2-16-2003

# Particle growth in urban and industrial plumes in Texas

Charles A. Brock
*National Oceanic and Atmospheric Administration*

Michael Trainer
*National Oceanic and Atmospheric Administration*

Thomas B. Ryerson
*National Oceanic and Atmospheric Administration*

J. Andrew Neuman
*National Oceanic and Atmospheric Administration*

David D. Parrish
*National Oceanic and Atmospheric Administration*

*See next page for additional authors*

## Recommended Citation

Brock, C. A., et al. (2003), Particle growth in urban and industrial plumes in Texas, J. Geophys. Res., 108, 4111, doi:10.1029/2002JD002746, D3.

## Authors

Charles A. Brock, Michael Trainer, Thomas B. Ryerson, J. Andrew Neuman, David D. Parrish, John S. Holloway, Dennis K. Nicks, Gregory J. Frost, Gerhard Hübler, Fred C. Fehsenfeld, J. Charles Wilson, J. Michael Reeves, Bernard G. Lafleur, Henrike Hilbert, Elliot L. Atlas, Stephen G. Donnelly Ph.D., Sue M. Schauffler, Verity R. Stroud, and Christine Wiedinmyer

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. D3, 4111, doi:10.1029/2002JD002746, 2003

# Particle growth in urban and industrial plumes in Texas

Charles A. Brock,[1] Michael Trainer, Thomas B. Ryerson, J. Andrew Neuman,[1]
David D. Parrish, John S. Holloway,[1] Dennis K. Nicks Jr.,[1] Gregory J. Frost,[1]
Gerhard Hübler,[1] and Fred C. Fehsenfeld[1]
Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA

J. Charles Wilson, J. Michael Reeves, Bernard G. Lafleur, and Henrike Hilbert
Department of Engineering, University of Denver, Denver, Colorado, USA

Elliot L. Atlas, Stephen G. Donnelly, Sue M. Schauffler, Verity R. Stroud,
and Christine Wiedinmyer
Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA

Received 11 July 2002; revised 17 September 2002; accepted 30 September 2002; published 7 February 2003.

[1] Particle size distributions and gas-phase particle precursors and tracer species were measured aboard an aircraft in the plumes downwind from industrial and urban sources in the vicinity of Houston, TX during the daytime in late August and early September 2000. Plumes originating from the Parish gas-fired and coal-fired power plant, petrochemical industries along the Houston ship channel, the petrochemical facilities near the Gulf coast, and the urban center of Houston were studied. Most of the particle mass flux advected downwind of Houston came from the industries and electrical utilities at the periphery of the city rather than from sources in the urban core. In $SO_2$-rich plumes that did not contain elevated concentrations of volatile organic compounds (VOCs), particle volume increased with increasing plume oxidation (age) at a rate consistent with condensation and neutralization of the gas-phase oxidation products of $SO_2$. In plumes that were rich in both $SO_2$ and VOCs, observed particle growth greatly exceeded that expected from $SO_2$ oxidation, indicating the formation of organic particulate mass. In plumes that were enhanced in VOCs but not in $SO_2$, and in the plume of the Houston urban center, no particle volume growth with increasing plume oxidation was detected. Since substantial particle volume growth was associated only with $SO_2$-rich plumes, these results suggest that photochemical oxidation of $SO_2$ is the key process regulating particle mass growth in all the studied plumes in this region. However, uptake of organic matter probably contributes substantially to particle mass in petrochemical plumes rich in both $SO_2$ and VOCs. Quantitative studies of particle formation and growth in photochemical systems containing nitrogen oxides ($NO_x = NO + NO_2$), VOCs, and $SO_2$ are recommended to extend those previously made in $NO_x$−VOC systems. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* aerosols, particles, plumes, oxidation, urban, industrial

**Citation:** Brock, C. A., et al., Particle growth in urban and industrial plumes in Texas, *J. Geophys. Res.*, *108*(D3), 4111, doi:10.1029/2002JD002746, 2003.

## 1. Introduction

[2] The metropolitan area of Houston, TX is home to more than four million people and the largest grouping of petrochemical industrial plants in the United States. During the summer, emissions of $NO_x$ and volatile organic compounds (VOCs) in combination with intense solar radiation and appropriate meteorological conditions lead to ozone concentrations that frequently exceed United States regulatory standards, sometimes by more than a factor of 2. The Houston metropolitan area may also be at risk of exceeding the proposed standards for the concentration of dry mass of aerosol particles with diameters <2.5 μm ($PM_{2.5}$). The sources of $PM_{2.5}$ in the Houston area are believed to include the gas-phase photooxidation of $SO_2$ and reactive organic

---

[1] Also at Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA.

0148-0227/03/2002JD002746

compounds, followed by condensation of the lower vapor pressure oxidation products. Other sources of $PM_{2.5}$ in the Houston area include dispersed, fixed urban sources such as light industry, cooking, and combustion, mobile sources such as diesel soot emissions and roadway-generated particles, and sea spray and windblown dust. A quantitative understanding of the relationship between emissions of primary particles and precursor gases and downwind aerosol properties is needed to develop effective mitigation strategies.

[3] The primary goal of the Texas Air Quality Study (TexAQS) 2000 was to improve understanding of the chemical and meteorological causes of ozone exceedance episodes in the Houston–Galveston and Dallas metropolitan areas [*Kleinman et al.*, 2002; *Wert et al.*, 2003; T. B. Ryerson et al., Effect of co-located petrochemical industrial emissions of reactive alkenes and $NO_x$ on tropospheric ozone formation, submitted to *Journal of Geophysical Research*, 2002, hereinafter referred to as Ryerson et al., submitted manuscript, 2002]. A further goal of the study was to investigate the sources and characteristics of aerosol particles in the study region. Airborne and surface observations, as well as modeling and forecasting tools, were used to achieve these program goals.

[4] From 16 August to 13 September 2000 measurements of particulate and gas-phase pollutants and tracer species were made on the Lockheed Electra aircraft, leased by the National Oceanic and Atmospheric Administration (NOAA) from the National Center for Atmospheric Research (NCAR), in a variety of power plant, petrochemical, and urban plumes in eastern Texas and Oklahoma. These flights, and those of other research aircraft, were supported by a network of Houston-area ground-based sites measuring photochemically active compounds, tracer species, photochemical oxidation products, and radiative and meteorological variables. Meteorological parameters were measured from a network of microwave wind profilers, and two additional sites were extensively instrumented with a variety of instruments for measuring gas-phase concentrations and the microphysical, optical, and chemical properties of aerosol particles. Meteorological and chemical modeling and efforts to refine emissions inventories were also integral components of the TexAQS 2000 program. This work will focus on reporting and interpreting particle size distribution measurements obtained aboard the Electra in plumes from specific sources in the Houston metropolitan area under meteorological conditions typified by relatively steady, moderate wind speeds. The major sources of enhanced particle volume and number are determined, their relative magnitudes are quantified, and the processes leading to particle production in this region in summertime are discussed.

## 2. Instruments and Methods

### 2.1. Particle Instruments

[5] Data collected aboard the Electra aircraft from a five-channel condensation particle counter (CPC) [*Brock et al.*, 2000], a laser optical particle counter (OPC) [*Jonsson et al.*, 1995], and a white-light OPC were combined to determine dry particle size distributions from 0.004 to 8 μm diameter with 1-s time resolution. Performance and calibration of the CPC and laser OPC, which together measure particle size distributions from 0.004 to 1.0 μm, are described by *Brock et al.* [2002]. The size distribution of particles with diameters from 0.4 to 8 μm was measured with a modified Climet 208A white-light OPC (Climet Instruments, Redlands, CA).

[6] Before, during, and after the TexAQS 2000 field project, the three particle instruments were calibrated with nearly monodisperse $(NH_4)_2SO_4$ particles with diameters from 0.05 to 1.6 μm. These particles were generated from an aqueous solution using an atomizer. The aerosol flow was dried and introduced into a cylindrical differential mobility analyzer (DMA) designed and built at the NOAA Aeronomy Laboratory. The particles were exposed to a 20 mCi bipolar ion source and classified within the DMA by electrical mobility. The nearly monodisperse particle stream was then introduced into the sampling plumbing at the location where the inlet sample line entered the aircraft fuselage. The concentration of calibration particles introduced at the inlet was determined with a separate CPC (Model 3760, TSI Inc., St. Paul, MN). Additionally, the size response of the Climet OPC, but not its counting efficiency, was determined for particles with diameters from 1.6 to 8 μm using polystyrene spheres and glass beads. Further calibrations of the five-channel CPC were also performed as described by *Brock et al.* [2000] prior to TexAQS 2000 using particles with diameters from 0.004 to 0.8 μm in diameter.

### 2.2. Low-Turbulence Inlet (LTI)

[7] The aerosol instruments sampled ambient air through a new inlet that uses active boundary layer suction to virtually eliminate turbulence while decelerating the 100 m $s^{-1}$ airflow to ~6 m $s^{-1}$ (Figure 1). This LTI was developed at the University of Denver. The LTI was mounted on the forwardmost window just aft of the cockpit and forward of upwash flow around the wing root area. The enhanced efficiencies with which particles of different sizes are transmitted through the LTI has been estimated by numerical simulation of particle trajectories within the external flow approaching the inlet tip, as well as within the decelerating and diverging internal flow within the inlet. Calculated enhancements in the sample airstream relative to the ambient air were negligible for particles with aerodynamic diameters <1 um, and factors of approximately 1.1, 1.3, and 1.7 for particles with aerodynamic diameters of 3, 5, and 8 μm, respectively. The data were corrected for these effects. After exiting the LTI, the sample airstreams were extracted from the center of the LTI flow and transported in stainless steel tubing distances <3 m to each of the instruments. The aerosol sample streams to the two OPCs were dried to <20% relative humidity with Nafion diffusion dryers.

### 2.3. Uncertainty Analysis

[8] A Monte Carlo simulation was used to propagate the random uncertainties due to calibration of particle size and concentration, and to in-flight measurement of flow rate, temperature, and pressure, through the numerical data processing algorithms, assuming typical background conditions measured during TexAQS 2000. The resulting estimated measurement precision for particle number is ±15% for 1-s data, while that for particle volume is ±34% with a sensitivity of 0.4 $\mu m^3$ $cm^{-3}$ for 1-s data. These precisions vary somewhat depending on the measured size distribution due to the differing accuracies of the three particle sizing instruments. Possible biases, due mainly to

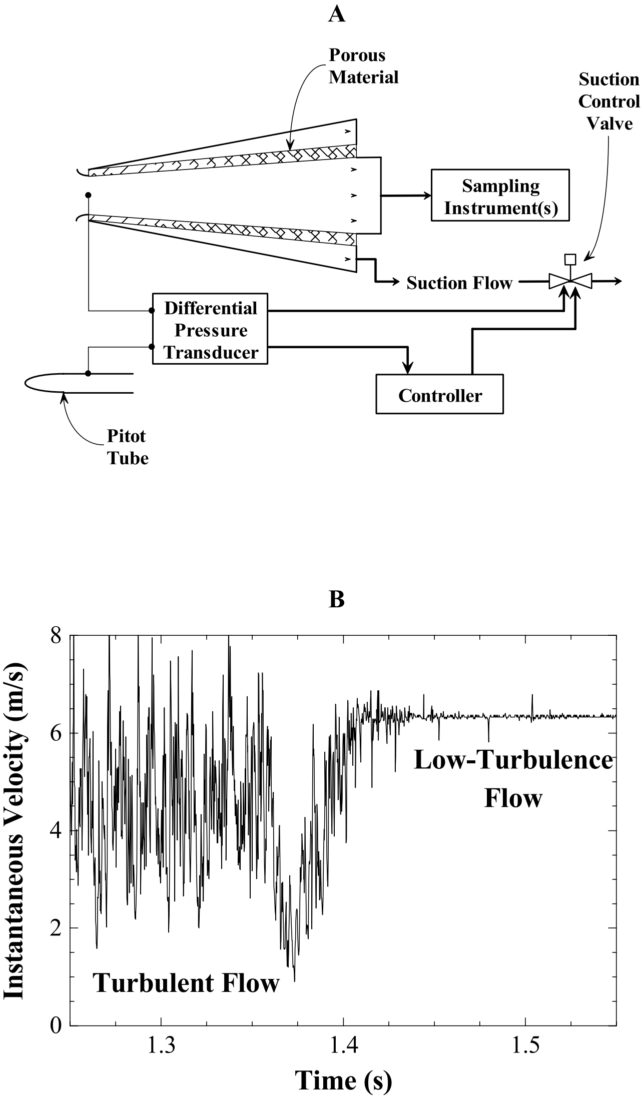

**Figure 1.** (a) Schematic diagram of the LTI used on the Electra aircraft during TexAQS 2000. Turbulent air is removed by suction through a porous material as it develops near the inlet wall, leaving a laminar core of air for the sampling instruments. Size-dependent particle enhancements occur where the sample flow decelerates and diverges. (b) Turbulence levels in the core sample flow at the diffuser exit as the suction flow is turned on.

uncertainties in particle refractive index and to uncharacterized sampling losses, are estimated to be <10% and <35% for particle number and volume concentrations, respectively. All particle parameters are reported in quantity per cubic centimeter of air at standard temperature and pressure (1013 hPa and 273.2 K).

### 2.4. Additional Measurements

[9] The analysis presented here makes use of measurements of photochemically reactive gases and tracer compounds to identify plumes, estimate dilution, and evaluate the mass budget of condensable compounds. These gas-phase measurements include NO, $NO_2$, $NO_y$, $O_3$, $SO_2$, CO, $CO_2$, and $HNO_3$ [*Ryerson et al.*, 1998; *Neuman et al.*, 2002]. All of these compounds were measured continuously with demonstrated instrumental response times of 1 s or faster (except for $SO_2$, with a response time of ~3 s) and accuracy and precision quantified by in-flight calibration and zeroing. Generally, the uncertainty of the $SO_2$ measurement was within ±10% for $SO_2$ levels well above the detection limit of approximately 0.5 ppbv. However, for the data on the two flights presented here this accuracy was sporadically degraded by short-term transients of up to several ppbv due to operational difficulties with the in-flight calibration system. These difficulties are considered in assigning the confidence limits to the results of the following analyses. Uncertainties for $NO_y$ and $HNO_3$, which are used quantitatively in this analysis, are ±(100 pptv + 10%) and ±(130 pptv + 10%), respectively. Individual whole-air canister samples were collected periodically over ~8-s intervals and were subsequently analyzed by chromatographic techniques [*Heidt et al.*, 1989; *Schauffler et al.*, 1999]. Analyzed species included alkyl nitrate compounds, alkanes, alkenes, alkynes, and several aromatic compounds with known secondary organic aerosol yields. Meteorological and navigational parameters reported by the Research Aviation Facility of NCAR (http://raf.atd.ucar.edu/Bulletins/bulletin9.html) were also used in the analysis.

## 3. Observations

[10] In this report, particle formation and growth in plumes observed on 27 and 28 August 2000 downwind of four clearly identifiable sources will be discussed. These sources are (Figure 2): (1) the Houston ship channel/west Galveston Bay area, containing multiple large petrochemical complexes and shipping and rail hubs within a low-density urban setting; (2) the Parish power plant, a coal-fired and natural gas-fired electric generation facility with no $SO_2$ gas scrubbers and located in open farmland southwest of Houston; (3) the Houston urban core, dominated by mobile tailpipe and dispersed local emissions; and (4) isolated large petrochemical complexes south of Houston.

[11] On both 27 and 28 August 2000, continuous southerly winds ranging from 3 to 6 m $s^{-1}$ were reported within the planetary boundary layer (PBL) throughout the Houston study area. The mid-PBL wind velocities on these days will be approximated as 4.5 ± 1 m $s^{-1}$. The relative constancy, direction and speed of the wind make it possible to readily identify the sources of many plumes, to track their locations >60 km downwind, and to accurately determine, from downwind distance, the time since the measured plume parcel was emitted, or plume age. The $NO_x$–$O_3$–VOC photochemistry within plumes from different sources on these days is discussed in detail by Ryerson et al. (submitted manuscript, 2002). Because of the continuous advection and dilution, the mixing ratios of $O_3$ at ground-based monitoring sites in the Houston metropolitan area did not exceed regulatory criteria on either 27 or 28 August nor were such mixing ratios observed onboard the Electra. There were no substantial unusual emissions, or upsets, of gas-phase or particulate pollutants from industries in the area on either day according to emissions data reported to and provided by the Texas Natural Resource Conservation Commission (TNRCC). Thus, these days appear to be typical of moderately polluted, well-ventilated, summertime conditions in the Houston metropolitan area. While these conditions do not

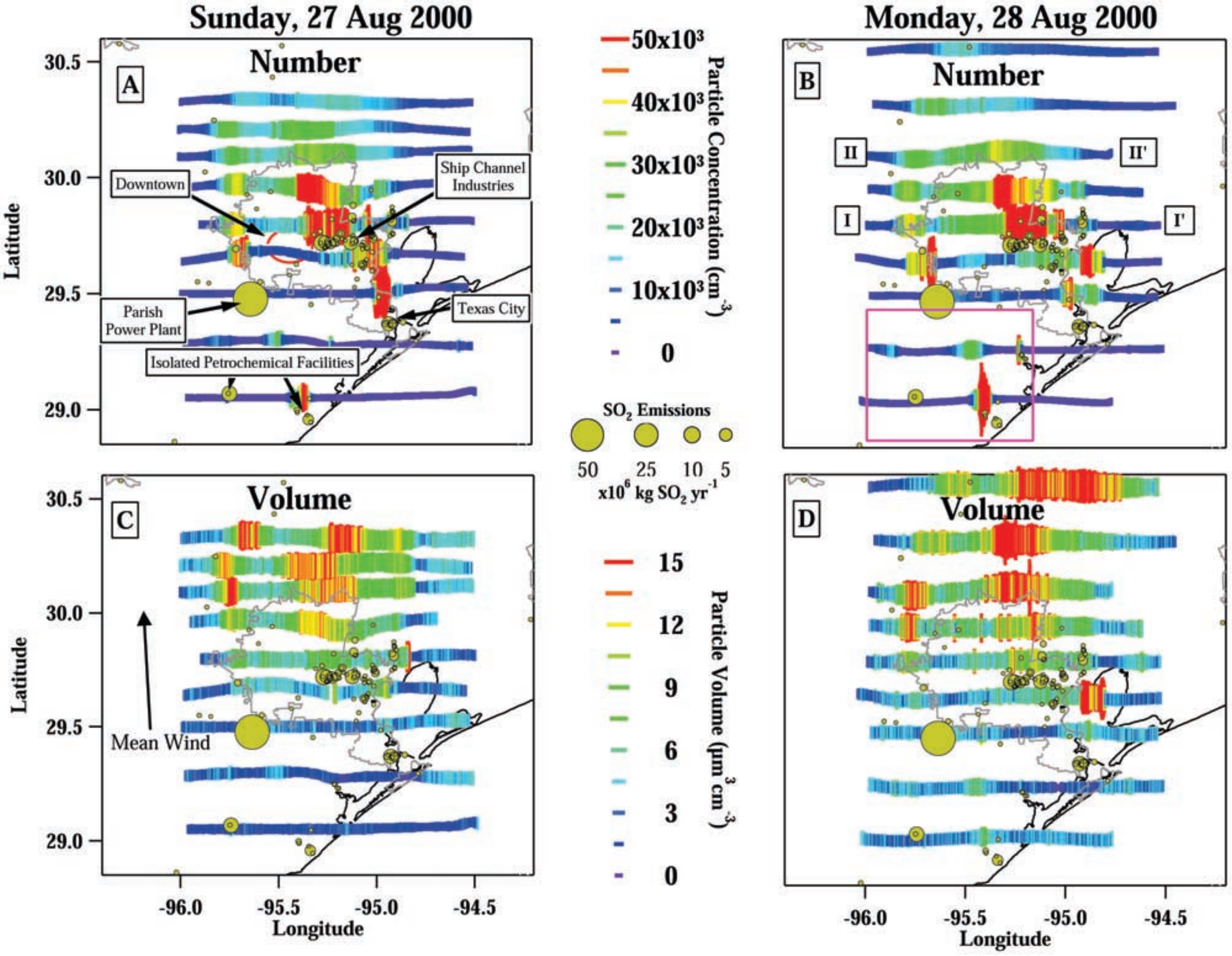

**Figure 2.** Map of the Houston area with flight track of the NCAR Electra aircraft during constant-latitude transects (approximately perpendicular to the prevailing southerly wind) within the PBL. The transects are color and size coded by particle number (a and b) and volume (c and d) concentration enhancements above background. (a) and (c) For 27 August 2000 and (b) and (d) for 28 August. Point sources of $SO_2$ are indicated by the circles, sized by annual emissions according to the 1999 TNRCC inventory. The Houston metropolitan area is outlined in gray, while the Texas coastline is in black. Time series data from the transects indicated by I-I′ and II-II′ in (b) are shown in Figure 3. Area indicated by the magenta box in (b) is shown in Figure 4.

result in concentrations of pollutants in excess of regulatory standards, they provide a relatively simple meteorological scenario in which to contrast the effects of different types of emissions on particle formation and growth. On 27 August, a Sunday, particle emissions from urban diesel vehicle traffic were probably significantly lower than on 28 August [e.g., *Dreher and Harley*, 1998; *Marr et al.*, 2002]. In contrast, inventoried emissions from stationary industrial sources were not substantially different on the two days.

[12] The Electra flew E-W transects approximately perpendicular to the southerly wind within the PBL at a typical height of 0.6–0.7 km above the surface on both days (Figure 2). The transects began well upwind of the Houston metropolitan area, proceeded over and downwind of Houston, and concluded >60 km downwind of the urban core. At the eastern or western termini of some of the transects, the aircraft climbed to determine the height of the PBL. Assuming approximately constant wind speed, as observed aboard the Electra over the course of the ~6-hour flights and from surface profiler sites, the furthest transect downwind of the Houston urban core and ship channel area corresponded to a plume age of >4 hours on each day. Because of the wind direction, identifiable plumes from the Parish coal-fired and gas-fired power plant, the downtown urban core of Houston, and the petrochemical industries located along the Gulf coast and the Houston ship channel were advected side-by-side to the north (Figure 2), with some merging of the plumes with increasing downwind distance.

### 3.1. Houston Ship Channel Industrial Complex

[13] The Houston ship channel is a narrow waterway extending eastward from downtown Houston to Galveston Bay (Figure 2). Extensive petrochemical complexes and shipping and rail hubs line both sides of the waterway. Colocated with the industries are fossil fuel-fired electrical generation and process heat facilities, some of which emit

**Table 1.** Plume Distances, Approximate Ages, and Mean and Maximum Number and Volume Concentrations Measured Downwind of the Parish Power Plant, the Houston Urban Core, and the Houston Ship Channel and in Background Air Southwest of Houston[a]

| Source | Date | Distance (km) | Plume Age (hours) | $N_{mean}$ ($\times 10^4$ cm$^{-3}$) | $N_{max}$ ($\times 10^4$ cm$^{-3}$) | $V_{mean}$ ($\mu m^3$ cm$^{-3}$) | $V_{max}$ ($\mu m^3$ cm$^{-3}$) |
|---|---|---|---|---|---|---|---|
| Background | 27 August | NA[b] | NA | ~0.3 | NA | ~7 | NA |
| | 28 August | NA | NA | ~0.3 | NA | ~9 | NA |
| Ship Channel | 27 August | 8 | 0.5 | 3.5 | 8.0 | 10.7 | 16.3 |
| | | 27 | 1.7 | 2.0 | 4.5 | 11.0 | 18.1 |
| | | 44(a) | 2.7 | 2.1 | 3.6 | 14.3 | 22.4 |
| | | 44(b) | 2.7 | 1.3 | 2.5 | 10.2 | 14.5 |
| | | 56 | 3.5 | 1.2 | 2.1 | 12.3 | 17.7 |
| | | 69 | 4.3 | 1.4 | 2.1 | 14.9 | 23.7 |
| | 28 August | 8 | 0.5 | 4.1 | 12 | 14.3 | 21.0 |
| | | 8 | 0.5 | 3.6 | 8.3 | 12.5 | 28.6 |
| | | 24 | 1.5 | 3.2 | 6.8 | 16.0 | 23.4 |
| | | 44 (a) | 2.7 | 2.2 | 4.1 | 17.9 | 43.4 |
| | | 44 (b) | 2.7 | 2.3 | 4.8 | 16.6 | 31.4 |
| | | 66 | 4.1 | 1.1 | 2.0 | 19.2 | 38.1 |
| | | 92 | 5.7 | 0.5 | 0.8 | 17.3 | 26.6 |
| Parish | 27 August | 23 | 1.4 | 3.4 | 6.3 | 9.0 | 12.2 |
| | | 36 | 2.2 | 3.0 | 4.5 | 10.0 | 14.5 |
| | | 56 | 3.5 | 2.0 | 3.6 | 12.1 | 18.7 |
| | | 71(a) | 4.4 | 1.4 | 2.3 | 12.9 | 22.9 |
| | | 71(b) | 4.4 | 1.5 | 2.2 | 10.5 | 13.9 |
| | | 83 | 5.1 | 1.1 | 2.1 | 11.2 | 18.8 |
| | | 96 | 5.9 | 1.1 | 1.8 | 13.2 | 22.1 |
| | 28 August | 18 | 1.1 | 4.2 | 12 | 11.8 | 14.3 |
| | | 38(a) | 2.3 | 2.4 | 4.2 | 13.4 | 19.1 |
| | | 38(b) | 2.3 | 2.0 | 3.3 | 13.4 | 17.5 |
| | | 54 | 3.3 | 2.7 | 3.6 | 17.0 | 23.7 |
| | | 69(a) | 4.3 | 1.9 | 2.9 | 16.9 | 24.6 |
| | | 69(b) | 4.3 | 1.8 | 2.7 | 16.6 | 26.5 |
| | | 93 | 5.7 | 2.1 | 2.6 | 15.8 | 20.3 |
| | | 120 | 7.4 | 1.6 | 2.0 | 15.8 | 21.5 |
| Urban Core | 27 August | ~8 | ~0.5 | 1.6 | 2.7 | 9.8 | 12.1 |
| | | 27 | 1.7 | 2.1 | 2.7 | 10.0 | 12.4 |
| | | 44 (a) | 2.7 | 1.8 | 2.2 | 9.8 | 15.1 |
| | | 44 (b) | 2.7 | 1.8 | 2.4 | 11.5 | 16.9 |
| | | 56 | 3.5 | 1.7 | 2.0 | 10.0 | 13.1 |
| | | 69 | 4.3 | 1.4 | 2.2 | 10.2 | 12.9 |
| | 28 August | ~8 | ~0.5 | 2.6 | 3.7 | 12.1 | 20.4 |
| | | ~8 | ~0.5 | 1.9 | 3.5 | 11.6 | 18.0 |
| | | 24 | 1.5 | 2.9 | 22 | 13.4 | 22.9 |
| | | 44 (a) | 2.7 | 2.3 | 2.9 | 13.6 | 16.8 |
| | | 44 (b) | 2.7 | 2.2 | 3.8 | 13.8 | 19.2 |
| | | 66 | 4.1 | 2.0 | 2.6 | 15.6 | 20.7 |
| | | 92 | 5.7 | 1.3 | 2.0 | 14.8 | 22.2 |

[a] See text for uncertainties.

[b] NA: Not applicable.

substantial amounts of $SO_2$ and $NO_x$. The collocation of $NO_x$ and VOC emissions, combined with intense insolation and light winds, can result in extremely high photochemical reactivity and rapid and efficient ozone formation [*Ryerson et al.*, 2001; *Neuman et al.*, 2002; *Kleinman et al.*, 2002].

[14] On both 27 and 28 August, the individual and merged plumes from industries in the ship channel region were crossed at five different downwind distances (Table 1 and Figure 2). The plumes were distinguished by differing concentrations and ratios of the tracer species $NO_y$, $CO_2$, CO, and $SO_2$, the photochemical reaction product $O_3$, and the number and volume concentrations of particles (Figure 3). As an example, in the transect made at 8 km downwind of the ship channel on 28 August, individual plumes from several separate sources within the ship channel could be discerned, as could the urban plume and that from the Parish power plant (Figure 3a). By 44 km downwind of the ship channel, boundary layer mixing had merged the multiple individual plumes from the ship channel to form a single coalesced plume with more uniform characteristics (Figure 3b). Also on this day, the plume from the Texas City industrial complex southeast of Houston could initially be identified over Galveston Bay (Figures 2b and 2d), but by 8 km downwind of the ship channel it was not possible to use the tracer measurements to discern the Texas City plume from the merged plume from the various ship channel industries. Further downwind, the western edge of the ship channel plume gradually blended with that from the Houston urban core, which was identifiable by elevated mixing ratios of CO from mobile sources and a relative lack of $SO_2$ and $CO_2$ from industrial sources.

[15] Particle volume concentrations within the plume from the ship channel industries increased substantially with increasing downwind distance, despite the dilution of the plume by entrainment of air with lower particle loadings from the west and east (Table 1 and Figures 2 and 3). On 28

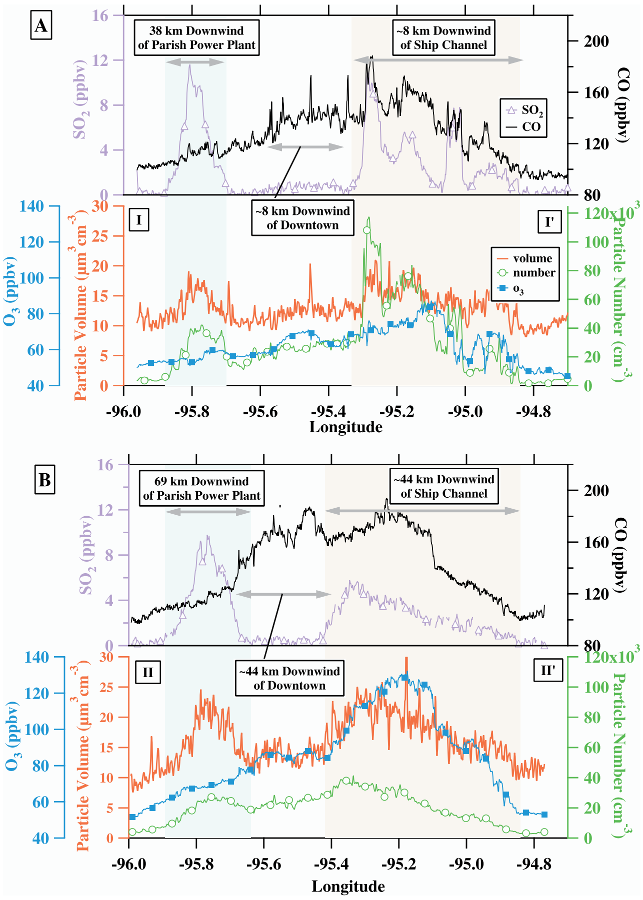

**Figure 3.** Measurements of $SO_2$, CO, $O_3$, and particle number and volume concentrations on 28 August 2000 downwind of the Parish power plant (shaded blue), the Houston urban core (unshaded), and the Houston ship channel industries (shaded peach). (a) Transect I-I′ on Figure 2, just downwind of the urban center and ship channel. (b) Transect II-II′ on Figure 2, further downwind at the northern edge of the Houston metropolitan area. Substantial increases in particle volume above background are clearly associated with the power plant and industrial plumes, indicated by enhanced $SO_2$ mixing ratios.

August, the peak enhancement above background in dry particle volume concentration was >17 µm$^3$ cm$^{-3}$ near the center of the plume at a distance of 92 km downwind. Assuming a dry particle density of ∼1.5 g cm$^{-3}$, this corresponds to an enhancement above background in particle mass concentration of >25 µg m$^{-3}$. The value, measured under well-ventilated meteorological conditions, may be compared with the proposed annual and 24-hour $PM_{2.5}$ national ambient air quality standards of 15 and 65 µg m$^{-3}$, respectively. Particle volume enhancements exceeding 12 µm$^3$ cm$^{-3}$ above background were found for >45 km along the flight path in this furthest transect >90 km downwind of the ship channel (Figure 2d). This substantial horizontal dispersion of enhanced particle volume concentrations illustrates the potential influence of the Houston-area petrochemical industries on regional air quality.

[16] In contrast to particle volume concentrations, particle number concentration maximized close to the sources (Table 1 and Figures 2a and 2b). The aerosol in these regions of high concentration was dominated by particles with diameters <0.05 µm which are unlikely to have been directly emitted but rather were formed from condensation from the gas phase [e.g., *Brock et al.*, 2002]. The highest particle concentrations were found in $SO_2$-rich portions of the ∼0.5-hour-old ship channel plume, indicating recent gas-to-particle formation from the oxidation products of $SO_2$. These observations are consistent with many earlier laboratory and field observations indicating that the oxidation products of $SO_2$ are critically important in the formation of new particles in polluted air, even when VOC concentrations are quite high [e.g., *Flagan et al.*, 1991; *Hoppel et al.*, 2001]. The rapid decrease in particle number concentration in the ship channel plume with increasing plume age is qualitatively consistent with expected high rates of coagulation of these nucleation-mode particles with themselves and with larger particles, combined with dilution by air with relatively low particle concentrations.

### 3.2. Parish Power Plant

[17] The W.A. Parish power plant is a large coal-fired and natural gas-fired electrical generation facility located southwest of the Houston metropolitan area. The plant emits approximately 5.7 × 10$^7$ kg yr$^{-1}$ of $SO_2$ and 3.2 × 10$^7$ kg yr$^{-1}$ of $NO_x$ (as $NO_2$). Compared with other Houston-area sources, it is not a large direct emitter of particulate matter or VOCs. On both 27 and 28 August 2000, the plume from the Parish power plant was advected northward over agricultural and suburban areas at the western edge of the Houston metropolitan area. On 27 August, transects were made perpendicular to the well-mixed plume at six downwind distances (Table 1 and Figures 2a and 2c) corresponding to approximate plume ages from 1.4 to 5.9 hours. On 28 August, transects across the well-mixed plume were also made at six distances, corresponding to approximate plume ages from 1.1 to 7.4 hours (Table 1 and Figures 2b and 2d).

[18] Although the photochemical evolution of the Parish plume was very similar on both 27 and 28 August, greater downwind coverage of the plumes by the aircraft makes the 28th better for in-depth study. By 38 km (2.3 hours) downwind distance (plume age) on 28 August, the eastward edge of the Parish plume had begun to blend with that from the Houston urban area (Figure 3a). By this time, peak enhancements above background in particle volume concentration of ∼8 µm$^3$ cm$^{-3}$ were observed within the Parish plume, while particle number concentrations reached ∼4 × 10$^4$ cm$^{-3}$ (Table 1). At 69 km (4.3 hours) distance from the power plant, the particle volume enhancement above background had reached its observed maximum of ∼16 µm$^3$ cm$^{-3}$. As in the plume from the ship channel, particle number concentrations, dominated by particles with diameters <0.05 µm produced from gas-to-particle conversion, reached a maximum close to the source and decreased rapidly with increasing plume age.

### 3.3. Houston Urban Core

[19] On both 27 and 28 August, the plume from the urban core of Houston was advected downwind between the plumes of the Parish power plant to the west and the petrochemical industries of the ship channel to the east (Figures 2 and 3). The urban area source is dominated by emissions from motor vehicles, which produce substantial

quantities of CO and $NO_x$, very little $SO_2$, and relatively small amounts of $CO_2$ compared with industrial point sources. Compared with the large increases in particle number and volume concentration observed in the plumes from the Parish power plant and the ship channel petrochemical industries, only relatively modest enhancements in particle volume and number above background were found within the Houston urban plume on either day (Table 1). There was no detectable systematic change in particle volume with age of the plume from the Houston urban center, suggesting that a large fraction of the particle mass was directly emitted and that rates of gas-to-particle conversion were low. Mean particle volume concentrations were $3-5$ $\mu m^3$ $cm^{-3}$ higher in the urban plume compared with background concentrations. On 27 August, a Sunday, particle volume enhancements above background were slightly lower (Table 1), perhaps reflecting a decrease in particle generation from vehicular traffic compared with the following workday. Mean particle number concentrations measured just downwind of the downtown core were a factor of $\sim$2 lower than those measured immediately downwind of the ship channel industries and the Parish power plant.

### 3.4. Geographically Isolated Refineries

[20] On both 27 and 28 August, the Electra sampled plumes from individual petrochemical complexes located on the coastal plain south of Houston near the town of Freeport, Texas (Figure 4). These industries are similar to those found along the Houston ship channel. However, because the Freeport-area plants are geographically isolated, with no significant upwind anthropogenic particle sources, they afford the opportunity to examine particle formation and growth in the absence of emissions from other nearby point, area, and mobile sources. Two discrete plumes have been identified as originating from two specific clusters of facilities: near the Dow Chemical Freeport B plant (Dow) and near the Gulf Chemical and Metallurgical plant (Gulf). The Dow facility, a group of plastics, epoxy, and hydrocarbon processing plants, combined with the nearby BASF Corp. plant, emit $13 \times 10^6$ kg $yr^{-1}$ of $NO_x$ and $2.4 \times 10^5$ kg $yr^{-1}$ of $SO_2$, while the Gulf plant, a catalyst manufacturing facility, together with two nearby facilities operated by Dow, emit less than half as much $NO_x$ and about 10 times more $SO_2$. These differences in $NO_x$ and $SO_2$ emissions and the >6 km spatial separation of the plants allow unambiguous identification of the plumes from the clusters of facilities during the flight transects (Figure 4).

[21] The plumes from these and other nearby plants were sampled during two downwind transects on 28 August, corresponding to approximate times since emission of 0.6 and 2.0 hours for the Dow plant and 0.8 and 2.2 hours for the Gulf plant (Figure 4). The further transect showed increases in particle volume concentration of $\sim$2 $\mu m^3$ $cm^{-3}$ above the surrounding background only in the plume of the Gulf plant, which is relatively rich in $SO_2$. Particle number concentration was also substantially enhanced above background in the relatively $SO_2$-rich Gulf plume, and not in the $SO_2$-poor Dow plume. These findings are very similar to those reported in industrial and power plant plumes in the south central United States, in which substantial increases in particle mass concentration above background are found only in plumes from large sources of $SO_2$ [*Brock et al.*, 2002].

[22] The gas-phase photochemical reactivity of these isolated petrochemical plumes has been documented by Ryerson et al. (submitted manuscript, 2002). The plumes have substantial and similar OH reactivity due in large part to the coemission of reactive alkenes with $NO_x$. Thus, if $SO_2$ is present, the oxidation of $SO_2$ by OH and the subsequent formation of condensable sulfate compounds is expected to proceed readily [*Meng et al.*, 1997; *Hoppel et al.*, 2001]. Measurements of the concentration of VOCs in the Dow and Gulf plumes indicate that both contain concentrations of aromatics and other VOC compounds well above background values (Table 2). Smog chamber studies using $NO_x$–VOC mixtures and concentrations atypical of those found in these petrochemical plumes have demonstrated that aromatic compounds can oxidize in photochemically active environments to produce particulate organic material [e.g., *Odum et al.*, 1996, 1997a, 1997b]. However, among plumes from the isolated petrochemical facilities studied here, particle volume growth above background was detected in only the Gulf plume, which contained $SO_2$. Oxidation and condensation of organic material in the $SO_2$-poor Dow plume was insufficient to produce detectable enhancements in particle volume in the conditions measured.

## 4. Analysis

### 4.1. Particle Fluxes

[23] The relative contribution of each of the major sources of particle volume in the Houston area cannot be determined from the observed concentrations alone because of the different spatial extent of the plumes. To account for varying plume dispersion, the observed enhancements above background were integrated across the width of the plume following the study of *Ryerson et al.* [1998]. Background values were determined for each transect from measurements west of the Parish power plant plume and east of the ship channel plume. The horizontal fluxes of particle volume and number were then calculated for the plumes from Parish power plant, the Houston urban core, and the ship channel industries, using an average wind velocity of 4.5 ± 1 m $s^{-1}$. To estimate the fluxes, the plume is assumed to be vertically well mixed throughout the PBL. The PBL height has been estimated as a function of geographic position and time of day based on vertical profiles made by the Electra aircraft at the termini of some of the transects, on data from a network of meteorological microwave profilers, and on vertical profiles of aerosol backscatter from a lidar system [*Senff et al.*, 1998] operated aboard a DC-3 aircraft in the same region on 28 August. The height of the PBL increased significantly northward and westward of the coastline on both days as the marine air was advected toward the north and became modified by surface heat fluxes. The PBL heights used in the flux estimates ranged from 1.3 to 2.5 km.

[24] Aerosol particles produced from the Houston ship channel industries dominated the particle number and volume mass fluxes downwind of the Houston metropolitan area (Figure 5). At the furthest downwind distances, the particle volume flux from the ship channel industries exceeded that from the Parish power plant by a factor of $\sim$4. The particle volume fluxes within the plume from the Houston urban core are difficult to estimate because there were only modest enhancements in particle volume above

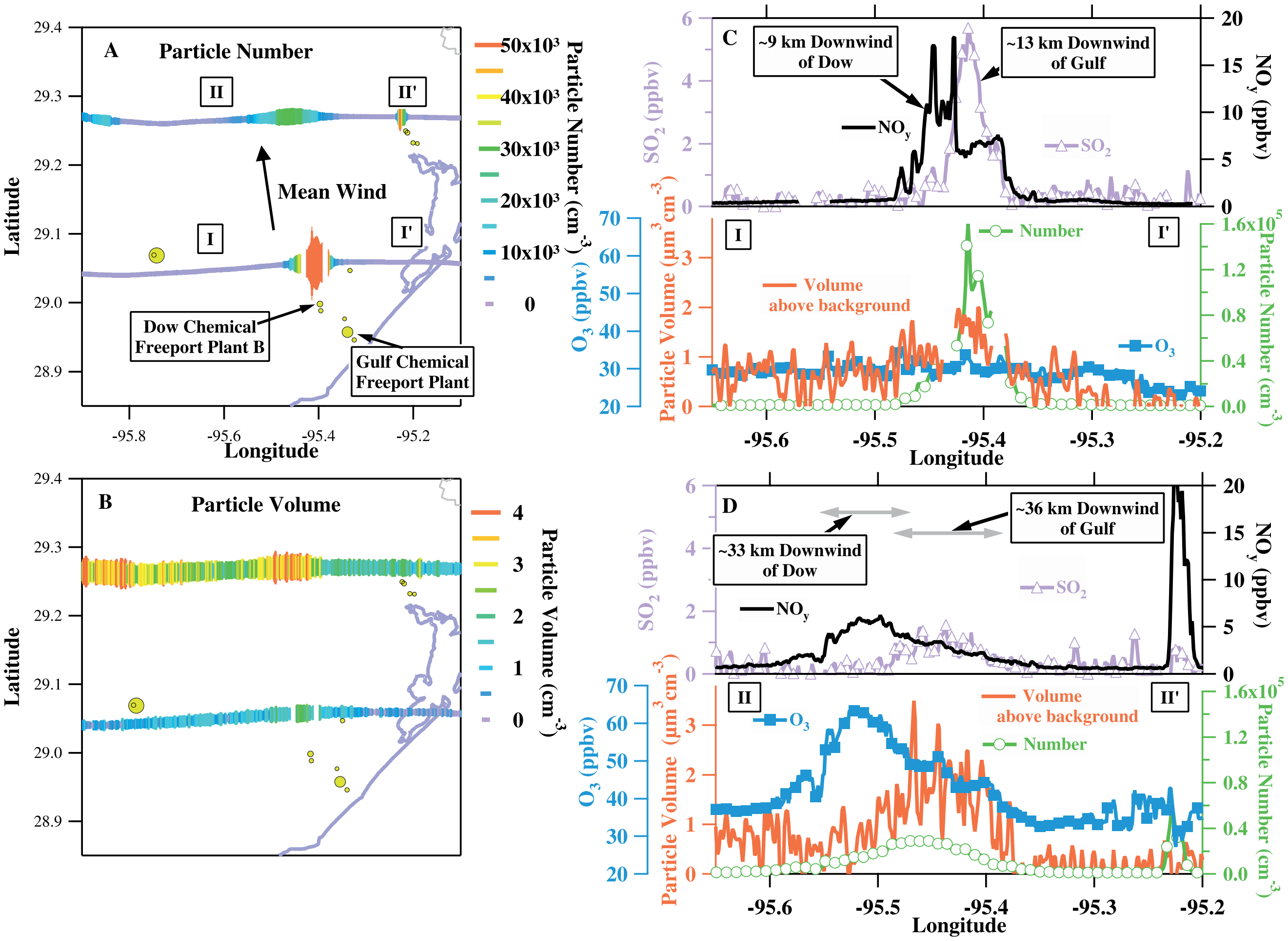

**Figure 4.** (a) Map of the coastal area south of Houston with flight track of the NCAR Electra aircraft during longitudinal transects (approximately perpendicular to the wind) within the PBL on 28 August 2000. The transects are color and size coded by particle number concentration. Portions of the flight track indicated by I-I′ and II-II′ are shown in (c) and (d). Significant sources of $SO_2$ are indicated by the circles, sized by annual emissions. The Texas coastline is in blue. (b) As in (a), but color and size coded by particle volume above background. (c) $NO_y$, $SO_2$, and $O_3$ mixing ratios and particle volume and number concentrations as a function of longitude for the portion of the transect indicated by I-I′ in (a), close to isolated industrial facilities. (d) As in (c), but for transect II-II′ in (a), further downwind of the industrial facilities.

the background, and because the Parish and ship channel plumes extended into the urban plume on either side. Because of this increasing encroachment of the surrounding industrial plumes into the Houston urban plume with increasing distance, the particle number and volume fluxes reported for the urban plume are upper limit estimates. For plume ages >3 hours, the particle volume flux within the Houston urban plume was ~1/2 that from the Parish power plant. Note that the particle volume fluxes from the ship channel industries and the Parish power plant continued to increase up to the maximum measured plume age, indicating continuing particle mass growth from gas-to-particle conversion in these plumes.

### 4.2. Sulfur Gas-to-Particle Conversion

[25] Particle volume concentration was positively correlated with $SO_2$ mixing ratio within the plume of the Parish power plant and within the plume from industries along the Houston ship channel. These data may be used to test if the observed increase in particle volume with increasing plume age is consistent with oxidation of $SO_2$ by OH and subsequent condensation of the sulfate oxidation products. This test involves assuming a composition for the particles and then examining the derived sulfur budget of the plume compared with that calculated with a numerical model of plume chemistry. Unpublished data from the TexAQS 2000 mission (R. Weber, personal communication, 2001) indicate that the sulfate aerosol within the Houston area during afternoons was usually fully neutralized by ammonium. If all of the enhancement in dry particle volume observed within a transect of a plume were caused by formation of $(NH_4)_2SO_4$, the fraction of total plume sulfur (particulate sulfur + $SO_2$) within the particles can be calculated from the measurements. With increasing plume age, and dependent upon the plume $NO_x$ and VOC concentrations and insolation, the slope of the regression between particulate and

**Table 2.** Measured Concentrations of Nonmethane Hydrocarbons (NMHCs) and Aromatics in Selected Petrochemical Plumes

| Source | Distance Downwind (km) | Plume Age (hours) | ΣNMHCs (ppbv) | Σaromatics (ppbv) |
|---|---|---|---|---|
| | 27 August 1999 | | | |
| Gulf of Mexico (background) | NA[a] | NA | 0.98 | 0.025 |
| Gulf Plant | 13 | 0.8 | 4.81 | 0.27 |
| Gulf + Dow | ~34 | ~2 | 3.09 | 0.13 |
| Gulf + Dow | ~34 | ~2 | 4.44 | 0.15 |
| Ship Channel (west side) | ~8 | ~0.5 | 5.97 | 0.54 |
| Ship Channel (east side) | ~8 | ~0.5 | 29.8 | 1.59 |
| Ship Channel (west side) | 27 | 1.7 | 22.6 | 0.96 |
| | 28 August 1999 | | | |
| Gulf of Mexico (background) | NA | NA | 1.12 | 0.028 |
| Gulf Plant | 13 | 0.8 | 5.02 | 0.43 |
| Dow Plant | 9 | 0.6 | 9.20 | 0.37 |
| Dow Plant | 33 | 2.0 | 5.67 | 0.099 |
| Ship Channel (west side) | ~8 | ~0.5 | 45.9 | 1.79 |
| Ship Channel (east side) | ~8 | ~0.5 | 28.7 | 0.51 |
| Ship Channel (west side) | 24 | 1.5 | 23.6 | 1.09 |
| Ship Channel (east side) | 24 | 1.5 | 19.2 | 1.01 |

[a] NA: Not applicable.

total plume sulfur should increase as a larger fraction of the $SO_2$ is oxidized by OH and the resulting sulfuric acid condenses on the particles and is neutralized to form $(NH_4)_2SO_4$ (Figure 6). This analysis is dependent upon the assumption that the particles are composed of $(NH_4)_2SO_4$, and the absence of substantial loss of plume sulfur through aqueous oxidation and dry deposition. In-cloud oxidation of $SO_2$ is believed to have been negligible because there were only scattered cumulus clouds on 27 and 28 August in the study region, and because, as discussed later, the ratio of $SO_2$ to $NO_y$ within the plumes did not vary substantially as a function of plume age. Loss of $SO_2$ due to dry deposition is not negligible, but will be ignored for the moment since it is incorporated in the numerical model of plume chemistry with which these data will be compared.

[26] Under these assumptions, the fraction of plume sulfur observed in the particulate phase (the slopes in Figure 6) should increase with increasing integrated exposure of emitted $SO_2$ to OH. If the assumptions regarding particle composition and losses of $SO_2$ are correct, the fraction should reach one when all of the $SO_2$ in the plume has oxidized and been converted to particulate $(NH_4)_2SO_4$. For the greatest plume age, 5.7 hours, the particulate sulfur fraction derived from the observations is 0.76 (Figure 6). However, based on plume flux estimates, only a small fraction (less than ~30%) of the $SO_2$ within the plume had been oxidized at this plume age. If a less neutralized sulfate composition, such as $(NH_4)HSO_4$ or $H_2SO_4$, is assumed, an even higher fraction of plume sulfur would be calculated to reside in the particulate phase. These discrepancies strongly suggest that the assumed predominantly sulfate composition is incorrect, and that compounds other than $(NH_4)_2SO_4$, such as nitrates or organics, contributed to most of the observed particle growth in the plume from the petrochemical industries along the Houston ship channel.

[27] This regression approach can be used to compare particle growth as a function of plume age among plumes from different sources with different emission characteristics. However, the oxidation rate of $SO_2$ is strongly affected by the concentration of OH, which in turn is highly depend-

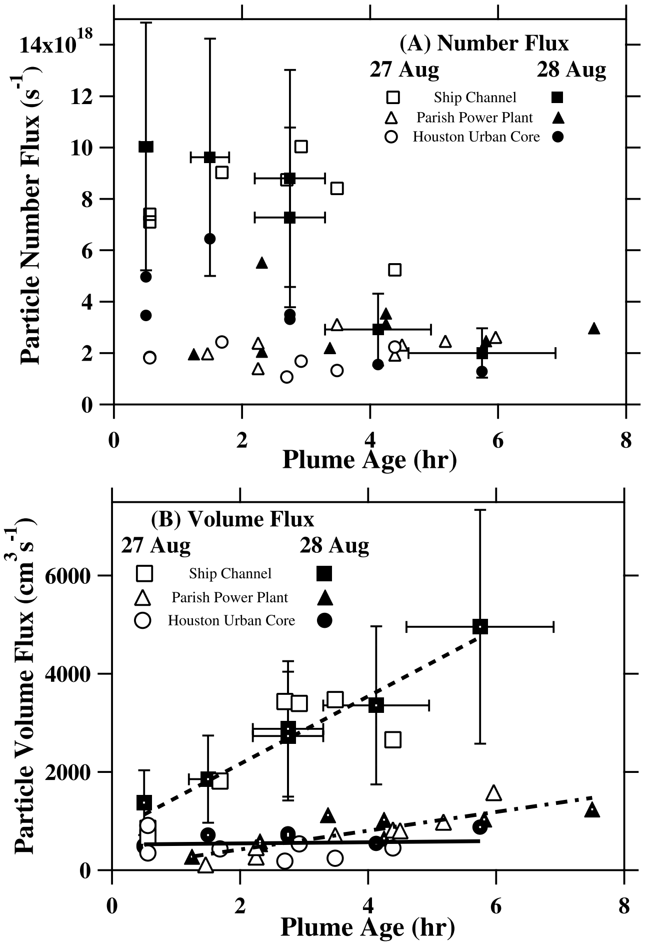

**Figure 5.** Horizontal flux of particle number (a) and volume (b) within the PBL from three different sources in the vicinity of the Houston metropolitan area as measured on 27 and 28 August 2000. Error bars (shown for a subset of the data for clarity) are calculated in quadrature from measurement uncertainties and estimated uncertainties in determining wind speed and boundary layer height.

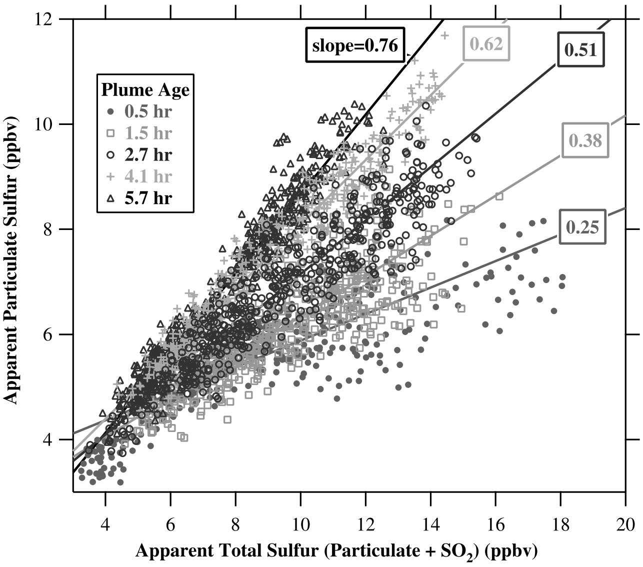

**Figure 6.** Apparent mixing ratio of sulfur in particles within the plume from the Houston ship channel industries calculated from observed particle volume assuming a composition of $(NH_4)_2SO_4$, plotted as a function of total plume sulfur (measured $SO_2$ + apparent particulate sulfur). Lines are least squares univariate linear regressions from data obtained on 28 August 2000 in the merged plumes of the industries located along the Houston ship channel during five different transects downwind. Since depositional and aqueous losses of $SO_2$ are small over the time period of the observations, the increase in slopes of the regression lines with increasing plume age is attributed to gas-to-particle conversion within the plume.

ent upon $NO_x$ and insolation, and will also differ between plumes depending on hydrocarbon concentrations and reactivity. Therefore, time since emission (plume age) does not effectively represent the photochemical oxidation history of a given plume parcel. Because $HNO_3$ is produced by oxidation of $NO_2$ by OH, the fraction of total odd nitrogen ($NO_y$) converted to $HNO_3$ is a better proxy for the integrated exposure of the plume to OH. The calculated fraction of total plume sulfur found in the particulate phase increases with increasing $HNO_3/NO_y$ for both the Parish and ship channel plumes on both 27 and 28 August (Figure 7). The apparent particulate sulfur fraction at a given value of $HNO_3/NO_y$ is substantially greater in the plume from the Houston ship channel than in that from the Parish power plant. Because particle volume, rather than mass, was measured, this difference between the plumes is critically dependent upon the assumption of a particle composition of $(NH_4)_2SO_4$. For example, if the particles in the ship channel plume are composed of a mixture of 30% by mass of organics (with a density of $\sim$1 g cm$^{-3}$) and 70% $(NH_4)_2SO_4$ (with a density of $\sim$1.8 g cm$^{-3}$), the actual particulate sulfur mass is lower by almost a factor of 2 compared with that calculated assuming a composition of pure $(NH_4)_2SO_4$. This analysis also assumes that the only substantial loss of $SO_2$ is due to oxidation and conversion to aerosol sulfate. Because the ratio of $SO_2$ to $NO_y$ remained approximately constant with increasing plume age (Figure 8), there do not appear to have been substantial sinks (such as aqueous reactions) that preferentially removed $SO_2$.

[28] The particulate sulfur fraction derived from the observations can be compared with the results from a numerical model of plume mixing and photochemistry that includes $SO_2$ oxidation processes. A Lagrangian model [*Trainer et al.*, 1991; *Wert et al.*, 2003; *Brock et al.*, 2002] was initialized with inventoried emissions of $NO_x$ and $SO_2$ in the Parish plume and inventoried $NO_x$ and observed $SO_2$ in the ship channel plume. Emissions of VOCs were estimated using their measured mixing ratios relative to $NO_y$ (for which demonstrably accurate emission rates are known), after accounting for the expected oxidation of the VOCs by OH since emission. The Gaussian dispersion of the plume was prescribed to match the observed plume dimensions. The model successfully simulates observed $O_3$ formation rates and yields (Ryerson et al., submitted manuscript, 2002), $NO_y$ partitioning [*Neuman et al.*, 2002], and formaldehyde production [*Wert et al.*, 2003] in the ship channel and Parish plume. The model includes $SO_2$ loss via reaction by OH and by dry deposition. Sulfur molecules oxidized by OH in the model are presumed to rapidly form condensable products and transfer to the particulate phase.

[29] The model predicts a conversion of $SO_2$ to condensable sulfate as a function of $HNO_3/NO_y$ that is approximately half of the central values calculated from observed particle growth in the $SO_2$-rich plume from the Parish power plant as it advected over terrain with low isoprene emissions and rural and suburban land use patterns (Figure 7). However, the modeled sulfur conversion fraction is still within the uncertainty estimate for the particulate sulfur fraction calculated from the observations using a compositional assumption of $(NH_4)_2SO_4$. In contrast to this relatively good agreement between model and measurement within the power plant plume, the model underpredicts particle growth in the VOC-rich and $SO_2$-rich plume from the combined industries located along the Houston ship channel by a factor ranging between 2 and 10 compared with the uncertainty range of the observations. The model accurately replicates observed gas-phase speciation and mixing ratios within the plume of the ship channel industries, implying that modeled OH concentrations are substantially correct. Also, the model faithfully simulates the observed $SO_2/NO_y$ ratios with increasing plume age (Figure 8), indicating that the heterogeneous $SO_2$ oxidation is not important in this data set and that the dry deposition parameterization in the model is appropriate. Therefore, the difference in particulate sulfur fraction between the model and measurements is probably caused by the assumption that the observed particle volume growth is due solely to the condensation of sulfate compounds and the subsequent formation of aerosol $(NH_4)_2SO_4$. The most likely explanation for the discrepancy (one supported by ground-based observations of submicron particle chemistry made a few km south of the ship channel during the TexAQS 2000 project (D. Worsnop, personal communication, 2002)) is that gas-to-particle conversion of organic matter produces a substantial fraction of the observed particle volume growth within the oxidized ship channel plume. Condensation of smaller quantities of organic matter, as well as area-source contributions to the particle loading, may explain why the model results for the Parish power plant plume are at the

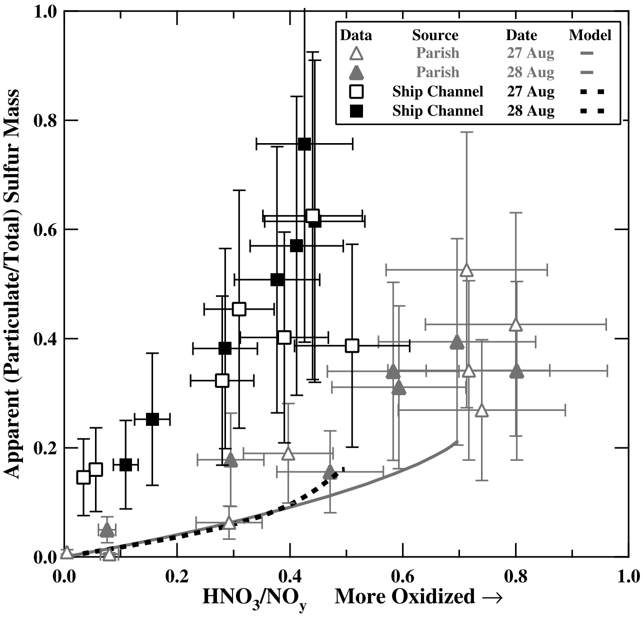

**Figure 7.** Apparent fraction of total plume sulfur in the particulate phase, determined as in Figure 6, plotted as a function of measured fraction of $NO_y$ converted to $HNO_3$ (an indicator of total OH exposure). Particles are assumed to be composed of $(NH_4)_2SO_4$. Lines give the same parameters determined from a Lagrangian model of plume chemistry (see text). Measured data and model calculations are for the plume of the Parish power plant (triangles and solid curve) and the merged ship channel industries (squares and dashed curve).

bottom limit of agreement with the observations within experimental uncertainties.

## 5. Discussion and Summary

[30] There are three principal findings to this work: (1) the petrochemical industries located along the Houston ship channel are the predominant source of particle number and volume (mass) flux downwind of the Houston metropolitan area, followed in importance by the Parish power plant and the urban core of Houston; (2) substantial increases in particle volume concentration with increasing plume age, indicating conversion of gas-phase compounds to the particulate phase, were found in only those plumes with detectable enhancements in $SO_2$; and (3) the particle growth in the plume of the Parish power plant was generally consistent with the condensation of the oxidation products of $SO_2$ alone, while particle growth within the VOC-rich ship channel plume exceeded that expected solely from $SO_2$ oxidation.

[31] Prior research [e.g., *Hewitt*, 2001; *Brock et al.*, 2002] has shown that particle mass fluxes from urban areas are often smaller than those within oxidized plumes from nearby, large point sources of $SO_2$. Similarly, the data presented here show that the particle volume flux within the oxidized plume from the Parish power plant exceeds that from the Houston urban core. What is more surprising is the observed association between $SO_2$ and particle volume in oxidized plumes downwind of petrochemical industries. One might expect particle growth in such plumes even in the absence of $SO_2$, since smog chamber and field studies in heavily urbanized areas such as Los Angeles show substantial organic particle formation and growth in environments rich in $NO_x$ and VOCs even in the absence of much $SO_2$ [e.g., *Collins et al.*, 2000; *Jacobson et al.*, 2000; *Turpin and Huntzicker*, 1991; *Odum et al.*, 1996, 1997a, 1997b]. However, these studies were accomplished with VOC mixtures and concentrations that may not be representative of those found in the plumes from the Houston petrochemical industries. In Houston, recent new particle formation and volume growth due to vapor condensation was evident in only those plumes characterized by detectable enhancements in $SO_2$. Yet, the amount of growth observed in the combined plume from the industries along the Houston ship channel was substantially greater than could be accounted for by condensation of the oxidation products of $SO_2$ alone, suggesting a linkage between sulfate and organic gas-to-particle conversion. Ground-based observations of particle composition at the LaPorte municipal airport a few km south of the ship channel support this speculation. Organic matter, which contributed >30% of the total volatile submicron particle mass during afternoon, photochemically active periods during the TexAQS 2000 project, was positively correlated with ammonium and sulfate, which contributed ~30–50% of the total volatile submicron mass during the same periods (D. Worsnop, personal communication, 2002).

[32] The partitioning of the semivolatile products of VOC oxidation between the gas and particulate phase is an area of active research. There are few data available on particle formation in VOC-rich mixtures at concentrations representative of actual atmospheric conditions. However, smog

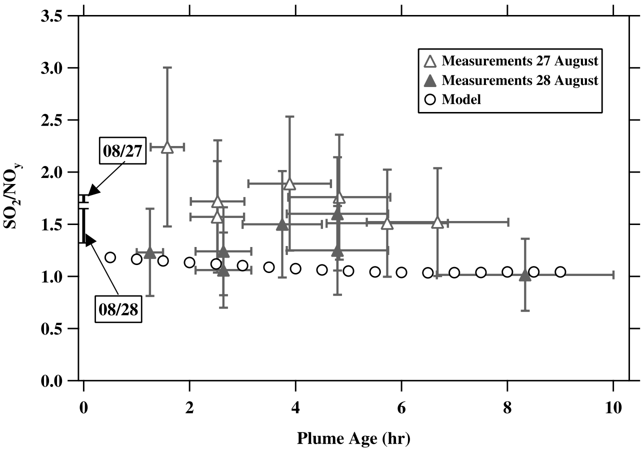

**Figure 8.** Ratios of $SO_2/NO_y$ observed as a function of the age of the Parish power plant plume on 27 and 28 August 2000 (triangles) and calculated from the photochemical plume model (circles). The vertical bars at a plume age of 0 hour show the range of $SO_2/NO_x$ (virtually all $NO_y$ emissions initially are in the form of $NO_x$) reported hourly from chemical emissions monitoring equipment at the power plant for the times corresponding to the emission times of the sampled plumes. There is no substantial change in the $SO_2/NO_y$ ratio with increasing plume age in either the model or the measurements, indicating that there is little heterogeneous oxidation of $SO_2$ and that the gas-phase oxidation and dry deposition processes within the model adequately represent the actual $SO_2$ losses.

chamber measurements of the fraction of organic matter forming in the particulate phase are in general agreement with absorptive partitioning theory for high concentrations of relatively simple mixtures of aromatic compounds [e.g., *Odum et al.*, 1996, 1997a, 1997b]. This theory indicates only a few to several percent of the total aromatic mass should oxidize, form semivolatile products, and partition to the particulate phase. Analysis of air samples collected during transects ~8 km downwind of the ship channel industries on both 27 and 28 August 2000 show mixing ratios of aromatic compounds (the only VOC aerosol precursors sampled) summing to <2 ppbv (Table 2). These mixing ratios are insufficient to explain the observed aerosol mass growth using absorptive partitioning theory in the absence of other unmeasured condensable organic species. Substantial quantities of unmeasured VOC compounds, such as organic acids, could have been present and served as the parent material for the formation of condensable organic mass. Alternately, heterogeneous mechanisms for the formation of secondary organic particle mass, such as acid-catalyzed reactions [e.g., *Jang and Kamens*, 2001], may have contributed the apparent organic particle formation within the plume of the Houston ship channel, and might explain the observed association of the particle growth with enhanced $SO_2$ concentrations.

[33] *Flagan et al.* [1991] and *Hoppel et al.* [2001] found that, in initially particle-free air rich in $NO_x$ and reactive VOCs in smog chambers, very rapid particle nucleation and growth occurred when $SO_2$ was added to the system. Without $SO_2$, the onset of detectable particle formation and condensational growth was substantially delayed and the initial rates of growth were smaller. Flagan et al. did not quantitatively determine whether the observed particle formation and volume growth was consistent with the mass budget of organic matter and $SO_2$ within the smog chamber. Hoppel et al. found that there was no detectable change in particulate organic yield whether $SO_2$ was present or absent. In neither experiment was the mix or concentration of reactive VOCs within the smog chamber representative of that found in the plumes of the petrochemical plants studied during TexAQS 2000. Further laboratory studies of particle mass growth and composition using $SO_2$, $NO_x$, and reactive VOC compounds at mixing ratios and timescales similar to those reported here may help elucidate the processes leading to particle formation and growth within the Houston metropolitan area.

[34] **Acknowledgments.** We thank the management, staff, and flight crew from the NCAR Research Aviation Facility for their exceptional support during this field mission and the preceding instrument integration. We also thank F. Brechtel, M. Canagaratna, J. Jimenez, R. Weber, and D. Worsnop for their contributions and comments. This work was supported in part by the TNRCC and the NOAA Health of the Atmosphere and Climate and Global Change Programs.

## References

Brock, C. A., F. Schröder, B. Kärcher, A. Petzold, R. Busen, and M. Fiebig, Ultrafine particle size distributions measured in aircraft exhaust plumes, *J. Geophys. Res.*, *105*, 26,555–26,567, 2000.

Brock, C. A., et al., Particle growth in the plumes of coal-fired power plants, *J. Geophys. Res.*, *107*, 4155, doi:10.1029/2001JD001062, 2002.

Collins, D. R., H. H. Jonsson, H. Liao, R. C. Flagan, J. H. Seinfeld, K. J. Noone, and S. V. Hering, Airborne analysis of the Los Angeles aerosol, *Atmos. Environ.*, *34*, 3155–4173, 2000.

Dreher, D. B., and R. A. Harley, A fuel-based inventory for heavy-duty diesel truck emissions, *J. Air Waste Manage. Assoc.*, *48*, 352–358, 1998.

Flagan, R. C., S.-C. Wang, F. Yin, J. H. Seinfeld, G. Reischl, W. Winklmayr, and R. Karch, Electrical mobility measurements of fine-particle formation during chamber studies of atmospheric photochemical reactions, *Environ. Sci. Technol.*, *25*, 883–890, 1991.

Heidt, L. E., J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, Trace gases in the Antarctic atmosphere, *J. Geophys. Res.*, *94*, 11,599–11,611, 1989.

Hewitt, C. N., The atmospheric chemistry of sulphur and nitrogen in power station plumes, *Atmos. Environ.*, *35*, 1155–1170, 2001.

Hoppel, W., et al., Particle formation and growth from ozonolysis of α-pinene, *J. Geophys. Res.*, *106*, 27,603–27,618, 2001.

Jacobson, M. C., H.-C. Hansson, K. J. Noone, and R. J. Charlson, Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, *38*, 267–294, 2000.

Jang, M., and R. M. Kamens, Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci. Technol.*, *35*, 4758–4766, 2001.

Jonsson, H. H., et al., Performance of a focused-cavity aerosol spectrometer for measurements in the stratosphere of particle size in the 0.06–2.0 μm diameter range, *J. Atmos. Oceanic Technol.*, *12*, 115–129, 1995.

Kleinman, L. I., P. H. Daum, D. Imre, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, and J. Rudolph, Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston, *Geophys. Res. Lett.*, *29*, 10.1029–10.1033, 2002.

Marr, L. C., D. R. Black, and R. A. Harley, Formation of photochemical air pollution in central California, 1, Development of a revised motor vehicle emission inventory, *J. Geophys. Res.*, *107*, doi:10.1029/2001JD000689, 2002.

Meng, Z., D. Dabdub, and J. H. Seinfeld, Chemical coupling between atmospheric ozone and particulate matter, *Science*, *277*, 116–119, 1997.

Neuman, J. A., et al., Fast-response airborne in situ measurements of $HNO_3$ during the Texas 2000 Air Quality Study, *J. Geophys. Res.*, *107*, doi:10.1029/2001JD001437, 2002.

Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld, Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, *30*, 2580–2585, 1996.

Odum, J. R., T. P. W. Jungkamp, R. J. Griffin, H. J. L. Forstner, R. C. Flagan, and J. H. Seinfeld, Aromatics, reformulated gasoline, and atmospheric organic aerosol formation, *Environ. Sci. Technol.*, *31*, 1890–1897, 1997a.

Odum, J. R., T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, and J. H. Seinfeld, The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, *276*, 96–99, 1997b.

Ryerson, T. B., et al., Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, *103*, 22,569–22,583, 1998.

Ryerson, T. B., et al., Observations of ozone formation in power plant plumes and implications for ozone control strategies, *Science*, *292*, 719–723, 2001.

Schauffler, S., E. Atlas, D. Blake, F. Flocke, R. Lueb, J. Lee-Taylor, V. Stroud, and W. Travnicek, Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, *104*, 21,513–21,535, 1999.

Senff, C. J., R. M. Hardesty, R. J. Alvarez II, and S. D. Mayor, Airborne lidar characterization of power plant plumes during the Southern Oxidants Study, *J. Geophys. Res.*, *103*, 31,173–31,189, 1998.

Trainer, M., M. P. Buhr, C. M. Curran, F. C. Fehsenfeld, E. Y. Hsie, S. C. Liu, R. B. Norton, D. D. Parrish, and E. J. Williams, Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, *96*, 3045–3063, 1991.

Turpin, B. J., and J. J. Huntzicker, Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations, *Atmos. Environ.*, *25A*, 207–215, 1991.

Wert, B. P., et al., Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQS 2000, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002502, in press, 2003.

---

E. L. Atlas, S. G. Donnelly, S. M. Schauffler, V. R. Stroud, and C. Wiedinmyer, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307, USA.

C. A. Brock, F. C. Fehsenfeld, G. J. Frost, J. S. Holloway, G. Hübler, J. A. Neuman, D. K. Nicks Jr., D. D. Parrish, T. B. Ryerson, and M. Trainer, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80306, USA. (cbrock@al.noaa.gov)

H. Hilbert, B. G. Lafleur, J. M. Reeves, and J. C. Wilson, Department of Engineering, University of Denver, Denver, CO 80208, USA.