Using observed urban NO\textsubscript{x} sinks to constrain VOC reactivity and the ozone and radical budget in the Seoul Metropolitan Area

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Abstract

Ozone (O₃) is an important secondary pollutant that impacts air quality and human health. Eastern Asia has high regional O₃ background due to the numerous sources and increasing and rapid industrial growth, which impacts the Seoul Metropolitan Area (SMA). However, SMA has also been experiencing increasing O₃ driven by decreasing NOₓ emissions, highlighting the role of local, in-situ O₃ production on SMA. Here, comprehensive gas-phase measurements collected on the NASA DC-8 during the NIER/NASA Korea United States-Air Quality (KORUS-AQ) study are used to constrain the instantaneous O₃ production rate over the SMA. The observed NOₓ oxidized products support the importance of non-measured peroxy nitrates (PNs) in the O₃ chemistry in SMA, as they accounted for ~49% of the total PNs. Using the total measured PNs (ΣPNs) and alkyl and multifunctional nitrates (ΣANs), unmeasured volatile organic compound (VOC) reactivity (R(VOC)) is constrained and found to range from 1.4 – 2.1 s⁻¹. Combining the observationally constrained R(VOC) with the other measurements on the DC-8, the instantaneous net O₃ production rate, which is as high as ~10 ppbv hr⁻¹, along with the important sinks of O₃ and radical chemistry, are constrained. This analysis shows that ΣPNs play an important role in both the sinks of O₃ and radical chemistry. Since ΣPNs are assumed to be in steady-state, the results here highlight the role ΣPNs play in urban environments in reducing net O₃ production, but ΣPNs can potentially lead to increased net O₃ production downwind due to their short lifetime (~1 hr). The results provide guidance for future measurements to identify the missing R(VOCs) and ΣPNs production.
Short Summary

Ozone (O₃) is a pollutant formed from the reactions of gases emitted from various sources. In urban areas, the density of human activities can increase the O₃ formation rate (P(O₃)); thus, impact air quality and health. Observations collected over Seoul, South Korea, are used to constrain P(O₃). A high local P(O₃) was found; however, local P(O₃) was partly reduced due to compounds typically ignored. These observations also provide constraints for unmeasured compounds that will impact P(O₃).
1. **Introduction**

Representing global and urban tropospheric ozone (O\textsubscript{3}) in chemical transport models (CTMs) is still challenging due to uncertainty in physical and chemical processes that control the O\textsubscript{3} budget (Archibald et al., 2020). One area of uncertainty is underestimated urban volatile organic compounds (VOCs) emissions (von Schneidemesser et al., 2023), which arise from a large number of sources, including some that are very hard to quantify (e.g., cooking and chemical product) (e.g., McDonald et al., 2018; Simpson et al., 2020). Intensive research is also ongoing as to why O\textsubscript{3} is increasing in recent years in urban areas, even with reductions in combustion emissions (e.g., Lyu et al., 2017; Colombi et al., 2023). This O\textsubscript{3} impacts the large populations in urban areas with harmful health effects, including premature mortality (e.g., Cohen et al., 2017).

Tropospheric O\textsubscript{3} production is driven by the catalytic cycling of nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) fueled by the photooxidation of VOCs, both of which can come from anthropogenic emissions. The chemistry producing O\textsubscript{3} is described in R1 – R6 in Table 1. During daylight hours, VOCs are oxidized by OH (or undergo photolysis) to form an organic peroxy radical (RO\textsubscript{2}) in R1\textsubscript{a} (R1\textsubscript{b}). If the RO\textsubscript{2} then proceeds through R2\textsubscript{a}, at least two O\textsubscript{3} molecules are produced. The first O\textsubscript{3} molecule is formed by the photolysis of NO\textsubscript{2} and the reaction of O(3P) with oxygen (R3 – R4). The second O\textsubscript{3} molecule is formed through the reaction of the alkoxy radical (RO\textsuperscript{•}) with oxygen to form the hydroperoxyl radical (HO\textsubscript{2}) (R5), which goes on to react with NO to produce NO\textsubscript{2} (R6) and the subsequent reactions described above (R3 – R4). However, some fraction of the time, depending on the number of carbons and functional group (e.g., Espada and Shepson, 2005; Perring et al., 2013; Yeh and Ziemann, 2014), alkyl or multifunctional nitrates (ANs = RONO\textsubscript{2}) are formed (R2\textsubscript{b}). The fraction of reactions to form ANs is described by the branching ratio, \(\alpha\). Reaction R2\textsubscript{b} has been shown to impact O\textsubscript{3} production, depending on the types of VOC emitted,
by reducing the fraction of NO$_2$ that photolyzes to form O$_3$ in source regions (R3 – R4) (Farmer et al., 2011). As $\alpha$ is a function of the individual VOC’s carbon backbone and functional group (e.g., Perring et al., 2013), any uncertainty related to primary VOC emissions and secondary chemistry will directly impact the ability to describe urban O$_3$ production.

One important subclass of VOCs—aldehydes (RCHO), which can either be directly emitted or produced via photooxidation of VOCs (Mellouki et al., 2015; de Gouw et al., 2018; Yuan et al., 2012; Wang et al., 2022). The photooxidation of the aldehyde (R7) in the presence of NO$_x$ can either form acyl peroxy nitrates (R8, PNs = R(O)O$_2$NO$_2$) or an organic peroxy radical (RO$_2^\cdot$) (R9). The competition between R8 to form PNs versus R9 to form RO$_2^\cdot$ depends on the NO-to-NO$_2$ ratio (Nihill et al., 2021). Further, R8 is in thermodynamic equilibrium due to the weak bond strength between the acyl peroxy radical (R(O)O$_2^\cdot$) and NO$_2$. Thus, formation of PNs pose only a temporary loss of NO$_2$. Finally, it has been observed that aldehydes with longer carbon backbones (e.g., C8s and C9s) from various anthropogenic activities, such as cooking (Coggon et al., 2024; Rao et al., 2010), may have mixing ratios as high as aldehydes typically quantified in field experiments (acetaldehyde and propaldehyde). However, there is larger uncertainty associated with these higher aldehydes in their fate to produce both PNs and ANs (e.g., Hurst Bowman et al., 2003). Missing both these emissions and subsequent chemistry would impact estimates of urban O$_3$ chemistry.

The fraction of RO$_2^\cdot$ forming ANs in R2b and the fraction of R(O)O$_2^\cdot$ forming PNs in R8 alter the instantaneous O$_3$ production (P(O$_3$)) by removing NO$_2$ and/or the radical species. This is further shown in Figure S1, where an analytical equation to describe R1 – R6 (Farmer et al., 2011), is used to explore how changes in the VOC reactivity (R(VOC)), radical production (P(HO$_x$)), and ANs production and branching ratio, $\alpha$ (R2b), impact the instantaneous P(O$_3$) (see Sect. S1 for the analytical equation and description). Any changes in P(HO$_x$), R(VOC), and/or $\alpha$ will impact both
the instantaneous P(O\textsubscript{3}) as well as the NO\textsubscript{x} mixing ratio corresponding to the maximum P(O\textsubscript{3}). As these parameters are generally interconnected, investigating all three is important to understand the sources and control of instantaneous P(O\textsubscript{3}). Further, R7 – R9 are not included in this traditional description of the analytical equation, as it is assumed PNs are in steady-state (Farmer et al., 2011).

Thus, if PNs are not in steady-state, their role in altering P(O\textsubscript{3}) may be underestimated.

Increasing surface O\textsubscript{3} is a concern throughout East Asia, including South Korea (Colombi et al., 2023; Gaudel et al., 2018; Kim et al., 2021; Yeo and Kim, 2021). The emissions associated with industry and other anthropogenic activities and the associated photochemistry have impacted regional air quality, leading to high O\textsubscript{3} backgrounds that can impact a country’s ability to achieve reduced O\textsubscript{3} exposure for new air quality standards (e.g., Colombi et al., 2023). However, local emissions and photochemistry still play an important role. For example, during the Korea-United States Air Quality (KORUS-AQ) campaign, it was observed between morning and afternoon in the Seoul Metropolitan Area (SMA), O\textsubscript{3} increased by ~20 parts per billion by volume (ppbv) over a background concentration of over 75 ppbv (Crawford et al., 2021). Thus, an understanding of the variables highlighted in Figure S1 are necessary to control both local and regional P(O\textsubscript{3}).

One tool typically used to understand the role of regional O\textsubscript{3} and transported O\textsubscript{3} on local O\textsubscript{3} and impacts of local emission controls on O\textsubscript{3} are CTMs. As shown in Park et al. (2021), for the SMA, CTMs typically underestimate the observed O\textsubscript{3} and formaldehyde. While the low O\textsubscript{3} could be partially related to underestimated transport (e.g., Seo et al., 2018) or resolution of the CTM (e.g., Jo et al., 2023; Park et al., 2021), the low bias also observed for modeled formaldehyde indicates overall (a) too little VOCs and thus too low R(VOC) (Brune et al., 2022; H. Kim et al., 2022), (b) missing photochemical products from missing VOCs, including oxygenated VOCs (OVOCs) that contribute to P(HO\textsubscript{x}) (Brune et al., 2022; H. Kim et al., 2022; Lee et al., 2022; Wang et al., 2022).
et al., 2022), and (c) likely missing PNs and ANs from the underestimated VOCs related to the underestimated R(VOC) (Lee et al., 2022; Park et al., 2021). Missing (a) – (c) will bias the instantaneous P(O₃) (Figure S1), impacting the ability to investigate what policies should be implemented to reduce O₃.

To better understand what controls the instantaneous P(O₃) over SMA, observations collected on the NASA DC-8 during KORUS-AQ are used to constrain the three variables highlighted in Figure S1—R(VOC), HOₓ production and loss, and ANs and PNs production. Observational constraints on these three parameters provide a means to investigate the instantaneous P(O₃) over SMA and the major classes of contributors to O₃ and HOₓ production and loss. These results are discussed and placed into the context of improving our knowledge about O₃ production in an urban environment.

2. Methods and Data Description

2.1 KORUS-AQ and DC-8 Descriptions

The KORUS-AQ campaign was a multi-national project that was conducted in May – June, 2016, led by South Korea’s National Institute of Environmental Research (NIER) and United States National Aeronautics and Space Administration (NASA). The project was conducted in South Korea and the surrounding seas with numerous airborne platforms, research vessels, and ground sites (Crawford et al., 2021). The study here focuses on the observations collected on the NASA DC-8.

The instrument payload, flights, and observations have been described in other studies (Crawford et al., 2021; Schroeder et al., 2020; Brune et al., 2022; Lee et al., 2022). Briefly, the DC-8 was stationed at Osan Air Force Base, Pyeongtaek, South Korea, which is approximately 60
km south of Seoul. A total of 20 research flights were conducted with the DC-8. Part of each research flights included a stereo-route in the SMA in the morning (~09:00 local time), midday (~12:00 local time), and afternoon (~15:00 local time), which included a missed approach over Seoul Air Base (< 15 km from Seoul city center) and a fly-over of the Olympic Park and Taehwa Forest Research sites (Figure 1). A total of 55 descents over Olympic Park and 53 spirals over Taehwa Forest Research site were conducted (Crawford et al., 2021). Only observations from the DC-8 after 11:00 local time are used here to ensure that the boundary layer has grown and stabilized and to minimize any influence from residual layer mixing into the boundary layer and/or titration of O₃ by NO (R10). We analyze data collected below 2 km and between 127.10 – 127.67°E and 37.22 – 37.69°N to focus on the boundary layer in the SMA without influence from industrial emissions along the western South Korean coast (Crawford et al., 2021).

During KORUS-AQ, four different meteorological periods, as described by Peterson et al. (2019), impacted the region. These periods included a Dynamic period from 1 – 16 May, where there were a series of frontal passages; a Stagnant period from 17 – 22 May, where it was dry, clear, and stagnant; Transport/Haze period from 25 – 31 May, where long-range transport and hazy conditions with high humidity and cloud cover prevailed; and, a Blocking period from 1 – 7 June, where blocking conditions minimized transport (Peterson et al., 2019). However, as discussed in Sect. 3.2, conditions did not impact the general trends and chemistry and thus the whole campaign has been analyzed together.

The observations used for the analysis are shown in Table 2, along with the associated references. The 1-min merged data from the DC-8 is used here (KORUS-AQ Science Team, 2023). For data missing due to frequency of measurements (e.g., VOCs from WAS), data was filled in a similar approach as Schroeder et al. (2020), in that VOCs with missing data were filled by the
linear relationship of that VOC with VOCs measured more frequently. This step was necessary for the observations used in the diel steady-state calculations described in Sect. 2.2. Note, the TD-LIF NO$_2$ (see Table 2) was used throughout this study and discussed in Sect. S2 and Figure S2–S3 as it generally agreed better with steady-state calculated NO$_2$-to-NO ratios than the chemiluminescence NO$_2$.

2.2 F0AM Box Model Diel Steady-State Calculations for Missing Reactivity and Peroxynitrate Budget Analysis

We use the F0AM box model (Wolfe et al., 2016) with chemistry from the MCMv3.3.1 (Jenkin et al., 2015) to simulate production of PNs and formaldehyde using 1-min merged data, as described in Sect. 2.1. As in Schroeder et al. (2020), we simulate each aircraft observation in diurnal cycle mode until the diurnal cycle for each species reaches convergence within 1%. We constrain concentrations of NO, O$_3$, H$_2$O$_2$, HNO$_3$, CO, CH$_4$, H$_2$, and all measured or estimated VOCs given in Table 2 and Table S1. We allow the model to freely calculate NO$_2$, formaldehyde, and all PNs, including PAN and PPN, for when calculating the budget of PNs. However, for the acyl peroxy radical mixing ratios to calculate O$_x$ and HO$_x$ budget (Sect. 2.3), PAN and PPN were constrained by observations. We use a dilution constant of 12 hours, according to Brune et al. (2022). Model evaluation is discussed in Sect. 3.4. The contribution of individual VOCs to PAN was calculated by reducing precursor VOCs by 20% and multiplying the resulting impact on the peroxy acetyl radical (CH$_3$C(O)O$_2$) by 5. Other acyl peroxy nitrates (higher PNs) are lumped into categories based on their primary precursor species from Table S2, species currently typically
measured (e.g., PPN) or contributes a large fraction of the total higher PNs budget (greater than
>2%; e.g., PHAN and MPAN).

2.3 Calculation of Instantaneous Ozone and HO\textsubscript{x} Production and Loss

An experimental budget for the production and loss of O\textsubscript{x} (O\textsubscript{x} = O\textsubscript{3} + NO\textsubscript{2}) and HO\textsubscript{x} (HO\textsubscript{x})
= OH + HO\textsubscript{2} + RO\textsubscript{2} + R(O)O\textsubscript{2}) is described here. NO\textsubscript{2} and O\textsubscript{3} are combined to reduce any potential
impact from titration via O\textsubscript{3} reaction with NO (R10). The budget analysis includes field-measured
quantities (mixing ratios and photolysis rates, Table 2), results from F0AM (Sect. 2.2), estimated
missing R(VOC) (Sect. 3.2) and published kinetic rate constants (see Table 1 for references). The
rate of production or destruction is calculated with the following equations (Eq. 1 – 7) below. Note,
these equations differ from Schroeder et al. (2020) in that (a) ANs and PNs chemistry are explicitly
included and (b) the reaction of O\textsubscript{3} with alkenes is excluded as this reaction contributed a minor
loss to O\textsubscript{3} (< 1%).

\[ P_{O_x} = \sum (1-\alpha_{eff})k_{RO_2} + k_{NO_2} \left[ NO \right] + k_{HO_2} \left[ HO_2 \right] \left[ NO \right] \]  
\[ (1) \]
\[ L_{O_x} = k_{NO_2} \left[ NO_2 \right] \left[ OH \right] + k_{O_3} \left[ O_3 \right] \left[ OH \right] + f \times j_{O_1} \left[ O_3 \right] + k_{HO_2} \left[ HO_2 \right] \left[ O_3 \right] + \text{net(PNs)} \]  
\[ (2) \]
\[ \text{net(PNs)} = \beta k_{R(O)O_2 + NO_2} \left[ R(O)O_2 \right] \left[ NO_2 \right] - (1-\beta)k_{\text{decomposition}} \left[ \text{PNs} \right] \]  
\[ (3) \]
\[ \beta = \frac{k_{R(O)O_2 + NO_2} \left[ NO_2 \right]}{k_{R(O)O_2 + NO_2} \left[ NO_2 \right] + k_{R(O)O_2 + NO} \left[ NO \right]} \]  
\[ (4) \]
\[ P(\text{HO}_x) = 2f \times j_{O_1} \left[ O_3 \right] + 2j_{H_2O_2} \left[ H_2O_2 \right] + 2j_{CH_2O \rightarrow H + HCO} \left[ CH_2O \right] + 2j_{CHCHO} \left[ CHCHO \right] + 2j_{CH_2OOH} \left[ CH_2OOH \right] + 2j_{CH_2CHO} \left[ CH_2CHO \right] + 2j_{CH_3C(O)CH_3} \left[ CH_3C(O)CH_3 \right] + 2j_{CH_2CH_2CH_2} \left[ CH_2CH_2C(O)CH_2 \right] \]  
\[ (5) \]
\[
L(\text{HO}_x) = k_{\text{NO}_2 \cdot \text{OH}}[\text{NO}_2][\text{OH}] + \sum_i \alpha_{\text{eff}} k_{\text{RO}_2,i \cdot \text{NO}}[\text{RO}_2,i][\text{NO}] + \\
2k_{\text{HO}_2 \cdot \text{HO}_2}[\text{HO}_2][\text{HO}_2] + 2k_{\text{RO}_2 \cdot \text{RO}_2}[\text{RO}_2][\text{RO}_2] + 2k_{\text{HO}_2 \cdot \text{RO}_2}[\text{HO}_2][\text{RO}_2] + \text{net(PNs)} \quad (6)
\]

\[
[\text{RO}_2] = \frac{\sum_i k_{\text{OH} \cdot \text{VOC}_i}[\text{VOC}_i][\text{OH}]}{(1-\alpha_{\text{eff}})k_{\text{RO}_2 \cdot \text{NO}}[\text{NO}] + k_{\text{RO}_2 \cdot \text{HO}_2}[\text{HO}_2]} \quad (7)
\]

Here, \( k \) is the rate constant for compound, \( i \), with the associated compound listed, \( \alpha_{\text{eff}} \) is the effective branching ratio for R2a and R2b for the observations (Sect. 3.2), \( f \) is the fraction that O\(^1\)D that reacts with water to form OH versus reacting with a third body molecule to form O\(^3\)P, \( \beta \) is the fraction the R(O)O\(_2\) that reacts with NO\(_2\) versus NO, and \( j \) is the measured photolysis frequency (Table 2). Note, R(O)O\(_2\) is not included in Eq. 7 as (a) it is assumed the initial production of R(O)O\(_2\) is captured with the reaction of OH with VOC and (b) R(O)O\(_2\) accounts for a small fraction of the total RO\(_2\) (<10%). Not including R(O)O\(_2\) in Eq. 7 may lead to a small underestimation of total RO\(_2\). Finally, HO\(_2\) calculated from F0AM is used in the equations to determine the O\(_x\) and HO\(_x\) budget.

3. Observational constraints on NO\(_x\), organic oxidation chemistry

In the Sect. 3.1, the detailed observations from the DC-8 during KORUS-AQ provided measurements that allow us to test our understanding of NO\(_x\) oxidation into total NO\(_z\) (NO\(_z = \) higher NO\(_x\) oxides, including \( \Sigma \)PNs, \( \Sigma \)ANs, HNO\(_3\) and particulate nitrate, pNO\(_3\)), which is needed for the remainder of the analysis. Sect. 3.2 to 3.4 will focus on the organic NO\(_x\) chemistry. This is due to the chemistry and dynamics impacting the total inorganic nitrate chemistry that has been discussed recently (Travis et al., 2022; Jordan et al., 2020).

3.1 NO\(_x\) and its oxidation products
The average NO\textsubscript{x} mixing ratios observed by the NASA DC-8 in the SMA below 2 km after 11:00 local time is shown in Figure 1. As NO\textsubscript{x} is mainly emitted from anthropogenic activities, such as combustion emissions, in an urban environment, the largest NO\textsubscript{x} mixing ratios are observed between Olympic Park and the missed approach, as this area included downtown SMA. As the DC-8 flies from the missed approach toward Taehwa Research Site, the NO\textsubscript{x} mixing ratios decrease. The combination of reduced emissions, chemical reactions, and dilution and mixing reduces the NO\textsubscript{x} mixing ratios away from the city. An understanding of these processes is important for urban P(O\textsubscript{x}).

On the DC-8, there were multiple measurements of various speciated and total family contribution towards NO\textsubscript{z} (Table 2). The comparison of the speciated and measured NO\textsubscript{z} is investigated in Figure 2 for observations over SMA. When only speciated PNs (GT) and ANs (CIT + WAS) and gas-phase nitrate (HNO\textsubscript{3}) are compared to the NO\textsubscript{z} (NO\textsubscript{z} (NCAR) – (NO (NCAR) + NO\textsubscript{2} (TD-LIF))), only 46% of the NO\textsubscript{z} can be explained. This is not completely unexpected, as multiple studies have indicated that the speciated ANs measurements are typically lower than the total ANs measurements (Perring et al., 2010; Fisher et al., 2016). Further, pNO\textsubscript{3} has been found to be important for total nitrate budget in the SMA (e.g., Travis et al., 2022). Chemiluminescence measurements of gas-phase NO\textsubscript{y} have been found to efficiently measure pNO\textsubscript{3}, depending on the sensitivity to pNO\textsubscript{3} enhancements or exclusions (Bourgeois et al., 2022); thus, it is expected that missing ANs and pNO\textsubscript{3} are necessary to close the NO\textsubscript{z} budget. Adding the measured pNO\textsubscript{3} to the speciated PNs (GT) and ANs (CIT + WAS) and gas-phase nitric acid, 81% of NO\textsubscript{z} can be explained. This barely overlaps the combined uncertainty of the measurements (~26%). Total PNs and ANs, measured by TD-LIF, are needed to close of the total NO\textsubscript{z} budget.
The breakdown of the NO\textsubscript{y} budget over the SMA as the airmasses photochemically ages (decreasing NO\textsubscript{x} contribution to total NO\textsubscript{y}) is shown in Figure 2b. During KORUS-AQ, ~56% of NO\textsubscript{y} was inorganic (gas- and particle-phase nitrate), ranging from 52% to 62%; the remaining NO\textsubscript{y} was organic (PNs and ANs). Approximately 74% of the total ANs were not speciated (range 73% to 76%). Speciated PNs species, such as PAN (peroxy acetyl nitrate), account for a mean 51% of the total PNs (range 47 to 59%), much lower than typically observed in prior studies (e.g., Wooldridge et al., 2010). In these prior studies, the speciated PN species (typically PAN + PPN (peroxy propionyl nitrate)) accounted for 90 – 100% of the ΣPNs, except for some select cases attributed to poor inlet design (Wooldridge et al., 2010). PAN accounted for the majority of the speciated PNs, with the remaining speciated PNs (PPN + PBzN (peroxy benzoyl nitrate) + APAN (peroxy acryloyl nitrate)) accounting for ~1%. However, during KORUS-AQ, Lee et al. (2022) observed that PAN contributed only 60% of calculated total PNs in industrial plumes near the SMA. Thus, the VOC emissions in and near SMA potentially lead to PNs typically not directly measured; this is explored more in Sect. 3.4

As NO\textsubscript{y} decreases from ~30 ppbv to 4 ppbv, the contribution of organic NO\textsubscript{y} increases (Figure 2b). At about 4 ppbv, the contribution of organic NO\textsubscript{y} starts to decrease. Further, the contribution of the different organic NO\textsubscript{y} species changes. For example, from ~30 ppbv to 4 ppbv, the un-speciated ΣPNs contributes the majority of the organic NO\textsubscript{y} budget (~39%). Below ~4 ppbv, the contribution of un-speciated ΣPNs decreases and the PAN contribution increases. The change in contribution of PNs is due to changes in the PN precursors (e.g., combination short-lived precursors oxidizing to CH\textsubscript{3}C(O)O\textsubscript{2} and thermal decomposition of the higher PNs (higher PNs = ΣPNs – PAN)). On the other hand, the contribution of un-speciated ΣANs remains relatively constant with NO\textsubscript{x} (~6% of total NO\textsubscript{y}). However, the type of ANs is most likely changing with
NOx due to the lifetime of the ANs precursors and/or the lifetime of ANs. Less is known about the lifetime of ANs derived from anthropogenically emitted VOCs compared to those from biogenic VOCs (González-Sánchez et al., 2023; Picquet-Varrault et al., 2020; Zare et al., 2018). On average unknown ANs and PNs account for ~24% of the observed NOx on average.

3.2 Meteorological impact on NOx oxidation

As discussed in Sect. 2.1 and various prior studies, four different meteorological conditions impacted the observations during KORUS-AQ (Peterson et al., 2019). The impact of the meteorological conditions on NOx oxidation was investigated by plotting two metrics of NOx oxidation—Ox versus ΣANs and ΣPNs versus formaldehyde (Figure 3). The implications of both plots are further discussed in Sect. 3.3 and 3.4, respectively. Briefly, Ox versus ΣANs and ΣPNs versus formaldehyde are competitive products from the reaction of RO2 or R(O)O2 with NOx (R2a versus R2b or R8 versus R9). The different meteorological periods corresponded to differences in temperatures and amount of photolysis due to cloud cover (Peterson et al., 2019). Thus, these different periods may impact gas-phase chemistry and/or VOC emissions. However, as demonstrated in Figure 3, there are minimal systematic differences in the trends observed for the two NOx oxidation products as there is no systematic shift in the trends or scatter observed in Figure 3. This suggests that the data does not have to be separated by meteorological conditions.

3.3 Production of ANs to constrain R(VOC)

Observations of un-speciated ANs and PNs imply missing VOCs that impact O3 chemistry. The relationship of ANs to Ox can provide a method to investigate this source. This relationship provides an estimate of the effective branching ratio, α, for the observed VOC mix (Perring et al.,
The value of this relationship stems from the reactions discussed above (R1 – R6) in that upon the oxidation of VOCs, some fraction of the time, RO$_2$ reacts with NO to form an AN molecule and the remainder of the time the reaction goes to form O$_3$. This is expressed with the following equations:

\[ P_{\Sigma AN} = \sum \alpha_i k_{OH+VOC_i}[OH][VOC_i] \quad (8) \]

\[ P(O_x) = \sum \gamma_i (1 - \alpha_i) k_{OH+VOC_i}[OH][VOC_i] \quad (9) \]

Here, \( \alpha \) is the effective branching ratio in the reaction of RO$_2$ with NO to form ANs versus RO$_2$ (R2), \( k \) is the OH rate constant with VOC$_i$, and \( \gamma \) is the number of O$_3$ molecules formed per oxidation of VOC$_i$. The \( \gamma \), calculated for the observed and calculated compounds from F0AM using the values from MCM (Jenkin et al., 2015), is found to be, on average, 1.53, which is lower than the value of 2 typically assumed in prior studies (e.g., Perring et al., 2013). This lower \( \gamma \) is due to the role of CO and CH$_2$O to the total reactivity. After the boundary layer height has stabilized (e.g., after 11:00 am LT used here) and is near enough (e.g., less than 1 day aging) to the VOC source to ignore deposition and entrainment, Eq. 8 and 9 can be combined to approximate the change in O$_x$ per molecule \( \Sigma AN \) formed:

\[ \frac{\Delta O_x}{\Delta \Sigma AN} \approx \frac{P_{O_x}}{P_{\Sigma AN}} \approx \frac{1.53(1-\alpha)}{\alpha} \quad (10) \]

For this equation to be valid, \( \alpha \) needs to be relatively small (\( \alpha \ll 1 \)), which is true for VOCs, as maximum \( \alpha \) for the conditions of KORUS-AQ is expected to be 0.35 (Orlando and Tyndall, 2012; Perring et al., 2013; Yeh and Ziemann, 2014). Note, though Eq. 10 can be used at short photochemical ages due to minimal impact from physical loss processes, chemical loss processes may impact the assumptions in Eq. 10 and are discussed in more detail below.

Over the SMA during KORUS-AQ, the slope between O$_x$ and \( \Sigma ANs \) was observed to be 40.5±1.8 (Figure 3a), with an \( R^2 = 0.60 \). Using Eq. 10, this translates to an effective branching
ratio ($\alpha_{\text{eff}}$), of 0.036. For other urban locations around the world, this slope has ranged from 13 – 47 (Farmer et al., 2011; Kenagy et al., 2020; Perring et al., 2010; Rosen et al., 2004), leading to an effective $\alpha$ between 0.04 and 0.15, assuming a $\gamma$ of 2 instead of the calculated $\gamma$ used here. Thus, the $\alpha_{\text{eff}}$ observed over SMA during KORUS-AQ is similar to other urban locations (Houston = 0.05 (Rosen et al., 2004) and South Korea = 0.05 (Kenagy et al., 2021)) but much lower than observed for Mexico City = 0.07 – 0.12 (Perring et al., 2010; Farmer et al., 2011) and Denver = 0.16 (Kenagy et al., 2020). This suggests that VOCs with low $\alpha$ dominate the total R(VOC) and production of ANs in SMA. The VOCs in SMA that dominate R(VOCs), including OVOCs, alkenes, and aromatics (Schroeder et al., 2020; Simpson et al., 2020), generally have lower $\alpha$ (Perring et al., 2013 and references therein; Orlando and Tyndall, 2012).

We use the observed VOCs (Table 2) to calculate $\alpha_{\text{eff}}$ from this mixture to compare to the calculated $\alpha_{\text{eff}}$ of 0.036 derived from the slope of $O_x$ versus $\Sigma$ANs in Figure 3a, as shown in Figure 4. The R(VOC) calculated from the observed VOCs and from the intermediates produced by the F0AM model, described in Sect. 2.2, are shown in Figure 4a, and the reactivity weighted $\alpha$ for the observations is shown in Figure 4b. As has been observed in other urban environments (e.g., Hansen et al., 2021; Whalley et al., 2016; Whalley et al., 2021; Yang et al., 2022), measured OVOCs contribute the most to the calculated R(VOC) for all NOx mixing ratios (32 – 48%). The unmeasured OVOCs (F0AM species) contributed 17 – 28% of the calculated reactivity. The F0AM species reactivity ranged from 0.45 – 1.78 s$^{-1}$, which is a similar increase in total OH reactivity observed by Brune et al. (2022) over South Korea. At higher NOx mixing ratios, primary, more reactive VOCs (e.g., alkanes, alkenes, aromatics) contribute an important fraction (> 25%) of the R(VOC). As there are interferences in the total OH reactivity measurement at high NOx (Brune et al., 2022), we are unable to determine the extent to which the observed and modeled reactivity
captures total OH reactivity in the SMA above a NO\textsubscript{x} value of approximately 4 ppbv. At lower NO\textsubscript{x} mixing ratios, ~33% of the R(VOC) is missing (calculated R(VOC), including F0AM species, ~3.0 s\textsuperscript{-1} and measured R(VOC) from Penn State—see Table 2—is 4.5 s\textsuperscript{-1}).

Numerous other urban studies have observed unmeasured OH reactivity, which is assumed to be unmeasured R(VOC), as the inorganic OH reactivity is typically well covered by measurements. This unmeasured R(VOC) has ranged from ~3 s\textsuperscript{-1} to ~10 s\textsuperscript{-1} (e.g., Brune et al., 2022; Hansen et al., 2021; Kim et al., 2016; Ma et al., 2022; Tan et al., 2019; Whalley et al., 2016; Whalley et al., 2021). Over the SMA, the difference between measured and calculated R(VOC) was ~1.5 s\textsuperscript{-1} at low NO\textsubscript{x} and unknown at high NO\textsubscript{x} mixing ratios. The lower difference may be related to the comparison occurring for observations at low NO\textsubscript{x}, when the very reactive material has either reacted into compounds measured on the DC-8 (e.g., formaldehyde, acetaldehyde, etc.), diluted to low enough concentrations to be negligible for R(VOC), or undergone deposition or partitioning to the particle-phase.

At higher NO\textsubscript{x} mixing ratios, which is more representative of fresh emissions, these more reactive compounds typically not measured are expected to lead to a higher difference between the calculated and observed R(VOC). Prior studies with more comprehensive measurements found these more reactive compounds and their secondary products contributed an important fraction towards the R(VOC) (e.g., Whalley et al., 2016). Thus, to determine if these unmeasured VOCs potentially contribute to the R(VOC), and thus P(O\textsubscript{x}), in SMA, another means to constrain their contributions is necessary. One potential means to constrain the total R(VOC) is by using the observed ΣANs and O\textsubscript{x} and assuming the observations are from the instantaneous production of both species (e.g., the assumption used for Figure 3a).
To estimate the unmeasured R(VOC), Eq. 10 is used without cancelling out terms and expanded into the measured and unmeasured R(VOC) and α:

\[
\frac{\Delta O_x}{\Delta \sum ANs} = \frac{\gamma RVOC_m[OH] + \gamma RVOC_u[OH] - \gamma \alpha_m RVOC_m[OH] - \gamma \alpha_u RVOC_u[OH]}{\alpha_m RVOC_m[OH] + \alpha_u RVOC_u[OH]}
\] (11)

Here, \( \frac{\Delta O_x}{\Delta \sum ANs} \) is the slope from Figure 3a, \( \gamma \) is the number of O\(_x\) molecules formed per oxidation of VOC, which is 1.53 for this study, R(VOC) is the VOC reactivity, which is its OH oxidation rate constant and its concentration (k×[VOC]) in units s\(^{-1}\), \( \alpha \) is the branching ratio for R2 (Table 1), and \( m \) and \( u \) correspond to measured and unmeasured RVOC and \( \alpha \). The rate constants for the measured VOCs are listed in Table 1, the reactivity for F0AM is taken directly from F0AM, and \( \alpha \) is either from MCM (Jenkin et al., 2015) or Perring et al. (2013) for observations or assumed to be 0.05 for F0AM secondary products. The equation is rearranged and solved for RVOC\(_u\), using different values of \( \alpha_u \) (e.g., 0.00 – 0.30, values typical \( \alpha \)).

As discussed in Sect. S3 in the Supp. Information, there are numerous assumptions and potential sources of uncertainty in the simplified version of Eq. 11. A thorough analysis and discussion of these assumptions are discussed in Sect. S3. The potentially most important assumption is that chemical loss is negligible in solving Eq. 11. However, due to the expected relatively short lifetime of \( \sum ANs \), the chemical loss of both O\(_x\) and ANs nearly cancel each other, leading to similar results in considering or neglecting these loss terms in Eq. 11. Further, as \( \sum ANs \) chemical loss has uncertainty, especially for ANs produced from anthropogenic VOC oxidation, the use of Eq. 11 reduces some of these uncertainties in comparison to Eq. S9. Thus, for the remainder of the paper, the values calculated from Eq. 11 will be used.

For the range of missing \( \alpha \) assumed, an \( \alpha = 0.10 \) for the unmeasured R(VOC) provides the best agreement with the observed R(VOC) (“From PSU” is the Penn State OH Reactivity with inorganic reactivity subtracted out) for all observations where NO\(_x\) < 4 ppbv. Further, it is found
that α ranging from 0.075 – 0.125 encompasses the associated uncertainty with the observed R(VOC) (±0.64 s⁻¹ (Brune et al., 2019)). This leads to an average unmeasured R(VOC) of 1.7⁺¹.⁴₋₀.₄.

The associated total missing R(VOC) for the assumed α of 0.10 ranges from 1.4 to 2.1 s⁻¹.

Assuming typical rate constants for emitted VOCs, assuming it is comparable to semi- and intermediate-VOCs, and their associated secondary products (~1 – 4×10⁻¹¹ cm³ molec⁻¹ s⁻¹ (Ma et al., 2017; Zhao et al., 2014)), the total missing reactivity would be equivalent to ~1 – 8 ppbv. Zhao et al. (2014) observed ~12 μg m⁻³ of semi- and intermediate-VOCs near Los Angeles, CA, during the CalNex study. Depending on the molecular weight assumed, this translates to ~1 to 2 ppbv. Nault et al. (2018) found that ~5 – 8 ppbv of VOCs were needed to explain the observed secondary organic aerosol production over the SMA, depending on the molecular weight assumed for the VOC. Further, Kenagy et al. (2021) also found that known chemistry could only account for ~33% of the observed ANs and missing sources of lower volatility VOCs to produce anthropogenically-derived ANs were necessary. Finally, Whalley et al. (2016) found that addition of unassigned VOCs and their associated oxidation products led to a reactivity of ~1.6 s⁻¹, leading to ~1 – 6 ppbv missing R(VOC). Thus, the reactivity and equivalent mixing ratios estimated here appear plausible and warrant future measurements to understand this unmeasured reactivity sources.

One important aspect of this unmeasured R(VOC) is that it should not be considered one or a couple of VOCs emitted and contributing 1 – 8 ppbv of VOC in the atmosphere. Instead, it will be the emitted VOCs and its oxidation products summed together to form the 1 – 8 ppbv of unmeasured VOCs in the atmosphere.

One possible missing VOC is nonanal, which is associated with cooking emissions (Rao et al., 2010; Sai et al., 2012; Schauer et al., 2002) and vegetative emissions (Hurst Bowman et al., 2003). Kim et al. (2018) observed cooking organic aerosols at a ground site in SMA, indicating...
that there should be associated gas-phase emissions from cooking. Nonanal has recently been
suggested to be a potential interference compound with isoprene measurements on a PTR-MS
(Coggon et al., 2024; Wargocki et al., 2023). Comparisons of isoprene measured by the PTR-MS
and WAS during KORUS-AQ (Figure S5) shows at increasing NOx mixing ratios (closer to
emission sources), the difference between the PTR-MS and WAS isoprene mixing ratios increases.
This suggests that there are potential unmeasured OVOCs and/or other C5H8 alkenes at high NOx
ratios that cannot be easily determined by the difference between the PTR-MS and WAS.
Continuing to use nonanal as a surrogate for this unmeasured OVOC, nonanal has a rate constant
consistent with the values used above for the missing R(VOC) (3.6×10^{-11} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1} (Hurst
Bowman et al., 2003)). Further, nonanal has an estimated high \( \alpha \) of \( \sim 0.2 \) (Hurst Bowman et al.,
2003). As typical nonanal mixing ratios have been observed or estimated to be < 500 pptv, this
suggests that nonanal or similar OVOCs may contribute to some of the missing reactivity (< 0.45
s^{-1}). Finally, nonanal may be an important higher PNs precursor (see Sect. 3.4 for more discussion
about un-speciated higher PNs).

OVOC emissions are generally considered to be an important fraction of R(VOC) for urban
emissions (de Gouw et al., 2018; Gkatzelis et al., 2021; McDonald et al., 2018; Ma et al., 2022;
Simpson et al., 2020; Wang et al., 2022; Yang et al., 2022). However, the \( \alpha \) for OVOC is
potentially smaller than alkanes, though it is highly unconstrained (Orlando and Tyndall, 2012).
Note, higher OVOCs have been understudied and thus may have higher \( \alpha \) (e.g., nonanal). Thus, if
the missing reactivity is mainly OVOCs and it is assumed their \( \alpha \) is low, compounds with \( \alpha > 0.15 
\) will be needed for the budget closure shown here. Likely compounds with high \( \alpha \) include alkenes,
cycloalkenes/alkenes, and aromatics, though the latter is also highly uncertain. Alkanes have
typically been a small source for the R(VOC) in urban environments (e.g., McDonald et al., 2018;
Though aromatics contribute a significant fraction of R(VOC) in different Asian urban environments (Brune et al., 2022; Schroeder et al., 2020; Simpson et al., 2020; Whalley et al., 2021), the majority of the aromatic R(VOC) is considered to be measured by WAS over SMA during KORUS-AQ (e.g., measured aromatics account for ~81% of aromatic reactivity in McDonald et al. (2018) and 98% of aromatic reactivity in Whalley et al. (2016), where both studies had more complete VOC measurements). Finally, the cycloalkenes/alkenes originate from numerous anthropogenic sources (e.g., McDonald et al., 2018; Simpson et al., 2020). One subclass of cycloalkenes includes monoterpenes. Similar to the comparison of isoprene between PTR-MS and WAS, the difference in monoterpenes between these two measurements increases with increasing NO$_x$ (Figure S6). As the interfering compound(s) measured by the PTR-MS and whether they are oxygenated or not is not known, only the WAS monoterpenes are used in this analysis of calculating R(VOC). Assuming the limonene rate constant, the difference between the PTR-MS and WAS monoterpenes raises the terpene reactivity by 0.05 – 0.30 s$^{-1}$. Though this does not include any associated photochemical products from the oxidation of monoterpenes and can improve the closure, it does not explain the total missing reactivity (1.4 – 2.1 s$^{-1}$). Thus, the missing R(VOC) is most likely a combination of OVOCs and cycloalkenes/alkenes.

### 3.4 Sources of PNs over SMA

As shown in Figure 2, ΣPNs account for a larger fraction of the total NO$_x$ budget than ΣANs. ΣPNs are known to be a temporary sink of NO$_x$ and radicals (R(O)O$_2$) due to their short thermal lifetime (~1 hr). Thus, the NO$_x$ emitted in SMA is being transported regionally, impacting the P(Ox).
In Figure 3b, ΣPNs shows some correlation with formaldehyde. Both are secondary products from the photooxidation of VOCs and have short lifetimes, leading to the correlation. However, above 4 ppbv formaldehyde, the correlation shifts as ΣPNs increases more rapidly than formaldehyde. As shown in Figure S7, this change in the relationship between ΣPNs versus formaldehyde is due to changes in the competition in the reaction of the acyl peroxy radical (R(O)O₂⁻) between NO₂ and NO. At low NO-to-NO₂ ratios, R8 is more favorable, leading to more efficient production of PNs over formaldehyde. As NO-to-NO₂ ratios increase (NO becomes comparable to NO₂), R9 becomes more dominant, leading to less production of PNs.

To further explore the sources of both PAN and the higher ΣPNs, the F0AM model (Wolfe et al., 2016) was used to predict ΣPNs, constrained by the observed VOCs precursors (Table 2). F0AM shows minimal bias in the predicted formaldehyde, NO₂, and OH (Figure S8). As discussed in Sect. 3.3, though, there is missing R(VOC) of 1.7\(^{+1.1}_{-0.3}\) s⁻¹. A sensitivity analysis in adding this missing reactivity to F0AM on predicted OH and formaldehyde was conducted (Sect. S4 and Figure S9 – S10). Both OH and formaldehyde are found to be buffered with the addition of this low amount of R(VOC). Thus, though there is good agreement in these intermediate products between observation and F0AM, this analysis for the sources of PAN and higher ΣPNs is expected to be a lower limit. This missing R(VOC) is further observed in the F0AM-predicted higher PNs (ΣPNs-PAN) versus formaldehyde, as a general underestimation in the total higher PNs compared to observations is observed (Figure 5a). PAN was excluded as F0AM overestimated the mixing ratios of PAN by approximately a factor of 2 (Figure S8e). Note, F0AM also overpredicted the PPN mixing ratios, but to a lesser extent than PAN (~50%; Figure S8f). The differences in predicted versus observed PNs may be associated with assumed background, dilution, and/or temperature used to reach steady-state (Schroeder et al., 2020). Thus, the results from F0AM will...
provide qualitative insight into sources and chemistry that should be investigated to better understand PN chemistry in SMA.

The classes of compounds producing higher PNs in F0AM are shown in Figure 5b. The classes of compounds were selected from the parent VOC which was oxidized into the higher PN (Table S2). Individual PNs with high contributions and/or are typically measured (PPN, PBzN, and MPAN (methacryloyl peroxy nitrate)) or are a large fraction of PNs but have yet to be measured in ambient conditions (PHAN) are shown without any connection to the parent VOC. Further, both PHAN and PPN have numerous precursors while many of the other higher PNs modeled by F0AM are generally associated with one precursor. At high NOx mixing ratios, the more reactive VOCs (aromatics, terpenes) contribute a large fraction of the higher PNs (>35% for NOx > 4 ppbv). As the air moves away from SMA (lower NOx mixing ratios), contributions of higher PNs from longer-lived compounds (e.g., alkanes) and later generation oxidation products start dominating.

An interesting trend is observed for PPN and PHAN. Both peroxy acyl radicals for PPN and PHAN (C2H5C(O)O2· and CH2(OH)C(O)O2·, respectively) are products from photooxidation of many VOCs, including aromatics, alkanes, and methyl ethyl ketone (MEK). However, the fractional contribution of PPN to higher PNs remains constant with decreasing NOx while the fractional contribution of PHAN increases with decreasing NOx (Figure 5b). This stems from the sources of C2H5C(O)O2· versus CH2(OH)C(O)O2·. The MCM mechanism, which is used for F0AM, produces C2H5C(O)O2· from the photooxidation from both short- and long-lived species (isoprene, C8-aromatics, toluene, ethanol, MEK, propane, and C4-alkanes) while CH2(OH)C(O)O2· is produced from the photooxidation of isoprene and ethene. For CH2(OH)C(O)O2·, the production is through minor channels in the photooxidation of isoprene.
(~3% yield directly from isoprene and ~20% as a secondary product (Galloway et al., 2011)). Ethene is relatively long-lived, with a lifetime ~7 hrs (OH = 5×10^6 molec. cm^-3) leading to the delay in the production of PHAN.

The results here in general indicate more speciated measurements of higher PNs are needed. However, as highlighted in Figure 5, improved detection of or measurements of PBzN, PHAN, and MPAN would allow for furthering our knowledge in PNs chemistry in urban environments and their role in controlling Oₓ production.

A qualitative investigation of the precursors of PAN predicted by F0AM are shown in Figure 5c. This provides a basis for further investigation of the sources over the SMA region for PAN as (a) F0AM over-predicts PAN, as noted above, (b) ethanol is currently estimated, similar to Schroeder et al. (2020), and (c) R(VOC) in F0AM is low due to missing precursors. Like the higher PNs, highly reactive R(VOC) contributes a large portion of the PAN budget at high NOₓ. The short-lived compounds contribute ~80% of PAN over SMA at the highest NOₓ mixing ratios. At lower NOₓ mixing ratios, moving away from SMA, longer-lived compounds, such as ethanol, contribute the most towards PAN production (~70%).

One of the interesting contributions not typically observed for PAN is MEK, which also contributes to PPN and PHAN. In prior studies, MEK mixing ratios were typically 0.5 to 2.0 ppbv (Bon et al., 2011; de Gouw et al., 2018; Liu et al., 2015). Over the SMA, 1.5 ppbv of MEK was observed on average with values as high as 8.3 ppbv. Due to the long lifetime of MEK (~30 hrs for the average photolysis rate measured and OH = 5×10^6 molec. cm^-3), the high mixing ratios of MEK are most likely due to direct emissions (e.g., de Gouw et al., 2005; Liu et al., 2015). Thus, there are potentially large sources of MEK in SMA that need to be considered in properly representing PAN chemistry.
Another potentially important compound for PAN production is ethanol. However, this compound was not measured during KORUS-AQ; instead, it was estimated based on previous ground-based observations, similar to Schroeder et al. (2020). Ethanol is considered to mainly come from vehicle emissions (e.g., Millet et al., 2012) and potentially cleaning agents (e.g., McDonald et al., 2018). As ethanol use is predicted to increase in the future (e.g., de Gouw et al., 2012) and cleaning agents and other volatile chemical products appear to scale with population (Gkatzelis et al., 2021), ethanol and MEK may continue contributing towards the PAN budget in the SMA in the future.

As a note, two other compounds potentially important for PAN production that were not measured on the DC-8 during KORUS-AQ include methylglyoxal and biacetyl (LaFranchi et al., 2009). In a forested environment that was partially impacted by urban outflow, these two components contributed on average 25% of the PAN budget (LaFranchi et al., 2009). In urban environments, methylglyoxal is believed to mainly originate from aromatic oxidation (Ling et al., 2020); whereas, biacetyl is believed to come from anthropogenic emissions (Xu et al., 2023). Further, as discussed in Sect. 4.3, these two compounds may potentially be important missing HOx sources, as well. Thus, measurements of these two compounds along with ethanol is necessary to better understand PAN chemistry.

4. Observational constraints of the HOx and Ox budget over SMA

As highlighted in Figure S1, the three factors impacting instantaneous P(Ox) are R(VOC), P(HOx), and NOx loss processes. In Sect. 3, the NOx loss processes were investigated and provided a constraint for R(VOC) to improve the investigation of P(Ox). With R(VOC) constrained, the RO2· concentration can be estimated, providing a means to calculate the net P(Ox) and to
investigate the major reactions leading to O\(_x\) loss and total HO\(_x\) (OH + HO\(_2\) + RO\(_2\)· + R(O)O\(_2\)·) loss. With the latter, this allows for an investigation of the major P(HO\(_x\)) reactions, assuming L(HO\(_x\)) equals P(HO\(_x\)) (see Eq. 1 – 7 in Sect. 2.3).

4.1 Net O\(_x\) production and sources of O\(_x\) loss

Using the total R(VOC) from Sect. 3.3 (Figure 4a), the net P(O\(_x\)) (Eq. 1 – 2) over SMA during KORUS-AQ has been determined (Figure 6a). The net P(O\(_x\)) peaked at 10.3 ppbv hr\(^{-1}\) at ~8 ppbv NO\(_x\). If only the measured and estimated R(VOC) from F0AM secondary products is used to calculate net P(O\(_x\)), the value decreases to 8.8 ppbv hr\(^{-1}\), but at the same NO\(_x\) mixing ratio. This value is similar to values observed in other urban locations around the world (~2 – 20 ppbv hr\(^{-1}\)), showing that many urban areas are still impacted by high P(O\(_x\)) values (Brune et al., 2022; Griffith et al., 2016; Ma et al., 2022; Ren et al., 2013; Schroeder et al., 2020; Whalley et al., 2016, 2018).

The NO\(_x\) distribution over SMA (Figure 1) shows a large area (~127.53°E to 127.18°E, or ~39 km) is near the NO\(_x\) mixing ratio with the maximum P(O\(_x\)) (Figure 6). Thus, a large portion of the SMA will have high instantaneous P(O\(_x\)) of ~10 ppbv hr\(^{-1}\). As the median wind speed over SMA during KORUS-AQ was ~5 m s\(^{-1}\), an air parcel would remain at the highest P(O\(_x\)) for ~2 hrs, leading to ~20 ppbv O\(_3\) being produced (not including dilution). This agrees with the ~20 ppbv increase in O\(_3\) observed over the Taehwa Research Forest supersite between midday and afternoon overpasses by the DC-8 during KORUS-AQ (Crawford et al., 2021). Thus, though there is a substantial O\(_3\) background observed over SMA (Colombi et al., 2023; Crawford et al., 2021), a large contribution of the O\(_3\) is due to photochemical production.

The major reactions leading to O\(_x\) loss (L(O\(_x\))) are shown in Figure 6b. The two major reactions that lead to O\(_x\) loss are net R8 (light and dark red), or the net production of PNs (which
includes losses), and R11, reaction of NO₂ with OH (blue) (see Table 1). Note, as discussed in Sect. 2.2, for the budget analysis conducted here, PAN and PPN were constrained to observations. At high NOₓ (near emissions, ~30 ppbv), R11 (NO₂ + OH) dominates the L(Oₓ) budget (> 60%), with net R8 (net PAN, dark red, and higher PNs, light red) contributing ~25%, and R12 – 14 accounting for the remaining 15% of Oₓ loss. As NOₓ mixing ratios decrease (moving away from emissions), the net R8 reaction, producing both PAN and higher PNs, starts contributing to larger total L(Oₓ), ranging from 30 – 40%. Furthermore, the net R8 reaction contribution towards L(Oₓ) remains relatively constants with NOₓ mixing ratios as the contribution from R11 (OH + NO₂) decreases. At NOₓ mixing ratios < 3 ppbv is when non-NOₓ reactions (R12 – 14) contribute greater than 30% of the L(Oₓ) budget. Thus, proper representation of PAN and higher PNs, both in precursors and speciation, is important in properly understanding the Oₓ budget in SMA.

4.2 HOₓ loss over the SMA

Similar to L(Oₓ), the major reactions leading to L(HOₓ) over the SMA during KORUS-AQ were the reactions of NOₓ with HOₓ, specifically NO₂ with OH (R11) and net PAN (dark red) and higher PNs (light red) production (R8). Reaction R11 is most important for NOₓ mixing ratios greater than 15 ppbv (50 – 65%). Between 5 and 15 ppbv, R11 is comparable to the net PN production (R8), where R11 comprises 35 – 50% of L(HOₓ) while net R8 (sum of higher ∑PNs and PAN) comprises 30 – 40% of L(HOₓ). At lower NOₓ mixing ratios, R11 is always smaller for L(HOₓ) than net R8, where R11 is about a factor of 2 lower than net R8. Production of ∑ANs played a minor role due to the low α_eff.

The self-reaction of HOₓ species (R15 – R16) contributes minimally to L(HOₓ) (less than 10%) for NOₓ mixing ratios greater than 8 ppbv. At lower NOₓ mixing ratios, R16 starts
dominating L(HO$_x$) budget, increasing from 8% at 8 ppbv to 50% of L(HO$_x$) at NO$_x$ mixing ratios less than 2 ppbv. Reaction R15 remains relatively small for the L(HO$_x$) budget, only reaching 7% of the L(HO$_x$) budget at NO$_x$ mixing ratios less than 2 ppbv.

### 4.3 Sources of HO$_x$ over SMA

The analysis conducted leads to the ability to constrain HO$_x$ losses over the SMA during KORUS-AQ. This is important as not all typical HO$_x$ sources were measured on the DC-8 during the project (e.g., nitrous acid, or HONO), and HO$_x$ production rates directly impacts P(O$_x$) (Figure S1). Prior studies (e.g., Griffith et al., 2016; Tan et al., 2019; Whalley et al., 2018) have demonstrated that in urban environments, sources of HO$_x$ include photolysis of O$_3$ and subsequent reaction with water vapor, formaldehyde photolysis, and HONO photolysis. Furthermore, recent studies have highlighted the potential importance of typically non-measured OVOCs in their contribution to P(HO$_x$) and subsequent P(O$_x$) in an urban environment (Wang et al., 2022). To constrain the P(HO$_x$) over SMA during KORUS-AQ, the P(HO$_x$) was assumed to be equal to the observationally constrained L(HO$_x$). Then, P(HO$_x$) was calculated for the measurements on the DC-8, including photolysis of O$_3$, formaldehyde, H$_2$O$_2$, and other measured OVOCs (Table 2).

Comparing the calculated P(HO$_x$) and L(HO$_x$), ~1.5 ppbv hr$^{-1}$ P(HO$_x$) (range 1.3 – 1.8 ppbv hr$^{-1}$) is not accounted for, leading to ~45% of the necessary L(HO$_x$) to maintain steady-state (Figure 7). For the calculated P(HO$_x$) budget, O$_3$ and formaldehyde photolysis contributed ~50% and 40% of the budget, respectively, with the remainder coming from photolysis of H$_2$O$_2$ and other measured OVOCs. Accounting for the unobserved P(HO$_x$), O$_3$ and formaldehyde photolysis contributed ~25% and ~20%, respectively.
Potential missing sources of P(HO\(_x\)) are briefly speculated here. First, one potential source is the photolysis of methylglyoxal. Using the F0AM predicted methylglyoxal, as it was not measured on the DC-8, methylglyoxal would contribute \(~0.24\) ppbv hr\(^{-1}\) P(HO\(_x\)), or \(~16\)% of the unobserved P(HO\(_x\)). Another OVOC not measured on the DC-8 and expected to originate from anthropogenic emissions and not from chemistry is 2,3-butanedione, or biacetyl (de Gouw et al., 2018; Grosjean et al., 2002; Schauer et al., 2002; Xu et al., 2023; Zhou et al., 2020). Prior studies observed 20 – 400 pptv of biacetyl (de Gouw et al., 2018; Xu et al., 2023), correspond to 0.04 – 0.74 ppbv hr\(^{-1}\), or 3 – 49% of the unobserved P(HO\(_x\)). Thus, between these two OVOCs, 19 – 66% of the unobserved P(HO\(_x\)) could be explained. Other unmeasured OVOCs could potentially contribute to the observed P(HO\(_x\)) (e.g., Wang et al., 2022); however, there is less constraints both on the speciation and photolysis rates for these OVOCs (e.g., Mellouki et al., 2015). Finally, HONO could contribute to this observed P(HO\(_x\)). Up to 700 pptv of HONO was observed in SMA during KORUS-AQ (Gil et al., 2021), though, this would quickly photolyze to the altitudes the DC-8 flew over SMA (Tuite et al., 2021). Even at 50 – 100 pptv HONO, photolysis of HONO would lead to 0.2 – 0.4 ppbv hr\(^{-1}\) P(HO\(_x\)), or 13 – 27% of the unobserved P(HO\(_x\)). Thus, between methylglyoxal, biacetyl, and HONO, between 32 – 92% of the unobserved P(HO\(_x\)) could be accounted for. This analysis highlights the importance of measuring these HO\(_x\) sources to better understand and constrain O\(_x\) chemistry in SMA and other urban environments.

One note about this analysis is that particulate matter collected onto the downwelling CAFS optics during KORUS-AQ (see Sect. S5, Table S3, and Figure S11). Corrections of up to 20% were determined, and the associated uncertainties were also increased by 20% due to the corrections. Thus, the exact amount of unmeasured P(HO\(_x\)) is potentially smaller than discussed.
5. Conclusions and Implications

In the Seoul Metropolitan Area (SMA), the ozone (O₃) mixing ratio often exceeds current standards and is increasing. Many processes can impact the O₃ mixing ratios and exceedances. Here, the processes that impact instantaneous O₃ production (P(Oₓ), where Oₓ is O₃ + NO₂ to account for possible O₃ titration) were investigated for observations collected on the NASA DC-8 during the 2016 NIER/NASA Korea United-States Air Quality (KORUS-AQ) study. The observations indicate missing oxidized NOₓ products (NOₓ) that include both the short-lived peroxy nitrates (ΣPNs) and alkyl and multi-functional nitrates (ΣANs). ΣPNs contributed the most for the organic NOₓ species. Only ~50% of the ΣPNs were speciated over SMA, which is atypical as prior studies typically show closure between the speciated and total PN measurements.

The un-speciated ΣPNs and ΣANs were used to constrain the missing volatile organic compound (VOC) reactivity (R(VOC)), as R(VOC) is important in constraining the instantaneous P(Oₓ). The missing R(VOC) was found to be 1.4 to 2.1 s⁻¹. The F0AM box model further supports the role of unmeasured ΣPNs as an important temporary NOₓ and radical sink over SMA. F0AM predicts ~50% of the higher ΣPNs (higher ΣPNs = ΣPNs − PAN), indicating missing R(VOCs) may explain the other 50%. Constraints from both the ΣPNs and ΣANs suggest that this missing R(VOC) would include oxygenated VOCs (OVOCs), including aldehydes such as octanal and nonanal from cooking, and alkenes from anthropogenic emissions.

With the constraints on the R(VOC), the net instantaneous P(Oₓ) was determined for SMA. It was found to peak at ~10 ppbv hr⁻¹ at ~8 ppbv NOₓ. A large fraction of the SMA area was, on average, at this mixing ratio of NOₓ, indicating high local P(Oₓ). This supports the increase of ~20 ppbv of O₃ observed in a downwind site (Taehwa Research Forest supersite) from midday to afternoon during KORUS-AQ.
With the comprehensive measurements on-board the DC-8, the F0AM model results, and the observationally constrained \(R(\text{VOC})\), a budget analysis on the sinks of \(\text{O}_3\) (\(L(\text{O}_3)\)) and \(\text{HO}_x\) (\(L(\text{HO}_x)\)), where \(\text{HO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2^- + \text{R(O)O}_2^-\)) was performed. Due to the high \(R(\text{VOC})\), type of VOC, and the \(\text{NO}_2\)-to-\(\text{NO}\) ratio, net \(\Sigma\text{PNs}\) production is surprisingly a large and important sink of \(\text{O}_x\) and \(\text{HO}_x\) over SMA (\(-25 \text{ -- } 40\\%\) and \(15 \text{ -- } 40\\%\) for \(L(\text{O}_3)\) and \(L(\text{HO}_x)\), respectively), with production of \(\text{HNO}_3\) and radical self-reactions accounting for the other \(L(\text{O}_3)\) and \(L(\text{HO}_x)\) losses. Net \(\Sigma\text{PNs}\) production as an important \(L(\text{O}_3)\) and \(L(\text{HO}_x)\) term is significant, as \(\Sigma\text{PNs}\) is a temporary reservoir of both \(\text{NO}_2\) and \(\text{R(O)O}_2^-\) but has not traditionally been included in these calculations. Downwind locations separated from the local \(\text{NO}_x\) and VOC emissions of the SMA will experience increased \(P(\text{O}_3)\) due to the release of \(\text{NO}_2\) and \(\text{R(O)O}_2^-\). With the constraint of \(L(\text{HO}_x)\), \(P(\text{HO}_x)\) was investigated, assuming steady-state, and unmeasured \(\text{HONO}\) plus unmeasured OVOCs were found to be necessary to explain the missing \(\text{HO}_x\) sources. Both sources of \(\text{HO}_x\) are either missing or highly uncertain in chemical transport models.

Though the high regional background and foreign sources of \(\text{O}_3\) and its precursors elevate the \(\text{O}_3\) levels in SMA and potentially already causes the SMA to be in exceedance for \(\text{O}_3\) concentrations, this study highlights the importance local, in-situ \(P(\text{O}_3)\) to the SMA area, which can further exacerbate the \(\text{O}_3\) concentrations for SMA and the surrounding region. The results support the observations of increasing \(\text{O}_3\) with decreasing \(\text{NO}_x\) that has been observed for SMA in prior studies. Further, the study highlights the important role of unmeasured VOCs and OVOCs and the necessity to understand their sources and role in \(\text{NO}_x\) and \(\text{O}_3\) chemistry. Further, the study demonstrates the interplay of direct emissions or secondary production of PN precursors and its role in net \(P(\text{O}_3)\). Attempts at specifically reducing the sources of PN may adversely impact net \(P(\text{O}_x)\), as lower net PN chemistry may increase \(\text{O}_3\) due to more \(\text{NO}_2\) being available.
Competing Interests

At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

Acknowledgements

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Data Availability
Version R6 1-min merged data used in this analysis available at DOI:10.5067/Suborbital/KORUSAQ/DATA01. The F0AM setup file, input file, and output files are all available at https://doi.org/10.5281/zenodo.1072327.

**Author Contribution**

BAN, KRT, and JHC designed the experiment and wrote the paper. BAN and KRT analyzed the data. KRT ran the F0AM model and KRT and BAN analyzed the model output. BAN, DRB, PCJ, RCC, JPD, GSD, SRH, LGH, JLJ, K-EK, YL, IJS, KU, and AW collected and QA/QC the data during KORUS-AQ. All authors contributed to the writing and editing of the paper.
References


Area during the Korea-US Air Quality study, Atmos Environ, 247, 118182, 2021.


### Table 1. Reactions described in text along with associated rate constants and references for those rate constants.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1a (\text{VOC}+\text{OH} + \text{O}_2 \rightarrow \text{RO}_2)</td>
<td>Varies</td>
<td>Atkinson (2003); Atkinson and Arey (2003); Atkinson et al. (2006); Bohn and Zetzsch (2012); Sprengnether et al. (2009)</td>
</tr>
<tr>
<td>R1b (\text{VOC}+h\nu + \text{O}_2 \rightarrow \text{RO}_2)</td>
<td>Varies/Measured</td>
<td>Shetter &amp; Müller (1999)</td>
</tr>
<tr>
<td>R2a (\text{RO}_2^+\text{NO} \rightarrow (1-\alpha) \text{RO}+ (1-\alpha) \text{NO}_2)</td>
<td>(2.7\times10^{11}\times\exp(390/T))</td>
<td>Burkholder et al. (2020)</td>
</tr>
<tr>
<td>R2b (\text{RO}_2+\text{NO} \rightarrow \alpha \text{RONO}_2)</td>
<td>(2.7\times10^{11}\times\exp(390/T))</td>
<td>Burkholder et al. (2020)</td>
</tr>
<tr>
<td>R3 (\text{NO}_2+h\nu \rightarrow \text{NO}+\text{O}(^3\text{P}))</td>
<td>Measured on DC-8</td>
<td>Shetter &amp; Müller (1999)</td>
</tr>
<tr>
<td>R4 (\text{O}(^3\text{P})+\text{O}_2 \rightarrow \text{O}_3)</td>
<td>(3.2\times10^{11}\times\exp(67/T))</td>
<td>Saunders et al. (2003)</td>
</tr>
<tr>
<td>R5 (\text{RO}+\text{O}_2 \rightarrow \text{R(O)}+\text{HO}_2)</td>
<td>Assumed Instantaneous</td>
<td>Saunders et al. (2003)</td>
</tr>
<tr>
<td>R6 (\text{HO}_2+\text{NO} \rightarrow \text{OH}+\text{NO}_2)</td>
<td>(3.45\times10^{12}\times\exp(270/T))</td>
<td>Saunders et al. (2003)</td>
</tr>
<tr>
<td>R7 (\text{RCHO}+\text{OH} + \text{O}_2 \rightarrow \text{R(O)}\text{O}_2)</td>
<td>Varies</td>
<td>Atkinson (2003); Atkinson and Arey (2003); Atkinson et al. (2006)</td>
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<td>R8a (\text{R(O)}\text{O}_2^+\text{NO}_2 \leftrightarrow \text{R(O)}\text{O}_2\text{NO}_2)</td>
<td>F: (8.69\times10^{12}) cm(^3) molec.(^{-1}) s(^{-1}) R: (4.30\times10^{-4}) s(^{-1})</td>
<td>Burkholder et al. (2020)</td>
</tr>
<tr>
<td>R9 (\text{R(O)}\text{O}_2+\text{NO} \rightarrow \text{RO}_2+\text{NO}_2)</td>
<td>(8.1\times10^{12}\times\exp(270/T))</td>
<td>Burkholder et al. (2020)</td>
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<tr>
<td>R10 (\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2)</td>
<td>(2.07\times10^{13}\times(\text{-1400}/T))</td>
<td>Burkholder et al. (2020)</td>
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<tr>
<td>R11b (\text{OH}+\text{NO}_2 \rightarrow \text{HNO}_3)</td>
<td>(1.24\times10^{11}) cm(^3) molec.(^{-1}) s(^{-1})</td>
<td>Burkholder et al. (2020)</td>
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<tr>
<td>R12 (\text{O}_3+h\nu \rightarrow 2\text{O}(^1\text{D}))</td>
<td>hv measured on DC-8: (2.14\times10^{10}) cm(^3) molec.(^{-1}) s(^{-1})</td>
<td>Shetter &amp; Müller (1999); Saunders et al. (2003)</td>
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<td>R13 (\text{O}_3+\text{OH} \rightarrow \text{HO}_2+\text{O}_2)</td>
<td>(1.7\times10^{12}\times\exp(\text{-940}/T))</td>
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<td>R14 (\text{O}_3+\text{HO}_2 \rightarrow \text{OH}+2\text{O}_2)</td>
<td>(1.0\times10^{14}\times\exp(\text{-490}/T))</td>
<td>Burkholder et al. (2020)</td>
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<td>R15b (\text{HO}_2+\text{HO}_2 \rightarrow \text{H}_2\text{O}_2)</td>
<td>(5.06\times10^{12}) cm(^3) molec.(^{-1}) s(^{-1})</td>
<td>Saunders et al. (2003)</td>
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<tr>
<td>R16 (\text{HO}_2+\text{RO}_2 \rightarrow \text{Products})</td>
<td>(2.91\times10^{13}\times\exp(1300/T))</td>
<td>Saunders et al. (2003)</td>
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<tr>
<td>R17 (\text{HO}_2+\text{OH} \rightarrow \text{Products})</td>
<td>(4.80\times10^{11}\times\exp(250/T))</td>
<td>Burkholder et al. (2020)</td>
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</table>
R18<sup>b</sup>  |  OH+NO → HONO  |  7.40×10<sup>-12</sup> cm<sup>3</sup> molec.<sup>-1</sup> s<sup>-1</sup>  |  Burkholder et al. (2020)  
---|---|---|---
R19  |  HO<sub>2</sub>+R(O)O<sub>2</sub> → Products  |  4.30×10<sup>-13</sup>×exp(1040/T)  |  Burkholder et al. (2020)  

<sup>a</sup>Only showing forward (F) and reverse (R) rate constant at 298 K and 1013 hPa and being a termolecular reaction.  
<sup>b</sup>Termolecular reaction; only showing rate at 298 K and 1013 hPa.
Table 2. List of instruments, compounds measured, accuracy/precision, and associated references used in this study.

<table>
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<tr>
<th>Instrument</th>
<th>Species</th>
<th>References</th>
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<tr>
<td>University of California, Irvine, Whole Air Sampler (WAS)</td>
<td>Ethane, Ethene, Ethyne, Propane, Propene, i-Butane, n-Butane, 1-Butene,</td>
<td>Simpson et al. (2020)</td>
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<td>i-Butene, trans-2-Butene, cis-2-Butene, i-Pentane, n-Pentane, 1,3-Butadiene, 1</td>
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<td>Isoprene, n-Hexane, n-Heptane, n-Octane, n-Nonane, n-Decane, 2,3-Dimethylbutane,</td>
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<td></td>
<td>2-Methylpentane, 3-Methylpentane, Cyclopentane, Methylcyclopentane,</td>
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<td>Cyclohexane, Methylcyclohexane, Benzene, Toluene, m+p-Xylene, o-Xylene,</td>
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<td>Ethylbenzene, Styrene, i-Propylbenzene, n-Propylbenzene, 3-Ethylltoluene,</td>
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<td>4-Ethylltoluene, 2-Ethylltoluene, 1,3,5-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1</td>
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<td>1,2,3-Trimethylbenzene, α-Pinene, β-Pinene, Methyl nitrate, Ethyl nitrate,</td>
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<td>i-Propyl nitrate, n-Propyl nitrate, 2-Butyl nitrate, 3-Pentyl nitrate, 2-Pentyl nitrate, 3-Methyl-2-Butyl nitrate</td>
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<td>The Pennsylvania State University Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS)</td>
<td>OH, HO₂, OH Reactivity</td>
<td>Faloona et al. (2004), Mao et al. (2009), Brune et al. (2019)</td>
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<td>University of California, Berkeley, Thermal Dissociation-Laser Induced Fluorescence (TD-LIF)</td>
<td>NO₂, ΣPNs, ΣANs</td>
<td>Thornton et al. (2000), Day et al. (2002), Wooldridge et al. (2010)</td>
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<td>NASA Langley Diode Laser Hygrometer (DLH)</td>
<td>H₂O</td>
<td>Diskin et al. (2002)</td>
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<td>NASA Langley Diode Laser Spectrometer Measurements (DACOM)</td>
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<td>Sachse et al. (1987)</td>
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<td>University of Colorado, Boulder, Compact Atmospheric Multi-species Spectrometer (CAMS)</td>
<td>CH₃O, C₂H₆</td>
<td>Richter et al. (2015), Fried et al. (2020)</td>
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<td>Gwangju Institute of Science and Technology Korean Airborne Cavity Enhances Spectrometer (K-ACES)</td>
<td>CHOCHO</td>
<td>Min et al. (2016), D. Kim et al. (2022)</td>
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<td>Instrument/Instrumentation</td>
<td>Analytes</td>
<td>References</td>
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<td>NCAR CCD Actinic Flux Spectroradiometers (CAFS)</td>
<td>j-values</td>
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<td>Georgia Institute of Technology Chemical Ionization Mass Spectrometer (GT)</td>
<td>SO₂, PAN, PPN, APAN, PBzN</td>
<td>Kim et al. (2007), Lee et al. (2022)</td>
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<td>NCAR 4-Channel Chemiluminescence Instrument (NCAR)</td>
<td>NO, NO₂, O₃, NO₃</td>
<td>Weinheimer et al. (1994)</td>
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<td>California Institute of Technology Chemical Ionization Mass Spectrometer (CIT)</td>
<td>Butene Hydroxynitrates, Butadiene Hydroxynitrates, Ethene Hydroxynitrates, Ethanal Nitrate, Isoprene Hydroxynitrates, Propene Hydroxynitrates, Propanal Nitrate, CH₃OOH, Peroxyacetic Acid, HNO₃, Hydroxyacetone, H₂O₂</td>
<td>Crounse et al. (2006), Teng et al. (2015)</td>
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<td>University of Oslo Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-MS)</td>
<td>Methanol, Acetaldehyde, Acetone+Propanal, Isoprene, MVK+MACR+ISOPOOH, Benzene, Toluene, C₈-alkylbenzenes, Monoterpenes, MEK</td>
<td>Müller et al. (2014)</td>
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<td>NSRC Meteorological and Geographical Data</td>
<td>Latitude, Longitude, Altitude, Temperature, Pressure</td>
<td>Crawford et al. (2021)</td>
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Figure 1. Binned NO\textsubscript{x} mixing ratios observed on the NASA DC-8 during the KORUS-AQ campaign. Note, the color bar scale is logarithmic. The binning is along the flight paths of the NASA DC-8 for any observations collected below 2.0 km and after 11:00 local time. The rest of the NASA DC-8 flight paths not included in the analysis are shown in grey. Three key areas from KORUS-AQ are highlighted—the Olympic Park ground site, the airfield where the NASA DC-8 conducted routine missed approaches, and the Taehwa Research ground site. The histograms above and to the left are the distribution of NO\textsubscript{x} mixing ratios longitudinally and latitudinally, respectively.
Figure 2. (a) Scatter plot of the summation of individual NO$_z$ (NO$_z$ is higher oxide NO$_x$ products) measured by GT, CIT, WAS, TD-LIF, and AMS versus NO$_x$ measured by difference between NO$_y$ and NO$_x$ (see Table 2 for compounds measured by each instrument). NO$_x$ is NO measured by NCAR and NO$_2$ measured by LIF. The observations are for when the DC-8 was over the SMA. (b) Average contribution of measured speciated NO$_z$ over the SMA during KORUS-AQ versus NO$_x$. Higher PNs is PPN + APAN + PBZN. ΣUn-speciated PNs is total peroxnitrates from TD-LIF minus total measurement from GT. Alkyl RONO$_2$ is the total small alkyl nitrate measurements from WAS. Multifunctional RONO$_2$ is the total measurements from CIT. ΣUn-speciated ANs is the total alkyl nitrates from TD-LIF minus total RONO$_2$ from CIT and WAS.
Figure 3. Scatter plot of (a) O₅ versus ΣANs and (c) ΣPNs versus formaldehyde (CH₂O) over SMA (see Figure 1 for area studied). Data is colored by meteorological periods discussed in Peterson et al. (2019). Data plotted here is after 11:00 am LT to minimize impact of growing boundary layer and nocturnal residual layer mixing. The curvature in (c) is further explored in Figure S7.
Figure 4. (a) Binned VOC reactivity versus NO\textsubscript{x} observed over SMA during KORUS-AQ (see Figure 1 for the area studied). The measured observed R(VOC), labeled as “From PSU”, where PSU is Pennsylvania State University, is the VOC reactivity calculated from the measured total OH reactivity with inorganic OH reactivity removed. As discussed in Brune et al. (2022), the OH reactivity has interferences at high NO\textsubscript{x} mixing ratios. The error bar is the uncertainty in the OH reactivity measurement (Brune et al., 2022). The red line represents the calculated unmeasured R(VOC), using Eq. 11, with an assumed \( \alpha = 0.10 \). The shaded area represents different calculated unmeasured R(VOC), assuming different \( \alpha \) for the unmeasured R(VOC) (see Eq. 11). (b) The calculated effective \( \alpha \) from observations versus NO\textsubscript{x}. The dashed purple line is the effective \( \alpha \) estimated from Eq. 10, using the slope from Figure 3a. For both (a) and (b), the colored stacked data is the calculated VOC reactivity (a) and weighted effective \( \alpha \) (b). The values from (b) are calculated using Eq. 11. Finally, for both (a) and (b), F0AM species is the reactivity for compounds not measured on the DC-8 predicted by F0AM with an estimated \( \alpha = 0.05 \). The associated uncertainty in using different \( \alpha \) for the F0AM predicted reactivity is explored in Figure S4.
Figure 5. (a) Scatter plot of binned higher ΣPNs calculated using F0AM (red) or binned higher ΣPNs from observations (black) versus formaldehyde (CH\textsubscript{2}O). Slopes shown are ODR fits to the binned data. (b) Fractional contribution of the higher PNs predicted from F0AM versus NO\textsubscript{x}. (c) Fractional contribution of different precursors to PAN, predicted by F0AM versus NO\textsubscript{x}. For both (b) and (c), Alk is all alkanes, Arom is all aromatics, and ≥C\textsubscript{4} Alk is all alkanes with 4 or more carbons. See Figure S8 for comparison of F0AM.
Figure 6. (a) Net \( \text{O}_x (\text{O}_3 + \text{NO}_2) \) production (see Eq. 1 and 2) predicted for SMA using measured and F0AM \( R(\text{VOC}) \) (dashed) or total \( R(\text{VOC}) \) (solid), from Figure 4a, versus \( \text{NO}_x \). (b) Contribution of different reactions to the total \( \text{O}_x \) loss versus \( \text{NO}_x \). (c) Contribution of different reactions to total \( \text{HO}_x \) (\( \text{HO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2 + \text{R}(\text{O})\text{O}_2 \)) loss versus \( \text{NO}_x \). The predicted \( \text{RO}_2 \) comes from the total VOC reactivity calculated in Figure 4a assuming steady-state (Eq. 7), and \( \text{HO}_2 \) the acyl peroxy radicals are from F0AM results. Note for both (b) and (c), net \( \text{RC}(\text{O})\text{O}_2 + \text{NO}_2 \) and net \( \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \) are described in Eq. 3. Radical reactions contributing < 1\% to the \( \text{L(O}_x \) or \( \text{L(HO}_x \) are not included.
Figure 7. Calculated HOx production from observations (colored stack) compared with the calculated HOx loss from Figure 6c over the SMA during KORUS-AQ.