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Revisiting the Effectiveness of HCHO/NO₂ Ratios for Inferring Ozone Sensitivity to Its Precursors using High Resolution Airborne Remote Sensing Observations in a High Ozone Episode during the KORUS-AQ Campaign

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Abstract. The nonlinear chemical processes involved in ozone production ($P(O_3)$) have necessitated using proxy indicators to convey information about the primary dependence of $P(O_3)$ on volatile organic compounds (VOCs) or nitrogen oxides (NO_x). In particular, the ratio of remotely sensed columns of formaldehyde (HCHO) to nitrogen dioxide (NO_2) has been widely used for studying O_3 sensitivity. Previous studies found that the errors in retrievals and the incoherent relationship between the column and the near-surface concentrations are a barrier in applying the ratio in a robust way. In addition to these obstacles, we provide calculational-observational evidence, using an ensemble of 0-D photochemical box models constrained by DC-8 aircraft measurements on an ozone event during the Korea-United States Air Quality (KORUS-AQ) campaign over Seoul, to demonstrate the chemical feedback of NO_2 on the formation of HCHO is a controlling factor for the transition line between NO_x -sensitive and NO_x -saturated regimes. A fixed value (~ 2.7) of the ratio of the chemical loss of NO_x (LNO_x) to the chemical loss of HO_2+RO_2 (LRO_x) perceptibly differentiates the regimes. Following this value, data points with a ratio of HCHO/ NO_2 less than 1 can be safely classified as NO_x -saturated regime, whereas points with ratios between 1 and 4 fall into one or the other regime. We attribute this mainly to the HCHO- NO_2 chemical relationship causing the transition line to occur at larger (smaller) HCHO/ NO_2 ratios in VOC-rich (VOC-poor) environments. We then redefine the transition line to $LNO_x/LRO_x \sim 2.7$ that accounts for the HCHO- NO_2 chemical relationship leading to $HCHO = 3.7 \times (NO_2 - 1.14 \times 10^{16} \text{ molec.cm}^{-2})$. Although the revised formula is locally calibrated (i.e., requires for readjustment for other regions), its mathematical format removes the need for having a wide range of thresholds used in HCHO/ NO_2 ratios that is a result of the chemical feedback. Therefore, to be able to properly take the chemical feedback into consideration, the use of $HCHO = a \times (NO_2 - b)$ formula should be preferred to the ratio in future works. We then use the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) airborne instrument to study O_3 sensitivity in Seoul. The unprecedented spatial ($250 \times 250 \text{ m}^2$) and temporal (\sim every two hours) resolutions of HCHO and NO_2 observations from the sensor enhance our understanding of $P(O_3)$ in Seoul; rather than providing a crude label for the entire city, more in-depth variabilities in chemical regimes are observed that should be able to inform mitigation strategies correspondingly.

Keywords: ozone sensitivity, remote sensing, formaldehyde, NO_2 , emissions, modeling

Introduction

The study of ozone concentrations in the troposphere is complicated by a number of factors including the nonlinearity of the net ozone production ($P(O_3)$) to its precursor sources, primarily from nitrogen oxides (NO_x) and volatile organic compound (VOC) emissions

[Sillman, 1999]. To precisely determine this complex chemical relationship, we either need to i) measure NO_x , VOC, and their chemical reactivity or ii) set up a well-established chemical transport model that can fairly reproduce the relevant species abundance. The former alternative is limited to spatially-sparse observations collected from campaigns and the latter is too optimistic given the underlying errors associated with model inputs and mechanisms [e.g., Choi and Souri, 2015a]. In absence of these models and observations, chemical proxies can be used to provide some insights into the ozone- NO_x -VOC relationship. Sillman [2002] validated the robustness of several proxy indicators and found $\text{H}_2\text{O}_2/\text{HNO}_3$ to be a solid way to diagnose O_3 sensitivity. This ratio is strongly proportional to the chemical loss of HO_2+RO_2 (LRO_x) over the chemical loss of NO_x (LNO_x) which was revisited later in Schroeder et al. [2017] who found it to be a reliable metric to locate the ridgelines in $\text{P}(\text{O}_3)$ isopleths. Unfortunately, the satellite-based measurements of these two compounds are limited to scarce limb soundings with limited sensitivity to the boundary layer [Mencaraglia et al., 2006; Rinsland et al., 2007].

The absorption lines of several molecules in UV-Visible spectral range allow the retrieval of HCHO [e.g., Chance et al., 1991, 1997, 2000; González Abad et al., 2015; De Smedt et al., 2015], and NO_2 [e.g., Martin et al., 2002; Boersma et al., 2002; Marchenko et al., 2015] from space [González Abad et al., 2019]. The availability of these observations with high spatial coverage has motivated scholars to leverage HCHO and NO_2 concentrations as proxies for VOC reactivity and NO_x , respectively [Tonnensen, and Dennis, 2000]. Using a synergy of model simulations and the Global Ozone Monitoring Experiment (GOME) HCHO/ NO_2 observations, Martin et al. [2004] made an early attempt showing that surface ozone production is more sensitive to NO_x than VOCs during the summers in Northern Hemisphere. Duncan et al. [2010] combined models and Ozone Monitoring Instrument (OMI) data to show certain ranges of HCHO/ NO_2 ratios that can be useful for classifying a region into NO_x -sensitive (i.e. NO_x -limited) or NO_x -saturated (i.e. VOC-limited) regimes. Following these results, the ratio has been widely used for studying weekly variations in HCHO/ NO_2 ratios over the U.S. [Choi et al., 2012], its long term trends in Iran [Choi and Souri, 2015b], Texas [Choi and Souri, 2015a], East Asia [Jin and Holloway, 2015; Souri et al., 2017], Colorado [Schroeder et al., 2017; Jeon et al., 2018], and on a global scale [Jin et al., 2017]. A study of the relative changes of the magnitude of the ratio in time and space is relevant; but the challenge is to whether we can quantitatively rely on the absolute values to complementarily inform emission regulations. A number of studies observed that differing HCHO/ NO_2 thresholds differentiate the transition in the chemical regimes [e.g., Schroeder et al., 2017; Jin et al., 2017]. They

suggested that the fuzziness in the thresholds arises mainly from the uncertainties associated with the retrievals, and the variable relationship between the column and the near-surface concentrations. While those sources of errors unquestionably limit the applications of column HCHO/NO₂, we hypothesize that inherent dependence of HCHO production on NO_x levels [Wolfe et al., 2016] can systematically result in varying HCHO/NO₂ thresholds, regardless. To investigate this hypothesis, we will focus on a chemically complex city in East Asia, Seoul, during the Korean-United States Air Quality (KORUS-AQ) campaign period. We will simulate an ensemble of 0-D box models constrained by aircraft observations, and validate the hypothesis to be able to reformulate the transition line to reflect the chemical conditions more realistically.

The advantage of focusing on the KORUS-AQ campaign period is the availability of a large suite of observations including those from airborne remote sensing [Nowlan et al., 2016; Nowlan et al., 2018; Souri et al., 2018], and in situ aircraft DC-8 observations. Particularly, we will use NO₂ and HCHO observations from the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) sensor. Because of relatively small footprint, several overpasses in a course of a day, solid sensor calibration, and the use of a very detailed surface bidirectional reflectance distribution function (BRDF), these airborne remote sensing measurements can be partly regarded as a proxy for the upcoming first geostationary satellite for monitoring air pollution in the U.S. by the Tropospheric Emissions: Monitoring Pollution (TEMPO) instrument [Chance et al., 2019; Zoogman et al., 2017], in East Asia by Geostationary Environment Monitoring Spectrometer (GEMS, Kim et al., 2019), and in Europe by the Sentinel-4 mission [Ingmann et al., 2012]. Using the airborne observations will allow us to understand to what extent we can classify the chemical conditions regimes by taking into account the reformulated transition line.

GeoTASO

Hyperspectral airborne images in the ultraviolet-visible spectrophotometry range 290 nm to 695 nm were captured by two 2-D CCD detector arrays using the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) instrument [Leitch et al., 2014]. The sensor was mounted on-board NASA's B200 aircraft flying at ~9 km altitude above sea level. A more detailed description of the engineering configuration for this sensor can be found in Nowlan et al. [2016]. Similar to other remotely sensed instruments, the size of the footprint is a function of sensor geometry, aperture, aircraft speed, altitude, and targeted signal-to-noise ratios. The synergy of all this factors resulted in a 250×250 m² spatial resolution which is ~300 times as fine as that of the Tropospheric Monitoring Instrument (TROPOMI) nadir pixels. A major

improvement in the sensor design compared to its former campaigns was a mirror replacement. This change led to mitigating stray light in the UV range, allowing for achieving a more robust retrieval.

The HCHO retrieval algorithm follows a conventional 2-step procedure: i) HCHO slant column is retrieved via direct non-linear least-squares fitting of a GeoTASO radiance spectrum (328.5 nm- 356.5 nm) taking into consideration wavelength registration, slit function calibration, under-sampling, closure polynomials that represent low frequency effects of aerosols and molecular scattering, interference molecules (e.g., O₃ and NO₂), and rotational Raman scattering [Chance et al., 2000; Nowlan et al., 2016; 2018], ii) HCHO vertical column is obtained by applying an air mass factor (AMFs) to each observation quantifying the light path through a simulated atmosphere using VLIDORT [Nowlan et al., 2016; 2018]. The first step requires a reference spectrum as a function of cross-track position, which is determined from spectra collected over a relatively clean region in the Taebaek Mountains on 25 May. The earthshine reference is preferred to a solar one because it permits more efficient removal of cross-track striping and biases [Nowlan et al., 2016; 2018]. The details of the retrieval and possible source of uncertainty for this product can be found in Nowlan et al. [2016]. The projected fitting uncertainty on the vertical column is found on average to be 3.53×10^{15} molec.cm⁻² in our case study.

The NO₂ retrieval follows the similar procedure done for HCHO, but with a different fitting window (425-460 nm) using the Differential Optical Absorption Spectroscopy (DOAS) technique. NO₂ vertical column density (VCD) data below the aircraft using the algorithm discussed in detail in Lamsal et al. [2017], with additional improvement for identification of a relatively pollution free reference location for the spectral fitting process by analyzing Pandora NO₂ observations at Songchon on 20 May, and proper accounting of NO₂ amount over the reference location. To convert the differential slant column densities (dSCDs) from the DOAS fit to VCDs, AMFs are calculated using the on-line radiative transfer calculation from VLIDORT. Inputs to the AMF calculation include the solar and observation geometry, high-resolution (1 km) Moderate Resolution Imaging Spectroradiometer (MODIS) BRDF [Schaaf et al., 2011] to provide an intrinsic characterization of surface anisotropy, and diurnally-varying NO₂ vertical profiles from a regional model constrained by OMI-derived NO_x emissions [Goldberg et al., 2019]. The latter two are spatially interpolated to the GeoTASO footprint. Other details on the retrievals and their uncertainties can be found in Lamsal et al. [2017]. For both data we consider only cloud-free pixels using cloud flags provided in the data.

An Ensemble of Photochemical Box Models

In order to calculate the chemical reaction rates of several species, we use the Framework for 0-D Atmospheric Modeling (F0AM) v3.1 [Wolfe et al., 2016]. The chemical mechanism deployed for the calculation is based on CB6r2 [Hildebrandt Ruiz and Yarwood, 2013] which includes more than 77 species and 216 chemical reactions. We use observations available on the DC8 platform for constraining the model by holding their values constant throughout model step. This includes the required meteorological variables, photolysis frequencies, and concentrations of various compounds. The averaging time for the observations is 10 s. Table 1 lists inputs and configurations used for the model. Since the target of this study focuses on the well-mixed boundary layer, we only incorporate those observations that are within this layer based on the study of Sullivan et al. [2019]. Therefore, we limit our study to afternoon only times, as the aircraft did not fly low enough during the morning. In about 15% of cases, we observe missing values in some compounds (VOC-specified gases sampling have different temporal resolutions). Accordingly, we fill the missing values using linear interpolation. For each sample, we assume that rapidly cycling species are in a diel steady state indicating that the loss and production of most of the reactive species are in balance. To be able to fulfill our assumption, we run the box model for five solar cycles consecutively. It is worth mentioning that the steady state assumption may not be valid if the air parcel is in the proximity of high emitters [Thornton et al., 2002]. The model integration time for each solar cycle is set to 30 min. To prevent the long-lived species from accumulating over time (due to the lack of transport and deposition components in the box model), we use a dilution constant equal to a 24-h lifetime.

To account for measurement random noises, we perform the simulation in a stochastic framework. Accordingly, in this study, the framework of the box modeling is based on an ensemble model ($R_i : i = 1, 2, \dots, k$) with 50 members ($k=50$) generated by applying randomness to the chemical compounds used for constraining the model. We focus on only perturbing the gas concentrations to generate the ensemble models. The randomness coefficients applied to each compound are drawn from a lognormal distribution with a mean of 1, and a variance equal to the measurement precision listed in Table 1.

One can calculate the mean (\bar{R}) and covariance (P) of the reaction rates from an ensemble of the box models:

$$\bar{R} = \frac{1}{k} \sum_{i=1}^k R_i \quad (1)$$

$$\mathbf{P} = \frac{1}{k-1} \sum_{i=1}^k (\mathbf{R}_i - \bar{\mathbf{R}})(\mathbf{R}_i - \bar{\mathbf{R}})^T \quad (2)$$

$$= \frac{1}{k-1} \mathbf{R} \mathbf{R}^T, \text{ where } \mathbf{R} \text{ is the vector of } \mathbf{R}_i - \bar{\mathbf{R}} \text{ (i.e., perturbations)}$$

Therefore, we are able to estimate a distribution for a number of variables including net ozone production ($P(O_3)$), LRO_x , LNO_x , and VOC reactivity (VOCR) rates. We calculate $P(O_3)$ by subtracting ozone loss mainly controlled by HO_x ($HO+HO_2$), the formation of HNO_3 , and O_3 photolysis followed by the reaction of $O(^1D)$ with water vapor from ozone formation (through removal of NO via HO_2 and RO_2) [Kleinman, 2005]:

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

VOCR is calculated as the sum of the product of the rate constants of $VOC+OH$ reactions ($k_{i,OH}$) and VOC concentration:

$$VOCR = \sum_i k_{i,OH+VOC_i}[VOC_i] \quad (4)$$

LRO_x is defined through the sum of primarily radical-radical reactions:

$$\begin{aligned} LRO_x = & k_{HO_2+HO_2}[HO_2]^2 + \sum k_{RO_{2i}+HO_2}[RO_{2i}][HO_2] \\ & + \sum k_{RO_{2i}+RO_{2i}}[RO_{2i}]^2 \end{aligned} \quad (5)$$

LNO_x mainly occurs via the NO_2+OH reaction:

$$LNO_x = k_{OH+NO_2+M}[OH][NO_2][M] \quad (6)$$

Figure 1 demonstrates important interactions involved in the formation of tropospheric ozone. Per one RO_x cycle (in the center of diagram), two molecules of ozone are generated. The availability of NO_2 and VOC concentrations dictates the controlling factor for driving the cycle. Assuming $NO_x \gg VOC$ leads to the removal of OH and NO_2 from the system (LNO_x) making $P(O_3)$ a function of VOC (NO_x -saturated). On the other hand, an environment with a $NO_x \ll VOC$ undergoes a change by which it loses HO_2 and RO_2 (LRO_x) molecules rendering $P(O_3)$ dependent on NO_x concentrations (NO_x -sensitive). Hence, the ratio of LNO_x to LRO_x offers a way to separate these two chemical condition regimes.

WRF-CMAQ

We simulate the atmospheric composition in East Asia using the CMAQ model [Byun and Schere, 2006] at 27 km spatial resolution with 328×323 grid size. We choose the CB05

gas-phase mechanism and the six-generation aerosol mechanism (AERO6). The location of this domain is shown in Figure 2. We process anthropogenic emissions for the CMAQ domain from the MIX emissions inventory 2010 [Li et al., 2015], which contains gridded ($0.25^\circ \times 0.25^\circ$) monthly emissions for black carbon, carbon monoxide (CO), carbon dioxide (CO₂), NO_x, ammonia (NH₃), organic carbon (OC), fine and coarse particulate matter (PM_{2.5} and PM₁₀), sulfur dioxide (SO₂), and NMVOC in the CB05 mechanism. A diurnal factor adopted from the EPA NEI2011 emissions is applied for the mobile sector. The FINN v1.6 emissions [Wiedinmyer et al., 2011] are extended to include biomass burning emissions with consideration of a plume height assumption commonly used in the GEOS-Chem model. For biogenic emissions, we use a standalone MEGAN (v2.1) [Guenther et al., 2006] model (offline), which incorporates a dynamic leaf area index from MODIS, a comprehensive climatology of plant functional maps (PFT) [Ke et al., 2012], and meteorological fields from the following weather model. In order to simulate the mesoscale meteorology, we use the Weather Research and Forecasting model (WRF) v3.9.1 [Skamarock et al., 2008]. The domain's grid is 342 steps west-east, 337 steps south-north, and 28 vertical pressure sigma levels. We use the ACM2 scheme [Pleim, 2007] for the planetary layer fluxes, Kain-Fritsch for cumulus parameterization [Kain, 2004], the WRF Single-Moment (WSM) 6-class scheme for microphysics [Hong and Lim, 2006], Noah Land-Surface Model for the surface physics [Chen and Dudhia, 2001], and Rapid Radiative Transfer Model (RRTM) for short- and long-wave radiation. We account for the horizontal turbulent diffusion based on the standard Smagorinsky first-order closure. The lateral boundary conditions and the grid nudging inputs come from the global Final (FNL) 0.25° resolution model. The diurnally lateral chemical conditions are generated by GEOS-Chem v10 [Bey et al., 2001] with the full chemistry mechanism (NO_x-O_x-HC-Aer-Br) spun up for a year.

Case Description

Between April and June 2016, a joint team of researchers from the U.S. and South Korea conducted an atmospheric chemistry field campaign over the Korean Peninsula and surrounding open waters [<https://espo.nasa.gov/korus-aq>, last access: 22 June 2019]. Observations were collected from a variety of observing systems encompassing surface sites, airborne remote sensing, and in-situ aircraft observations. Figure 3 shows contour maps of simulated surface ozone concentrations overlapped by 500 mb geopotential heights and 700 mb wind vectors in East Asia during the June 7th-10th 2016 period. A low pressure system aloft over the very northern part of China associated with the trough (purple line) is responsible for carrying on the continental polluted air masses from the west while obstructing those from

clean maritime regions coming from the south. In addition, the development of an atmospherically stagnant condition over the North China Plain and the Yellow Sea from June 8th till June 9th 2016, evident in the expansion of the isobars, resulted in elevated ozone concentrations over East Asia. For instance, ozone levels within the first 2 km altitude on June 9th 2016 around the Seoul metropolitan area are found to be 107 ± 14 ppbv [Figure S1]. By virtue of the favorable atmospheric conditions for the formation of ozone, and the availability of qualified GeoTASO and DC8 observations on June 9th 2016, we focused our study on this ozone episode day. It is worth noting that on any other day during the campaign, the coincidence of GeoTASO and DC8 measurements was suitable to draw statistically significant conclusions on the relationship between $P(O_3)$ and ozone precursors.

Ozone chemistry analysis during the episode — DC8

Prior to assessing the usefulness of GeoTASO at pinpointing the sensitivity of ozone to its precursors, we find it essential to study the relevant chemical rates at which ozone is being formed/removed. We first validate the performance of the ensemble of box models by comparing OH and HO₂ measurements to the simulated values, and those from NASA Langley Research Center (LaRC) box model (<https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq>, Last access: Dec 2019). Comparing to the observations, we observe a reasonable performance in our box model with respect to correlation and bias for OH ($R^2=0.43$, +27%) and HO₂ ($R^2=0.71$, -20%). Moreover, both box models agree well within 10% and 34% range in terms of OH and HO₂, respectively [Figure S2 and S3]. Figure 4 shows the DC-8 measurements of NO₂, HCHO, O₃ below 2 km, and the simulated VOCR from the box model on June 9th 2016 afternoon (1400-1600 LST). The borders are administration subdivisions. The rough threshold of mixing layer height is derived from ceilometer backscatter profiles shown in Sullivan et al. [2019]. The altitude of the aircraft is demonstrated in Figure S4. To gather a better qualitative picture of the spatial variations in NO₂ and HCHO, we plot their vertical columns observed by GeoTASO in the background. We find a fair correlation ($R^2=0.47$ for HCHO, and $R^2=0.69$ for NO₂) between the collocated pixels and the DC-8 measurements within a 500 m radius.

Not surprisingly, high concentrations of NO₂ are seen in the city mainly due to anthropogenic NO_x emissions. The MIX-Asia 2010 emissions inventory suggest that the primary source of NO_x emissions in the Seoul metropolitan area is the mobile sector (67%, 74 ton/day) followed by the residential (22%, 21 ton/day) (not shown). The measured NO₂ columns pinned to the city are exceptionally high (~ 3.1 DU = 8.3×10^{16} molec.cm⁻²) such that Pandora ground-based NO₂ column observations located in Yonsei University (Seoul) from 16th May to 11th June 2016 only observed such a value or higher with less than 1% occurrence

[Herman et al., 2018].

The retrieval of HCHO has intrinsically been difficult primarily due to the weaker molecular absorption which leads to a relatively higher detection limit and noisier values [Chance et al., 1991, 2000]. As a result, former studies mapping HCHO values on urban scales using satellite observations had to oversample years of data at a cost of losing temporal information [Zhu et al., 2014; Souri et al., 2017; Zhu et al., 2018]. The uniqueness of GeoTASO lies in its capability to observe elevated HCHO values at sub-urban scales with just one overpass [Nowlan et al., 2016], as seen in Figure 4. Souri et al. [2017] calculated the average total HCHO columns from the Ozone Monitoring Instrument (OMI) in 2005-2014 and found them to be comparatively high over Seoul, possibly a result of anthropogenic emissions. Similarly, the combination of GeoTASO and DC-8 observations reveals a pronounced level of HCHO in the urban area. A myriad of VOC compounds with various emissions sources can contribute to the formation of HCHO [Seinfeld and Pandis, 2016]. A comprehensive source apportionment study using VOC measurements in Seoul during the years of 2013-2015 suggested that the major contributor to VOC concentrations were from the solvent use and mobile emissions [Song et al., 2019]. Likewise, the DC-8 aircraft measure high concentrations of ethane, ethene, and methanol in the proximity of the city, all of which are largely utilized in vehicle fuels [Figure S5-S7]. High toluene concentrations (a major product from solvent use) are mostly observed in the southern part of the city (> 5 ppbv) [Figure S8]. As another major source of VOC (and HCHO), we find high concentrations of isoprene (0.74 ± 0.23 ppbv) over Seoul (Olympic Park) [Figure S9].

A major assumption in using HCHO/NO₂ ratio for gaining some insights into ozone formation is that HCHO is a proxy for total VOCR [Duncan et al., 2010]. To reassess this assumption, we plot the DC-8 HCHO versus the simulated VOCR values on June 9th 2016 afternoon (1400-1600 LST) in Figure 5. A significant coefficient of determination ($R^2=0.90$) is found between DC-8 HCHO levels and the logarithm-transformed VOCR. The logarithmic dependence indicates that two quantities begin to diverge at high values. For example, the Pearson correlation coefficient between VOCR and HCHO changes from 0.9 for VOCR below 4 s^{-1} to 0.6 for VOCR above 4 s^{-1} . This drift is in agreement with Valin et al. [2016] who found that HCHO levels under high VOCR ($>8 \text{ s}^{-1}$) are primarily dependent on OH concentrations rather than VOCR at midday (see Eq1 in the paper). Therefore, the assumption of HCHO being a proxy for VOCR might not hold for VOC-rich environments.

A second assumption in using the ratio is that it might be a proxy for the magnitude of

LNO_x/LRO_x ratios [Duncan et al., 2010; Schroeder et al., 2017]. Figure 6 depicts the relationship between the measured ratios versus the modeled LNO_x/LRO_x. Both quantities are transformed logarithmically. A high degree of negative correlation between the two variables ($R^2=0.96$) underscores the relevance of HCHO/NO₂ ratios to LNO_x/LRO_x values. Kleinman et al., [2001] and Kleinman, [2005] found that P(O₃) is proportional to VOCR for those LNO_x/LRO_x ratios near to 1 or higher (i.e., NO_x-saturated), while for lower values, it becomes independent of VOCR (i.e., NO_x-sensitive). Schroeder et al. [2017] further reassessed this indicator (i.e. LNO_x/LRO_x) during the Colorado DISCOVER-AQ campaign and found out the LNO_x/LRO_x cut-off value should be increased to ~2.8 to correctly locate the P(O₃) turnaround point mainly due to the inclusion of NO_z in their box model calculation. Assuming a NO_x/VOC transition at LNO_x/LRO_x =1, the fitted curve in Figure 6 suggests that the transition occurs at a HCHO/NO₂ ratio close to 2.8, while considering LNO_x/LRO_x=2.8 leads to the ratio ~1.8. We will investigate the dependency of P(O₃) on HCHO/NO₂ ratios later.

In general, the observed ambient ozone concentrations neither correlate with HCHO nor NO₂, as they are influenced by a combination of a non-linear chemistry, dry deposition, background values, photochemistry, meteorology and stratosphere-troposphere exchange [Cooper et al., 2012]. To elucidate the chemistry, we plot the major loss and formation pathways in P(O₃) calculated from the box model in Figure 7. In the presence of both relatively high VOCR rates and NO_x concentrations, we observe several ozone production hot spots through the reactions of HO₂+NO and RO₂+NO over the downtown and the downwind area (the predominant surface wind is weak northwesterly). The major pathway of chemical ozone loss in the city is through the formation of HNO₃. O₃ photolysis by the reaction of O(¹D)+H₂O is the second factor for the photochemical ozone loss. The mean P(O₃) is estimated at 7.66±2.52 ppbv hr⁻¹ with a maximum value up to 14.41 ppbv hr⁻¹. The elevated P(O₃) is majorly observed over areas in which we see simultaneously high concentrations of HCHO (from isoprene) and NO₂ [Sullivan et al., 2019].

To shed light on the dependency of P(O₃) on its major precursors (i.e., NO_x and VOCs), we conduct two experiments; the first experiment follows an observationally stand-alone framework involving the comparison of observed NO concentrations from DC-8 with P(O₃). Such an experiment is limited to the range of observed values, thus to be able to extrapolate the analysis, the second experiment makes use of the constrained box model changing the concentrations of NO and VOCs. Here, we detach the model from the HCHO constraint to allow it to respond to changes in the primary VOCs. To perturb the values, we use a linear factor stretching from 0.1 to 15 with a 0.1 step (150 values). We apply this factor to all

constrained VOCs and NO_x (excluding HCHO and aromatic VOCs) to be able to create a 150×150 grid in NO_2 -HCHO space.

Figure 8 (left panel) demonstrates the relationship between the logarithm-transformed NO and $\text{P}(\text{O}_3)$ colored by various VOCR rates for observations further than 50 km from Seoul on the same day (mainly rural). The $\text{P}(\text{O}_3)$ values increase monotonically for all ranges of NO illustrated by a high degree of correlation between them. The increases in $\text{P}(\text{O}_3)$ relative to NO are steeper for larger VOCR rates. The right panel in Figure 8 shows the same relationship but for those observations closer to the city (<50 km); we find that the $\text{P}(\text{O}_3)$ dependence on NO follows a quadratic function. The $\text{P}(\text{O}_3)$ values increase for $\text{NO} < \sim 1$ ppbv, but slow down afterward. Theoretically, the location of the $\text{P}(\text{O}_3)$ turnover point depends on VOCR mainly due the fact that a high reactive VOC yields a larger amount of RO_2 to react with NO [e.g., Schroeder et al., 2017]. Under high NO concentrations (a typical urban setting), air parcels with high VOCR are usually associated with ample RO_2 or HO_2 molecules which enhance the conversion of NO to NO_2 , whereas in a low VOCR environment the radical termination becomes prominent removing NO_2 from the cycle. To some extent, we observe the same tendency in Figure 8, but the number of observations (over Seoul) is not adequate to statistically associate the sensitivity of $\text{P}(\text{O}_3)$ with NO given a certain VOCR rate. A striking difference between the two sets of observations is having much more variability for observations close to Seoul, which in turn, results in increased uncertainty in the maxima (1.2-2.46 ppbv for NO). This indicates the presence of diverse emissions sources, and more complex chemical condition regimes, making necessary performing the second experiment for expanding our data.

We next explore the $\text{P}(\text{O}_3)$ isopleths as a function of HCHO and NO_2 concentrations based on the average of all perturbed observations located in the proximity of Seoul (<50 km) on June 9th (1400-1600 LST) (Figure 9). We furthermore overplot the associated $\text{LNO}_x/\text{LRO}_x$ isopleths (purple lines). The chemical transition point is found at $\text{LNO}_x/\text{LRO}_x \sim 2.7$ which is in strong agreement with those values reported in Schroeder et al. [2017]. At points on the right side of this line, $\text{P}(\text{O}_3)$ mostly is a function of HCHO, thus reducing VOCs turns out to be a practical way to reduce $\text{P}(\text{O}_3)$. In contrast, moving toward the left side of the line renders $\text{P}(\text{O}_3)$ dependent on NO_x concentrations. The $\text{LNO}_x/\text{LRO}_x$ contours also hint about the relationship between HCHO- NO_2 - O_3 . Enhancement of NO_2 concentrations leads to an exponential increase in $\text{LNO}_x/\text{LRO}_x$, evident in the smaller changes in the x-intercepts of the $\text{LNO}_x/\text{LRO}_x$ lines. This is essentially due to that fact that the relationship between NO_x emissions and NO_2 concentrations changes from a linear form to an exponential one [Souri et al., 2017] mainly because of the feedback of NO_x on its own lifetime. Another distinct feature is that the slope

of the LNO_x/LRO_x lines becomes less steeper as NO_2 concentrations increase. Under rich VOC environments, the LNO_x/LRO_x ratios seem to be more buffering with respect to NO_2 changes. A possible explanation for this tendency can be due to the HCHO- NO_2 relationship [Wolfe et al., 2016; Chan Miller et al., 2017].

Martin et al. [2004] suggested that the transition between VOC-sensitive and NO_x -sensitive regimes occurs at a HCHO/ NO_2 ratio of 1. Figure 9 shows that the majority of data points can safely be described as NO_x -saturated as long as HCHO/ NO_2 is lower than 1. On the contrary, any data point that results in a larger value than 1 may fall into either NO_x -sensitive or NO_x -saturated regime. Duncan et al. [2010] defined an ambiguous region ranging from 1-2 and classified NO_x -sensitive regimes if $HCHO/NO_2 > 2$. According to Figure 9, using this threshold, we would misclassify a sizable proportion of the data. We observe that the discrepancy between the $HCHO/NO_2 = 2$ line and that of $LNO_x/LRO_x = 2.7$ is larger for VOC rich environments. In fact, to stay on $LNO_x/LRO_x = 2.7$, HCHO/ NO_2 can have a wide extent of values ranging from 1 to 4, questioning the robustness of this indicator to ascribing the chemical condition regimes. Using observations measured in DISCOVER-AQ Colorado, Schroeder et al. [2017] similarly discovered that a broad range of column HCHO/ NO_2 ratios between 1.1 and 3.3 can fall into the ambiguous class. They attributed this to the inhomogeneous vertical distributions of HCHO and NO_2 . However, there is a feature in our second experiment which carries over quantitatively to the more fundamental problem which is the dependence of HCHO production on NO_x [Wolfe et al., 2016]. This initial finding motivates us to further investigate this relationship by comparing NO_2 concentrations with the HCHO formation.

Figure 10a depicts the HCHO formation isopleths for different NO_2 and VOCs concentrations. At low VOC environments, the HCHO formation is dampened by increasing NO_2 (due to OH suppression and formation of organic nitrates), whereas at high VOC conditions, the availability of RO_2 and HO_2 results in enhancing VOC oxidation (thus larger HCHO formation) with respect to NO_2 for given NO_2 levels (< 6 ppbv). Revisiting Figure 9, at a point that HCHO = 22 ppbv and $NO_2 = 8$ ppbv, the $LNO_x/LRO_x = 2.7$ line suggests that this data point is in NO_x -saturated while the conventional threshold ($HCHO/NO_2 = 2$) indicates otherwise. According to Figure 10a, an increase in NO_2 at this point should naturally result in reducing HCHO formation, which in turn, moves this point to the bottom and the right side of the $P(O_3)$ isopleth (i.e., toward NO_x -saturated regime). This provides theoretical evidence that the hypothesis on this point being NO_x -sensitive regime (by $HCHO/NO_2 = 2$) is spurious. Likewise, at a point that HCHO = 2 ppbv and $NO_2 = 2$ ppbv, the transitional line indicates that

this point should be labeled in the NO_x-sensitive regime, whereas the threshold suggests the NO_x-saturated. The wide range of HCHO/NO₂ ratios that the transition line falls in can be partly explainable by the impact of NO₂ on HCHO formation. Under VOC-rich environments, the feedback of NO₂ on HCHO formation increases the numerator of the HCHO/NO₂ ratios (and denominator of LNO_x/LRO_x) indicating the transition occurs at larger ratios. On other hand, under VOC-poor environment, the same chemical feedback decreases the numerator suggesting that the transition occurs at the smaller ratios. The inherit dependence of HCHO formation on NO_x concentrations have comprehensively studied in Marias et al. [2012], Valin et al. [2016], and Wolfe et al. [2016]. The major driver for this chemical feedback is by OH production/loss. To better demonstrate this, we plot the contour map of OH concentration from the same analysis done for HCHO formation in Figure 10b. The figure shows enhanced OH mainly due to RO₂+NO reaction for given NO₂ concentrations (depending on the abundance of VOCs), but reduced OH afterward primary due to NO₂+OH reaction. Therefore, the more reactive a VOC compound is, the larger NO_x can boost HCHO production, thus complicating the HCHO/NO₂ ratio. We observe the same chemical tendency by calculating the derivative of HCHO columns with respect to the NO_x emissions using the CMAQ Direct Decoupled Method (DDM) [Cohan et al., 2005] during afternoon in May-June 2016 [Figure S10].

With this caveat in mind, we define our case-specific transition line for mapping GeoTASO columns into the different regimes by fitting a line to the LNO_x/LRO_x=2.7 which results in the following equation:

$$HCHO = 3.7 \times (NO_2 - 2.2 \text{ ppbv}) \quad (7)$$

It is worth pointing out here that this is for the local relationship under a well-mixed planetary boundary condition, which may not translate easily to the ratio of the columns. In fact, the variable relationship between the columns and the near-surface concentrations can provide another source of error that has been comprehensively studied in Duncan et al. [2010], Jin et al. [2017] and Schroeder et al. [2017]. However, on this specific day, the assumption of a well-mixed boundary, evident in the strong degree of correlation between GeoTASO and DC8, allowed us to isolate the chemical feedback, an overlooked error in the use of the ratio. To convert the intercept to column, we assume uniformly mixed NO₂ concentrations (2.2 ppbv) from 0 to 2 km above ground level and for higher altitudes; we follow the CMAQ-WRF profiles over Seoul. The use of the model is due to the lack of DC-8 spiral measurements over Seoul on this day. The converted formula to the columns is:

$$HCHO = 3.7 \times (NO_2 - 1.14 \times 10^{16} \text{ molec. cm}^{-2}) \quad (8)$$

Mapping Chemical Conditions over Seoul — GeoTASO

To proceed further with the link between the transition line derived from the second experiment and GeoTASO HCHO/NO₂ columns, will first require a comparison of DC-8 HCHO/NO₂ ratios to those of GeoTASO on June 9th 2016 at 1400-1600 LST. Figure 11 shows a point-to-point comparison of these two datasets collocated spatially. The temporal co-registration of both datasets is not feasible; we have to assume that both datasets are exposed to the same atmospheric condition in the 1400-1600 LST window. The comparison suggests that DC-8 fairly captures ~60% of the variance in GeoTASO. However, GeoTASO HCHO/NO₂ ratios tend to be higher than those of DC-8. A number of factors contribute to the disagreement between two datasets: i) the accuracy in the retrievals [Nowlan et al., 2016; Nowlan et al., 2018; Lamsal et al., 2017] can directly contaminate HCHO/NO₂ column, ii) the assumption of the effective vertical diffusion mechanism within the mixed layer should not rule out the impact of the free troposphere on the magnitude of column, and iii) the spatial heterogeneity in the observations inevitably leads to some degree of disagreements.

We further use Eq.8 to classify the Seoul metropolitan area into NO_x-saturated and NO_x-sensitive regimes at different times of the day (1000-1600 LST), shown in Figure 12. Compared with former studies using satellite observations [Choi and Souri, 2015a,b; Jin and Holloway, 2015; Duncan et al., 2010; Choi et al., 2012; Chang et al., 2016; Jin et al., 2017; Souri et al., 2017], GeoTASO with unprecedented spatial and temporal resolutions provides much more in-depth information at a fine scale. In a broad picture, NO_x-sensitive regimes are primarily observed in suburbs, whereas the NO_x-saturated regimes are mostly confined to urban settings. Areas that are located in NO_x-saturated regime change over time, shrinking from the morning time to the afternoon which is mainly associated with photochemistry, although the impact of meteorology and traffic patterns cannot be neglected. We constantly observe how the Olympic Park (shown with a red circle) falls into NO_x-saturated regime suggesting that the abrupt increase in isoprene in this area [Figure S9] can strongly enhance P(O₃). Based on OMI observations from 2005-2015, Jin et al. [2017] labeled Seoul as the transitional regime in warm seasons. Integrating all pixels from GeoTASO leads to the same conclusion (assuming $1 < \text{HCHO/NO}_2 < 2$ as the transitional class), suggesting that the broad picture of the latter remains correct; however, the finer resolution of GeoTASO allows the regimes to be further broken out into smaller segments, showing significant spatial variations in HCHO/NO₂ ratios. To better demonstrate how a finer spatial resolution can be critical for our application, we chose an area in Incheon by putting together the CMAQ-derived ratios in 27×27 km² and those of GeoTASO, shown in Figure 13. Unfortunately, the OMI data are unavailable on this day

because of technical issues in the sensor; therefore we resorted to using a model for this analysis. By virtue of having a large portion (63%) of NO_x -saturated regime observed by GeoTASO, the CMAQ model correctly labels this area as the same category, but according to GeoTASO, the sub-pixel variabilities are large suggesting that high resolution sensors offer a potential basis for designing more specific mitigation strategies.

Summary

Persistent increases in stagnation, continental background concentrations, and photochemistry go hand-in-hand and lead to an ozone extreme event in the Seoul metropolitan area on June 9th 2016, making this day an interesting target to study ozone sensitivity. Specifically, DC-8 measurements observed mixing-layer NO_2 and HCHO concentrations up to 30 and 9 ppbv respectively over the city during the afternoon, which is an indication of an exceptionally degraded air quality. To study ozone chemistry, we conduct an ensemble of steady-state box models constrained by qualified observations within the mixing-layer (<2 km). The ensemble of models suggests elevated volatile organic compound reactivity (VOCR) rates ($\sim 8 \text{ s}^{-1}$) close to the Olympic Park in eastern Seoul mainly due to abundance of both isoprene and NO_x , resulting in enhancement of net ozone production rate ($P(\text{O}_3)$) by 12 ppbv hr^{-1} . The same observations are captured in Sullivan et al. [2019].

We further study the $P(\text{O}_3)$ dependency on NO by differentiating observations in rural areas (>50 km far from Seoul) and urban ones (< 50 km). In the rural areas, a strong linear relationship between the two quantities is found mainly due to abundant VOCs; the relationship turns into a quadratic form in the urban areas resulting from $\text{NO}_2 + \text{OH}$ reaction. The maxima of this quadratic function occurs at a wide range of NO (1.2-2.46 ppbv) giving a strong indication of the presence of diverse emissions. We extrapolate our analysis by perturbing the primary compounds and find that the loss of NO_x (LNO_x) to the loss of $\text{HO}_2 + \text{RO}_2$ (LRO_x) which is roughly equivalent to $\text{HNO}_3/\text{H}_2\text{O}_2$ suggested by Sillman et al. [2002] is a robust way to differentiate NO_x -sensitive (i.e. NO_x -limited) or NO_x -saturated (i.e. VOC-limited) [Schroeder et al., 2017]. Following the ratio of $\text{LNO}_x/\text{LRO}_x \sim 2.7$ describing the transition line, the conventional thresholds of HCHO/ NO_2 ratios, a proxy indicator commonly applied using satellite-derived observations, are not always applicable. Our theoretically observational-calculational experiment indicates that NO_2 -HCHO chemical relationship plays a major role in usefulness of the mathematical formulation of HCHO/ NO_2 . Under VOC-rich environment, the acceleration of HCHO formation with respect to NO_2 suggests that the transition line occurs at larger HCHO/ NO_2 ratios (up to 4), whereas under VOC-poor environment, the suppression of HCHO formation due to NO_2 indicates that the transition line happens at the smaller ratios.

Our analysis highlights the limitation of using the HCHO/NO₂ ratios at pinpointing the regimes from a chemical point of view. This means that the conventional approach of formulating this indicator is facing problems under both VOC-rich and VOC-poor environments, thereby a fundamental reformulation might be needed. We then reformulate the indicator to be able to match with $LNO_x/LRO_x \sim 2.7$ which leads to $HCHO = 3.7 \times (NO_2 - 1.14 \times 10^{16} \text{ molec.cm}^{-2})$. The advantage of using this mathematical format over a ratio lies in the fact that it removes the need for providing a wide range of thresholds depending on VOC environment, although the numbers here have been calibrated locally. This means that the coefficients provided here in the new formula might not be applicable for other regions around the globe; accordingly, we encourage only the use of $HCHO = a \times (NO_2 - b)$ formula in future works for other regions in which the coefficients will be adjusted with respect to field measurements.

Making use of newly available airborne remotely sensed data at unprecedented spatial and temporal resolutions, we use the redesigned formula in an effort to classify the chemical condition regimes over Seoul. Compared to a crude classification suggested in former studies using coarse satellite observations [Souri et al., 2017; Jin et al., 2017], the Geostationary Trace gas and Aerosol Sensor Optimization (GeoTASO) airborne instrument reveals more in-depth spatial and temporal variabilities associated with the regimes. We observe a larger ring of NO_x-saturated regimes at 10-12 LST compared to the afternoon possibly due to less active photochemistry. The Olympic Park in which P(O₃) is high is constantly observed in NO_x-saturated regime throughout the daytime. Results ensure the capability of future geostationary satellites at better capturing the chemical condition regimes with much improved spatial and temporal coverage.

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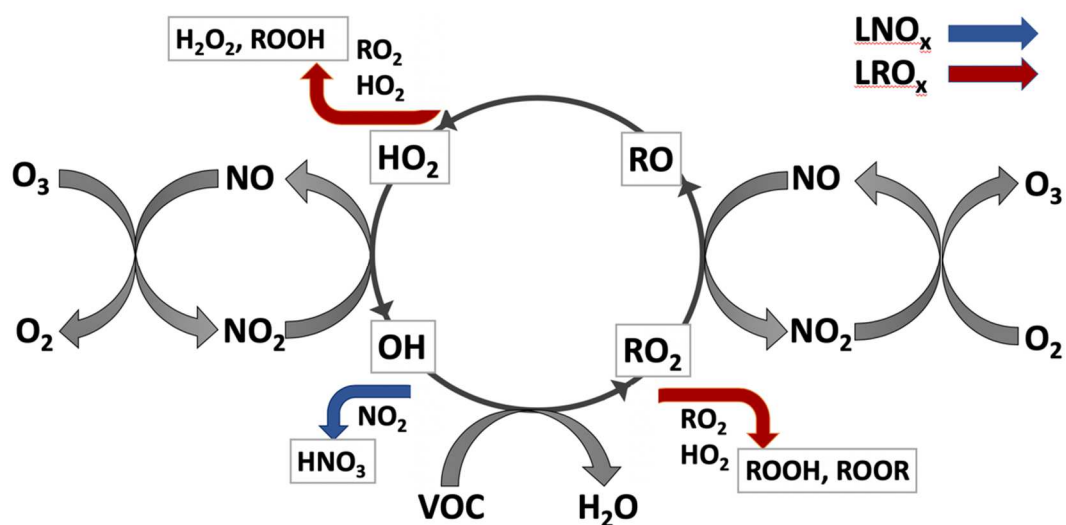
Tables

Table1. The box model configurations and inputs.

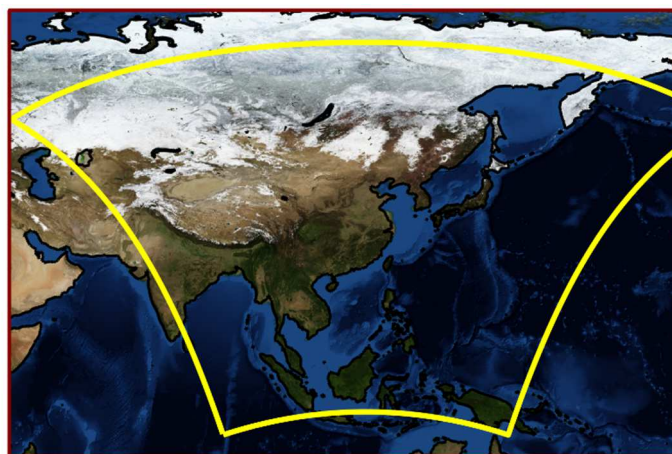
Time Steps	30 mins
Number of Solar cycles	5
Dilution constant	1/86400 (s ⁻¹)
Meteorological Inputs	Pressure, Temperature, Relative Humidity
Photolysis frequencies	Measured by NCAR's CCD Actinic Flux Spectroradiometers
Chemical Levels (Instrument#*, Precision) used for constraining the box model	H ₂ (1,5%), O ₃ (2,10%), CO (4,2%), H ₂ O ₂ (5,30%), HNO ₃ (5,30%), NO ₂ (2,30%), SO ₂ (6,30%) , CH ₄ (4,0.1%), PAN (6,20%), Alkyl nitrates (10,10%), Isoprene (1,5%), Monoterpene (9,33%), HCHO (7,3.3%), Acetone (9,3%), Ethene (1,5%), Ethyne (1,5%), Ethane (1,5%), Methanol (9,3%), CHOCHO (8,15%), Propane (1,5%), Benzene (1,5%), Xylene (1,5%), Toluene (1,5%), Acetaldehyde (9,8%)
Chemical Levels (Instrument#*, Precision) used only for initializing the box model	OH (3,32%), HO ₂ (3,32%), NO (2,20%)
Chemical Mechanism	CB6r2

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

805 **Figures:**



806
807 **Figure 1.** A representation of the important interactions in the daytime chemistry of the
808 tropospheric ozone formation.



810
811 **Figure 2.** The location of CMAQ 27 km domain which covers China, Japan, India, South
812 Korea, Taiwan and some portions of Russia and South Asia.

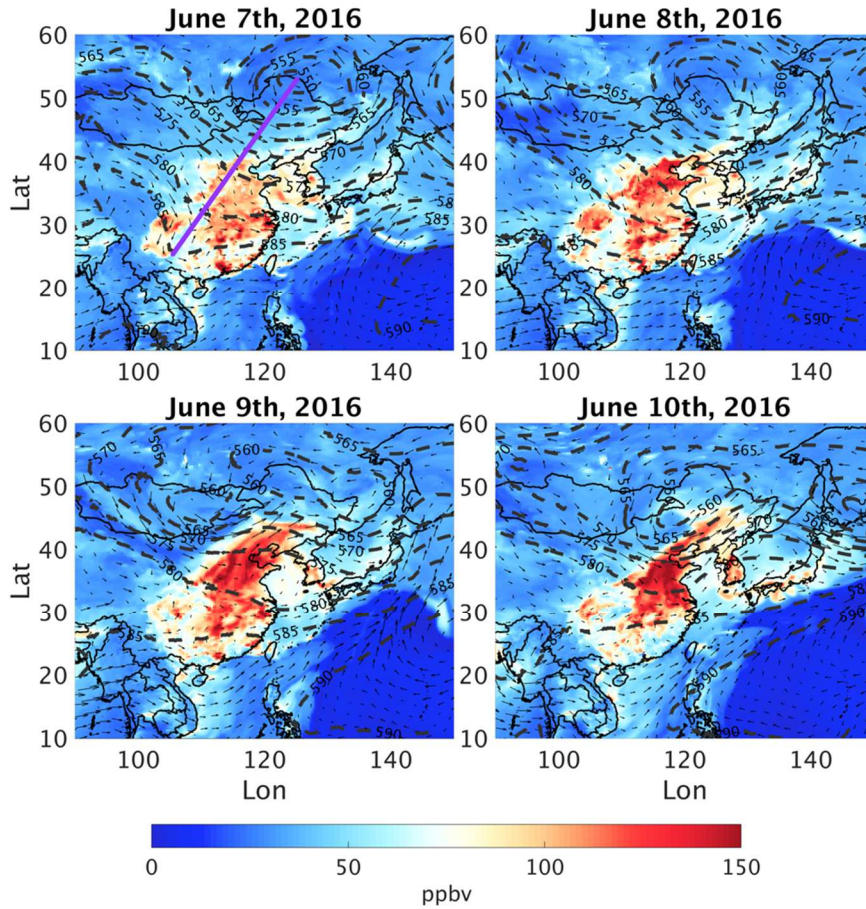


Figure 3. Synoptic-scale atmospheric conditions for East Asia at 0600 UTC on four different days (June 7th-10th 2016). The background color indicates surface ozone mixing ratios (ppbv) simulated by the WRF-CMAQ model. Black dashed lines represent 500 hPa geopotential heights (decameters), and the black vectors show 700 hPa winds.

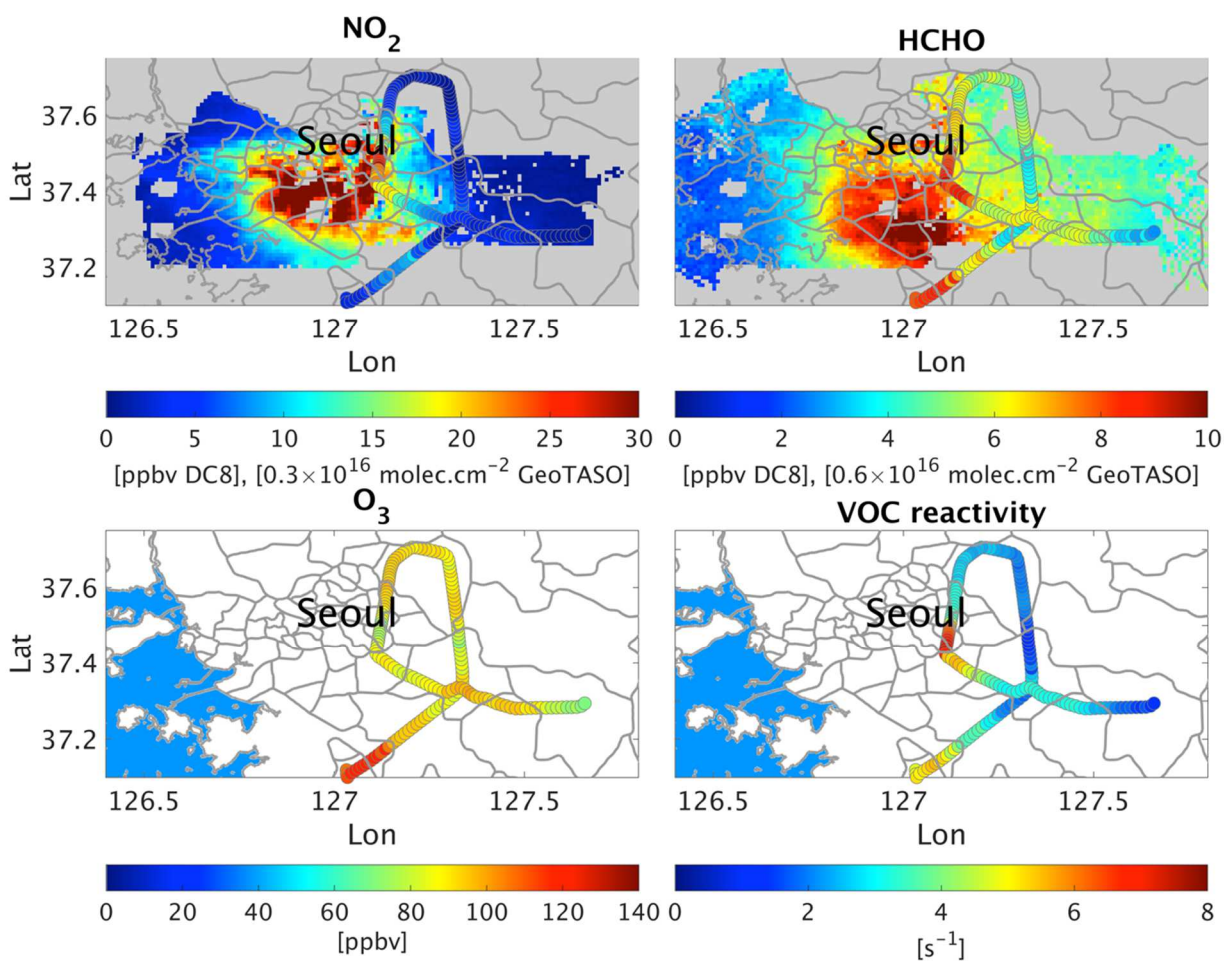


Figure 4. Contour maps of GeoTASO NO_2 and HCHO columns overlapped with DC-8 measurements on June 9th 2016 afternoon (1400-1600 LST) (first row). The measured O_3 levels and simulated VOCR based on the ensemble of box models (second row). For inferring the columns, a factor provided in captions should be applied to the colorbar values.

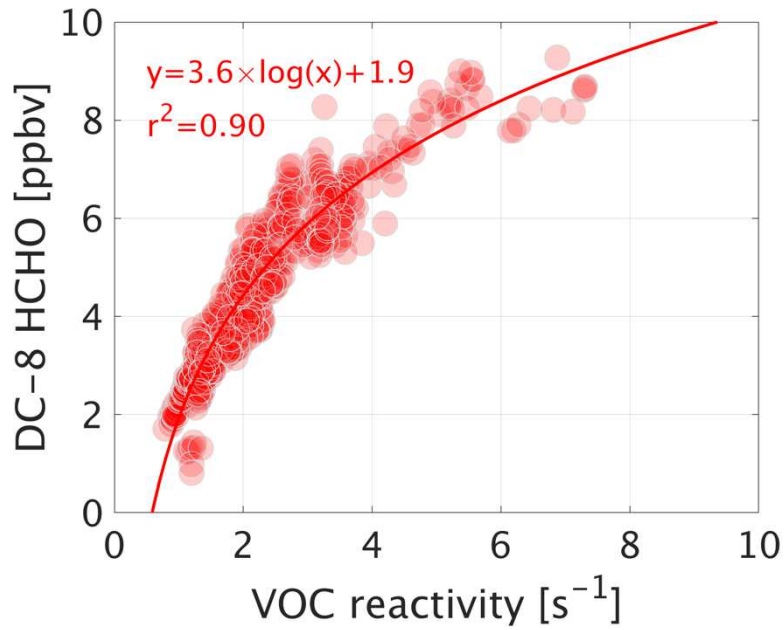


Figure 5. Point-to-point comparison of simulated VOCR rates using the constrained ensemble of box models with measured HCHO values on June 9th 2016 afternoon (1400-1600 LST). Only observations with less than a 2 km altitude are considered in the analysis. The black line denotes the identity line.

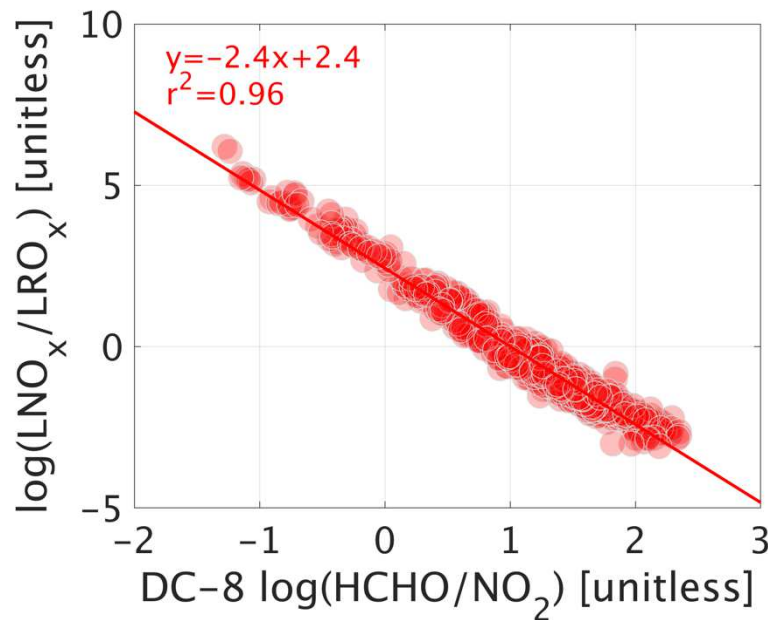
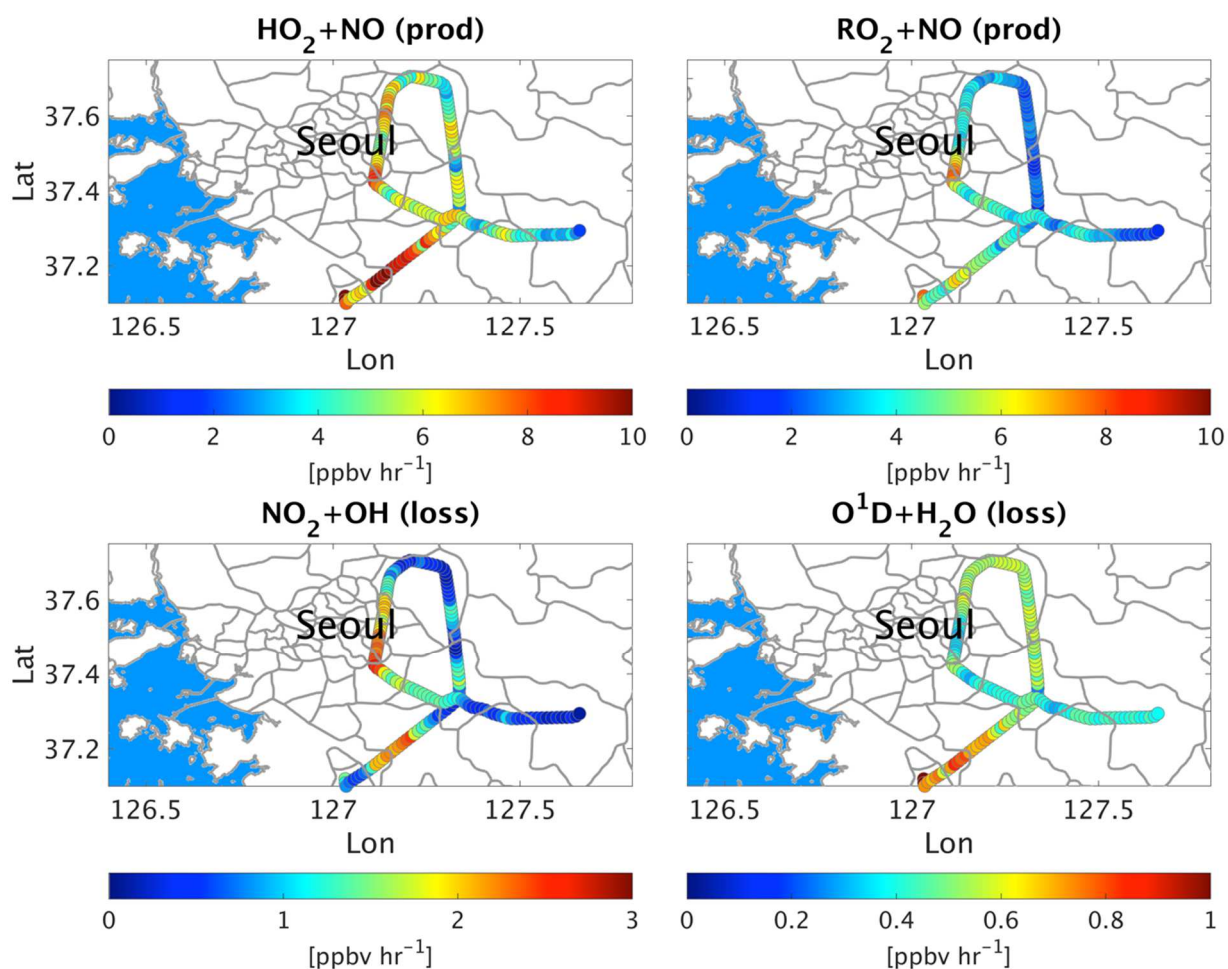


Figure 6. Point-to-point comparison of the logarithm-transformed DC-8 HCHO/NO₂ ratios vs simulated LNO_x/LRO_x values using the constrained ensemble of box models on June 9th 2016 afternoon (1400-1600 LST). Only observations with less than a 2 km altitude (mixing layer) are considered in the analysis.

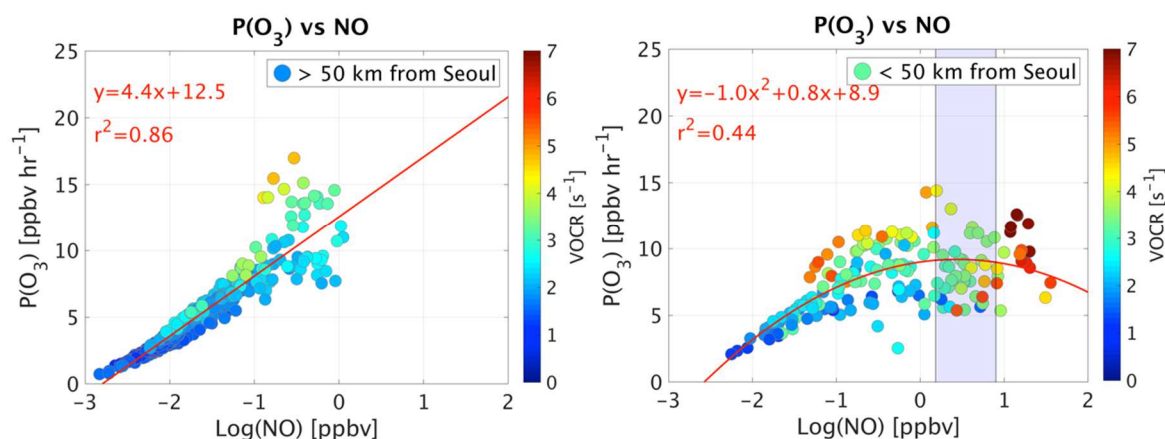
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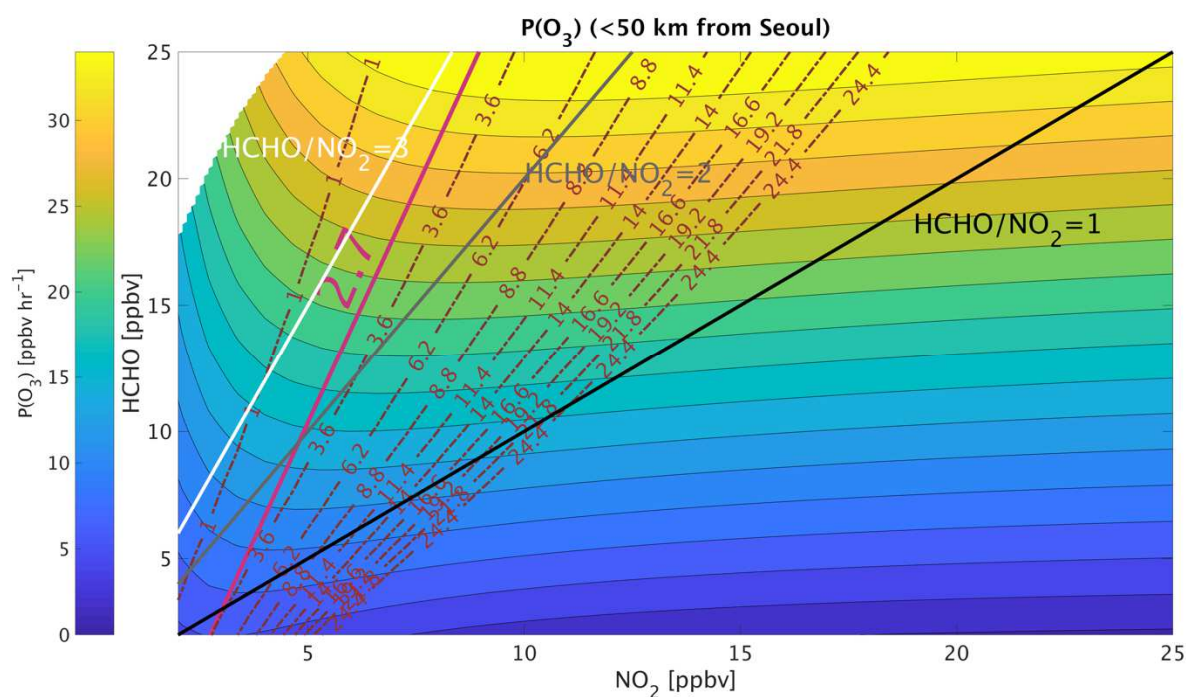
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838 **Figure 7.** The simulated major pathways of photochemical ozone production (first row) and
 839 loss (second row).

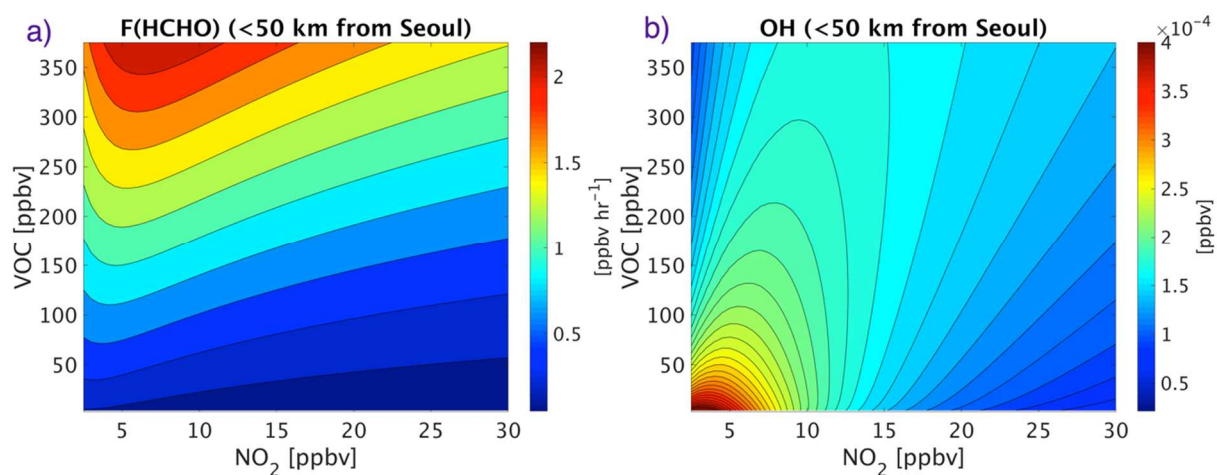
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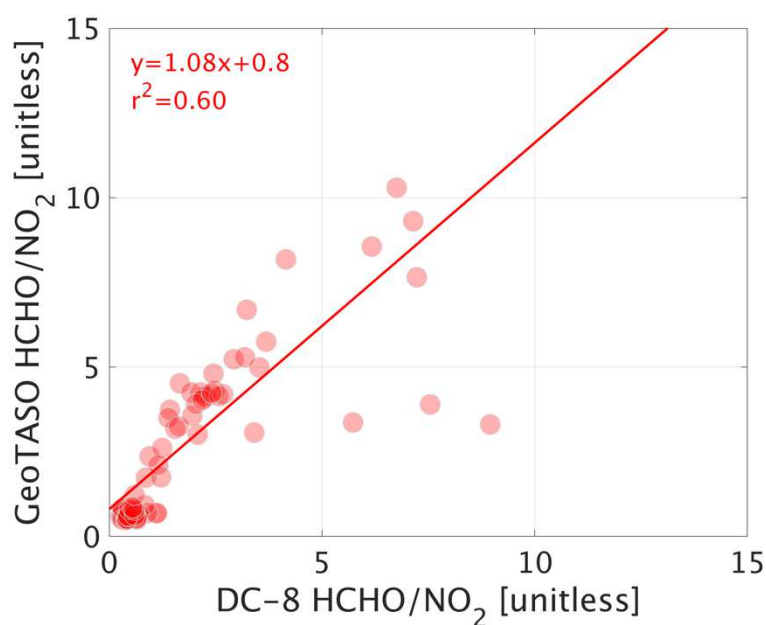
841
 842 **Figure 8.** The relationship between observed NO and simulated P(O₃) using the constrained
 843 ensemble of box models for different regions (>50 km from Seoul in the left panel and <50 km
 844 in the right). The shade area in the right panel indicates the range of location that local maxima
 845 may fall in (at 95% confidence level).
 846



847
 848 **Figure 9.** The P(O₃) isopleths as a function of NO₂ and HCHO concentrations overlaid by the
 849 LNO_x/LRO_x contours (purple lines). Data points used for this plot are generated by perturbing
 850 NO_x and primary VOCs (excluding HCHO and aromatic VOCs) using the box model described
 851 in Table 1. The data are collected from DC-8 on June 9th 2016 afternoon (1400-1600 LST).
 852



853
 854 **Figure 10.** (a) The HCHO production isopleths, and (b) the OH concentrations isopleths as a
 855 function of NO_2 and VOC concentrations.



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 857 **Figure 11.** The comparison of GeoTASO HCHO/ NO_2 ratios versus those of DC-8.
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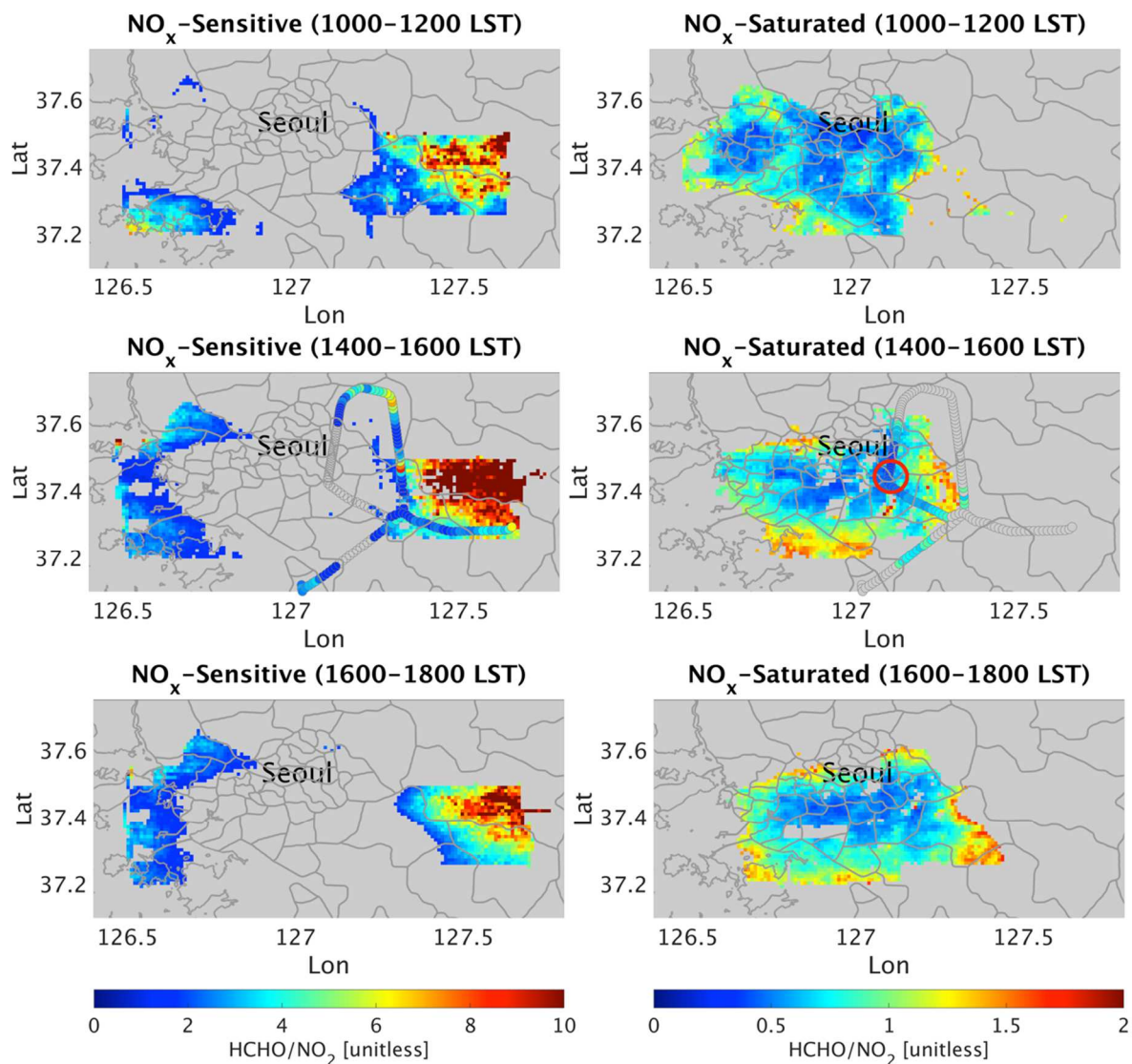


Figure 12. The contour maps of GeoTASO HCHO/NO₂ ratios labeled into two different chemical conditions regimes based on the transition line derived from this study. The observations are collected on June 9th 2016. The red circle shows the location of Olympic Park.

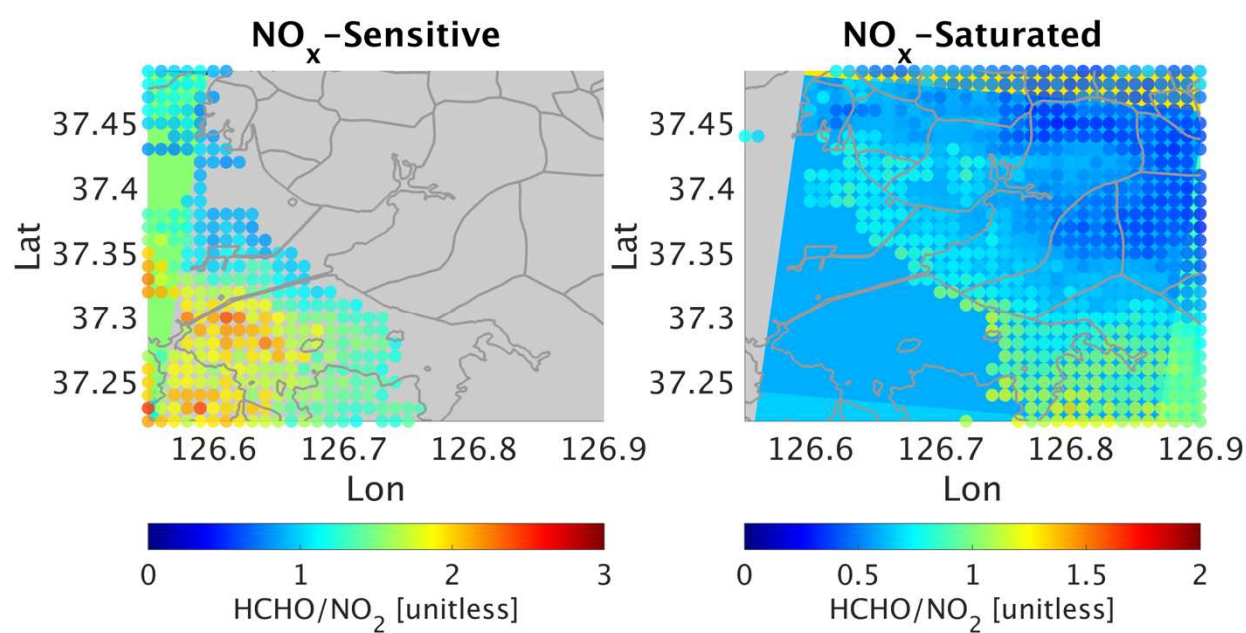


Figure 13. The spatial representation of HCHO/NO₂ ratios of CMAQ (background) overlaid by those of GeoTASO for an area in Incheon, South Korea.