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## 1. INTRODUCTION

Particles are formed within the plumes from industrial facilities from condensation of the oxidation products of SO<sub>2</sub> and other compounds. A quantitative understanding of the relationship between emissions of precursor gases such as SO<sub>2</sub> and downwind aerosol properties is needed for mitigation efforts.

During the Texas 2000 Air Quality Study, airborne measurements of particle size distributions were made in a variety of power plant, petrochemical, and urban plumes. Data from a 5channel condensation particle counter (Brock et al., 2000), a laser optical particle counter (Jonsson et al., 1995), and a white light optical particle counter (a modified Climet 208A) were combined to determine particle size distributions from 0.004-10 mm diameter with 1 second resolution. Estimated uncertainties for particle number and volume concentrations are given in Table 1.

	Number	Volume
Precision	±15%	±34%
Bias	< 8%	< 40%

The instruments were operated on the National Center for Atmospheric Research Electra aircraft sampling from a new inlet that used active boundary layer suction to virtually eliminate turbulence while decelerating the 100 m s<sup>1</sup> airflow (Fig. 1). This low turbulence inlet, developed at the University of Denver, allowed particle transmission to be quantitatively calculated and corrected for.

The analysis presented here makes use of measurements of photochemically reactive gases and tracer compounds (Ryerson et al. 1998, 2000; Huey et al., 1998) to identify plumes, estimate dilution, and evaluate the mass budget of condensable compounds.

## 2. OBSERVATIONS

Measurements were made in the plumes downwind of large fossil-fueled power generation stations and from



Figure 1. Schematic of the University of Denver low turbulence inlet used on the NCAR Electra aircraft during the Texas 2000 Air Quality Study.

petrochemical facilities (which often included co-located power generation units and transportation centers). Downwind of these sources, substantial enhancements in particle mass were found in only those plumes rich in SO<sub>2</sub>. Even in the plumes downwind of petrochemical complexes with large tabulated emissions of NOx and aromatic volatile organic compounds (VOCs) south of Houston, particle enhancements were not detected in the absence of SO<sub>2</sub>. Nearby, modest sources of SO<sub>2</sub> produced detectable enhancements in particle volume (Fig. 2).

Particle growth in the plumes of geographically isolated refineries upwind of the Houston metropolitan area was guite modest on the two days they were studied. However, particle growth in the coalesced plume downwind of the industrial complexes located along the Houston ship channel on the east side of the metropolitan area was substantial on every day the plume was encountered. For example, on 28 August, the ship channel plume produced enhancements above background in particle volume that exceeded those found at similar plume ages downwind of the Parish power plant, and which were much larger than those from the urban center of Houston (Fig. 3). Similar, large increases in particle volume concentration were repeatedly found in the plumes downwind of the ship channel throughout the study period. There were no reported large "upsets", or unusual emissions, from industries in the area on the study days. In steady wind conditions the estimated flux of particles in the ship channel plume exceeded that from the urban core of Houston and that from the Parish power plant. Thus, we believe that that the industries located along the

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Figure 2. Top panel: map of the Electra flight track on 28 August 2000 showing locations of  $NO_x$  sources (diamonds) and  $SO_2$  sources (circles), sized by source strength. Bottom panel: time plot from AB, showing particle volume (circles),  $NO_y$  (triangles) and  $SO_2$  (line). Although the Dow Freeport B plant is a large source of some aromatic organic compounds, particle volume was not detectably enhanced above background in its plume, while particle volume increased in the relatively  $SO_2$ -rich Gulf Freeport plume.

Houston ship channel provide the largest source of submicron particle mass in the Houston area in typical summertime conditions. Large enhancements in particle volume observed in the plumes downwind of individual sources in the Houston area and in the coalesced plume downwind of the ship channel industries were always associated with detectable increases above background in SO<sub>2</sub>, suggesting a strong photochemical link between SO<sub>2</sub> and particle mass growth.

## 3. ANALYSIS

In the absence of in-cloud oxidation, particulate sulfate is produced by condensation of gas-phase sulfuric acid, the end product of oxidation of SO<sub>2</sub> by OH Similarly, gas-phase HNO3 is in the atmosphere. produced by the oxidation of NO<sub>2</sub> by OH. Thus, the fraction of plume NO<sub>x</sub> oxidized to HNO<sub>3</sub> roughly indicates total parcel exposure to OH. Assuming a constant composition of 50% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, the fraction of plume S found in the particulate phase was calculated as function of HNO<sub>3</sub>/NO<sub>y</sub> and compared with a 2dimensional numerical model of plume chemistry and dvnamics. This Gaussian plume model uses the chemical scheme of Trainer et al. [1991] and plume dynamics similar to that of Sillman [2000], constrained



Figure 3. Top panel: map of the Electra flight track on 28 August 2000 showing the Houston metropolitan area and major point sources of  $SO_2$  (circles), size by source strength. Bottom panel: transect from AB, showing particle volume (circles), CO (triangles) and  $SO_2$  (line). CO is an indicator of industrial and urban emissions. The urban center of Houston is not a significant source of  $SO_2$  but has large emissions of CO from mobile sources. Particle volume enhancements are clearly associated with the SO2 plumes from the Parish power plant and the ship channel industries.

by observed plume dimensions. Because the model closely replicates the observed ozone and  $HNO_3$  yieldand the nitrogen partitioning in the plumes of the Parish power plant and petrochemical complexes, we believe that it adequately represents the time evolution of OH concentrations and thus the oxidation of SO<sub>2</sub> by OH.

For this analysis, we assume that the observed increase in particulate volume with increasing plume oxidation occurs while particle composition remains constant at 50% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by volume. This compositional assumption is consistent with unpublished airborne and ground-based measurements (see presentations 10.1 and 10.13 of these Proceedings). Because 50% of the particle volume is also not sulfate. we implicitly assume that additional condensation of nonsulfate species must occur as the plume oxidizes and particulate volume increases.



Figure 4. Fraction of total plume sulfur found in the particulate phase as estimated from measurements within the Parish power plant (triangles) and Houston ship channel (circles) plumes assuming a constant particle composition of 50% ( $NH_4$ )<sub>2</sub>SO<sub>4</sub> by volume. The dashed and solid lines show calculations by a two-dimensional plume photochemistry model of the fraction of plume SO<sub>2</sub> oxidized by OH within the ship channel and Parish plumes, respectively. The model cannot account for the observed particle growth in the ship channel plume but reasonably replicates the growth seen in the Parish power plant plume.

Using these assumptions regarding particle composition, we can calculate the fraction of total plume S found in the particulate phase and compare it to themodel simulations of SO<sub>2</sub> oxidation in the measured plumes (Fig. 4). In the plume of the Parish power plant, the apparent increase in the fraction of total plume S found in the particulate phase with increasing OH exposure is well simulated by the model. However, in the merged industry plume from the Houston ship channel, the apparent increase in the fraction of plume S in the particulate phase is underpredicted by the model. This difference may be due to model formulation errors, unaccounted SO<sub>2</sub> losses, or to particle growth by nonsulfate species beyond the 50% by volume already assumed. Similar analysis of observations from the previous day produces very similar results; particulate mass growth in the plume of the Parish power plant is reasonably accounted for by SO2 oxidation, while growth in the coalesced ship channel plume exceeds that predicted from SO<sub>2</sub> oxidation.

The fact that detectable particle growth is not seen in the plumes of isolated petrochemical refineries that do not emit large quantities of  $SO_2$  strongly indicates that  $SO_2$  oxidation products are required for such growth, even in the presence of substantial quantities of potential organic particle precursor gases such as aromatic compounds (Fig. 2). These data are further supported by the strong correlation between  $SO_2$  and particle volume enhancements downwind of the Houston urban/industrial area (Fig. 3). Our results suggest that co-condensation of nonsulfate compounds is important within the plume of the petrochemical complexes in the ship channel area, yet the observations also point to the oxidation of SO<sub>2</sub> as the primary process regulating particulate mass formation from the studied industrial sources. We recommend studies of the aerosol-forming potential of mixtures of reactive VOCs (particularly aromatics), NO<sub>x</sub>, and SO<sub>2</sub> to extend previous work on NO<sub>x</sub>-VOC systems (*e.g.*, Odom *et al.*, 1997; Jacobson *et al.*, 2000).

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