Formaldehyde columns from the Ozone Monitoring Instrument: Urban versus background levels and evaluation using aircraft data and a global model

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[1] We combine aircraft measurements (Second Texas Air Quality Study, Megacity Initiative: Local and Global Research Observations, Intercontinental Chemical Transport Experiment: Phase B) over the United States, Mexico, and the Pacific with a 3-D model (GEOS-Chem) to evaluate formaldehyde column (Ω_HCHO) retrievals from the Ozone Monitoring Instrument (OMI) and assess the information they provide on HCHO across local to regional scales and urban to background regimes. OMI Ω_HCHO correlates well with columns derived from aircraft measurements and GEOS-Chem (R = 0.80). For the full data ensemble, OMI’s mean bias is −3% relative to aircraft-derived Ω_HCHO (−17% where Ω_HCHO > 5 × 10^15 molecules cm^-2) and −8% relative to GEOS-Chem, within expected uncertainty for the retrieval. Some negative bias is expected for the satellite and model, given the plume sampling of many flights and averaging over the satellite and model footprints. Major axis regression for OMI versus aircraft and model columns yields slopes (95% confidence intervals) of 0.80 (0.62–1.03) and 0.98 (0.73–1.35), respectively, with no significant intercept. Aircraft measurements indicate that the normalized vertical HCHO distribution, required by the satellite retrieval, is well captured by GEOS-Chem, except near Mexico City. Using measured HCHO profiles in the retrieval algorithm does not improve satellite-aircraft agreement, suggesting that use of a global model to specify shape factors does not substantially degrade retrievals over polluted areas. While the OMI measurements show that biogenic volatile organic compounds dominate intra-annual and regional Ω_HCHO variability across the United States, smaller anthropogenic Ω_HCHO gradients are detectable at finer spatial scales (~20–200 km) near many urban areas.


1. Introduction

[2] Formaldehyde (HCHO) is a common product in the oxidation of atmospheric volatile organic compounds (VOCs), with a typical lifetime (against photolysis and oxidation by OH) of a few hours in daytime [Sander et al., 2006]. While methane oxidation is the largest HCHO source to the global troposphere, HCHO variability over land is dominated by its production from nonmethane VOCs [Millet et al., 2006; Stavrakou et al., 2009b]. Primary HCHO emissions from combustion [Garcia et al., 2006] and vegetation [Janson et al., 1999; Kesselmeier and Staudt, 1999; Martin et al., 1999; Seco et al., 2007] also contribute but are minor compared to secondary formation. Measurements of HCHO columns (Ω_HCHO, molecules cm^-2) from the Ozone Monitoring Instrument (OMI) and other space-borne sensors can provide local-to-global constraints on the emission sources and photochemical processing of VOCs [Chance et al., 2000; Abbot et al., 2003; Palmer et al., 2003, 2006, 2007; Wittrock et al., 2006; Millet et al., 2006, 2008; Fu et al., 2007; Stavrakou et al., 2009a; Duncan et al., 2010; Curci et al., 2010]. Here we combine OMI Ω_HCHO data, aircraft measurements (collected over the United States, Mexico and the Pacific Ocean) and a chemical transport model (GEOS-Chem) to evaluate OMI measure-
ments and assess the information they provide on HCHO in urban versus background regimes.

[1] Space–borne sensors for measuring atmospheric HCHO include the Global Ozone Monitoring Experiment (GOME-1 [Burrows et al., 1999; Chance et al., 2000] and GOME-2 [Callies et al., 2000]), the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) [Burrows et al., 1995; Bovensmann et al., 1999], and OMI [Levelt et al., 2006]. In each case $\Omega_{HCHO}$ is determined from solar backscatter measurements in near-UV wavelengths (310–365 nm). Of the available sensors, OMI’s high spatial resolution (13 × 24 km$^2$ at nadir) and daily global coverage offer substantial advantages for resolving spatial variability and reducing measurement uncertainty through improved sampling statistics. The small footprint also reduces data contamination by clouds, the primary source of error in the retrieval [Millet et al., 2006].

[4] Research to date has applied HCHO column data to study anthropogenic and biogenic VOC emissions from North and South America [Abbot et al., 2003; Palmer et al., 2003, 2006, 2007; Barkley et al., 2008; Millet et al., 2006, 2008], Europe [Dufour et al., 2009; Curci et al., 2010], Asia [Fu et al., 2007], and the globe [Wittrock et al., 2006; Stavrakou et al., 2009a, 2009b; Shim et al., 2005], and to examine ozone chemistry over the United States [Martin et al., 2004b; Duncan et al., 2010]. Quantitative interpretation of $\Omega_{HCHO}$ retrievals requires error characterization and consistency evaluation against other data sets, but opportunities for direct validation have so far been limited, particularly for OMI. Millet et al. [2008] compared OMI $\Omega_{HCHO}$ with GOME-1 and found differences of 2%–14% (with OMI lower), less than the estimated measurement uncertainty. Others have compared HCHO retrievals from SCIAMACHY with ground-based UV/visible light and Fourier transform infrared measurements [Wittrock et al., 2006; Vigouroux et al., 2009]. Earlier work by Ladstätter-Weißenmayer et al. [2003] and Martin et al. [2004a] carried out comparisons between GOME-1 HCHO and some of the limited aircraft measurements then available; both studies found agreement between satellite and in situ measurements within instrument uncertainty, including where $\Omega_{HCHO}$ was near the detection limit (4.0 × 10$^{15}$ molecules cm$^{-2}$) [Chance et al., 2000].

[5] Here we use aircraft measurements (collected over the United States, Mexico and the Pacific Ocean) and a chemical transport model (GEOS-Chem) to evaluate and interpret OMI $\Omega_{HCHO}$ measurements. The present analysis builds on previous work by directly evaluating OMI $\Omega_{HCHO}$ and its variability across marine to urban regimes. We then apply the OMI data to examine HCHO gradients over North America across urban-to-background regimes as a function of season. We interpret our findings with respect to their implications for uncertainty in $\Omega_{HCHO}$ retrievals from OMI and similar space–borne sensors.

2. Data Sources

2.1. Aircraft Campaigns

[6] Figure 1 shows flight tracks for the aircraft campaigns used here: the Second Texas Air Quality Study (TexAQS II)
2.2. Ozone Monitoring Instrument

[8] OMI is on board NASA’s EOS Aura satellite at ~705 km altitude in a Sun-synchronous orbit with 98° inclination and 1338 local equator crossing time [Levett et al., 2006]. Aura’s period is approximately 99 min, providing 14 to 15 orbits and global coverage daily. OMI is a UV/visible light nadir solar backscatter CCD spectrometer covering the spectral range 270–500 nm with a resolution of 0.45 nm between 310 and 365 nm. OMI has a 114° swath angle covering approximately 2600 km on Earth; its 60 pixels have footprints ranging from 13 × 24 km2 at nadir to 28 × 160 km2 at swath edges. OMI reads out a single cross-track swath line approximately every 3.5 s yielding 1644 swaths per orbit.

[10] For our analysis we use the standard OMI HCHO data product version 2.0 (Collection 3). Column values are subject to a number of quality checks. Aside from cloud screening (see below), only column values flagged as “good” in the product are included [Kurosu, 2008]. Across-track striping (discontinuities across the swath), arising from imperfect cross-calibration and different dead/hot pixel masks for the 60 CCD detector regions that provide the across-track coverage, has a significant effect on HCHO due to the small atmospheric optical density of this absorber. The derivation of the OMI HCHO data product includes methods to minimize this effect, including use of an earthshine radiance from the remote Pacific in lieu of a solar irradiance reference, residual outlier screening during the nonlinear least squares fitting procedure, and the application of a postretrieval across-track smoothing filter. Temporal averaging over longer time periods further removes the impact of the stripes. During June 2007 OMI developed an anomaly affecting radiance measurements in cross-track positions 53 and 54 (0-based) caused by a partial external blockage of the radiance port. This so-called row anomaly expanded over time to other cross-track positions and is being actively monitored by the instrument team (http://www.knmi.nl/omi/research/product/rowanomaly-background.php). We remove these pixels from consideration in all postanomaly orbits.

[11] For comparing OMI with the aircraft data we restrict flight data to times bracketing the OMI nadir overpass (1200–1500 LT), a criterion that excludes 33 of 71 total flights (Figure 1). We also restrict the use of OMI pixels to those at solar zenith angle (SZA) ≤80° (see http://eospspo.gsfc.nasa.gov/eos_homepage/for_scientists/atbd/viewInstrument.php?instrument=13/) and cloud fraction ≤0.4 [Chance et al., 2000; Palmer et al., 2001; Millet et al., 2006], eliminating OMI retrievals during 7 of the 38 remaining flights.

2.3. GEOS-Chem Chemical Transport Model

[12] We use the GEOS-Chem 3-D model of atmospheric chemistry to simulate \( \Delta_{\text{HCHO}} \) for cross-evaluation with OMI and the aircraft data, and to specify the HCHO vertical profile shapes needed in the OMI retrieval (see section 3.1).
GEOS-Chem v8.2 (http://www.GEOS-Chem.org/) is a 3-D Eulerian global chemical transport model including detailed ozone-NOx-VOC chemistry [Bey et al., 2001]. The chemical mechanism includes >80 species and >300 reactions including heterogeneous chemistry, with aerosols simulated as described by Park et al. [2004]. GEOS-Chem uses assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-5) including mixing height and surface characteristics (3 hour temporal resolution), wind, convective and advective mass transport, clouds, temperature and precipitation (6 hour resolution) [Bey et al., 2001; Park et al., 2004]. The meteorological data have 0.5° x 0.667° spatial resolution (latitude x longitude) and 72 vertical layers, which we degrade to 2° x 2.5° and 47 vertical layers for computational expediency. Anthropogenic and biogenic emissions used here are described elsewhere [Millet et al., 2010]. For consistency with the aircraft data we sample the model along each flight track at the time and location of the in situ measurements and calculate HCHO columns as described in section 3.

3. HCHO Column Determination

3.1. OMI HCHO Column Retrievals

[13] HCHO column abundance is retrieved from OMI observations of solar radiation backscattered and reflected from Earth’s atmosphere and surface. Radiiances are processed through spectral fitting algorithms in the 327.5–356.5 nm window based on nonlinear least squares minimization to retrieve the HCHO abundance along the viewing path (slant column). The ratio of the slant column to the vertical column amount (air mass factor, AMF) is a function of viewing geometry, surface reflectance, atmospheric scattering, and the normalized vertical distribution of HCHO (shape factor) [Palmer et al., 2001]. Here we compute AMFs with a lookup table derived using the Doubling Adding KNMI (DAK) radiative transfer model [Stamnes, 2001]. In calculating the AMF for each OMI pixel we use GEOS-Chem to estimate the HCHO shape factor at the location and time of the satellite overpass. This approach assures self-consistency when comparing retrieved columns to those simulated by GEOS-Chem but may introduce model bias in the retrieval, as discussed below. Sources of error in the AMF, in addition to the specification of the shape factor, include cloud and aerosol effects and the surface albedo. In previous work, Millet et al. [2006] found the combination of these to result in an overall AMF uncertainty of ≈20% for a scene with a cloud fraction of 0.2.

[14] The spectral fitting uncertainty for OMI HCHO slant columns ranges from 40% to 100%, comparable to the instrument’s predecessors, though this uncertainty can be significantly reduced through the increased sampling made possible by OMI’s small footprint and high temporal coverage. For comparison with aircraft data we average all OMI pixels transected by a flight track. This approach reduces the effective spatial resolution, particularly for long flight tracks, but also reduces random error in the comparisons. The number of OMI observations averaged together for any given flight ranges from 7 to 199 (median = 69) resulting in an average uncertainty for all flights of 29% (relative standard error of all OMI scenes) or 15% where \( \Omega_{\text{HCHO}} > 5.0 \times 10^{15} \) molecules cm\(^{-2}\).

3.2. HCHO Vertical Profiles and Columns Computed From Aircraft Measurements and GEOS-Chem

[15] Figure 2 compares mean HCHO vertical profiles measured aboard the aircraft (averaged in 50 hPa bins) to those simulated by GEOS-Chem for each of the aircraft campaigns. The ordinate value of each data point is determined as the average altitude of all HCHO measurements in each bin. Over land and in continental outflow (e.g., MILAGRO, TexAQS II) we observe the highest HCHO concentrations near the surface, decreasing strongly with height above the boundary layer. Over the remote ocean (e.g., INTEX-B) we see low concentrations throughout the atmospheric column with little vertical gradient. These patterns reflect the predominant terrestrial source of HCHO precursors combined with the short atmospheric lifetime of HCHO. On average GEOS-Chem captures the observed HCHO profile shape, providing support for its use in computing the AMF. An exception is over and downwind of Mexico City (MILAGRO campaign), where a low model bias is evident compared to highly variable in situ observations. A. Fried et al. (manuscript in preparation, 2010) discuss the potential cause for analogous box model underestimates in this regime.

[16] We estimate \( \Omega_{\text{HCHO}} \) from the observed and modeled profiles on each flight day (1200–1500 LT) by integrating the mean vertical HCHO profile (expressed in number concentration, molecules cm\(^{-3}\)) from the flight floor to the flight ceiling. To estimate HCHO abundance above and below each profile, we extrapolate the topmost measured mixing ratio as constant to the tropopause (zero above the tropopause) and the bottommost measured mixing ratio as constant to the surface. The tropopause is taken as the average altitude of all HCHO measurements in the last bin with a mixing ratio above 5.0 × 10\(^{15}\) molecules cm\(^{-2}\). Surface altitude is determined from a 10 min resolution topographic map.
Figure 3. OMI HCHO columns versus model (red) and aircraft (black) profile-derived HCHO columns. Dashed lines are best fit (major axis regression), with regression parameters given in the inset. Dotted lines show the 95% confidence interval for the best-fit line. Vertical error bars show the standard error in the OMI column values, and horizontal error bars show the estimated uncertainty in each profile-derived column.

The mean flight floor across flights ranges from 308 to 532 m for the various campaigns. During TexAQS II, with its urban focus, the fraction of measurements taken in the boundary layer ranges between 51% and 100% for the two aircraft (versus 14%–59% and 2%–37% for INTEX-B and MILAGRO, respectively). We discard any computed columns where the extrapolated fraction (above and below the measured HCHO profile) exceeds 50% of the total computed HCHO column, leaving a total of 29 flights for the comparison. The GEOS-Chem HCHO columns computed in this way agree well with the average of the full model columns over transected grid squares (weighted by the number of measurements over each) \( R = 0.98 \), slope = 1.10 (0.99–1.21), intercept = –0.02 (–0.08–0.05) (95% confidence interval (CI)), demonstrating the reliability of the overall extrapolation approach.

We estimate the uncertainty in the extrapolated columns by computing upper and lower limits as follows. We recalculate \( \Omega_{\text{HCHO}} \) using the vertical profiles of mean HCHO concentration ±1σ (standard deviation) for each vertical bin and extrapolate using the flight’s mean tropopause height and mean surface altitude ±1σ. We find in this way that most of the uncertainty in the extrapolated columns stems from HCHO ambient variability over the domain of each flight (on average 67% of total uncertainty), with a smaller error introduced by extrapolating to the surface (20% of total uncertainty) and tropopause (13% of total uncertainty). Over all flights, the uncertainty in the HCHO columns derived in this way ranges from −17% to +17% (mean = 6%), which is similar to the level of agreement between the GEOS-Chem extrapolated and full vertical HCHO columns.

4. Comparing OMI HCHO Columns With Modeled and in Situ Values

Figure 3 compares OMI \( \Omega_{\text{HCHO}} \) with columns derived from the measured and simulated profiles. Note that negative \( \Omega_{\text{HCHO}} \) values can occur in the OMI retrieval as the result of minimizing residuals during the spectral fitting when HCHO is close to or below the sensor detection limit (OMI HCHO columns flagged as “good” and used here are ≥0 within 2σ fitting uncertainties). Discarding those negative values would produce an erroneously high bias in any temporal or spatial averaging. The OMI HCHO columns are well correlated with those derived from the aircraft and model profiles: \( R = 0.81 \) (0.68–0.91) and 0.80 (0.75–0.88) (95% CI), respectively. Major axis regression of OMI versus model \( \Omega_{\text{HCHO}} \) yields a best-fit line of \( Y = 0.98 (0.73–1.35)X - 0.03 \) (−0.28–0.17) (95% CI). The corresponding fit for OMI versus aircraft columns is \( Y = 0.80 (0.62–1.03)X - 0.01 \) (−0.23–0.18) (95% CI). These statistics include only columns with extrapolated fraction <50%. A more restrictive criterion (<20%) yields regressions with very similar slopes and intercepts but reduces the correlation (to 0.69 versus the measurements and 0.79 versus the model).

This data set represents a challenging test case for both the satellite and the model since many flights focused on sampling polluted urban and biomass-burning plumes, which may be diluted by averaging over the satellite/model footprint (up to 28 × 160 km² and 2° × 2.5°). Nevertheless, as shown in Figure 4, OMI’s relative bias compared to the aircraft columns is less than 3% for the full data ensemble and −17% when HCHO is elevated \( \left( \Omega_{\text{HCHO}} > 5 \times 10^{15} \text{ molecules cm}^{-2} \right) \), values that are within the expected uncertainty in satellite-based HCHO column measurements [Millet et al., 2006] and comparable to the level of uncertainty in extrapolating full columns from the flight-track data. This bias is also similar to what was found earlier (−2 to −14%) for OMI relative to GOME-1 [Millet et al., 2008]. The average bias

Figure 4. OMI relative bias as a function of HCHO column abundance relative to in situ (black) and modeled (red) columns.
for the GEOS-Chem columns compared to the aircraft values is −5% for all flights and −23% when $\Omega_{\text{HCHO}} > 5 \times 10^{15}$ molecules cm$^{-2}$.

[21] Computing the AMF in the HCHO retrieval requires a priori the normalized vertical distribution of HCHO (shape factor) for each satellite pixel. This information may be taken from climatology or provided by a 3-D model (here we use GEOS-Chem). To see how this parameter affects the OMI retrievals, we recomputed the AMFs using the measured in situ HCHO profiles for each flight in lieu of the corresponding modeled profiles. AMFs calculated using the measured HCHO profiles were on average 95% ± 15% (1σ) of those calculated using shape factors from GEOS-Chem. The overall level of agreement between OMI and aircraft HCHO columns did not improve with the use of measured HCHO profiles in the retrieval.

5. Temporal and Spatial Gradients in HCHO Over North America as Observed by OMI

[22] In this section we apply the OMI data to investigate spatial and temporal patterns in urban versus rural HCHO across the United States, and the extent to which these patterns are modified by anthropogenic VOCs in a way that is detectable from space.

[23] Figure 5 shows monthly mean OMI $\Omega_{\text{HCHO}}$ retrievals over North America for April–October during 2005–2007. Individual OMI pixels are projected onto, and averaged over, a $0.25^\circ \times 0.25^\circ$ grid. There is a clear seasonal cycle over North America, especially pronounced in the U.S. Southeast, which is consistent with the distribution of biogenic VOC emissions and changes in solar radiation and temperature during the growing season. Despite significant (albeit declining) anthropogenic VOC emissions in the United States [Parrish, 2006] and OMI’s high spatial resolution, observed HCHO columns over urban areas generally do not (at any time of year) exhibit the dramatic enhancements seen over the U.S. Southeast during the growing season. Variability in $\Omega_{\text{HCHO}}$ reflects the emission strength and near-field HCHO yield of precursor VOCs. As seen in Figure 5, the product of the two is dominated by biogenic VOCs over the United States (and in particular by isoprene emissions [Palmer et al., 2003; Millet et al., 2006]). On the other hand, an anthropogenic contribution to the HCHO column may be apparent at finer scales around urban areas; we return to this question below. Strong $\Omega_{\text{HCHO}}$ enhancements are visible over the Yucatan Peninsula during April and May, reflecting extensive biomass burning in this region during the dry season [Yokelson et al., 2009].

[24] The observed HCHO distribution contrasts with that of NO$_2$, which is dominated by anthropogenic emissions over the continental United States [Hudman et al., 2007]. Figure 6 illustrates this contrast, showing OMI $\Omega_{\text{HCHO}}$ and $\Omega_{\text{NO}_2}$ for June-August during 2005–2007 (9 months total) binned by population density over four quadrants of the United States (25°–50°N, 65°–130°W, sectioned at 98°W and 38°N) (OMI NO$_2$ data provided by KNMI in collaboration with NASA, http://www.temis.nl/; population data sourced from 2005 Gridded Population of the World v.3, CIESIN/SEDAC, Columbia University, http://sedac.ciesin.columbia.edu/gpw/). The OMI data shown in Figure 6 are first gridded to $0.25^\circ \times 0.25^\circ$ and then binned such that the mean population density changes by approximately a factor of 2 between bins. Employing population- and land area–weighted schemes (plots not shown), in which each bin represents equal land area or an equal fraction of the total population, produces similar results. The total number of OMI observations averaged in each bin in Figure 6 varies (10th–90th percentile) from 9,602 to 135,292 (median = 46,855) and the resulting uncertainty (standard error) varies (10th–90th percentile) from $3.2 \times 10^{13}$ to $1.3 \times 10^{14}$ molecules cm$^{-2}$ (median = $5.75 \times 10^{13}$ molecules cm$^{-2}$).

[25] For each U.S. quadrant in Figure 6, $\Omega_{\text{NO}_2}$ increases strongly in the most densely populated areas, but in general this is not the case for $\Omega_{\text{HCHO}}$. For instance, in the U.S. Southwest and Northwest, median $\Omega_{\text{NO}_2}$ increases by more than a factor of 4 from remote to urban areas (first and last bins in Figure 6)
while $\Omega_{\text{HCHO}}$ changes by <15%. Only in the U.S. Northeast (and perhaps the Southwest) does $\Omega_{\text{HCHO}}$ exhibit a discernable increase in densely populated areas. The stronger relationship between $\Omega_{\text{HCHO}}$ and population density for the U.S. Northeast may reflect the fact that this quadrant contains nearly half the U.S. population (45% of the population total, versus 27%, 19% and 9% for the Southeast, Southwest and Northwest, respectively), and the higher associated anthropogenic VOC emissions. On the other hand, the population distribution is biased to the southern part of this quadrant, so that temperature also increases with population density here (not shown). The observed $\Omega_{\text{HCHO}}$ trend may therefore reflect an underlying temperature-isoprene correlation. In any case, even in the Northeast the relationship between $\Omega_{\text{HCHO}}$ and population density is much weaker than for NO$_2$; median $\Omega_{\text{HCHO}}$ increases on average 7% between bins versus 25% for $\Omega_{\text{NO2}}$.

[26] As in Figure 5, we see in Figure 6 that the western regions lack the broad HCHO enhancements seen in the eastern United States, with the highest $\Omega_{\text{HCHO}}$ values in the U.S. Southeast owing to strong regional isoprene emissions. This region also exhibits the weakest relationship between $\Omega_{\text{NO2}}$ and population density. This may reflect higher regional OH (due to high water vapor concentrations and actinic fluxes) and therefore shorter NO$_2$ lifetime, or it may reflect the population distribution within the region. We return to this point below in the context of HCHO. Finally, the anomalously low column values for HCHO and NO$_2$ in the first and second bins for this quadrant reflect low-population grid squares straddling the Gulf of Mexico coastline in Louisiana, Texas and Florida which are influenced by clean marine air.

[27] Figure 6 illustrates broad differences between HCHO and NO$_2$ column amounts in urban versus rural locations in the United States, but does not resolve any geographic biases that might exist within quadrant (for instance, populations predominantly on coasts versus inland). To examine urban-rural differences in more detail, and to assess the extent to which anthropogenic contributions to $\Omega_{\text{HCHO}}$ are detectable from the satellite, we plot $\Omega_{\text{HCHO}}$ in Figure 7 as a function of radial distance from the city center (population density-weighted city centroid) for selected major cities within each of the four U.S. quadrants. Data shown are averaged by season for 2005–2007 (inclusive) and show only HCHO column measurements over land. Ordinate scales in Figure 7 vary by quadrant to provide better resolution.

[28] The extent to which urban areas make a discernable contribution to $\Omega_{\text{HCHO}}$ variability over the United States via oxidation of reactive anthropogenic VOCs should manifest in Figure 7 as elevated $\Omega_{\text{HCHO}}$ values over the city, decreasing with distance from the city center. Relatively long-lived anthropogenic VOCs can also react to produce HCHO, but this contribution is spread out spatially and does not contribute to detectable variation from the perspective of the satellite instrument [Palmer et al., 2003].
Figure 7 reveals such gradients (high $\Omega_{\text{HCHO}}$ near the city center, low farther away) for some but not all cities, influenced by season and the local geography. In all seasons (most notably in summer) Los Angeles and New York stand out as the strongest examples of elevated $\Omega_{\text{HCHO}}$ in the city, compared to surrounding areas. During summer months, HCHO columns over the center of Los Angeles and New York are on average 128% and 67% higher than they are 200 km away, respectively.

The strength of the anthropogenic signal for each city in Figure 7 depends in part on regional HCHO levels and therefore on regional biogenic isoprene emissions. For example, over Atlanta during summer, $\Omega_{\text{HCHO}}$ declines only weakly with distance from the city center, dropping by <13% over 200 km. However, rural $\Omega_{\text{HCHO}}$ values outside Atlanta are 2–4 times higher than outside New York or Los Angeles, masking any urban enhancement that might otherwise be detectable. Another factor attenuating the gradients in Figure 7 might be differing vegetation (cover and type) inside versus outside cities, resulting in lower isoprene emissions in urban than in rural environments.

Portland exhibits the same general behavior as New York and Los Angeles, though to a lesser extent. Seattle is anomalous, with lower $\Omega_{\text{HCHO}}$ over the urban core compared to the surroundings; one likely explanation is inbound transport of clean marine air. Houston is also an interesting case, with elevated urban $\Omega_{\text{HCHO}}$ values during spring and fall (~30% higher in urban than in rural areas), but little or no apparent gradient (10% or less) during summer. Houston has high reactive olefin emissions from the local petrochemical industry [Jobson et al., 2004; Leuchner and Rappenglück, 2010] (centered around the Houston ship channel, ~60 km from the Houston city center), but their summertime contribution to HCHO columns may be obscured in Figure 7 by increased isoprene columns from the surrounding areas.

Figure 8 shows the seasonality of OMI $\Omega_{\text{HCHO}}$ observations over the same eight cities shown in Figure 7, in comparison with terrestrial and oceanic background levels. Mean $\Omega_{\text{HCHO}}$ values for specific cities are determined as a built area-weighted average of OMI $\Omega_{\text{HCHO}}$ values within 100 km of each city’s center (population density-weighted centroid). Terrestrial background $\Omega_{\text{HCHO}}$ values are determined for each U.S. quadrant as an average of all 0.25° grid squares in the region with ≤1% built area (comprising 77%, 48%, 73% and 37% of the land area in the U.S. Northwest, Northeast, Southwest and Southeast regions, respectively). Northern Hemispheric (0°–64°N) ocean background is determined as an average $\Omega_{\text{HCHO}}$ over marine grid squares.

We see in Figure 8 that the urban HCHO columns tend to exhibit similar seasonality and dynamic range as the nonurban terrestrial background levels within each region. In the West, urban HCHO columns are similar to marine background levels during fall and spring, and are elevated by only 23%–92% compared to the marine background in summer. In the East, urban HCHO levels are higher during...
summer, but still fall within the terrestrial background range seen within the quadrant (Atlanta lies outside the 0.1–0.9 background quantiles plotted in Figure 8, but inside the full range). In general, the seasonality in urban \( W \text{HCHO} \) is consistent with that seen in the surrounding nonurbanized region. We examined a range of other major U.S. cities with comparable results.

6. Discussion

[33] Formaldehyde column (\( \Omega_{\text{HCHO}} \)) measurements from the Ozone Monitoring Instrument (OMI), with \( 13 \times 24 \text{ km}^2 \) nadir footprint and daily global coverage, provide a highly resolved data set for examining biogenic and anthropogenic sources of VOCs. Here we used vertical profile measurements of HCHO from recent aircraft missions, combined with a global 3-D model (GEOS-Chem), to evaluate OMI HCHO retrievals and their fidelity in terms of resolving urban versus background HCHO column abundance. The average bias in the OMI columns was \(<3\%\) relative to the aircraft values for the full data set, and \(-17\%\) where \( \Omega_{\text{HCHO}} > 5 \times 10^{13} \text{ molecules cm}^{-2} \). The \(-17\%\) bias is within the expected uncertainty for space-borne HCHO retrievals, but may also reflect the aircrafts’ preferential sampling of polluted plumes, which are averaged over the satellite footprint. This level of error is also similar to the uncertainty we expect for extrapolating in situ measurements to full HCHO columns. Further evaluation would be useful to determine the extent to which the discrepancy reflects retrieval bias rather than just representation error for this particular case. We discuss this issue further below.

[34] On average, GEOS-Chem reproduces the shape of the HCHO vertical profiles measured onboard the aircraft. The use of measured HCHO shape factors (normalized vertical profile) in the AMF computation did not improve the level of agreement with the aircraft data compared to using shape factors from GEOS-Chem, despite the \( 2^\circ \times 2.5^\circ \) model resolution and urban focus of several of the flights. On this basis, we conclude that use of shape factors from a global model does not introduce a significant bias in satellite measurements of HCHO over urban areas.

[35] OMI \( \Omega_{\text{HCHO}} \) correlates well with columns extrapolated from the aircraft profiles and with those derived from GEOS-Chem sampled along the flight tracks (\( R = 0.80 \) and 0.81). This finding suggests OMI and similar instruments reliably capture horizontal gradients in HCHO given sufficient averaging over time and/or space to reduce random noise in the retrieval.

[36] HCHO columns measured by OMI over North America and the Pacific exhibit temporal and spatial patterns consistent with biogenic VOCs as the dominant cause of variability, as has been demonstrated previously [Abbot et al., 2003; Martin et al., 2004a; Millet et al., 2006; Shim et al., 2005]. HCHO columns over urban areas generally exhibit similar seasonality as the nonurban terrestrial background for the surrounding region. However, fine-scale spatial gradients are detectable in the vicinity of certain urban areas, for instance in New York and Los Angeles, where \( \Omega_{\text{HCHO}} \) can...
decrease by >50% between the urban core and locations 200 km from the city. While detectable, in an absolute sense these gradients are much smaller than those associated with spatial and temporal changes in biogenic isoprene emission over the United States.

[37] While OMI and similar satellite sensors provide a rich global data set for understanding hydrocarbon emissions and chemistry, the scarcity of in situ HCHO measurements for coincident validation remains an issue. One way to address this would be a ground-based remote sensing network spanning urban to forested locales. This would provide a complementary data stream with high sensitivity to trace gases in the planetary boundary layer, and a means to cross-compare the current generation of satellite sensors and the upcoming GEO-CAPE instrumentation.

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