Factors controlling surface ozone in the Seoul Metropolitan Area during the KORUS-AQ campaign

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Abstract

To understand the characteristics of air quality in the Seoul Metropolitan Area, intensive measurements were conducted under the Korea-United States Air Quality (KORUS-AQ) campaign. Trace gases such as O₃, NOₓ, NO₂, SO₂, CO, and volatile organic compounds (VOCs), photochemical byproducts such as H₂O₂ and HCHO, aerosol species, and meteorological variables including planetary boundary layer height were simultaneously measured at Olympic Park in Seoul. During the measurement period, high O₃ episodes that exceeded the 90 ppbv hourly maximum occurred on 14 days under four distinct synoptic meteorological conditions. Furthermore, local circulation such as land–sea breeze and diurnal evolution of the boundary layer...
were crucial in determining the concentrations of precursor gases, including NO\textsubscript{x} and VOC as well as O\textsubscript{3}. During such episodes, the nighttime NO\textsubscript{x} and VOC and daytime UV levels were higher compared to non-episode days. The overall precursor levels and photochemical activity were represented fairly well by variations in the HCHO, which peaked in the morning during the high O\textsubscript{3} episodes. This study revealed that toluene was the most abundant VOC in Seoul, and its concentration increased greatly with NO\textsubscript{x} due to the large local influence under stagnant conditions. When O\textsubscript{3} was highly elevated concurrently with PM\textsubscript{2.5} under dominant westerlies, NO\textsubscript{x} and VOCs were relatively lower and CO was noticeably higher than in other episodes. Additionally, the O\textsubscript{3} production efficiency was the highest due to a low NO\textsubscript{x} with the highest NO\textsubscript{y}/NO\textsubscript{z} ratio among the four episodes. When westerlies were dominant in transport-south episode, the nighttime concentration of O\textsubscript{3} remained as high as 40–50 ppbv due to the minimum level of NO\textsubscript{x} titration. Overall, the Seoul Metropolitan Area is at NO\textsubscript{x}-saturated and VOC-limited conditions, which was diagnosed by indicator species and VOC/NO\textsubscript{x} ratios.

**Keywords**

KORUS-AQ; Air quality; Ozone; NO\textsubscript{x} and VOCs; PM\textsubscript{2.5}; SMA (Seoul Metropolitan Area)

### 1. Introduction

Tropospheric ozone (O\textsubscript{3}), which is known as a short-lived climate pollutant, is a potent greenhouse gas that acts as a product and initiator in environmental photochemical reactions (IPCC, 2007). It has been a critical cause of the increasing rate of climate change over the years and is harmful to human health, vegetation, and ecosystems due to its strong oxidation capacity (Benton et al., 2000; Fuhrer, 2003; Kampa and Castanas, 2008; Karnosky et al., 2005; Thompson, 1992; Thurston and Ito, 2001). Ozone is primarily transported from the stratosphere and produced via photochemical reactions that involve nitrogen oxides (NO\textsubscript{x}), volatile organic compounds (VOCs), and carbon monoxide (CO) in the presence of sunlight (NRC, 1991). These O\textsubscript{3} precursors are emitted into the atmosphere from many diverse sources (e.g., vehicle exhaust, industrial activities, residences, and biogenic activities). Ozone is produced rapidly under highly elevated NO\textsubscript{x} and VOC concentrations, which may lead to severe surface O\textsubscript{3} pollution (Jacob, 1999). Many metropolitan areas across the globe have suffered from extreme O\textsubscript{3} pollution, with severe exceedances of the National Ambient Air Quality Standards (NAAQS). For example, in North America and Europe, the number of severe O\textsubscript{3} pollution events rose in the 1990s, which were alleviated by imposing strict emission controls (Chang et al., 2017; Cooper et al., 2014). Significant research has been conducted for several decades on alleviating air pollution in urban areas in Europe and North America (Jenkin and Clemitshaw, 2000; Singh et al., 2006; Solomon et al., 2000). For example, Los Angeles was troubled with photochemical smog in the 1900s; however, the O\textsubscript{3} was alleviated after research was conducted and stringent control strategies were implemented on emissions (Fenger, 1999; Jacob, 1999). Similarly, Houston suffered from extreme O\textsubscript{3} pollution in the summer of 2000 and the Texas Air Quality Study (TexAQS) was conducted to determine why the city frequently faced severe O\textsubscript{3} exceedances of the NAAQS (Banta et al., 2005). In Mexico City, a high population density and local geographical features facilitated the O\textsubscript{3} and PM\textsubscript{2.5} pollution; therefore, the “Megacity
Initiative: Local and Global Research Observations-the Mexico City Metropolitan Area (MILAGRO-MCMA) campaign was conducted to improve the Mexico City Metropolitan Area emissions inventory and to understand the overall atmospheric pollution (Molina et al., 2006; Song et al., 2010).

The highest concentrations of O$_3$ and other pollutants frequently occur in major metropolitan areas in South and East Asia owing to urbanization and industrialization, which is causing significant increases in O$_3$ precursor emissions (Akimoto, 2003; McGranahan and Murray, 2012; Molina and Molina, 2004). In China, Beijing is one of the most populated cities and suffers from the high O$_3$ pollution with severe NAAQS exceedances (Wang et al., 2006; Wang et al., 2017; Xu et al., 2011). To improve the understanding of VOC-NO$_x$-O$_3$ chemistry, the Campaign of Air Quality Research in Beijing and surrounding areas (CARE-Beijing) was conducted in 2006 (Chou et al., 2009).

The Seoul Metropolitan Area (SMA) accounts for approximately 44% of South Korea’s population (51 million), which has approximately 10 million registered vehicles (KOSTAT, 2019). Thus, the SMA suffers from high NO$_x$ and VOC concentrations, which is a major hindrance in maintaining good air quality (An et al., 2015; Iqbal et al., 2014; Na et al., 2003). In Seoul, primary pollutants such as CO and SO$_2$ decreased sharply until the early 2000s and have remained low since then (KMOE, 2017). The mean annual PM$_{2.5}$ concentration has also decreased (Seoul, 2017). However, the O$_3$ levels have clearly increased since 2005, in spite of the NO$_2$ decrease. Han et al. (2013) suggested that the increased O$_3$ concentration in Seoul adequately represents the complex nonlinearity between O$_3$ and its precursors. In Seoul, the highest hourly O$_3$ mixing ratio reached approximately 150 ppbv in the spring of 2017 (KMOE, 2017), and thus the reduction of O$_3$ and its precursors has become an imminent environmental issue as well as further reduction in PM$_{2.5}$ concentrations.

To investigate and identify the key constituents and parameters involved in the photochemical formation of O$_3$, which eventually leads to O$_3$ pollution, a multi-year study was conducted in the eastern parts of Seoul (at Olympic Park and Korea University) from 2004–2005 (Lee et al., 2008b; Shon et al., 2007). Moreover, the Megacity Air Pollution Study-Seoul (MAPS-Seoul) was conducted to investigate the meteorological and chemical factors that contribute to O$_3$ formation in May and June of 2015 (Kim and Lee, 2018). The main result of these study was that O$_3$ formation in Seoul is generally VOC-sensitive (Kim et al., 2018a; Lee et al., 2008a).

The Korea-United States Air Quality (KORUS-AQ) campaign, performed in the spring of 2016, was a comprehensive measurement study to investigate the diverse aspects of air quality problems in East Asia and to evaluate the air quality of the SMA (KORUS-AQ mission whitepaper, 2015). This study, which was conducted as part of the KORUS-AQ campaign, aims to understand the photochemical mechanisms of O$_3$ formation in the SMA, diagnose its sensitivity, and identify the crucial factors that control O$_3$ formation in early summer (May–June).
2. Experimental methods

2.1. Measurements

Seoul, the capital of South Korea, is a basin surrounded by mountains with the Han River flowing across the center from east to west. The old town is located in the northern part of the Han River and forms a historical and political center, while the south is a newly developed area that serves as a residential and economic center. Ground measurements were conducted at Olympic Park, located in southeastern Seoul, from May 10 to June 12, 2016 (Figure 1). Olympic Park (37.52 N, 127.12 E) is surrounded by trees, main roads (400–600 m away), and residential areas. All measurement instruments were installed in a two-story container house, which was located close to a small lake (~50 m) and swimming stadium with a parking lot (~200 m).

During the field measurements, trace gases including O$_3$, NO$_x$, NO$_y$, SO$_2$, CO, and VOCs, aerosol species, and photochemical indicators (e.g., H$_2$O$_2$ and HCHO) were measured simultaneously. The Korea Research Institute of Standards and Science (KRISS) measured the O$_3$, NO$_x$, CO, and SO$_2$ concentrations using a series of KENTEK instruments (South Korea) utilizing UV absorption (Mezus 410), chemiluminescence with a photolytic converter (Mezus 210P), non-dispersive infrared technique (Mezus 310), and UV fluorescence (Mezus 110), respectively. The detection limit was 0.5 ppbv for O$_3$, NO, NO$_2$, and SO$_2$, and 50 ppbv for CO. The NO$_x$, SO$_2$, and CO instruments were calibrated every three days against zero air and span gas (400 ppbv for NO$_x$ and SO$_2$; 4 ppm for CO). The O$_3$ monitor was calibrated before and after the field campaign using the standard reference photometer of KRISS. The NO$_x$ measurement (T200U, Teledyne, USA) was made by Kunsan National University. To minimize the loss of reactive nitrogen oxide (e.g., PAN, HNO$_2$, and HNO$_3$) in the sample, the molybdenum converter was mounted externally, close to the sample inlet. The detection limit of NO$_y$ was 0.5 ppbv. Three calibrations were performed by KRISS against NO (101.26 μmol/mol) and NO$_2$ (50.05 μmol/mol) using a Teledyne (T700) calibrator. The concentration change was verified for 30 min to 1 h after injecting zero and standard gas (400 ppbv) directly through the sample line.

For VOCs, of the total 56 species of O$_3$ precursors species, C6–C12 (34 species) and C2–C5 (22 species), were measured at Olympic Park and a nearby Gwangjin site (37.55 N, 127.09 E), respectively, by the Seoul Research Institute of Public Health and Environment (SRI) utilizing a gas chromatography flame ionization detector (GC-FID). In addition, the National Institute of Environmental Research (NIER) operated a proton-transfer-reaction mass spectrometer (PTR-MS) in Olympic Park to detect acetone, acetaldehyde, and methyl ethyl ketone (MEK). A detailed description of the VOC species is summarized in Kim et al., 2020.

The United States Environmental Protection Agency (EPA) installed Aerodyne quantum cascade lasers (TDL Wintel v14.91) in the second floor of container house to detect formaldehyde (HCHO). The instrument accuracy was 10%, and its precision was 0.06 ppbv (Spinei et al., 2018). A quantum cascade-tunable infrared laser differential absorption spectrometer (QC–TILDAS) was used by the Hankuk University of Foreign Studies (HUFS) to measure hydrogen peroxide (H$_2$O$_2$) and nitrous acid (HONO).
PM$_{2.5}$ mass concentration and composition were measured by the SRI. The mass was monitored every 5 min utilizing beta attenuation techniques (FH 62 C14 series, Thermo Fisher Scientific). The composition was analyzed every hour for soluble ionic species using a monitoring of aerosols and gases system (MARGA, model ADI 2080, DOGA Limited, Turkey).

Meteorological parameters were monitored on site by NIER. In particular, the planetary boundary layer (PBL) height was retrieved from the continuous backscatter profiles obtained from a ceilometer (CL-51, Vaisala Inc.) by the EPA. At a nearby Jungnang site (37.5907°N 127.0794°E) that is located 8.5 km northwest of Olympic Park, vertical wind profiles were continuously monitored by pulsed Doppler wind lidar (Leosphere, Windcube-200) (Park et al., 2017). These two sets of measurements provide a unique opportunity to investigate the role of boundary layer dynamics in air quality. Considering the different time resolutions of the various measurements, all measured species were averaged hourly and merged into a dataset for further analysis in this study.

2.2. Model description

The air-mass trajectory was traced backward using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model with a global data assimilation system (GDAS, 1 degree) from the U.S. National Oceanic and Atmospheric Administration (NOAA) (Draxler and Hess, 1998; Stein et al., 2015), and the trajectories were calculated and plotted using Trajstat software (Wang, 2014).

This study used the framework for 0-D atmospheric modeling (F0AM) to simulate diurnal O$_3$ variations using measured NO$_x$ and VOC concentrations as hourly averages. The F0AM was initially introduced as an advanced version of 1D chemistry for the atmosphere-forest exchange (CAFE) model (Wolfe et al., 2016), but was applied to various types of experiments and analyses. The F0AM provides a chemical mechanism, such as a master chemical mechanism (MCM) or a regional atmospheric chemistry mechanism (RACM), and facilitates the simulation of an atmospheric chemistry system, including the time evolution of photochemical process, VOC oxidation, radical production, and photolysis. In this study, MCMv3.3.1, written in MATLAB, was utilized as the chemical mechanism.

3. Results and discussion

3.1. Measurement overview

The measurement results of the trace gases (e.g., O$_3$, NO$_x$, NO$_2$, SO$_2$, HCHO, CO, and VOCs), PM$_{2.5}$, and meteorological factors are presented for the May 10 to June 12 study period (Figure 2), and the VOCs are given for each of the sub-classes. During the entire measurement period, the daily maximum 1- and 8-h average O$_3$ mixing ratios were 128 ppbv and 96 ppbv, respectively, and were observed on June 10, 2016 (Table 1). The O$_3$ mixing ratios showed a variation that is typical of polluted urban sites; these variations were characterized by a clear maximum during the day and a very low level at night. The O$_3$ mixing ratios, however, occasionally remained high (greater than 40 ppbv) at night with a low NO$_x$. The average NO$_x$ mixing ratio for the entire study period was 30 ± 23 ppbv (NO:
6.2 ± 12.1 ppbv and NO₂: 23.9 ± 14.4 ppbv) within a range of 0.1 to 148.9 ppbv. The highest NOₓ was observed at night on May 18. At night, the NOₓ frequently exceeded 50 ppbv and exceeded 100 ppbv for 5 consecutive days. NOₓ variations showed similar patterns to NOₓ and ranged from 2.8 to 145.0 ppbv with a mean of 35.6 ± 23.3 ppbv. Furthermore, NOₓ as [NOₓ] – [NOₓ] ranged from 1 to 20.0 ppbv, with an average of 5.9 ppbv. The total oxidant (Oₓ) as the sum of O₃ and NO₂ exhibited a typical distribution similar to that of O₃ with a maximum of 144 ppbv at 15:00 on June 10. In this case, O₃ accounted for almost 90% of the Oₓ in the daytime, and the concentration of NO₂ was mainly high during the nighttime.

As a byproduct of VOCs oxidation, HCHO was measured from May 12 to June 11, and the mean was 3.6 ± 1.6 ppbv. From May 18 to May 23, when NOₓ was the highest, the HCHO was also elevated, and the highest HCHO was 9.6 ppbv on May 20.

During the entire experiment, the mean and maximum PM₂.₅ were 29 ± 16 μg m⁻³ and 88 μg m⁻³, respectively. The PM₂.₅ concentration exceeded the daily standard of 35 μg m⁻³ from May 25 to May 31. During this period, the major ionic species, including nitrate (NO₃⁻), sulfate (SO₄²⁻), and ammonium (NH₄⁺), were highly elevated and accounted for nearly one-third of the PM₂.₅ mass. In conjunction with an increase in PM₂.₅, the CO increased to 1112 ppbv, which is more than twice the average CO mixing ratio (537 ± 190 ppbv). In addition, the SO₂ increased and remained high during this period. Unlike inorganic species, organic carbon (OC) was the most abundant from May 20–23 when PM₂.₅ concentrations were relatively low.

In this study, the four VOC sub-classes were considered as O₃ precursors and included in the total VOCs (TVOCs): alkanes, alkenes and alkynes, aromatics, and oxygenated VOCs (OVOCs). Of these, the C₂–C₅ species were measured at the Gwangjin site near Olympic Park. Due to the scarcity of VOC measurements, it was not feasible to investigate the spatial homogeneity of the two sites. In Seoul, however, the OH reactivity and temporal variability of light VOCs were generally less than that of heavy VOCs (Seoul City, 2017). Therefore, the measurements from the two sites were combined for further discussion.

Among these, the alkanes were the most abundant and accounted for 40% of the total VOCs, followed by OVOCs, aromatics, and alkenes (Figure 2). The highest concentration among the individual species was acetone, followed by ethane and toluene. The highest toluene and acetone mixing ratios, 16 and 13 ppbv, respectively, occurred on June 10.

The temperature gradually increased from May to June, and the daily maximum temperature exceeded 30°C for four days during the entire period. The relative humidity varied from 16.6 to 97.8% and the PBL height significantly varied from 121 to 3,507 m according to the meteorological conditions.

### 3.2. High O₃ episodes

#### 3.2.1. O₃ and PM₂.₅ standard exceedance

In South Korea, the NAAQS for O₃ are 100 and 60 ppbv for the 1- and 8-h averages, respectively. Based on these criteria, the O₃ exceeded the NAAQS on 6 and 26 days, respectively, which means that the 8-h O₃ standard was violated for approximately two-thirds of the experiment period. In this
context, the high \( \text{O}_3 \) episodes were selected for which the daily maximum \( \text{O}_3 \) exceeded 90 ppbv (96th percentile) in the present study. This concurred with the “moderate” phase of the Comprehensive Air-quality Index (CAI) that classifies ambient air quality according to the health risks of air pollution. As a result, in total, 14 days were chosen as high \( \text{O}_3 \) episodes. Over the same period, \( \text{PM}_{2.5} \) exceedance occurred on 10 days, when the daily \( \text{PM}_{2.5} \) concentration was higher than 35 \( \mu \text{g m}^{-3} \) (1-day NAAQS for \( \text{PM}_{2.5} \)).

3.2.2. Synoptic weather condition—Because the study region was under the influence of the East Asian Monsoon, northerly winds were dominant from December to February, while southerly winds brought heavy rain from July to September. Before the summer monsoon season, there is a transition period during which air masses are frequently stagnant, with a low wind speed (<2 m/s), and high radiant heating during the day in May and June (Kim et al., 2018a). For the KORUS-AQ period, meteorological conditions showed dynamic variations, leading to an increase in \( \text{O}_3 \) or \( \text{PM}_{2.5} \) concentrations (Kim et al., 2018b; RSSR, 2017). While high \( \text{O}_3 \) events were identified under various synoptic weather conditions like the stagnant, transport, and blocking periods (Peterson et al., 2019), the \( \text{PM}_{2.5} \) exceedance days occurred mostly during the transport period.

With the HYSPLIT model, the 24 h backward trajectories of air masses arriving at an altitude of 500 m, were analyzed every 3 h for the entire experiment period. Through cluster analysis, these trajectories were separated into four groups (Figure 3), in which the 14 days of high \( \text{O}_3 \) episodes were found in groups according to synoptic weather conditions. As a result, the four trajectory clusters were connected with the distinct synoptic weather periods, representing the mean trajectories of air masses for the stagnant (C1), blocking (C2), and transport (C3 and C4) periods.

The episodes from May 18–23 belonged to C1 under a high-pressure system residing over the Korean Peninsula (except for May 21). Similarly, C2 included the high \( \text{O}_3 \) events that occurred in June under a blocking pattern over East Asia (June 2, 5, 7, 9, and 10). In contrast, the episodes of C3 and C4 were characterized by highly elevated \( \text{PM}_{2.5} \) concentrations under the influence of dominant westerlies. While C3 included the impact of Northern China, including North Korea (May 17, 29, and 30), C4 was distinguished by the air mass from the southeastern part of China (May 25) (Peterson et al., 2019). Thus, the transport period was split into transport-north (C3) and transport-south (C4) period. The measurements of reactive gases and meteorological parameters were sorted by episode and compared with each other and with those of non-episode periods (Figure 4).

This study focused on the 14 days of high \( \text{O}_3 \) episodes that were categorized into the four groups (C1–C4), for which the relevant reactive precursors were comprehensively analyzed and the factors affecting the \( \text{O}_3 \) level were thoroughly investigated in the following section.

Temperature and relative humidity showed a gradual change from C1 to C4. Likewise, the \( \text{PM}_{2.5} \), \( \text{SO}_2 \), and \( \text{CO} \) concentrations increased from C1 to C4. In comparison, VOC and \( \text{NO}_x \) were similar in variation to those of UV and PBL height and noticeably higher in C1 than in C4. While \( \text{O}_3 \) levels were comparable during the day, the nighttime concentration was clearly higher in C4. Among the four episodes, C1 was characterized by high
temperatures, PBL heights, and NO\textsubscript{x} concentrations. In contrast, C4 was distinguished by a concurrent increase in O\textsubscript{3} and PM\textsubscript{2.5}, with high SO\textsubscript{2} and low NO\textsubscript{x} concentrations. The similarities and differences in the measured variables between the four episodes reveal key factors controlling the air quality and indicate the intimate coupling between chemical and meteorological processes at local and regional scales.

### 3.2.3. Diurnal evolution of O\textsubscript{3} and its precursors

The UV and precursor levels were noticeably high during the high O\textsubscript{3} episodes compared to the non-episode periods (Figure 4) and their diurnal evolution varied from episode to episode (Figure 5). In this section, therefore, the diurnal variations of the chemical species and meteorological variables were examined in detail for the four episodes. For instance, the UV level was highly variable and did not directly correlate with the O\textsubscript{3} (Figure 5). In a previous study, the UV level was not a key factor that determined high O\textsubscript{3} concentrations (Lee et al., 2008b). In this study, the UV level variations were related to cloud coverage (low and medium levels). In C4, the UV level was low due to a thick cloud cover in the morning, but it rapidly increased with a decrease in cloud coverage around noon, leading to a sharp O\textsubscript{3} peak at 15:00 (Figure 5d). On the contrary, the O\textsubscript{3} peak time was 14:00 during the non-episode period, with increased cloud coverage in the afternoon (Figure 5e). Therefore, these four high O\textsubscript{3} episodes demonstrate the weather conditions that meet the prerequisites for high O\textsubscript{3} formation.

One of the main results of the KORUS-AQ campaign revealed that mesoscale circulation, such as the land–sea breeze, was a critical factor determining the O\textsubscript{3} level in Seoul (Peterson et al., 2019; RSSR, 2017). This was observed in the C1 episode, when stagnant condition and weak synoptic flow enhanced land-sea breeze (Peterson et al., 2019). On May 20, the O\textsubscript{3} level increased abruptly and reached a maximum at 18:00.

As a major source and sink of odd-hydrogen radicals, the variations of HCHO and H\textsubscript{2}O\textsubscript{2} were examined under different conditions during the four high O\textsubscript{3} episodes and non-episode (Figure 5). Previous studies reported that HCHO reached a maximum at 10:00–11:00 or 14:00–15:00, which varied based on the season (Li et al., 2014; Pang and Mu, 2006). Most interestingly, there were three HCHO peaks identified in the present study, one in the morning, afternoon, and evening. The morning peak appeared right after the maximum NO\textsubscript{x} occurred and was most pronounced in C1 when there was no typical afternoon maximum for HCHO (Figure 5a). Instead, the HCHO increased with NO\textsubscript{x} at night, which was the most noticeable on May 21 and 22 (Figure 2). This is primarily related to the daily evolution of boundary layer.

In the stagnant condition (C1), NO\textsubscript{x} and VOC levels were highly elevated at night, but at a minimum in the afternoon. While the shallow PBL resulted in the enrichment of precursors at night, all precursor levels were at their minimum levels when the boundary layer was the deepest in the afternoon. In the morning, the UV level was the highest for all four episodes, which likely expedited VOC oxidation and led to HCHO formation, and in turn, HO\textsubscript{2} radical production. It was recently hypothesized that OH radicals produced from HONO photolysis initiated VOC oxidation early in the morning during the high O\textsubscript{3} episodes (Gil et al., 2020). It is likely to be a plausible reason for the morning HCHO peaks observed in this study.
In general, the afternoon peak was evident and represented the daily maximum HCHO, which was the most pronounced on May 25 (C4) (Figure 5d). The daily maximum was not significantly different between episodes (5–6 ppbv), although it was substantially lower during non-episodes. Likewise, the background HCHO level was higher during the high O₃ episodes (~4 ppbv) than during non-episodes (~3 ppbv). Furthermore, the morning and night HCHO peaks agreed well with the VOC and NOₓ levels. These results imply that HCHO serves as a robust tracer for the overall VOC activity that leads to O₃ formation.

The minimum HCHO for the entire measurement period, which was no less than 2 ppbv, indicates that it needs to be further investigated to determine whether it was a result of primary or secondary sources.

In the four episodes, the diurnal variation of H₂O₂ was different in the peak time between 14:00 and 19:00. Except for C1, H₂O₂ reached its maximum around 17:00, after the O₃ peak. In C1, the H₂O₂ mixing ratio increased in the early morning and showed a broad maximum around 14:00, before the O₃ maximum (Figure 5a). This is likely associated with the morning HCHO peak, which readily produced HO₂ radicals and promoted HO₂ formation. In the present study, the H₂O₂ levels were higher during the high O₃ episodes than during the non-episodes; however, the maximum barely exceeded 1 ppbv due to the high NOₓ, which was particularly high at night. In C1, the boundary layer was the most intensively expanded during the day, and the levels of primary species rapidly decreased accordingly, creating a favorable condition for H₂O₂ formation.

These findings demonstrate that the photochemical characteristics differed between episodes and that the cycle of odd-hydrogen radicals was closely related to the overall precursor level and meteorological conditions.

3.3. Planetary boundary layer effects on air quality

In Northeast Asia, atmospheric pollutant levels are significantly affected by synoptic weather conditions, which was also observed in this study (Jordan et al., 2020; Peterson et al., 2019). Additionally, the daily evolution of the boundary layer has been found to be a critical factor determining urban air quality (e.g., Huang et al., 2018). As expected, in the present study, O₃ and CO were positively and negatively correlated with the PBL height, respectively (Figure 6). The measurement data presented for each episode shows that the boundary layer was deeper in C1 and C2 than in C3 and C4. Nevertheless, O₃ levels were comparable for the four episodes because a deep boundary layer not only promotes O₃ production through NOₓ dilution, but also dilutes photochemically produced O₃. In Figure 6a, outliers were mostly observed in C1 and C2. Especially, on May 20 (C1), the O₃ concentration rapidly increased with a decrease in the PBL height, reaching up to 113 ppbv at 18:00. It turned out that this was caused by mesoscale circulation, such as a land–sea breeze (Peterson et al., 2019).

The relationship between PBL height and CO demonstrates that the CO level was affected by the PBL because it was diluted during the day and accumulated at night (Figure 6b) and was evidently higher during transport episodes (C3 and C4) than the other episodes. This characteristic was partially attributed to the change in the PBL height under different synoptic meteorological conditions. Like CO, PM₂.₅ concentration was inversely related
to the PBL height (Figure 6c). Considering that the highest PM\textsubscript{2.5} was due to secondary inorganic ions at night in C4 episode, this relationship suggests that there must be other mechanisms responsible for nighttime increases in PM\textsubscript{2.5} than accumulation or transport, which is addressed in Jordan et al. (2020).

In addition to the high O\textsubscript{3} occurrence observed on May 20, O\textsubscript{3} often increased or remained high after sunset, which was associated with the low PBL height as shown in Figure 6a. On May 23–24 and June 5–6, the O\textsubscript{3} increase was accompanied with an increase in H\textsubscript{2}O\textsubscript{2} and a decrease in CO from 00:00–02:00 (Figure 7a and b). These events took place in association with a rapid change in the PBL height (C1 and C2, respectively). In comparison, the nighttime O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} enhancement was concurrent with an increase in CO and PM\textsubscript{2.5} on May 25–26 and 30–31, during which the PBL height remained low (C3 and C4, respectively) (Figure 7c and d). The PBL was overlaid with the vertical wind vectors measured by the Doppler wind lidar in Figure 7, which revealed the detailed boundary layer structure, particularly when the PBL was shallow at night.

For cases C1 and C2, the PBL change was associated with strong southerly winds above the boundary layer and at the surface, respectively. These horizontal winds were possibly due to local circulation such as land and mountain breezes, which caused the boundary layer to become unstable and the nocturnal residual layer was mixed down. The PBL primarily stayed shallow under constant westerlies; however, it was slightly increased when winds were strong, as indicated in C4 (Figure 7d). In this case, CO and PM\textsubscript{2.5} concentrations increased with O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} increases. As a result of the KORUS-AQ campaign, the elevated CO/CO\textsubscript{2} ratio was suggested to be an indicator of Chinese influences (Tang et al., 2018). It is mainly attributed to the CO enhancement, which is evident in the transport regimes of C3 and C4.

Given that all these enhanced O\textsubscript{3} events at night occurred during the high O\textsubscript{3} episodes, the likely cause is the vertical mixing of air enriched with photochemical byproducts in the residual layer. In previous studies, the nighttime O\textsubscript{3} increase has been explained by nocturnal residual layer entrainment (Aneja et al., 2000; Jackson and Hewitt, 1996; Lee et al., 2008b). Therefore, the results of this study demonstrated that, in addition to synoptic circulation, the daily boundary layer evolution was responsible for the O\textsubscript{3} and PM\textsubscript{2.5} short-term variations as well as primary pollutants such as CO. The enhanced nighttime O\textsubscript{3} level was not as high as the episodes during the day; however, it was greater than 60 ppbv and could thus contribute to the 8-h NAAQS violations. It is also note-worthy that the nighttime increase was accompanied by an increase in H\textsubscript{2}O\textsubscript{2}; thereby suggesting that it is a useful tracer for residual layer entrainment.

### 3.4. Characteristics of O\textsubscript{3} precursors

3.4.1. Nitrogen oxide—In general, O\textsubscript{3} is titrated by NO\textsubscript{x} under a high NO\textsubscript{x} environment; this is a major process of O\textsubscript{3} loss in urban areas. Thus, O\textsubscript{3} (NO\textsubscript{2}+O\textsubscript{3}) represents the actual O\textsubscript{3} level and is a better indicator for understanding O\textsubscript{3} chemistry (Lei et al., 2007; Lin et al., 2008). As shown in Figure 4, the O\textsubscript{3} level was comparable in all four cases. For O3, the daytime levels were in a similar range, but the nighttime levels were clearly different from episode to episode, leading to a large difference in the O\textsubscript{3}/O\textsubscript{3} ratio.
at night caused by a difference in NO$_x$, which were highest in C1 and lowest in C4. The difference of nighttime O$_3$/O$_x$ ratios in the C1 and C4 demonstrates that the NO$_x$-titration effect is significant even during the high O$_3$ episodes in Seoul. It is also noteworthy that the nighttime O$_3$ concentration remained as high as 40–50 ppbv under the low NO$_x$ condition in C4, which is comparable to the mode concentration of O$_3$ (59 ppbv) observed from shipboard measurements in the Yellow Sea during the KORUS-AQ (Seo et al., 2019).

Like NO$_x$, the NO$_y$ mixing ratio was two times higher in C1 (52.5 ppbv) than in C4 (24.8 ppbv). In contrast, NO$_z$, calculated as [NO$_y$] – [NO$_x$], was the highest in C4, in which NO$_z$ accounted for approximately 40% of the NO$_y$. It is well known that the NO$_z$/NO$_y$ ratio provides information about the photochemical aging of air masses (Marion et al., 2001; Perros and Marion, 1999; Wood et al., 2009). The NO$_z$/NO$_y$ ratio was higher in C3 and C4 than in C1 and C2, as expected from the meteorological regime of the air mass. NO$_z$ is discussed further in Section 3.5.2 to evaluate O$_3$ production efficiency.

### 3.4.2. Volatile organic compounds

The reactions of NO with HO$_2$ and RO$_2$ radicals produced from VOC oxidation are the major pathway for radical cycling that leads to O$_3$ formation. In general, VOC reactivity varies over a wide range and individual VOC species make different contributions to O$_3$ formation in the atmosphere (Atkinson et al., 2000). The TVOC mixing ratios were higher during the high O$_3$ episodes (203.0 ppbC) than during the non-episodes (154.7 ppbC). Among the four episodes, TVOCs were the highest in C1, followed by C3, and the lowest in C4 (Figure 8a). Toluene was the most abundant VOC compound, accounting for nearly 15% of the TVOCs, followed by acetone and n-butane. It was the highest in C1 among the four episodes.

To compare the contribution of each VOC species to O$_3$ formation, their OH reactivity was calculated (Atkinson et al., 2003) including NO$_2$ and CO (Figure 8b). Although alkanes were abundant in Seoul, they were less reactive than the aromatics such as xylene and toluene or OVOCs such as acetaldehyde and HCHO. These aromatic VOCs were found to significantly influence O$_3$ production during the KORUS-AQ (Schroeder, 2020). Despite their low mixing ratios, 1,3,5-trimethylbenzene and styrene exhibited a considerably high contribution to OH reactivity.

The OH reactivity of CO and NO$_2$ comprised approximately half of the total reactivity for all episodes. Interestingly, the CO contribution increased with the decrease in NO$_2$ reactivity from the C1 to C4 episodes. CO has not been regarded as a major O$_3$ precursor in urban chemistry due to its low reactivity and long lifetime (cf., Jacobson, 2002; Sze, 1977); however, its contribution was reported to be significant in previous studies (Di Carlo et al., 2004; Jeffries, 1995; Vukovich, 2011) and increased under a transport regime in this study. Since the results of this study are based entirely on measurements, the CO contribution to the total OH reactivity may be over-estimated due to missing OH reactivity or VOC measurement uncertainty. Basically, the increased contribution of OH reactivity was due to the elevated CO under transport regime in the C3 and C4 episodes, during which the average OH reactivity of CO was 3.1 and 2.8 s$^{-1}$, respectively, compared to the average OH reactivity of CO was 2.1 s$^{-1}$ for the entire period. This analysis shows
that the photochemical properties vary depending on weather conditions, which may have implications for policy making.

As the most abundant carbonyl compounds in an urban area, formaldehyde and acetaldehyde significantly contributed to OH reactivity (15%) during the high O$_3$ episodes. These compounds are mainly produced by secondary formations from the breakdown of VOCs or directly emitted from a variety of sources (Luecken et al., 2012; Ling et al., 2017). In previous studies, their importance to O$_3$ formation was demonstrated in many regions, including the SMA (Shao et al., 2009; Kim et al., 2015).

### 3.5. O$_3$ formation diagnosis

#### 3.5.1. Ozone formation sensitivity

O$_3$ formation sensitivity to NO$_x$ or VOCs is driven by odd-hydrogen chemistry, which can be diagnosed by photochemical indicator species such as H$_2$O$_2$, HNO$_3$, HCHO, and NO$_2$ (Milford et al., 1994; Sillman, 1995; Sillman et al., 1997). In models, NO$_x$- and VOC-sensitive regimes were associated with the high and low values of H$_2$O$_2$/HNO$_3$, O$_3$/NO$_2$, and O$_3$/NO$_y$ ratios. In the present study, the evidence for O$_3$ formation sensitivity was obtained from NO$_y$, NO$_z$, HCHO, and H$_2$O$_2$ measurements.

The split values of various indicators (Sillman, 1995; Sillman et al., 1997) and the percentage of measurements that fit into these criteria are summarized in Table 2. For the NO$_x$ indicator, 63% of the measurements fell into the VOC-sensitive regime. When the H$_2$O$_2$/NO$_y$ ratio was applied, 96% of all the measurements fell into the VOC-sensitive regime. All the other indicator species ratios tested in this study, including O$_3$/NO$_x$, H$_2$O$_2$/NO$_z$, and HCHO/NO$_x$, consistently indicated that O$_3$ formation is more sensitive to the VOC than the NO$_x$ in Seoul (Table 2). This result demonstrates that VOCs play a more critical role than NO$_x$ in O$_3$ production, thereby suggesting VOC control for O$_3$ abatement.

Before this approach was developed, the relative ratio of VOCs to NO$_x$ was utilized as a diagnostics tool to evaluate the O$_3$ production regime (United States Environmental Protection Agency, 1989). The TVOCs-to-NO$_x$ ratios greater than 15 and less than 4 are often considered as NO$_x$- and VOC-sensitive regimes, respectively (NRC, 1991). Thus, this method was applied to this study, and the daily averaged VOC and NO$_x$ mixing ratios were obtained as shown in Figure 9a. Consistent with the results presented earlier, the O$_3$ formation was found to be VOC-limited and 13 of the 14 high O$_3$ days fell into the line of TVOCs: NO$_x$ between 4 and 8. In comparison, a few non-episode days were found in the transition regime. The indicator species ratio and the relative ratio of TVOCs to NO$_x$ consistently indicated that O$_3$ formation is NO$_x$-saturated and VOC-limited in Seoul, and therefore VOCs need to be reduced to decrease the O$_3$ concentration. It is also noteworthy that although the TVOCs/NO$_x$ ratios are similar for high O$_3$ episodes, the individual NO$_x$ and VOC mixing ratios were spread in a wide range and are not distinguished from those of non-episode days, except for C1. In this regard, the detailed chemical mechanisms tightly linked with meteorological conditions of the high O$_3$ episodes should be thoroughly understood when establishing an O$_3$ abatement policy.
3.5.2. Ozone production efficiency—In addition to the sensitivity regime, ozone production efficiency (OPE) is another key factor in determining \( \text{O}_3 \) mixing ratio in the \( \text{NO}_x \)-saturated regime (Kleinman et al., 2002a; Zaveri, 2003). OPE can be practically determined from a linear regression of \( \text{O}_3 \) or \( \text{O}_x \) against \( \text{NO}_x \) (Kleinman et al. 2002b; Trainer et al., 1993). In previous studies, OPE has been found to be as high as 10 in low \( \text{NO}_x \) conditions (Li et al., 1997; Trainer et al., 1993). In urban conditions, low OPEs were found as follows: 8 in Houston during the DISCOVER-AQ campaign (Mazzuca et al., 2016), 5.9 in Texas during the TexAQS 2006 field study (Neuman et al., 2009), 5.4 during the TexAQS 2000 (Ryerson et al., 2003), 2.2–4.2 in New York City (Kleinman et al., 2000), and 6 and 5 for urban and power plant plumes in Nashville, respectively (St John et al., 1998).

In this study, OPE was determined as a slope of \( \text{O}_x \) against \( \text{NO}_x \) between 12:00 and 16:00. For each high \( \text{O}_3 \) episode, it ranged from 3.1 to 6.3 mol/mol (Figure 9b). As expected, it was the highest in \( \text{C} 4 \) (6.3 mol/mol), which was twice as high as the other episodes (\~{}3 mol/mol), suggesting that \( \text{O}_3 \) production was more efficient under the transport regime. In the \( \text{C} 4 \) episode, \( \text{NO}_x \) and VOC levels were significantly lower; however, the \( \text{NO}_x \) levels and the \( \text{NO}_x/\text{NO}_y \) ratios were considerably higher than in the other episodes (Figure 4). The \( \text{O}_x \) to \( \text{NO}_x \) ratio also serves as an indicator for \( \text{O}_3 \) formation sensitivity and is higher under \( \text{NO}_x \)-sensitive and lower under VOC-sensitive regimes (Kleinman et al. 2002b; Sillman et al., 1995). This result implies that the \( \text{NO}_x \) titration effect is substantial in Seoul and reducing \( \text{NO}_x \) will increase OPE and thus \( \text{O}_3 \). Currently, high PM\(_{2.5}\) concentrations have become a national issue, and the \( \text{NO}_x \) reduction policy has been implemented to combat PM\(_{2.5}\). In this respect, an integrated understanding of PM\(_{2.5}\) and \( \text{O}_3 \) formation is required when establishing policies to improve urban air quality.

3.6. Effect of \( \text{NO}_x \) and VOC reduction on \( \text{O}_3 \)

In the present study, the precursor levels were higher in the high \( \text{O}_3 \) episodes than the non-episodes and the \( \text{O}_3 \) formation was controlled by VOCs during high \( \text{O}_3 \) episodes. In this study, the FOAM modeling was utilized to examine how \( \text{O}_3 \) level changed as precursor levels were reduced to non-episode levels. Evaluating the \( \text{NO}_x \) and VOC reduction effect on \( \text{O}_3 \) production is crucial for implementing \( \text{O}_3 \) policies. First, the \( \text{O}_3 \) mixing ratio was simulated for episodes \( \text{C} 1, \text{C} 2, \) and \( \text{C} 3 \) with the average diurnal profiles of \( \text{NO}_x \) and VOCs. In this simulation, \( \text{C} 4 \) was not considered because the \( \text{NO}_x \) and VOC levels were lower than during the non-episodes. Next, \( \text{O}_3 \) was calculated with the three reduced scenarios of \( \text{NO}_x \), VOCs, and combined \( \text{NO}_x \) and VOC. Then, the peak \( \text{O}_3 \) level of each run was compared (Table 3). The detailed photochemical model information used for this calculation can be found in Gil et al., 2020. Considering the abundance and OH reactivity, ten VOC species were chosen for simulation including acetaldehyde, acetone, BTX, and isoprene. These species account for nearly two-thirds of the total OH reactivity of the 56 VOC species.

For the \( \text{C} 1 \) episode, \( \text{NO}_x \) and VOC levels were reduced by 49% and 45%, respectively, compared to the base run. For \( \text{C} 2 \) and \( \text{C} 3 \), the \( \text{NO}_x \) and VOC reductions were 24% and 16%, and 31% and 34%, respectively. As expected from the \( \text{O}_3 \) formation sensitivity, \( \text{O}_3 \) increased with a reduction in \( \text{NO}_x \) but decreased with a reduction in VOCs in all three episodes. While the increased \( \text{O}_3 \) was not related to the \( \text{NO}_x \) reduction, the \( \text{O}_3 \) decrease was proportional...
to the VOC reduction. When reducing both NO\textsubscript{x} and VOCs, the decrease in O\textsubscript{3} was less than the VOC-only reduction. This model simulation highlights that the chemical regime creating high O\textsubscript{3} mixing ratio was highly saturated with NO\textsubscript{x} and the daily maximum O\textsubscript{3} was reduced by 0.57% per 1% reduction in VOCs regardless of the NO\textsubscript{x} level and VOC composition.

4. Conclusion

As a part of the KORUS-AQ campaign, comprehensive measurements were conducted at several ground sites in South Korea. At Olympic Park in Seoul, reactive gases including O\textsubscript{3}, NO\textsubscript{x}, NO\textsubscript{y}, CO, and SO\textsubscript{2}, and VOCs, photochemical byproducts such as HCHO and H\textsubscript{2}O\textsubscript{2}, PM\textsubscript{2.5} composition, and meteorological parameters such as PBL height were continuously measured from May 10 to June 12, 2016. In this experiment, the maximum hourly O\textsubscript{3} (127 ppbv) and PM\textsubscript{2.5} (88 µg m\textsuperscript{-3}) occurred on June 10 and May 31, respectively. The average NO\textsubscript{x} and TVOC were 30.0 and 39.3 ppbv, respectively. As the most dominant VOCs, the toluene mixing ratio reached 16.0 ppbv with an average of 3.9 ppbv.

During the experiment, the O\textsubscript{3} level violated the 8-h standard of 60 ppbv for 26 days and the 1-h standard of 100 ppbv for 6 days. For an in-depth analysis of this study, the high O\textsubscript{3} episode was defined as occurring when the daily O\textsubscript{3} maximum exceeded 90 ppbv (96\textsuperscript{th} percentile). The 14 days of high O\textsubscript{3} episodes occurred under distinct weather conditions that were separated into stagnant, transport, and blocking periods. The transport regime was further divided into two periods involving different air masses from the southwest (transport-south) and northwest (transport-north). As the experiment was conducted before the summer monsoon started, the synoptic meteorology played a significant role in determining the air quality. For example, PM\textsubscript{2.5} and O\textsubscript{3} were imported in aged plumes transported over the Yellow Sea under the constant westerlies and the local influences were more significant as westerlies were weakened. When the extreme stagnation developed under a persistent anticyclone, the evolution of boundary layer played an important role.

Under a persistent high pressure, NO\textsubscript{x} and VOC were greatly elevated, particularly at night by the emissions of the SMA. During mornings when the UV level was high under a clear sky, the VOC oxidation resulted from a clear morning peak in HCHO. In the afternoon, all precursor levels decreased below those of the non-episode days due to deep mixing. During stagnant periods, O\textsubscript{3} occasionally increased in the evening and at night, which was associated with mesoscale circulation and was evident in the vertical wind profile.

Similarly, the air was stagnated under blocking condition. In this condition, the precursor levels were lower than in the stagnant episode and the levels and variations of photochemical byproducts highlight that the air was photochemically more aged with higher HCHO and NO\textsubscript{y} levels during the day. Accordingly, the highest O\textsubscript{3} concentration was observed in this episode.

When the air mass was transported across the Yellow Sea, O\textsubscript{3} was concurrently enhanced with PM\textsubscript{2.5}. This episode is characterized by high CO and SO\textsubscript{2} levels, but low NO\textsubscript{x} and VOC concentrations. As a result, O\textsubscript{3}/O\textsubscript{x} and NO\textsubscript{y}/NO\textsubscript{y} ratios were high, implying that the
air was photochemically aged. At night, O₃ concentrations remained in the range of 40–50 ppbv with an O₃/Oₓ ratio as high as 0.8, indicating the O₃ titration by NOₓ is substantial and played a critical role in determining the O₃ level in Seoul. In addition, the OH reactivity of CO was increased with a decrease in NO₂. CO was highly enhanced with O₃ under the northerly wind at the end of May.

For the high O₃ episodes, the O₃ formation was diagnosed as VOC-sensitive from the photochemical indicator species ratios such as H₂O₂, HCHO, and NOₓ, and from the TVOC and NOₓ levels. In addition, the ozone production efficiency evaluated from the ΔOₓ/ΔNOₓ of the linear regression between Oₓ and NOₓ was higher in the transport regime than in the other episodes, which was further demonstrated from the model simulation. Because the precursor levels were higher during the high O₃ episodes than during the non-episodes, the diurnal variation of O₃ was simulated for the three episodes (C1–C3) with the NOₓ and VOC levels of the non-episode. Under the NOₓ-saturated condition, the NOₓ reduction increased the O₃ concentration. In contrast, the daily maximum O₃ was reduced proportionally with the VOC reduction rate; therefore, reducing NOₓ would exacerbate air quality in terms of O₃. In the SMA, air quality improvement should be attained, based on a comprehensive understanding of the O₃ and PM₂.₅ formation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data Accessibility Statement

Surface data during the KORUS-AQ in South Korea were obtained from the NASA data archive at https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq. The cloud coverage and UV data were obtained from the Korea Meteorological Administration website (http://www.data.kma.go.kr).

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Figure 1: Map showing the Korean Peninsula and the capital city, Seoul. Olympic Park, utilized as a ground measurement site in Seoul, is located in the southeast portion of Seoul (37.52° N, 127.12° E). DOI: https://doi.org/10.1525/elementa.444.f1
Figure 2: Time-series variation of reactive gases (O$_3$, NO, NO$_2$, NO$_y$, CO, SO$_2$, and HCHO), PM$_{2.5}$ mass and composition (NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and OC), meteorological parameters (temperature, relative humidity, and boundary layer height), and total VOCs classified into four subgroups (alkanes, alkenes and alkynes, aromatics, and OVOCs). The C2–C5 hydrocarbons were measured at the Gwangjin site near Olympic Park. The PM$_{2.5}$ composition is given as the daily average. DOI: https://doi.org/10.1525/elementa.444.f2
Figure 3: Four trajectories identified from air mass cluster analyses at 500 m for 24-h using NOAA HYSPLIT model. The high-O₃ episode days belong to these four clusters: stagnation to C1, blocking to C2, transport-north to C3, and transport-south to C4. DOI: https://doi.org/10.1525/elementa.444.f3
Figure 4: Box-whisker plots of major chemical and meteorological species and their ratios. Categorized into four high O$_3$ episodes, then further divided into day (06:00–19:00) and night (20:00–05:00) and compared with the non-episode periods. UV is colored in red and cloud coverage in blue. DOI: https://doi.org/10.1525/elementa.444.f4
Figure 5: Diurnal variations of O$_3$, PM$_{2.5}$, cloud coverage, and UV (upper panel), and aromatics, NO$_x$, HCHO, and H$_2$O$_2$ (lower panel) for four high O$_3$ episodes. (a) C1, (b) C2, (c) C3, and (d) C4, and (e) the non-episode. DOI: https://doi.org/10.1525/elementa.444.f5
Figure 6: Correlation between planetary boundary layer (PBL) height and (a) O₃, (b) CO, and (c) PM₂.₅ for the high O₃ episodes and a non-episode.
DOI: https://doi.org/10.1525/elementa.444.f6
Figure 7: Diurnal variations of O$_3$, PM$_{2.5}$, CO, and H$_2$O$_2$ at night with the boundary layer height (white line) and vertical wind profile (wind speed and direction) up to 3 km measured by a pulsed Doppler wind lidar at the Jungmang site near Olympic Park on (a) May 23–24, (b) June 5–6, (c) May 30–31, and (d) May 25–26.
DOI: https://doi.org/10.1525/elementa.444.f7
Figure 8: (a) Abundance of the four VOC sub-classes and individual VOC species and (b) their relative OH reactivity with that of NO$_2$ and CO during the four high O$_3$ episodes. For this analysis, the missing C2–C5 alkane measurements during June 8–12 were estimated from a linear regression between alkanes and aromatics ($R^2 = 0.65$) and are presented separately with a red dashed line. DOI: https://doi.org/10.1525/elementa.444.f8
Figure 9: (a) Daily averaged TVOCs and NO<sub>x</sub> concentrations and (b) correlation of NO<sub>2</sub> with O<sub>x</sub> between 12:00 and 16:00, signifying OPE during the four high O<sub>3</sub> episodes.

In (a), the line denotes the TVOCs/NO<sub>x</sub> ratio of 15, 8, and 4. The estimated TVOCs (see Figure 8) are presented as open squares for June 8–12. DOI: https://doi.org/10.1525/elementa.444.f9
Table 1:
Measurement statistics of O$_3$, PM$_{2.5}$, NO$_x$, NO$_y$, CO, SO$_2$, VOCs, HCHO, and meteorological parameters during the KORUS-AQ campaign, and the number of days (out of total 34 days) during which O$_3$ and PM$_{2.5}$ values exceeded the NAAQS. DOI: https://doi.org/10.1525/elementa.444.t1

| Species    | Mean ± SD (ppbv) | Maximum (ppbv) | Exceedance days |
|------------|------------------|----------------|-----------------|
| O$_3$      | 39 ± 27          | 128            | $6^a, 26^b$     |
| PM$_{2.5}$ | 29 ± 16 ($\mu$g m$^{-3}$) | 88 ($\mu$g m$^{-3}$) | 23$^c$         |
| NO$_x$     | 30 ± 23          | 149            | –               |
| NO$_y$     | 36 ± 23          | 145            | –               |
| CO         | 537 ± 190        | 1113           | –               |
| SO$_2$     | 4.2 ± 2.1        | 15.0           | –               |
| TVOCs      | 39 ± 18          | 105            | –               |
| Alkanes    | 16 ± 11          | 69             | –               |
| Alkenes and Alkynes | 4 ± 1  | 8        | –               |
| Aromatics  | 9 ± 5            | 27             | –               |
| OVOCs      | 10 ± 3           | 26             | –               |
| Formaldehyde | 3.6 ± 1.6         | 9.6           | –               |
| Temperature (°C) | 20.8 ± 4.8      | 30.6          | –               |
| Relative Humidity (%) | 60.7 ± 19.4    | 97.8         | –               |
| Planetary Boundary Layer Height (m) | 774 ± 513       | 2624       | –               |
| Wind Speed (m/s) | 0.5 ± 0.4    | 2.3            | –               |

$^a$Exceedance of 1-h standard of 100 ppbv.

$^b$Exceedance of 8-h standard of 60 ppbv.

$^c$Exceedance of 24-h standard of 35 µg m$^{-3}$.
Table 2:
Percentage of measurements that meet the criteria of each indicator for VOC- and NOX-sensitive regimes.

DOI: https://doi.org/10.1525/elementa.444.t2

| Indicators | VOC-sensitive | NOX-sensitive |
|------------|---------------|---------------|
| NOx        | 63% (> 20 ppbv) | 11% (< 10 ppbv) |
| O3/NOx     | 85% (< 6) | 9% (> 7.5) |
| H2O2/NOx   | 96% (< 0.15) | 0% (> 0.3) |
| H2O2/NOz   | 75% (< 0.2) | 9% (> 0.35) |
| HCHO/NOy   | 69% (< 0.2) | 4% (> 0.4) |
Table 3:
Average concentration of O₃, PM₂.₅, NOₓ, and TVOCs during the four high O₃ episodes, as well as the non-episode periods, and the rate of change in O₃ maximum concentration with a reduction in NOₓ, VOCs, and combination of both. DOI: [https://doi.org/10.1525/elementa.444.t3](https://doi.org/10.1525/elementa.444.t3)

| Species (unit) | Stagnation (C1) | Blocking (C2) | Transport-North (C3) | Transport-South (C4) | Non-episodes |
|----------------|-----------------|---------------|----------------------|----------------------|--------------|
|                | May 18–23       | June 2, 5, 7, 9, and 10 | May 17, 29, and 30 | May 25               |              |
| O₃ (ppbv)      | 38              | 39             | 44                   | 59                   | 39           |
| PM₂.₅ (μg m⁻³) | 30              | 29             | 39                   | 53                   | 27           |
| NOₓ (ppbv)     | 48              | 33             | 36                   | 16                   | 25           |
| TVOCs (ppbC)   | 246             | 162            | 232                  | 108                  | 155          |
| NOₓ control    | +12%            | +9%            | +10%                 | N/A                  |              |
| VOCs control   | −35%            | −13%           | −26%                 | N/A                  |              |
| NOₓ and VOCs control | −25% | −4% | −17% | N/A |

¹ NOₓ, ² VOCs, and ³ NOₓ and VOC concentrations were reduced to that of the non-episode.