Characterization of Errors in Satellite-based HCHO/NO₂ Tropospheric Column Ratios with Respect to Chemistry, Column to PBL Translation, Spatial Representation, and Retrieval Uncertainties

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Abstract.

The availability of formaldehyde (HCHO) (a proxy for volatile organic compound reactivity) and nitrogen dioxide (NO₂) (a proxy for nitrogen oxides) tropospheric columns from Ultraviolet-Visible (UV-Vis) satellites has motivated many to use their ratios to gain some insights into the near-surface ozone sensitivity. Strong emphasis has been placed on the challenges that

48 come with transforming what is being observed in the tropospheric column to what is actually in
49 the planetary boundary layer (PBL) and near the surface; however, little attention has been paid to
50 other sources of error such as chemistry, spatial representation, and retrieval uncertainties. Here
51 we leverage a wide spectrum of tools and data to quantify those errors carefully.
52   Concerning the chemistry error, a well-characterized box model constrained by more than
53 500 hours of aircraft data from NASA's air quality campaigns is used to simulate the ratio of the
54 chemical loss of HO_2+RO_2 (LROx) to the chemical loss of NO_x (LNOx). Subsequently, we
55 challenge the predictive power of $HCHO/NO_2$ ratios (FNRs), which are commonly applied in
56 current research, at detecting the underlying ozone regimes by comparing them to LROx/LNOx.
57 FNRs show a strongly linear (R^2=0.94) relationship to LROx/LNOx, but only in the logarithmic
58 scale. Following the baseline (i.e., ln(LROx/LNOx) = -1.0±0.2) with the model and mechanism
59 (CB06, r2) used for segregating NOx-sensitive from VOC-sensitive regimes, we observe a broad
60 range of FNR thresholds ranging from 1 to 4. The transitioning ratios strictly follow a Gaussian
61 distribution with a mean and standard deviation of 1.8 and 0.4, respectively. This implies that FNR
62 has an inherent 20% standard error (1-sigma) resulting from not accurately describing the ROx-
63 HOx cycle. We calculate high ozone production rates (PO_3) dominated by large $HCHO \times NO_2$
64 concentration levels, a new proxy for the abundance of ozone precursors. The relationship between
65 PO_3 and $HCHO \times NO_2$ becomes more pronounced when moving towards NOx-sensitive regions
66 due to non-linear chemistry; our results indicate that there is fruitful information in the
67 $HCHO \times NO_2$ metric that has not been utilized in ozone studies. The vast amount of vertical
68 information on HCHO and NO_2 concentration from the air quality campaigns enables us to
69 parameterize the vertical shapes of FNRs using a second-order rational function permitting an
70 analytical solution for an altitude adjustment factor to partition the tropospheric columns to the
71 PBL region. We propose a mathematical solution to the spatial representation error based on
72 modeling isotropic semivariograms. Based on summertime averaged data, Ozone Monitoring
73 Instrument (OMI) loses 12% of spatial information at its native resolution with respect to a high-
74 resolution sensor like TROPOspheric Monitoring Instrument (TROPOMI) ($>5.5 \times 3.5$ km^2). A
75 pixel with a grid size of 216 km^2 fails at capturing ~65% of the spatial information in FNRs at a
76 50 km length scale comparable to the size of a large urban center (e.g., Los Angeles). We
77 ultimately leverage a large suite of in-situ and ground-based remote sensing measurements to draw
78 the error distributions of daily TROPOMI and OMI tropospheric NO_2 and HCHO columns. At a
79 68% confidence interval (1 sigma), errors pertaining to daily TROPOMI observations, either
80 HCHO or tropospheric NO_2 columns, should be above $1.2\text{-}1.5 \times 10^{16}$ molec.cm^{-2} to attain 20-30%
81 standard error in the ratio. This level of error is almost non-achievable with OMI, given its large
82 error in HCHO.
83   The satellite column retrieval error is the largest contributor to the total error (40-90%) in
84 the FNRs. Due to a stronger signal in cities, the total relative error (<50%) tends to be mild,
85 whereas areas with low vegetation and anthropogenic sources (e.g., Rocky Mountains) are
86 markedly uncertain (>100%). Our study suggests that continuing development in the retrieval
87 algorithm and sensor design and calibration is essential to be able to advance the application of
88 FNRs beyond a qualitative metric.

89 **1. Introduction**

90   Accurately representing the near-surface ozone (O_3) sensitivity to its two major precursors,
91 nitrogen oxides (NOx) and volatile organic compounds (VOCs), is an imperative step in
92 understanding non-linear chemistry associated with ozone production rates in the atmosphere.
93 While it is often tempting to characterize an airshed as NOx or VOC-sensitive, both conditions are

94 expected as VOC-sensitive (ozone production rates sensitive to VOC) conditions near NOx
95 sources transition to NOx-sensitive (ozone production rates sensitive to NOx) conditions
96 downwind as NOx dilutes. Thus, reducing the footprint of ozone production can mostly be
97 achieved through NOx reductions. VOCs are key to determining both the location and peak in
98 ozone production, which varies nonlinearly to the NOx abundance. Thus, knowledge of the relative
99 levels of NOx and VOCs informs the trajectory of ozone production and expectations of where
100 peak ozone will occur as emissions change. While a large number of surface stations regularly
101 monitor the near-surface ambient nitrogen dioxide (NO_2) concentrations, the measurements of
102 several VOCs with different reactivity rates with respect to hydroxyl (OH) are not routinely
103 available. As such, our knowledge of where and when ozone production rates are elevated, and
104 their quantitative dependence on a long list of ozone precursors, is fairly limited, except for
105 observationally-rich air quality campaigns. This limitation has prompted several studies, such as
106 Sillman et al. (1990), Tonnesen and Dennis (2000a,b), and Sillman and He (2002), to investigate
107 if the ratio of certain measurable compounds can diagnose ozone regimes meaning if the ozone
108 production rate is sensitive to NOx (i.e., NOx-sensitive) or VOC (i.e., VOC-sensitive). Sillman
109 and He (2002) suggested that H_2O_2/HNO_3 was a robust, measurable ozone indicator as this ratio
110 could well describe the chemical loss of HO_2+RO_2 (LROx) to the chemical loss of NOx (LNOx)
111 controlling the O_3-NOx-VOC chemistry (Kleinman et al., 2001). Nonetheless, both H_2O_2 and
112 HNO_3 measurements are limited to a few spatially-sparse air quality campaigns.
113   Formaldehyde (HCHO) is an oxidation product of VOCs, and its relatively short lifetime
114 (~1-9 hr) makes the location of its primary and secondary sources rather identifiable (Seinfield and
115 Pandis, 2006; Fried et al., 2020). Fortunately, monitoring HCHO abundance in the atmosphere has
116 been a key goal of many Ultraviolet-Visible (UV-Vis) viewing satellites for decades (Chance et
117 al., 1991; Chance et al., 1997; Chance et al., 2000; González Abad et al., 2015; De Smedt et al.,
118 2008, 2012, 2015, 2018, 2021) with reasonable spatial coverage. Additionally, the strong
119 absorption of NO_2 in the UV-Vis range has permitted measurements of NO_2 columns from space
120 (Martin et al., 2002; Boersma et al., 2004, 2007, 2018).
121   Advancements in satellite remote-sensing of these two key compounds have encouraged
122 many studies to elucidate if the ratio of $HCHO/NO_2$ (hereafter FNR) could be a robust ozone
123 indicator (Tonnensen and Dennis, 2000b; Martin et al., 2004; Duncan et al., 2010). Most studies
124 using the satellite-based FNR columns attempted to provide a qualitative view of the underlying
125 chemical regimes (e.g., Choi et al., 2012; Choi and Souri, 2015a,b; Jin and Holloway, 2015; Souri
126 et al., 2017; Jeon et al., 2018; Lee et al., 2021). Relatively few studies (Duncan et al., 2010; Jin et
127 al., 2017; Schroeder et al., 2017; Souri et al., 2020) have carefully tried to provide a quantitative
128 view of the usefulness of the ratio. For the most part, the inhomogeneous vertical distribution of
129 FNR in columns has been emphasized. Jin et al. (2017) and Schroeder et al. (2017) showed that
130 differing vertical shapes of HCHO and NO_2 can cause the vertical shape of FNR not to be
131 consistent throughout the troposphere leading to a variable relationship between what is being
132 observed from the satellite and what is actually occurring in the lower atmosphere. Jin et al. (2017)
133 calculated an adjustment factor to translate the column to the surface using a relatively coarse
134 global chemical transport model. The adjustment factor showed a clear seasonal cycle stemming
135 from spatial and temporal variability associated with the vertical sources and sinks of HCHO and
136 NO_2, in addition to the atmospheric dynamics. In a more data-driven approach, Schroeder et al.
137 (2017) found that the detailed differences in the boundary layer vertical distributions of HCHO
138 and NO_2 lead to a wide range of ambiguous ratios. Additionally, ratios were shown to shift on high
139 ozone days, raising questions regarding the value of satellite averages over longer timescales. Our

140 research aims to put together an integrated and data-driven mathematical formula to translate the
141 tropospheric column to the planetary boundary layer (PBL), exploiting the abundant aircraft
142 measurements available during ozone seasons.
143   Using observationally-constrained box models, Souri et al. (2020) demonstrated that there
144 was a fundamentally inherent uncertainty related to the ratio originating from the chemical
145 dependency of HCHO on NO_x (Wolfe et al., 2016). In VOC-rich (poor) environments, the
146 transitioning ratios from NOx-sensitive to VOC-sensitive occurred in larger (smaller) values than
147 the conventional thresholds defined in Duncan et al. (2010) due to an increased (dampened) HCHO
148 production induced by NOx. To account for the chemical feedback and to prevent a wide range of
149 thresholds on segregating NOx-sensitive from VOC-sensitive regions, Souri et al. (2020)
150 suggested using a first-order polynomial matched to the ridgeline in $P(O_3)$ isopleths. Their study
151 illuminated the fact that the ratio suffers from an inherit chemical complication. However, Souri
152 et al. (2020) did not quantify the error, and their work was limited to a subset of atmospheric
153 conditions. To challenge the predictive power of FNR from a chemistry perspective, we will take
154 advantage of a large suite of datasets to make maximum use of varying meteorological and
155 chemical conditions.
156   Not only are satellite-based column measurements unable to resolve the vertical
157 information of chemical species in the tropospheric column, but they are also unable to resolve the
158 horizontal spatial variability due to their spatial footprint. The larger the footprint is, the more
159 horizontal information is blurred out. For instance, Souri et al. (2020) observed a substantial spatial
160 variance (information) in FNR columns at the spatial resolution of 250×250 m^2 observed by an
161 airborne sensor over Seoul, South Korea. It is intuitively clear that a coarse-resolution sensor
162 would lose a large degree of spatial variance (information). This error, known as the spatial
163 representation error, has not been studied with respect to FNR. We will leverage what we have
164 learned from Souri et al. (2022), which modeled the spatial heterogeneity in discrete data using
165 geostatistics, to quantify the spatial representation error in the ratio over an urban environment.
166   A longstanding challenge is to have a reliable estimate of the satellite retrieval errors of
167 tropospheric column NO_2 and HCHO. Significant efforts have been made recently to assemble,
168 analyze, and estimate the retrieval errors for two key satellite sensors, TROPOspheric Monitoring
169 Instrument (TROPOMI) and Ozone Monitoring Instrument (OMI), using various in-situ
170 measurements (Verhoelst et al., 2021; Vigouroux et al., 2020, Choi et al., 2020; Laughner et al.,
171 2019; Zhu et al., 2020). This study will exploit paired comparisons from some of these new studies
172 to propagate individual uncertainties in HCHO and NO_2 to the FNR errors.
173   The overarching science goal of this study is to address the fact that the accurate diagnosis
174 of surface O_3 photochemical regimes is impeded by numerous uncertainty components, which will
175 be addressed in the current paper, and can be classified into four major categories: i) inherent
176 uncertainties associated with the approach of FNRs to diagnose local O_3 production and sensitivity
177 regimes, ii) translation of tropospheric column satellite retrievals to represent PBL- or surface-
178 level chemistry, iii) spatial representativity of ground pixels of satellite sensors, and iv)
179 uncertainties associated with satellite-retrieved column-integrated concentrations of HCHO and
180 NO_2. We will address all of these sources of uncertainty using a broad spectrum of data and tools.
181   Our paper is organized into the following sections. Section 2 describes the chemical box
182 model setup and data applied. Sections 3.1 to 3.4 deal with the chemistry aspects of FNRs and
183 show the results from a box model. Section 3.5 introduces a data-driven framework to transform
184 the FNR tropospheric columns to the PBL region. Section 3.6 offers a new way to quantify the
185 spatial representation error in satellites. Section 3.7 deals with the satellite error characterization

186 and its impacts on the ratio. Section 3.8 summarizes the fractional contribution of each error to the
187 combined error. Finally, Section 4 provides a summary and conclusions of the study.

2. Photochemical Box Modeling and Aircraft Data Used

189   To quantify the uncertainty of FNR from a chemistry perspective and to obtain several
190 imperative parameters, including the calculated ozone production rates and the loss of NO_x (LNO_x)
191 and RO_x (LRO_x), we utilize the Framework for 0-D Atmospheric Modeling (F0AM) v4 (Wolfe et
192 al., 2016). We adopt the Carbon Bond 6 (CB06, r2) chemical mechanism, and heterogenous
193 chemistry is not considered in our simulations. The model is initialized with the measurements of
194 several compounds, many of which constrain the model by being held constant for each timestep
195 (see Table 1).
196   Figure 1 shows the map of data points from Deriving Information on Surface Conditions
197 from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ)
198 Baltimore-Washington (2011), DISCOVER-AQ Houston-Texas (2013), DISCOVER-AQ
199 Colorado (2014), and Korea United States Air Quality Study (KORUS-AQ) (2016).
200 Meteorological inputs come from the observed pressure, temperature, and relative humidity. The
201 measurements of photolysis rates are not available for all photolysis reactions; therefore, our initial
202 guess of those rates comes from a look-up-table populated by the National Center for Atmospheric
203 Research (NCAR) Tropospheric Ultraviolet And Visible (TUV) model calculations. These values
204 are a function of solar zenith angle, total ozone column density, surface albedo, and altitude. We
205 set the total ozone column and the surface albedo to fixed numbers of 325 (Dobson) DU and 0.15,
206 respectively. The initial guess is then corrected by applying the ratio of observed photolysis rates
207 of NO_2+hv (jNO_2) and/or O_3+hv (jO^1D) to the calculated ones to all j-values (i.e., wavelength-
208 independent). If both observations of jNO_2 and jO^1D are available, the correction factor is
209 averaged. The KORUS-AQ campaign is the only one that provides jO^1D measurements; therefore,
210 the use of the wavelength-independent correction factor based on the ratio of observed to
211 calculated jNO_2 values for all j-value is a potential source of error in the model especially when
212 aerosols are present. The model calculations are based on the observations merged to a temporal
213 resolution varying from 10 to 15 seconds. Each calculation was run for five consecutive days with
214 an integration time of 1 hour to approach diel steady state. We test the number of solar cycles
215 against ten days on the KORUS-AQ setup and observe no noticeable difference in simulated OH
216 and HCHO (Figure S1), indicating that five solar cycles suffice. Some secondarily-formed species
217 must be unconstrained for the purpose of model validation. Therefore, the concentrations of several
218 secondarily-formed compounds, such as HCHO and PAN, are unconstrained. Nitric oxide (NO)
219 and NO_2 are also allowed to cycle while their sum (i.e., NOx) is constrained. Because the model
220 does not consider various physical loss pathways, including deposition and transport, which vary
221 by time and space, we oversimplify their physical loss through a first-order dilution rate set to
222 $1/86400-1/43200$ s^{-1} (i.e., 24- or 12-hr lifetime), which in turn prevents relatively long-lived
223 species from accumulating over time. Our decision on unconstraining HCHO, a pivotal compound
224 impacting the simulation of HOx, may introduce some systematic biases in the simulation of
225 radicals determining ozone chemistry (Schroeder et al., 2020). Therefore, to mitigate the potential
226 bias in HCHO, we set the dilution factor to maintain the campaign-averaged bias in the simulated
227 HCHO with respect to observations of less than 5%. However, it is essential to recognize that
228 HCHO can fluctuate freely for each point measurement because the dilution constraint is set to a
229 fixed value for an individual campaign. Each time tag is independently simulated, meaning we do
230 not initialize the next run using the simulated values from the previous one; this in turn, permits
231 parallel computation. Regarding the KORUS-AQ campaign where HOx observations were

232 available, we only ran the model for data points with HOx measurements. Similar to Souri et al.
233 (2020), we filled gaps in VOC observations with a bilinear interpolation method with no
234 extrapolation allowed. In complex polluted atmospheric conditions such as that over Seoul, South
235 Korea, Souri et al. (2020) observed that this simple treatment yielded comparable results with
236 respect to the NASA LaRC model (Schroeder et al. 2020), which incorporated a more
237 comprehensive data harmonization. Table 1 lists the major configuration along with the
238 observations used for the box model.

239   Several parameters are calculated based on the box model outputs. LRO$_x$ is defined through
240 the sum of primarily radical-radical reactions:

$$LRO_x = k_{HO_2+HO_2}[HO_2]^2 + \sum k_{RO_{2i}+HO_2}[RO_{2i}][HO_2] + \sum k_{RO_{2i}+RO_{2i}}[RO_{2i}]^2 \tag{1}$$

241 where k is the reaction rate constant. LNO$_x$ mainly occurs via the NO$_2$+OH reaction:

$$LNO_x = k_{OH+NO_2+M}[OH][NO_2][M] \tag{2}$$

242 where M is a third body. We calculate P(O$_3$) by subtracting the ozone loss pathways dictated by
243 HO$_x$ (HO+HO$_2$), NO$_2$+OH, O$_3$ photolysis, ozonolysis, and the reaction of O(^{1}D) with water vapor
244 from the formation pathways through the removal of NO via HO$_2$ and RO$_2$:

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_{2i}+NO}[RO_{2i}][NO] - k_{OH+NO_2+M}[OH][NO_2][M] - P(RONO_2) - k_{HO_2+O_3}[HO_2][O_3] - k_{OH+O_3}[OH][O_3] - k_{O(^1D)+H_2O}[O(^1D)][H_2O] - L(O_3 + alkenes) \tag{3}$$

3. Results and Discussion

3.1. Box Model Validation

247   There are uncertainties associated with the box model (e.g., Brune et al., 2022; Zhang et
248 al., 2021; Lee et al., 2021), which can be attributed to: i) the lack of inclusion of physical processes
249 such as entrainment/detrainment and diffusion, ii) discounting the heterogeneous chemistry, iii)
250 invalid assumption of the diel steady state in areas close to large emission sources or in
251 photochemically less active environments (Thornton et al., 2002; Souri et al., 2021), iv) errors in
252 the chemical mechanism and v) errors in the measurements. These limitations necessitate a
253 thorough validation of the model using unconstrained observations. While models have been
254 known for a long time not to be 100% accurate (Box, 1976), it is important to characterize whether
255 the model can effectively represent reality. For instance, if the simulated HCHO is poorly
256 correlated with observations and/or displayed large magnitude biases, it will be erroneous to
257 assume that the sources of HCHO, along with relevant chemical pathways, are appropriate. It is
258 important to acknowledge that the VOC constraints for these model calculations are incomplete,
259 especially for the DISCOVER-AQ campaigns, which lacked comprehensive VOC observations.
260 Nevertheless, we will show that the selected VOCs are sufficient to reproduce a large variance
261 (>70%) in observed HCHO.

262   We diagnose the performance of the box model by comparing the simulated values of five
263 compounds to observations: HCHO, NO, NO$_2$, PAN, hydroperoxyl radical (HO$_2$), and OH. Figure
264 2 depicts the scatterplot of the comparisons along with several statistics. HCHO observations are
265 usually constrained in box models to improve the representation of HO$_2$ (Schroeder et al., 2017;

266 Souri et al., 2020; Brune et al., 2022); however, this constraint may mask the realistic
267 characterization of the chemical mechanism with respect to the treatment of VOCs. Additionally,
268 it is important to know if the sources of HCHO are adequate. Therefore, we detach the model from
269 this constraint to perform a more fair and stringent validation.

270   Concerning HCHO, our model does have considerable skill at reproducing the variability
271 of observed HCHO (R^2=0.73). To evaluate if this agreement is accidentally caused by the choice
272 of the dilution factor and to identify if our VOC treatment is inferior compared to the one adopted
273 in the NASA LaRC (Schroeder et al., 2021), we conducted three sets of sensitivity tests for the
274 KORUS-AQ campaign, including ones with and without considering a dilution factor and another
275 one without HNO_3 and H_2O_2 constraints (Figure S2). The lack of consideration of a dilution factor
276 results in no difference in the variance in HCHO captured by our model (R^2=0.81). Our model
277 without the dilution factor is still skillful at replicating the magnitude of HCHO with less than 12%
278 bias. This is why the optimal dilution factor for each campaign is within 12 hr to 24 hr, which is
279 not different from other box modeling studies (e.g., Brune et al., 2022; Miller and Brune, 2022).
280 We observe no difference in the simulated HCHO when HNO_3 and H_2O_2 values are not
281 constrained. The unconstrained NASA LaRC setup oversampled at 10-sec frequency captures 86%
282 variance in the measurements, only slightly (6%) outperforming our result. However, the
283 unconstrained NASA LaRC setup greatly underestimates the magnitude of HCHO compared to
284 our model results.

285   The model performs well with regard to the simulation of NO (R^2=0.89) and NO_2 (R^2=0.99)
286 in the logarithmic scale. Immediately evident is the underestimation of NO in highly polluted
287 regions, contrary to an overestimation in clean ones. This discrepancy leads to an underestimation
288 (overestimation) of NO/NO_2 in polluted (clean) regions. The primary drivers of NO/NO_2 are jNO_2
289 and O_3, both of which are constrained in the model. What can essentially deviate the partitioning
290 between NO and NO_2 from that of observations in polluted areas is the assumption of the diel
291 steady state, which is rarely strictly valid where measurements are close to large emitters. The
292 overestimation of NO in low NO_x areas is often blamed on the lack of chemical sink pathways of
293 NO in chemical mechanisms (e.g., Newland et al., 2021). The relatively reasonable performance
294 of PAN (R^2=0.63) is possibly due to constraining some of the oxygenated VOCs, such as
295 acetaldehyde. Xu et al. (2021) observed a strong dependency of PAN concentrations on NO/NO_2
296 ratios. Smaller NO/NO_2 ratios are usually associated with larger PAN mixing ratios because NO
297 can effectively remove peroxyacetyl radicals. We observe an overestimated PAN (0.27 ppbv),
298 possibly due to an underestimation of NO/NO_2. Moreover, we should not rule out the impact of
299 the first-order dilution factor, which was only empirically set in this study. For instance, if we
300 ignore the dilution process for the KORUS-AQ campaign, the bias of the model in terms of PAN
301 will increase by 33% resulting in poor performance (R^2=0.40) (Figure S3). We notice that this
302 poor performance primarily occurs for high altitude measurements where PAN is thermally stable
303 (Figure S4); therefore, this does not impact the majority of rapid atmospheric chemistry occurring
304 in the lower troposphere, such as the formation of HCHO. Schroeder et al. (2020) found that proper
305 simulation of PAN in the polluted PBL during KORUS-AQ required a first-order loss rate based
306 on thermal decomposition at the average PBL temperature, which was more realistic than the
307 widely varying local PAN lifetimes associated with temperature gradients between the surface and
308 the top of the PBL. This solution is computationally equivalent to the dilution rate used in this
309 study.

310   KORUS-AQ was the only field campaign providing OH and HO_2 measurements.
311 Concerning HO_2, former studies such as Schroeder et al. (2017), Souri et al. (2020), and Brune et

al. (2022) managed to reproduce HO_2 mixing ratios with R^2 ranging from 0.6 to 0.7. The performance of our model (R^2=0.66) is similar to these past studies, with nearly negligible biases (<1%). One may argue that the absence of the HO_2 uptake by aerosols is contributing to some of the discrepancies we observe in the HO_2 comparison. Brune et al. (2022) provided compelling evidence showing that considering the HO_2 uptake made their results significantly inconsistent with the observations suggesting that the HO_2 uptake might have been inconsequential during the campaign. Our model manages to reproduce 64% of the variance of observed OH outperforming the simulations presented in Souri et al. (2020) and Brune et al. (2022) by >10%. The slope (= 1.03) is not too far from the identity line, indicating that our box model systematically overestimates OH by 0.62×10^6 cm^{-3}. This may be attributed to a missing OH sink in the mechanism or the lack of inclusion of some VOCs. A sensitivity test involving removing the first-order dilution process demonstrates that the simulation of HOx is rather insensitive to this parameter (Figure S5). In general, the model performance is consistent, or outperforms, results from recent box modeling studies, indicating that it is at least roughly representative of the real-world ozone chemistry and sensitivity regimes.

3.2.   Can HCHO/NO₂ ratios fully describe the HOx-ROx cycle?

Kleinman et al. (2001) demonstrated that LROx/LNOx is the most robust ozone regime indicator. Thus, the predictive power of FNR at detecting the underlying chemical conditions can be challenged by comparing FNR to LROx/LNOx. Ideally, if they show a strong degree of correspondence (i.e., R^2=1.0), we can confidently say that FNR can realistically portray the chemical regimes. Any divergence of these two quantities indicates the inadequacy of the FNR indicator. Souri et al. (2020) observed a strong linear relationship between the logarithmic transformed FNR and those of LROx/LNOx. Our analysis in this study will be based on the simulated values to ensure that the relationship is coherent based on a realization from the well-characterized box model. As pointed out by Schroeder et al. (2017) and Souri et al. (2020), a natural logarithm of LROx/LNOx roughly equal to -1.0 (i.e., LROx/LNOx = 0.35-0.37) perceptibly separates VOC-sensitive from NOx-sensitive regimes, which would make this threshold the baseline of our analysis.

Figure 3 demonstrates the log-log relationship of LROx/LNOx and FNR, and P(O₃), from all four air quality campaigns. The log-log relationships from each individual campaign are shown in Figure S6-S9. We overlay the LROx/LNOx baseline threshold along with two commonly used thresholds for FNR suggested by Duncan et al. (2010); they defined the VOC-sensitive regimes if FNR<1 and the NOx-sensitive ones if FNR>2. Any region undergoing a value between these thresholds is unlabeled and considered to be in a transitional regime. The size of each data point is proportional to the HCHO×NO₂ concentration magnitude. One striking finding from this plot is that there is indeed a strong linear relationship between the logarithmic-transformed LROx/LNOx and FNR (R^2=0.91). A strong linear relationship between the two quantities in the log-log scale indicates a power law dependence (i.e., $y=ax^b$). A strong power law dependency means that these two quantities have a poor correlation at their low and high values. This is mainly caused by the fact that HCHO does not fully describe VOC reactivity rates in environments with high and low VOC concentrations (Souri et al., 2020). The question is, what range of FNR will fall in ln(LROx/LNOx) = -1.0±0.2? Following the baseline, the transitioning ratios follow a normal distribution with a mean of 1.8, a standard deviation of 0.4, and a range from 1 to 4 (Figure S10). We define the chemical error in the application of FNR to separate the chemical regimes as the relative error standard deviation (i.e., σ/μ) of the transitioning ratios leading to ~ 20%. These numbers are based on a single model realization and can change if a different mechanism is used;

nonetheless, the model has considerable skill at reproducing many different unconstrained compounds, especially OH, suggesting that it is a rather reliable realization. Comparing the transitioning FNRs to the NO_2 concentrations suggests no correlation (r=0.02), whereas there is a linear correlation between the transitioning ratios and the HCHO concentrations (r=0.56). This tendency reinforces the study of Souri et al. (2020), who, primarily due to the HCHO-NO_2 feedback, observed a larger FNR threshold in VOC-rich environments to be able to detect the chemical regimes.

3.3. Large PO_3 rates occur in regions with large HCHO×NO_2 concentrations when moving toward NOx-sensitive regions

A striking and perhaps intuitive tendency observed from Figure 3 is that large PO_3 rates are mostly tied to higher HCHO×NO_2. But this relationship gradually weakens as we move towards VOC-sensitive regions (smaller LROx/LNOx ratios). This is a textbook example of non-linear ozone chemistry. In VOC-sensitive areas, PO_3 can be strongly inhibited by NO_2+OH and the formation of organic nitrates despite the abundance of the precursors. In the application of remote-sensing of ozone precursors, the greatest unused metric describing the mass of the ozone precursors is HCHO×NO_2. However, this metric should only be used in conjunction with FNR. To demonstrate this, based on what the baseline (LROx/LNOx) suggests against thresholds on FNRs defined by Duncan et al. (2010), we group the data into four regions: NOx-sensitive – NOx-sensitive, NOx-sensitive–transitional, VOC-sensitive–transitional, and VOC-sensitive–VOC-sensitive. A different perspective on this categorization is that the transitional regimes are a weaker characterization of the main regime; for instance, NOx-sensitive–transitional regions are less NOx-sensitive than NOx-sensitive – NOx-sensitive. Subsequently, the cumulative distribution functions (CDFs) of PO_3 and HCHO×NO_2 with respect to the aforementioned groups are calculated, which is shown in Figure 4. Regarding NOx-sensitive—NOx-sensitive regions, we see the PO_3 CDF very quickly converging to the probability of 100%, indicating that the distribution of PO_3 is skewed towards very low values. The median of PO_3 for this particular regime (where CDF = 50%) is only 0.25 ppbv/hr. This agrees with previous studies such as Martin et al. (2002), Choi et al. (2012), Jin et al. (2017), and Souri et al. (2017), reporting that NOx-sensitive regimes dominate in pristine areas. The PO_3 CDFs between NOx-sensitive—transitional and VOC-sensitive—VOC-sensitive are not too distinct, whereas their HCHO×NO_2 CDFs are substantially different. The non-linear ozone chemistry suppresses PO_3 in highly VOC-sensitive areas such that those values are not too different from those in mildly polluted areas (NOx-sensitive—transitional). Perhaps the most interesting conclusion from this figure is that elevated PO_3 values (median = 4.6 ppbv/hr), a factor of two larger than two previous regimes, are mostly found in VOC-sensitive—transitional. This is primarily due to two causes: i) this particular regime is not strongly inhibited by the nonlinear chemistry, particularly NO_2+OH, and ii) it is associated with abundant precursors evident in the median of HCHO×NO_2 being three times as large of those in NOx-sensitive—transitional. This tendency illustrates the notion of non-linear chemistry and how this may affect regulations. Simply knowing where the regimes are might not suffice to pinpoint the peak of PO_3, as this analysis suggests that we need to consider both FNR and HCHO×NO_2; both metrics are readily accessible from satellite remote-sensing sensors.

3.4. *Can we estimate PO_3 using the information from HCHO/NO_2 and HCHO×NO_2?*

It may be advantageous to construct an empirical function fitted to these two quantities and elucidate the maximum variance (information) we can potentially gain to recreate PO_3. After several attempts, we found a bilinear function ($z=a_0+a_1x+a_2y+a_3xy$) to be a good fit without

403 overparameterization. Due to presence of extreme values in both FNR and HCHO×NO$_2$, we use a
404 weighted least squares method for the curve fitting based on the distance of the fitted curve to the
405 data points (known as bi-squares weighting). The best fit with R^2 equals to 0.94 and an RMSE of
406 0.60 ppbv/hr is:

$$PO_3 = 0.74 - 0.09\,x - 0.02\,y + 0.25xy \tag{4}$$

407 where x and y are FNR (unitless) and HCHO×NO$_2$ (ppbv^2), respectively. The residual of the fit is
408 shown in Figure S11. The gradients of PO$_3$ with respect to x and y are:

$$\frac{dPO_3}{dx} = 0.25y - 0.09 \tag{5}$$

$$\frac{dPO_3}{dy} = 0.25x - 0.02 \tag{6}$$

409 An apparent observation arises from these equations that is the derivative of PO$_3$ to each
410 metric depends on the other one underscoring their interconnectedness. For instance, Eq. (6)
411 suggests that larger FNRs (x) result in a larger gradient of PO$_3$ to the abundance of HCHO×NO$_2$
412 (y). In very low FNRs, this gradient can become very small, rendering PO$_3$ insensitive (or in
413 extreme cases, negatively correlated) to HCHO×NO$_2$. This analysis provides encouraging results
414 about the future application of the satellite-derived HCHO×NO$_2$; however, the wide class of
415 problems relating to the application of satellite-derived FNR columns, such as satellite errors in
416 columns or the translation between columns to PBL is also present in Eq. (4), even in a more
417 pronounced way due to HCHO×NO$_2$ and HCHO^2 (= xy). This new perspective on PO$_3$ estimation
418 deserves a separate study.

3.5. Altitude dependency and its parametrization

420 A lingering concern over the application of satellite-based FNR tropospheric columns is
421 that the vertical distribution of HCHO and NO$_2$ are integrated into columns; thus, this vertical
422 information is permanently lost. Here, we provide insights into the vertical distribution of FNR
423 within the tropospheric column. This task requires information about the differences between i)
424 the vertical shape of HCHO and that of NO$_2$ and ii) the vertical shape in the sensitivity of the
425 retrievals to the different altitude layers (described as scattering weights). Ideally, if both
426 compounds show an identically relative shape, the FNR columns will be valid for every air parcel
427 along the vertical path (i.e., a straight line). Previous studies such as Jin et al. (2017) and Schroeder
428 et al. (2017) observed a large degree of vertical inhomogeneity in both HCHO and NO$_2$
429 concentrations suggesting that this ideal condition cannot be met. We do not always have precise
430 observations of HCHO and NO$_2$ vertical distributions, but we can constitute some degree of
431 generalization by leveraging the measurements made during the aircraft campaigns. As for the
432 differences in the vertical shapes (i.e., the curvature) of the sensitivity of the retrievals between
433 HCHO and NO$_2$ channels (i.e., ~ 340 nm and ~440 nm), under normal atmospheric and viewing
434 geometry conditions, several studies such as Nowlan et al. 2018 and Lorente et al. 2017 showed
435 small differences in the vertical shapes of the scattering weights in the first few kilometers altitude
436 above the surface where the significant fluctuations in FNRs usually take place. Therefore, our
437 analysis does not consider the varying vertical shapes in the scattering weights. However, this
438 assumption might not hold for excessive aerosol loading with variable extinction efficiency
439 between ~340 nm and ~440 nm wavelengths or extreme solar zenith angles.

440 Figure 5 demonstrates the violin plot of the afternoon (> 12:00 LT) vertical distribution of
441 HCHO, NO$_2$, and FNR observed by NASA's aircraft during the four field campaigns analyzed in
442 this study superimposed by the simulated PO$_3$ rates. The vertical layers are grouped into sixteen

443 altitudes ranging from 0.25 km to 7.75 km. Each vertical layer incorporates measurements ±0.25
444 km of the mid-layer height. The observations do not follow a normal distribution, particularly in
445 the lower parts of the atmosphere; thus, medians are preferred to represent the central tendency.
446 While the largest PO_3 rates tend to occur in areas close to the surface (< 2 km agl), a nonnegligible
447 fraction of the elevated PO_3 rates are also observed in other parts of the atmosphere, such as in the
448 free troposphere.
449   Several intriguing features are observed in Figure 5: First, up to the 5.75 km range, which
450 encompasses the PBL area and a large portion of the free troposphere, NO_2 concentrations tend to
451 decrease quicker than those of HCHO in line with previous studies such as Schroeder et al. (2017),
452 Jin et al. (2017), Chan et al. (2019), and Ren et al. (2022). Second, above 5.75 km, HCHO levels
453 off, whereas NO_2 shows an increasing trend. Finally, due to their different vertical shapes, we
454 observe nonuniformities in the vertical distribution of FNR: they become more NOx-sensitive with
455 altitude up to a turning point at 5.75 km and then shift back to the VOC-sensitive direction.
456   It is attractive to model these shapes and apply parameterizations to understand how their
457 shapes will complicate the use of tropospheric column retrieval from satellites. First order rational
458 functions are a good candidate to use. Concerning the vertical dependency of HCHO and NO_2, we
459 find reasonable fit (R^2=0.73) as:

$$HCHO, NO_2 = \frac{a_0 z + a_1}{z + a_2} \tag{7}$$

460 where z is altitude in km. a_i (i=0,1,2) are fitting parameters. From this equation it is determined
461 that FNRs follow a second order rational function:

$$f(z) = \frac{HCHO}{NO_2} = \frac{b_0 z^2 + b_1 z + b_2}{b_3 z^2 + b_4 z + b_5} \tag{8}$$

462 where b_i (i=0, … , 5) are fitting parameters. One can effortlessly fit this function to different bounds
463 of the vertical distribution of FNR such as the 25th and 75th percentiles, and subsequently estimate
464 the first moment of the resultant polygon along z divided by the total area bounded to the polygon
465 (the centroid, G) via:

$$G(z_1, z_2) = \frac{1}{2A} \int_{z1}^{z2} f^2(z)_{75th} - f^2(z)_{25th} \, dz \tag{9}$$

466 where A is the area of the polygon bounded by the 75th percentiles, $f(z)_{75th}$, and the 25th
467 percentiles ($f(z)_{25th}$) of FNR (shown in Figure 5 as solid black lines). We define an altitude
468 adjustment factor (f_{adj}) such that one can translate an observed FNR tropospheric column ratios,
469 such as those retrieved from satellites, to a defined altitude and below that point (zt) through:

$$f_{adj} = \frac{G(0, z_t)}{G(0, 8\ km)} \tag{10}$$

470 where zt can be interchanged to match the PBLH. This definition is more beneficial than using the
471 entire tropospheric column to the surface conversion (e.g., Jin et al., 2017) because ozone can form
472 in various vertical layers. Using the observations collected during the campaign, we estimate Eq.
473 (10) along with ±1σ boundaries shown in Figure 6. To determine the adjustment factor error, we
474 reestimate Eq.9 with ±1σ level in the coefficients obtained from Eq.8. The resultant error is shown
475 in the dashed red line in Figure 6. This error results from uncertainties associated with assuming
476 that the second-order rational function can explain the vertical distribution of FNRs. The shape of
477 the resulting adjustment factor is in line with the vertical distribution of FNR (see Figure 5): the
478 adjustment factor curve closer to the surface has values smaller than one, increases to values larger
479 than one in the mid-troposphere, and finally, converges to one near the top of measured
480 concentrations. If one picks out an altitude pertaining to a PBLH, one can easily apply f_{adj} to the

481 observed FNR columns to estimate the corresponding ratio for that specific PBLH. A more evolved
482 PBLH (i.e., a large zt) results in stronger vertical mixing, rendering f_{adj} closer to one. The standard
483 error deviation of this conversion is around 19%. The relatively low fluctuations in the adjustment
484 factor around one suggest that under the observed atmospheric conditions (clear-sky afternoon
485 summers), the columnar tropospheric ratios do not poorly represent the chemical conditions in the
486 PBL region.
487   It is beneficial to model this curve to make this data-driven conversion easier for future
488 applications. A second-order polynomial can well describe (R^2=0.97) this curve:

$$f_{\text{adj}} = az_t^2 + bz_t + c \qquad\qquad a = -0.01, b = 0.15, c = 0.78 \qquad\qquad (11)$$

489 Although Eq. (11) does not include observations above 8 km, the area bounded between $f(z)_{75th}$
490 and $f(z)_{25th}$ in higher altitudes is too small to make a noticeable impact on this adjustment factor.
491   One may object that since we estimated the adjustment factor based on two boundaries
492 (25th and 75th percentiles) of the data, we are no longer really dealing with 50% of features
493 observed in the vertical shapes of FNR. This valid critique can be overcome by gradually relaxing
494 the lower and upper limits and examining the resulting change in f_{adj}. When we reduce the lower
495 limit in Eq. (9) from the 25th to 1st percentiles, the optimal curve is similar to the one shown in
496 Figure 6 (Figure S12). However, when we extend the upper limit from the 75th percentile to greater
497 values, we see the fit becoming less robust above the 80th percentile, indicating that the formulation
498 applies to ~80% of the data. The reason behind the poor representation of the adjustment factor
499 for the upper tail of the population is the extremely steep turning point between 5.5 and 6.0 km,
500 necessitating a higher-order rational function to be used for Eq. (7) and Eq. (8). We prefer to limit
501 this analysis to both boundaries and the order defined in Eq. (8) and Eq. (9) because extreme value
502 predictions usually lack robustness.
503   A caveat with these results is that our analysis is limited to afternoon observations because
504 we focus on afternoon low-orbiting sensors such as OMI and TROPOMI. Nonetheless, Schroeder
505 et al. (2017) and Crawford et al. (2021) observed large diurnal variability in these profiles due to
506 diurnal variability in sinks and sources of NO_2 and HCHO and atmospheric dynamics. The diurnal
507 cycle has an important implication for geostationary satellites such as Tropospheric Emissions
508 indeed: Monitoring of Pollution (TEMPO) (Chance et al., 2019). Limiting the observations to
509 morning time results in a smaller adjustment factor for altitudes close to the surface resulting from
510 steeper vertical gradients of HCHO/NO_2 (Figures S13 and S14). This tendency agrees with Jin et
511 al. (2017), who observed a larger deviation from one in an adjustment factor used for the column-
512 surface conversion in winter.
513   Another important caveat with our analysis is that it is based upon four air quality
514 campaigns in warm seasons that avoid times/areas with convective transport; as such, our analysis
515 needs to be made aware of the vertical shapes of FNR during convective activities and cold
516 seasons. However, a few compelling assumptions can minimize these oversights: first, it is very
517 atypical to encounter elevated ozone production rates during cold seasons with few exceptions
518 (Ahmadov et al., 2015; Rappenglück et al., 2014); second, the notion of ozone regimes is only
519 appropriate in photochemically active environments where the ROx-HOx cycle is active; an
520 example of this can be found in Souri et al. (2021) who observed an enhancement of surface ozone
521 in central Europe during a lockdown in April 2020 (up to 5 ppbv) compared to a baseline which
522 was explainable by the reduced O_3 titration through NO in place of the photochemically induced
523 production. An exaggerated extension to this example is the nighttime chemistry where NO-O_3-
524 NO_2 partitioning is the primary driver of negative ozone production rates; at night, the definition
525 of NOx-sensitive or VOC-sensitive is meaningless, so it is in photochemically less active

526 environments; third, it is rarely advisable to use cloudy scenes in satellite UV-Vis gas retrievals
527 due to the arguable assumption on Lambertian clouds and highly uncertain cloud optical centroid
528 and albedo; accordingly, atmospheric convection occurring during storms or fires is commonly
529 masked in satellite-based studies. Therefore, the limitations associated with the adjustment factor
530 are mild compared to the advantages.

3.6. Spatial Heterogeneity

531

532 The spatial representation error resulting from unresolved processes and scales (Janić et
533 al., 2016; Valin et al., 2011; Souri et al., 2022) refers to the amount of information lost due to
534 satellite footprint or unresolved inputs used in satellite retrieval algorithms. Unfortunately, this
535 source of error cannot be determined when we do not know the true state of the spatial variability.
536 There is, however, a practical way to resolve this by conducting multi-scale intercomparisons of a
537 coarse spatial resolution output against a finer one. Yet, despite the absence of the truth in this
538 approach, we tend to find their comparisons useful in giving us an appreciation of the error.
539 We build the reference data on qualified pixels (qa_value> 0.75) of offline TROPOMI
540 tropospheric NO_2 version 2.2.0 (van Geffen et al., 2021; Boersma et al., 2018) and total HCHO
541 columns version 2.02.01 (De Smedt et al., 2018) oversampled at 3×3 km^2 in summer 2021 over
542 the US. Figure 7 shows the map of those tropospheric columns as well as FNR. Encouragingly,
543 the small footprint and relatively low detection limit of TROPOMI compared to its predecessor
544 satellite sensors (e.g., OMI) enable us to have possibly one of the finest maps of HCHO over the
545 US to date. Large values of HCHO columns are found in the southeast due to strong isoprene
546 emissions (e.g., Zhu et al., 2016; Wells et al., 2020). Cities like Houston (Boeke et al., 2011; Zhu
547 et al., 2014; Pan et al., 2015; Diao et al., 2016), Kansas City, Phoenix (Nunnermacker et al., 2004),
548 and Los Angeles (de Gouw et al., 2018) also show pronounced enhancements of HCHO possibly
549 due to anthropogenic sources. Expectedly, large tropospheric NO_2 columns are often confined to
550 cities and some coal-fired power plants along the Ohio River basin. Concerning FNR, low values
551 dominate cities, whereas high values are found in remote regions. An immediate tendency
552 observed from these maps is that the length scale of HCHO columns is longer than that of NO_2.
553 This indicates that NO_2 columns are more heterogeneous. Because of this, we observe a large
554 degree of spatial heterogeneity with respect to FNRs.
555 Here we limit our analysis to Los Angeles due to computational costs imposed by the
556 subsequent experiment. To quantify the spatial representation errors caused by satellite footprint
557 size, we upscale the FNRs by convolving the values with four low pass box filters with the size of
558 13×24, 36×36, 108×108, and 216×216 km^2, shown in the first column of Figure 8. Subsequently,
559 to extract the spatial variance (information), we follow the definition of the experimental
560 semivariogram (Matheron, 1963):

$$\gamma(\boldsymbol{h}) = \frac{1}{2N(\boldsymbol{h})} \sum_{|x_i - x_j| - |\boldsymbol{h}| \leq \varepsilon} [Z(x_i) - Z(x_j)]^2 \qquad (12)$$

561 where $Z(x_i)$ (and $Z(x_j)$) is discrete pixels of FNRs, $N(\boldsymbol{h})$ is the number of paired pixels separated
562 by the vector of $\boldsymbol{h}$. The $|.|$ operator indicates the length of a vector. The condition of $|x_i - x_j| -$
563 $|\boldsymbol{h}| \leq \varepsilon$ is to permit certain tolerance for differences in the length of the vector. Here, we ignore
564 the directional dependence in $\gamma(\boldsymbol{h})$ which makes the vector of $\boldsymbol{h}$ scalar ($h = |\boldsymbol{h}|$). Moreover, we bin
565 γ values in 100 evenly-spaced intervals ranging from 0 to 5 degrees. To remove potential outliers
566 (such as noise), it is wise to model the semivariogram using an empirical regression model. To
567 model the semivariogram, we follow the stable Gaussian function used by Souri et al. (2022):

$$\gamma(h) = s(1 - e^{-(\frac{h}{r})^{c_0}}): c_0 = 1.5 \tag{13}$$

where r and s are fitting parameters. For the most part, geophysical quantities become spatially uncorrelated at a certain distance called the range, and the variance associated with that distance is called the sill. The fitting parameters, r, and s, describe these two quantities as long as the stable Gaussian function can well fit to the shape of semivariogram. The semivariograms, and the fits, associated with each map are depicted in the second column of Figure 8.

The modeled semivariograms suggest that a coarser field comes with a smaller sill, implying a loss in the spatial information (variance). The length scale (i.e., the range) only sharply increases at coarser footprints ($>36\times36$ km^2). This indicates that several coarse-resolution satellite sensors, such as OMI (13×24 km^2), are rather able to determine the length scales of FNR over a major city such as Los Angeles. By leveraging the modeled semivariograms, we can effortlessly determine the spatial representation error for specific scale (e.g., h=10 km) through

$$e^2(h) = 1 - \frac{\gamma(h)}{\gamma_{ref}(h)} \tag{14}$$

where $\gamma(h)$ and $\gamma_{ref}(h)$ are the modeled semivariogram of the target and the reference fields (3×3 km^2). This equation articulates the amount of information lost in the target field compared to the reference. Accordingly, the proposed formulation of the spatial representation error is relative. Figure 9 depicts the representation errors for various footprints. For the most part, the OMI nadir pixel (13×24 km^2) only has a ~12% loss of the spatial variance. On the contrary, a grid box with a size of 216×216 km^2 fails at capturing ~65% of the spatial information in FNR with a 50 km length scale comparable to the extent of Los Angeles. The advantage of our method is that we can mathematically describe the spatial representation error as a function of the length of our target. The present method can be easily applied to other atmospheric compounds and locations. We have named this method SpaTial Representation Error EstimaTor (STREET) which is publicly available as an open-source package (Souri, 2022).

An oversight in the above experiment lies in its lack of appreciation of unresolved physical processes in the satellite measurements: a weak sensitivity of some retrievals to the near-surface pollution due to the choice of spectral windows used for fitting (Yang et al., 2014), using 1-D air mass factor calculation instead of 3-D (Schwaerzel et al., 2020), and neglecting aerosol effect on the light path are just a few examples to point out. To account for the unresolved processes, one can recalculate Eqs. (12)-(14) using outputs from different retrieval frameworks, which is beyond the scope of this study.

3.7.   Satellite errors

3.7.1. Concept

Two types of retrieval errors can affect our analysis: systematic errors (bias) and unsystematic ones (random errors). In theory, it is very compelling to understand their differences. In reality, the distinction between random and systematic errors is not as clear-cut as it seems. For example, one may wish to establish the credibility of a satellite retrieval by comparing it to a sky-radiance measurement over time. Because each measurement is made at a different time, their comparison is not a repetition of the same experiment; each time, the atmosphere differs in some aspects, so each comparison is unique. Adding more sky-radiance measurements will add new experiments. For each paired data point, many unique issues contribute differently to errors; as such, our problem is grossly under-determined (i.e., more unknowns for a given observation).

608 Here, we do not attempt to separate random from systematic errors in the subsequent analysis,
609 thereby limiting this study to the total uncertainty.
610   We focus on analyzing the statistical errors drawn from the differences between the
611 benchmark and the retrievals on daily basis. Two sensors are used for this analysis: TROPOMI
612 and OMI. To propagate individual uncertainties in HCHO and NO_2 to FNRs, we follow an
613 analytical approach involving Jacobians of the ratio to HCHO and NO_2. Assuming that errors in
614 HCHO and NO_2 are uncorrelated, the relative error of the ratio can be estimated by:

$$\frac{\sigma}{ratio} = \sqrt{\left(\frac{\sigma_{HCHO}}{HCHO}\right)^2 + \left(\frac{\sigma_{NO_2}}{NO_2}\right)^2} \tag{15}$$

615 where σ_{HCHO} and σ_{NO_2} are total uncertainties of HCHO and NO_2 observations. It is important to
616 recognize that the errors in HCHO and NO_2 are not strictly uncorrelated due to assumptions made
617 in their air mass factor calculations.

3.7.2. Error Distributions in TROPOMI and OMI

619   We begin our analysis with the error distribution of daily TROPOMI tropospheric NO_2
620 columns (v1.02.02) against 22 MAX-DOAS instruments from May to September in 2018-2021.
621 The data are paired based on the criteria defined in Verhoelst et al. (2021). The spatial locations
622 of the stations are mapped in Figure S15. Figure 10a shows the histogram of the TROPOMI minus
623 the MAX-DOAS instruments. The first observation from this distribution is that it is skewed
624 towards lower differences, evident in the skewness parameter around -4.6. As a result of the
625 skewness, the median should better represent the central tendency which is around -1×10^{15}
626 molec./cm^2. In general, TROPOMI tropospheric NO_2 columns show a low bias. We fit a normal
627 distribution to the data using the non-linear Levenberg-Marquardt method. This fitted normal
628 distribution (R^2=0.94) is used to approximate σ_{NO_2} for different confidence intervals, and to
629 minimize blunders. To understand how much of these disagreements are caused by systematic
630 errors as opposed to random errors, we redo the histogram using monthly-based observations
631 (Figure S16). A slight change in the dispersions between the daily and the monthly-basis analysis
632 indicates the significance of unresolved systematic (or relative) biases. This tendency suggests that
633 when conducting the analysis on a monthly basis, the relative bias cannot be mitigated by
634 averaging. Verhoelst et al. (2021) rigorously studied the potential root cause of some discrepancies
635 between MAX-DOAS and TROPOMI. An important source of error stems from the fundamental
636 differences in the vertical sensitivities of MAX-DOAS (more sensitive to the lower tropospheric
637 region) and TROPOMI (more sensitive to the upper tropospheric area). This systematic error can
638 only be mitigated using reliably high-resolution vertical shape factors instead of spatiotemporal
639 averaging of the satellite data.
640   The error analysis for OMI follows the same methods applied for TROPOMI; however,
641 with different benchmarks. We follow the comparisons made between the operational product
642 version 3.1 and measured columns derived from NCAR's NO_2 measurements integrated along
643 aircraft spirals during four NASA's air quality campaigns. More information regarding this data
644 comparison can be found in Choi et al. (2020). Figure 10b shows the histogram of OMI minus the
645 integrated spirals. Compared to TROPOMI, the OMI bias is worse by a factor of two. The standard
646 deviation calculated from a Gaussian fit (2.31×10^{15} molec./cm^2) is not substantially different from
647 that of TROPOMI (2.11×10^{15} molec./cm^2).
648   As for the error distribution of TROPOMI HCHO columns (version 1.1.(5-7)), we use 24
649 FTIR measurements during the same time period based on the criteria specified in Vigouroux et

al. (2020). The stations are mapped in Figure S15. The frequency of the paired data is daily. Figure 11a depicts the error distribution. The distribution is slightly broader compared to that of NO_2, manifested in a larger standard deviation 4.32×10^{15} molec./cm^2. This is primarily due to two facts: i) HCHO optical depths generally peak in the UV range (<380 nm), where the large optical depths of ozone and Rayleigh scattering result in weaker and noisier signals (Gonzalez Abad et al., 2019), and ii) the broader and stronger NO_2 optical depths in the ViS range (400-500 nm), where the signal-to-noise ratio is typically more outstanding, permit better quality retrievals. Similar to the NO_2, we fit a normal distribution (R^2=0.90) to specify σ_{HCHO} for different confidence intervals.

Concerning OMI HCHO columns from SAO version 3 (Gonzalez Abad et al., 2015), we follow the intercomparison approach proposed in Zhu et al. (2020). Based on this approach, the benchmarks come from GEOS-Chem simulated HCHO columns corrected by in-situ aircraft measurements. The measurements were made during ozone seasons from KORUS-AQ, DISCOVERs, FRAPPE, NOMADSS, and SENEX campaigns (see Table 1 in Zhu et al. 2020). OMI values ranging from -0.5×10^{15} molec./cm^2 and 1.0×10^{17} molec./cm^2 with effective cloud fraction between 0.0 and 0.3, and SZA between 0 and 60 degrees are only considered in the comparison. Any pixels from OMI and grid boxes from the corrected GEOS-Chem simulation that fall into a polygon enclosing the campaign domain are used to create the error distribution shown in Figure 11b. The distribution has much denser data because the model output covers a large portion of the satellite swath. The error distribution suggests that OMI HCHO is inferior to TROPOMI evident in larger bias and standard deviation. The OMI bias is twice as large as that of TROPOMI. De Smedt et al. (2021) observed the same level of bias from their comparisons of OMI/TROPOMI with MAX-DOAS instruments (see Table 3 in their paper). Moreover, their OMI vs MAX-DOAS comparisons were severely scattered. Likewise, we observe the standard deviation of OMI from the fitted Gaussian function to be roughly five times as large of that TROPOMI. This can be primarily due to a weaker signal-to-noise (and sensor degradation) in OMI. It is because of this reason that OMI HCHO should be averaged over several months. Another possible reason for the large standard deviation is the fact that the benchmark arises from a modeling experiment whose ability at resolving spatiotemporal variations in HCHO may be uncertain. This partly leads to the performance of OMI to look poor.

3.7.3. The impact of retrieval error on the ratio

Following Eq. (15), we calculate the standard error for a wide range of NO_2 and HCHO columns at a 68% confidence interval (1 sigma) for both TROPOMI and OMI derived from the fitted Gaussian function to the histograms; the standard errors are shown in Figure 12. We observe smaller errors to be associated with larger tropospheric column concentrations. As for TROPOMI, either daily HCHO or tropospheric NO_2 columns should be above $1.2-1.5\times10^{16}$ molec./cm^2 to achieve 20-30% standard error. The TROPOMI errors start diminishing the application of FNR when both measurements are below this threshold. Regarding OMI, it is nearly impossible to get the standard error below of 20-30% given its problematically large HCHO standard deviation. For 50% error, the daily HCHO columns should be above 3.2×10^{16} molec./cm^2. This range of error can also be achieved if OMI tropospheric NO_2 columns are above 8×10^{15} molec./cm^2.

3.8. The fractional errors to the combined error

The ultimate task is to compile the aforementioned errors to gauge how each individual source of error contributes to the overall error. Although each error is different in nature, combined they explain the uncertainties of one quantity (FNR) and can be roughly considered independent; therefore, the combined error is given by:

$$\sigma_{total} = \sqrt{\sigma^2_{Col2PBL} + \sigma^2_{SpatialRep} + \sigma^2_{Retreival}} \tag{16}$$

$\sigma_{Col2PBL}$ is the error in the adjustment-factor defined in this study. We calculated a 26% standard error for a wide range of PBLHs. Therefore, $\sigma_{Col2PBL}$ equals to 19% of the observed ratio (i.e., magnitude dependent). $\sigma_{SpatialRep}$ is more complex. It is a function of the footprint of the satellite (or a model), the spatial variability of the reference field, which varies from environment to environment, and the length scale of our target (e.g., a district, a city, or a state). Eq. (14) explicitly quantifies this error. The product of the square root of that value and the observed ratio defines $\sigma_{SpatialRep}$. The last error depends on the magnitude of HCHO and NO_2 tropospheric columns. It can be estimated from Eq. (15) times the observed ratio. We did not include the chemistry error in Eq. (16) because it was suited only for segregating the chemical conditions; it does not describe the level of uncertainties that comes with the observed columnar ratio. Figure 13 shows the total relative error given the observed TROPOMI ratio seen in Figure 7. We consider the OMI spatial representation error (13% variance loss) for this case that was computed in a city environment. The retrieval errors are based on TROPOMI sigma values. Areas associated with relatively small errors (<50%) are mostly seen in cities due to a stronger signal (smaller $\sigma_{Retreival}$). Places with low vegetation and anthropogenic sources (i.e., Rocky Mountains) possess the largest errors (>100%).

To produce some examples of the fractional errors to the combined error, we focus on two different environments with two different sets of HCHO and NO_2 columns. One represents a heavily polluted area, and the other one is a moderately polluted region. We also include two footprints: OMI (13×24 km^2) and a 108×108 km^2 pixel. Finally, we calculate the percentage of each error component for both OMI and TROPOMI sensors. Figure 14 shows the pie charts describing the percentage of each individual error to the total error for TROPOMI. Unless the footprint of the sensor is coarse enough (e.g., 108 km^2) to give rise to the spatial representation error dominance, the retrieval error stands out. New satellites are not expected to have very large footprints; as such, retrieval errors appear to be the major obstacle to using FNR in a robust manner. Figure 15 shows the same calculation but using OMI errors; the retrieval errors massively surpass other errors. This motivates us to do one more experiment; we recalculate the HCHO error distribution in OMI using monthly-averaged data instead of daily (Figure S17). This experiment suggests a standard deviation of 9.4×10^{15} molec./cm^2, with which we again observe the retrieval error to be the largest contributor (>80%) of the combined error (Figure S18). A recent study (Johnson et al., 2022) also suggests that retrieval errors can result in considerable disagreement between FNRs from various sensors and retrieval frameworks.

4. Summary

The main goal of this study was to characterize the errors associated with the ratio of satellite-based HCHO to NO_2 columns, which has been widely used for ozone sensitivity studies. From the realization of the complexity of the problem, we now know that four major errors should be carefully quantified so that we can reliably represent the underlying ozone regimes. The errors are broken down into i) the chemistry error, ii) the column to the PBL translation, iii) the spatial representation error, and iv) the retrieval error. Each error has its own dynamics and has been tackled differently by leveraging a broad spectrum of tools and data.

The chemistry error refers to the predictive power of the HCHO/NO_2 ratio (hereafter FNR) in describing the HOx-ROx cycle, which can be well explained by the ratio of the chemical loss

737   of HO_2+RO_2 (LROx) to the chemical loss of NOx (LNOx). Because those chemical reactions are
738   not directly observable, we set up a chemical box model constrained with a large suite of in-situ
739   aircraft measurements collected during DISCOVER-AQs and KORUS-AQ campaigns (~ 500 hr
740   of flight). Our box model showed a reasonable performance at recreating some unconstrained key
741   compounds such as OH (R^2=0.64, bias=17%), HO_2 (R^2=0.66, bias<1%), and HCHO (R^2=0.73).
742   Subsequently, we compared the simulated FNRs to LROx/LNOx. They showed a high degree of
743   correspondence (R^2=0.93) but only in the logarithmic scale; this indicated that FNRs do not fully
744   describe the HOx-ROx cycle (i.e., the sensitivity of ozone production rates to NOx and VOC) for
745   heavily polluted environments and pristine ones. Following a robust baseline indicator
746   (ln(LROx/LNOx) = -1.0 ± 0.2) segregating NOx-sensitive from VOC-sensitive regimes, we
747   observed a diverse range of FNR ranging from 1 to 4. These transitioning ratios had a Gaussian
748   distribution with a mean of 1.8 and a standard deviation of 0.4. This implied that the relative
749   standard error associated with the ratio from the chemistry perspective at a 68% confidence interval
750   was 20%. Although this threshold with its error was based on a single model realization and can
751   be different for a different chemical mechanism, it provided a useful universal baseline derived
752   from various chemical and meteorological conditions. At a 68% confidence level, any uncertainty
753   beyond 20% in the ozone regime identification from FNRs likely originates from other sources of
754   error, such as the retrieval error.
755   Results from the box model showed that ozone production rates in extremely polluted
756   regions (VOC-sensitive) were not significantly different from those in pristine ones (NOx-
757   sensitive) due to non-linear chemical feedback mostly imposed by NO_2+OH. Indeed, the largest
758   PO_3 rates (median = 4.6 ppbv/hr) were predominantly seen in VOC-sensitive regimes tending
759   towards the transitional regime. This was primarily caused by the abundance of ozone precursors
760   (i.e., HCHO×NO_2) and the diminished negative chemical feedback. We also revealed that
761   HCHO×NO_2 could be used as a sensible proxy for the ozone precursors' abundance. In theory,
762   this metric, in conjunction with the ratio, provided reasonable estimates of PO_3 rates (RMSE =
763   0.60 ppbv/hr).
764   We then analyzed the afternoon vertical distribution of HCHO, NO_2, and their ratio
765   observed from aircraft during the air quality campaigns binned to the near-surface to 8 km. For
766   altitudes below 5.75 km, HCHO concentration steadily decreased with altitude but at a lower rate
767   than NO_2. Above that altitude, NO_2 concentrations stabilized and slightly increased due to
768   lightning and stratospheric sources. The dissimilarity between the vertical shape of NO_2 versus
769   HCHO resulted in a rather non-linear shape of FNR. This non-linear shape necessitated a
770   mathematical formulation to transform an observed columnar ratio to a ratio at a desired vertical
771   height expanding from the surface. We fit a second-order rational function to the profile and
772   formulated the altitude adjustment factor, which followed a second-order polynomial function
773   starting from values below 1 for lower altitudes, following values above 1 for some high altitudes,
774   and finally converging to 1 at 8 km. This behavior means that the ozone regime tends to get pushed
775   slightly towards the VOC-sensitive regime near the surface for a given tropospheric columnar
776   ratio. This tendency was more pronounced in morning times when the non-linear shape of FNRs
777   was stronger. This data-driven adjustment factor exclusively derived from afternoon aircraft
778   profiles during warm seasons in non-convective conditions had a standard error of 19%.
779   An important error in the satellite-based observations stemmed from unresolved spatial
780   variability in trace gas concentrations within a satellite pixel (Souri et al., 2022; Tang et al., 2021).
781   The amount of unresolved spatial variability (the spatial representation error) can in principle be
782   modeled if we base our reference on a distribution map made from a high spatial resolution dataset.

783 We modeled semivariograms (or spatial auto-correlation) computed for a reference map of FNR
784 observed by TROPOMI at 3×3 km^2 over Los Angeles. Subsequently, we coarsened the map to
785 13×24, 36×36, 108×108, and 216×216 km^2 and modeled their semivariograms. As for 13×24 km^2,
786 which is equivalent to the OMI nadir spatial resolution, around 12% of spatial information
787 (variance) was lost due to its footprint. The larger the footprint, the bigger the spatial representation
788 error. For instance, a grid box with a size of 216×216 km^2 lost 65% of the spatial information in
789 the ratio at a 50 km length scale. Our method is compelling to understand and easy to apply for
790 other products and different atmospheric environments. Based on this approach, we developed an
791 open-source package called SpaTial Representation Error EstimaTor (STREET) (Souri, 2022).
792 We presented estimates of retrieval errors associated with daily TROPOMI and OMI
793 tropospheric NO$_2$ columns by comparing them against a large suite of MAX-DOAS (Verhoelst et
794 al. 2021) and vertically-integrated measurements from aircraft spirals (Choi et al., 2020). Both
795 products were smaller than the benchmark. Furthermore, they show a relatively consistent
796 dispersion at a 68% confidence level ($\sim2\times10^{15}$ molec./cm^2) suggested by fitting a normal function
797 ($R^2>0.9$) to their error distributions. As for daily TROPOMI and OMI HCHO products, we used
798 global FTIR observations (Vigouroux et al., 2020) and data-constrained GEOS-Chem outputs from
799 multiple campaigns (Zhu et al., 2020), respectively. TROPOMI HCHO indeed outperforms OMI
800 HCHO with respect to bias and dispersion on a daily basis. The standard deviation of OMI HCHO
801 was found to be roughly five times as large compared to TROPOMI. While this error can be partly
802 reduced by oversampling over a span of a month or a season, it is critical to recognize that ozone
803 events are episodic; thus, daily observations should be the standard mean for understanding the
804 chemical pathways for the formation of tropospheric ozone. After combining the daily biases from
805 both HCHO and NO$_2$ TROPOMI comparisons, we concluded that either daily HCHO or
806 tropospheric NO$_2$ columns should be above 1.2-1.5×10^{16} molec./cm^2 to achieve 20-30% standard
807 error in the ratio. Due to the large error in daily OMI HCHO, it was nearly impossible to achieve
808 20-30% standard error given the observable range of HCHO and NO$_2$ columns over our planet. To
809 reach 50% error using daily OMI data, HCHO columns should be above 3.2×10^{16} molec./cm^2 or
810 tropospheric NO$_2$ columns should be above 8×10^{15} molec./cm^2.
811 To build intuition in the significance of the errors above, we finally calculated the
812 combined error in the ratio by linearly combining the root sum of the squares of the TROPOMI
813 retrieval errors, the spatial representation error pertaining to OMI nadir footprint over a city-like
814 environment, and the altitude adjustment error for a wide range of observed HCHO and NO$_2$
815 columns over the US. These observations were based on the TROPOMI in the summertime of
816 2021. The total errors were relatively mild (<50%) in cities due to a stronger signal, whereas they
817 easily exceeded 100% in regions with low vegetation and anthropogenic sources (i.e., Rocky
818 Mountains). The retrieval error was the dominant source of the combined error (40-90%).
819 All of these aspects highlight the necessity of improving the trace gas satellite retrieval
820 algorithms in conjunction with sensor calibration, although with the realization that a better
821 retrieval is somewhat limited by the advancements made in other disciplines, such as atmospheric
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862

Data Access
864 The FTIR and MAXDOAS data used in this publication were partly obtained from the Network
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866 NDACC website www.ndacc.org. The spatial representation error is estimated based on publicly
867 available package, SpaTial Representation Error EstimaTor (STREET)
868 (https://github.com/ahsouri/STREET). DISCOVER-AQ and KORUS-AQ aircraft data can be
869 downloaded from https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html and
870 https://www-air.larc.nasa.gov/missions/korus-aq/. TROPOMI NO_2 and HCHO data can be
871 downloaded from https://disc.gsfc.nasa.gov/datasets/S5P_L2__NO2___1/summary and
872 https://disc.gsfc.nasa.gov/datasets/S5P_L2__HCHO___1/summary. The box model results can be
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874

Author contributions

AHS designed the research, analyzed the data, conducted the simulations, made all figures, and wrote the paper. MSJ, SP, XL, and KC helped with conceptualization, fundraising, and analysis. GMW helped with configuring the box model. AF, AW, WB, DRB, AJW, RCC, KM, and CC measured various compounds during the air quality campaigns. JHC orchestrated all these campaigns and contributed to the model interpretation. TV, SC, and GP provided paired MAX-DOAS and TROPOMI tropospheric NO_2 observations. CV and BL provided paired FTIR and TROPOMI HCHO observations. SC and LL provided paired integrated aircraft spirals and OMI tropospheric NO_2 observations. LZ and SS provided the paired observations between the corrected GEOS-Chem HCHO and OMI HCHO columns. All authors contributed to the discussion and edited the paper.

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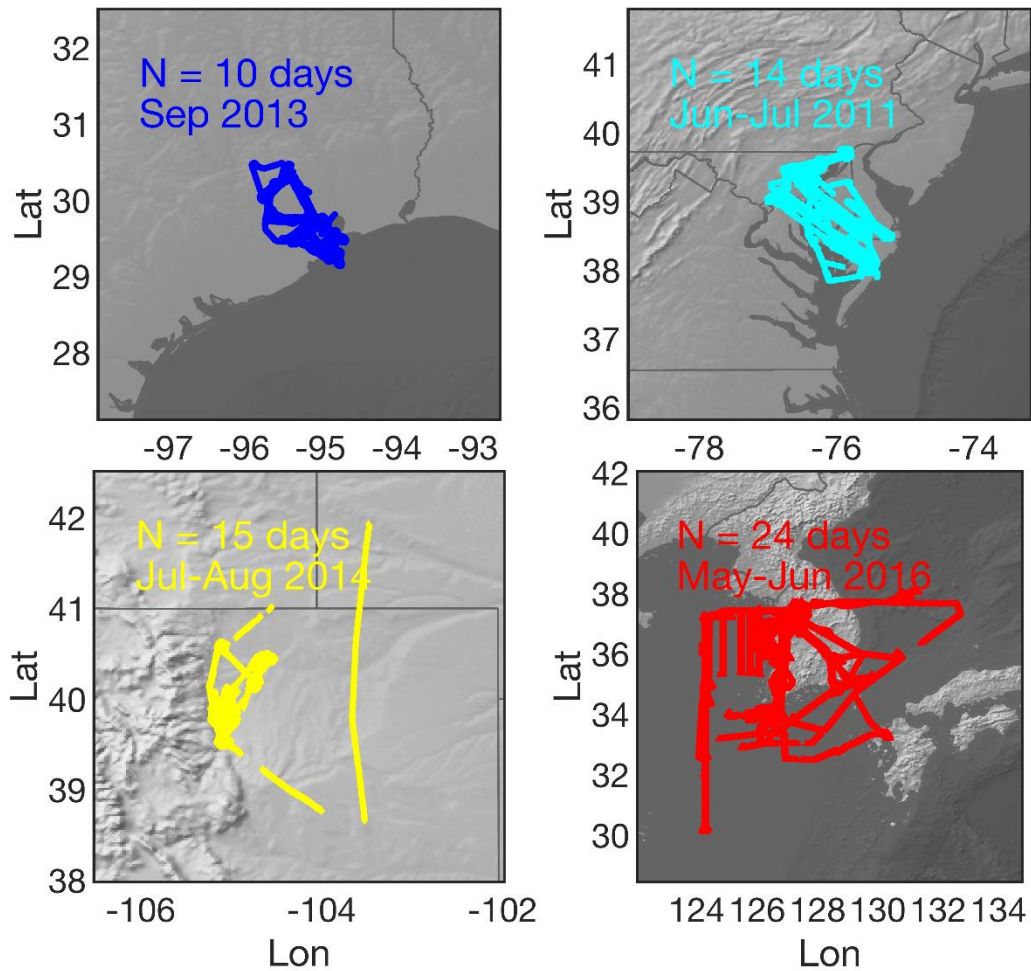
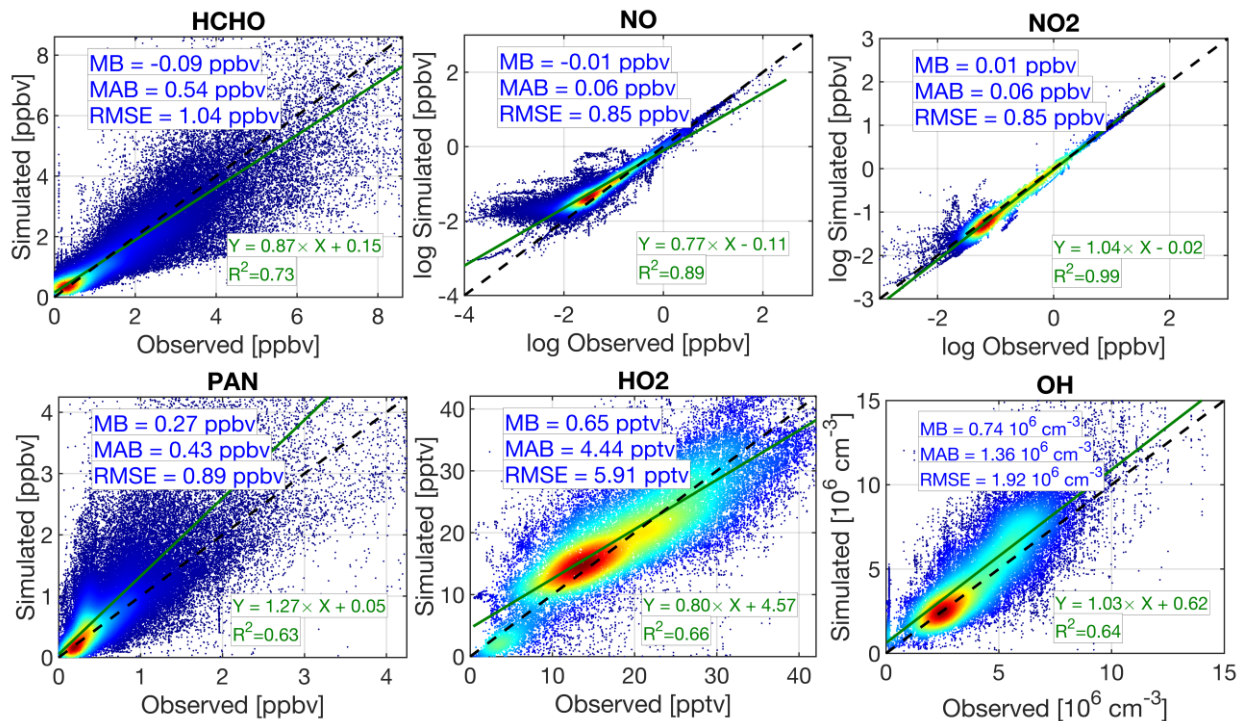
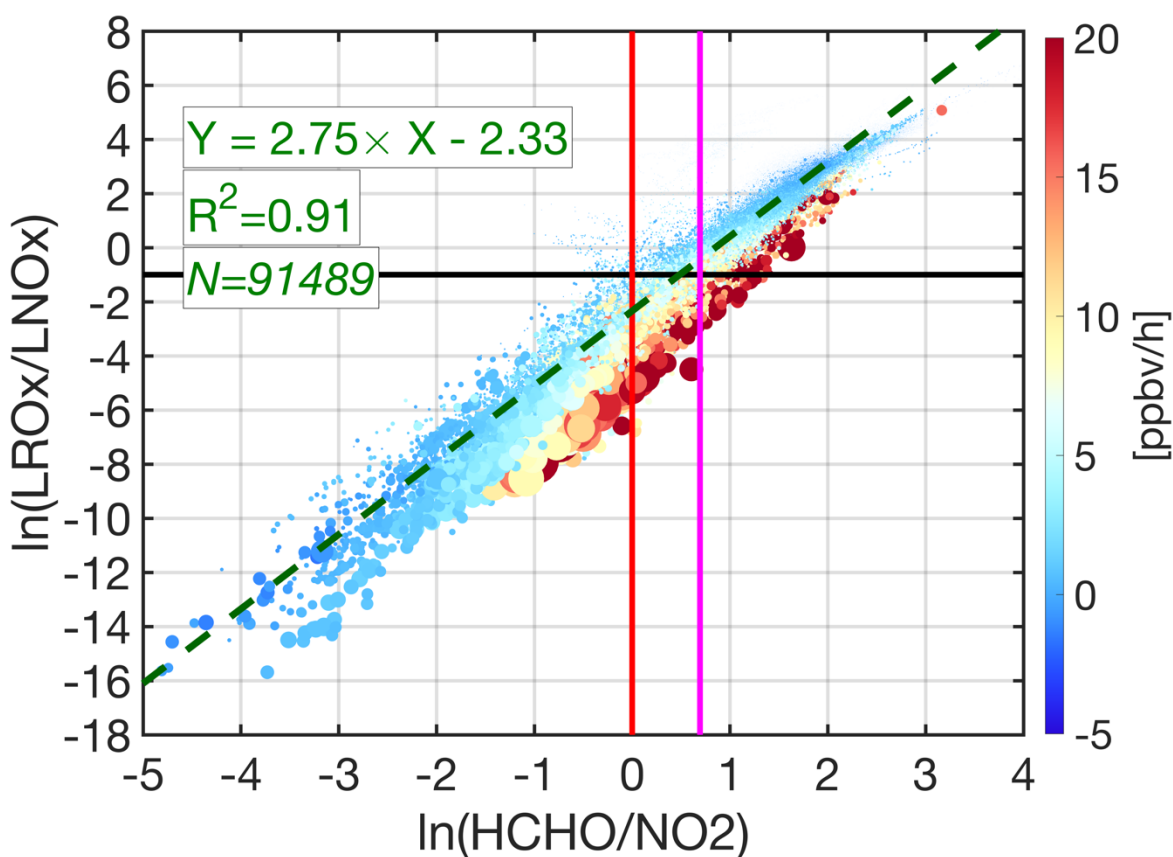
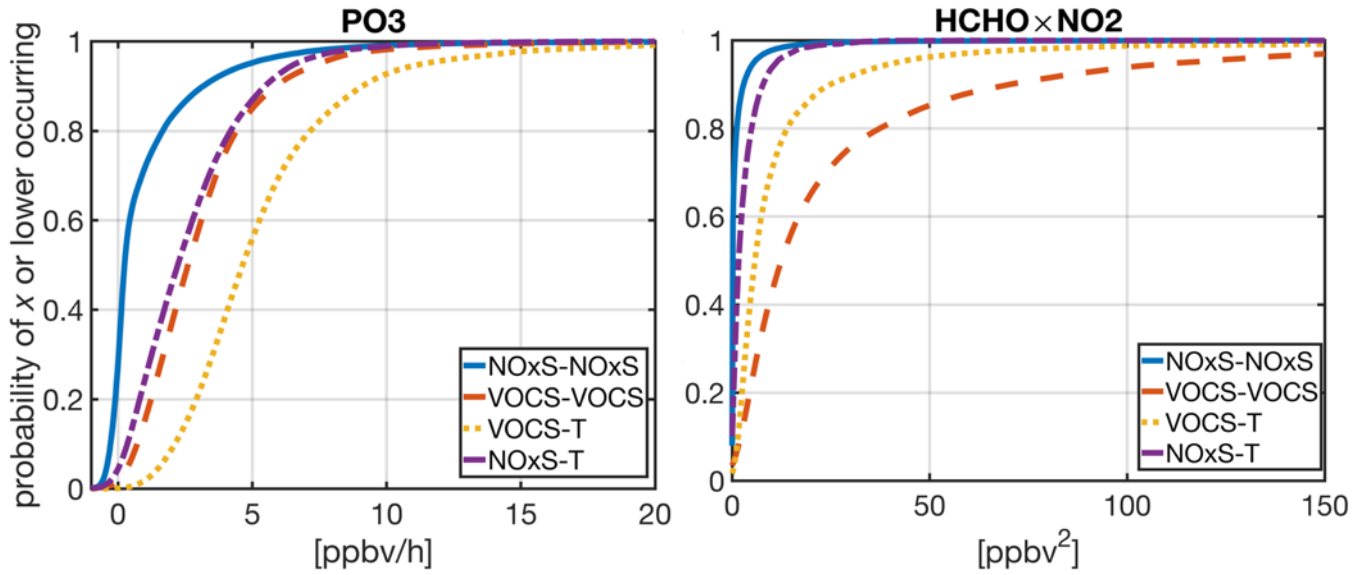
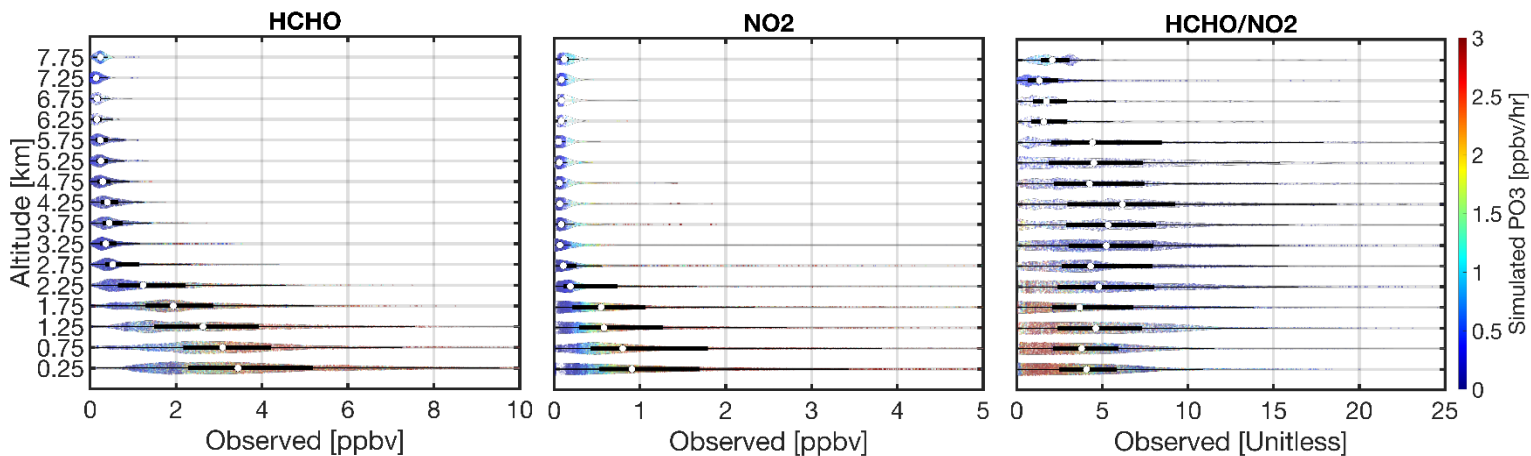
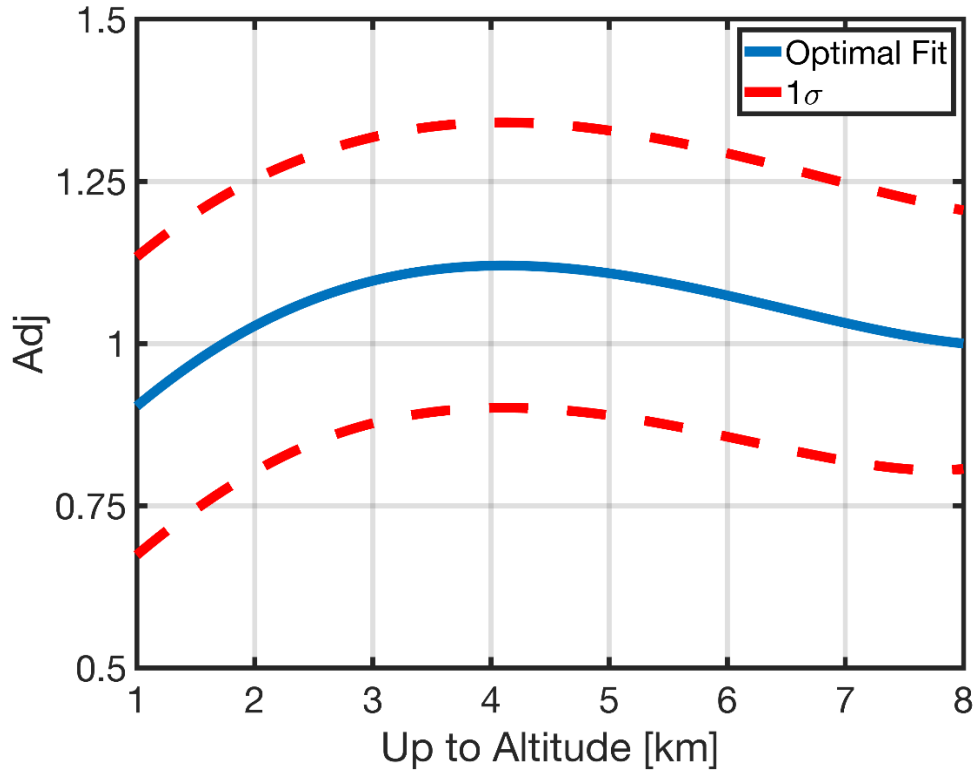
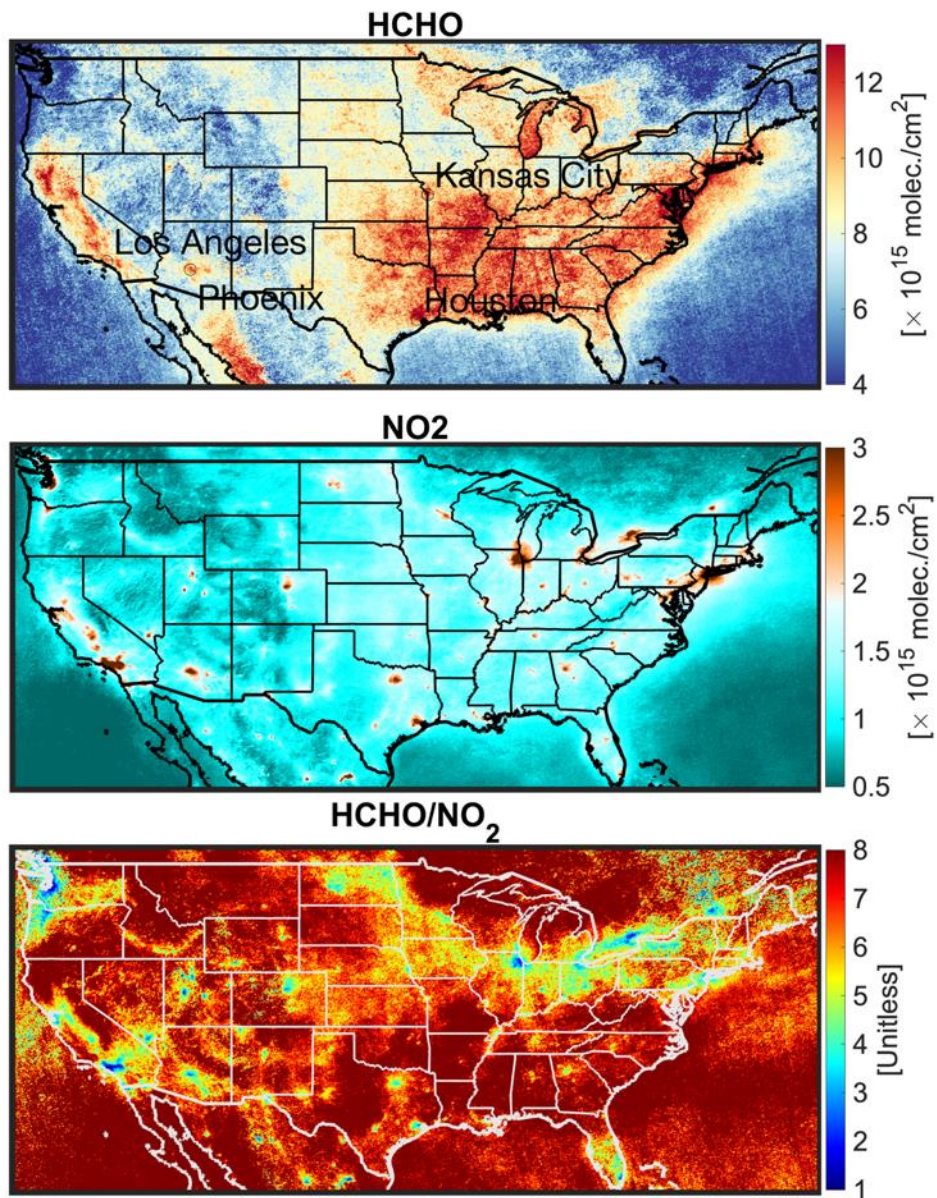
1253   **Table1.** The box model configurations and inputs.

Temporal resolution of samples	10-15 sec
Time steps	1 hour
Number of solar cycles	5
Dilution constant	$1/86400 - 1/43200$ (s^{-1})
Meteorological Inputs	Pressure, Temperature, and Relative Humidity
Photolysis frequencies estimates	LUT based on the NCAR TUV model calculations
Photolysis frequencies constraints (campaign#‡)	Measured jNO_2 (1-4) and jO^1D (4)
Compounds (Instrument#†, campaign#‡) used for constraining the box model	H_2(1, 4)§, CO (4, 1-4), NO_x (2, 1-4), O_3 (2, 1-4), SO_2 (6, 4) , CH_4 (4, 1-4), HNO_3 (10, 1-4), Isoprene (9, 1-4), Monoterpenes (9, 1-4), Acetone (9, 1-4), Ethylene (1, 4), Ethane (1, 4), Methanol (9, 1-4), Propane (1, 4), Benzene (1 or 9, 2-4), Xylene (1 or 9, 1 and 4), Toluene (1 or 9, 1-4), Glyoxal (8, 4), Acetaldehyde (9, 1-4), Methyl vinyl ketone (9, 1-4), Methyl Ethyl Ketone (9, 2-4), Propene (1 or 9, 2 and 4), Acetic acid (9, 2-4), Glycolaldehyde (5, 4), H_2O_2 (5, 4)
Unconstrained compounds (Instrument#†, campaign#‡) used for validation	HO_2 (3, 4), OH (3, 4), NO (2, 1-4), NO_2 (2, 1-4), PAN (10, 1-4), HCHO (7, 1-4)
Chemical Mechanism	CB06

1254
1255   † (1) UC Irvine's Whole Air Sampler (WAS), (2) NCAR 4-Channel Chemiluminescence, (3) Penn
1256   State's Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS), (4) NASA Langley's DACOM
1257   tunable diode laser spectrometer, (5) Caltech's single mass analyzer, (6) Georgia Tech's ionization
1258   mass spectrometer, (7) The University of Colorado at Boulder's the Compact Atmospheric Multi-
1259   species Spectrometer (CAMS), (8) Korean Airborne Cavity Enhances Spectrometer, (9)
1260   University of Innsbruck's PTR-TOF-MS instrument, and (10) University of California, Berkeley's
1261   TD-LIF.

1262
1263   ‡ (1) DISCOVER-Baltimore-Washington, (2) DISCOVER-Texas-Houston, (3) DISCOVER-
1264   Colorado, and (4) KORUS-AQ

1265
1266   § In the absence of measurements, a default value of 550 ppbv is specified.
1267

1268

1269
1270
1271 **Figure 1.** The spatial distributions of aircraft measurements collected during NASA's a)
1272 DISCOVER-AQ Houston-Texas, b) DISCOVER-AQ Baltimore-Washington, c) DISCOVER-AQ
1273 Colorado, and d) KORUS-AQ. The duration of each campaign is based on how long the aircraft
1274 was in the air.
1275

1276
1277
1278 **Figure 2.** The comparisons of the observed concentrations of several critical compounds to those
1279 simulated by our F0AM box model. Each subplot contains mean bias (MB), mean absolute bias
1280 (MAB), and root mean square error (RMSE). The least-squares fit to the paired data, along with
1281 the coefficient of determination (R^2) are also individually shown for each compound. Note that we
1282 do not account for the observations errors in the x-axis. The concentrations of NO and NO_2 are
1283 log-transformed.

1284
1285
1286 **Figure 3.** The scatterplot of natural logarithm-transformed of $HCHO/NO_2$ versus $LROx/LNOx$
1287 based on the simulated values performed by the F0AM box model. The heat color indicates the
1288 calculated ozone production rates (PO_3). The size of each data point is proportional to
1289 $HCHO \times NO_2$. The black line is the baseline separator of NOx-sensitive (above the line) and VOC-
1290 sensitive (below the line) regimes. We overlay $HCHO/NO_2=1$ and $HCHO/NO_2=2$ as red and
1291 purple lines, respectively. The dashed dark green line indicates the least-squares fit to the paired
1292 data. The $HCHO/NO_2 = 1.8$ with a 20% error is the optimal transitioning point based on this result.
1293

129
Figure 4. Cumulative distribution functions of PO$_3$ and HCHO×NO$_2$ simulated by the box model constrained by NASA's aircraft observations. Four regions are shown: NOx-sensitive — NOx-sensitive, NOx-sensitive—transitional, VOC-sensitive—transitional, and VOC-sensitive—VOC-sensitive. The first name of the regime is based on the baseline (ln(LROx/LNOx)=-1.0), whereas the second one follows those defined in Duncan et al. (2010): VOC-sensitive if HCHO/NO$_2$<1, transitional if 1<HCHO/NO$_2$<2, and NO$_x$-sensitive if HCHO/NO$_2$>2.

1303 **Figure 5.** The violin plots of the afternoon vertical distribution of HCHO, NO$_2$, and HCHO/NO$_2$
1304 observations collected during DISCOVER-AQ Texas, Colorado, Maryland, and KORUS-AQ campaigns.
1305 The violin plots demonstrate the distribution of data (i.e., a wider width means a higher frequency). White
1306 dots show the median. A solid black line shows both the 25th and 75th percentiles. The heatmap denotes
1307 the simulated ozone production rates.
1308

1309
1310
1311 **Figure 6.** The adjustment factor is the ratio of the centroid of the polygon bounding 25th and 75th
1312 percentiles of the observed HCHO/NO$_2$ columns by NASA's aircraft between the surface to 8 km
1313 to the ones between the surface and the desired altitude. This factor can be easily applied to the
1314 observed HCHO/NO$_2$ columns to translate the value to the desired altitude stretching down to the
1315 surface (i.e., PBLH). The optimal curve follows a quadratic function formulated in Eq.11.
1316

1317
Figure 7. Oversampled TROPOMI total HCHO columns (top), tropospheric NO$_2$ columns (middle), and the ratio (bottom) at 3×3 km^2 from June till August 2021 over the US. The ratio map is derived from the averaged maps shown in the top and middle panels.

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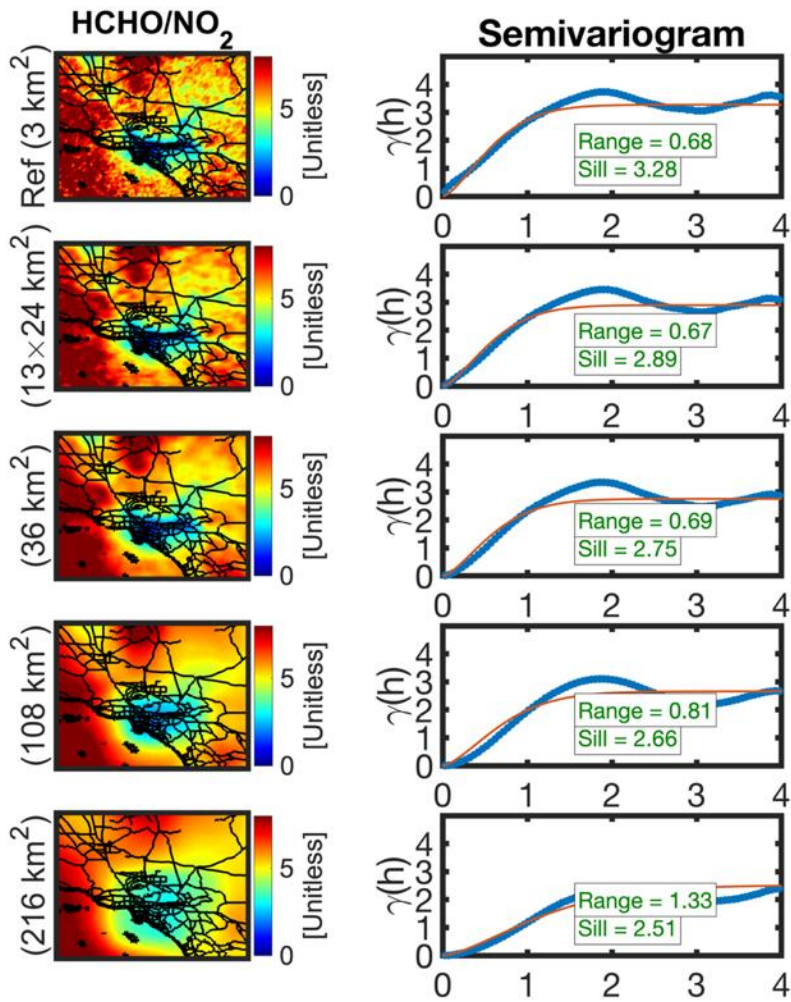
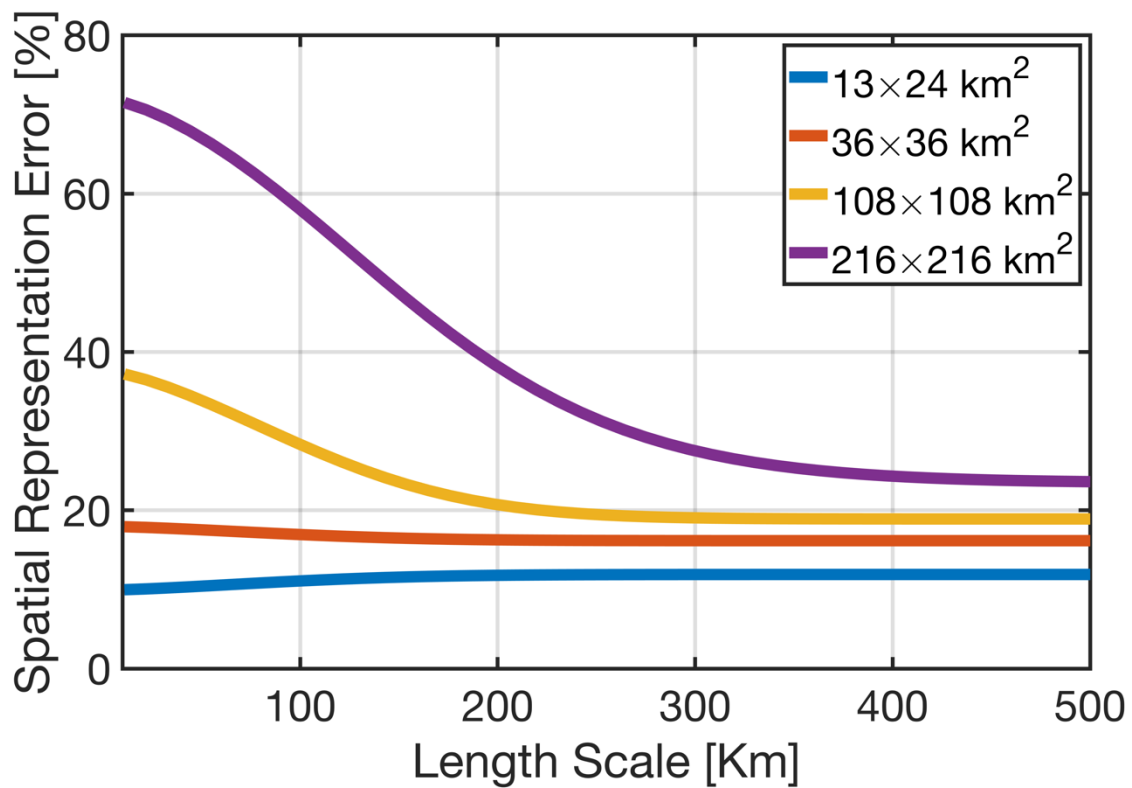
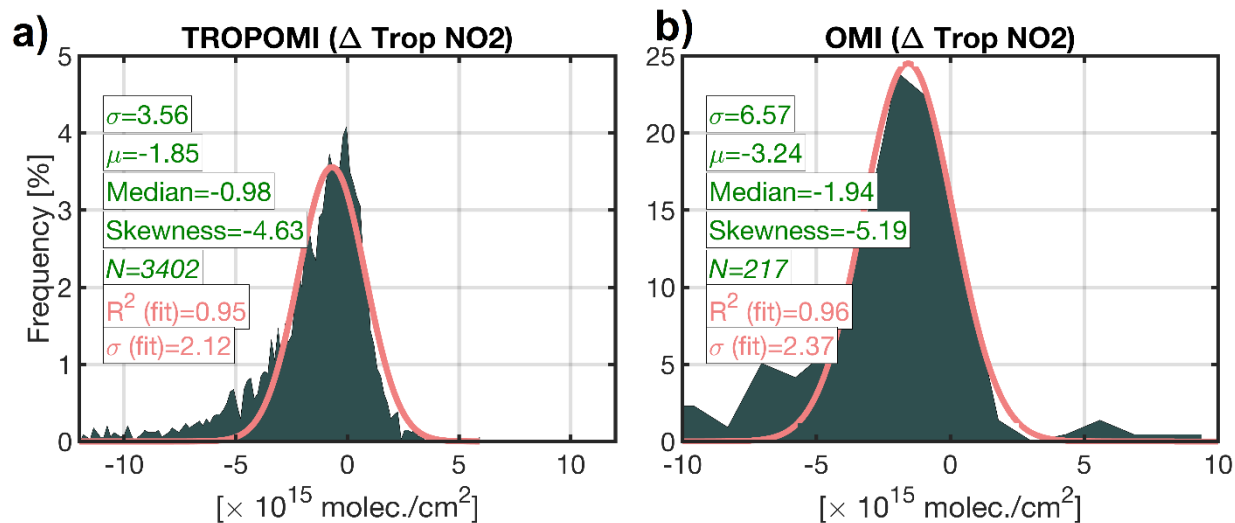
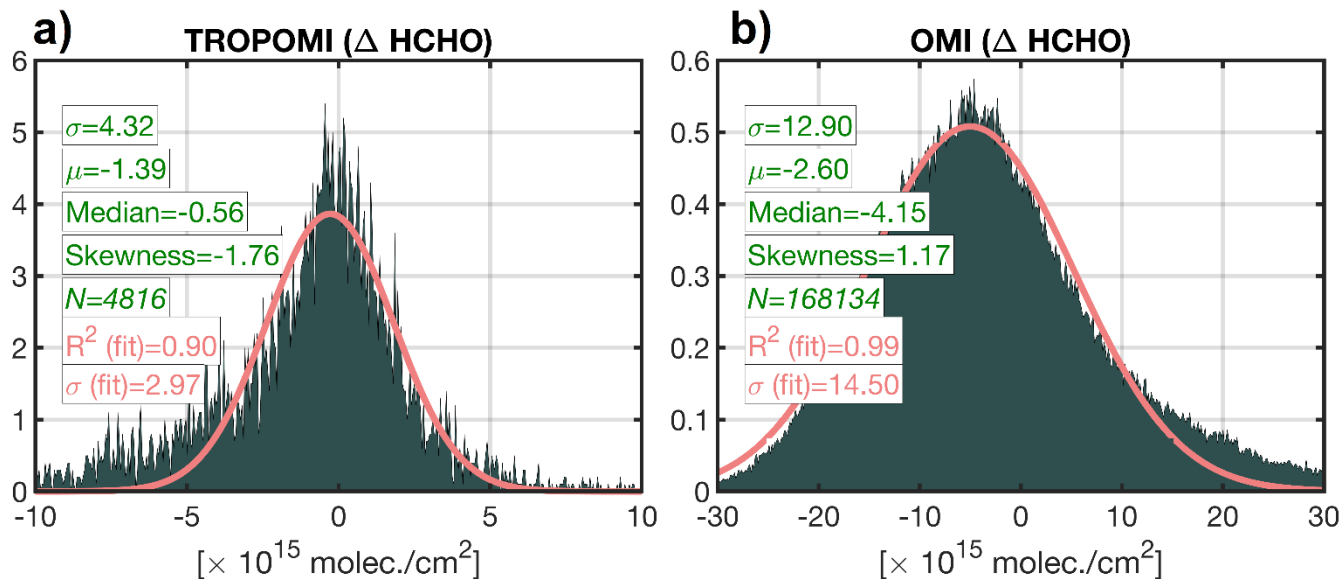
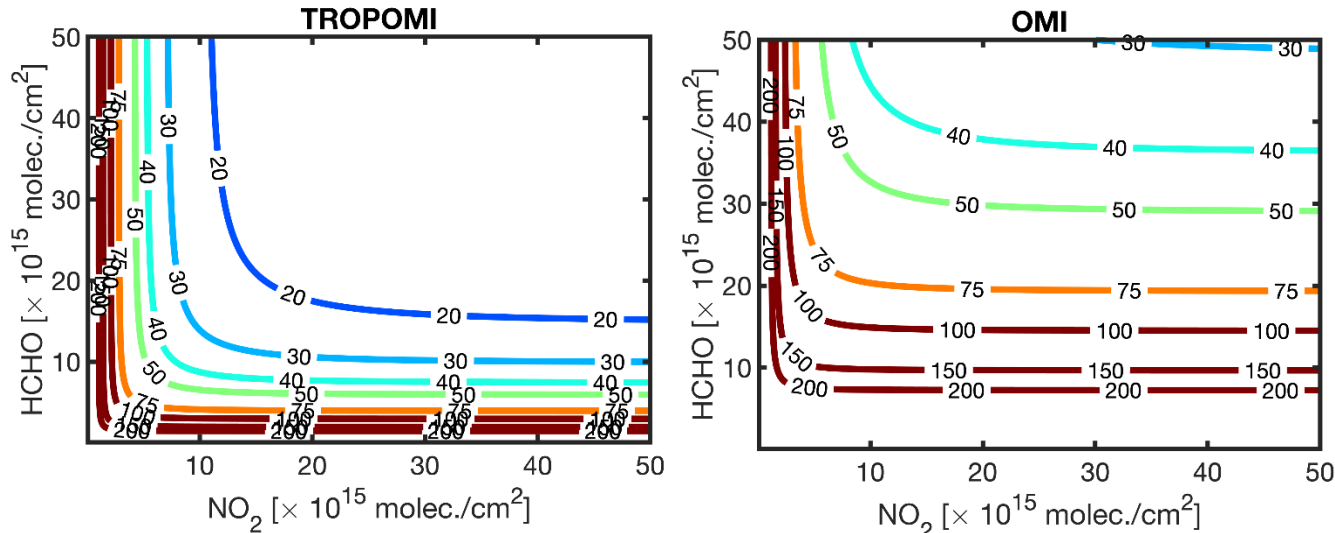
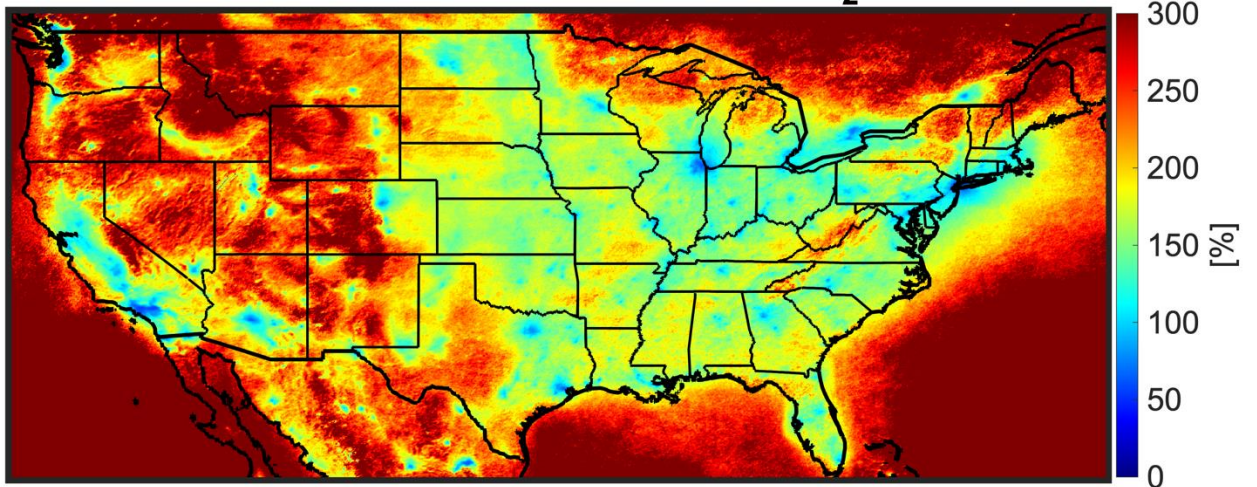
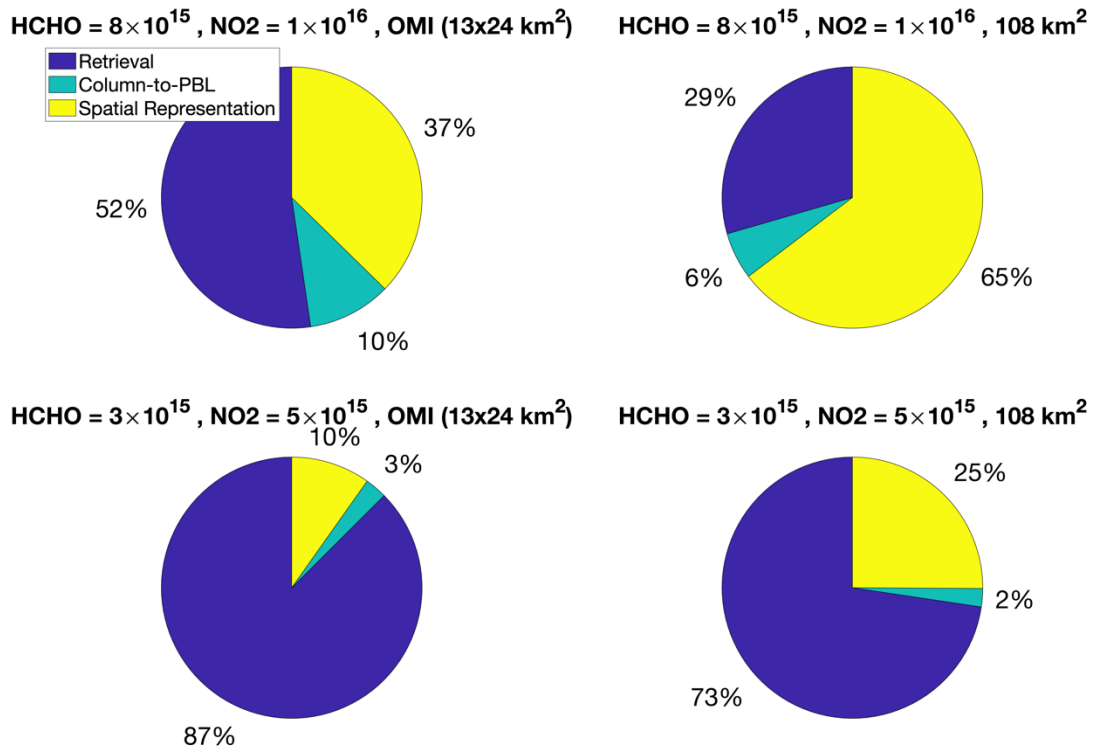
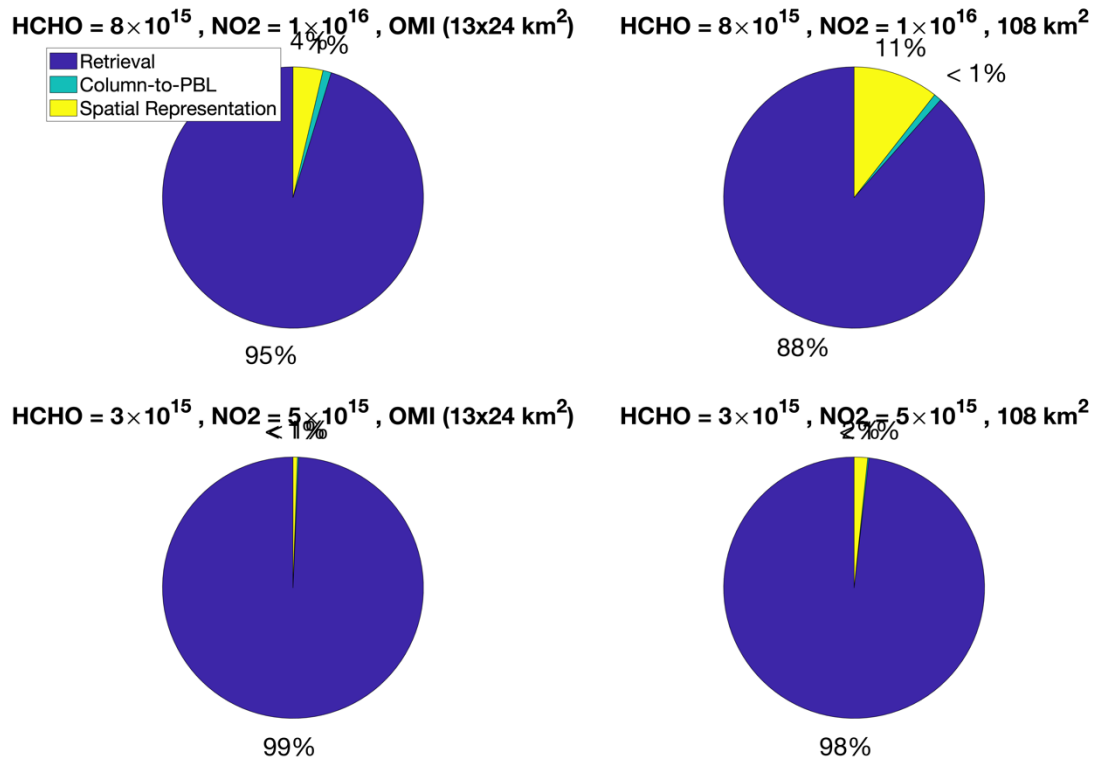

1322
Figure 8. The first column represents the spatial map of HCHO/NO$_2$ ratios over Los Angeles from June till August 2021 at different spatial resolutions. To upscale each map to a coarser footprint, we use an ideal box filter tailored to the target resolution. The second column shows the semivariograms corresponding to the left map along with the fitted curve (red line). The sill and the range are computed based on the fitted curve. The x-axis in the semivariogram is in degrees (1 degree ~ 110 km).

1330
1331 **Figure 9.** The spatial representation errors quantified based on the proposed method in this study.
1332 The error explains the spatial loss (or variance) due to the footprint of a hypothetical sensor at
1333 different length scales. To put this error in perspective, a grid box with 216×216 km^2 will naturally
1334 lose 65% of the spatial variance existing in the ratio at the scale of Los Angeles, which is roughly
1335 50 km wide. All of these numbers are in reference to the TROPOMI 3×3 km^2.
1336

1337
1338 **Figure 10.** The histogram of the differences between TROPOMI and OMI and benchmarks. MAX-
1339 DOAS and integrated aircraft spirals are the TROPOMI and the OMI benchmarks, respectively.
1340 The data curation and relevant criteria on how they have been paired can be found in Verholest et
1341 al. (2021) and Choi et al. (2020). The statistics in green are based on all data, whereas those in
1342 pink are based on the fitted Gaussian function.
1343

1345 **Figure 11.** The histogram of the differences between TROPOMI and OMI and benchmarks. FTIR
1346 and corrected GEOS-Chem simulations are the TROPOMI and the OMI benchmarks. The data
1347 curation and relevant criteria on how they have been paired can be found in Vigouroux et al. (2021)
1348 and Zhu et al. (2020). The statistics in green color are based on all data, whereas those in pink are
1349 based on the fitted Gaussian function.
1350
1351

1352
1353   **Figure 12.** The contour plots of the relative errors in TROPOMI (left) and OMI (right) based on
1354   dispersions derived from Figures 10 and 11. The errors used for these estimates are based on daily
1355   observations.
1356

Total Relative Error in HCHO/NO$_2$

1357
1358 **Figure 13.** The total relative error for observed TROPOMI HCHO/NO$_2$ ratios considering the
1359 daily TROPOMI retrieval errors (σ_{NO_2}= 2.11×10^{15} molec./cm^2 and σ_{HCHO}= 2.97×10^{15}
1360 molec./cm^2), the spatial representation pertaining to OMI footprint over a city environment (13%
1361 loss in the spatial variance), and the column to the PBL translation parameterization (19%)
1362 proposed in this study. Please note that the observed FNR is based on mean values from June to
1363 August 2021, while the uncertainties used for error calculation are on a daily-basis.
1364
1365

1366
1367 **Figure 14.** The fractional errors of retrieval (blue), column to PBL translation (green), and spatial
1368 representation (yellow) of the total error budget for different concentrations and footprints based
1369 on TROPOMI sigma values. The retrieval error used for the error budget is on a daily basis.

1370
1371   **Figure 15.** Same as Figure 14 but based on OMI sigma values.
1372