Evaluation of simulated O$_3$ production efficiency during the KORUS-AQ campaign: Implications for anthropogenic NO$_x$ emissions in Korea

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We examine O$_3$ production and its sensitivity to precursor gases and boundary layer mixing in Korea by using a 3-D global chemistry transport model and extensive observations during the KOReA-US cooperative Air Quality field study in Korea, which occurred in May–June 2016. During the campaign, observed aromatic species onboard the NASA DC-8 aircraft, especially toluene, showed high mixing ratios of up to 10 ppbv, emphasizing the importance of aromatic chemistry in O$_3$ production. To examine the role of VOCs and NO$_x$ in O$_3$ chemistry, we first implement a detailed aromatic chemistry scheme in the model, which reduces the normalized mean bias of simulated O$_3$ mixing ratios from –26% to –13%. Aromatic chemistry also increases the average net O$_3$ production in Korea by 37%. Corrections of daytime PBL heights, which are overestimated in the model compared to lidar observations, increase the net O$_3$ production rate by ~10%. In addition, increasing NO$_x$ emissions by 50% in the model shows best performance in reproducing O$_3$ production characteristics, which implies that NO$_x$ emissions are underestimated in the current emissions inventory. Sensitivity tests show that a 30% decrease in anthropogenic NO$_x$ emissions in Korea increases the O$_3$ production efficiency throughout the country, making rural regions ~2 times more efficient in producing O$_3$ per NO$_x$ consumed. Simulated O$_3$ levels overall decrease in the peninsula except for urban and other industrial areas, with the largest increase (~6 ppbv) in the Seoul Metropolitan Area (SMA). However, with simultaneous reductions in both NO$_x$ and VOCs emissions by 30%, O$_3$ decreases in most of the country, including the SMA. This implies the importance of concurrent emission reductions for both NO$_x$ and VOCs in order to effectively reduce O$_3$ levels in Korea.

Keywords: Ozone; Ozone production efficiency (OPE); KORUS-AQ; Chemical Transport model

1. Introduction

Air pollution in East Asia has been an important issue especially for densely populated mega-cities with the rapid development over the past few decades. Although stringent air pollution controls have been executed in countries including Japan, Korea, and recently China, surface ozone (O$_3$), which is a key secondary air pollutant that affects human health and the ecosystem, has shown an increasing trend over the past two decades (2000–2017) (Chang et al., 2017; Li et al., 2019). Moreover, key controlling factors for the O$_3$ formation still remain uncertain especially in East Asia (Park and Kim, 2014).

O$_3$ is photochemically produced in the lower troposphere from the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO$_x$ = NO + NO$_2$) (WHO, 2003). Identifying sources of O$_3$ precursors and quantifying the effect of the reduction of emissions on ambient O$_3$ levels are necessary to address the environmental threat that O$_3$ pollution poses to the public.

Reducing precursor emissions does not always lead to a reduction in O$_3$ levels because of the nonlinear relationship of O$_3$ with its precursor concentrations (Lin et al., 1988). The Korean government has put an effort on regulating major emission sectors such as mobile and industrial sources since the 1990s. As a result, emissions and ambient concentrations of NO$_x$ and VOCs showed significant
decreases in the Seoul Metropolitan Area (SMA), where almost half the population reside in (Kim and Lee, 2018). However, despite the successful reductions of precursor emissions, urban \(O_3\) levels have consistently increased nationwide during the past two decades (Susaya et al., 2013). Therefore, understanding the regional characteristics of photochemical \(O_3\) production based on the ambient VOCs or NO\(_x\) concentrations is essential to formulate an effective control policy (Liu et al., 1987).

There have been several studies using observed \(O_3\), NO\(_x\), and total reactive nitrogen (NO\(_y\)) from field campaigns to investigate the features of \(O_3\) production in both rural, urban, and industrial areas in the United States and Europe (Imhoff et al., 1995; Kleinman et al., 1994; Nunnermacker et al., 2000; Olszyna et al., 1994; Rickard et al., 2002; Trainer et al., 1993). In Korea, most studies have focused on identifying the contribution of various chemical and physical factors to explain \(O_3\) production characteristics in the SMA, as the increasing trend in ground level \(O_3\) is more evident in urban areas (Lee et al., 2007; Ryu et al., 2013). Kim et al. (2018) stated that the increasing trend of \(O_3\) is mainly because of NO\(_x\) reductions, and Shin et al. (2013) suggested a control strategy on solvent and traffic emissions of VOCs to reduce \(O_3\) levels in Seoul. Susaya et al. (2013) extended the study on ground level \(O_3\) in Seoul and conducted a trend analysis of urban air quality for six additional major cities, but did not cover any suburban or rural areas.

Along with observations, chemical transport models (CTMs) and box model simulations have been used to test the nonlinear sensitivity of \(O_3\) production to ambient conditions (Kleinman et al., 2002; Mazzuca et al., 2016; Ninneman et al., 2017; Zaveri et al., 2003). CTMs have been used as an effective tool for evaluating the emissions inventory and testing the atmospheric response to changes in precursor emissions (Jeong et al., 2012; Kim et al., 2015; Kim, 2011). However, simulated \(O_3\) concentrations in Korea and East Asia have generally been underestimated in CTMs (Han et al., 2008; Kang et al., 2016), which might be due to a combination of several factors including horizontal and vertical resolutions, uncertainty in meteorological parameters, vertical mixing schemes, and chemical mechanisms (Han et al., 2008; Kang et al., 2016).

In this study, we examine the characteristics of photochemical \(O_3\) production in Korea using aircraft (DC-8) measurements during the international KOREa-US cooperative Air Quality field study in Korea (KORUS-AQ). During the campaign, high \(O_3\) episodes exceeding 100 ppbv were reported along with high levels of reactive precursor (e.g., NO\(_x\), aromatic VOCs) mixing ratios. We compare the results of an observation-constrained 0-D photochemical box model with a 3-D global CTM to analyze the sensitivity of \(O_3\) production to various atmospheric processes including chemical mechanisms, emissions, and vertical mixing. We also conduct several sensitivity simulations by perturbing emissions of \(O_3\) precursors and suggest the possible implication for future \(O_3\) levels based on the emissions reduction plan by the Korean Ministry of Environment.

2. Methods

2.1 KORUS-AQ field campaign

The atmospheric chemical composition over the Korean peninsula is influenced by a combination of many different sources. Due to the high population density, local anthropogenic emissions are dominant in urban cities, such as the SMA and Busan. Local emissions from power plants, petrochemical and other manufacturing industries also affect regional air quality (NIER and NASA, 2017). Furthermore, a large proportion of the country is covered with mountains, which serve as a profound source of biogenic emissions (Kim et al., 2014) (Figure 1). Meanwhile, due to the geographic location and meteorological conditions, Korea is often influenced by anthropogenic emissions and soil dust transported from China (Lee et al., 2019) and biomass burning from Siberia (Jung et al., 2016).

![Figure 1: Spatial distribution of observed and simulated \(O_3\). Spatial distribution of the observed and simulated \(O_3\) mixing ratios along the DC-8 flight track during 13–16 LST (averaged below 1.5 km). Geographic locations of industrial and populated large cities are indicated with white circles. DOI: https://doi.org/10.1525/elementa.394.f1](https://doi.org/10.1525/elementa.394.f1)
KORUS-AQ is an international air quality field study that was held in Korea, May–June 2016, which aimed to understand the factors controlling air quality across urban, rural, and coastal interfaces. During the campaign, extensive surface and airborne observations with high temporal resolutions were conducted using various instruments.

Measurements of reactive gaseous species onboard the NASA DC-8 aircraft enable a comprehensive analysis on the chemical formation and distribution of air pollutants. Airborne measurements used in this study include O3, NO, NO2, NOy, OH, HOx, and speciated VOCs. O3, NOy, and NOx measurements were conducted using the NCAR NO–NOy instrument which uses the chemiluminescence of NO by reaction with O3 with a detection limit of 5–10 pptv/s (Ridley and Grahek, 1990). OH and HOx were measured using the Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) with a detection limit of 0.01 and 0.1 pptv (Brune et al., 1995).

Speciated VOCs including alkanes, alkenes, and aromatic hydrocarbons were collected in Whole Air Samples (WAS) and identified by laboratory analysis using gas chromatography with flame ionization detection, electron capture detection, and mass spectrometric detection. The detection limits for the VOCs are 2–3 pptv (https://airbornescience.nasa.gov/instrument/WAS_UCI). Isoprene, acetaldehyde (CH3CHO), and formaldehyde (HCHO) measurements were also conducted using the Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) (Müller et al., 2014) and the Compact Atmospheric Multispecies Spectrometer (CAMS) (Richter et al., 2015).

All research flights during the campaign landed and returned back to the air base at 16 LST (Local Standard Time), and O3 observations showed highest values in the planetary boundary layer (PBL) during 13–16 LST. In order to focus on O3 and its production characteristics, we used 60 second averaged DC-8 observations for cases where the plane flew over inland areas or near the coast with an altitude below 1.5 km during the photochemically active hours, 13–16 LST, in our analysis.

### 2.2 O3 production efficiency (OPE) during KORUS-AQ

The production of O3 varies nonlinearly with VOCs and NOx concentrations (Lin et al., 1988). The OPE, which is an effective metric to examine the nonlinearity of O3 production (Lin et al., 1988), is defined as the number of O3 molecules produced per NOx molecules consumed, $P_{O3}/L_{NOx}$, assuming a steady state for NOx. Values are typically high (>10) in a clean rural region and low (<5) in a polluted urban region (Kleinman et al., 2002). In this study, we use this metric to understand the characteristics of O3 formation in Korea.

Several observation-based studies used the regression slopes of the observed concentrations of O3 versus NOx oxidation products (NOy = NOy − NOx) to obtain the OPE, and reported values ranging from 2 to 12, where the lowest values were observed in plumes with high NOx conditions (Zaveri et al., 2003). However, this approach may lead to an ambiguous interpretation because observations contain air parcels with different photochemical histories and ages (Trainer et al., 2000). Furthermore, the magnitude of NOx mixing ratios may differ depending on reactive nitrogen species that are included in defining NOx (NOy, PANs, HONO, NOy, NOy, N2O5, organic nitrates, particulate nitrate, etc.). To avoid such issues, we explicitly calculate the instantaneous formation ($F_{O3}$), destruction ($D_{O3}$), net production rates of O3 ($P_{O3} = F_{O3} - D_{O3}$) and the loss rate of NOx ($L_{NOx}$) using equations (1–4) below in 3-D chemical transport simulations that we discuss in detail in section 2.3.

Equation (1) describes the daytime O3 formation starting with the reaction of NO with the hydroperoxy radical (HO2) and organic peroxy radicals (RO$_2$) to produce NOx. Equation (2) represents the O3 destruction rate, which includes the photolysis (followed by the reaction of O(1D) with H2O) and the reaction of O$_3$ with HOx, OH, VOCs (alkenes) and NO (followed by the reaction of NOx with OH). NOx loss rate is calculated by equation (4), where NOx is oxidized by OH to produce HNO3, which is scavenged by wet or dry deposition (Finlayson-Pitts and Pitts Jr., 2000).

$$F_{O3} = k_{NOx-NO2}[NO][HO2] + \sum k_{NOx-RO2}[NO][RO_2]$$  \(1\)

$$D_{O3} = k_{OH}[O(1D)][H2O] + k_{NO-NO2}[NO][HO2] + k_{OHx-NOx}[NOx][OH] + \sum k_{ROx-NOx}[VOC][NOx][OH]$$  \(2\)

$$P_{O3} = F_{O3} - D_{O3}$$  \(3\)

$$L_{NOx} = k_{NOx-NO2}[NOx][OH]$$  \(4\)

Instantaneous OPE is the rate of net O3 production per the rate of NOx loss, which can be obtained using equation (5).

$$OPE = \frac{P_{O3}}{L_{NOx}}$$  \(5\)

Time-dependent observation-constrained O-D photochemical box modeling was conducted by the NASA Langley Research Center (LaRC) to simulate the oxidation and photochemical processes during KORUS-AQ. Model inputs derived from 1 second-merged DC-8 measurements of temperature, pressure, photolysis rates, O3, CO, NO, H2O, CH3OH, HNO3, PAN, HCHO, and VOCs were used as constraints to calculate diurnal steady state concentrations of radical species. Using a customized chemical mechanism with reaction rates based on NASA JPL 2012 (https://jpldataeval.jpl.nasa.gov/index.html) and IUPAC 2006 recommendations, concentrations of NOx, OH, HOx, and RO2 were simulated (Crawford et al., 1999; Schroeder et al., 2017). The model also calculated instantaneous production and loss rates of O3 and NOx, as described in equations (1–4). The box model calculations include dry deposition loss, and rainout loss based on Logan et al. (1981), but do not include any heterogeneous chemistry and convection. A full list of detailed chemical mechanisms used in the box model can be found in the supporting information of Schroeder et al. (2017).

Using the box model results and DC-8 measurements, instantaneous $F_{O3}$, $D_{O3}$, net $P_{O3}$, and $L_{NOx}$ rates were calculated along the DC-8 flight track. Box model predictions...
of NO$_x$, OH, and peroxy radicals are in good agreements with observations (Figure S1), and are further discussed in (Schroedel et al., in prep.). Therefore, we assume that the observation-constrained box model represents the true atmosphere and we use the box-model calculated OPE values to evaluate 3-D model simulations.

### 2.3 GEOS-Chem Chemical Transport Model

We use a 3-D global chemical transport model (GEOS-Chem v10-01) (Bey et al., 2001) and its nested configuration to simulate gas and aerosol species in Korea during the campaign. The model is driven by GEOS-FP (Forward Processing) assimilated meteorology provided by the GMAO at NASA Goddard Space Flight Center. The nested model covers the East Asian domain ($70^\circ$E–$140^\circ$E, $15^\circ$N–$55^\circ$N) with a horizontal resolution of $0.25^\circ \times 0.3125^\circ$ and 47 vertical layers. Boundary conditions are provided from a global simulation with $2^\circ \times 2.5^\circ$ horizontal resolution. A one-month spin-up was conducted for both the global and nested simulations.

We update the default NO$_x$-O$_3$-VOC chemistry to represent all the VOC species with updated kinetic rates and photolysis parameters. We also update the default NO$_x$-hydrocarbon aerosol chemistry to represent aromatic hydrocarbons with updated kinetic rates and photolysis parameters. We update the default NO$_x$-VOC chemistry to represent aromatic hydrocarbons with updated kinetic rates and photolysis parameters.

### 3. Effect of aromatic chemistry on simulated O$_3$ production

We first evaluate the baseline model (BASE) performance by comparing observed and simulated O$_3$ mixing ratios during the campaign. Figure 1 shows the spatial distribution of observed and simulated mean O$_3$ mixing ratios averaged for 13–16 LST of the campaign below 1.5 km along the DC-8 flight track. The model generally captures the observed spatial distribution, i.e., high in urban areas and low in rural areas, but fails to capture the magnitude of measurements.

Figure 2 shows scatter-plot comparisons of the observed and simulated O$_3$ and NO$_x$ mixing ratios during the campaign. The BASE model significantly underestimates O$_3$ and NO$_x$, although no significant low biases are shown for reactive VOCs (Figure S2). We find that the update of aromatic chemistry in the model (AROM) substantially increases O$_3$ mixing ratios, which are in better agreement with the observations relative to those of the BASE model. This increase in O$_3$ production mainly results from more NO to NO$_2$ conversion driven by aromatic VOCs oxidation, especially by toluene and xylene, which show decreases with the update in the model. As a result, we find a large low bias of simulated NO$_x$ levels in the AROM model. This bias can be attributed to the increase in NO$_x$ production from aromatic VOCs.

### Table 1: Summary of the model (GEOS-Chem) simulations conducted in this study. DOI: https://doi.org/10.1525/elementa.394.11

<table>
<thead>
<tr>
<th>Model name</th>
<th>Chemistry</th>
<th>PBL height</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>Default</td>
<td>Default</td>
<td>Default</td>
</tr>
<tr>
<td>AROM</td>
<td>Updated aromatic chemistry</td>
<td>Default</td>
<td>Default</td>
</tr>
<tr>
<td>PBL</td>
<td>Updated aromatic chemistry</td>
<td>Scaled PBL height</td>
<td>Default</td>
</tr>
<tr>
<td>PBL+NO$_x$</td>
<td>Updated aromatic chemistry</td>
<td>Scaled PBL height</td>
<td>50% increased NO$_x$</td>
</tr>
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is also associated with increased formation of organic nitrates and PAN (Figure S2), which are important NO reservoirs produced during the oxidation of VOCs. Despite the decrease in NO mixing ratios, we find that the chemistry update effectively converts NO to organic nitrates, resulting in better agreements with observations.

We compare the instantaneous O₃ formation, O₃ destruction, and NO₃ loss rates from the model as calculated using equations (1–4) with results from the observation-constrained box model described in section 2.2. Each term comprises the OPE and mean values averaged during the campaign are shown in Figure 3.

The O₃ formation rate, \( F_{O_3} \), is calculated as the sum of the reaction rates of peroxy radicals and NO. Compared to the BASE simulation, updated aromatic chemistry increases both “HO₂+NO” and “RO₂+NO” terms but still underestimates \( F_{O_3} \) compared to the box model. Figure S1 shows that RO₂ is overestimated and HO₂ is underestimated in GEOS-Chem. Therefore, NO₃ underestimation appears to be the main cause of the low formation rates compared to the box model.

While the O₃ destruction rate, \( D_{O_3} \), is also underestimated in GEOS-Chem, O₃ losses by the “O₂+HO₂” and “NO₂+OH” reactions show largest discrepancies between the two models (Figure 3 (b)). An O₂ destruction increase by the “O₂+HO₂” reaction in the AROM model is associated with the increase in HO₂ mixing ratios. Despite the increase in the AROM model, the “O₂+HO₂” term is still smaller in GEOS-Chem than that of the box model, which can be explained by the underestimation of O₂ and HO₂ mixing ratios (Figure S1). The overestimation of >C3 alkenes (Figure S2) causes the overestimation of the “O₃+VOCs” term. The “NO₂+OH” contribution, which represents an O₃ loss by the reaction with NO, does not show a significant change from the BASE model to the AROM model. In both model runs, the underestimation of NO₃ shown in Figure 2 is the main contributor to the underestimation of O₃ loss rates by the “NO₂+OH” reaction relative to the box model result.

The difference between \( F_{O_3} \) and \( D_{O_3} \) is the net O₃ production rate, which is shown in Figure 3 (c). Updated aromatic chemistry increases the simulated net O₃ production and NO₃ loss rates in GEOS-Chem by 37% and 22%. This explains the increase in O₃ and the decrease in NO₃ mixing ratios shown in Figure 2. However, because NO₃ is highly underestimated in GEOS-Chem, \( L_{NO_3} \) underestimation still exists.

NO₃ underestimation may imply either the underestimation of emissions or model uncertainties in chemical, thermodynamic or physical processes such as NO₃ recycling, NO₂ partitioning or boundary layer mixing (Bertram et al., 2013), which will be further discussed in section 4.2.

4. Sensitivity of the model to PBL height and NO₃ emissions

4.1 Model sensitivity to PBL height

The PBL height (i.e., mixing layer height) is a key factor that controls the vertical mixing and surface concentrations of pollutants (Tong et al., 2011). In this section, we examine the sensitivity of the model to changes in PBL heights, which are constrained by the lidar observations. In addition, we conduct model sensitivity analyses to anthropogenic NOx emission changes and their effects on the simulated O₃ formation.

Figure 2: Scatter-plot comparisons of observed and simulated O₃ and NO₃. Simulated (GEOS-Chem) versus observed (DC-8) concentrations of O₃ and NO₃ below 1.5 km during 13–16 LST. For all panels the axes indicate DC-8 observations (x-axis) and simulations (y-axis). The regression equation are stated in the upper corners. The normalized mean bias (NMB) between the model and observation is calculated as \( \frac{\sum_{i=1}^{N} (M_i - O_i)}{N} \), where N denotes the total number of data points, M indicates the model value and O indicates the observed value. DOI: https://doi.org/10.1525/elementa.394.f2
Previous studies have reported that air quality models generally overestimate the daytime evolution of the PBL heights compared to lidar or ceilometer measurements (Haman et al., 2014; Scarino et al., 2014). Scarino et al. (2014) described that the discrepancy could be due to model resolutions, which are generally too coarse to account for the sub-grid scale variation of terrain heights, while Haman et al. (2014) explained that the modeled PBL showed too rapid growth driven by faster wind speeds than observations.

PBL heights are commonly observed by the inversion of the potential temperature profile or as a peak in low level wind (Grossman and Gamage, 1995; Holzworth, 1964). Lidar backscatter profiles are also widely used to examine the structure and variability of PBL heights (Brooks, 2003). During the campaign, PBL heights were measured at Seoul National University (SNU, 126.95°E, 37.46°N) using lidar observations with the retrieval algorithm introduced by Brooks (2003) and are used for the model evaluation in this study. Figure 4 compares simulated versus observed hourly PBL heights at SNU averaged for the campaign and we find large discrepancies of up to a factor 1.3 during 13–15 LST in the model relative to the lidar-derived values.

**Figure 3: Comparison of simulated $F_{O_3}$, $D_{O_3}$ and OPE.** Average a) $O_3$ formation rate, b) $O_3$ destruction rate, and c) OPE during the campaign. Different shades indicate each term that comprises the total quantities. DOI: https://doi.org/10.1525/elementa.394.f3
The lidar-derived PBL height indicates the height of transition from a particle-rich layer near the surface to a cleaner layer aloft. Therefore, lidar-derived PBL heights are often higher than the meteorological transition heights during the nighttime when the residual layer and mixing layer coexist (Bravo-Aranda et al., 2017). Due to the residing or transported aerosol layer existing above 0.7–0.8 km, there could be few cases where the retrieved nighttime PBL heights might be overestimated. However, these cases did not affect the average diurnal profile of the whole period and even for our analysis, which mainly focuses on the daytime.

In order to test the effect of boundary layer mixing within the PBL in the model, we used average diurnal profiles of the PBL to calculate hourly scale factors based on the discrepancy between the model and lidar observations at SNU. Although the hourly scale factors are based on model evaluation at only one grid box, the same scale factors were applied to other grid boxes for the rest of South Korea. The scaled PBL heights are lower in the daytime and higher in the nighttime compared to the PBL heights in the baseline model, reducing the gap between the model and lidar observations as shown in Figure 4.

Constraining the daytime PBL heights based on the lidar-derived observations increases O$_3$ and its precursors mixing ratios in the model. Correspondingly, both the $P_0$ and $L_{NO}$ terms increase and show better agreements with the box model results (Figure 3).

Figure 5 shows the mean vertical profiles of NO$_x$ mixing ratios averaged in urban and rural regions, respectively, and over the whole Korea. Urban regions include major metropolitan cities such as the SMA, Busan, Daegu and Ulsan (indicated in Figure 1). The AROM model fails to capture the vertical gradient shown in DC-8 observations.

**Figure 4:** Diurnal profiles of observed (lidar) and simulated PBL heights. Mean diurnal profiles of modeled (colored) and lidar-derived (black) PBL heights at Seoul National University. Red and blue solid lines each indicate the modeled PBL height with no modification and the constrained PBL height using hourly scale factors, respectively. DOI: [https://doi.org/10.1525/elementa.394.f4](https://doi.org/10.1525/elementa.394.f4)

**Figure 5:** Vertical profiles of observed and simulated NO$_x$. Mean vertical profiles of observed (black) and simulated NO$_x$ mixings. Colored lines indicate simulated NO$_x$ profiles, and dotted lines indicate results using scaled PBL heights. The number of averaged data is denoted on the left sides of each panel. DOI: [https://doi.org/10.1525/elementa.394.f5](https://doi.org/10.1525/elementa.394.f5)
and shows that model underestimation is mostly located near the surface. Although the simulated NO$_x$ mixing ratios show a 5% increase when the PBL height is scaled based on the observation (Figure 2), this is not large enough to reduce the discrepancy in the model. Moreover, NO$_x$ levels are still significantly underestimated in the model for both urban and rural areas.

4.2 Model sensitivity to local NO$_x$ emissions
Based on the model underestimation of surface NO$_x$ levels we increased NO$_x$ emissions in South Korea by 50%. Figure 5 shows that when the emissions are increased, simulated NO$_x$ mixing ratios are significantly enhanced and become much closer to the observations especially above 1 km. It appears that the model still underestimates observed NO$_x$ levels at the surface and the further increase in NO$_x$ emissions could decrease the simulated discrepancy, but our analysis of total reactive nitrogen (NO$_3$) and O$_3$ production characteristics below does not allow for this.

We further separated the analyses into four different periods (dynamic weather, stagnant, extreme pollution, blocking pattern) based on synoptic weather conditions during the campaign (Peterson et al., in review) to separate the effects of transboundary transport versus local emissions on ambient NO$_x$ and NO$_2$ levels in Korea. Figure S3 shows mean sea level pressures (SLP) and wind vectors in the model for each period. Unlike the dynamic weather period, the influence of local emissions was dominant for the Korean peninsula during the stagnant period due to weak wind speeds and inefficient mixing associated with a persistent high pressure system located over East Asia. We found the highest levels of surface pollutants such as O$_3$ and PM$_{2.5}$ during the extreme pollution period, exceeding the Korea air quality standards (NIER and NASA, 2017). During this period, due to weakening of the polar jet stream over Central Asia and the weaker vertical motion, direct transport from China accompanied with the westerlies was important, causing high levels of pollutants in surface air in Korea (Peterson et al., in review).

Figure 6 shows that during the dynamic weather and extreme pollution periods, modeled NO$_3$ and NO$_2$ levels are higher than observations in all four sensitivity simulations. In contrast, during the stagnant and blocking pattern periods with dominant effects of local emissions, model results with increased NO$_x$ emissions show better agreement with observations, especially in urban areas. This indicates that local NO$_x$ sources are likely underestimated in the inventory.

Model results from the PBL+NO$_x$ model show increases in NO$_x$ mixing ratios as well as $L_{NOx}$ (Figures 2 and 3). We find model improvements in the regression slope of $L_{NOx}$ (0.83) and correlation (0.58) with the box model relative to other simulations. Model performance in simulating O$_3$ also shows improvements in terms of both the normalized mean bias (~11%) and correlation (0.70) with observations.

Despite the 50% increase in NO$_x$ emissions, Figure 2 shows that the model still underestimates NO$_x$ mixing ratios compared to the observations. Recent studies suggest that additional mechanisms such as nitril chloride chemistry (Sarwar et al., 2012) and nitrate photolysis (Ye et al., 2017) can improve the simulations of nitrogen chemistry in air quality models. Choi et al. (2019) implemented particulate nitrate photolysis in GEOS-Chem using parameters from Ye et al. (2017) and found a significant improvement in particulate nitrate, HONO, and NO$_2$ simulations. Our study focuses on constraining NO$_x$ emissions based on the model evaluation regarding O$_3$ production characteristics, but there still remains a limitation. A further study is necessary to account for the additional NO$_3$ chemistry that is currently absent in the model.

Figure 7 shows the VOCs and NO$_x$ dependency of instantaneous OPEs calculated in the box model and GEOS-Chem. VOCs include ethane, propane, large alkanes.
>C4), large alkenes (>C3), benzene, toluene, xylene, isoprene, monoterpenes, methyl ethyl ketone (MEK), and acetaldehyde. In the observation-constrained box model, low OPE values are shown above the 10:1 line, indicating that urban areas in Korea are VOC-limited. Rural areas tend to have higher OPE values that are located below the 10:1 line. General characteristics of the observed OPE dependency on precursor concentrations also appear in GEOS-Chem. However, due to the underestimation of NOx, GEOS-Chem results are slightly shifted to a NOx-limited regime compared to the box model.

The simulated results with scaled PBL heights shown in Figure 7 (c) and (d) show larger scatters compared to Figure 7 (b), elongating the location of the points diagonally, which is caused by the lower PBL height. Decreased PBL heights tend to decrease species mixing ratios in upper levels (~1.5 km) compared to the base PBL simulation. This results in decreases of NOx and VOCs mixing ratios around 1.5 km, which correspond to the data points located in the lower left corners in Figure 7 (c) and (d).

The overall comparison of GEOS-Chem to the observation-constrained box model indicates that the PBL+NOx model (Figure 7 (d)) shows the best performance in reproducing the observed O3 production regimes in Korea.

Considering the underestimation of aromatic VOCs in GEOS-Chem (Figure S2), we additionally doubled toluene emissions to investigate the sensitivity of OPE to aromatic VOCs emissions. Although we see a slight increase in the OPE, a negligible change is found compared to Figure 7 (d) and therefore we conclude that the OPE is more sensitive to NOX emissions than aromatic VOCs emissions in Korea.

5. Sensitivity of OPE to emission changes in Korea

The Korean government aims to achieve a 30% reduction of domestic emissions (from industries, powerplants, diesel cars, etc) by 2022 as part of the PM2.5 concentrations reduction policy (Ministry of Environment, 2017). However, this emission change may also have a profound impact on O3 levels in Korea. To estimate the effect of regulation we conduct sensitivity simulations and investigate the change in O3 and the OPE with respect to emissions control in the future. Using our best-performing model (PBL+NOx) as the base run, we compare the results with 30% decreased NOX and anthropogenic VOCs emissions over Korea.

Figure 8 shows the spatial distributions of simulated ground level OPEs during May 2016. Typical features of the OPE such as high in clean regions and low in polluted regions are well captured. In the base run, we find maximum OPE of ~20 along the mountain range located in the middle, where biogenic VOCs emissions are dominant, and minimum values in high NOx regions such as the SMA. In both the sensitivity runs the reduction in emissions increases the OPE throughout the country. When only NOx emissions are controlled, the OPE reaches up
to 30 in rural regions, indicating that these NO\textsubscript{x}-limited regions become much more efficient in producing O\textsubscript{3} with the same amount of NO\textsubscript{x}. With NO\textsubscript{x} and VOCs emissions controlled together, the OPE increase is less prominent, showing a maximum of ~25. 

**Figure 9** shows the OPE, O\textsubscript{3} mixing ratios, and NO\textsubscript{x} lifetime changes as a response to the emissions control. We find that the decrease in precursor emissions does not have a linear impact on O\textsubscript{3}. In rural regions where NO\textsubscript{x} plays the major role in O\textsubscript{3} production, O\textsubscript{3} mixing ratios decrease and the NO\textsubscript{x} lifetime increases due to less oxidation by OH (i.e., decrease in NO\textsubscript{x} loss). In urban (e.g., Seoul, Busan) and industrial areas (e.g., Daesan, Pohang, Ulsan, Yeosu) which are under VOC-limited conditions, O\textsubscript{3} increases (~6)

**Figure 8:** Spatial distributions of simulated OPEs and responses to emission change. Spatial distributions of simulated OPE at surface level and responses to NO\textsubscript{x} and VOCs emission changes in South Korea. All simulations are run using the same configuration as the PBL+NO\textsubscript{x} model. Major metropolitan and industrial areas are indicated with stars and circles, respectively. DOI: https://doi.org/10.1525/elementa.394.f8

**Figure 9:** Spatial distributions of simulated OPE, O\textsubscript{3}, and NO\textsubscript{x} lifetime changes. Spatial distributions of changes (modified emissions run minus base run) in simulated surface a) OPE, b) O\textsubscript{3} levels, and c) NO\textsubscript{x} lifetime as a response to emission changes. Major metropolitan and industrial areas are indicated with stars and circles, respectively. DOI: https://doi.org/10.1525/elementa.394.f9
ppbv) and NO\textsubscript{x} lifetimes show noticeable decreases as a result of NO\textsubscript{x} reductions. With concurrent VOCs reductions, although there are some signals of O\textsubscript{3} increase in industrial areas the magnitudes are significantly smaller than those without VOCs reductions, and O\textsubscript{3} decreases are shown in major metropolitan areas.

Table 2 summarizes the changes of O\textsubscript{3} production characteristics that appear in different regimes in the sensitivity simulations. In VOC-limited regions (i.e., urban and industrial), a decrease in NO\textsubscript{x} emissions results in an increase in O\textsubscript{3} levels. Two contributing factors, an increase of the O\textsubscript{3} formation rate due to faster NO\textsubscript{3} recycling (i.e., higher OPE) and a decrease of the O\textsubscript{3} destruction rate via NO\textsubscript{x} titration result in an increase of O\textsubscript{3} mixing ratios. Despite the decrease in ambient NO\textsubscript{x} mixing ratios (~36%), \(F_{O_3}\) shows an increase (+9%) due to the efficient HO\textsubscript{2}–NO\textsubscript{x} cycling. Because the decrease in \(L_{NO_3}\) (~19%) reflects the decrease of NO\textsubscript{x} titration, we can imply that the impact of less titration is the predominant factor that causes the O\textsubscript{3} increase in these areas. With an additional VOCs reduction, the decrease of O\textsubscript{3} precursors results in a decrease of net production. On the other hand, NO\textsubscript{x} titration is of less importance for O\textsubscript{3} levels in NO\textsubscript{x}-limited regions. The 30% decrease in precursor emissions does not directly decrease O\textsubscript{3} mixing ratios by 30% because of the nonlinear chemistry. However, the simulation results show that the tendency of O\textsubscript{3} production follows the change in precursor emissions in rural areas.

6. Summary and Conclusions
An observation-constrained box model and a 3-D chemical transport model (GEOS-Chem) were used to obtain instantaneous O\textsubscript{3} production efficiencies (\(OPE = P_{O_3}/L_{NO_3}\)) in Korea during May–June 2016. The sensitivity of simulated OPE was tested to examine the effect of aromatic chemistry and anthropogenic NO\textsubscript{x} and VOC emissions on O\textsubscript{3} production.

Table 2: Relative differences of O\textsubscript{3}, NO\textsubscript{x}, O\textsubscript{3} production, and destruction terms with respect to the base run. DOI: https://doi.org/10.1525/elementa.394.t2

<table>
<thead>
<tr>
<th>Urban &amp; Industrial areas</th>
<th>Rural areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>(30% \text{NO}_3) decrease</td>
<td>(30% \text{NO}_x) &amp; VOCs decrease</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>(+3%)</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>(-36%)</td>
</tr>
<tr>
<td>(F_{O_3})</td>
<td>(+9%)</td>
</tr>
<tr>
<td>(D_{O_3})</td>
<td>(-9%)</td>
</tr>
<tr>
<td>(P_{O_3})</td>
<td>(+13%)</td>
</tr>
<tr>
<td>(L_{NO_3})</td>
<td>(-19%)</td>
</tr>
<tr>
<td>OPE</td>
<td>(+40%)</td>
</tr>
</tbody>
</table>

\*The relative difference between the base and sensitivity run is calculated as \(\text{Difference} = \frac{A - B}{B} \times 100\%\), where S indicates the sensitivity run and B indicates the base run value.

Based on box model calculations, O\textsubscript{3} production in urban areas in Korea showed VOC-limited characteristics and OPE values were less than 10 in general. In rural areas, O\textsubscript{3} production tended to be more NO\textsubscript{x}-limited and OPE values were higher than 20. Average OPE values over Korea calculated from the box model and GEOS-Chem with default chemistry and updated aromatic chemistry were 19.8, 16.5, and 17.2, respectively.

Our model evaluation showed that aromatic chemistry itself can increase the average net O\textsubscript{3} production in Korea by 37%. The overestimation of the daytime PBL height in the model was found to be responsible for ~10% decrease in both the net O\textsubscript{3} production and NO\textsubscript{x} loss rates. The vertical distribution of simulated and observed NO\textsubscript{x} mixing ratios and comparison of O\textsubscript{3} production regimes in different model runs clearly showed the underestimation of NO\textsubscript{x} was mainly caused by the underestimation of NO\textsubscript{x} emissions in the current inventory. Increasing 50% of NO\textsubscript{x} emissions in the model improved model performance in reproducing the observed O\textsubscript{3} production and NO\textsubscript{x} loss rates.

Sensitivity tests showed that the 30% decrease in anthropogenic emissions increases the OPE throughout the country, making rural regions ~2 times more efficient in producing O\textsubscript{3}. However, without the VOCs emissions reduction, the NO\textsubscript{x} emissions reduction alone can result in significant increases in O\textsubscript{3} levels in both urban and industrial regions. This implies the importance of concurrent emission reductions for both NO\textsubscript{x} and VOCs in order to effectively reduce O\textsubscript{3} levels in Korea.

Data Accessibility Statement
Observational data from KORUS-AQ used in this study can be downloaded in the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) format through the data archive website (https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq).

Supplemental files
The supplemental files for this article can be found as follows:

- **Figure S1.** Comparison of observed and simulated NO\textsubscript{2} and radical species. DOI: https://doi.org/10.1525/elementa.394.s1
- **Figure S2.** Comparison of observed and simulated organic nitrates, PAN, and speciated VOCs. DOI: https://doi.org/10.1525/elementa.394.s1
- **Figure S3.** Mean sea level pressures (SLP) and wind vectors in GEOS-Chem during four different synoptic weather patterns in East Asia. DOI: https://doi.org/10.1525/elementa.394.s1
- **Table S1.** Gas phase reactions of aromatic chemistry in GEOS-Chem based on Henze et al. (2008). DOI: https://doi.org/10.1525/elementa.394.s1
- **Table S2.** Gas phase reactions of aromatic chemistry added in GEOS-Chem based on Porter et al. (2017). DOI: https://doi.org/10.1525/elementa.394.s1
- **Table S3.** Aromatic species and reaction intermediates added in GEOS-Chem. DOI: https://doi.org/10.1525/elementa.394.s1
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Competing interests

The authors have no competing interests to declare.

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• Contributed to analysis and interpretation of data: YJO, RJP, JRS, JHC
• Drafted and/or revised the article: YJO, RJP, JHC, SWK
• Approved the submitted version for publication: RJP, JHC

References


