

## Evaluation of GOME satellite measurements of tropospheric NO<sub>2</sub> and HCHO using regional data from aircraft campaigns in the southeastern United States

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[1] We compare tropospheric measurements of nitrogen dioxide (NO<sub>2</sub>) and formaldehyde (HCHO) from the Global Ozone Monitoring Experiment (GOME) satellite instrument with in situ measurements over eastern Texas and the southeast United States. On average, the GOME and in situ measurements of tropospheric NO<sub>2</sub> and HCHO columns are consistent despite pronounced sampling differences. The geometric mean in situ to GOME ratios over the campaign are 1.08 for NO<sub>2</sub> and 0.84 for HCHO, with corresponding geometric standard deviations of 1.27 and 1.38. The correlation of the observed column spatial variability between the two NO<sub>2</sub> measurement sets is encouraging before ( $r^2 = 0.54$ ,  $n = 18$ ) and after ( $r^2 = 0.67$ ,  $n = 18$ ) correcting for a sampling bias. Mean relative vertical profiles of HCHO and NO<sub>2</sub> calculated with a global three-dimensional model (GEOS-CHEM) and used in the GOME retrieval are highly consistent with in situ measurements; differences would affect the retrieved NO<sub>2</sub> and HCHO columns by a few percent. GOME HCHO columns over eastern Texas include contributions from anthropogenic volatile organic compound (VOC) emissions but are dominated by biogenic VOC emissions at the regional scale in August–September when HCHO columns are within 20% of those over the southeastern United States. In situ measurements show that during summer the lowest 1500 m (the lower mixed layer) contains 75% of the tropospheric NO<sub>2</sub> column over Houston and Nashville, and 60% of the HCHO column over Houston. Future validation of space-based measurements of tropospheric NO<sub>2</sub> and HCHO columns over polluted regions should include coincident in situ measurements that span the entire satellite footprint, especially in the heterogeneous mixed layer. *INDEX TERMS*: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 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; 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS*: ozone, GOME, TEXAQS, Houston, nitrogen dioxide, formaldehyde

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### 1. Introduction

[2] Surface ozone is deleterious to human health, crops, and ecosystems [*National Research Council*, 1991]. Uncertainty in the relative abundance of the two main ozone precursors, nitrogen oxides (NO<sub>x</sub> ≡ NO + NO<sub>2</sub>) and volatile organic compounds (VOCs) remains a primary obstacle to improving surface air quality [*Sillman*, 1999]. Observational constraints of ozone precursors traditionally rely on in situ measurements at the local to regional scale. More recently constraints at the regional to global scale are being provided by satellite instruments such as the Global Ozone Monitoring Experiment (GOME) [*European Space Agency*, 1995; *Burrows et al.*, 1999]. Validation of GOME observations with coincident in situ measurements at the regional scale is a prerequisite for using GOME to link regional and global-scale processes.

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**Table 1.** Time and Date of Aircraft Flights Used for Validation<sup>a</sup>

SOS			TEXAQS		
Date	Takeoff	Land	Date	Takeoff	Land
6/24	2310	0144	8/16	1703	2130
6/30	1625	2342	8/18	1738	2154
7/3	1645	0015	8/20	2156	2722
7/4	2016	0412	8/23	1630	2252
7/6	1610	2352	8/25	1628	2232
7/11	1701	0106	8/27	1720	2348
7/12	1755	0033	8/28	1641	2305
7/13	1652	0002	8/30	1517	2236
7/14	1757	2309	9/1	1444	2055
7/17	1557	2329	9/3	1542	2219
7/19	1552	2220	9/6	1534	2158
			9/7	1555	2226
			9/10	1547	2158
			9/13	1552	2141

<sup>a</sup>Aircraft takeoff time (GMT) for the date specified. Landing times earlier than 0500 are for the following day in GMT. Local time is about GMT -5 hours.

[3] The GOME instrument provides the capability to observe tropospheric nitrogen dioxide (NO<sub>2</sub>) and formaldehyde (HCHO) columns at a spatial resolution of 40 km × 320 km. GOME observations are being applied to a wide range of issues including continental outflow [Spichtinger *et al.*, 2001; Richter and Burrows, 2002; Stohl *et al.*, 2003; Wenig *et al.*, 2003], constraints on emission inventories of NO<sub>x</sub> [Leue *et al.*, 2001; Martin *et al.*, 2003b; Beirle *et al.*, 2003; Jaeglé *et al.*, 2004] and VOCs [Abbot *et al.*, 2003; Palmer *et al.*, 2003], and to distinguish between NO<sub>x</sub>-sensitive and NO<sub>x</sub>-saturated regimes of ozone production [Martin *et al.*, 2004]. However, evaluations of GOME with in situ observations have been limited by sparse spatial sampling in the lower mixed layer [Heland *et al.*, 2002; Ladstätter-Weißmayer *et al.*, 2003]. Here we examine the consistency of tropospheric NO<sub>2</sub> and HCHO retrieved from GOME with measurements from aircraft over eastern Texas and the southeastern United States, and discuss the needs for future satellite validation.

[4] In situ measurements revealed that petrochemical emissions of reactive VOCs in the presence of NO<sub>x</sub> play the dominant role in the most extreme ozone episodes over and downwind of Houston during August–September [Kleinman *et al.*, 2002; Roberts *et al.*, 2003; Ryerson *et al.*, 2003; Wert *et al.*, 2003a]. Enhancements of HCHO reflect oxidation of VOC emissions from biogenic [Lee *et al.*, 1998; Palmer *et al.*, 2003] and anthropogenic [Wert *et al.*, 2003a] sources. We use GOME observations of HCHO columns to examine the regional scale and temporal variation of VOC emissions over eastern Texas.

## 2. In Situ Measurements From Aircraft

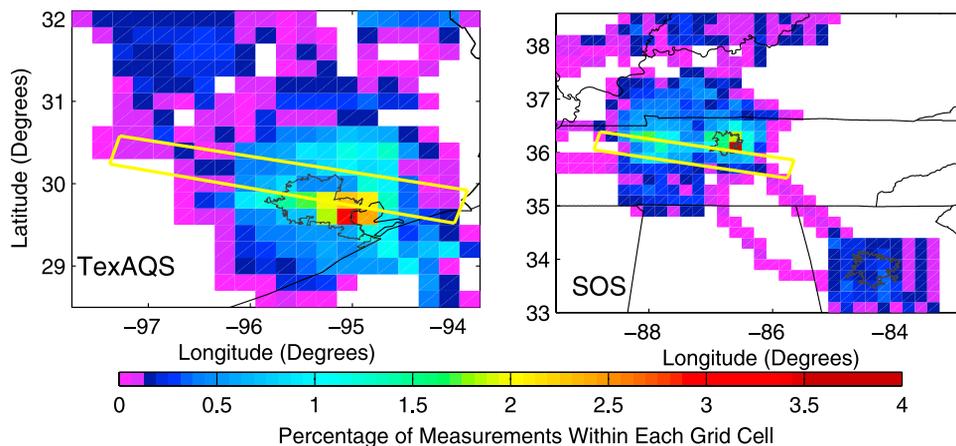
[5] Tropospheric NO<sub>2</sub> and HCHO were measured from aircraft over eastern Texas on 14 separate flights during late morning and afternoon over 16 August to 13 September 2000 as part of the Texas Air Quality Study (TexAQS) and as part of the Southern Oxidants Study (SOS) near Tennessee on 11 separate flights over 24 June to 19 July 1999. Table 1 specifies the date and time of each flight. Measurements typically commenced in late morning and continued for about six hours. Flights frequently occurred on days

with little cloud cover, similar to the conditions observed by GOME. In both campaigns NO<sub>2</sub> was measured by photolysis of NO<sub>2</sub> and chemiluminescence detection of the product NO with a total uncertainty of ±(200 pptv + 15%) for a 1-s average in 1999 and ±(40 pptv + 8%) for a 1-s average in 2000 [Ryerson *et al.*, 2000; Ryerson *et al.*, 2003]. For SOS, NO<sub>2</sub> above 2 km was determined from photochemical steady state calculations of measured ozone, NO, and  $J(\text{NO}_2)$ . HCHO was measured as part of TexAQS using tunable diode laser absorption spectroscopy at 10-s resolution with a total uncertainty better than ±(120 pptv + 10%) prior to 1 September, and at 1-s resolution with a total uncertainty better than ±(400 pptv + 10%) during 1–13 September [Wert *et al.*, 2003b]. For SOS, a liquid phase derivitization technique was used to measure HCHO [Lee *et al.*, 1998], but instrumental issues resulted in data loss at altitudes above 2000 m, precluding reconstruction of HCHO columns for comparison to GOME for this mission.

[6] Figure 1 shows the spatial distribution of in situ measurements during TexAQS and SOS. Flight tracks for TexAQS targeted plumes from the Houston metropolitan area, the Dallas-Fort Worth area, power plants, and petrochemical facilities. Flight tracks for SOS targeted power plant plumes, and the urban centers of Nashville and Atlanta. The spatial extent of aircraft flights during the campaign is comparable to the scale of a GOME footprint. All measurements occurred below 7000 m, and 80% of the measurements were below 1500 m.

[7] Figure 2 shows the vertical profiles of NO<sub>2</sub> and HCHO measured during TexAQS and SOS. Mean NO<sub>2</sub> mixing ratios over Houston and Nashville are 2–3 ppbv below 900 hPa, decrease sharply near 900 hPa, and are 50–200 pptv for pressures less than 800 hPa. Measurements show large variability over urban areas near the surface, reflecting the large spatial variability in emissions. The NO<sub>2</sub> enhancement near 830 hPa over Atlanta is highly localized to the Bowen power plant plume encountered by the aircraft on 6 July. Mean NO<sub>2</sub> mixing ratios over the Texas coast show a shallow mixed layer with NO<sub>2</sub> mixing ratios 25% of those over Houston. Over Houston, the vertical gradient in the HCHO profile is less pronounced than in the NO<sub>2</sub> profile due to chemical production of HCHO above the mixed layer and the decline in the NO<sub>2</sub>/NO ratio with increasing altitude. Maximum HCHO mixing ratios of 3–5 ppbv over Houston between the surface and 900 hPa decrease to 1 ppbv at 800 hPa and 150 pptv at 600 hPa. HCHO mixing ratios near the surface over the Texas coast are 75% of the mixing ratios over Houston, reflecting a more spatially uniform HCHO source than NO<sub>x</sub> source.

[8] The airborne measurements show that the largest contributions to tropospheric NO<sub>2</sub> and HCHO columns are within the mixed layer. The lowest 1500 m contains 80% of the NO<sub>2</sub> column below 6 km, and 64% of the HCHO column below 6 km. We relate the column below 6 km to a tropospheric column using results from a global 3-D model simulation (GEOS-CHEM model, see Appendix A). The mean residual column in the GEOS-CHEM model simulation between 6 km and the tropopause over the southern United States during summer is  $5 \times 10^{14}$  molecules cm<sup>-2</sup> for NO<sub>2</sub>, and  $1.3 \times 10^{15}$  molecules cm<sup>-2</sup> for HCHO, comprising only 6% of the total column for both gases. Combining the modeled and measured values reveals



**Figure 1.** Spatial distribution of aircraft measurements. (left) The percentage of 1-s in situ NO<sub>2</sub> measurements within a  $0.2^\circ \times 0.2^\circ$  grid cell as part of the Texas Air Quality Study (TexAQS) during 16 August to 13 September 2000. (right) The corresponding distribution of 1-s NO<sub>2</sub> measurements as part of the Southern Oxidants Study (SOS) during 24 June to 19 July 1999. White areas indicate regions without measurements. Yellow lines show a nominal GOME footprint. Gray lines denote boundaries of the Houston, Nashville, and Atlanta metropolitan areas. More than 200,000 1-s NO<sub>2</sub> measurements were taken during each campaign.

that the lowest 1500 m contains 75% of the tropospheric NO<sub>2</sub> column, and 60% of the HCHO column.

### 3. Space-Based Observations of Tropospheric NO<sub>2</sub> and HCHO

[9] The GOME instrument on board the European Remote Sensing-2 satellite provides the capability for continuous global monitoring of NO<sub>2</sub> and HCHO atmospheric columns through observation of solar backscatter. The satellite was launched in April 1995 into a Sun-synchronous orbit, crossing the equator at 1030 local time (LT) in the descending node. The GOME instrument observes the atmosphere in the nadir view with a typical surface spatial resolution of 40 km along track by 320 km across track, using a scanning mirror to measure 3 such scenes across the flight track. Global coverage is achieved every 3 days after 43 orbits. Table 2 shows the specific dates of GOME measurements. The GOME overpass time is within 1615–1715 GMT for Nashville and 1630–1730 GMT for Houston, varying with GOME scan position.

[10] We use the algorithms described in the work of *Martin et al.* [2002b, 2003b] to retrieve tropospheric NO<sub>2</sub> columns and those described in the work of *Chance et al.* [2000] and *Abbot et al.* [2003] to retrieve HCHO columns. These algorithms include the air mass factor (AMF) formulation of *Palmer et al.* [2001] to convert slant columns into vertical columns by computing the AMF as the integral of the relative vertical distribution of the trace gas (shape factor) weighted by the local sensitivity to the trace gas of the solar radiation backscattered to space (scattering weights). The local shape factor is specified from a GEOS-CHEM simulation. The scattering weights are calculated with the Linearized Discrete Ordinate Radiative Transfer (LIDORT) model [*Spurr*, 2002], using local monthly mean surface reflectivity retrieved from GOME [*Koелеmeijer et al.*, 2003], accounting for cloud scattering in partly cloudy scenes using local cloud

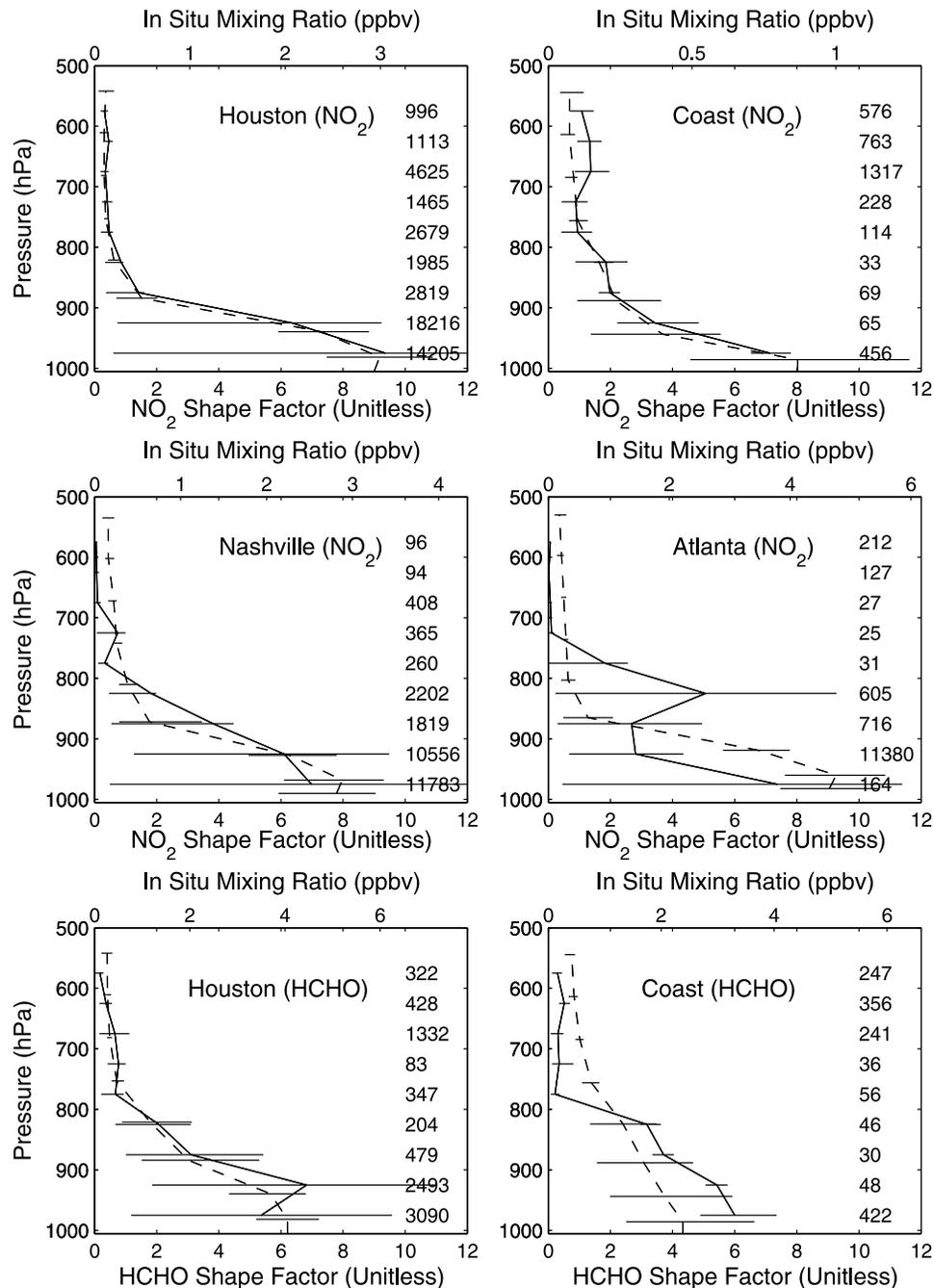
information retrieved from GOME [*Kurosu et al.*, 1999], and using aerosol information from a 3-D aerosol simulation (GOCART model [*Chin et al.*, 2002]). We exclude observations in which the fraction of backscattered intensity from clouds exceeds 50% for each scene.

[11] Uncertainties for each GOME scene include absolute errors of  $1 \times 10^{15}$  molecules cm<sup>-2</sup> for tropospheric NO<sub>2</sub> [*Martin et al.*, 2002b] and  $4 \times 10^{15}$  molecules cm<sup>-2</sup> for HCHO [*Chance et al.*, 2000] from the spectral fitting, the stratospheric NO<sub>2</sub> column, and instrumental artifacts. Uncertainties for each scene also include a relative error of 40% from the AMF that contains both random and systematic contributions from surface reflectivity, clouds, aerosols, and the trace gas profile [*Martin et al.*, 2003b]. The monthly mean uncertainty is  $\pm(5 \times 10^{14}$  molecules cm<sup>-2</sup> + 30%) for tropospheric NO<sub>2</sub> and  $\pm(2 \times 10^{15}$  molecules cm<sup>-2</sup> + 30%) for HCHO, accounting for random errors.

## 4. Evaluation of the GOME Retrieval

### 4.1. Shape Factors

[12] Independent information on the relative vertical profile of the trace gas is necessary for determination of column abundance from GOME [*Palmer et al.*, 2001]. Figure 2 compares campaign-averaged shape factors of NO<sub>2</sub> and HCHO measured from aircraft with those calculated with the GEOS-CHEM model as used in the GOME retrieval. The aircraft measurements and model calculation are highly consistent providing confidence in the AMF calculation, and in the ability of the GEOS-CHEM model to represent trace gas gradients in the lower troposphere. The AMF calculated from the campaign-averaged in situ profile generally is within a few percent of the AMF determined from simulated profiles. The largest discrepancy occurs for HCHO over the Texas coast where the AMF calculated with the measured profile is 6% lower than the AMF calculated with the simulated profile.



**Figure 2.** Shape factors (relative vertical distribution) of NO<sub>2</sub> and HCHO over Houston (29°N–31°N, 96.25°W–93.75°W) and the Texas coast (27°N–29°N, 96.25°W–93.75°W) and of NO<sub>2</sub> over Nashville (35°N–37°N, 88.75°W–86.25°W) and Atlanta (33°N–35°N, 86.25°W–83.75°W) averaged over the entire campaign. The solid lines show the shape factors determined from in situ measurements. The shape factor is calculated as the mixing ratio times the ratio of the vertical column of air to the vertical column of the trace gas [Palmer *et al.*, 2001]. The dashed lines show the shape factors calculated with the GEOS-CHEM model and used in the GOME retrieval. Solid lines also indicate the mean mixing ratio determined from in situ measurements. The number of measurements within each 50 hPa interval are shown in the right of each panel. Error bars represent the 17th and 83rd percentiles. All model and in situ data are taken within 2 hours of the GOME observation time of about 1615–1730 GMT.

#### 4.2. Tropospheric Columns

[13] Comparison of satellite retrievals with in situ measurements requires reconciling their different sampling characteristics. Satellite validation exercises traditionally relate a single aircraft spiral to a coincident space-based

observation. We do not validate individual GOME retrievals here. Rather, we compare averages over the entire campaign since individual flights do not span the GOME footprint, spatial heterogeneity makes the relationship between an individual flight and a single GOME measurement sensitive

**Table 2.** Dates of GOME Observation of the Regions in Figure 1<sup>a</sup>

TexAQS	SOS
8/16	7/1
8/17	7/3
8/19	7/4
8/20	7/5
8/26	7/7
8/29	7/8
9/1	7/16
9/2	7/17
9/5	7/19
9/11	

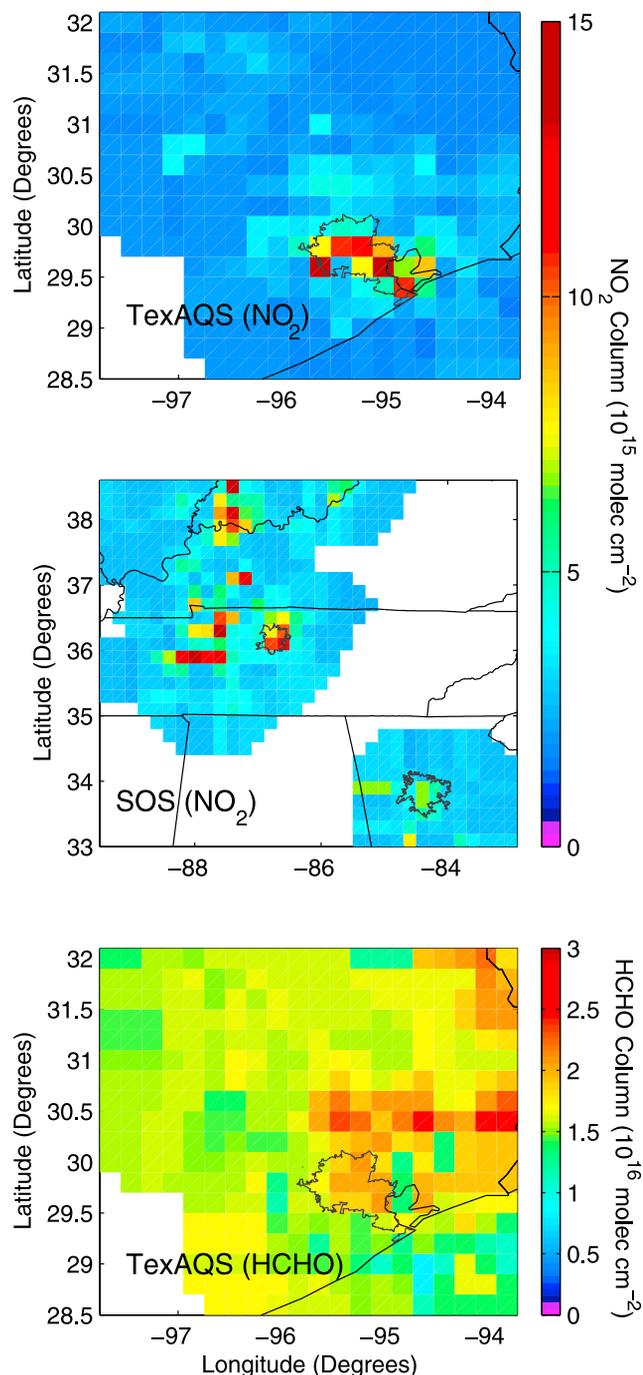
<sup>a</sup>Dates are reported only when the backscattered intensity from clouds is less than that from clear sky.

to where the aircraft flew within the footprint, there were no coincident spirals during GOME overpasses, and the aircraft was at a fixed altitude during most of the flight on the few days of coincident measurements. However care must be taken in a campaign average comparison to address bias from temporal variation and in particular when preferential plume sampling occurs during pronounced shifts in wind direction.

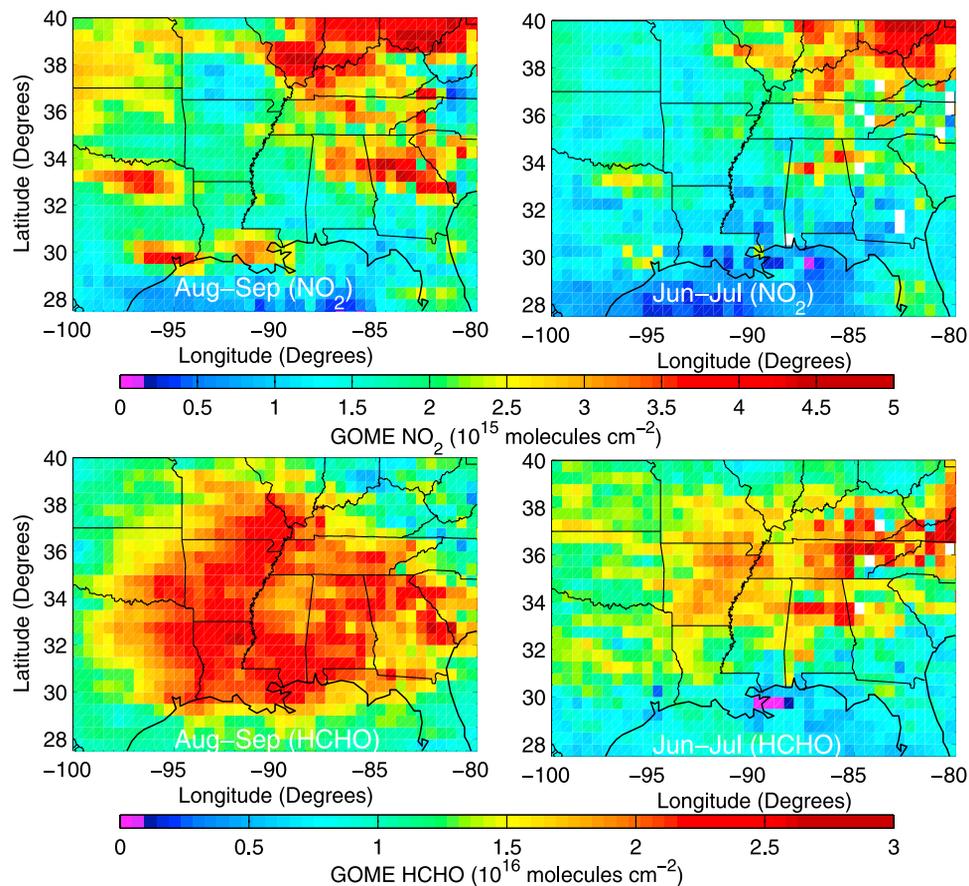
[14] The GOME instrument has nearly uniform sensitivity over the entire spatial footprint. However, the aircraft spatial sampling characteristics are not uniform across the GOME footprint as evident in Figure 1. We achieve more uniform spatial weighting by averaging columns calculated from in situ aircraft measurements over the scale of the GOME footprint, giving equal weight to each cell. Cells without any measurements below 1500 m are assigned the mean column value of the four adjacent 0.2 degree cells. Such assignments occurred for 25% of the cells. Boxes more than 0.5° away from any measurements are excluded from further analysis. We represent the contribution from 6 km to the tropopause by adding the GEOS-CHEM calculation of  $5 \times 10^{14}$  molecules  $\text{cm}^{-2}$  to all tropospheric NO<sub>2</sub> columns and  $1.3 \times 10^{15}$  molecules  $\text{cm}^{-2}$  to all HCHO columns. We calculate partial columns from the airborne measurements by integrating the average NO<sub>2</sub> and HCHO number density in 200 m increments from the surface to 6 km for each 0.2° cell. For the 200 m increments without in situ measurements, we calculate the partial column from the 17th percentile (i.e., one standard deviation below the mean for a normal distribution) of all NO<sub>2</sub> mixing ratios at that altitude for the appropriate campaign, and from the median of all HCHO mixing ratios at that altitude. Inspection of the in situ profiles in Figure 2 guided the selection of the 17th percentile for NO<sub>2</sub> and the median for HCHO to represent measurements over remote regions. Mean NO<sub>2</sub> mixing ratios over the Texas coast are comparable to the 17th percentile over Houston, Nashville, and Atlanta. In contrast, mean HCHO mixing ratios over the Texas coast are not markedly different from those over Houston. Probability distributions reflect these differences. The NO<sub>2</sub> distribution is highly skewed with a median that is half of the mean, indicative of direct NO<sub>x</sub> emissions with high spatial heterogeneity. The HCHO measurements are normally distributed reflecting chemical production from VOC oxidation [Lee *et al.*, 1998; Wert *et al.*, 2003a] and more spatially homogeneous sources.

[15] Figure 3 shows the resulting tropospheric columns. The top two panels illustrate stark spatial heterogeneity in

NO<sub>2</sub>. Tropospheric NO<sub>2</sub> columns over Houston are a factor of 5 larger than those a degree to the south. Tropospheric NO<sub>2</sub> columns over power plants to the west of Nashville are a factor of 5 larger than over neighboring regions. The coefficient of variation (standard deviation divided by the mean) of the in situ NO<sub>2</sub> columns in the east-west direction ranges from 20% over remote regions to 80% over Houston, providing a measure of the subpixel variation over the GOME footprint. The bottom panel shows that HCHO



**Figure 3.** Tropospheric NO<sub>2</sub> and HCHO columns determined from in situ measurements. The gray lines denote boundaries of the Houston, Nashville, and Atlanta metropolitan areas.



**Figure 4.** Tropospheric NO<sub>2</sub> and HCHO columns retrieved from the GOME satellite instrument and regridded at  $0.5^\circ \times 0.5^\circ$  resolution. The two left panels show the mean over 16 August to 13 September 2000. The two right panels show the mean over 24 June to 19 July 1999. White areas indicate regions where the backscattered intensity from clouds persistently exceeds that from the clear sky, a threshold that occurs more frequently at the wavelengths used to retrieve NO<sub>2</sub> (423–451 nm) than HCHO (337–356 nm).

columns exhibit much weaker spatial variation with surprisingly little enhancement from petrochemical facilities downwind of the Houston ship channel. *Wert et al.* [2003a] measured maximum HCHO mixing ratios of 30 ppbv in plumes of highly concentrated alkenes. However mean HCHO mixing ratios below 1500 m over the ship channel are 4–8 ppbv. Maximum HCHO columns are found north and east of Houston, regions of higher isoprene emission from hardwood forests [*Wiedinmyer et al.*, 2001]. The coefficient of variation of the HCHO columns in the east-west direction ranges from 5% to 20%.

[16] Figure 4 shows the tropospheric NO<sub>2</sub> and HCHO columns that we have retrieved from GOME for the TexAQS and SOS campaigns. We regrid the GOME data by weighting each observation by the fractional area covered by the GOME footprint for each  $0.5^\circ$  grid box. Variation in the location of the GOME footprint with successive overpasses reveals some detail finer than the GOME footprint, but horizontal smearing persists. The top panels show local enhancements in tropospheric NO<sub>2</sub> over Houston ( $29.5^\circ\text{N}$ ,  $95^\circ\text{W}$ ), Dallas/Fort Worth ( $32.5^\circ\text{N}$ ,  $97^\circ\text{W}$ ), Nashville ( $36^\circ\text{N}$ ,  $87^\circ\text{W}$ ), and Atlanta ( $34^\circ\text{N}$ ,  $84.5^\circ$ ). A regional enhancement in the tropospheric NO<sub>2</sub> column exists over southern Illinois, Indiana, and Ohio. The smaller NO<sub>2</sub> columns during June–July reflect the shorter NO<sub>x</sub> lifetime.

[17] Earlier manuscripts illustrating tropospheric NO<sub>2</sub> from GOME [i.e., *Martin et al.*, 2002b] showed no clear enhancement over Houston. The apparent discrepancy arises largely from the resolution at which the GOME data are regridded. *Martin et al.* [2002b] regridded the GOME data to a resolution of  $2^\circ \times 2.5^\circ$  for comparison with a GEOS-CHEM model simulation at that resolution. The  $0.5^\circ$  resolution in the present manuscript resolves smaller features. Tropospheric NO<sub>2</sub> columns over Houston regridded at  $2^\circ \times 2.5^\circ$  resolution for July 2000 are 10% higher than those presented in the work of *Martin et al.* [2002b] for July 1996.

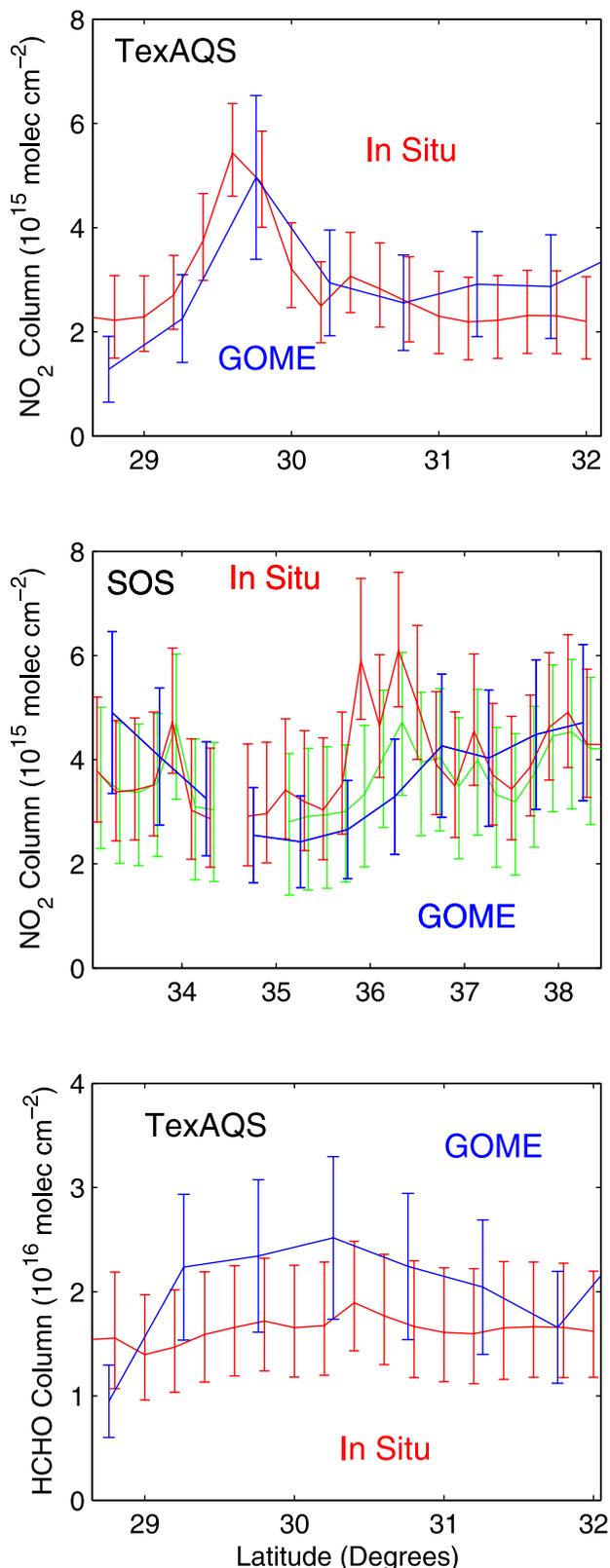
[18] The bottom panel of Figure 4 shows the GOME tropospheric HCHO columns. A broad enhancement is centered on Tennessee during June–July, largely due to isoprene oxidation [*Lee et al.*, 1998; *Palmer et al.*, 2003]. This enhancement progresses southwest into Louisiana and Texas during August–September. The GEIA biogenic isoprene emission inventory shows a similar southwestward seasonal progression of isoprene emissions into northeastern Texas. GOME HCHO columns over eastern Texas are within 20% of mean HCHO columns over the southeast United States. We find that the August–September enhancement in HCHO columns over eastern Texas and the surrounding area is associated with little change in the

frequency of exceedences of the 8-hour standard in the Houston area as reported by the Texas Natural Resource Conservation Commission, consistent with the expectation that regional isoprene emissions have little effect on surface ozone in Houston. However a marked increase in the

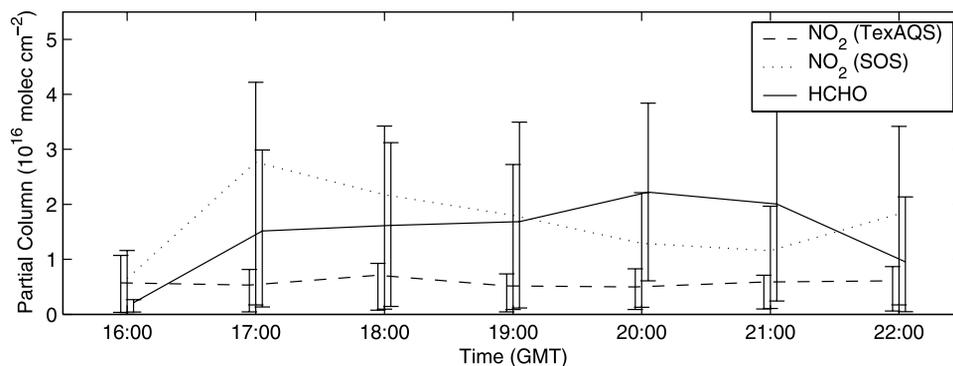
frequency of ozone exceedences to the north and east of Houston occurs in mid-August to mid-September; further work is needed to determine coincidence or causality.

[19] Figure 5 compares tropospheric NO<sub>2</sub> and HCHO columns retrieved from GOME with those calculated from in situ measurements as a function of latitude. The center of the footprint of the GOME data included in the comparison spans 1.5°, resulting in consistent longitudinal coverage between the two measurements since the GOME footprint is 3.3° wide. Error bars indicate the sensitivity of the in situ columns to the assumed percentiles for altitudes without measurements. The two measurement techniques are generally consistent within their uncertainty. Both show a clear NO<sub>2</sub> column enhancement near 29.7°N due to NO<sub>x</sub> emissions from the Houston area. The most prominent discrepancy occurs in the middle panel near 36°N. Aircraft measurements in this region (36°N, 88°W) sampled power plant plumes twice as frequently as GOME by sampling air to the north when winds were from the south and sampling air to the south when winds were from the north. The mean absolute difference between the GOME and in situ measurements for NO<sub>2</sub> is  $6.0 \times 10^{14}$  molecules cm<sup>-2</sup> with a coefficient of determination,  $r^2$ , between the two measurements of 0.54 ( $n = 18$ ). The geometric mean in situ to GOME ratio  $m$  is 1.08, with a small geometric standard deviation  $\sigma$  of 1.27 (i.e., 67% of the values are between  $m/\sigma$  and  $m\sigma$ ). The green line in Figure 5 shows the in situ NO<sub>2</sub> columns after correcting for the sampling bias by excluding the flights on 12 and 13 July when winds were from the north. The mean absolute difference improves to  $4.9 \times 10^{14}$  molecules cm<sup>-2</sup>, the  $r^2$  improves to 0.67, the geometric mean ratio to 1.00, and the geometric standard deviation to 1.24.

[20] The bottom panel shows little spatial variation in the two measurement techniques for HCHO. A weak maximum in the GOME HCHO columns occurs between 29.5°N–30.5°N. Figure 3 shows a similar latitudinal enhancement in the in situ data east of 96°W, but lower HCHO columns to the west. The mean absolute difference for HCHO is  $5.5 \times 10^{15}$  molecules cm<sup>-2</sup>. The geometric mean in situ to GOME ratio for HCHO is 0.84 with a geometric standard deviation of 1.38. The coefficient of determination ( $r^2 = 0.07$ ,  $n = 7$ ) is less representative since the uncertainty in each measurement technique is much larger than the spatial variation.



**Figure 5.** Comparison of tropospheric NO<sub>2</sub> and HCHO columns retrieved from GOME with those determined from in situ measurements. The top and bottom panels show the in situ and GOME columns averaged over 97.75°W–93.75°W. The middle panel shows the in situ and GOME measurements averaged over 85.5°W–89.5°W for latitudes north of 34.5°N and averaged over 82.5°W–86.5°W for latitudes south of 34.5°N. The green line shows NO<sub>2</sub> columns determined from in situ measurements after correcting for a sampling bias. Red and green error bars are derived from column calculations using the 5th and 30th instead of the 17th percentile for NO<sub>2</sub> and the 30th and 70th percentile instead of the median for HCHO for altitudes without measurements. GOME error bars show the retrieval uncertainty discussed in section 3.



**Figure 6.** Diurnal variation of HCHO and NO<sub>2</sub> columns below 3 km. Values are calculated by integrating the mean of all measurements within an hour of the indicated time. Error bars show columns calculated with the 17th and 83rd percentiles instead of the mean.

Pronounced temporal variation and differences in temporal sampling also play a role as discussed below.

## 5. Observed Temporal Variation

[21] Tables 1 and 2 show that the aircraft and space-based measurements were usually not coincident in day or time. Isolation of either temporal or spatial variation is prohibited by the simultaneous change in both the time and location of each measurement. Section 4 assumed that temporal variation in NO<sub>2</sub> and HCHO was small with respect to spatial variation. Here we examine that assumption with particular attention to HCHO.

[22] Figure 6 shows the diurnal variation in partial columns calculated from in situ measurements below 3 km. In situ measurements above 3 km were infrequent. Partial NO<sub>2</sub> columns below 3 km for TexAQS show little diurnal variation, indicating little bias in the comparison with GOME measurements. Partial NO<sub>2</sub> columns for SOS show a maximum at 1700 GMT that coincides with in situ measurements in power plant plumes at that time, and is likely unrelated to temporal variation in the NO<sub>2</sub> column. The mean NO<sub>2</sub> columns in Figure 6 are similar in magnitude to the maximum values in Figure 3, indicating the high frequency of measurements in plumes. HCHO columns exhibit a more pronounced diurnal variation, with a maximum in late afternoon. HCHO columns at the GOME observation time of about 1700 GMT are 5% less than the mean, suggesting that diurnal variation could mask a slightly larger bias between GOME and in situ HCHO measurements.

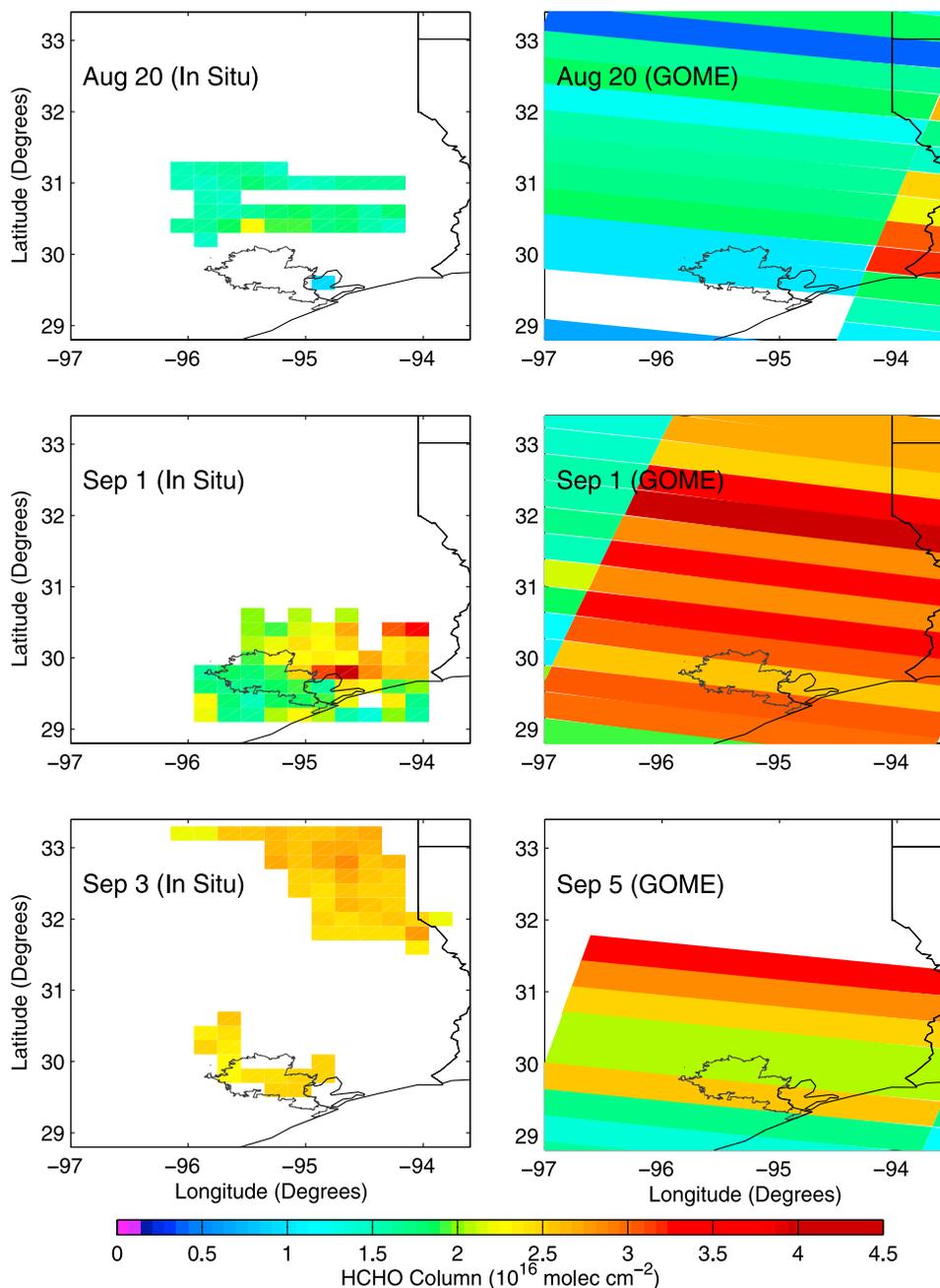
[23] We examine the daily variation in HCHO columns over eastern Texas by assuming that the spatial variation in HCHO is weaker than the daily variation. Figure 3 provides evidence that such an assumption is possible for HCHO, but would be unrealistic for NO<sub>2</sub>. The aircraft often flew at a fixed altitude, providing more spatial than vertical information. We calculate partial columns at altitudes without in situ measurements at a given location from the median HCHO measured elsewhere during the flight, similar to section 4. Figure 7 shows the daily variation in HCHO columns over eastern Texas on two days of coincident measurements. (The coincident 16 August transit flight had sparse in situ measurements.) The limited 3-D sampling of a single aircraft flight prevents quantitative comparison with the

large GOME footprint for validation purposes, but both techniques exhibit qualitatively consistent temporal variation of more than a factor of 2. The pronounced day-to-day variation in HCHO columns suggests that temporal variation may contribute to the differences between the two measurement techniques shown in Figure 5 for HCHO.

[24] We briefly interpret the daily variation in HCHO columns to address the relative contributions of anthropogenic and biogenic VOCs to the GOME HCHO columns in Figure 7. On 20 August, HCHO columns determined from both GOME and aircraft measurements are about 75% of the August–September mean. Ground monitors reported no ozone exceedences in Texas on 20 August. A major episode occurred on 1–5 September when surface temperatures exceeded 35°C and 8-hour surface ozone exceeded 85 ppbv throughout eastern Texas. In situ measurements show HCHO column enhancements to the east of Houston on 1 September when westerly winds transported rapidly produced ozone and HCHO in petrochemical plumes from the Houston ship channel to southeast Texas [Wert *et al.*, 2003a]. Coincident GOME HCHO columns are also 50–100% higher than the August–September mean over southeast Texas with further increase to the north where there were no aircraft measurements. Winds were again westerly on 3 September; in situ measurements show enhanced HCHO columns over a large area of northeast Texas with strong biogenic isoprene emissions [Wiedinmyer *et al.*, 2001; Wert *et al.*, 2003a]. Subsequent GOME measurements on 5 September again show increasing HCHO columns to the north, but clouds prohibit observation north of 32°N. It appears that GOME observations of HCHO columns over eastern Texas include contributions from highly concentrated petrochemical plumes in southeast Texas, but biogenic isoprene emissions dominate over a large area in northeast Texas.

## 6. Conclusion and Recommendations for Future Evaluation

[25] We have evaluated the consistency of space-based observations of tropospheric NO<sub>2</sub> and HCHO columns with in situ measurements of NO<sub>2</sub> and HCHO over urban regions. The in situ measurements were part of the Southern Oxidants Study (SOS) in June–July 1999 and the Texas Air Quality Study (TexAQS) in August–September 2000. The



**Figure 7.** Daily HCHO columns determined from aircraft and GOME. White areas in the left panels indicate regions without measurements below 1500 m. White areas in the right panels indicate regions where the backscattered intensity from clouds exceeds that from the clear sky.

space-based observations were retrieved from the Global Ozone Monitoring Experiment (GOME) satellite instrument during the aircraft campaigns. We focused the comparison on averages over the entire campaign since individual flights do not span the GOME footprint, and there were no coincident spirals during GOME overpasses.

[26] We found that during summer nearly 75% of the tropospheric NO<sub>2</sub> column is below 1500 m over Houston and Nashville, and that 60% of the HCHO column is below 1500 m over Houston. The relative vertical profiles of the in situ measurements were compared with those used in the GOME retrieval. The retrieval uses local profiles from a global 3-D model (GEOS-CHEM). The campaign-averaged

model and in situ profiles are highly consistent. Use of the campaign-averaged in situ profiles in the GOME retrieval would change the campaign-averaged retrieved columns by a few percent.

[27] The average GOME and in situ measurements are generally consistent despite large sampling differences. In situ measurements show detailed spatial structure within the scale of a GOME footprint of 40 km by 320 km. Nonetheless, the mean absolute difference between the two techniques is within their combined uncertainty:  $6.0 \times 10^{14}$  molecules  $\text{cm}^{-2}$  for NO<sub>2</sub> and  $5.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  for HCHO. The geometric mean in situ to GOME ratios are 1.08 for NO<sub>2</sub> and 0.84 for HCHO, with respective

geometric standard deviations of 1.27 and 1.38 (i.e., 67% of the ratios for NO<sub>2</sub> are between 0.85 and 1.37). Both NO<sub>2</sub> measurement techniques show a pronounced local maximum over Houston. The coefficient of determination ( $r^2$ ) of the in situ and GOME observations as a function of latitude is 0.54 for NO<sub>2</sub> ( $n = 18$ ). The largest discrepancy in NO<sub>2</sub> measurements occurs downwind of power plants in Tennessee and arises from differences in spatial sampling. Correcting this sampling bias improves the mean absolute difference to  $4.9 \times 10^{14}$  molecules cm<sup>-2</sup>, the  $r^2$  to 0.67, the geometric mean ratio to 1.00, and the geometric standard deviation to 1.24. A poor spatial correlation for HCHO ( $r^2 = 0.07$ ) reflects a spatial variation that is much less than the measurement uncertainty.

[28] We examined the diurnal and daily temporal variation. Tropospheric NO<sub>2</sub> columns exhibit little diurnal variation, in contrast with HCHO columns which reach a maximum in late afternoon. The mean of the in situ derived HCHO columns for the hour of the GOME overpass is 5% less than the mean of all of the in situ derived HCHO columns, suggesting that diurnal variation could mask a slightly larger bias between GOME and in situ HCHO measurements. The daily variation in HCHO columns is comparable in magnitude to their spatial variation. Differences in daily sampling between GOME and the in situ measurements likely contribute to the poor spatial correlation for the campaign-average HCHO comparison.

[29] GOME measurements show that HCHO columns over eastern Texas during August–September are within 20% of those over the southeastern United States where HCHO columns reflect oxidation of biogenic VOCs. Aircraft measurements indicate that GOME HCHO columns in eastern Texas include a larger contribution from anthropogenic VOCs, especially in southeast Texas, but biogenic VOCs appear to dominate the HCHO budget on a regional scale, especially in northeast Texas. Seasonal and daily enhancements in the GOME HCHO columns are associated with violations of the 8-hour surface ozone standard to the north and east of Houston, but causality of this relationship has not been established.

[30] The aircraft observations used in this study were not intended for GOME validation. Deliberate validation using vertical spirals coincident in time and space with satellite overpasses is obviously needed in the future. This is an important issue for the new generation of nadir sensors capable of measuring tropospheric NO<sub>2</sub> and HCHO from space, SCIAMACHY [Bovensmann *et al.*, 1999] on board Envisat and OMI on board Aura. Vertical spirals should attempt to span the entire troposphere. Only 5% of the column may reside above 6 km over polluted regions, but convective enhancements must be ruled out. More than 10% of the column could reside below 150 m. Ideally the aircraft profiles should be complemented with surface observations to provide continuity down to the surface. Ground-based measurements of the vertical profiles, e.g., using balloons, would also provide this continuity. A validation location without major point sources (i.e., with horizontally homogeneous concentrations) is needed to reduce the consequences of unavoidable mismatch in the horizontal footprint between the aircraft and the satellite. This homogeneity should be verified with the aircraft by conducting a mixed layer horizontal leg over the satellite footprint prior to

the spiral. Minimizing or accounting for horizontal heterogeneity is more of a challenge for GOME because of the large footprint ( $320 \times 40$  km<sup>2</sup>) than for SCIAMACHY ( $60 \times 30$  km<sup>2</sup>) or OMI ( $24 \times 13$  km<sup>2</sup>).

## Appendix A: GEOS-CHEM Model Description

[31] The retrieval of tropospheric NO<sub>2</sub> and HCHO columns requires independent information on their relative vertical profile. A global 3-D model of tropospheric chemistry is the best source of this information. We use here the GEOS-CHEM model [Bey *et al.*, 2001] version 4.26 (<http://www-as.harvard.edu/chemistry/trop/geos/>) [Martin *et al.*, 2003a]. The model is driven by assimilated meteorological data from the Goddard Earth Observing System of the NASA Data Assimilation Office. The meteorological data include 3-D fields updated every 3 hours for surface fluxes and mixing depths, and every 6 hours for other variables. We use for this study the GEOS data for 1996–1997, available with a resolution of 2° latitude by 2.5° longitude and 46 sigma levels in the vertical extending up to 0.1 hPa. The five lowest levels are centered at 50, 250, 600, 1100, and 1700 m for a column based at sea level. For computational expedience in GEOS-CHEM the vertical levels above the lower stratosphere are merged, retaining a total of 26. We retain the original horizontal resolution. The tropopause in the model is determined using the World Meteorological Organization standard criterion of a 2 K km<sup>-1</sup> lapse rate.

[32] The GEOS-CHEM model includes a detailed simulation of tropospheric ozone-NO<sub>x</sub>-hydrocarbon chemistry, originally described by Horowitz *et al.* [1998] and updated as described in several papers [Bey *et al.*, 2001; Fiore *et al.*, 2002; Martin *et al.*, 2002a, 2003a]. Reactions in aerosols, including N<sub>2</sub>O<sub>5</sub> hydrolysis (reaction probability 0.1), are described by Jacob [2000]. The chemical evolution of about 120 species is computed with a Gear solver [Jacobson and Turco, 1994]. Photolysis frequencies are computed using the Fast-J radiative transfer algorithm [Wild *et al.*, 2000] which includes Rayleigh scattering as well as Mie scattering by clouds and aerosols. Aerosol fields affecting radiation and heterogeneous chemistry are 3-D monthly means from a 1996–1997 simulation with the GOCART model [Chin *et al.*, 2000; Ginoux *et al.*, 2001; Chin *et al.*, 2002] which uses the same GEOS meteorological fields and transport algorithms as GEOS-CHEM.

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