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Hotspot of Glyoxal Over the Pearl River Delta Seen from the OMI Satellite Instrument: Implications for Emissions of Aromatic Hydrocarbons

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Abstract. The Pearl River Delta (PRD) is a densely populated hub of industrial activity located in southern China. OMI satellite observations reveal a large hotspot of glyoxal (CHOCHO) over the PRD that is almost twice as large as any other in Asia. Formaldehyde (HCHO) and NO_2 observed by OMI are also high in the PRD but no more than in other urban/industrial areas of China. The CHOCHO hotspot in the PRD can be explained by industrial paint and solvent emissions of aromatic volatile organic compounds (VOCs), with toluene being a dominant contributor. By contrast, HCHO in the PRD originates mostly from VOCs emitted by combustion (principally vehicles). By applying a plume transport model to wind-segregated OMI data, we show that the CHOCHO and HCHO enhancements over the PRD observed by OMI are consistent with current VOC emission inventories. Prior work using CHOCHO retrievals from the SCIAMACHY satellite instrument suggested that aromatic VOC emissions in the PRD were too low by a factor of 10-20; we attribute this result in part to bias in the SCIAMACHY data and in part to underestimated CHOCHO yields from oxidation of aromatics. Our work points to the importance of better understanding CHOCHO yields from the oxidation of aromatics in order to interpret CHOCHO observations from space.

1 Introduction

The Pearl River Delta (PRD) is a metropolis of nine cities on the southern coast of China with 57 million people as of 2013. Rapid economic growth over the past three decades has created a serious air quality problem within the region, with ozone (O_3) and particulate matter (PM) air quality standards frequently violated. Volatile organic compounds (VOCs) are important O_3 and PM precursors. Our recent retrieval of atmospheric glyoxal (CHOCHO) from the OMI satellite instrument, including a number of corrections to previous retrievals, finds the CHOCHO column concentrations over the PRD to be the highest in the world (Chan Miller et al., 2014). Here we investigate the sources of CHOCHO in the PRD, their representation in current VOC emission inventories used by atmospheric models.

The PRD has undergone rapid industrialization since 1980 when a series of economic reforms reduced restrictions on foreign investment. The PRD is now referred to as the "World Factory", producing 25% of China's exports (Guangdong

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Statistical Yearbook, 2010). Major industries include printing, oil refining, chemical production, and automobile and electronics manufacturing (Zhong et al., 2013).

This industrialisation has led to worsening air quality throughout the region. Surface O_3 and PM are routinely in excess of the Chinese national ambient air quality standards (NAAQS) of 81.5 ppbv for O_3 and 35 μg m^{-3} for $PM_{2.5}$ (MEP, 2012). Ozone production in the PRD is predominantly VOC-limited (Zhang et al., 2007, 2008; Wang et al., 2010; Shao et al., 2009; Xue et al., 2014), and the aromatic species toluene and xylene play a dominant role (Xue et al., 2014). Aromatics have also been identified as an important regional source of secondary organic aerosol via reactive uptake of their oxidation products (Li et al., 2013).

CHOCHO is a high-yield product of aromatic oxidation (Nishino et al., 2010), thereby making satellite CHOCHO observations a valuable proxy for their emission. Previous satellite observations have suggested that inventories underestimate aromatic emissions over China. Stavrakou et al. (2009) used 2005 observations of CHOCHO and HCHO from the SCIAMACHY satellite instrument and found the global RETRO VOC inventory (Maarten van het Bolscher, 2007) to be too low in the PRD by over a factor of 2. Liu et al. (2012) used 2007 SCIAMACHY CHOCHO observations and found the INTEX-B East Asian inventory (Zhang et al., 2009) underestimated emissions in the PRD by 10 - 20-fold.

Our OMI CHOCHO retrieval is systematically lower than the older SCIAMACHY data, with very different patterns, as a result of improved background corrections and removal of NO_2 interferences (Chan Miller et al., 2014). Another recent OMI retrieval (Alvarado et al., 2014) is also systematically lower than SCIAMACHY. This calls for revisiting the interpretation of CHOCHO data from space. Focus on the PRD not only targets a hotspot in the OMI data, but enables comparison to a highly detailed local VOC inventory for the region (Zheng et al., 2009a, b).

2 Data and Methods

The Ozone Monitoring Instrument (OMI) was launched onboard the NASA Aura satellite in July 2004 (Levelt et al., 2006). Aura is in sun-synchronous orbit with an equatorial crossing time of 13:38 local. OMI measures backscattered solar radiation at a nadir spatial resolution of 13km$\times$24km and achieves daily global coverage by cross-track imaging. Spectral fitting yields slant columns of CHOCHO, HCHO and NO_2 along the optical path. These are converted to vertical columns using air mass factors (AMFs) that combine scattering weights and vertical concentration profiles (González Abad et al., 2015). We use CHOCHO data from Chan Miller et al. (2014), and HCHO and NO_2 data from the OMI Version 3 product release (González Abad et al., 2015; Bucsela et al., 2013). Vertical profiles for the AMF computation are from the GEOS-Chem chemical transport model (v9-01-3; http://geos-chem.org). GEOS-Chem was originally described by Bey et al. (2001) and the glyoxal simulation was first introduced by Fu et al. (2008). The general chemical mechanism in v9-01-3 is described in Mao et al. (2013).

Observations are averaged on a $0.25^\circ \times 0.3125^\circ$ grid using an area-weighted tessellation algorithm (Spurr, 2004). We exclude observations from the first and last cross track positions, those that fail the retrieval algorithm statistical quality checks, and those impacted by the row anomaly (http://www.knmi.nl/omi/research/product/rowanomaly-background.php). Validation with aircraft data indicates that the OMI HCHO and NO_2 retrievals are accurate within 20% and 30% respectively (Lamsal et al.,

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2014; Zhu et al., 2015). CHOCHO/HCHO column ratios from OMI are consistent with aircraft observations (Kaiser et al., 2015), whereas previous SCIAMACHY retrievals showed large discrepancies (DiGangi et al., 2012).

We relate the CHOCHO and HCHO satellite observations over the PRD to VOC emissions using a 1-D advective-reactive plume model (Beirle et al., 2011; Valin et al., 2013), assuming a constant wind u, and treating the PRD as a Gaussian-distributed source ($N(x;\sigma)$) orthogonal to the wind with total emission rate E_i (e.g. mol s^{-1}). Let l_i represent the vertical column density of VOC species i integrated in the horizontal orthogonally to the wind (molecules cm^{-1}). The continuity equation is written;

$$\frac{\partial l_i(x,t)}{\partial t} + u\frac{\partial l_i(x,t)}{\partial x} = E_i(t)N(x;\sigma) - k_i[OH](t)l_i(x,t) \quad (1)$$

Here k_i is the rate constant of the reaction of VOC i with the hydroxyl radical OH (the main sink for the VOCs of interest). The local diurnally-varying concentration of OH is calculated from GEOS-Chem and peaks at 1.5×10^7 molecules cm^{-3} at local noon, close to observed values in the PRD (Hofzumahaus et al., 2009). E_i varies diurnally using source scaling factors from GEOS-Chem (van Donkelaar et al., 2008). We use the NO_2 plume as a proxy to derive the along-trajectory width of the VOC source region (σ), using the exponential decay model from Beirle et al. (2011). The derived half-maximum width (~ 85 km) is reasonable given the observed extent of PRD urban landcover from MODIS (Figure 3).

CHOCHO is treated as a product of VOC oxidation with yield α_i from VOC i, and is lost by reaction with OH and photolysis (rate constants k_g and J_g respectively). The CHOCHO vertical column density integrated in the horizontal orthogonal to the wind ($g(x,t)$) is then given by

$$\frac{\partial g(x,t)}{\partial t} + u\frac{\partial g(x,t)}{\partial x} = \sum_i \alpha_i k_i[OH](t)l_i(x,t) - \{k_g[OH](t) + J_g(t)\}\, g(x,t) \quad (2)$$

A similar equation holds for HCHO. J_g is calculated using the Fast-JX radiative transfer model (Wild et al., 2000; Neu et al., 2007). The yields (α_i) are calculated for a 1-day VOC aging time using the box model simulation of Palmer et al. (2006) with the MCMv3.2 chemical mechanism(Jenkin et al., 1997, 2003), and assuming a high-NO_x regime where organic peroxy radical products of VOC oxidation react mainly with NO.

We apply the plume model to VOC emissions from five different inventories - RETRO (Maarten van het Bolscher, 2007), MACCity (Granier et al., 2011), REASv2 (Kurokawa et al., 2013), INTEX-B (Zhang et al., 2009), and the local PRD inventory from Zheng et al. (2009a).

3 Results and Discussion

Figure 1 shows the mean 2006-2007 vertical columns of CHOCHO, HCHO, and tropospheric NO_2 over China. OMI CHOCHO columns in the PRD (23°N, 113°E) peak at 1.0×10^{15} molecules cm^2, the highest in the world on an annual basis (Chan Miller et al., 2014). HCHO in the PRD is also high but comparable to values in the industrial Szechuan Basin to the northwest and in the densely populated East China Plain. NO_2 is high but less than in the East China Plain. As pointed out previously by Liu

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et al. (2012) and Li et al. (2014), the unusually high CHOCHO concentrations over the PRD can be attributed to high emissions of aromatic VOCs.

The Zheng et al. (2009a) PRD emissions inventory includes detailed VOC speciation profiles of local sources (Liu et al., 2008a; Lai et al., 2009), resolving 91 individual VOCs, and adds biogenic VOC emissions from GloBEIS (Zheng et al., 2009c). The inventory does not contain primary CHOCHO emissions, and primary HCHO emissions are negligibly small.

Figure 2 shows the VOC emissions from Zheng et al. (2009a) and the corresponding HCHO and CHOCHO production rates. Aromatic VOCs have higher CHOCHO yields than other precursors, and their emissions are high enough to dominate CHOCHO production. Paints and solvents are the largest source of aromatics in the inventory, responsible for over 50% of benzene, toluene and xylene emissions. Atmospheric VOC observations in the PRD are consistent with that solvent/paint signature (Liu et al., 2008b; Barletta et al., 2008), in contrast to other Chinese cities where VOC emissions are predominantly from combustion (Barletta et al., 2005). Acetylene emitted from combustion has a 64% ultimate yield of CHOCHO (Fu et al., 2008) but its lifetime is too long (about 10 days) to make a major contribution to the local CHOCHO budget.

HCHO is produced with a more consistent yield from different VOCs, as shown in Figure 2. VOCs emitted by vehicles including alkenes and $\geq C_4$ alkanes play a dominant role in HCHO production, with biogenic isoprene making an additional seasonal contribution. This explains why OMI HCHO columns in the PRD are comparable to other Chinese urban areas (Figure 1).

Figure 3 shows mean 2006-2007 OMI columns over the PRD segregated by northeasterly, easterly, and calm (< 2 m s^{-1}) wind conditions. The segregation is based on GEOS-5 surface wind data at Shenzhen (23.5°N, 114°E). The shape of the urban plume is consistent with wind direction. 90% of northeasterly conditions are in fall and winter. 50% of calm conditions are in summer, and easterly conditions are evenly spread over the seasons. These seasonal dependences explain the higher HCHO columns under calm conditions, as biogenic VOCs make a larger contribution in summer (Zheng et al., 2010a). On the other hand, NO_2 is lower because of faster photochemical loss. CHOCHO shows much less variability between wind sectors, consistent with a dominant anthropogenic source and with photochemistry driving both production and loss.

We select observations from the northeasterly sector for comparison to the Zheng et al. (2010b) inventory using the advective-reactive plume model. Wind under these conditions is relatively steady, with low diurnal variability, and the urban plume is transported over flat terrain. The prevailing fall/winter conditions minimize the influence of biogenic VOCs.

Figure 4 shows cross-wind integrals of CHOCHO and HCHO vertical column densities as a function of transport time calculated from the trajectories using the mean wind field, and initialised upwind of the PRD. A regional background has been subtracted prior to integration using observations in a sector upwind of the plume source (114-116°E, 22-23°N). We ascribe a 20% relative error to the observations from systematic AMF uncertainties (Vrekoussis et al., 2010) and a spatially-uniform error from uncertainty in the background correction (Zhu et al., 2014).

Also shown in Figure 4 are the results from the advective-reactive plume model using the Zheng et al. (2009a) PRD emission inventory for individual VOCs, with MCMv3.2 yields for HCHO and CHOCHO (Figure 2). The model does not include biogenic emissions (isoprene, monoterpenes, and methanol), which are relatively weak in fall/winter and would be included in

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the regional background. The anthropogenic emissions are released at $t = 6.5$ h for CHOCHO and $t = 7$ h for HCHO, based on the location of the observed maximum during calm conditions (Figure 3).

Figure 4 shows that the model can replicate the observed concentrations (line densities) CHOCHO and HCHO as a function of transport time. Specification of OH concentrations and photolysis rates is likely the largest source of uncertainty in the model. We estimate a 30% uncertainty in OH concentrations, and a 20% uncertainty for photolysis rates, with the latter driven by aerosol scattering (Martin et al., 2003). Integrating the plume model results between $t = 5$ and $t = 20$ h in Figure 4, we find good agreement with OMI for both CHOCHO (370 $\pm$ 50 kmol modeled vs 350 $\pm$ 90 kmol OMI) and HCHO (3.2 $\pm$ 0.6 Mmol modeled vs 2.6 $\pm$ 0.7 Mmol OMI), and conclude that the PRD inventory of Zheng et al. (2009a) is consistent with observations.

We repeated the same plume model calculation with the INTEX-B, REASv2, RETRO, and MACCity emission inventories for the PRD. All inventories are for 2006 except RETRO (2000). Figure 5 shows the emissions from each inventory, together with integrated CHOCHO and HCHO plume enhancements in the PRD integrating the OMI observations and plume model results in Figure 4 between $t = 5$ and $t = 20$ h. With the exception of RETRO, all inventories have similar total VOC emissions on a per C basis, though they differ in speciation, and they reproduce the observed CHOCHO and HCHO plumes within 40% for CHOCHO and 55% for HCHO.

The good agreement between VOC emission inventories and satellite observations of CHOCHO and HCHO is in sharp disagreement with Liu et al. (2012), who inferred a 10 - 20-fold underestimation of PRD aromatic emissions in the INTEX-B inventory using SCIAMACHY CHOCHO observations. The same inventory in our plume model underestimates the OMI CHOCHO concentration by only a factor of 2. Increasing aromatic VOC emissions by a factor of 10 would also overestimate HCHO by more than a factor of 2.

Annually averaged SCIAMACHY CHOCHO columns are $\sim 60\%$ higher than OMI in the PRD, and this is not enough to explain the difference between our study and Liu et al. (2012). Different aromatic CHOCHO yields likely play a larger role in the discrepancy. Molar yields in Liu et al. (2012) were 25% for benzene, 16% for toluene, and 16% for xylenes, based on a literature-based average of chamber experiments compiled by Fu et al. (2008). By contrast the MCMv3.2 molar yields used are 75% for benzene, 70% for toluene, and 36% for xylenes.

Figure 6 shows the pathways to CHOCHO formation from toluene in MCMv3.2. Approximately half of CHOCHO formation in MCMv3.2 is produced as a first generation product via a bicyclic intermediate (TLBIPERO). The rest of CHOCHO production involves intermediate products, implying delays and additional uncertainties.

Studies reporting CHOCHO yields at the lower end of the range reported in Fu et al. (2008) were conducted under very high NO_x conditions, resulting in OH-adduct reactions (pink pathway, Figure 6) that would suppress CHOCHO formation (Nishino et al., 2010). The highest yield of $39.0 \pm 10.2\%$ measured by Volkamer et al. (2001) was performed under NO_x levels closer to ambient conditions, however it was later revised to $30.6 \pm 6.0\%$ after CHOCHO measurements from the experiment were revised downward based on more accurate CHOCHO absorption cross sections (Volkamer et al., 2005). Nishino et al. (2010) corrected for NO_2 reactions in their kinetics analysis to determine a yield of $26.0 \pm 2.2\%$, in close agreement with Volkamer et al. (2001). In both studies, CHOCHO production was from first generation production. This is very consistent with the 32%

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first-generation CHOCHO yield from MCMv3.2 via TLBIPERO (Figure 6). Thus the higher yield of CHOCHO from toluene in the MCMv3.2 mechanism relative to the Fu et al. (2008) compilation is due to the accounting of later-generation production.

Bloss et al. (2005) experimentally observed CHOCHO production from butenedial (MALDIAL), confirming the existence of later-generation CHOCHO production from toluene. Other later-generation CHOCHO formation pathways in MCMv3.2 still need to be experimentally confirmed. However, the combined data on CHOCHO and HCHO from the satellite observations do provide additional constraints. If the CHOCHO yield from aromatics were much lower than MCMv3.2, then aromatic emissions would need to be increased in a way that would be inconsistent with the HCHO data.

The CHOCHO hotspot over the PRD seen by the OMI satellite instrument can thus be explained by a very large industrial source of aromatic VOCs, consistent with current emission inventories used in atmospheric models. There has been little confidence in the past in interpreting CHOCHO data from space, in part because of inconsistency with surface observations (DiGangi et al., 2012). This issue seems to be resolved with the OMI observations, and we find CHOCHO to be an excellent tracer of aromatic VOC emissions where these are high. Further work will need to examine other sources of CHOCHO relevant to interpreting satellite observations, in particular biogenic isoprene. The CHOCHO yields from atmospheric oxidation of aromatic VOCs also need to be better established in order to improve the quantitative interpretation of CHOCHO data from space.

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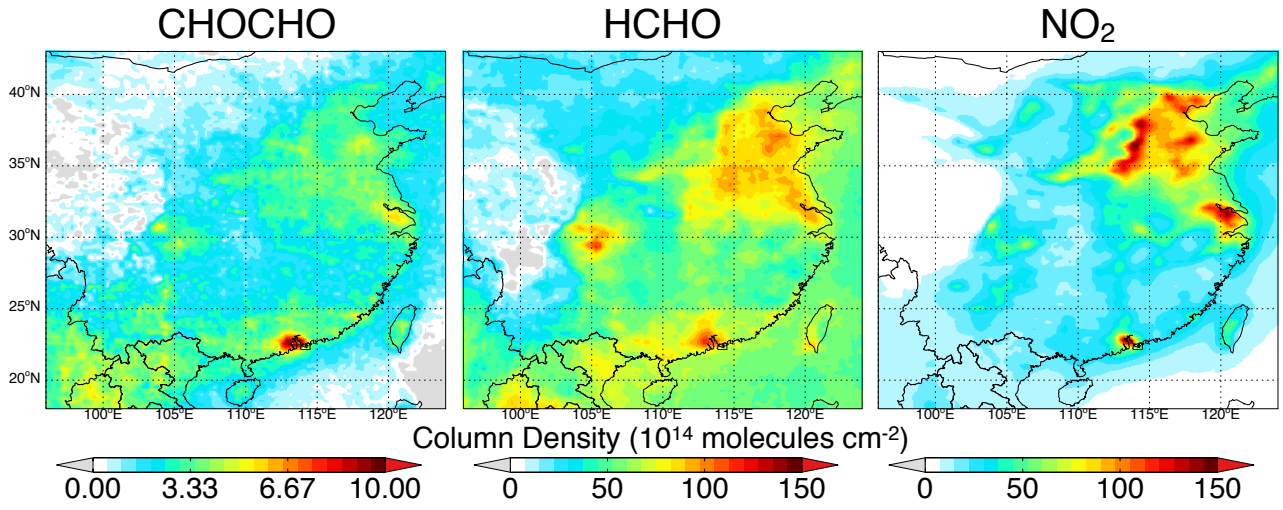

Figure 1. Annual mean vertical column densities of NO_2, HCHO, and CHOCHO for 2006-2007. Values are OMI observations from Chan Miller et al. (2014) for CHOCHO, González Abad et al. (2015) for HCHO, and Bucsela et al. (2013). for NO_2

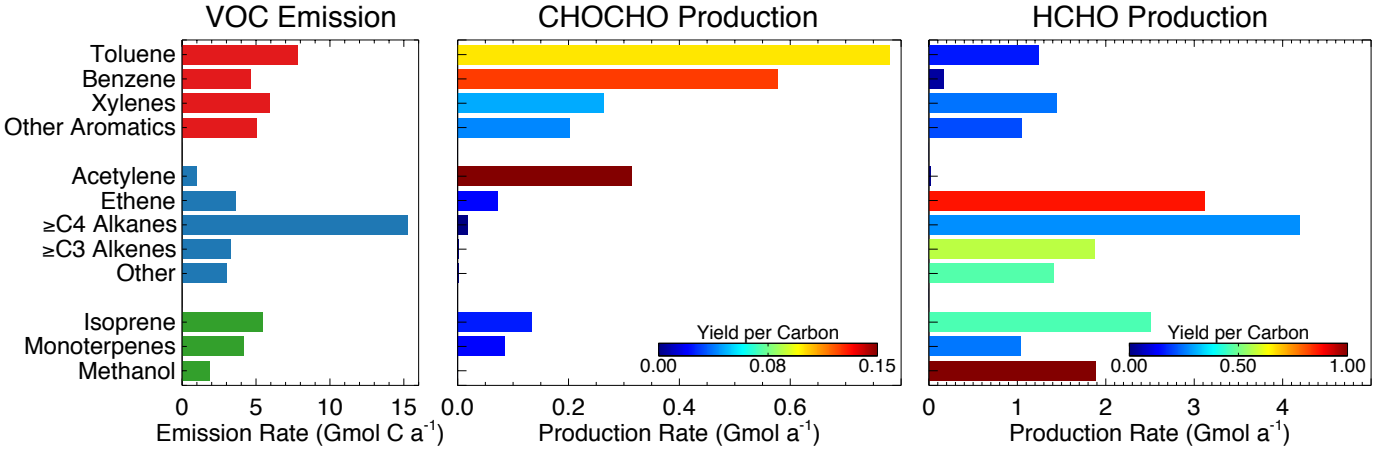

Figure 2. Yearly VOC emissions (2006) in the PRD ($21.5-24°$N, $112-115.5°$E) and corresponding yields and production rates of CHOCHO and HCHO over one day of aging. VOC emissions are from Zheng et al. (2009a). Yields are computed using the MCMv3.2 chemical mechanism(Jenkin et al., 1997, 2003).

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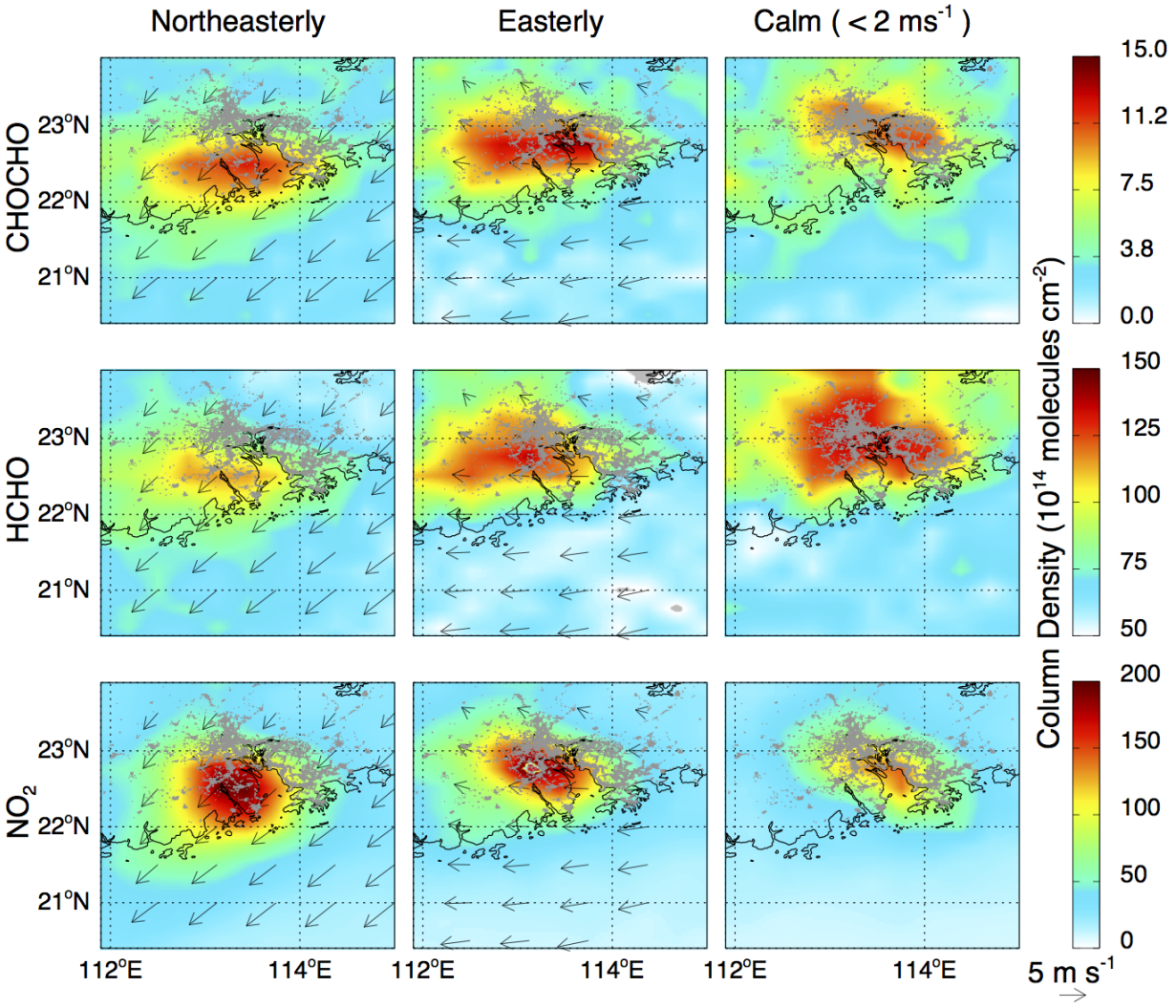

Figure 3. Mean OMI vertical column densities of CHOCHO, HCHO, and NO_2 over the PRD for 2006 to 2007, segregated by wind direction. Winds vectors at 60-m altitude are from the NASA GEOS-5 assimilated meteorology product. The distribution of urban landcover from the MODIS type 5 land cover product is shown in grey.

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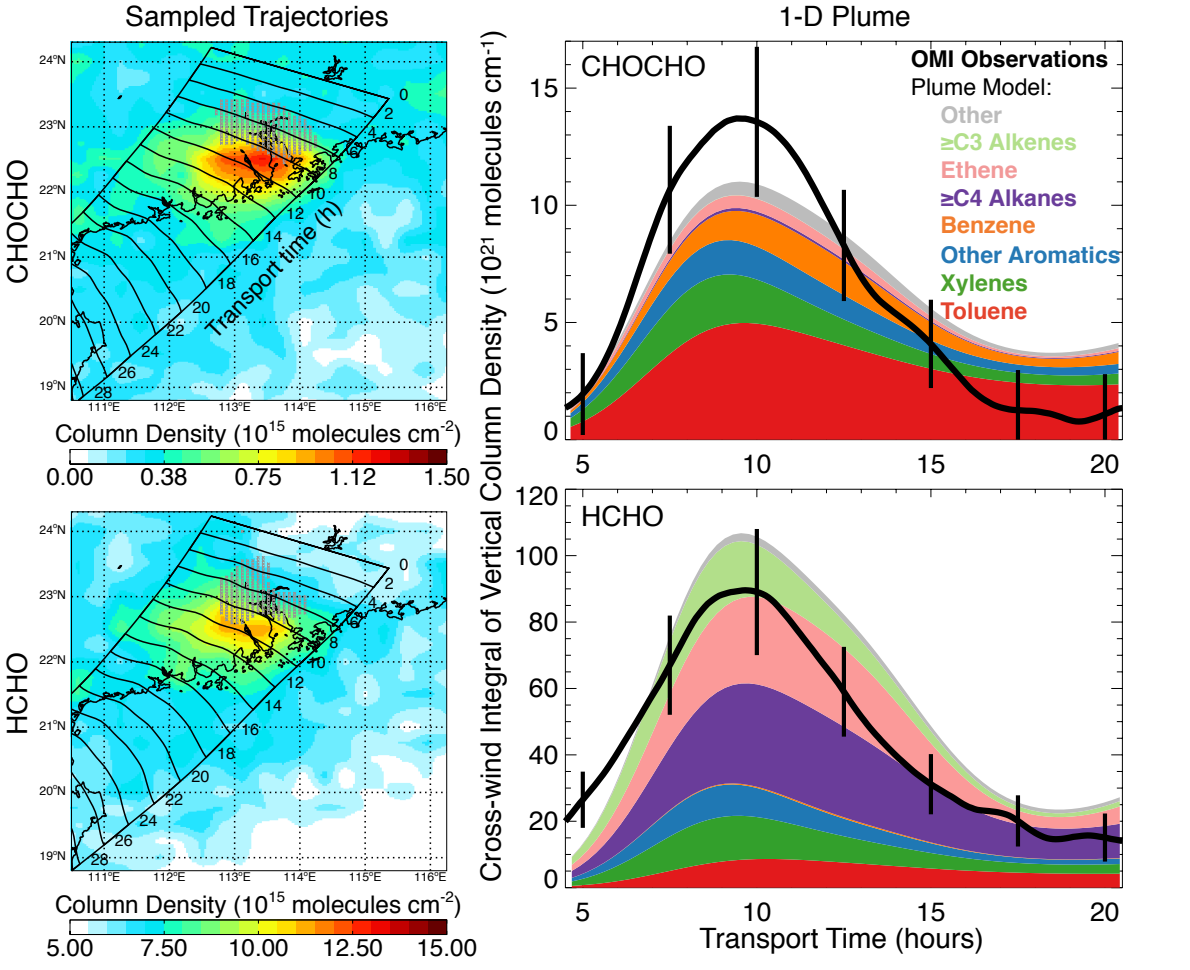

Figure 4. Mean CHOCHO and HCHO PRD plumes under northeasterly flow conditions. **Left:** Vertical column densities, overlaid with surface air (60 m) trajectories for the mean wind field of Figure 3. The trajectories are initialized upwind of the PRD ($t = 0$), and transport times in hours along the trajectories are indicated. The grey hatched area indicates the location of maximum emissions as diagnosed by the peak concentrations for the calm wind conditions in Figure 3 (8×10^{14} and 1.25×10^{16} molecules cm^{-2} for CHOCHO and HCHO respectively). **Right:** CHOCHO and HCHO cross-wind integrals of vertical column density. The OMI observations are line integrals across the trajectories in the left panels, and vertical bars are retrieval uncertainties. The stacked contours are results from the 1-D plume model showing the contributions from individual VOCs as given by the Zheng et al. (2009a) PRD inventory, combined with the CHOCHO and HCHO yields of Figure 2. VOC emissions in the plume model for CHOCHO and HCHO are centered at transport time $t = 6.5$ and $t = 7.0$ hours respectively, based on the plume location during calm wind conditions.

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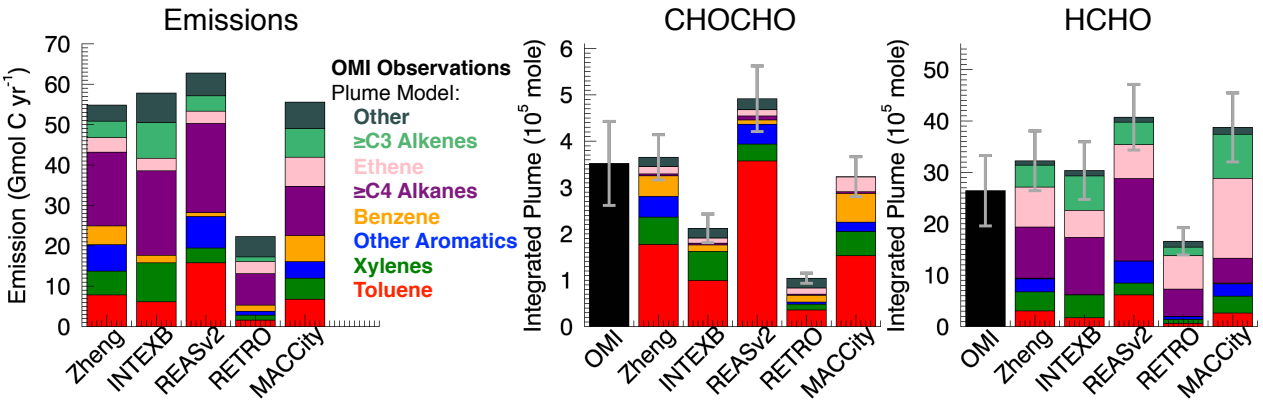

Figure 5. VOC emissions in the PRD from five different inventories (see text), and corresponding plume amounts of CHOCHO and HCHO as computed from the plume model discussed in the text and integrated from $t = 5$ to $t = 20$ h on the trajectory time grid shown in Figure 4. Model uncertainty bars are from uncertainties in OH concentrations and photolysis rates (see text). OMI observations integrated on the same trajectory grid are also shown.

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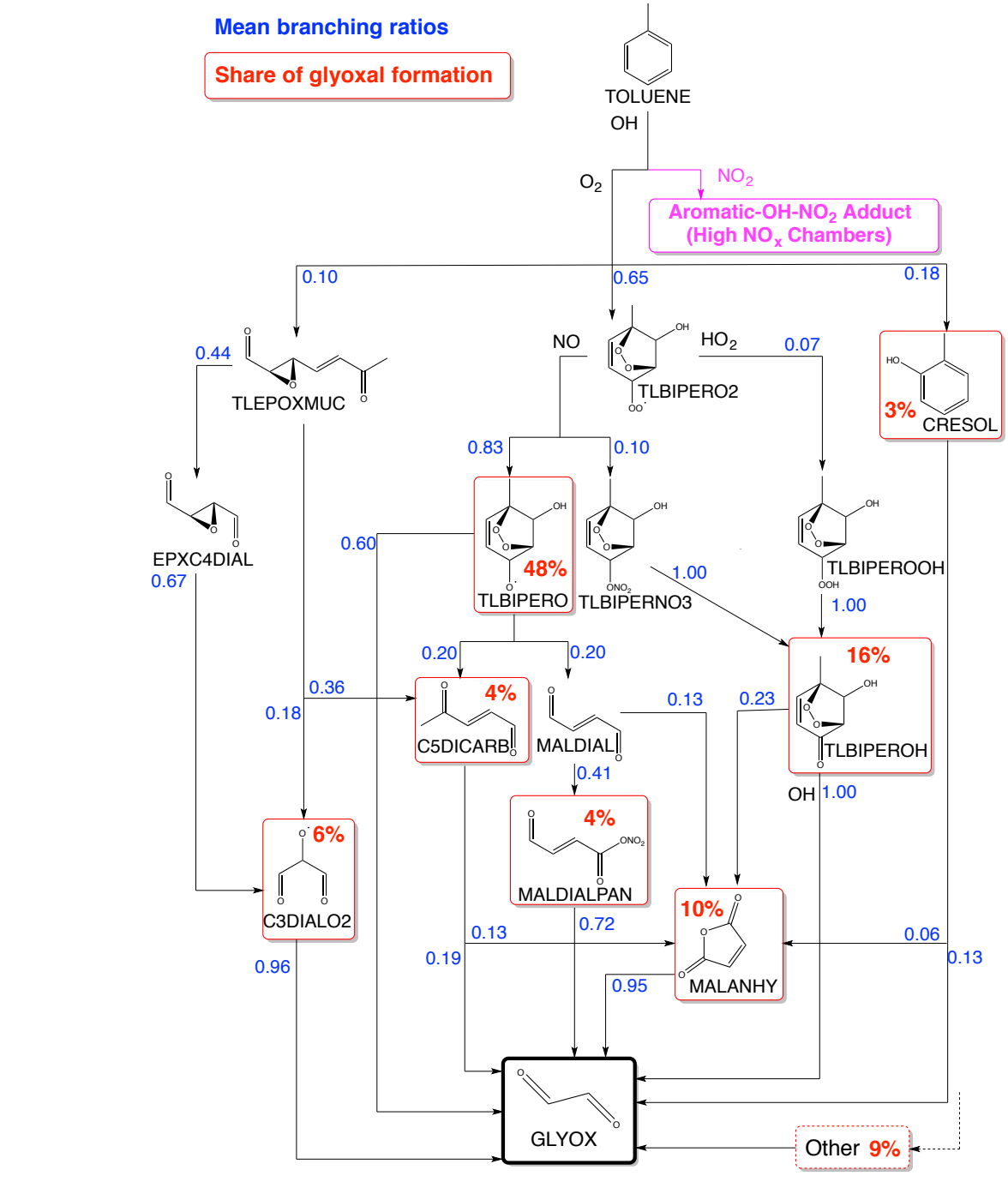

Figure 6. Pathways to glyoxal formation from toluene oxidation by OH in MCMv3.2. Only species relevant to CHOCHO formation are shown, and are labeled by their MCMv3.2 name. Branching ratios (blue) and the share of glyoxal formation from each boxed species (red) are from the 24 h box model simulation described in the text. The high NO_2 pathway (not in MCMv3.2 but relevant in chamber studies) is indicated in pink.