample Description	Sample Vol, m3	[SO ₄], ug/m3	[NH ₄], ug/m3	[NO ₃], ug/m3	Corr. ⁺ NH ₄ ⁺ /SO ₄ ⁻
23 Aug 98	Flt 6 bkgd	32.30	12.59	0.29	2.77	1.137
23 Aug 98	Flt 6, 19 km downwind	13.91	11.32	0.29	2.29	1.038
23 Aug 98	Flt 6, 54 km downwind	15.50	18.23	1.29	3.95	1.045
24 Aug 98	Flt 7, bkgd	26.12	11.95	0.87	2.53	1.015
25 Aug 98	Flt 8, bkgd	45.53	10.59	0.94	3.51	1.632
25 Aug 98	Flt 8, 19 km downwind	11.60	13.81	2.66	4.33	1.374
25 Aug 98	Flt 8, 56 km downwind	6.83	10.39	3.84	3.63	1.292
26 Aug 98	Flt 9, bkgd	23.06	15.59	1.07	4.11	1.300
26 Aug 98	Flt 9, 28 km downwind	5.05	20.17	2.02	5.31	1.249
26 Aug 98	Flt 9, 74 km downwind	8.94	22.78	1.03	4.77	1.046
29 Jun 99	Flt 3, bkgd	16.02	5.05	0.86	0.18	1.114
29 Jun 99	Flt 3, 19 km downwind	6.28	3.95	0.80	MDL	1.382
29 Jun 99	Flt 3, 67 km downwind	3.99	Not valid	0.48	0.95	Not valid
04 Jul 99	Flt 5, bkgd	31.96	5.66	1.48	0.34	1.303
04 Jul 99	Flt 5, 37 km downwind	8.14	9.76	Not valid	MDL	Not valid
04 Jul 99	Flt 5, 56 km downwind	5.52	11.23	Not valid	MDL	Not valid
06 Jul 99	Flt 6 bkgd	32.15	4.06	1.22	0.54	1.397
06 Jul 99	Flt 6,56 km downwind	6.80	6.47	Not valid	3.65	Not valid
13 Jul 99	Flt 8 bkgd	20.25	14.03	3.50	0.37	1.288
13 Jul 99	Flt 8, 14 km downwind	3.81	33.08	2.99	0.37	0.465
13 Jul 99	Flt 8, 35 km downwind	4.58	14.27	3.32	0.48	1.187
15 Jul 99	Flt 10, bkgd	16.03	10.77	1.58	0.84	0.884
15 Jul 99	Flt 10, 14.5 km downwind	4.58	16.73	2.27	1.92	0.753
15 Jul 99	Flt 10, 55 km downwind	6.90	9.09	2.36	2.84	1.299
15 Jul 99	Flt 10, 95 km downwind	11.61	14.30	1.60	1.52	0.604

⁺ corrected for the portion of the ammonium associated with observed nitrate.

"positive artifact nitrate" might have occurred. Of course, if significant portions of the nitric acid are removed in the inlet, this would of course disturb the nitric acid-ammonia-nitric acid equilibrium leading to the evaporation of ammonium nitrate if present, leading to negative errors in calculated particulate nitrate concentrations.

Another assumption that is implicit in this sampling approach is that the fine particles present in the plume (mostly from background air) constitute an internal mixture with respect to extractable nitrate and sulfate. To the extent that this is not true (external mixture, for example), ammonium nitrate and acidic sulfate might co-exist in the aerosol. Due to the large surface area of quartz filters, it is possible for collected particles from externally mixed ambient aerosols to be preserved in filter samples, and for small amounts of nitric acid released from quartz-collected ammonium nitrate particles when flushed with air from which nitric acid has been removed to be retained by sorption on the filter (Tanner et al., 1989). Whether all of these effects result in a net negative or positive bias for particulate nitrate collected in the CUF plume cannot be determined from the data taken in this study.

Despite these limitations, we feel that it is useful to compare these filter data with the continuous data results for "NITR", the sum of inorganic nitrate and nitric acid determined from the $\text{NO}_y\text{-NO}_y^*$ signal. We converted the HiVol nitrate data to ppbv values (at 25°C), then calculated an average plume NITR above background from the $\text{NO}_y\text{-NO}_y^*$ data. The results are presented in Table 5. The data show considerable

Table 5. Particulate Fraction of Inorganic Nitrate

Date	Description	ΔHiVol (pNO_3) ppbv	Ave Plume NITR, ppbv	Fraction pNO_3/NITR , %
23 Aug 98	Flt 6, 19 km downwind	<0	Missing	Loss
23 Aug 98	Flt 6, 54 km downwind	0.47	Missing	Missing
25 Aug 98	Flt 8, 19 km downwind	0.32	2.0	16
25 Aug 98	Flt 8, 56 km downwind	0.05	2.1	2.4
26 Aug 98	Flt 9, 28 km downwind	0.47	8	6
26 Aug 98	Flt 9, 74 km downwind	0.26	No data	No data
29 Jun 99	Flt 3, 19 km downwind	<0	4-5	Loss
29 Jun 99	Flt 3, 67 km downwind	0.30	1.5	20
06 Jul 99	Flt 6, 56 km downwind	1.23	3.5	35*
13 Jul 99	Flt 8, 14 km downwind	0.0	7	0
13 Jul 99	Flt 8, 35 km downwind	0.04	5.5	<1
15 Jul 99	Flt 10, 14.5km downwind	0.43	3.0	14
15 Jul 99	Flt 10 55 km downwind	0.79	2.4	33
15 Jul 99	Flt 10 95 km downwind	0.27	2.4	11

* May have been influenced by urban plume nitrate.

variability from day to day and plume distance to plume distance. However, a range of from about 65 to essentially 100% of the observed nitrate was in the form of nitric acid (fraction of particulate nitrate $\leq 35\%$). In fact, for some of the close-in distances, c.f., Flight 6/1998 and Flight 3/1999, the filter sample shows less particulate nitrate than the background, indicating net loss of collected particulate nitrate, possibly due to the effect of acidic plume particles on the background aerosol. Although there is only a limited amount of data, they suggest that plume-generated NITR is mostly in the form of nitric acid and does not on average increase ambient levels of $PM_{2.5}$ significantly due to formation of particulate nitrate.

We note that these measurements were taken under warm, summertime conditions during which ambient levels of $p\text{-NO}_3^-$ in the eastern US are generally very low (Blanchard et al., 2000). The potential contributions to ambient levels of $p\text{-NO}_3^-$ in other seasons, or in locations (e.g., large urban areas or areas of intense animal husbandry) where the NH_3 concentrations are high, cannot be discounted on the basis of these measurements.

◆ *Tests of hypothesis two: primary emissions of fine particles from units equipped with high-efficiency SO_2 scrubbers make only minor contributions to ambient $PM_{2.5}$ levels.*

Particulate emissions are characterized in the plume by measurements made with the PCASP instrument, with which measurements of the numbers of particles in 15 size bins are made. By subtracting out the contributions from the surrounding background, the number of plume-excess particles in each size bin can be determined during each plume traverse at each sampled distance from the source (stack). In Figure 2 is shown the average excess particle volume for a close-in (18 km), a middle (56 km) and a far distance (110 km) for each particle size during the Aug. 25, 1998 flight, compared to the average background volume and to the background variability. The number concentrations in each bin are converted to volume concentrations in constructing this plot, assuming spherical particles of the mean diameter of that bin, and are averaged over all traverses at a given distance. Note that it is the **variability** in the background number concentrations used to calculate volumes which determines whether the plume contribution can be "seen above the background", not the absolute background concentrations themselves. The background variability is clearly smaller than the volume contributions for the PCASP data in size bins between 0.1 and 0.2 μm as shown in Figure 2. Therefore, although the contribution of particles in the 0.1-0.2 μm size range (bins 1-3) is clearly discernable above the variability in the background, and plume-excess number concentrations exceed their inter-traverse variability for close-in distances, these particles contribute very little volume or mass to the background aerosol (note that the plot is semi-logarithmic for clarity).

The mass contribution from primary emissions is thus low and is concentrated in the 0.1-0.2 μm size range, consistent with the results of stack emissions characterization study conducted by TVA in 1995 at the CUF (unpublished Executive Summary, TVA, July 18, 1996). These emissions apparently do not grow into or make a significant contribution

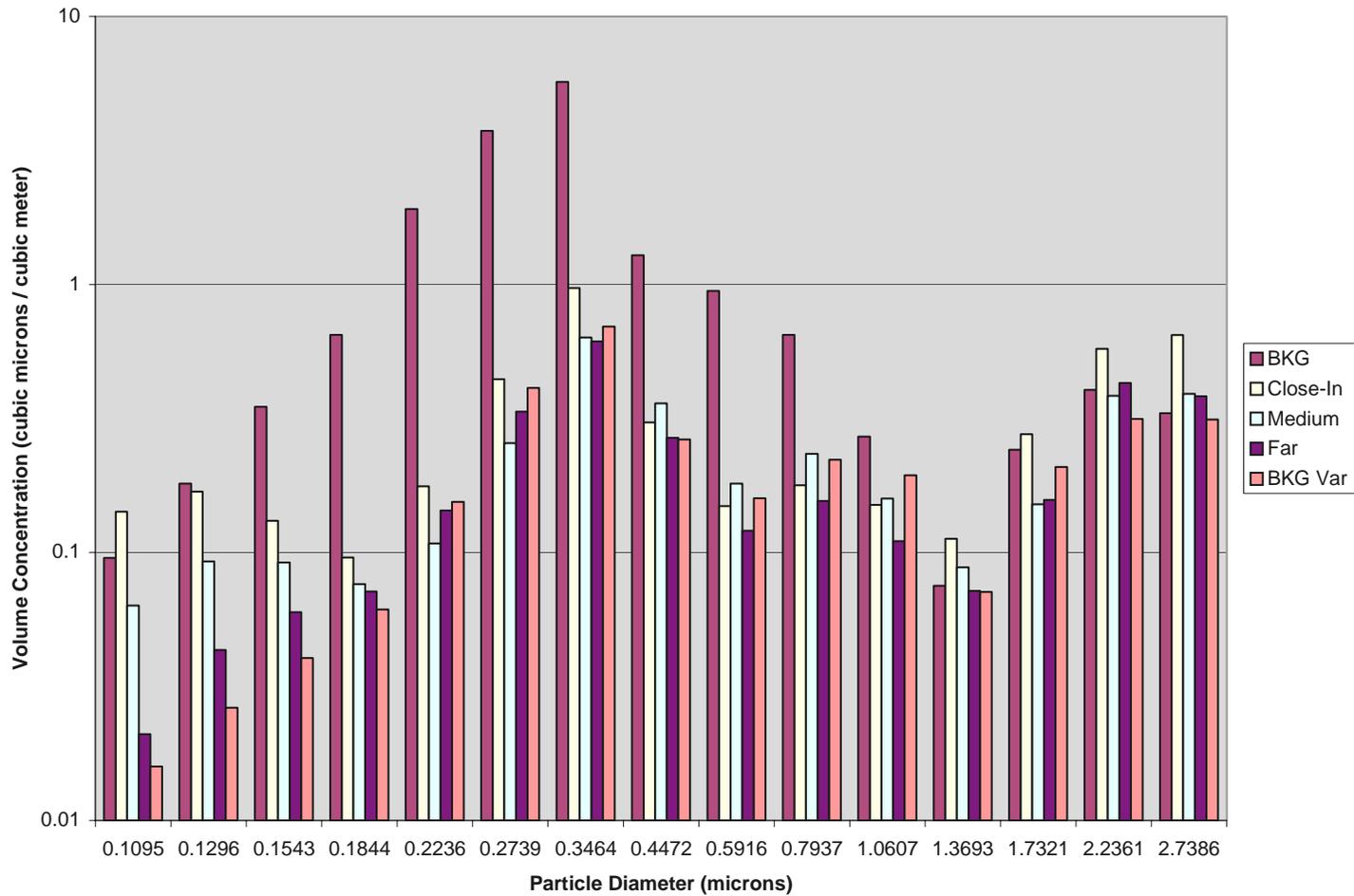


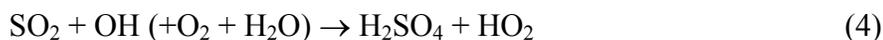
Figure 2. Comparison of the excess particle volume for each particle size to the average background volume and to the background variability during the Aug. 25, 1998 flight. The background variability is characterized by the standard deviation of the background.

to the plume-excess accumulation aerosol mass or to light scattering therefrom, as shown in Figure 2. The high correlation between plume-excess particle volumes and plume-excess NO_y concentrations, excess plume NO_y (mostly NO_x near the stack) clearly being a primary emission, indicates that these particle emissions are primary although their contribution to the plume aerosol volume is low (Figure 3).

That neither primary nor secondary particles formed in the FGD-scrubbed plume contribute much to plume excess particle volume and light scattering is shown in Figure 4, in which the PCASP particle volume and nephelometer light scattering (3-wavelength instrument, with blue, standard green, and red scattering) are plotted for a representative intermediate-distance traverse, along with NO_y and SO₂ concentrations to identify the extent of the plume. For this intermediate plume transport distance, it is difficult to distinguish the plume from the background based on plume particle volume by PCASP or particle light scattering by nephelometer. The plume excess light scattering and aerosol volume are more noticeable at the third distance sampled during this flight (110 km downwind) but still amount to only about a maximum of about a 15% increase in scattering near the plume centerline compared to background.

◆ *Tests of hypothesis three: secondary sulfate formation in-plume under cloud-free, summertime conditions has decreased proportionately to SO₂ emissions reductions.*

The extent to which reductions in SO₂ emissions have resulted in corresponding decreases in ambient aerosol sulfate levels is a crucial policy-relevant question for future SIP development if needed. Thus it comprised a major motivation for this study. It is critical to note that two major and distinctly different conversion processes determine the yield of sulfate aerosols from SO₂ emissions into the atmosphere. One is the gas-phase oxidation of SO₂, the net reaction for which is:



The second process is the aqueous phase process by which dissolved SO₂ (sulfite) is oxidized to sulfate in cloud droplets by peroxides (mostly H₂O₂), and, at higher pH, by dissolved ozone or oxygen catalyzed by Fe and Mn:



This second process may also occur to a lesser extent in aerosol droplets at high RH.

Since this study focused on summertime, largely cloud-free conditions, the results therefrom could only be used to determine if the rate of **gas-phase** SO₂-to-sulfate conversion has changed significantly in the CUF plume as a result of the 95% reduction in SO₂ emissions brought about by the installation of the FGD scrubbers in late 1994. This study could not address whether aqueous phase SO₂ oxidation rates might have concomitantly changed. In addition, its results cannot be used to argue that regional levels of sulfate would be expected to change in a manner reflecting the CUF SO₂ emissions reductions,

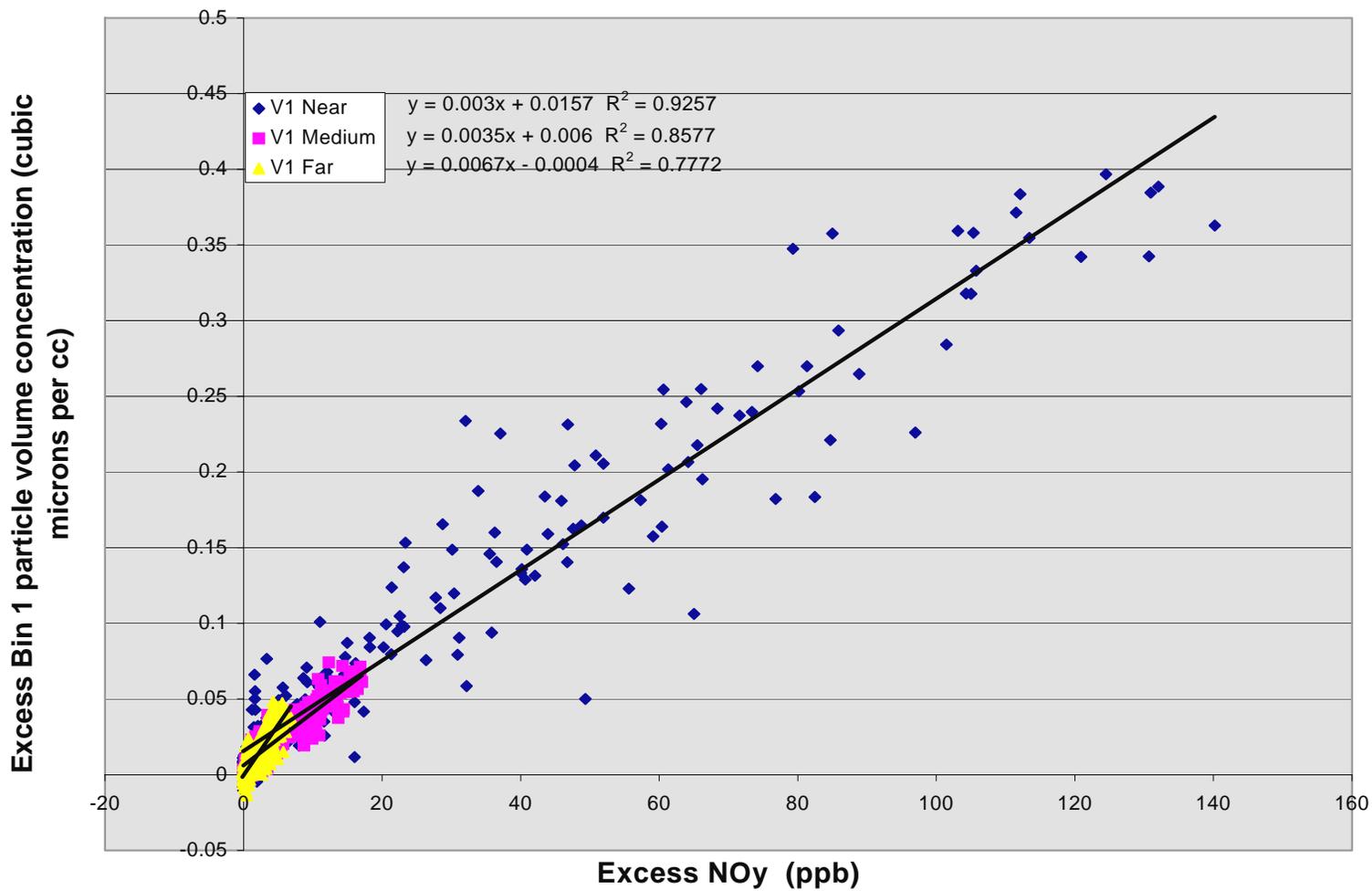


Figure 3. Scatter plot of excess volume concentration in PCASP bin 1 versus excess NO_y at three distances for a 1998 flight.



TANSPED version 2.3

5-Second Data for TVA Helicopter
Julian Day: 237 1998 (8/25/98) Plume Number: 007

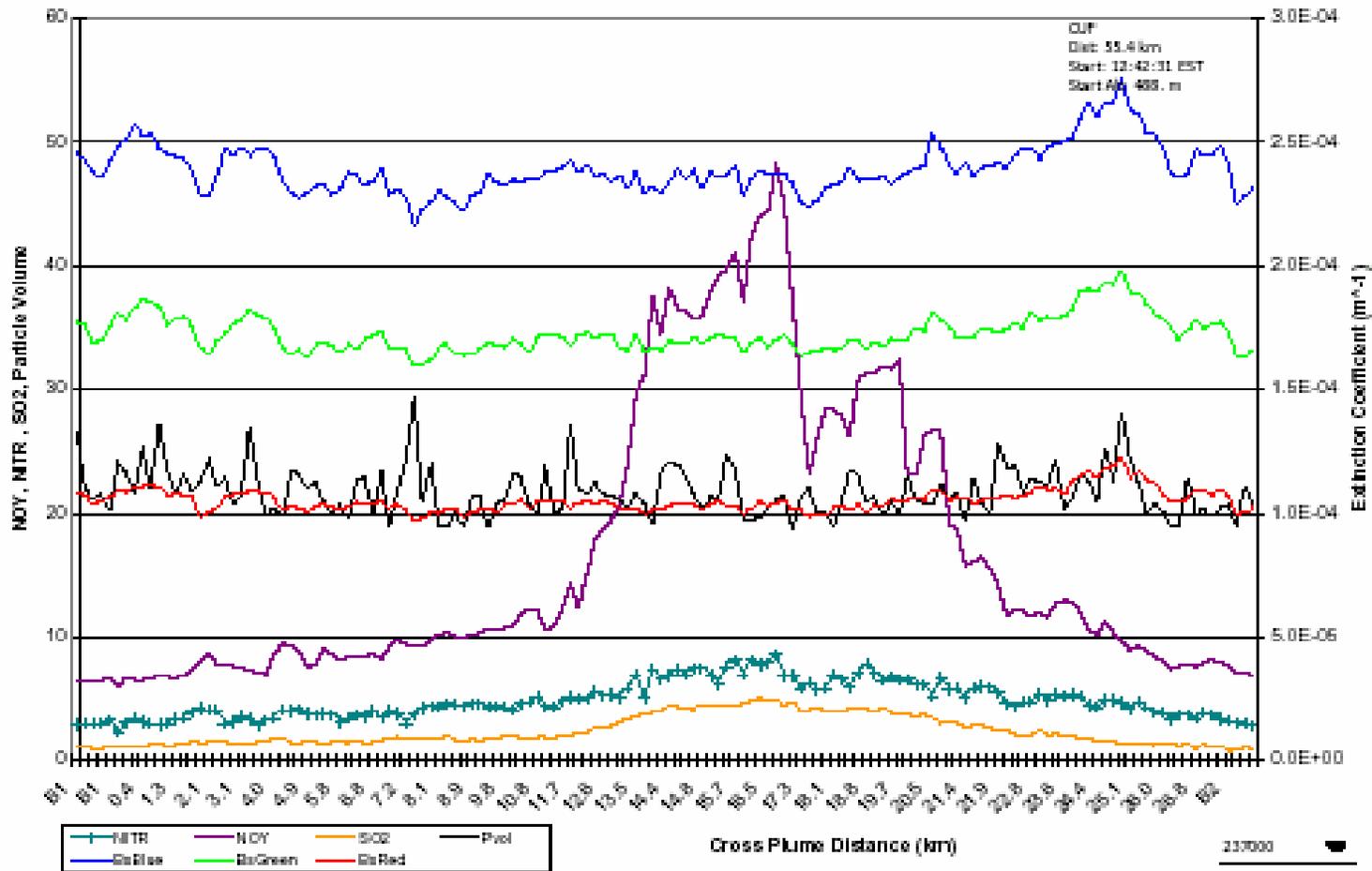


Figure 4. Particle and Gas Concentrations, CUF Plume 7, 55 km, 8/25/98.

since regional sulfate levels are affected by a large number of emissions sources as well as by mean regional meteorological conditions.

A principal focus of this aspect of the study was then to determine rates of gas-phase conversion and see if those rates had changed significantly since the last time extensive plume measurements had been made in the late 1970s. In addition to the observation that in-plume oxidation rates on cloud-free days were about the same as before scrubbers were installed, we found that light scattering measurements could no longer be used to locate and follow the plume, and that the apparent reason for this is that plume dispersion now occurs at a rate faster than in-plume accumulation of light scattering particles. There was also some indication of cross-plume structure in the rates of oxidation in the CUF plume, with higher rates near the edges. This observation has been reported previously by Gillani et al. (1981) and by McMurry et al. (1981) in the pre-FGD scrubbed CUF plume and we have discussed it further in Imhoff et al. (2001). It is analogous to, but less pronounced, than the ozone wings associated with ozone formation in point-source NO_x plumes.

Results related to determining the rates of SO_2 -to-sulfate conversion based on measurements in this study have been reported in two refereed publications in the Journal of the Air and Waste Management Association in 2000 and 2001. These are attached to this report as Appendices A and B, respectively

In Imhoff et al., (2000), The Evolution of Particles in the Plume from a Large Coal-Fired boiler with Flue Gas Desulfurization, taken from a presentation made the PM 2000 Conference in Charleston, SC, and included herein as Appendix A, we reported airborne measurements made of gaseous and particulate species in the CUF plume after flue gas desulfurization (FGD) controls were installed, and compared them with measurements made before FGD controls. Two series of eight research flights each were performed in the Cumberland plume in the summers of 1998 and 1999 and the resulting data were used to investigate the oxidation processes in the scrubbed plume. The Cumberland plume did not mix with plumes from adjacent power plants during two of those sampling flights, enabling a conversion rate to be estimated from plume samples taken at three downwind distances. The light scattering and number and volume distributions of plume excess particles were determined by nephelometry and PCASP optical particle techniques, respectively. The plume impact based on optical measurements was much lower than that observed in earlier measurements. Indeed, plume excess volumes as a function of particle size were of the same magnitude as the variability of the background volume distribution (see Figure 2 above). In situ excess plume scattering actually decreased with distance from the source, in contrast to pre-FGD conditions.

The upper limit for the dry rate of SO_2 -to-sulfate conversion was estimated directly from plume excess volume measurements, and found to be about $4\% \text{ hr}^{-1}$. This is slightly greater than the upper limit, $3.5\% \text{ hr}^{-1}$, estimated by earlier researchers (McMurry et al., 1981; Gillani and Wilson, 1981), but did not differ significantly from the value estimated using the same technique but with the earlier data.

The cross-plume profile of volume suggests SO₂-to-sulfate conversion is highest at the plume edges. The greatest benefit of SO₂ reduction on plume excess volume and visibility appear to occur far downwind of the source.

In a follow-up manuscript, Rates of Conversion of Sulfur Dioxide to Sulfate in a Scrubbed Power Plant Plume, Luria et al. (2001) (see Appendix B) re-estimated the rate of conversion of SO₂ to sulfate for the Cumberland plume after including corrections for dry depositional losses. The plume of the 2600 MW plant now has a relatively low ratio of SO₂ to NO_y emissions (~0.1 prior to the recent installation of low-NO_x burner equipment lowering NO_x emissions) compared with a ratio of approximately 2 before the installation of the SO₂ scrubbers in 1994. Removal rate constants for the sum of oxidation and (dry) deposition were calculated and those rate constants for the August 25, 1998, flight are shown in Figure 5. After taking into account best estimates of dry deposition losses, and considering the fact that plume SO₂ levels are no longer in large excess compared with SO₄²⁻ levels, an upper limit for just the conversion rate was estimated based on plume excess aerosol volume. The upper limit value estimated for the 1998 flight is 0.069 h⁻¹ while the same value for 1999 is 0.034 h⁻¹. While the 1999 rate is comparable with values estimated earlier for non-scrubbed plumes, the 1998 value is somewhat higher than expected, suggesting a possible deviation from a linear relationship between SO₂ emissions and sulfate formation, although the error bars for the two estimations do overlap.

◆ *Tests of hypothesis four: changes in SO₂ oxidation rates with NO_x emission reductions*

The study was not really designed to test this hypothesis—that lower NO_x emission rates lead to lower OH concentrations and thus to lower SO₂ conversion rates, or that lower NO_x emission rates might increase the rates of aqueous phase SO₂ conversion by increasing peroxide levels through NO_x-limited ozone chemistry. We note that the measurements were made during summertime, mostly clear sky conditions. In the absence of extensive cloud cover, the conversion of SO₂ to sulfate is generally determined by the gas phase reaction with OH (see reaction (1)), hence is controlled by the levels of atmospheric OH. OH levels are determined by the concentrations of a large number of atmospheric species, hence the reduction of NO_x emissions from a single point source, even a large one, is unlikely to affect regional OH levels. It is possible that at least locally, the reduction in NO_x emissions may result in higher HO₂ levels, hence in an increased rate of production of H₂O₂ from the recombination reaction. In the presence of clouds this could lead to more rapid aqueous-phase SO₂-to-SO₄²⁻ production. However, as noted above, flights were generally limited to clear sky conditions, and since observable effects of NO_x reductions from a single point source were likely small and unquantifiable, we could not test this hypothesis.

◆ *Tests of hypothesis five: ozone formation in large point-source plumes*

Recent studies have added much to our knowledge of ozone formation in point-source and urban plumes (Ryerson et al., 1998; Gillani et al., 1998; Nunnermacker et al., 1998;

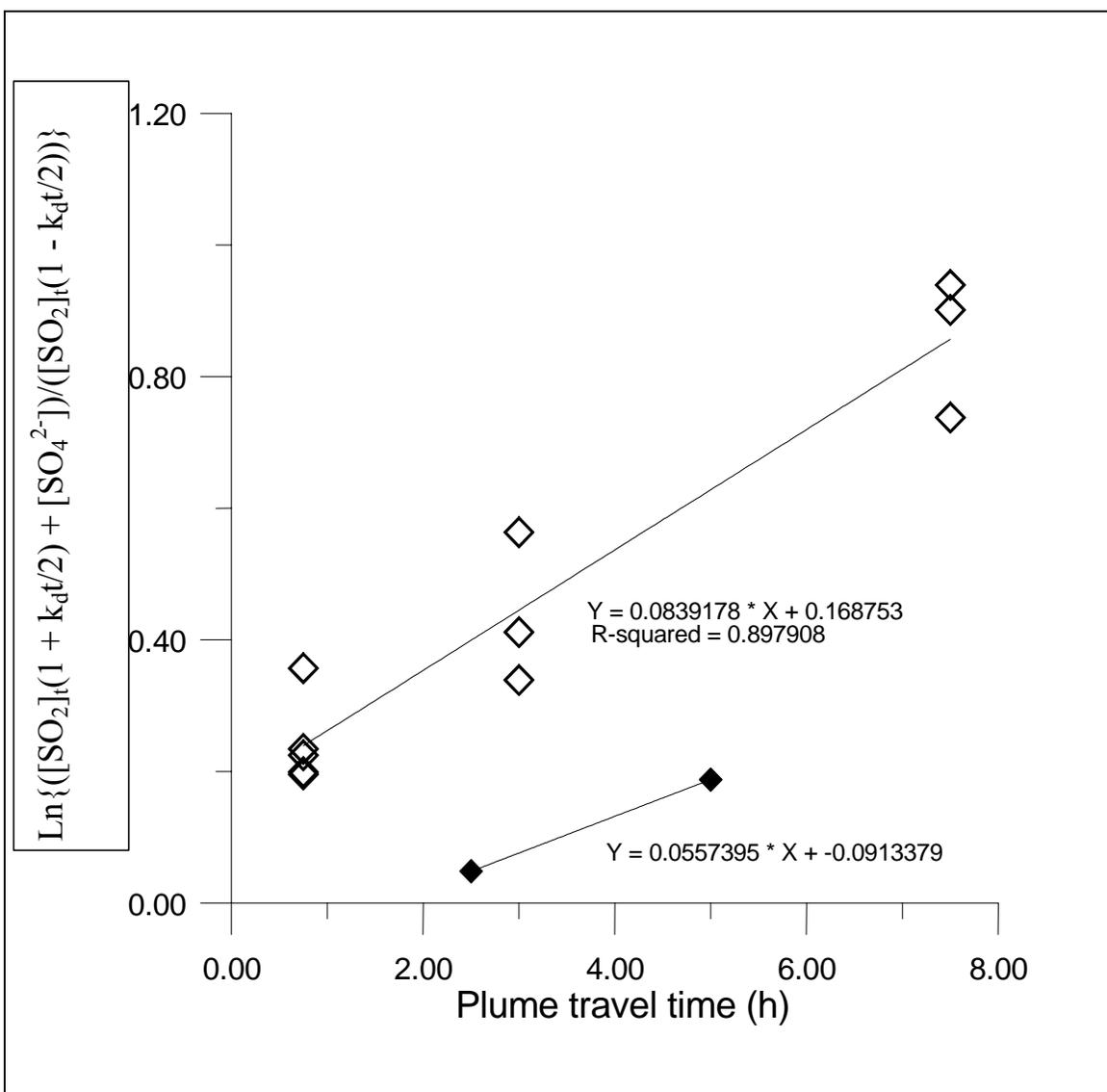


Figure 5. Estimation of the sum of the removal rate constants (oxidation and deposition) for the Cumberland plume in flight 8, August 25, 1998, using equation xxx? and assuming a dry deposition rate constant of 0.015 hr^{-1} .

Valente et al., 1998; Luria et al., 1999). It is clear that the extent of impact of these plumes depends on three principal factors: the magnitude of the emission rate, the availability and reactivity of the VOCs (especially naturally emitted species such as isoprene and terpenes) involved in the ozone formation process, and boundary layer meteorological conditions such as temperature, BL height, wind speed, etc. which affect the degree of dispersion of the plume. This study has contributed measurably to the understanding of plume ozone formation in at least three major areas: the effect of the emission rate of NO_x on the efficiency with which ozone is formed, the structure of the plumes with respect to ozone formation, and the rate at which the plume becomes

"mature" and stops producing ozone faster than it can be dispersed to the surrounding background.

In this regard, we have recently drafted a manuscript which compares the photochemical reactivity and dispersion of the CUF plume based on 1998 and 1999 missions, and have submitted it to Atmospheric Environment for publication: Luria et al., 2002, Ozone Production Efficiency in a Large Power Plant Plume (see Appendix C). The plume of coal fired Cumberland power plant was sampled during several days in the summer of 1998 and 1999 from an instrumented helicopter. The plume was sufficiently isolated from other point sources on four days to allow analysis of ozone formation in the CUF plume. The formation and removal processes of the various NO_y species in the plume were estimated and were found to be similar during three of the sampling days (see Table 6). On the fourth day the plume was significantly slower due to poor dispersion conditions, and was not within experimental error different from zero. For the other three days ozone production efficiency, was estimated to be in the range of 2.1 to 5.4 when calculated directly from the integrated plume excess ozone and NO_y ratios. These values, as shown below, are upper limits to the true OPE values if NO_z product species such as nitric acid are lost from the plume at rates exceeding that of ozone and/or SO₂. Correcting for differential losses of NO_y species during plume transport, the OPEs (OPE* in Table 6)

Table 6. Summary of calculated ozone production efficiencies and concentration ratios

<i>Parameter</i>	Flight 8/98 25 Aug 1998	Flight 6/99 6 July 1999	Flight 8/99 13 July 1999	Flight 10/99 15 July 1999
OPE derived from integrated ratios (No. of Data Points)	2.1±0.8 (4)	2.7±0.3 (3)	NA	5.4±1.1 (3)
In plume SO ₂ /NO _y	Increase with distance from 0.1 up to 0.25	Very slight increase with distance	Data too scattered	Starts high (≈0.2), and increases to 0.5
OPE*	1.5±1.0	2.6±0.3	NA	2.0±0.55
Bkgd. NO _z /NO _y	0.86-0.95	0.8-0.9	0.86-0.94	0.88-0.95
NO _z /NO _y (at D3, max) Bkg NO _z /NO _y	0.65 >0.9	0.54 >0.9	NA	0.85 >0.9
NIT/NO _y (at LT ^a , max)	0.51-0.54	0.46-0.54	0-0.08	0.44-0.51
ONIT/NO _y (at LT,max)	0.04-0.19	0.02-0.04	NA	0.33-0.41

^aLT (last traverse), is the furthest downwind sampling distance.

were re-estimated to be in the range of 1.5-2.6 molecules of O₃ produced per one molecule of NO_x emitted.

One hypothesis that was not originally formulated as part of this project, but which has turned out to be significant in the evaluation of ozone yields and production efficiencies in large point sources of NO_x, is as follows:

◆ *Are the products of NO_x photochemistry, abbreviated NO_z, lost from the plume during its chemical evolution at a rate significantly faster than SO₂ or ozone, and does this materially affect the estimates of ozone production efficiencies (or yields)?*

The development of optimized ozone control strategies based on NO_x reductions from specific sources is critically dependent on estimates of ozone yields and production efficiencies. This project has provided data that suggests that plume loss of the NO_z portion of NO_y can be significant, that the extent of loss varies significantly from day to day depending on meteorological conditions, and that these apparent losses are unlikely to be caused solely by measurement uncertainties. A short communication on the effect of differential losses of NO_z species on the apparent ozone production efficiency in the CUF plume has now been published (Imhoff et al., 2001) and is attached as Appendix D. This communication contains data from 1998 flights and is a follow-up to Gillani et al., (1998). Airborne measurements performed in the plume of the Cumberland Power Plant during August 1998 using a highly sensitive SO₂ instrument as well as the suite of nitrogen oxide instruments (NO_y, NO_y^{*}, NO, and NO₂). These measurements confirmed suggestions by Gillani et al. (1998) that NO_y species are removed from the plume at a faster rate than SO₂. The differential removal rate (the difference between the loss rate of NO_y and that of SO₂) was estimated to be 0.06 h⁻¹, which is in the middle of the range of previous observations. This value implies that NO_y loss rate is in the range of 0.09-0.14 h⁻¹. In a mature plume with a chemical age (NO_z/NO_y) of the order of 80% and assuming the loss rates of NO and NO₂ are much smaller than for SO₂ and ozone, this corresponds to a deposition rate of NO_z from the plume of about 4 cm/s for a boundary layer 1 km in height. Then if the principal NO_z species lost from the plume were nitric acid, typically about 60% of NO_z in a large point source plume (Tanner et al., 1998), this would correspond to a nitric acid deposition rate of 7 cm/s (± ca. 50%). This rate is higher than the accepted deposition rate for HNO₃, but the uncertainties in the estimation are sufficiently large to maintain the plausibility of this explanation of in-plume losses, and justify the need to adjust for these losses when determining ozone production efficiencies in power plant plumes.

Some investigators have maintained that these apparent NO_y losses are mostly due to inlet losses of NO_z species, particularly nitric acid. This explanation is not supported by the analysis shown in Luria et al., 2002, (Appendix D) in which a maximum apparent loss of 20% could have been observed due to measurement errors, based on uncertainties in the calibrations and observed in-flight drifts of the NO_y and NO_y^{*} instruments, observed pre- and post-flight NO_y-to-NO conversion efficiencies, and direct measurements of inlet transmission efficiencies for nitric acid (the latter observed in the laboratory). We cannot exclude the possibility of in-plume conversion of NO_x to an NO_y species which is not

converted to NO in the gold-CO converters, but this seems unlikely, since the literature shows that known species including NO₂, p-NO₃⁻, HNO₃, PANs and organic nitrates and nitrites are converted to NO with high efficiency in the gold-CO converter.

In this study, the application of a mathematical argument, based on the convolution integral (see Data Acquisition Procedures section on *The convolution process*, pp. 7-8), enabled the improved synchronization of the data from the SO₂ and NO_y instruments. Examination of the synchronized data revealed that the ratio between SO₂ and NO_y varies across the plume. For near-source traverses (up to 63 km) it is higher at the wings of the plume, while in the core of the plume it is similar to the ratio at the release point. Three possible explanations of the observations are: experimental measurement problems including inlet losses of NO_z species, in-plume conversion to non-measured NO_y species, and in-plume loss of NO_y (as HNO₃) via dry deposition. From the analysis above, we conclude that the upper limit for experimental measurement problems including inlet losses of NO_z species is about one-third of the observed losses, and it is implausible that problems of inlet losses, etc. should vary widely from day to day. We cannot exclude the formation of unmeasured NO_z species in the plume, e.g., particulate organic nitrates or dinitrates, but these products have not been reported in the literature to be present in large amounts. The most likely explanation is relatively rapid losses of nitric acid and possibly other NO_z species by deposition to the surface.

Summary

In this project, the rate of conversion of SO₂ to SO₄²⁻ was estimated from measurements made in the plume of the Cumberland power plant to determine the effects of installation of flue gas desulfurization (FGD) scrubbers for SO₂ removal in 1994. The ratio of SO₂ to NO_y emissions into the plume was reduced to ~0.1, compared with a pre-scrubber value of ~2. The data were used to determine whether the SO₂ emissions reduction has correspondingly reduced plume-generated particulate SO₄²⁻ production by comparing the rates of conversion after scrubber installation with pre-scrubber estimates developed from measurements made during the Tennessee Plume Study in the late 1970s. The post-scrubber estimates are based upon two series of research flights in the summers of 1998 and 1999. During two of these flights the Cumberland plume did not mix with adjacent power plant plumes and complete data sets were available, enabling rate constants for conversion to be estimated from samples taken in the plume at three downwind distances. Dry deposition losses and the fact that SO₂ is no longer in large excess compared with SO₄²⁻ were taken into account, and an upper limit for the conversion rate constant was determined based on plume excess aerosol volume. The estimated upper limit values are 0.069 hr⁻¹ and 0.034 hr⁻¹ for the 1998 and 1999 data, respectively. The 1999 rate is comparable with earlier values for non-scrubbed plumes, and although the 1998 upper limit value is higher than expected, these estimates do not, within experimental error, provide significant evidence for deviation from a linear relationship between SO₂ emissions and SO₄²⁻ formation by gas-phase processes.

On the three more 'reactive' days during this study in which it could be determined, ozone production efficiency (OPE) in the CUF plume was found to be in the range of 1.5-

2.6 molecules of O₃ produced per molecule of NO_x emitted, consistent with the relatively low OPEs reported in the literature for large point sources of NO_x. This body of work also suggests that the rates of all processes involved in plume evolution and ozone formation—ozone formation rates, yield and production efficiency, photochemical chain length, and rates of conversion of NO_x to NO_z ($\Delta[\text{chemical age}]/\Delta t$), and loss rates of NO_z during plume evolution—are variable from day to day. This variability depends on the availability of VOCs (mostly isoprene during summertime in the region into which the CUF plume is usually transported), the rate and extent of plume dispersion, and, less directly, on other meteorological parameters. No strong evidence was found in data from the 1999 flights that OPEs were higher in the CUF plume which had reduced NO_x emission rates compared with 1998 (see Table 6), but the day to day variability of ozone formation may have masked any existing trends.

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LIST OF APPENDICES

APPENDIX A

Imhoff, R.E., R.L. Tanner, R.J. Valente, and M. Luria, The Evolution of Particles in the Plume from a Large Coal-Fired boiler with Flue Gas Desulfurization (2000) *J. Air & Waste Manage. Assoc.* **50**, 1207-1214.

APPENDIX B

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APPENDIX C

Luria, M., R.E. Imhoff, R.J. Valente, and R.L. Tanner, Ozone Production Efficiency in a Large Power Plant Plume, (2002), *Atmos. Environ.*, submitted.

APPENDIX D

Imhoff, R.E., M. Luria, R.J. Valente, and R.L. Tanner, NO_y Removal from the Cumberland Power Plant Plume, (2001) *Atmos. Environ.* **35**, 179-183.