Revisiting the Effectiveness of HCHO/NO$_2$ 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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TEMPO Meeting 2020 August
Background

• The non-linear chemical processes involved in ozone production $P(O_3)$ have necessitated using proxy indicators to convey information about the dependence of $P(O_3)$ on VOCs or $NO_x$.

• A number of these indicators are introduced and tested in Sillman et al. [2002]:
  • e.g., $O_3/NO_y$, $O_3/HNO_3$, $H_2O_2/NO_z$, and $H_2O_2/HNO_3$. 
Background

- \( \text{H}_2\text{O}_2/\text{HNO}_3 \) is rather a robust proxy, since:
- \( \text{HNO}_3 \) is a primary product from the removal of \( \text{NO}_2 \) (urban setting), whereas high \( \text{H}_2\text{O}_2 \) levels give a strong indication of \( \text{HO}_2+\text{HO}_2 \) reaction that typically occurs in remote areas (rural setting).
- This ratio which lines up with loss of radicals (Q) over loss of NOx (L) was revisited later as a solid way to locate the ridgelines in \( \text{P(O}_3 \) isopleths in Schroeder et al., [2017].
- Unfortunately, the satellite-based measurements of these two compounds are limited to scarce limb soundings.
Background

• The absorption lines of several molecules in UV-Vis range allow the retrieval of HCHO [Chance et al., 1991, 1997, 2000], and NO$_2$ [Boersma et al., 2002] from space (a comprehensive review can be found in Gonzalez 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 [Martin et al., 2004; Duncan et al., 2010].

• HCHO/NO$_2$ ratio has never been theoretically endorsed, but its accessibility from space has put more gravity on its usage.
Background

- The ratio has been widely used for studying its spatiotemporal variability [Choi et al., 2012; Choi and Souri, 2015b; Choi and Souri, 2015a; Jin and Holloway, 2015; Souri et al., 2017; Schroeder et al., 2017; Jeon et al., 2018; Jin et al., 2017].

- A number of studies observed that differing HCHO/NO\textsubscript{2} thresholds differentiates 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 incoherent relationship between the column and the near-surface concentrations.

- While those sources of errors unquestionably limit the applications of column HCHO/NO\textsubscript{2}, we hypothesize that the NO\textsubscript{2}-HCHO chemical feedback can systematically result in varying HCHO/NO\textsubscript{2} thresholds, regardless.
Methods (0-D Box Modeling)

- In order to calculate the chemical reaction rates of several species, we used 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 only qualified observations available on the DC8 platform for constraining 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 (< 2km).

- 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.
Methods (0-D Box Modeling)

• As the observations are intrinsically affected by random noise, it is important to perform the simulation in a stochastic framework.

• Accordingly, in this study, the framework of the box modeling is based on an ensemble model \( (R_i : i = 1,2, \ldots, k) \) 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.

• Therefore, we are able to estimate a distribution for a number of variables including net ozone production \( (P(O_3)) \), L, Q, and VOC reactivity \( (VOCR) \) rates.
**Methods (0-D Box Modeling)**

<table>
<thead>
<tr>
<th>Time Steps</th>
<th>30 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Solar cycles</td>
<td>5</td>
</tr>
<tr>
<td>Dilution constant</td>
<td>$1/86400, (s^{-1})$</td>
</tr>
<tr>
<td>Meteorological Inputs</td>
<td>Pressure, Temperature, Relative Humidity</td>
</tr>
<tr>
<td>Photolysis frequencies</td>
<td>Measured by NCAR's CCD Actinic Flux Spectroradiometers</td>
</tr>
</tbody>
</table>

**Chemical Levels (Instrument#*, Uncertainty) used for constraining the box model**

- $H_2 (1.5\%)$, $O_3(2.10\%)$, $CO\ (4.2\%)$, $H_2O_2\ (5.30\%)$, $HNO_3\ (5.30\%)$, $NO_2\ (2.30\%)$, $SO_2\ (6.30\%)$, $CH_4\ (4.0.1\%)$, 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#*, Uncertainty) used only for initialization 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.
Methods (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, which includes chlorine chemistry and the six-generation aerosol mechanism (AERO6) which considers sea salt and aqueous/cloud chemistry.
- We process anthropogenic emissions for the CMAQ domain from the MIX emissions inventory 2010 [Li et al., 2015].
- The FINN v1.6 emissions [Wiedinmyer et al., 2011] are extended to include biomass burning emissions.
- We use a standalone MEGAN (v2.1) [Guenther et al., 2006] model to include biogenic emissions.
- 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.
Methods (WRF-CMAQ)

- In order to simulate the mesoscale meteorology, we use the Weather Research and Forecasting model (WRF) v3.9.1 [Skamarock et al., 2008].
- The lateral boundary conditions and the grid nudging inputs come from the global Final (FNL) 0.25° resolution model.
- Physical options include: KF sub-grid cumulus parametrization, WSM-6 for microphysics, Yonsei University (YSU) scheme for the planetary layer fluxes, Noah Land-Surface Model for the surface physics, and Rapid Radiative Transfer Model (RRTM) for short- and long-wave radiation.
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.

- The sensor was mounted on-board NASA’s B200 aircraft flying around 9 km altitude above sea level.

- 250×250 m² spatial resolution which is ~400 times as fine as that of the TROPOspheric Monitoring Instrument (TROPOMI) nadir pixels.

- The HCHO retrieval algorithm follows a conventional 2-step procedure:
  
i) HCHO slant column is retrieved via direct non-linear least-squares fitting of GeoTASO radiance spectrum (328.5–356.5 nm) taking into consideration wavelength registration, slit function calibration, under-sampling, closure polynomials, interference molecules (e.g., O₃ and BrO), and Raman scattering [Chance et al., 2005; Nowlan et al., 2016; 2018].

  ii) HCHO vertical column is obtained by applying air mass factors (AMFs) to each observation quantifying the light path through a simulated atmosphere using VLIDORT [Gonzalez Abad et al., 2015].
GeoTASO

- The first step requires reference spectra which were taken over a relatively clean region in the Taebaek Mountains on 25 May as a function of cross-track position.

- 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].

- We only considered cloud-free pixels using cloud flags provided in the data.

- The NO₂ retrieval follows the same procedure done for HCHO with a different fitting window (425-460 nm) using the Differential Optical Absorption Spectroscopy (DOAS) technique [e.g., Lamsal et al., 2017].

- The reference spectra were chosen over a Pandora surface station located in Songchon.
Case Description

- A favorable synoptic condition for ozone formation in the June 7th-10th 2016 period.
- 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.
GeoTASO vs DC8

NO₂

[ppbv DC8], [0.3×10^{16} molec.cm^{-2} GeoTASO]

HCHO

[ppbv DC8], [0.6×10^{16} molec.cm^{-2} GeoTASO]

O₃

[VOC reactivity]

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HCHO Chemistry — DC8

- We find the reaction of ISO2 (peroxy radical from OH addition to isoprene) and NO (0.54±0.21 ppbv hr⁻¹) as the main contributor to HCHO production in the east of Seoul (where the hotspot of HCHO concentrations is mostly seen). This is mainly because of the atypically high concentrations of isoprene (0.74±0.23 ppbv) in this specific location (Olympic Park).

- The coincidently high levels of isoprene in this region make isoprene the largest contributor to VOCR (2.7 s⁻¹, 38% of total) coinciding with a study by Kim et al. [2018].

<table>
<thead>
<tr>
<th>Groups</th>
<th>Urban (s⁻¹)</th>
<th>Non-urban (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkenes (Ethene, Ethane, Ethyne, and Propane)</td>
<td>0.22±0.06</td>
<td>0.10±0.07</td>
</tr>
<tr>
<td>Aromatics (Beneze, Xylene, and Toluene)</td>
<td>0.62±0.16</td>
<td>0.43±0.30</td>
</tr>
<tr>
<td>oVOC (Acetaldehyde, Glyoxal, Methanol, and Acetone)</td>
<td>1.78±0.38</td>
<td>1.08±0.44</td>
</tr>
<tr>
<td>HCHO</td>
<td>1.50±0.21</td>
<td>1.09±0.36</td>
</tr>
<tr>
<td>BVOC (Monoterpene and Isoprene)</td>
<td>1.01±0.72</td>
<td>0.25±0.21</td>
</tr>
</tbody>
</table>
**VOCR — DC8**

- A major assumption in using HCHO/NO$_2$ ratio for gaining some insights into ozone formation is that HCHO is a proxy for total VOCR.

- The logarithmic dependence indicates that two quantities begin to diverge at high values.

- This drift is in agreement with Valin et al. [2016] who found that HCHO levels under high VOCR (>8 s$^{-1}$) are primarily dependent on OH concentrations rather than VOCR.

- **VOC rich/poor environment?**
Ozone Chemistry — DC8

- The P(O₃) values in rural setting increase monotonically for all ranges of NO illustrated with a high degree of correlation between them.
- For those observations closer to the city (<50 km); we find that the P(O₃) dependence on NO follows a quadratic function.
- More scattered = diverse emissions sources, and more complex chemical condition
To be able to extrapolate the analysis, the second experiment makes use of the constrained box model by changing the concentrations of NO and VOCs (excluding HCHO and aromatic VOCs).

Purple lines are LNOx/LROx (L/Q).

Here, we detach the model from the HCHO constraint.
Ozone Chemistry — DC8

- A wide range of HCHO/NO₂ ratios fall into the transition line.
- Can this be due the feedback of NO₂ on HCHO formation?
Ozone Chemistry — DC8

- Increasing NO$_2$ after/before a certain level decreases/increases the formation of HCHO.
Ozone Chemistry — DC8

- 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).
Redesigning the transition line

• This provides theoretical evidence that the hypothesis on this point being $NO_x$-sensitive regime (by $HCHO/NO_2=2$) is spurious.

• The wide range of $HCHO/NO_2$ 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 L/Q) indicating the transition occurs at larger ratios. Opposite trends for VOC poor environments.

• We see an opposite trend under VOC poor environments.

• 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 $L/Q=e$ which results in the following equation:

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

- A comparison of DC-8 HCHO/NO₂ ratios to those of GeoTASO on June 9th 2016 at 1400-1600 LST.

- The comparison suggests that DC-8 fairly captures ~70% of the variance in GeoTASO.

- However, GeoTASO HCHO/NO₂ ratios tend to be higher (~30%) than those of DC-8.
Chemical Conditions over Seoul

NO$_x$-Sensitive (1000–1200 LST)

NO$_x$-Saturated (1000–1200 LST)

NO$_x$-Sensitive (1400–1600 LST)

NO$_x$-Saturated (1400–1600 LST)

NO$_x$-Sensitive (1600–1800 LST)

NO$_x$-Saturated (1600–1800 LST)
Spatial Representivity

- 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.
Unexpected Results: Seoul (8-10 AM)

- An unexpected observation was seen during early morning.
- We would intuitively expect higher NO\textsubscript{2} levels (traffic and minimal photochemistry) at 8-10 AM compared to 10-12 AM, thus more NO\textsubscript{x}-saturated regime.
- Confusing, but possible reasons: Organic nitrate and PAN from earlier day? Breeze (sea and mountains)? Discontinuity in surface/column? Dry deposition? Photochemistry at accelerates RO\textsubscript{2}/HO\textsubscript{2}+NO later hours? or simply the retrieval?

**NO\textsubscript{x}–Sensitive (0800–1000 LST)**

**NO\textsubscript{x}–Saturated (0800–1000 LST)**

![Map of Seoul showing NO\textsubscript{x}–Sensitive and NO\textsubscript{x}–Saturated regions.](image)
Conclusion

• The ensemble of box models suggests elevated volatile organic compound reactivity (VOCR) rates (~ 8 s\(^{-1}\)) close to the Olympic Park in eastern Seoul mainly due to abundance of both isoprene resulting in enhancement of net ozone production rate (P(O\(_3\)) by 12 ppbv hr\(^{-1}\).

• We revisited that loss of radicals (L) to loss of NO\(_x\) (Q) which is roughly equivalent to HNO\(_3\)/H\(_2\)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].
Conclusion

• Following the ratio of $L/Q\sim e$ 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$_2$.

• This means that the conventional approach of formulating this indicator is facing problems under VOC rich and VOC poor environments, thereby a fundamental reformulation might be needed.
Conclusion

• We then reformulate the indicator to be able to match with $L/Q \sim e$ which leads to $HCHO = 3.7 \times (NO_2 - 1.14 \times 10^{16} \text{molec.cm}^{-2})$.

• 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 $P(O_3)$ is found high is constantly observed in $NO_x$-saturated regime.

• Results ensure the capability of future geostationary satellites at better capturing the chemical condition regimes with much improved spatial and temporal coverage.
This study is partially funded by NASA Aura Science Team (#NNX17AH47G).
The simulations were run on the Smithsonian Institution High Performance Cluster (SI/HPC).

Thanks for your attention!