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Citation
Zhu, Lei, Daniel J Jacob, Loretta J Mickley, Eloïse A Marais, Daniel S Cohan, Yasuko Yoshida, Bryan N Duncan, Gonzalo González Abad, and Kelly V Chance. 2014. “Anthropogenic Emissions of Highly Reactive Volatile Organic Compounds in Eastern Texas Inferred from Oversampling of Satellite [OMI] Measurements of HCHO Columns.” Environmental Research Letters 9 (11) (November 1): 114004. doi:10.1088/1748-9326/9/11/114004.

Published Version
doi:10.1088/1748-9326/9/11/114004

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Accessibility
Anthropogenic emissions of highly reactive volatile organic compounds in eastern Texas inferred from oversampling of satellite (OMI) measurements of HCHO columns

Lei Zhu 1, Daniel J Jacob 1, Loretta J Mickley 1, Eloïse A Marais 1, Daniel S Cohan 2, Yasuko Yoshida 3, Bryan N Duncan 4, Gonzalo González Abad 5 and Kelly V Chance 5

1 School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
2 Civil and Environmental Engineering, Rice University, Houston, TX, USA
3 Science Systems and Applications, Inc., Lanham, MD, USA and NASA Goddard Space Flight Center, Greenbelt, MD, USA
4 NASA Goddard Space Flight Center, Greenbelt, MD, USA
5 Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA

E-mail: leizhu@fas.harvard.edu

Received 12 June 2014, revised 7 October 2014
Accepted for publication 8 October 2014
Published 3 November 2014

Abstract
Satellite observations of formaldehyde (HCHO) columns provide top-down constraints on emissions of highly reactive volatile organic compounds (HRVOCs). This approach has been used previously in the US to estimate isoprene emissions from vegetation, but application to anthropogenic emissions has been stymied by lack of a discernable HCHO signal. Here we show that temporal oversampling of HCHO data from the Ozone Monitoring Instrument (OMI) for 2005–2008 enables detection of urban and industrial plumes in eastern Texas including Houston, Port Arthur, and Dallas/Fort Worth. By spatially integrating the HCHO enhancement in the Houston plume observed by OMI we estimate an anthropogenic HCHO source of 250 ± 140 kmol h⁻¹. This implies that anthropogenic HRVOC emissions in Houston are 4.8 ± 2.7 times higher than reported by the US Environmental Protection Agency inventory, and is consistent with field studies identifying large ethene and propene emissions from petrochemical industrial sources.

Keywords: HCHO, ozone monitoring instrument, anthropogenic, highly reactive VOC, oversampling

1. Introduction
Anthropogenic highly reactive volatile organic compounds (AHRVOCs) with atmospheric lifetimes of less than a day are important precursors of ozone and organic aerosols in urban air and industrial plumes. Their sources are poorly quantified in emission inventories, as shown by air quality studies in eastern Texas (Ryerson et al 2003, Parrish et al 2012) and in an oil/gas field of northern Colorado (Gilman et al 2013). Satellite column measurements of formaldehyde (HCHO), a high-yield product from atmospheric oxidation of VOCs, have been used to constrain AHRVOC emissions in East Asia (Fu et al 2007) and Nigeria (Marais et al 2014a). However, detection of AHRVOC emissions in the US from satellite HCHO data has been elusive (Martin et al 2004, Millet et al 2008). The highest-resolution data are from the Ozone Monitoring Instrument (OMI), which provides daily global
coverage of HCHO columns by cross-track scanning with 13×24 km² nadir pixel resolution (Levelt et al 2006). An analysis of OMI urban data in the US by Boeke et al (2011) found only weak HCHO enhancements in the New York and Los Angeles urban cores in summer, and in the Houston urban core in spring and fall.

The difficulty of observing US AHRVOC emissions from space likely reflects their relatively small magnitude. The single-retrieval detection limit for OMI HCHO is 2×10¹⁶ molecules cm⁻² (Millet et al 2008), which corresponds to ∼4 ppb HCHO in a 2 km deep boundary layer. HCHO concentrations of ∼10 ppb are commonly observed in urban air and industrial plumes (Wert et al 2003, Buzcu Guven and Olaguer 2011, Lin et al 2012, Zheng et al 2013) but would be diluted on the scale sampled by the satellite pixels. Temporal averaging of the satellite data greatly improves the detection limit (Boeke et al 2011), though quantifying this improvement is difficult as it depends on the random versus systematic character of the retrieval error. The urban signal can also be masked by large regional emissions of isoprene, the dominant biogenic HRVOC contributing to HCHO (Palmer et al 2003, Martin et al 2004, Boeke et al 2011).

Here we demonstrate that quantitative detection of AHRVOC emissions in eastern Texas can be achieved by oversampling of the OMI HCHO data. ‘Oversampling’ refers to temporal averaging of the satellite data on a spatial grid finer than the pixel resolution on the instrument. The technique achieves high signal-to-noise ratio at high spatial resolution by sacrificing temporal resolution, i.e., averaging over a long time period. It takes advantage of the spatial offset and changing geometry (from off-track viewing) of the satellite pixels from day to day. Oversampling of OMI data has been applied previously with success to detection of SO₂ and NO₂ from urban and point sources (de Foy et al 2009, Fioletov et al 2011, McLinden et al 2012, Lu et al 2013). We demonstrate here its application to HCHO.

2. Data and methods

OMI is a UV/Vis nadir solar backscatter spectrometer launched in 2004 on the Aura satellite (Levelt et al 2006). It achieves daily global coverage with an equator crossing time of 13:38 local time. HCHO slant column densities (SCD) along the solar backscatter optical path are fitted in the spectral window 327.5–356.5 nm (Chance et al 2000). We use OMI HCHO Version 2.0 (Collection 3) SCD retrievals for 2005–2008 (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/onmchho_v003.shtml) that (1) pass all fitting and statistical quality checks, (2) have a cloud fraction less than 0.3 and solar zenith angle less than 60°, and (3) are not affected by the ‘OMI row anomaly’ (www.knmi.nl/omi/research/product/rowanomaly-background.php). Drift from instrument aging (Marais et al 2012) is removed with a linear temporal regression of background SCD over the North Pacific (130°–125°W, 35°–40°N).

The air mass factor (AMF = SCD/VCD) to convert SCD to vertical column density (VCD, column hereafter) is computed following Palmer et al (2001) with the LIDORT radiative transfer model (Spurr et al 2001). Satellite viewing geometry, cloud fraction, and cloud centroid pressure are from the OMI data. The AMF calculation requires information on HCHO and aerosol vertical distributions, and these are specified locally from the GEOS-Chem model with 0.5°×0.667° horizontal resolution over North America (Zhang et al 2011). Oversampling uses a higher horizontal resolution for the OMI data than 0.5°×0.667°, but we expect that the error from subgrid variability in the HCHO and aerosol vertical distributions is small relative to other sources of error.

Wintertime observations would avoid biogenic interference on HCHO but we find that OMI HCHO columns are then indistinguishable from noise over the US including over Houston. This does not reflect loss of measurement sensitivity as the mean AMF over Houston in winter (December–February; AMF = 0.99±0.17) is actually higher than in summer (May–August; AMF = 0.78±0.13). The higher AMF in winter is due to longer light path and lower cloud cover, more than compensating for the effects of reduced UV light penetration and shallower planetary boundary layer (PBL). We attribute the lack of detectable HCHO in winter to low OH concentrations, delaying the oxidation of AHRVOCs to HCHO and thus smearing the HCHO signal. Average 12:00–15:00 (local time) OH concentrations in the GEOS-Chem model over Houston are a factor of 5 lower in December–February than in May–August. Mean surface wind speeds are 30% higher in December–February than May–August (www.wunderground.com), also contributing to the smearing. We limit our attention here to May–August HCHO columns.

We oversample the OMI HCHO data over eastern Texas (99.5°–92.5°W, 28°–34°N) for May–August 2005–2008 by averaging individual pixels onto a 0.02°×0.02° (~2×2 km²) grid. In this procedure, the column measurement for a given pixel is assumed to apply to a circle defined by the center point of the pixel and an ‘averaging radius’ of 24 km. Previous OMI oversampling studies have used the same strategy. Fioletov et al (2011) chose an averaging radius of 12 km for oversampling OMI SO₂ pixels, and McLinden et al (2012) used 20 km and 24 km for OMI NO₂ and SO₂ pixels, respectively. We find that a 12 km or 20 km averaging radius for HCHO pixels leads to excessive noise. Our oversampling approach leads to ~800 OMI measurements being averaged in each 0.02°×0.02° grid square.

3. Results and discussion

Figure 1 (left) shows the oversampled OMI HCHO concentrations for May–August 2005–2008. Urban/industrial sources in and near Houston, Port Arthur, and Dallas/Fort Worth are clearly detected. Urban areas of Austin and San Antonio are less industrial and only marginally detected. The Houston and Port Arthur plumes are transported northward by the prevailing SSE wind. The enhancement west of Dallas/
Environmental Protection Agency (EPA) as implemented by Stuart McKeen (Brioude et al. 2011, Kim et al. 2011). The Houston plume outline (gray) is used in the text to estimate AHRVOC emissions from the HCHO data. The boundary of the Houston–Galveston–Brazoria urban metropolitan area (HGB) is shown as the thin blue outline.

Fort Worth can be attributed to AHRVOC emissions from the Barnett Shale, the largest onshore natural gas field in the US. The high values over Northeast Texas are due to isoprene emission as discussed below.

HCHO columns over the Houston urban area peak at $1.4 \times 10^{16}$ molecules cm$^{-2}$ near the Houston ship channel where major refineries and petrochemical industries emit large amounts of HRVOCs. Johansson et al. (2014) previously reported HCHO columns in the channel of up to $2.4 \times 10^{16}$ molecules cm$^{-2}$ from ground-based remote sensing in May 2009. Our mean column of $9.4 \times 10^{15}$ molecules cm$^{-2}$ in the Houston–Galveston–Brazoria urban metropolitan area (HGB; figure 1, thin blue line) corresponds to a mean HCHO mixing ratio of 2.4 ppb for a 1.7 km deep PBL (Haman et al. 2012). This result agrees with the mean HCHO concentration of 2.4 ppb measured in the HGB during the summer 2006 Texas Air Quality Study (TexAQS) (Gilman et al. 2009). HGB concentrations measured during that study ranged from 1 to 20 ppb (Zhang et al. 2013).

The right panel of figure 1 shows HRVOC emissions for eastern Texas estimated from current inventories. These include MEGAN v2.1 for biogenic isoprene (Guenther et al. 2012) and the 2005 National Emission Inventory (NEI05) of the US Environmental Protection Agency (EPA) as implemented by Stuart McKeen (see Brioude et al. 2011, Kim et al. 2011). Here AHRVOCs are defined as having atmospheric lifetimes of less than 1 day against oxidation by OH. Table 1 lists the main NEI05 AHRVOCs emitted in the Houston plume area defined in figure 1 (gray line). Ethene and propene are the most important HCHO precursors, as also observed in the TexAQS campaigns (Wert et al. 2003, Parrish et al. 2012). Wert et al. (2003) found from speciated VOC samples that 78% of the HCHO production potential was from terminal alkenes including 30% from ethene, 22% from propene, 14% from isoprene, and 12% from other alkenes.

Biogenic isoprene makes a large background contribution to HCHO over eastern Texas, as seen in figure 1 and previously noted by Martin et al. (2004). Isoprene emissions in MEGAN v2.1 are particularly high over forested Northeast Texas, explaining the high OMI HCHO columns there. Some distinction between biogenic and anthropogenic contributions to OMI HCHO can be made on the basis of correlation with surface air temperature. Isoprene emission increases exponentially with temperature (Guenther et al. 2006), and this dependence is apparent in regional HCHO satellite data over the Southeast US (Palmer et al. 2006). Figure 2 shows the relationships of OMI HCHO with surface air temperature over Northeast Texas and the Houston core for May–September 2006–2008. The data over Northeast Texas show a strong exponential relationship with temperature ($R^2=0.64$) with an argument of 0.11 K$^{-1}$, consistent with that expected for isoprene emission (Guenther et al. 2006, Palmer et al. 2006). By contrast, OMI HCHO columns over the Houston core show no significant relationship with temperature ($R^2=0.03$), supporting the dominant anthropogenic influence. The lack of correlation in the Houston data partly reflects a cluster of three points in figure 2 with $T>300$ K and HCHO column $<2 \times 10^{15}$ molecules cm$^{-2}$, but even excluding these points the relationship with temperature yields only $R^2=0.34$. Some correlation of HCHO with temperature would be expected even over Houston due to (1) the regional HCHO background contributed by isoprene (Wert et al. 2003), (2) the temperature dependence of AHRVOCs oxidation, and (3) the association of high temperature with stagnation.

![Figure 1. OMI HCHO columns and HRVOC emission inventories for eastern Texas. The left panel shows OMI HCHO columns averaged over May–August 2005–2008 and oversampled to a 0.02°×0.02° resolution using an averaging radius of 24 km. Crosses indicate city centers. The right panel shows the May–August 2008 biogenic isoprene emissions and the major anthropogenic HRVOC (AHRVOC, table 1) point sources (dots) with emission larger than 3 kg C h$^{-1}$ binned on a 0.02°×0.02° grid. Isoprene emissions are computed with MEGAN v2.1 (Guenther et al. 2012). AHRVOC emissions are from the 2005 National Emissions Inventory (NEI05) of the US Environmental Protection Agency (EPA) as implemented by Stuart McKeen (Brioude et al. 2011, Kim et al. 2011). The Houston plume outline (gray) is used in the text to estimate AHRVOC emissions from the HCHO data. The boundary of the Houston–Galveston–Brazoria urban metropolitan area (HGB) is shown as the thin blue outline.](image-url)
A number of previous studies have used satellite HCHO data to constrain isoprene emissions by assuming a local relationship between the two from a chemical transport model (CTM) (Palmer et al 2003, Fu et al 2007, Millet et al 2008, Barkley et al 2008, Marais et al 2012) or by applying a more elaborate inversion method (Shim et al 2003, Fu et al 2007, Marais et al 2014b). In our case, the AHRVOC enhancement is on top of a large regional background (figure 1). We constrain AHRVOC emissions for the Houston plume area by integrating the OMI HCHO enhancement over the Houston plume as the difference between the observed HCHO column ($\Omega$) and the regional background ($\Omega_0$) contributed by biogenic and long-lived anthropogenic emissions. From the HCHO lifetime ($\tau_{\text{HCHO}}$) we deduce the corresponding HCHO source $S$ per unit time as

$$S = \frac{1}{\tau_{\text{HCHO}}} \int (\Omega - \Omega_0) dA, \tag{1}$$

where the integral is over the area $A = 1.9 \times 10^{4} \text{km}^{2}$ of the plume as defined in figure 1. This represents the total emission of AHRVOCs within the plume area weighted by their prompt yield of HCHO. We can convert this quantity to a total AHRVOC emission ($E$) by applying independent estimates of the fraction $f_i$ of the total emission contributed by species $i$ and the corresponding HCHO yield $Y_i$ (table 1):

$$E = \frac{S}{\sum_i f_i Y_i}. \tag{2}$$

Here we estimate the regional background ($\Omega_0$) as the HCHO column downwind of the discernible Houston plume, corresponding roughly to the green color in figure 1 (8–10 $\times 10^{15}$ molecules cm$^{-2}$). Figure 3 shows HCHO columns averaged across the prevailing wind as a function of the distance from Houston city center. The plume decays to a regional background value at about 110 km downwind of the city center. For a mean wind speed of 3.3 m s$^{-1}$ (www.wunderground.com/) this corresponds to an aging time of 9.3 h, long relative to the lifetimes of ethene and propene (table 1). From the downwind asymptote of the plume we

**Table 1. NEI estimates of Houston AHRVOC emissions and HCHO yields.**

| Species    | Lifetime$^a$ (h) | Emission$^a$ (kmol h$^{-1}$) | Molar HCHO yield$^a$ | HCHO production (kmol h$^{-1}$) |
|------------|------------------|-------------------------------|----------------------|-------------------------------|
| Ethene     | 2.9              | 16                            | 1.6                  | 27                            |
| Propene    | 0.8              | 6.3                           | 1.8                  | 12                            |
| Higher alkenes | 0.6$^b$          | 5.3                           | 0.6$^b$              | 3.2                           |
| Formaldehyde | 1.6$^c$          | 9.4                           | 1.0                  | 9.4                           |
| Acetaldehyde | 1.6              | 1.2                           | 1.0                  | 1.2                           |
| Other$^d$  | 0.4$^b$          | 0.7                           | 0.6$^b$              | 0.7                           |
| Total      | —                | 39                            | —                    | 52                            |

$^a$ Mean emissions for May–August 2005 from the US EPA National Emission Inventory (NEI05) implemented by Stuart McKeen (Brisoule et al 2011, Kim et al 2011, ftp://ftp.fsl.noaa.gov/divisions/taq) over the area of the Houston plume defined by the OMI HCHO data (figure 1, gray outline).

$^b$ Lifetime against oxidation by OH computed using a mean OH concentration of 1.1 $\times 10^{7}$ molecules cm$^{-3}$ for 09:30–13:30 local time taken from Mao et al 2009. Kinetic data are from the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al 1997, Saunders et al 2003, http://mcm.leeds.ac.uk/MCM).

$^c$ Prompt yield of HCHO realized within one day of initial oxidation, as computed using MCM v3.2 for oxidation by OH in the high-NO$_x$ regime.

$^d$ Using 1-butane as representative species.

$^e$ Also includes photolysis, using a mean 09:30–13:30 photolysis frequency of 8.1 $\times 10^{-5}$ s$^{-1}$ computed with the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (http://cprm.acd.ucar.edu/Models/TUV/). HCHO loss is 46% from photolysis and 54% from oxidation by OH.

$^f$ Including dienes, glyoxal, and styrene.

$^g$ Using 1,3-butadiene as representative species.
derive a best estimate for the regional background of \( \Omega_0 = 9.6 \pm 0.3 \times 10^{15} \) molecules cm\(^{-2} \) (Figure 3). The actual uncertainty in the regional background is likely larger considering the fine-scale heterogeneity in isoprene emissions (Gulden, Yang Z L 2006). We therefore adopt \( \Omega_0 = 9.6 \pm 0.5 \times 10^{15} \) molecules cm\(^{-2} \) as a more conservative estimate of the uncertainty. The uncertainty in the HCHO plume enhancement (\( \Omega - \Omega_0 \)) is largely defined by the uncertainty in \( \Omega_0 \), considering that any systematic errors in the retrieval would likely be canceled in computing the difference between \( \Omega \) and \( \Omega_0 \). We thus obtain a total HCHO column enhancement integrated over the plume of 400 ± 180 kmol (red area in Figure 3).

Loss of HCHO is by photolysis and oxidation by OH. From Table 1, we estimate \( \tau_{\text{HCHO}} \) to be 1.6 h. Photolysis accounts for half of total HCHO loss and is relatively well constrained. Loss by reaction with OH is not as well constrained because of uncertainty in OH concentrations. Here we adopted a mean OH concentration of 1.1 × 10\(^7\) molecules cm\(^{-3} \) at 09:30–13:30 local time from measurements in downtown Houston (Mao et al 2009) and estimate the overall uncertainty in \( \tau_{\text{HCHO}} \) to be 30%. The resulting anthropogenic HCHO source \( S \) over the area of the plume is 250 ± 140 kmol HCHO h\(^{-1} \), propagating in quadrature our estimated uncertainty in \( \tau_{\text{HCHO}} \).

Combining this result with the data on \( f_i \) and \( Y_i \) in Table 1, we deduce a total AHRVOC emission \( E \) for the HGB of 190 ± 100 kmol h\(^{-1} \), which can be compared to the NEI05 estimate of 39 kmol h\(^{-1} \) from Table 1. The OMI observations thus suggest that AHRVOC emissions in the Houston plume area are underestimated by a factor of 4.8 ± 2.7 in the NEI05 inventory for 2005–2008. This is consistent with previous studies pointing to a large underestimate of alkene emissions in the HGB (e.g., Wert et al 2003, de Gouw et al 2009, Parrish et al 2009, Mellqvist et al 2010). Our estimate of the HCHO source in the Houston plume is consistent with the estimate of 240 ± 90 kmol HCHO h\(^{-1} \) from Parrish et al (2012) computed using an improved alkene inventory (Kim et al 2011) with updated ethene and propene emission factors from petrochemical facilities (Mellqvist et al 2010).

Previous analyses of HCHO data in Houston have reached contradictory conclusions on whether most of the HCHO is primary, i.e., directly emitted (Rappengluck et al 2010, Buzcu Guven and Olaguer 2011, Olaguer et al 2013, Johansson et al 2014) or secondary, i.e., produced within the plume from alkene oxidation (Friedfeld et al 2002, Wert et al 2003, Parrish et al 2012, Zhang et al 2013). The distinction is important because primary HCHO would accumulate at night and photolyze in early morning, providing a source of radicals to initiate ozone formation. Our inability to detect the Houston urban plume in winter from the OMI data (see above) argues against a major primary source of HCHO. We attempted to constrain the speciation of AHRVOCs by using the shape of the OMI plume in Figure 3 and a simple constant-wind model, as primary HCHO would decay closer to the core. We were unsuccessful, partly because of the complexity arising from primary emissions at night and in early morning when the HCHO lifetime is long.

We see from Figures 1 and 3 that the anthropogenic HCHO enhancements in the Houston plume and elsewhere are on top of a larger regional background (\( \Omega_0 \)). This background is dominated from biogenic isoprene. For the Houston plume area in Figure 3, the 24 h average isoprene emission calculated by MEGAN in May–August is 95 kmol h\(^{-1} \). Assuming a HCHO molar yield of 2.3 from isoprene oxidation (Millet et al 2006), this yields a HCHO production rate of 220 kmol h\(^{-1} \), comparable in magnitude to the anthropogenic source.

Observations from the TexAQS aircraft campaigns in 2000 and 2006 documented a decrease of AHRVOC emissions from the HGB over that period. Gilman et al (2009) reported 56% and 51% decreases in ethene and propene median concentrations, respectively; Washenfelder et al (2010) found emission decreases in the Houston ship channel of 41% for ethene and 8% for propene from 1999 to 2006. Presently the useful OMI HCHO record is limited to 2005–2008; data after 2008 are too noisy for trend analysis because of the row anomaly. De Smedt et al (2010) used data from the GOME and SCIAMACHY satellite instruments to infer global 1997–2009 trends in HCHO, but we find that the pixel resolution of these instruments is too coarse for detection of the Houston plume. Post-2008 OMI data are expected to be corrected in a future product (González Abad et al 2014), which will then allow analysis of AHRVOC trends as well as examination of AHRVOC emissions associated with the large increase in oil/gas exploration across the US over the past five years.
4. Conclusions

We have shown that multi-year oversampling of summertime OMI HCHO satellite data enables detection of HCHO enhancements from large US urban/industrial sources of anthropogenic highly reactive volatile organic compounds (AHRVOCs). The enhancement in the Houston urban plume is sufficiently extensive to allow quantitative interpretation in terms of AHRVOC emissions. Our resulting estimate of AHRVOC emissions for Houston is 4.8 ± 2.7 times higher than the US EPA inventory and consistent with previous field estimates that identified large ethene and propene emissions from the petrochemical industry. The lack of detectable OMI HCHO enhancements in winter suggests that anthropogenic HCHO is mainly produced by photochemical oxidation of alkenes rather than directly emitted.

Acknowledgements

This work was supported by the NASA Aura Science Team and Air Quality Applied Sciences Team. The authors thank Barry Lefer and James Flynn at the University of Houston and Xiong Liu at the Harvard-Smithsonian Center for Astrophysics for their help. We thank two anonymous reviewers who provided thorough and thoughtful comments.

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