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### Title

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### Permalink

<https://escholarship.org/uc/item/0wt202qv>

### Journal

Elementa: Science of the Anthropocene, 8(1)

### ISSN

2785-4558

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### Publication Date

2020

### DOI

10.1525/elementa.400

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## RESEARCH ARTICLE

# Observation-based modeling of ozone chemistry in the Seoul metropolitan area during the Korea-United States Air Quality Study (KORUS-AQ)

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The Seoul Metropolitan Area (SMA) has a population of 24 million and frequently experiences unhealthy levels of ozone ( $O_3$ ). In this work, measurements taken during the Korea-United States Air Quality Study (KORUS-AQ, 2016) are used to explore regional gradients in  $O_3$  and its chemical precursors, and an observationally-constrained 0-D photochemical box model is used to quantify key aspects of  $O_3$  production including its sensitivity to precursor gases. Box model performance was evaluated by comparing modeled concentrations of select secondary species to airborne measurements. These comparisons indicate that the steady state assumption used in 0-D box models cannot describe select intermediate species, highlighting the importance of having a broad suite of trace gases as model constraints. When fully constrained, aggregated statistics of modeled  $O_3$  production rates agreed with observed changes in  $O_3$ , indicating that the box model was able to represent the majority of  $O_3$  chemistry.

Comparison of airborne observations between urban Seoul and a downwind receptor site reveal a positive gradient in  $O_3$  coinciding with a negative gradient in  $NO_x$ , no gradient in  $CH_2O$ , and a slight positive gradient in modeled rates of  $O_3$  production. Together, these observations indicate a radical-limited (VOC-limited)  $O_3$  production environment in the SMA. Zero-out simulations identified  $C_{7+}$  aromatics as the dominant VOC contributors to  $O_3$  production, with isoprene and anthropogenic alkenes making smaller but appreciable contributions. Simulations of model sensitivity to decreases in  $NO_x$  produced results that were not spatially uniform, with large increases in  $O_3$  production predicted for urban Seoul and decreases in  $O_3$  production predicted for far-outlying areas. The policy implications of this work are clear: Effective  $O_3$  mitigation strategies in the SMA must focus on reducing local emissions of  $C_{7+}$  aromatics, while reductions in  $NO_x$  emissions may increase  $O_3$  in some areas but generally decrease the regional extent of  $O_3$  exposure.

**Keywords:** Ozone; Air quality; Photochemistry; Korea; Seoul

## 1. Introduction

Rapid industrial growth and urban expansion in South Korea over the past several decades has been accompanied by increased exposure to criteria pollutants such as

ozone ( $O_3$ ), particularly in the Seoul Metropolitan Area (SMA) (Jo and Nam, 1999; Ghim and Chang, 2000; Chang et al., 2017; Kim and Lee, 2018; Seo et al., 2018; Fleming et al., 2018). Exposure to high levels of  $O_3$  is deleterious to

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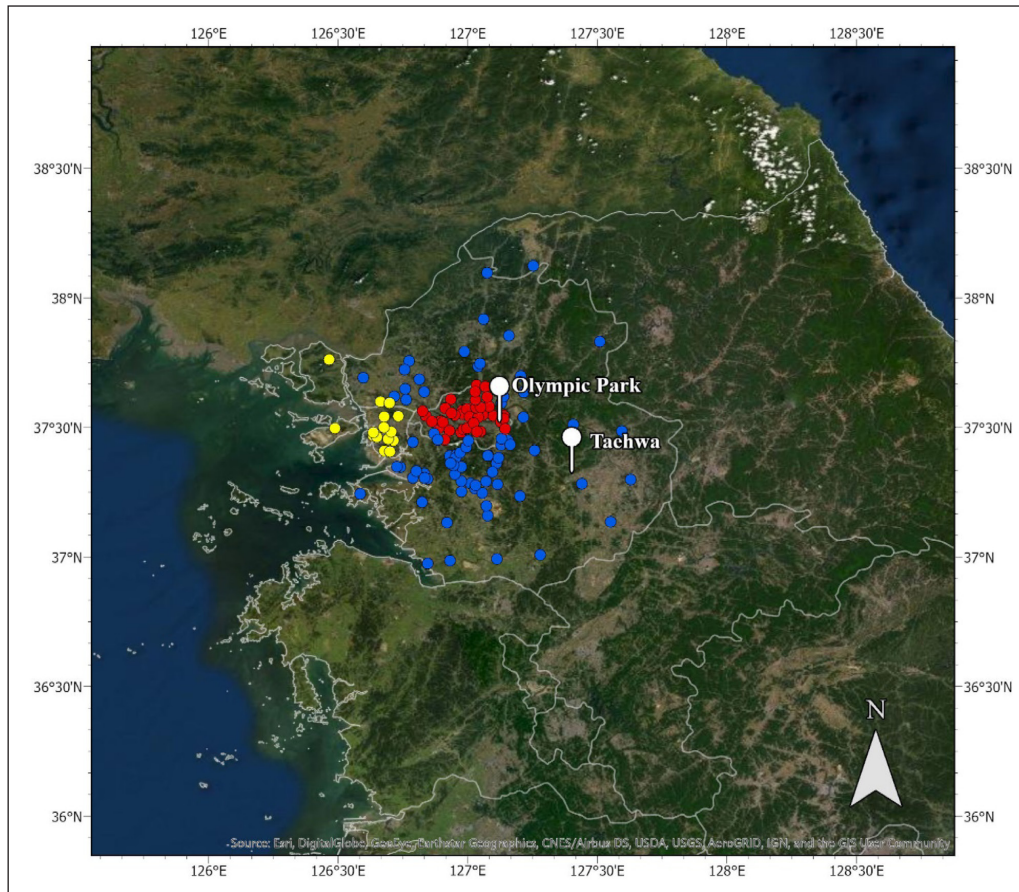
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human health and the environment, and has been linked to increased human mortality and decreased crop yields (Haagen-Smit et al., 1952; Heck et al., 1982; Chameides et al., 1999; Kim et al., 2004; Jerrett et al., 2009). Fleming et al. (2018) noted that the annual fourth-highest maximum daily 8-hour average (MDA8)  $O_3$  value increased at an average rate of 2 ppbv per year between 2000–2014, and the number of days with 8-hour  $O_3$  values greater than 70 ppbv increased by up to two days per year across South Korea. While ambient  $O_3$  levels in South Korea have been increasing for some time, recent work by Jung et al. (2018) suggests that the rate of increase has risen in recent years. Broader analysis of trends across greater East Asia has shown that  $O_3$  values throughout the region have been increasing in the past decade, raising questions about the influence of regional versus local emissions on air quality in the SMA (Chang et al., 2017). However, the trends noted by Fleming et al. (2018) and Chang et al. (2017) were significantly more prevalent at urban sites in South Korea than at rural sites, indicating that, while long-range transport may contribute to increasing background levels of  $O_3$ , local emissions must be addressed in order to improve air quality. In this work, data collected during the Korea United States Air Quality Study (KORUS-AQ) are used to better understand the primary drivers for  $O_3$  in the SMA.

There are no primary emission sources of  $O_3$ , and instead it is formed through the photochemical interaction between emissions of volatile organic compounds (VOCs) and nitrogen oxides ( $NO_x = NO + NO_2$ ). Therefore, strategies to reduce  $O_3$  in the SMA must focus on reducing local and regional emissions of these precursor species. However,  $O_3$  chemistry is complex and varies non-linearly with respect to precursor concentrations, and therefore a detailed understanding of the sensitivity of local  $O_3$  formation to changes in the precursor environment is essential for drafting effective mitigation strategies. This non-linear response of  $O_3$  to concentrations of its precursors results in the presence of two distinct photochemical regimes, often referred to as “ $NO_x$ -limited” and “radical-limited” (also called “VOC-limited” due to the relationship between VOCs and radicals) (Sillman et al., 1990; Kleinman, 1994). Understanding local  $O_3$  sensitivity (i.e. whether  $O_3$  formation is  $NO_x$ -limited or radical-limited) is a crucial first step for drafting targeted mitigation strategies. Formation of  $O_3$  in the background troposphere is typically  $NO_x$ -limited, while the urban areas around many megacities are often radical-limited (Duncan et al., 2010). However, these terms should not be taken to imply either/or solutions for ozone mitigation. For instance, megacities are not radical-limited because of minimal VOC emissions, but rather because of an overabundance of  $NO_x$ , making the term “ $NO_x$ -saturated” a more appropriate term. In such “ $NO_x$ -saturated” environments, reduction of  $NO_x$  is necessary to achieve long-term ozone reduction but would be expected to lead to short-term ozone increases without concurrent action to reduce VOC emissions. In this work, the terms “radical-limited”, “VOC-limited”, and “ $NO_x$ -saturated” are taken to have the same meaning, and we choose to use “radical-limited” for simplicity.

While classifying regional  $O_3$  production as  $NO_x$ -limited or radical-limited is an important first step, we must note that “VOCs” refers to a collection of hundreds of distinct trace gases arising from a variety of anthropogenic and natural sources, each with unique rates of reaction with OH and unique radical yields upon oxidation. Therefore, in radical-limited (i.e. VOC-limited) environments, investigating the sensitivity of  $O_3$  to individual VOCs or subsets of similar VOCs is necessary for developing mitigation strategies that target emissions sectors that contribute disproportionately to local  $O_3$  formation.

Effective  $O_3$  control strategies rely on accurate understanding of how ambient  $O_3$  levels would respond to reductions in precursor emissions; thus, potential biases or uncertainties from model-based and observation-based studies must be taken into consideration. 3D models that include emissions, transport, and chemistry are well-suited for exploring the response of simulated  $O_3$  to reductions in modeled emissions, but are subject to large uncertainties in many parameters (particularly emissions) that lead to uncertainties in simulated  $O_3$  and the simulated dependence of  $O_3$  on its precursors (Sillman, 1995, 2003; Sillman et al., 1998; Zhou et al., 2013; Choi and Souri, 2015; Goldberg et al., 2016). Ground-based studies that make use of  $O_3$  sensitivity indicators (as described in Sillman and He (2002) and Schroeder et al. (2017)) have the advantage of making direct observations of the real atmosphere, but may be limited to one location, making it difficult to understand how representative they are of a broader region (Thornton et al., 2002; Mao et al., 2010; Edwards et al., 2013; Ren et al., 2013). Furthermore, recent work has highlighted the presence of vertical gradients in  $O_3$  precursors within the boundary layer, suggesting that significant bias can arise if surface observations are used to infer integrated rates of  $O_3$  production throughout the boundary layer (Zhang et al., 2016). Airborne studies, on the other hand, provide measurements of  $O_3$  and its precursors over large geographical areas, allowing for calculation of  $O_3$  production rates and  $O_3$  sensitivity at local and regional scales across vertical gradients (Kleinman et al., 2001, 2002; Mazzuca et al., 2016; Schroeder et al., 2017). This work uses data collected onboard the NASA DC-8 aircraft during the Korea-United States Air Quality Study (KORUS-AQ; May 2–June 11, 2016) to explore gradients in  $O_3$  and its chemical precursors in the SMA, and uses an observationally-constrained box model to quantify the response of simulated  $O_3$  production rates to perturbations in the precursor environment. While much can be learned from analysis of box model calculations, care must be taken to ensure that the constraints used to drive the model and the underlying chemical mechanism within the model adequately represent conditions in the SMA. For this reason, a large portion of this work (Section 4) is dedicated to analysis of model performance against a number of metrics, including comparison of model-calculated abundances of secondary “test species” to observations, and comparison of calculated rates of  $O_3$  production to observed changes in  $O_3$ .



**Figure 1:** Map of  $O_3$  monitors in the SMA, with pins showing the locations of Olympic Park and Taehwa Forest, two key sites that will be discussed in greater detail in Section 3.  $O_3$  monitors are colored by subregion within the SMA: Urban Seoul (red), Incheon (yellow), and Gyeonggi (blue). DOI: <https://doi.org/10.1525/elementa.400.f1>

## 2. Distribution of surface $O_3$ in the SMA during KORUS-AQ

To help place the KORUS-AQ observations into context, it is useful to first examine the distribution of surface ozone observed by the AirKorea network of air quality monitoring sites. KORUS-AQ was conducted during the climatological peak of  $O_3$  season in South Korea that occurs during the pre-monsoon period in late spring/early summer, typically during May and June (Ghim and Chang, 2000; Jo et al., 2000; Kim et al., 2006). Therefore, the timing of the field deployment is germane to exploring spatiotemporal tendencies in  $O_3$  and conducting policy-relevant analysis of the key drivers of  $O_3$  formation.

The SMA has a population of approximately 25 million, divided into three main regions: Urban Seoul (population 10 million), the Incheon metropolitan city (population 3 million), and the surrounding Gyeonggi province (population 12 million). **Figure 1** shows the location of air quality monitoring sites maintained in these three regions by the National Institute of Environmental Research (NIER) as part of the larger country-wide AirKorea network. Statistics for observations across these sites are summarized in **Table 1**. Percentile statistics for sites across the three regions are provided for MDA8  $O_3$ , associated levels of  $O_x$  ( $O_3 + NO_2$ ), and number of exceedance days in each region. Exposure to high  $O_3$  levels is significantly greater

for sites in Gyeonggi province with monitors recording MDA8  $O_3$  values in excess of the Korean standard of 60 ppbv roughly half of the time. Seoul and Incheon experience such values, but only violate the Korean standard a little over a quarter of the time with lower  $O_3$  values that tend to be about 10 ppbv less than those observed in Gyeonggi province. This difference can be better understood when looking at statistics for the associated  $O_x$  values, which show Seoul to have values that run a few ppbv higher than Gyeonggi due to the proximity to greater  $NO_x$  emissions. While Incheon values of  $O_x$  are still lower than Gyeonggi, the regional difference in  $O_x$  is smaller than that for  $O_3$ . Based on these statistics, the greater number of exceedance days for Gyeonggi province can be attributed mainly to the lower  $NO_x$  levels in comparison to Seoul and Incheon rather than higher overall oxidant levels. These observations drive the motivation for this work, which broadly aims to answer the following two questions: 1) Which  $O_3$  precursor species are the primary drivers of  $O_3$  production in the SMA? And 2) What mitigation strategies would be most effective for achieving reductions in  $O_3$  across the SMA? This work uses measurements made onboard the NASA DC-8 aircraft during KORUS-AQ and observation-based modeling to explore these questions and provide policy-relevant information about the local photochemical environment.



**Table 1:** Percentile statistics for maximum daily average 8-hour (MDA8)  $O_3$ , MDA8  $O_x$ , and the number of days with at least one monitor in exceedance (MDA8  $O_3 > 60$  ppbv) for AirKorea monitors in Seoul, Incheon, and Gyeonggi provinces during the KORUS-AQ study period, May 2–June 11, 2016. DOI: <https://doi.org/10.1525/elementa.400.t1>

Location (color in Fig. 1)	Urban Seoul (red)	Incheon (yellow)	Gyeonggi (blue)
Percentile Statistics for MDA8 $O_3$ at AirKorea monitors (units: ppbv)			
95 <sup>th</sup>	82.0	83.0	90.6
75 <sup>th</sup>	62.5	63.6	72.6
Median	49.5	50.9	60.0
25 <sup>th</sup>	36.3	41.5	48.7
5 <sup>th</sup>	21.1	29.5	35.5
Percentile Statistics for MDA8 $O_x$ ( $O_3 + NO_2$ ) at AirKorea monitors (units: ppbv)			
95 <sup>th</sup>	120.7	110.3	115.8
75 <sup>th</sup>	99.3	87.5	95.9
Median	83.8	73.3	80.0
25 <sup>th</sup>	69.4	61.8	66.7
5 <sup>th</sup>	53.6	48.0	52.7
Number of Exceedance Days (at least one monitor with MDA8 $O_3 > 60$ ppbv)			
# Days	33	26	39

### 3. Methods

#### 3.1. KORUS-AQ Observations

KORUS-AQ was a multi-agency, multi-platform international field campaign that took place in South Korea from May 2–June 11, 2016. As part of KORUS-AQ, the NASA DC-8 aircraft performed 20 local research flights over South Korea. A map showing all local DC-8 flights during KORUS-AQ is shown in the top panel of **Figure 2**. During most research flights, the DC-8 flew a standard route over the SMA that was repeated during the morning (~9:00 local time), midday (~12:30 local time), and afternoon (~3:30 local time). This route is shown in the bottom panel of **Figure 2**, which descends over the city and passes over two instrumented supersites. The descent over the city began from ~2.5 km at the northern end of urban Seoul, passing over the Olympic Park site at ~0.5 km before coming within meters of the surface over the runway of Seoul Air Base, located about 8 km south of Olympic Park. From Seoul AB, the DC-8 proceeded at low altitude to pass over the Taehwa Forest research site at ~0.3 km before performing a wide ascending spiral up to ~10 km in the area to the east of Taehwa. Sampling along this route was performed on fifty-five occasions under a wide variety of air quality conditions. This provides a strong statistical basis for exploring the spatial and temporal variability over short term time scales (i.e. diurnal variability within one day) and relatively long time scales (i.e. day-to-day variability over the study period). The pri-

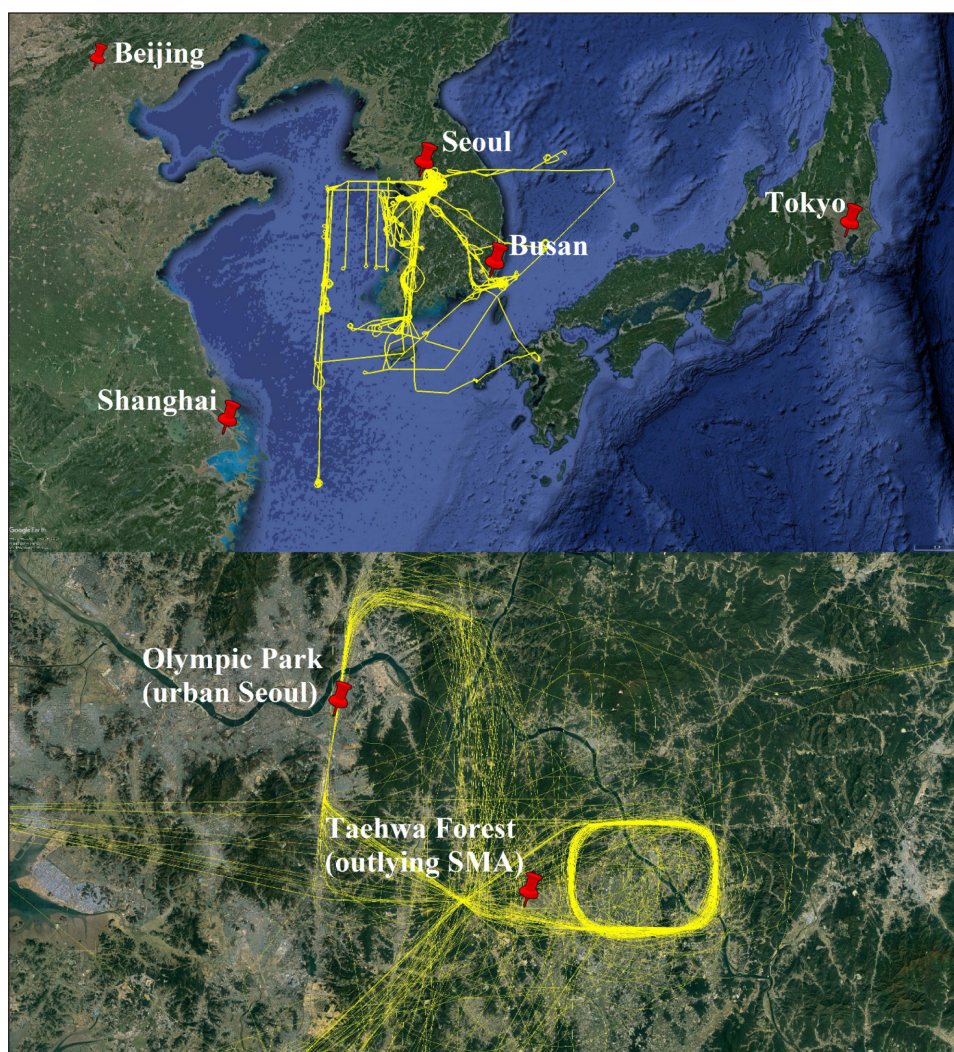
mary objective of KORUS-AQ was to collect measurements that would facilitate a better understanding of the chemical and physical processes that control air quality over South Korea, with an emphasis on collecting observations that could improve satellite-based remote sensing of air pollution. Because of this, the majority of flights during KORUS-AQ were conducted during sunny or partly cloudy conditions, which are also conducive to  $O_3$  formation. Much of the KORUS-AQ study period was characterized by consistent high pressure with relatively weak synoptic flow. Under these conditions, characterized by stagnant airmasses in the morning and a building westerly sea breeze through the afternoon, Taehwa forest acted as a receptor site for outflow from urban Seoul.

The instrument payload of the DC-8 was designed to allow for detailed studies of gas phase and condensed phase chemical processes. The subset of airborne measurements that are directly related to this work include trace gases ( $O_3$ , NO,  $NO_2$ , CO, water vapor,  $CH_2O$ , PAN,  $H_2O_2$ ,  $HNO_3$ , and speciated VOCs), meteorological variables, and photolysis rates. All DC-8 measurements used in this work are summarized in **Table 2**.

#### 3.2. Box model setup

The observationally-constrained NASA Langley Research Center (LaRC) 0-D time-dependent photochemical box model was used to simulate ozone photochemistry during KORUS-AQ. The model was constrained by coincident observations of trace gases such as  $O_3$ , NO, CO,  $CH_4$ ,  $CH_2O$ , water vapor, and non-methane hydrocarbons; by meteorological parameters such as temperature and pressure; and by photolysis rates derived from actinic flux observations. The model calculates the diurnal steady-state profiles of radicals and other computed species for each set of measurements along the flight path (Crawford et al., 1999; Olson et al., 2001, 2006). In effect, the model is integrated forward in time until all calculated species exhibit a reproducible diurnal cycle (i.e. convergence is met for each calculated species). Values are extracted for the specific time of the flight measurement to enable the calculation of instantaneous ozone production rates associated with the measurements along the flight path. During the simulated diurnal cycle, all constraining species are held constant.  $NO_x$  requires special treatment to allow interconversion between NO,  $NO_2$  and other short-lived reactive nitrogen species during the diurnal cycle. In this case, the total abundance of  $NO_x$  is held constant but calculated to be consistent with the observed NO mixing ratio at the time of the measurement. The diurnal variation of photolysis frequencies is calculated for clear-sky conditions and scaled by the ratio of observed-to-clear-sky values at the time of the measurement. The most recent update to the chemical mechanism, including a complete list of all reactions used in the model is provided in Schroeder et al. (2017); however, updates to the aromatic chemistry mechanism have been made and are described later in this section.

In highly polluted conditions, the appropriateness of the steady-state assumption becomes less valid. For instance, Fried et al. (2011) demonstrated that model estimates of  $CH_2O$  can be biased in pollution plumes when short-lived



**Figure 2:** Maps of all DC-8 flights in the broader context of East Asia (top panel), and the repeated stereo route over the SMA (bottom panel). DOI: <https://doi.org/10.1525/elementa.400.f2>

**Table 2:** Summary of DC-8 measurements used in this work. DOI: <https://doi.org/10.1525/elementa.400.t2>

Instrument Name	Species Measured	Reference(s)
Diode Laser Hygrometer (DLH)	water vapor	(Diskin et al., 2002)
Differential Absorption CO Measurement (DACOM)	CO, CH <sub>4</sub>	(Sachse et al., 1991)
NO <sub>x</sub> O <sub>3</sub> Chemiluminescence	O <sub>3</sub> , NO, NO <sub>2</sub>	(Weinheimer et al., 1994)
Compact Atmospheric Multi-species Spectrometer (CAMS)	CH <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub>	(Weibring et al., 2010; Richter et al., 2015)
Proton Transfer Time of Flight Mass Spectrometer (PTR-TOF-MS)	methanol, acetone + propanal, isoprene, MVK + MACR, benzene, toluene, C <sub>8</sub> aromatics	(Muller et al., 2014)
Whole Air Sampler (WAS) <sup>a</sup>	C <sub>2</sub> -C <sub>10</sub> alkanes, C <sub>2</sub> -C <sub>4</sub> alkenes, C <sub>6</sub> -C <sub>9</sub> aromatics, isoprene	(Colman et al., 2001)
Georgia Tech Chemical Ionization Mass Spectrometer (GTCIMS)	PAN	(Slusher et al., 2004)
California Institute of Technology Chemical Ionization Mass Spectrometer (CIT-TOF-CIMS)	H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> OOH	(Crouse et al., 2006)
CCD-Based Actinic Flux Spectrometers (CAFS)	4π sr actinic flux and derived photolysis frequencies	(Shetter et al., 1999)

<sup>a</sup> All measurements taken at a minimum frequency of 1 Hz except WAS. WAS sample frequency ranged from every 0.5–5 min, depending on aircraft location relative to points of interest, with each canister requiring 0.5 to 1.5 min to fill. On a typical 8 hour flight, about 170 whole air samples were collected.



species dominate the model photochemistry, e.g., highly-reactive VOCs such as biogenic isoprene or alkenes from industrial sources. Under such conditions, using observations to constrain  $\text{CH}_2\text{O}$  and other important radical reservoirs instead of calculating them will improve model calculations of the radical pool responsible for ozone production. The intricacies of the steady-state assumption will be explored further in Section 4 using comparisons of fully-constrained and minimally-constrained model runs. Additional model uncertainties arise from uncertainties in measured constraints and uncertainties in kinetic and photolytic rates.

Model inputs for each flight were derived from DC-8 1-s merges (available at <https://www-air.larc.nasa.gov/missions/korus-aq/index.html>). However, creating 1-s model inputs from these DC-8 1-s merges involved many steps to maximize the number of data points that could be run by the model. At a minimum, The LaRC 0-D photochemical box model must be constrained by coincident measurements of  $\text{CH}_4$ , CO, NO,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ , and photolysis rates. To maximize the number of points that could be run by our model, an iterative median smoothing process was performed to fill in missing data points for these species. Missing data were replaced with the median of the surrounding  $\pm 3n$  data points, where  $n = 1, 2, 3, 4$ . In effect, this allows for the smallest smoothing window possible to be used for each missing value. First, we attempted to replace missing values with the median of the surrounding  $\pm 3$  data points (i.e.  $n = 1$ ), under condition that at least half of the data points within the window were not missing themselves. If that condition was not met, median smoothing was attempted with a window of the surrounding  $\pm 6$  data points (i.e.  $n = 2$ ), onwards until a final smoothing window of  $\pm 12$  data points (i.e.  $n = 4$ ) was reached. Flying at an altitude of 1 km, the DC-8 would travel a distance of about 3 km in 24 seconds (i.e. the time duration of the maximum smoothing window,  $n = 4$ ), and a maximum vertical distance of about 120 meters (the DC-8 typically ascended/descended at a maximum rate of 5 m/s). For the subset of KORUS-AQ data highlighted in this paper, i.e., less than 2 km altitude over the SMA (36.9–37.73 N, 126.65–127.83 E), this smoothing process contributed to 8% of the CO and  $\text{CH}_4$  observations (consistent with the frequent calibration of the instrument every 5 min), 2.6% of the water vapor observations, and less than 2% of the  $\text{O}_3$  and NO observations. This enabled just over 77,000 unique calculations accounting for 80% of the DC-8 flight time over the SMA.

This median smoothing process was also applied to the following non-critical constraints:  $\text{CH}_2\text{O}$ , PAN and methanol. These are species that can be calculated by the model if not available to constrain the calculations. Smoothed data contributed to roughly 4% of  $\text{CH}_2\text{O}$ , 9% of PAN, and less than 2% of methanol data used in the calculations enabling constraint of these species for all but a handful of model runs. In the case of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ , the smoothing process was not effective in adding much additional information, but observations were still available to constrain over 80% of the model runs. Fortunately, constraining these species had a negligible effect on calculations

for the conditions encountered over the SMA during the study period (see discussion in Section 4).

A final step in preparing the model inputs required special consideration for non-methane hydrocarbons. Fortunately a subset of important hydrocarbons were measured at 1 Hz:  $\text{C}_2\text{H}_6$  by CAMS and aromatics and isoprene by PTR-TOF-MS (see **Table 1** for complete list). The large number of other hydrocarbon compounds were derived from whole air samples collected at discrete time intervals (see **Table 1** for details). For these species, “pseudo” 1 Hz interpolated values were derived using 1 Hz measurements of  $\text{C}_2\text{H}_6$ . Taking the ratio of each WAS measurement of  $\text{C}_2\text{H}_6$  to the average of 1 Hz measurements during the WAS integration time resulted in a small correction factor for each sample. Taking these correction factors, the full timeline of 1 Hz  $\text{C}_2\text{H}_6$ , including time gaps between WAS samples, was normalized by applying the average ratio between consecutive samples from the middle of one sample integration period to the next. This “adjusted 1 Hz ethane” was then used to derive 1 Hz inputs for other WAS species having anthropogenic sources. For example, a “pseudo” 1 Hz propane input was derived by taking the propane-to-ethane ratio for each WAS measurement. These ratios were then applied to the “adjusted 1 Hz ethane” again using the average ratio between consecutive WAS samples from the middle of one sample integration period to the next. This scheme was applied to derive 1 Hz inputs for lumped  $\text{C}_{4+}$  alkanes, ethene, lumped  $\text{C}_{3+}$  alkenes, ethyne, and benzene. Similar to the correction of 1 Hz  $\text{C}_2\text{H}_6$ , isoprene measurements from WAS canisters and 1 Hz PTR-TOF-MS data were used to derive an “adjusted 1 Hz isoprene” input. PTR-TOF-MS measurements of toluene and  $\text{C}_8$  aromatics were found to be in very good agreement with WAS measurements, so 1 Hz measurements of these species were used as-is for model inputs. Remaining VOC inputs, such as methanol and acetone, were only measured by PTR-TOF-MS and therefore used as-is for model inputs.

Model calculations of the free radical species that mediate ozone production allowed for the determination of instantaneous rates of net ozone production,  $P(\text{O}_3)$ , with individual terms given in the equation below.

$$P(\text{O}_3) = k[\text{HO}_2][\text{NO}] + \sum k_i[\text{RO}_2]_i[\text{NO}] - k[\text{O}^1\text{D}][\text{H}_2\text{O}] - k[\text{O}_3][\text{OH}] - k[\text{O}_3][\text{HO}_2] - k[\text{OH}][\text{NO}_2] - \sum k_i[\text{O}_3][\text{NMHC}]$$

The first two terms represent ozone formation from the conversion of NO to  $\text{NO}_2$  by hydroperoxy ( $\text{HO}_2$ ) radicals and the numerous organoperoxy ( $\text{RO}_2$ ) radicals resulting from hydrocarbon oxidation. Loss terms include the reaction of  $\text{O}^1\text{D}$  from ozone photolysis with water, direct reaction of ozone with OH and  $\text{HO}_2$ , reaction of  $\text{NO}_2$  with OH to form nitric acid (an indirect ozone loss via odd oxygen,  $\text{O}_x \equiv \text{O}_3 + \text{NO}_2$ ), and ozonolysis reactions with hydrocarbon species.

As noted above, a minor adjustment to the model mechanism was made in response to the dominance of  $\text{C}_{7+}$  aromatic compounds in the SMA. In previously modeled environments, including airborne field campaigns

over remote areas and polluted cities in the USA, aromatic species had never played a dominant role. For example, the mean mixing ratio of  $C_{7+}$  aromatics below 1 km over Seoul during KORUS-AQ was a factor of five higher than observed below 1 km over Houston during the DISCOVER-AQ airborne campaign (Summer 2013). This led to scrutiny of the OH reaction rate constant for the lumped  $C_{7+}$  aromatic compounds (AROM) when initial model calculations produced unrealistic results for peroxyacetyl nitrate (PAN) and  $CH_2O$ , indicating that the modeled radical environment (and modeled rate of  $P(O_3)$ ) was also unrealistic. Specifically, using the original OH rate constant for  $C_{7+}$  aromatics led to model over-prediction of PAN in Seoul by a factor of 10–15 and  $CH_2O$  by a factor of 2–3. The rate constant, one of only a few still based on the Lurmann et al. (1986) lumped hydrocarbon mechanism, was found to significantly overpredict the rate of aromatic oxidation by OH when considering current literature for toluene and higher aromatic reaction rates. To best represent aromatic oxidation, the rate constant for AROM + OH was updated to take the following form:

$$k_{\text{AROM}+\text{OH}} = A * (1.8 \times 10^{-12}) * e^{(340/T)}$$

This equation combines the rate constant for toluene with a simple scaling factor, A, accounting for the ratio of  $C_8$  aromatics to toluene for a given model run. The calculation of A took the following form:

$$A = ([C_8 \text{ aromatics}] * 2.43 + [\text{Toluene}]) / [\text{lumped } C_{7+} \text{ aromatics}]$$

The scaling factor of 2.43 was derived by assessing the relative OH reactivity of toluene versus  $C_8$  aromatics ( $k_{C_8 \text{ aromatics} + OH} / k_{\text{Toluene} + OH}$ ) for the mean mixing ratios of aromatics measured in the whole air samples. For a scaling factor of  $A = 1.4$  (median value for calculated over Seoul) and a temperature of 298 K, the revised rate constant is about 50% lower than the original rate constant. In addition, the stoichiometric yields of glyoxal and methyl glyoxal from  $C_{7+}$  oxidation under high- $NO_x$  conditions have been adjusted from 0.18 and 0.72 to 0.27 and 0.3 to better reflect results from chamber experiments (Tuazon et al., 1984; Smith et al., 1998) and to better agree with lumped chemical mechanisms used in 3D models, such as CAM-Chem (Louisa Emmons, private communication, 2018). These changes combined to lower the calculated  $P(O_3)$  below 2 km over the SMA by an average of 20%, but at low altitudes over Seoul, where observations of  $C_{7+}$  aromatics were highest, these changes resulted in up to a 65% decrease in calculated  $P(O_3)$ . Outputs from all box model simulations are available on the KORUS-AQ archive: <https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq?MODEL=1>.

#### 4. Evaluation of model performance

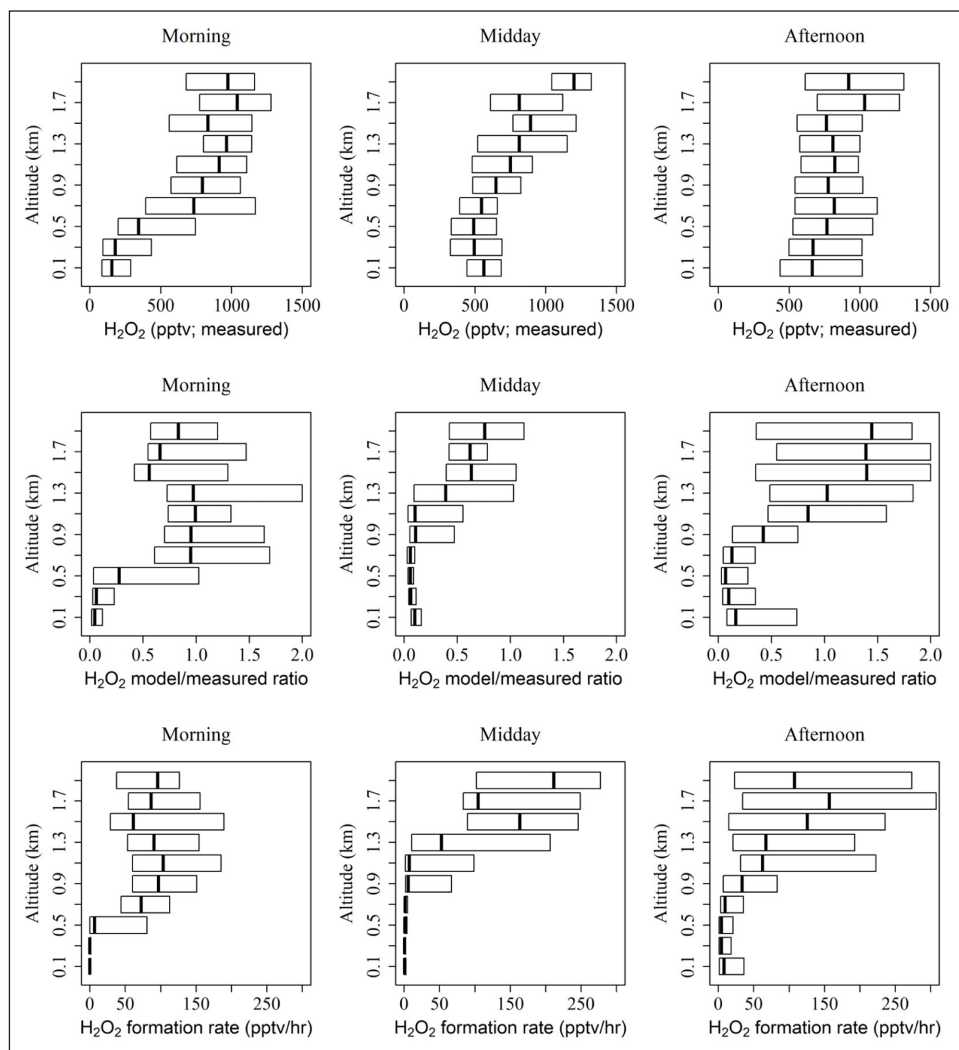
To provide confidence in model-calculated rates of  $P(O_3)$ , which cannot be directly observed, an objective assessment of model performance is enabled by observed species that can either be used to constrain the model as an

input or be calculated to be in photochemical steady state. Comparison of calculated and observed values for these test species can provide important insights on the aspects of the photochemistry that are being well represented and the sensitivity of the model to aspects that are not well represented. Limitations of the model are exacerbated for species with longer lifetimes, which are less likely to be in photochemical steady state, and conditions under which physical processes such as transport, deposition, or wet removal are dominating over photochemistry. It is also useful to have a large number of observations over which to test model performance as there are many conditions that can perturb local steady state for individual runs but not induce a bias in the overall statistics. For instance, measurements in a partially cloudy field can have large fluctuations in measured photolysis frequencies. Radical species can rapidly respond to such fluctuations, but longer-lived species will not be in photochemical equilibrium, and will deviate from model predictions both positively and negatively. Because the destruction of some secondary species (such as  $CH_2O$ , PAN,  $H_2O_2$ , and  $HNO_3$ ) provides chemical feedback into the modeled radical pool, over-prediction of these species by box models can have cascading effects on modeled rates of  $O_3$  formation. The broad suite of measurements and the diverse set of chemical and meteorological conditions sampled during KORUS-AQ provide a unique platform to evaluate model performance and evaluate the importance of observing these species to constrain  $O_3$  production estimates in a complex, heterogeneous megacity such as Seoul.

As noted in Section 3.2, model calculations were constrained by as many species as possible, including  $CH_2O$ , PAN,  $H_2O_2$ , and  $HNO_3$  when measurements were available to allow for the most accurate representation of the feedback that these species provide. Although this set of highly-constrained calculations is expected to yield the most realistic estimates of radical abundances and rates of  $O_3$  production, much can be learned about model sensitivity and local chemistry by comparing results of highly-constrained model runs to those using fewer constraints. For this comparison, four additional set of model calculations were performed. All inputs were identical to those in the highly-constrained set of runs, except each set left one of the secondary species unconstrained:  $CH_2O$ , PAN,  $H_2O_2$ , and  $HNO_3$ . The following discussion examines the comparison between model calculations for each of these species with their observed values, the reasons for differences, and the significance of these differences to model estimates of net  $O_3$  production.

**Figures 3, 4 and 5** examine observed versus calculated vertical profiles of  $H_2O_2$ , PAN, and  $CH_2O$  for the descents of the DC-8 over Seoul. Each figure is separated into morning, midday, and afternoon, showing how observed and modeled vertical profiles evolve throughout the day. The top row of each figure shows the statistics of observed vertical profiles, the middle row shows the ratio of modeled/measured mixing ratios from “unconstrained” calculations, and the bottom row shows the calculated lifetimes of the given test species. The diurnal evolution of ambient  $H_2O_2$  in the top panels of **Figure 3**





**Figure 3:** Vertical profiles of measured mixing ratios of  $H_2O_2$  (top), the ratio of modeled/measured  $H_2O_2$  from the “ $H_2O_2$ -unconstrained” set of simulations (middle), and the formation rate for  $H_2O_2$  (bottom). All data and calculations are from DC-8 profile descents over Seoul, and are broken up to show diurnal trends across morning (left), midday (middle), and afternoon (right). All data were divided into 0.2 km bins, and the box and whisker plots represent the median value and interquartile range for each bin. DOI: <https://doi.org/10.1525/elementa.400.f3>

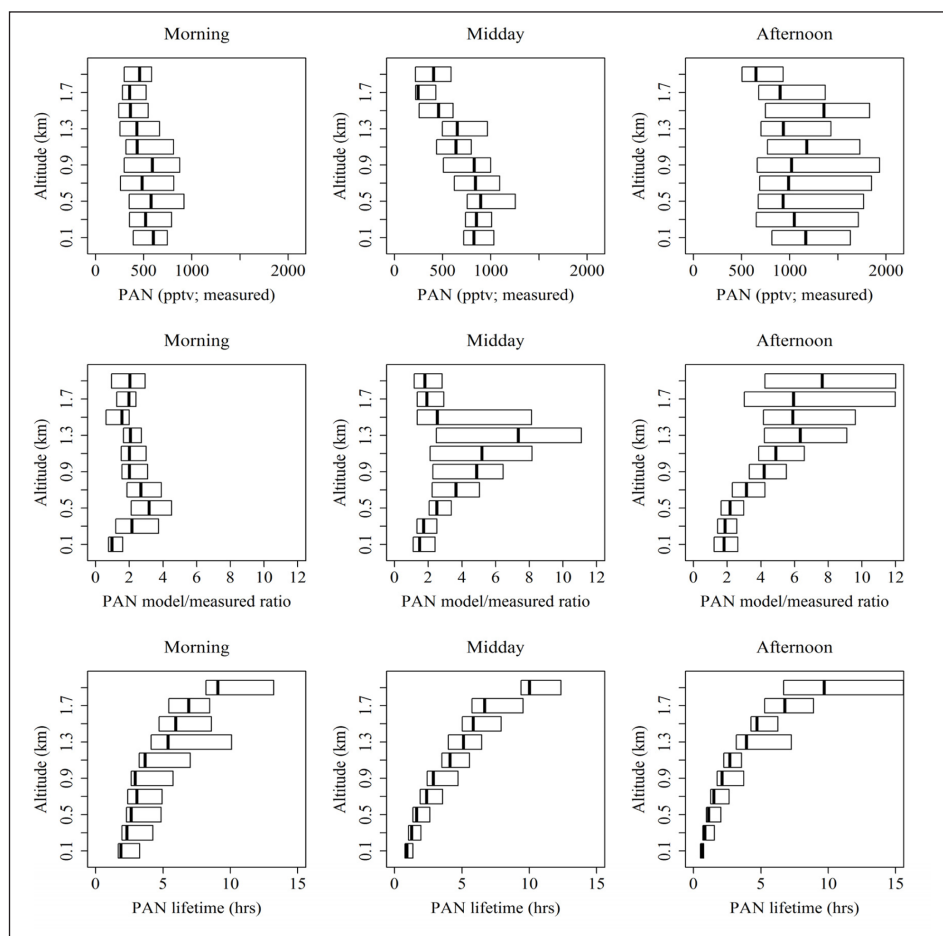
exhibits the combined influences of chemistry, deposition, and vertical mixing. In the morning,  $H_2O_2$  was present in low amounts in the shallow boundary layer (median values below 200 pptv), while a reservoir of relatively high  $H_2O_2$  (median values greater than 700 pptv) was present above 1 km. Here, we refer to the boundary layer as the lowermost region of the atmosphere that is directly impacted by surface emissions, which is typically very shallow (a few hundred meters) in the morning, and extends up to 1–2 km by the afternoon. The low mixing ratios of  $H_2O_2$  in the morning boundary layer result from inhibited photochemical production of  $H_2O_2$  as well as deposition throughout the night. Due to an overabundance of  $NO_x$ , photochemistry in Seoul was radical-limited during KORUS-AQ (described in greater detail in Section 5), which limits chemical formation of  $H_2O_2$  since reaction of  $HO_2$  with  $NO$  dominates over the  $HO_2$  self-reaction. This is exacerbated in the morning, when low photolysis, low vertical mixing, and strong  $NO_x$  emissions would act to strengthen the radical-limited conditions. As the day progresses, mixing ratios of  $H_2O_2$  at low altitudes increase, while mixing ratios aloft remain relatively

constant. By the afternoon, there is little vertical gradient in  $H_2O_2$ ; however, mixing ratios at lower altitudes never exceed those of the reservoir aloft. This behavior is consistent with  $H_2O_2$  in the boundary layer over Seoul being largely driven by entrainment of air from the residual layer aloft. The vertical profiles of the ratio of modeled/measured  $H_2O_2$  further support this hypothesis. Model/measured ratios of  $H_2O_2$  at higher altitudes are closer to one than at low altitudes, indicating that the air in the residual layer is better described by the steady state assumption than air in the boundary layer. In the morning, for example, modeled/measured  $H_2O_2$  ratios in the boundary layer were extremely low (below 0.1 at the lowest level), indicating model under-prediction of  $H_2O_2$ , while modeled/measured  $H_2O_2$  ratios in the residual layer were typically between 0.5–1.5. The calculated lifetimes for  $H_2O_2$  due to photochemical loss and deposition were on the order of 15–20 hrs and did not vary substantially with altitude. Comparatively, the  $H_2O_2$  formation rates shown in **Figure 3** exhibited large gradients with altitude and was driven primarily by the abundance of  $NO$ . As the day progressed, this led to underpredictions

of  $H_2O_2$  at higher altitudes as high  $NO$  values were mixed higher into the growing boundary layer. In effect, model calculations of  $H_2O_2$  did not match measurements within the boundary layer because of the large variation in local formation rates versus the more dominant influence of vertical mixing (not accounted for in the model) delivering higher abundances of  $H_2O_2$  produced aloft under conditions of much lower  $NO$ .

PAN, presented in **Figure 4**, exhibited small vertical gradients with higher mixing ratios tending toward lower altitudes. Values also increased throughout the day at all altitudes with afternoon values roughly double those observed in the morning. This behavior suggests that photochemical production from surface emissions drove the diurnal evolution of PAN observations. This is also consistent with the vertical gradient observed at midday when the boundary layer is still growing and the effect of surface emissions has yet to reach the top of the measured profile. Looking at modeled/measured mixing ratios, PAN was generally overestimated by the model, but the modest overestimates in the morning can be sharply contrasted with the large overestimates aloft later in the day. This model behavior can be best understood in the context of the PAN lifetime shown at the bottom of **Figure 4**. Model performance was best at the

lowest altitudes where PAN lifetime was shortest and the expectation of steady-state the best. Nevertheless, the slight tendency to overestimate at these altitudes likely resulted from mixing of PAN from above where  $NO_x$  was less abundant, but the lifetime of PAN was longer. The highest modeled/measured ratios occurred between 400–800 m in the morning, between 900–1,400 m at midday, and between 1,200–2,000 m in the afternoon. These altitudes roughly correspond to the range of boundary layer heights for those times of day. Those altitudes correspond to the longest PAN lifetimes in the profile that also have enough  $NO_x$  to sustain a large PAN production rate. Also note that the largest discrepancies occur at the highest (coldest) altitudes only when sufficient  $NO_x$  has mixed to those altitudes. As was the case for  $H_2O_2$ , these model discrepancies are ultimately caused by the vertical mixing that is not represented in the model. For PAN, it is the mixing from below that prevents the build-up of PAN to steady-state values at higher altitudes where PAN lifetimes are longer than the timescale for mixing. The widening of the range of modeled/measured PAN ratios at higher altitudes also reflects daily variability in the boundary layer height. For example, during Research Flight 7, the top of the boundary layer at midday was 1.5 km (as indicated by



**Figure 4:** Vertical profiles of measured mixing ratios of PAN (top), the ratio of modeled/measured PAN from the “PAN\_unconstrained” set of simulations, and the calculated lifetime of PAN. All data and calculations are from DC-8 profile descents over Seoul, and are broken up to show diurnal trends across morning (left), midday (middle), and afternoon (right). All data were divided into 0.2 km bins, and the box and whisker plots represent the median value and interquartile range for each bin. DOI: <https://doi.org/10.1525/elementa.400.f4>

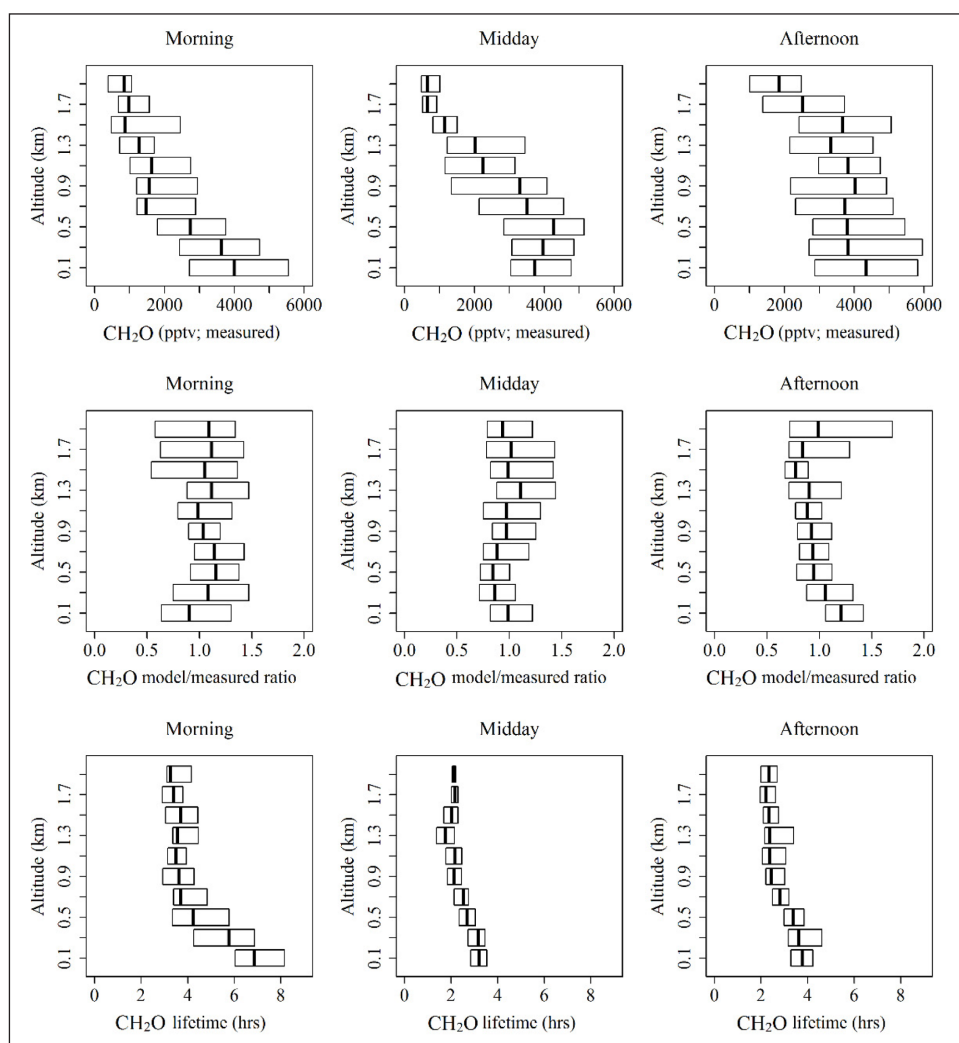
gradients in the test species and other short-lived species, such as  $\text{NO}_x$ ). During this time, the model/measured ratio increased with altitude before reaching a maximum value at 1.5 km, coincident with the top of the boundary layer. During Research Flight 10, on the other hand, the top of the boundary layer at midday was 1.3 km, and the maximum PAN modeled/measured ratio occurred at this height as well.

The vertical profiles of  $\text{CH}_2\text{O}$  presented in **Figure 5** also indicate photochemical production within the mixed layer. However, in contrast to PAN, model calculations of  $\text{CH}_2\text{O}$  reasonably match observations at all altitudes and all times of day. One reason for this can be attributed to the much shorter calculated lifetimes for  $\text{CH}_2\text{O}$  over Seoul which also had much less vertical variability than calculated PAN lifetimes; thus, the expectation for  $\text{CH}_2\text{O}$  to approach steady-state is much greater for  $\text{CH}_2\text{O}$  than either  $\text{H}_2\text{O}_2$  or PAN. Because  $\text{CH}_2\text{O}$  is closely related to the rate of VOC oxidation and the abundance of radical species (Wert, 2003; Parrish et

al., 2012; Valin et al., 2015; Schroeder et al., 2016; Wolfe et al., 2016), model-measurement agreement indicates that the VOC mixture used to constrain the model and the underlying chemical mechanism are adequate to represent of ambient conditions for  $\text{CH}_2\text{O}$ .

$\text{HNO}_3$  (not shown) is another secondary species that was calculated in an unconstrained simulation. Modeled  $\text{HNO}_3$  consistently exceeded observations by greater than a factor of 10 within the boundary layer. This can be attributed in part to the lack of adequate sinks in the model, which did not account for uptake of  $\text{HNO}_3$  to form particulate nitrate.

Having shown that the steady-state assumption is inadequate for describing some species in Seoul, it is important to assess the associated feedbacks that these species have on modeled rates of net  $\text{O}_3$  production,  $P(\text{O}_3)$ , in Seoul. In addition to the previously-described sets of model calculations, an additional set simulations were run whereby all four test species were unconstrained. Comparison of these six sets of simulations (constrained,



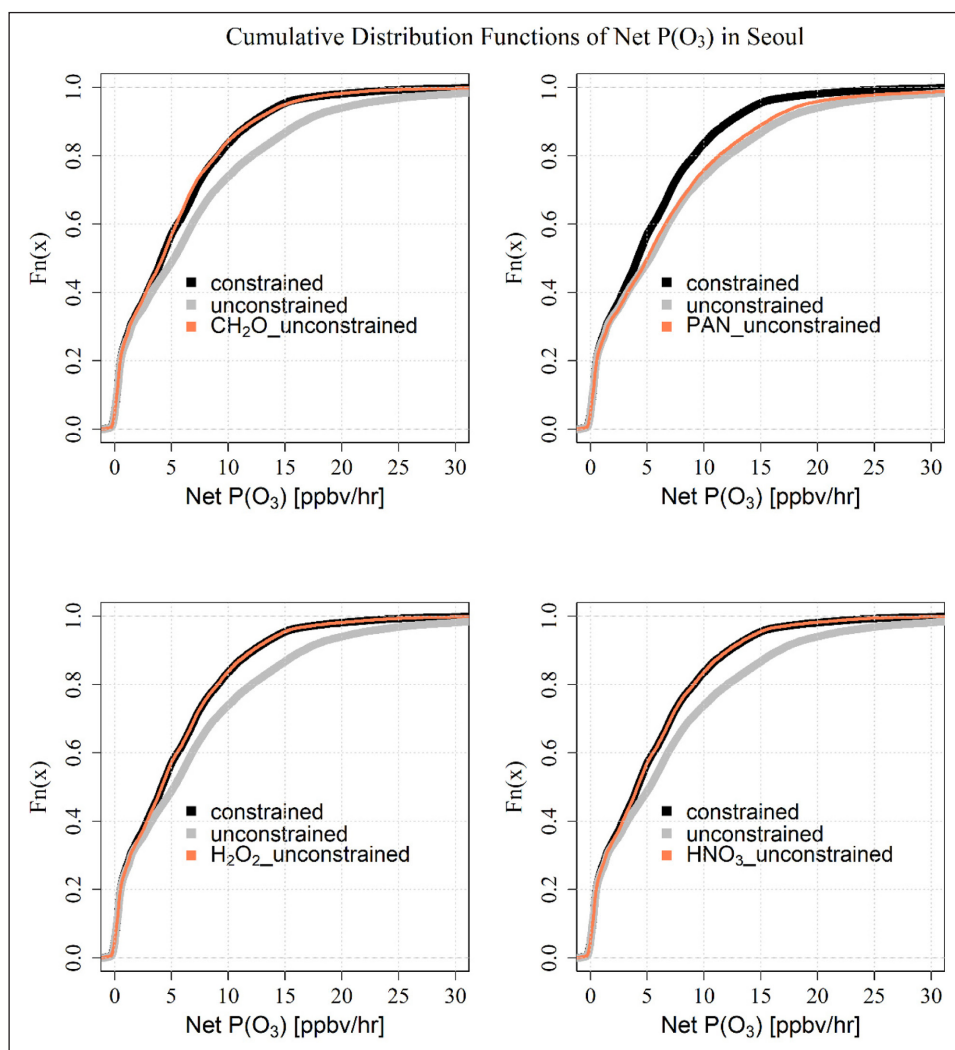
**Figure 5:** Vertical profiles of measured mixing ratios of  $\text{CH}_2\text{O}$  (top), the ratio of modeled/measured  $\text{CH}_2\text{O}$  from the “ $\text{CH}_2\text{O}_{\text{unconstrained}}$ ” set of simulations, and the calculated lifetime of  $\text{CH}_2\text{O}$ . All data and calculations are from DC-8 profile descents over Seoul, and are broken up to show diurnal trends across morning (left), midday (middle), and afternoon (right). All data were divided into 0.2 km bins, and the box and whisker plots represent the median value and interquartile range for each bin. DOI: <https://doi.org/10.1525/elementa.400.f5>

unconstrained, and the four simulations with each species unconstrained individually) allows for such an evaluation. **Figure 6** shows cumulative distributions of calculated  $P(O_3)$  from each of these model simulations. Between the constrained (black line) and unconstrained (gray line), there is a shift towards higher rates of  $P(O_3)$  in the unconstrained runs. To understand this difference, these two sets of model runs are compared with those for each of the individually unconstrained species runs. A quick examination shows that the difference is entirely due to the constraint of PAN. This is due to the additional production of organic peroxy radicals resulting from the overpredicted PAN abundances in the unconstrained runs. The lack of model sensitivity to  $H_2O_2$  and  $HNO_3$  is due to their weak roles as radical reservoirs in the polluted Seoul environment such that radical abundances and resulting rates of  $O_3$  production do not rely on their being well-represented in the model. Conversely,  $CH_2O$  is a strong peroxy radical source, but it is generally well predicted by the model with model/measurement discrepancies that are evenly distributed around the observed values. Thus, differences in individual model runs between constrained

and unconstrained calculations do not affect the overall distribution of  $P(O_3)$ . While it is difficult to quantify specifically, it is expected that the interpolation of hydrocarbon observations makes a large contribution to the discrepancies for individual model calculations while having no detectable impact on the aggregated statistics.

The exercises described above serve to highlight the importance of having a wide suite of measurements to constrain a box model in heavily polluted environments. In complex environments such as Seoul, where a confluence of strong time-varying local emissions, local meteorology, and background or residual pollution act to reduce the applicability of the steady-state assumption, the importance of model constraints is very high. In this case, without measurements of PAN to constrain the model, calculated rates of  $P(O_3)$  in Seoul would be biased high by more than 40% when integrated over the distribution of calculated rates.

This bias related to overprediction of PAN is of particular concern given the intent to use the model to examine the sensitivity of  $P(O_3)$  to changes in precursors. Such calculations must be conducted without constraining PAN



**Figure 6:** Cumulative distribution functions from different simulations using inputs derived from profile descents over Seoul. The same set of model inputs were used for each simulation, but the number of species used to constrain the model was varied between simulations, as indicated by the legend. DOI: <https://doi.org/10.1525/elementa.400.f6>



as its abundance must be allowed to change along with precursors. While the reason for the PAN discrepancy is tied to the physical process of boundary layer mixing, it is necessary to represent this impact in the box model with a chemical analog. As noted earlier, the strong temperature dependence of PAN thermal decomposition leads to a large range of lifetimes for PAN (e.g., up to 10–15 hours near 2 km as shown in **Figure 4**). Such lifetimes are unrealistic, given the expectation of a much shorter time for vertical mixing in the boundary layer; thus, a first-order loss of PAN was introduced into the model that was based on thermal decomposition at the average temperature in the lowest 2 km during daily descents over Seoul. Given both daily and diurnal temperature changes, the average temperature was determined for each individual descent over Seoul to determine the first order loss rate to apply to each data point. This loss was calculated to be half the rate of thermal decomposition at the average temperature for the profile below 2 km. This first-order loss is artificial in that it represents non-local decomposition as air is vertically exchanged, acting to limit the buildup of PAN at higher altitudes where lifetimes were too long and also effecting minor reductions of PAN at lower altitudes where precursor abundances were much higher than other altitudes in the boundary layer profile. This procedure was applied not only to PAN, but also to other peroxyacyl nitrates in the model (e.g., PPN derived from alkanes, TPAN derived from aromatics, and MPAN derived from isoprene).

Conducting unconstrained model calculations with this additional loss term for peroxyacyl nitrates had a dramatic impact on model performance. The regression of model-calculated PAN against observations improved substantially, showing both a reduction in the bias and an improvement in the correlation between calculated and observed PAN. The PAN regression slope for Seoul decreased from 4.8 to 0.92, the intercept changed from  $-50$  to  $-25$ , and the  $R^2$  increased from 0.33 to 0.49. The constrained calculations were also adjusted to include the new treatment of other peroxyacyl nitrates (PPN, TPAN, and MPAN), resulting in an 11% reduction in the integrated ozone production shown in **Figure 6**. Most importantly, the bias in ozone production between constrained and unconstrained calculations was dramatically reduced with integrated ozone production for the unconstrained calculations being only 8% lower than the constrained calculations. This modification to the model as applied to KORUS-AQ conditions allows for a more confident analysis of ozone production sensitivity to precursors, which is pursued in subsequent sections.

A final point of comparison is obtained by comparing calculated rates of net  $O_3$  production to observed changes in  $O_3$ . For this comparison, results from the constrained set of model runs (with updated treatment of peroxyacyl nitrates) are examined for the repeated profiling by the DC-8 over Seoul during the descents over Olympic Park which consistently sampled the same ground track from an altitude of 1 km down to a few tens of meters above the surface.

**Table 3** shows statistics for average  $O_x$ ,  $O_3$ , and model-calculated  $P(O_3)$  from the morning, midday, and

**Table 3:** Column averaged values of observed  $O_x$  ( $O_3$  in parentheses) and modeled  $P(O_3)$  below 1 km during Seoul missed approach profiles. DOI: <https://doi.org/10.1525/elementa.400.t3>

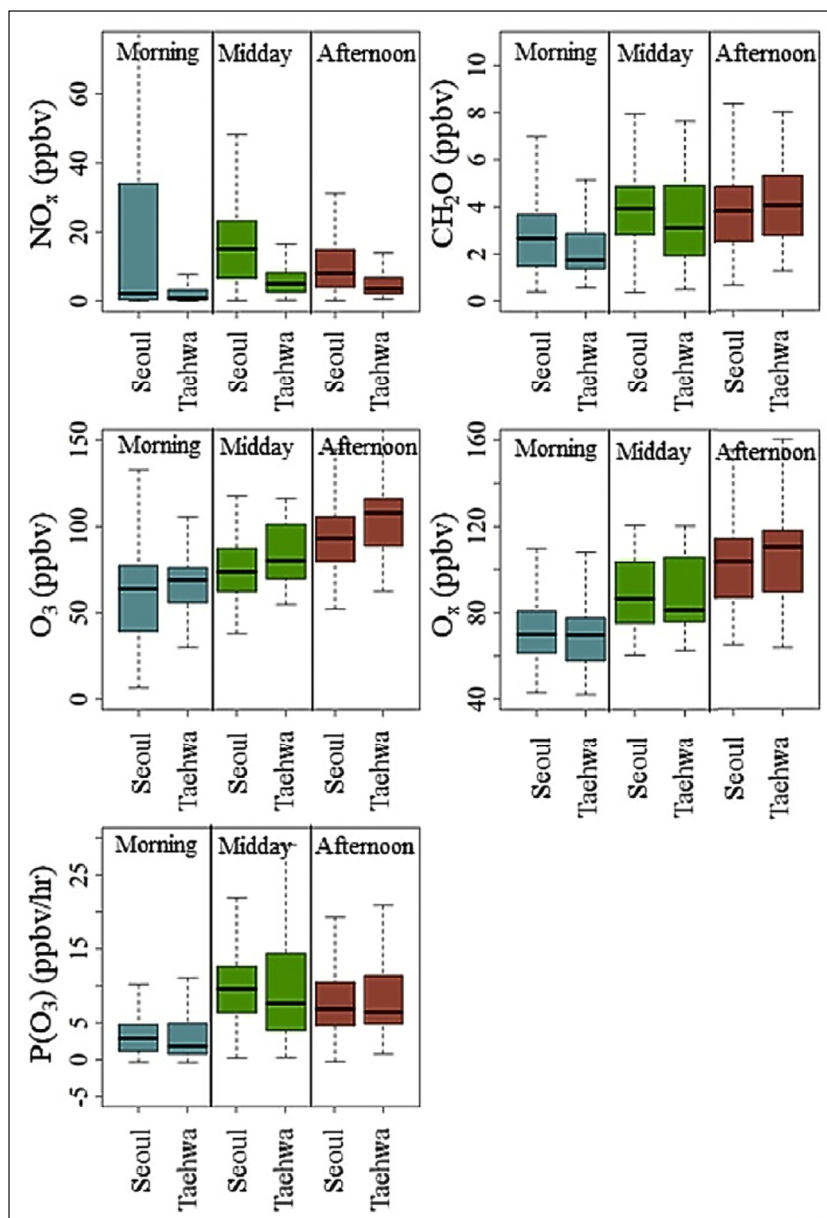
Profile Time	Average $O_x$ ( $O_3$ ) [ppbv]	Average $P(O_3)$ [ppbv/hr]	Average local time
Morning	71 (59)	3.2	08:25
Midday	88 (75)	8.1	12:06
Afternoon	104 (95)	7.5	15:29

afternoon descents over Seoul. From the morning to midday, an average change of 17 ppbv of  $O_x$  (16 ppbv of  $O_3$ ) over a period of 3.5 hours yields an observed rate of change of  $O_x$  (and  $O_3$ ) of  $\sim 4.8$  ppbv/hr, compared to the average calculated  $P(O_3)$  between morning and midday of 5.6 ppbv/hr. Likewise, from midday to afternoon, the observed change of 16 ppbv of  $O_x$  (20 ppbv of  $O_3$ ) over a period of  $\sim 3.5$  hours yields an observed rate of change of  $O_x$  of  $\sim 4.6$  ppbv/hr (and  $\sim 5.7$  ppbv/hr for  $O_3$ ) compared to the average calculated  $P(O_3)$  between midday and afternoon of 7.8 ppbv/hr.

These aggregate statistics demonstrate the strong role of photochemistry in the  $O_3$  changes observed over Seoul. It is also important, however, to recognize that other influences on  $O_3$  such as advection, entrainment from above, and surface deposition are not represented in the box model. Each of these factors should reduce  $O_3$  on average since Seoul is a strong source region and may explain the higher calculated rates of production as compared to observed changes.

## 5. $O_3$ Sensitivity in the SMA

Understanding  $O_3$  sensitivity, that is, whether local  $O_3$  production is  $NO_x$ -limited or radical-limited (VOC-limited), is a critical step towards drafting effective mitigation policies. During KORUS-AQ, DC-8 flights took advantage of natural gradients in  $O_3$  and its precursors by repeatedly overflying Seoul and Taehwa forest, located  $\sim 30$  km to the southeast, on many different days and under different conditions. A summary of these DC-8 observations for altitudes below 1 km is shown in **Figure 7**, contrasting data from the overflight of the two sites in the morning, midday, and afternoon. The most noticeable difference is that  $NO_x$  mixing ratios were always lower over Taehwa than over Seoul at all times of day with median values that were 2–6 times lower over Taehwa, Seoul also exhibited a much wider range of extreme values, especially in the morning when emissions were concentrated near the surface before substantial boundary layer growth had occurred.  $NO_x$  levels were lower outside the city due to dilution of the primary emissions as they moved downwind, as well as chemical processing. By contrast,  $CH_2O$ , an excellent proxy for VOC chemistry, was very similar between the two sites (with the exception of Taehwa in the morning), and roughly constant throughout the day. This is consistent with the continuous oxidation of VOCs and the short lifetime of  $CH_2O$ . The lower morning  $CH_2O$  at Taehwa also suggest a role for biogenic VOC emissions which increase throughout the day with temperature.  $O_3$  and  $O_x$  increased stead-



**Figure 7:** Diurnal distributions of observed  $\text{NO}_x$ ,  $\text{CH}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{O}_x$  and modeled  $\text{P}(\text{O}_3)$  over Seoul and Taehwa. Distributions are represented as box-whisker plots, where the thick black line represents the median value, the bounds of the box represent the interquartile range, and the whiskers represent the 5<sup>th</sup> and 95<sup>th</sup> percentiles. DOI: <https://doi.org/10.1525/elementa.400.f7>

ily from morning to afternoon at both sites, consistent with a photochemical source. While  $\text{O}_x$  distributions were similar,  $\text{O}_3$  tended to be higher over Taehwa in relation to Seoul due to the partitioning between  $\text{O}_3$  and  $\text{NO}_2$  under the high  $\text{NO}_x$  conditions in Seoul. The bottom left panel in **Figure 7** shows net  $\text{O}_3$  production rates calculated from the constrained set of model runs. Compared to the observed quantities,  $\text{P}(\text{O}_3)$  behaves most like  $\text{CH}_2\text{O}$ , as both map closely to photochemistry with lower morning values versus midday and afternoon. The lack of change in  $\text{P}(\text{O}_3)$  across the large  $\text{NO}_x$  gradient demonstrates the  $\text{NO}_x$ -saturated behavior in the model calculations. This allows sustained ozone production to increase both  $\text{O}_3$  and  $\text{O}_x$  across the region throughout the day. Thus, these observations provide a natural experiment whereby  $\text{O}_3$  production is sustained over a large  $\text{NO}_x$  gradient, without an associated gradient in VOCs (based on the  $\text{CH}_2\text{O}$  proxy), demonstrat-

ing that  $\text{O}_3$  production across the SMA was radical-limited (i.e. VOC-limited or  $\text{NO}_x$ -saturated). This builds upon recent work by Kim et al., (2018), who used measurements from an instrumented ground site in Seoul to identify conditions as radical-limited, by using airborne measurements throughout the boundary layer over a large area to understand  $\text{O}_3$  sensitivity over the broader SMA.

### 5.1. Model sensitivity to VOC classes

The findings highlighted in the previous section indicate that effective  $\text{O}_3$  mitigation strategies in the SMA must include reductions in VOC emissions. However, because VOCs as a class contain a broad spectrum of different species with a wide range of reactivities and radical yields, exploring the contributions of individual VOCs or classes of VOCs to the overall rate of  $\text{O}_3$  production is a crucial next step towards identifying emissions sectors that contribute

disproportionately to  $O_3$  production. To better understand the sensitivity of  $O_3$  to specific VOC classes, additional box model simulations were conducted whereby select VOC constraints were set to zero in the model. For these simulations, the model was not constrained by observations of  $CH_2O$ , PAN,  $HNO_3$ , and  $H_2O_2$  because of the associated feedback that removal of VOCs would have on these species. **Figure 8** shows the distribution of calculated  $O_3$  production rates over Seoul using a complete suite of DC-8 observations (black dashed line) compared to simulations where a single hydrocarbon or group of hydrocarbons were removed from the model (orange line in each panel). Note that because of the complex feedback that VOCs have on radical abundances and  $HO_x/NO_x$  partitioning, the percent reductions shown in **Figure 8** do not add up to 100%. The general shape of the  $P(O_3)$  distribution in the black dashed line (i.e. base-case) shows two distinct modes: one centered around 0–1 ppbv/hr and one centered around 4–5 ppbv/hr. In general, the lower mode contains data collected in the morning, at higher altitudes (1–2 km), and features low concentrations of  $NO_x$  (mean 0.3 ppbv) and low concentrations of short-lived hydrocarbons (for example, a median isoprene concentration of 0). The data that make up this mode are characterized as clean or aged airmasses above the boundary layer that were not recently impacted by surface emissions. The second mode, centered around 4–5 ppbv/hr, features data that contain characteristics of urban pollution, with relatively high  $NO_x$  (mean 11 ppbv) and VOCs.

$C_{7+}$  Aromatic compounds (which include toluene, ethylbenzenes, and xylenes) are shown to have the greatest impact on modeled  $O_3$  production, with a 32% reduction in mean  $P(O_3)$  and a sharp change in the distribution, with a large reduction in the amount of data falling above 5 ppbv/hr. Modeled  $O_3$  production was also fairly sensitive to isoprene, with removal of isoprene yielding a 15% reduction in mean  $P(O_3)$  over Seoul. Alkenes (which include ethene, propene,  $C_4$  alkenes, and  $C_5$  alkenes) also were found to contribute an important amount to  $O_3$  production in Seoul, with removal of alkenes resulting in a 14% reduction in mean  $P(O_3)$ . In contrast to  $C_{7+}$  Aromatics, removal of either isoprene or alkenes from the model resulted in little change in the modeled distribution of  $P(O_3)$  above 5 ppbv/hr. In effect, removing  $C_{7+}$  Aromatics from the model had a large effect on points with very high values of  $P(O_3)$ , while removing isoprene or alkenes tended to mostly impact points that were producing below 5 ppbv/hr in the base-case simulation. Other VOCs, including light alkanes, heavy alkanes, methanol, and CO (not shown) had negligible effect on modeled  $P(O_3)$ . **Figure 8** shows results of sensitivity simulations over Seoul, but similar results were noted when the study area was expanded to the entire SMA: Removal of  $C_{7+}$  Aromatics yielded a 36% reduction in mean  $P(O_3)$ , isoprene a 13% reduction, alkenes a 13% reduction, and all other species yielded 7% or less. Additionally, the results shown in **Figure 8** include all data collected below 2 km, which may mask the contribution of very short-lived VOCs, like isoprene, which have vertical profiles that are weighted towards the surface. When data are filtered to only include data collected below 1 km

over Seoul, the percent reductions in mean  $P(O_3)$  become 34% ( $C_{7+}$  Aromatics), 16% (isoprene), 13% (alkenes), 3% ( $C_{4+}$  alkanes), 1% (light alkanes), and 6% (methanol). Thus, no matter how the data are filtered (Seoul only, whole SMA, low altitudes only, etc.), the results suggest that reductions in anthropogenic emissions, particularly  $C_{7+}$  Aromatics (and alkenes, to a lesser extent), could provide an attractive target for reductions in local  $O_3$  production. This finding will benefit from source apportionment work being conducted by other KORUS-AQ investigators to characterize sources and quantify emissions of these species in the SMA. By contrast, the natural source of isoprene from vegetation does not offer an effective target for emissions reduction but must be considered to understand the response of  $O_3$  chemistry to emissions reductions for anthropogenic VOCs.

## 5.2. Model sensitivity to $NO_x$ reductions

While reductions in  $C_{7+}$  aromatics would benefit local  $O_3$  production in Seoul, the regional extent of downwind production must also be considered. The higher levels of  $O_3$  and  $P(O_3)$  at Taehwa (see **Figure 7**), despite the lower concentrations of  $NO_x$ , highlights the regional impact that the very high  $NO_x$  in Seoul has on sustaining  $O_3$  production downwind and across the surrounding region. Thus, despite the large gradient in  $NO_x$  from inside Seoul and into the surrounding region shown in **Figure 7**, conditions remain conducive to high rates of  $O_3$  production over a very large area and the only way to limit the regional extent of ozone production is to also target  $NO_x$  emissions for reduction.

In a strongly radical-limited environment, initial reductions in  $NO_x$  for a given VOC abundance will result in an increase in  $P(O_3)$ . After a sufficient amount of  $NO_x$  is removed, modeled  $P(O_3)$  will reach a maximum at the point where  $O_3$  sensitivity transitions to a  $NO_x$ -limited environment. Further reductions in  $NO_x$  beyond this point result in decreases in  $P(O_3)$  relative to the maximum, though  $P(O_3)$  may still be higher than at the starting point. To assess the impact of  $NO_x$  reductions, model sensitivity to  $NO_x$  was evaluated using three additional simulations whereby model input values for NO were reduced by 25%, 50%, and 75% while all other inputs were kept the same. Two additional simulations were performed where  $NO_x$  and all relatively-short-lived anthropogenic VOCs (i.e. all VOCs except methane, CO, and isoprene) were reduced by 10% and 25%. **Table 4** shows the mean relative increase in modeled  $P(O_3)$  from these experiments, filtered to show data from the entire SMA, Seoul, and non-Seoul SMA below 2 km. Over the entire SMA, reducing model input NO by 25% yielded a mean relative increase in modeled  $P(O_3)$  by 5%, becoming 11% when NO was reduced by 50%. Upon reducing input NO by 75%,  $P(O_3)$  was still higher than the base simulation by 10% on average, but was slightly lower than the simulations where NO was reduced by 50%. This indicates that, aggregated over the entire SMA,  $O_3$  sensitivity changed from radical-limited to  $NO_x$ -limited over this experimental range of NO reductions. In simulations where both  $NO_x$  and VOCs were reduced, mean  $P(O_3)$  decreased relative to the base simulation, demonstrating the value in concurrent reduction in emissions for both.



**Table 4:** Sensitivity of modeled  $P(O_3)$  to reductions in input NO, shows as mean relative increases compared to base simulations (i.e. unchanged DC-8 observations). Data are filtered to compare sensitivity of  $P(O_3)$  to  $NO_x$  over the entire SMA, Seoul, and non-Seoul SMA.

Model Simulation	Mean Relative Change in Modeled $P(O_3)$		
	All SMA <2 km	Seoul <2 km	non-Seoul SMA <2 km
NO -25%	+5%	+7%	+4%
NO -50%	+11%	+22%	+6%
NO -75%	+10%	+43%	-4%
NO + VOC -10%	-1%	-2%	-2%
NO + VOC -25%	-3%	-6%	-6%

When only data from urban Seoul are considered, reductions in NO always lead to an increase in  $P(O_3)$ , with the percent increase becoming higher with each subsequent NO reduction. This indicates that even with a 75% reduction in NO, the photochemical environment in urban Seoul is largely radical-limited. Interestingly, the changes in  $P(O_3)$  from urban Seoul suggest that it is substantially more radical-limited than the SMA taken as a whole. Because of this, suppression of radicals (and  $P(O_3)$ ) in urban Seoul leads to a lower base-case  $P(O_3)$  compared to the entire SMA, and therefore a larger relative increase in  $P(O_3)$  as the photochemical environment approaches the transition point where  $O_3$  production is most efficient. When only non-Seoul data were considered, the calculated mean relative increases in modeled  $P(O_3)$  with NO reductions were lower than the other two datasets (i.e. all SMA and urban Seoul), and the mean relative change in  $P(O_3)$  finally goes negative with the -75% simulation. As such, the “starting point” in the base-case simulation for non-Seoul was closer to the photochemical transition point than all SMA or urban Seoul.

These observations, combined with the results presented in Section 5.1, might suggest that reductions in VOC emissions should be a sole priority for reducing  $O_3$  in the SMA, and that reductions in  $NO_x$  emissions would exacerbate the problem. While reducing  $NO_x$  in our simulations resulted in increases in modeled  $P(O_3)$  in all but one case, it is also important to consider the associated feedbacks on key  $O_3$  precursors, particularly  $NO_x$  itself. Because  $NO_x$  has a lifetime on the order of hours, ambient  $NO_x$  mixing ratios are the result of a balance between  $NO_x$  emissions and  $NO_x$  removal. While reductions in  $NO_x$  emissions would certainly lead to reductions in ambient  $NO_x$  mixing ratios, we must also consider how the lifetime of  $NO_x$  changes in response to associated changes in the photochemical environment. **Table 5** shows weighted averages of instantaneous  $NO_x$  lifetimes as calculated by our model, assuming that formation of  $HNO_3$  is the only  $NO_x$  removal process. Reductions in constraining NO resulted in generally lower  $NO_x$  lifetimes compared to the base-case simulation, with the -75% simulation in urban Seoul yielding the largest reduction: a 66% decrease in

**Table 5:** Weighted average instantaneous  $NO_x$  lifetimes (hours), weighted by  $F(O_3)$ .

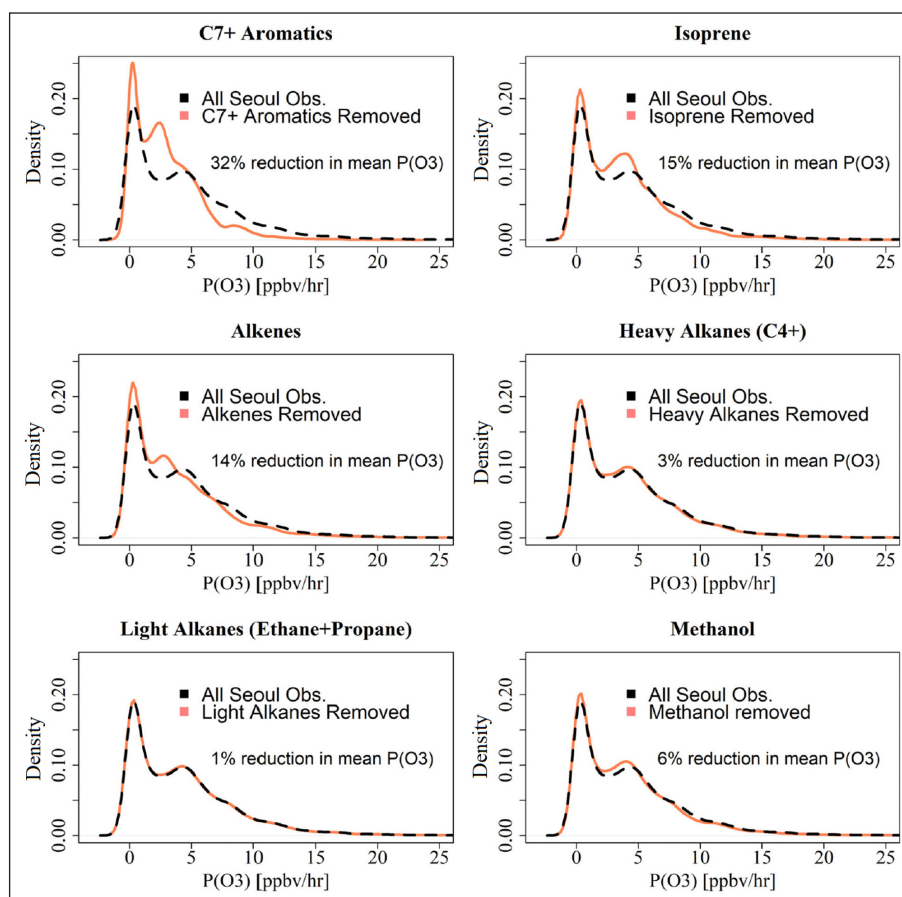
Simulation	weighted average of $\tau_{NO_x}$ (hrs), weighted by $F(O_3)$		
	All SMA <2 km	Seoul <2 km	non-Seoul SMA <2 km
Base	7.7	11.6	6.1
-25%	6.0	8.2	5.0
-50%	4.7	5.7	4.2
-75%	4.0	4.1	4.0

the  $NO_x$  lifetime relative to the base-case simulation. This is important for two reasons: 1) Reduction in  $NO_x$  emissions will result in amplified reductions in ambient  $NO_x$  mixing ratios (for example, a 25% reduction in  $NO_x$  emissions should be expected to produce ambient  $NO_x$  reductions in excess of 25%, all else being equal, because of associated reduction in the  $NO_x$  lifetime), and 2) A shorter duration of  $O_3$  production as airmasses move downwind from urban Seoul. While select VOCs, such as isoprene, are very short-lived, the majority of VOCs that were abundant in Seoul have lifetimes that are longer than  $NO_x$ , including aromatics (toluene, for example, has a lifetime of 1–2 days). In an environment such as the SMA, where VOCs are dominated by aromatics and emissions of biogenic VOCs persist throughout the region, the duration of  $O_3$  production for a given polluted airmass as it moves downwind is essentially limited by the lifetime of  $NO_x$  in that airmass. Therefore, even though reductions in NO resulted in increased rates of  $O_3$  production throughout the SMA in our simulations, the regional extent of  $O_3$  production would be reduced. In **Figure 7**, we showed that a receptor site at Taehwa Forest consistently had lower  $NO_x$  mixing ratios than urban Seoul. If  $NO_x$  mixing ratios in urban Seoul were reduced by some amount,  $NO_x$  mixing ratios at receptor sites such as Taehwa would be expected to be reduced by a larger amount, since a higher percent of  $NO_x$  would be chemically removed while in transit (owing to the shorter  $NO_x$  lifetime). In effect, while reductions in  $NO_x$  emissions could result in locally higher rates of  $O_3$  production in urban Seoul, regions outside of urban Seoul should benefit if the associated  $NO_x$  reductions push them far enough into the  $NO_x$ -limited regime. Fully quantifying the effects of  $NO_x$  reductions on  $O_3$  throughout the SMA requires the use of 3D models that can account for emissions, transport, and chemistry, and is beyond the scope of this work, but this question is being pursued by other KORUS-AQ investigators (Oak et al., 2019).

## 6. Summary and Conclusions

As South Korea has experienced rapid industrial growth over the past few decades, exposure to unhealthy levels of  $O_3$  has emerged as a public health concern, particularly in the SMA (population 25 million). Data collected by a network of ground stations in the SMA during KORUS-AQ indicated that  $O_3$  exceed the Korean 8-hour AQS value on 39 days during the 41-day study period.





**Figure 8:** Modeled distributions of P(O<sub>3</sub>) over Seoul from the “base case” simulation (black dashed line in each panel), and from the zero-out simulation shown in each panel (orange line). DOI: <https://doi.org/10.1525/elementa.400.f8>

Furthermore, O<sub>3</sub> was observed to be highest in outlying suburban regions, particularly Gyeonggi province, rather than urban Seoul. In this work, airborne observations of O<sub>3</sub> and other trace gases were used alongside an observationally-constrained 0-D photochemical box model to explore the sensitivity of O<sub>3</sub> to changes in its precursors. The fidelity of these photochemical calculations was explored using a series of additional simulations, and it was found that the steady state assumption used in 0-D box models cannot describe select intermediate species, particularly PAN, H<sub>2</sub>O<sub>2</sub>, and HNO<sub>3</sub>, while ambient CH<sub>2</sub>O observations were well-represented by our model. Model shortcomings in the prediction of H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> had no impact on model-calculated rates of O<sub>3</sub> production, while model results not constrained by PAN observations over-predicted average O<sub>3</sub> production in Seoul by more than 40%. This was mitigated by introducing a first order loss for PAN and other thermally labile peroxyacyl nitrates based on the average temperature in the boundary layer profiles of Seoul, providing much better agreement between constrained and unconstrained calculations of O<sub>3</sub> production. When fully constrained, aggregate statistics for model-predicted rates of O<sub>3</sub> production agreed well with average observed changes in ambient O<sub>3</sub>.

Observed gradients in O<sub>3</sub> and its precursors between urban Seoul and a downwind receptor site (Taehwa Forest) indicated that O<sub>3</sub> production in the SMA was radical-limited (i.e. VOC-limited) over the study period. Additional zero-out simulations were performed whereby

select VOCs were removed from the model, allowing for diagnosis of model sensitivity to individual VOCs. These simulations identified C<sub>7+</sub> aromatics (i.e. toluene, xylenes, ethylbenzenes, etc.) as the dominant VOC contributor to O<sub>3</sub> production in the region, with a 32% reduction in mean O<sub>3</sub> production calculated when C<sub>7+</sub> aromatics were removed from the model. Isoprene was found to be the second most important VOC with respect to contribution to O<sub>3</sub> production (15% reduction in mean O<sub>3</sub> production), and anthropogenic alkenes were the third most important (14% reduction in mean O<sub>3</sub> production).

Though the SMA was identified as radical-limited, analysis of model simulations in which NO<sub>x</sub> was reduced provided insight on competing effects. When constraining NO was reduced by up to 75% in our model, O<sub>3</sub> production increased in Seoul but began to decrease for the surrounding area. Thus, areas outside of Seoul were found to transition from a radical-limited to a NO<sub>x</sub>-limited environment within the range of NO<sub>x</sub> reductions studied here, while urban Seoul remained radical-limited even at a 75% reduction in constraining NO. Furthermore, we found that in all regions of the SMA, reductions in constraining NO lead to decreases in the modeled NO<sub>x</sub> lifetime. The results of a shortened NO<sub>x</sub> lifetime could be two-fold: 1) as the plume from urban Seoul moves downwind towards receptor sites, the time-duration over which that plume is capable of producing high amounts of O<sub>3</sub> would be shortened, and 2) reductions in NO<sub>x</sub> emissions should be accompanied by reductions in the NO<sub>x</sub> lifetime, meaning

that for a given reduction in  $\text{NO}_x$  emissions, a larger decrease in ambient  $\text{NO}_x$  mixing ratios could be expected. These results indicate that, even though the SMA was identified as radical-limited, reductions in  $\text{NO}_x$  emissions would have complex effects on  $\text{O}_3$  in the SMA, whereby  $\text{O}_3$  in urban Seoul would likely increase as a result of reduced  $\text{NO}_x$  emissions, but regions outside of urban Seoul, particularly Gyeonggi province, could benefit. Additional benefits of  $\text{NO}_x$  reductions include reductions in ambient  $\text{NO}_2$  (which is a criteria pollutant itself), and potential for reductions in fine particulate matter. However, analysis of these co-benefits is beyond the scope of this work.

The policy implications of this work are clear: reductions in VOCs, particularly  $\text{C}_{7+}$  aromatic compounds, provide an effective pathway for reducing  $\text{O}_3$  production in the SMA. Anthropogenic alkenes, such as ethylene and propylene, also provide an attractive target for emissions reductions, but certainly should not be prioritized over  $\text{C}_{7+}$  aromatics. Isoprene, while an important contributor to  $\text{O}_3$  production, does not represent a viable target for emissions reductions, owing to the biogenic nature of its source. The KORUS-AQ dataset can be utilized to classify and quantify sources of VOCs in the SMA, which may provide fruitful information for policymakers in drafting targeted mitigation strategies aimed at specific emissions sectors. Although  $\text{O}_3$  production in the SMA is radical-limited, reductions in  $\text{NO}_x$  emissions should also be considered with the intent of reducing the regional extent of  $\text{O}_3$  production. Broad-scale measurements of VOCs and  $\text{NO}_x$  in the SMA must be continued to understand changes in source contributions throughout the year, and to understand the effectiveness of any policies that are implemented. Long-term ground-based studies could provide continuous measurements at discrete locations, and follow-up airborne studies could be leveraged to explore emissions trends and gradients over larger spatial scales. While the  $\text{O}_3$  sensitivity analysis provided in this work and other studies that analyze in-situ measurements from KORUS-AQ can point to specific emissions sources that would make for attractive targets for emissions reductions, fully understanding the effects of emissions reductions on future air quality requires the use of 3D models that implement emissions, transport, and chemistry. Because of this, it is imperative that the emissions parameterizations used in 3D models are realistic, and the measurements from KORUS-AQ can provide an attractive dataset to test and validate 3D models. Additional studies that compare the chemical mechanisms used in 3D models and other models (such as the LaRC box model used in this study) may also highlight potential strengths or shortcomings of the underlying chemical mechanisms used in 3D models. If veracity can be obtained for modeled emissions and chemistry, a larger degree of confidence in the outcomes of simulations with different emissions reductions scenarios can be gained.

#### Data Accessibility Statement

Outputs from all box model simulations used in this work are available on the KORUS-AQ archive: <https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq?MODEL=1>.

#### Acknowledgements

The KORUS-AQ study was jointly funded by NASA and the Korean National Institute of Environmental Research (NIER). Special thanks goes to all who made the DC-8 flights over Seoul and in Korean airspace possible. This includes civil and military air traffic coordinators, DC-8 pilots and crew, and the scientists who negotiated the flight paths and permissions needed to collect these observations. The members of the PTR-MS instrument team (P. Eichler, L. Kaser, M. Müller) are acknowledged for their support with instrument preparation and field work.

#### Funding information

PTR-ToF-MS measurements aboard the NASA DC-8 during KORUS-AQ were supported by the Austrian Federal Ministry for Transport, Innovation and Technology (bmvit) through the Austrian Space Applications Programme (ASAP) of the Austrian Research Promotion Agency (FFG).

#### Competing interests

The authors have no competing interests to declare.

#### Author contributions

- Contributed to conception and design: JRS and JHC
- Contributed to acquisition of data: all authors
- Contributed to analysis and interpretation of data: JRS and JHC
- Drafted, revised, and approved of manuscript for submission: JRS and JHC

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**How to cite this article:** Schroeder, JR, Crawford, JH, Ahn, J-Y, Chang, L, Fried, A, Walega, J, Weinheimer, A, Montzka, DD, Hall, SR, Ullmann, K, Wisthaler, A, Mikoviny, T, Chen, G, Blake, DR, Blake, NJ, Hughes, SC, Meinardi, S, Diskin, G, Digangi, JP, Choi, Y, Pusede, SE, Huey, LG, Tanner, DJ, Kim, M and Wennberg, P. 2020. Observation-based modeling of ozone chemistry in the Seoul metropolitan area during the Korea-United States Air Quality Study (KORUS-AQ). *Elem Sci Anth*, 8: 3. DOI: <https://doi.org/10.1525/elementa.400>

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**Knowledge Domain:** Atmospheric Science

**Part of an *Elementa* Special Feature:** KORUS-AQ

**Submitted:** 03 May 2019

**Accepted:** 16 November 2019

**Published:** 13 January 2020

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