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CHEMICAL EVOLUTION OF A POWER-PLANT PLUME

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1. INTRODUCTION

During the Texas 2000 Air Quality Study (TexAQS 2000), the DOE G-1 research aircraft was used to characterize pollutant distributions in and around the greater Houston metropolitan area. These measurements were part of a large cooperative effort designed to understand the factors controlling the formation, transport and fate of air pollutants in this region. The high density of pollutant sources related to transportation, industrial petrochemical processing and power generation complicate the assessment of individual contributions to the overall air quality. Sampling from isolated sources in the region is one approach to studying differences between these sources and the subsequent transformations of their atmospheric discharges.

2. OBSERVATIONS

The G-1 flew twenty sampling missions during TexAQS 2000. These flights were primarily flown within a ~90-km distance from the center of Houston. One flight was devoted to study the processing of stack emissions from an isolated power-plant plume well removed from urban influences.

2.1 *Source Characteristics*

The Sandow power plant, located in Milam County, TX, consists of three 125-MW electrical generation units built in the 1950's and a fourth 545-MW unit constructed in 1981. The four units provide power for a co-located aluminum smelter with excess power from Unit 4 added to the commercial grid. The site is located next to Sandow mine which supplies lignite coal for the boilers. Emission levels from 1999 are shown in TABLE 1.

TABLE 1

	SO_2	NO_x	CO	PM_{10}	NMOC
	(ktons/y)				
Σ Units 1-3	61	20	22	1.3	1.6
Unit 4	29	9	1	1.0	0.1
Total	90	29	23	2.3	1.7

1999 TNRCC, Point Source Emission Inventory

2.2 *Sampling Conditions*

The research flight was conducted on September 10, 2000, a day following widespread precipitation and the air was relatively clean upwind from the source. Beginning at 14:30 local standard time, the aircraft repeatedly transected the plume for ~1 h at downwind distances from <4 to 65 km. Based on an average wind speed of 4 m/s, as measured aloft, the plume age when sampled ranged from ~10 min to ~4 h. Winds in the plume region were steady from the SE during the sampling period. A constant altitude of 580 m (MSL) or ~435 m (AGL) was maintained while tracking the plume. At 65-km downwind, the aircraft returned to the plant while climbing steadily. The mixing layer height at that time was 1800 m (MSL) or 1650 m (AGL) as marked by scattered cumulus clouds and a slight increase in potential temperature.

2.3 *Measurements*

Species measured included O_3, NO, NO_2, NO_y, CO, SO_2, speciated VOC (canister samples analyzed at York University), H_2O_2, organic peroxides (Zheng et al., 2001), formaldehyde (Lee et al., 1998), a full range of aerosol size spectra between 3 nm - 16 µm (Buzorius et al., 2001), aerosol chemical composition (Lee et al., 2001) and meteorological parameters. O_3 and SO_2 were measured by commercial instruments modified to achieve response times of ~10 s. Nitrogen species were measured with a three-channel chemiluminescent instrument. NO_2 was converted to NO by UV photolysis. NO_y was converted to NO by a Mo catalyst heated to 350°C and mounted externally in the free airstream. The response time for the three channels was <4 s. VOC canisters took ~45 s to fill. Measurements made from the G-1 for the entire TexAQS 2000 and ancillary materials are available by anonymous ftp from: ftp://aerosol.das.bnl.gov/pub/Houston00/.

3. RESULTS AND DISCUSSION

The spatial distribution of the plume shown in Fig. 1 was generated by the two-dimensional interpolation of SO_2 data measured along the flight track.

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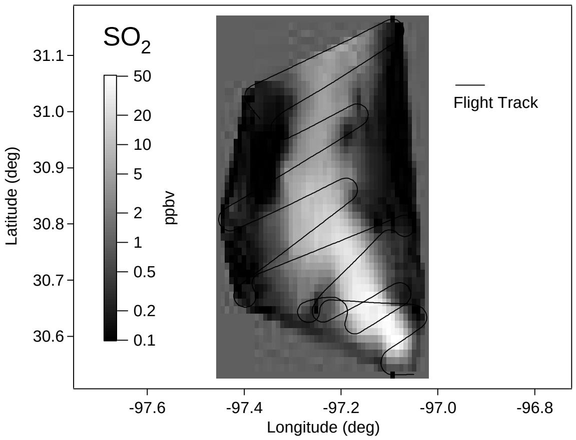

Figure 1 Plume visualization from SO_2 signal.

The meandering nature of the plume apparent in Fig. 1 is due to changes in the wind field over time. The edges of the plume are clearly identified as the concentration of SO_2 reached background levels (<0.2 ppbv) at the ends of each transect. Gridding of flight-track data, as shown in Fig. 1, also allows interpolation to span short periods of missing data arising from instrument zeros or calibrations.

The plume changes direction at a latitude of ~30.8 N. This is consistent with a change in wind direction roughly 2 hours earlier. Beyond this point the cross-plume integrated values of SO_2 and NO_y decrease markedly. It appears that after a plume age of ~2 hours, the transects are following only a portion of the original plume. Possible reasons for this include venting out of the boundary layer and/or shearing of the plume away from the sampling altitude. In the absence of vertical sampling data, the three-dimensional flow cannot be definitively characterized.

3.1 *Gaseous Species*

Vertical dispersion through diffusion and advection makes absolute quantitative analysis of components problematic. The consistent ratio of SO_2 to NO_y over a 4-h period as shown in Fig. 2 is used as one indication of measurement validity.

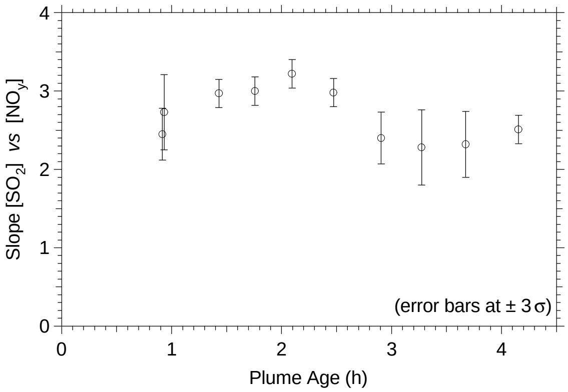

Figure 2 Relative plume composition over 4 h of transport.

SO_2 is removed from the plume by oxidation to sulfate, but at time scales longer than 4 h. NO_y is an aggregate measurement of all odd-nitrogen species. The relative concentrations of individual NO_y components change as NO is photochemically processed, ultimately forming HNO_3. Over 90% of the NO_x emitted is oxidized during the 4 hours studied. Loss of HNO_3 due to dry deposition is minimal in a 4-h period, thus the total NO_y in the plume should remain constant. As expected, the ratio of SO_2 to total NO_y is shown to be roughly constant over the age of the plume in Fig. 2. The weighted mean of SO_2 to NO_y is 2.7 (σ=0.3). This measured value is consistent with a molar ratio of 2.1 calculated from TABLE 1 given the variabilities introduced by the implementation of emissions controls, day-to-day boiler conditions and inventory uncertainties.

The ratio of NO_x to total NO_y decreases as the plume ages and is used as an indicator of the plume's photochemical age. For each transect, the slope of NO_x *vs* NO_y is plotted in Fig. 3.

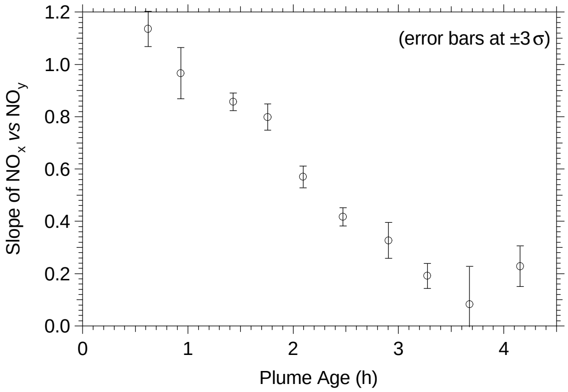

Figure 3 Photochemical processing consumes NO_x as a fraction of total NO_y.

The data of Fig. 3 indicate a loss rate for NO_x of ~0.5 h^{-1}. This is consistent with a loss rate of ~0.4 h^{-1} reported for a Nashville, TN power plant (Nunnermacker et al., 2001). If the loss of NO_x is due solely to the reaction of NO_2 with OH, then [OH] = 1.6×10^7 molec/cm^3. This value is roughly 3X [OH] calculated using a constrained steady state (CSS) photochemical box model (Kleinman et al., 2001). This discrepancy has several possible explanations. First, total processing time may be as much as 50% longer than indicated in Fig. 3, as wind speeds generally increase in the afternoon. Processing time was calculated using winds measured at the time of sampling. On this day, Continuous Air Monitoring Station (CAMS) sites in the region show a moderate increase in surface wind speed (TNRCC, 2001) in the hours prior to sampling. Second, appreciable photochemical processing occurred at times closer to solar noon than reflected in the model calculations which used the local sampling time. A third reason for the discrepancy may be the loss of NO_x through other channels involving organic nitrates and PAN. The relative magnitudes of these effects are being studied.

The O_3 production efficiency is an estimate of the O_3 produced per NO_x consumed (Trainer et al., 1993; Olszyna et al., 1994; Daum et al., 2000). At each transect, this is calculated from the slope of O_x *vs.* NO_z as shown in Fig. 4 (where $[O_x] = [O_3] + [NO_2]$).

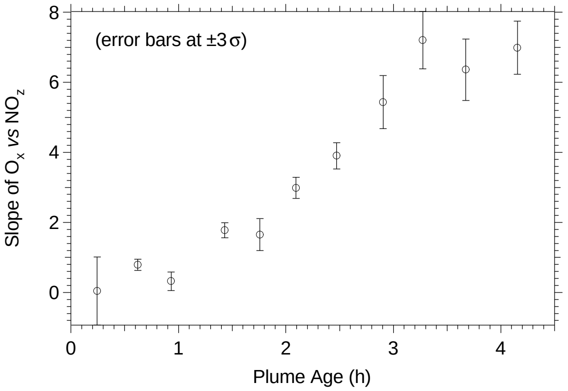

Figure 4 O_3 production efficiency increases with plume age.

The efficiency increases with plume age to a final level of ~6. This efficiency is consistent with that reported for a power plant in Nashville (Ryerson et al., 2001). Although both the production efficiency and the concentration of NO_x are quite high in this plume, the overall increase in O_3 is relatively modest. After 4 h, the O_3 concentration in the plume is ~15 ppbv above background levels. We ascribe the limited increase to dilution of the plume as it wafts downwind.

Three hydrocarbon samples were acquired in and around the plume region. Two different reactivities were calculated for each sample, a total reactivity for OH + VOC and a second reactivity including only biogenic hydrocarbons. As expected, the background samples exhibited low reactivities (k_{total}= 0.37 s^{-1}, $k_{biogenic}$=0.13 s^{-1}). The sole sample taken within the plume showed both elevated OH total reactivity (k_{total}= 8.2 s^{-1}), and elevated reactivity from species not associated with a power-plant plume ($k_{biogenic}$= 3.8 s^{-1}). The in-plume VOC sample was taken at a plume age of ~2h by which time appreciable dilution had reduced the NO_x concentration to 2-3 ppbv. The plume at this point has high VOC reactivity and low NO_x concentration leading to NO_x limited O_3 production. The presence of biogenic species in the plume cannot be explained by direct stack emissions. Entrainment of hydrocarbon-rich air near the surface is suggested as a possible explanation for this observation.

3.2 *Particulates*

The increase in particle concentrations was particularly striking. The absolute concentration of accumulation-mode particles (0.1 - 3 μm) increased by a factor of two over the course of the plume. Over this same distance, the concentration of SO_2 at the center line decreased by ~2 orders of magnitude. SO_2 is assumed to be a conservative tracer and its decrease in concentration is thereby a measure of dilution. When normalized for dilution, the relative concentration of accumulation-mode aerosol particles increases by more than a factor of 200 as shown in Fig. 5.

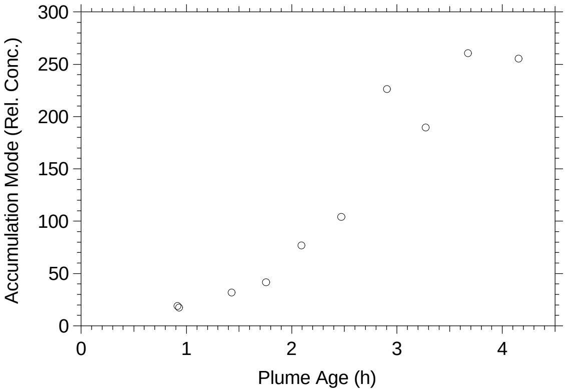

Figure 5 Increase in particles with plume age. Total accumulation mode (PCASP) normalized to SO_2 concentrations to remove the effects of dilution. Particles dominated by sizes < 0.4 μm.

4. CONCLUSIONS

Measurements made from the DOE G-1 aircraft were used to calculate the rate and efficiency of O_3 production downwind of an isolated, coal-fired power plant. The plume was transected 12 times at distances ranging to 65 km from its source (corresponding to an age of ~4 h assuming constant wind velocity). For NO_x, a loss rate of 0.5 h^{-1} was calculated. If reaction with OH was the sole loss mechanism, then an $[OH] = 1.6 \times 10^7$ molec/cm^3 is inferred, which is ~2 - 3X values calculated using a box model constrained by observations. Possible explanations for this discrepancy are discussed. O_3 production per molecule of NO_x approached 6-8 after the plume had aged >3h. Peak O_3 concentrations were 15 ppbv above background. Dilution appears to limit the peak O_3 concentration despite the high production efficiency. Hydrocarbon samples indicate high levels of VOC reactivity (~8 s^{-1}) in the plume. The number concentration of accumulation mode particles increases significantly with plume age indicating a rapid formation of aerosol mass.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Buzorius, G., Brechtel, F., Zelenyuk, A., Imre, D., Angevine, W.M., 2001: Observations of recent new particle formation in Houston during TexAQS-2000. *Fourth Conference on Atmospheric Chemistry*.

Amer. Meteor. Soc., Orlando, Fl, Poster P1.21.

Daum, P.H., Kleinman, L.I., Imre, D.G., Nunnermacker, L.J., Lee, Y.-N., Springston, S.R., Newman, L., 2000: Analysis of the processing of Nashville urban emissions on July 3 and July 18, 1995. *J. Geophys. Res.*, **105**, 9107-9119.

Gillani, N.V., Meagher, J.F., Valente, R.J., Imhoff, R.E., Tanner, R.L., Luria, M., 1998: Relative production of ozone and nitrates in urban and rural power plant plumes 1. Composite results based on data from 10 field measurement days. *J. Geophys. Res.*, **103**, 22593-22615.

Kleinman, L.I., Daum, P.H., Lee, Y.-N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2001: Sensitivity of ozone production rate to ozone precursors. *Geophys. Res. Lett.*, **28**, 2903-2906.

Lee, Y.-N., Zhou, X., Kleinman, L.I., Nunnermacker, L.J., Springston, S.R., Daum, P.H., Newman, L., Keigley, W.G., Holdren, M.W., Spicer, C.W., Young, V., Fu, B., Parrish, D.D., Holloway, J., Williams, J., Roberts, J.M., Ryerson, T.B., Fehsenfeld, F.C., 1998: Atmospheric chemistry and distribution of formaldehyde and several multioxygenated carbonyl compounds during the 1995 Nashville/Middle Tennessee Ozone Study. *J. Geophys. Res.*, **103**, 22449-22462.

Lee, Y.-N., Song, Z., Liu, Y., Daum, P., Weber, R., Orsini, D., Laulainen, N., Hubbe, J., Morris, V., 2001: Aerosol chemical characterization on board the DOE G1 aircraft using a Particle-into-Liquid Sampler (PILS) during the TexAQS 2000 Experiment. *Fourth Conference on Atmospheric Chemistry*. Amer. Meteor. Soc., Orlando, Fl, Paper 10.13.

Nunnermacker, L.J., Kleinman, L.I., Imre, D., Daum, P.H., Lee, Y.-N., Lee, J.H., Springston, S.R., Newman, L., Gillani, N., 2001: NO_y lifetimes and O_3 production efficiencies in urban and power plant plumes: Analysis of field data. *J. Geophys. Res.*, **105**, 9165-9176.

Olszyna, K.J., Bailey, E.M., Simonaitis, R., Meagher, J.F., 1994: O_3 and NO_y relationships at a rural site. *J. Geophys. Res.*, **99**, 14557-14563.

Ryerson, T.B., Trainer, M., Holloway, J.S., Parrish, D.D., Huey, L.G., Sueper, D.T., Frost, G.J., Donnelly, S.G., Schauffler, S., Atlas, E.L., Kuster, W.C., Goldan, P.D., Hubler, G., Meagher, J.F., Fehsenfeld, F.C., 2001: Observations of ozone formation in power plant plumes and implications for ozone control strategies. *Science*, **292**, 719-723.

TNRCC, 2001: Continuous Air Monitoring Site web site. http://www.tnrcc.state.tx.us/cgi-bin/monops/daily_summary.

Trainer, M., Parrish, D.D., Buhr, M.P., Norton, R.B., Fehsenfeld, F.C., Anlauf, K.G., Bottenheim, J.W., Tang, Y.Z., Wiebe, H.A., Roberts, J.M., Tanner, R.L., Newman, L., Bowersox, V.C., Meagher, J.F., Olszyna, K.J., Rodgers, M.O., Wang, T., Berresheim, H., Demerjian, K.L., Roychowdhury, U.K., 1993: Correlation of ozone with NO_y in photochemically aged air. *J. Geophys. Res.*, **98**, 2917-2925.

Zheng, J., Alaouie, A., Weinstein-Lloyd, J., Springston, S., Nunnermacker, L., Lee, Y.-N., Brechtel, F., Kleinman, L., Daum, P., 2001: Measurement of hydroperoxides during the Texas 2000 Air Quality Study. *Fourth Conference on Atmospheric Chemistry*. Amer. Meteor. Soc., Orlando, Fl, Poster P1.22.