Understanding Ozone Formation and Carbonyl Contributions in the Seoul Metropolitan Area

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ABSTRACT

With strong air quality policies in place in China and South Korea in recent years, it is important to understand the changing situation to address the increasing surface ozone problem in Korea. We revisited the ozone formation condition and investigated the contribution of each component using observations of routinely measured volatile organic compounds (VOCs) and, for the first time, employed multiyear ground observations of carbonyl compounds (formaldehyde, acetone, and acetaldehyde) from the two sites in Seoul Metropolitan Area (SMA), Seoul and Incheon, during the 2016–2018 ozone season (May–September). We found a significant fraction of carbonyl compounds (formaldehyde) based on ground observations, accounting for 51% (38%) and 37% (25%) of the total VOCs in Seoul and Incheon. To determine the ozone production regime, we used OH reactivities of NOx and VOCs, including carbonyl compounds. We found that while Seoul is still in the NOx-saturated regime, Incheon is already almost in a transition regime regardless of including carbonyl compounds. Since both regions are changing toward the transition regime, it is important to manage the NOx and VOC concentrations in a balanced manner. We calculated the ozone formation potential (OFP) of each VOC species using Maximum Incremental Reactivity (MIR). The results showed that formaldehyde contributes the most to OFP both in Seoul and Incheon, accounting for 45% and 29%, respectively. This study highlights the importance of carbonyl compounds in ozone formation in SMA, and it is recommended that formaldehyde be monitored with finer time resolution at monitoring stations co-located with other VOC monitoring stations in SMA for more reliable investigations.

Keywords: Ozone formation potential, OH reactivity, VOCs, Formaldehyde, MIR

1 INTRODUCTION

Exposure to high concentrations of ozone at the ground level has adverse effects on human health (Thurston and Ito, 2001; U.S. EPA, 2013) and the ecosystem (Fuhrer, 2003; Hogrefe et al., 2004; Hubbell et al., 2005; Karnosky et al., 2005). The Korean government has set national air quality standards for daily maximum 8-hour ozone (MDA8) of 60 ppb and 1-hour ozone (MDA1) of 100 ppb since 1993. In 2015, there were 256 valid monitoring stations nationwide, increasing to 431 by 2021, during which time less than 1% (42%) of the monitoring stations complied with the MDA8 (MDA1) standard each year, and ozone concentrations continued to increase (KME, 2021).
Especially, the increasing ozone in Seoul Metropolitan Area (SMA, including Seoul, Incheon, and Gyeonggi province) is of great concern (Kim et al., 2018; Seo et al., 2014; Yeo and Kim, 2021) because approximately 44% of the nation’s population (51 million) is concentrated in the SMA. Recent studies have shown that ozone concentrations in the SMA are influenced by increases in East Asian regional background ozone, but also show a unique behavior that distinguishes them from the rest of the country due to intensive local NOx emissions (Colombi et al., 2022; Lee and Park, 2022). Therefore, there is a need to understand better the effects of local-scale ozone formation in the SMA in Korea.

Tropospheric ozone is a secondary air pollutant formed through a series of chemical reactions between volatile organic compounds (VOCs) and nitrogen oxides (NOx = NO + NO2) in the presence of solar radiation. Each VOC has a different ozone formation potential (OFP) and the composition of VOCs varies by region. In urban and suburban areas with heavy traffic and anthropogenic activities, toluene and m,p-xylene were found to be the most effective in ozone formation (Feng et al., 2019; Kumar et al., 2018), while biogenic VOCs such as monoterpenes and isoprene were the most effective in rural or forested sites (Gómez et al., 2020). Oxygenated VOCs (OVOCs) are a considerable portion of VOCs, and carbonyls (formaldehyde, acetaldehyde, and acetone) are one of the most abundant groups of OVOCs in urban air (Legreid et al., 2007). The importance of formaldehyde in ozone formation has been suggested in several studies in urban areas (Duan et al., 2008; Lei et al., 2009; Wang et al., 2017). Formaldehyde can be directly emitted from incomplete combustion processes (primary formaldehyde) or produced by photo-oxidation of hydrocarbons (secondary formaldehyde). The major loss processes of formaldehyde are photolysis and reaction with the hydroxyl radical (OH). Formaldehyde serves as an important primary source for the hydroperoxyl radical (HO2) and contributes to other odd hydrogen radicals through the radical propagation processes leading to ozone production (Lei et al., 2009).

Kim et al. (2015) identified uncertainties in ozone formation mechanisms in SMA, suggesting the important role of OVOCs as a source and sink of radicals, but until recently, carbonyls, including formaldehyde, were excluded from domestic ozone formation analysis due to the lack of continuous observations (Kim et al., 2018; Shin et al., 2013a). In 2016, during the Korean-US Air Quality Study (KORUS-AQ campaign) OVOCs, including formaldehyde, were measured for about a month from May to June. Schroeder et al. (2020) investigated ozone chemistry using KORUS-AQ observations and found formaldehyde to be enriched among VOCs, and Travis et al. (2022) found strong relationships between surface ozone observations with formaldehyde column amount derived from the NASA DC-8 research aircraft and Pandora during the campaign. Although satellite observations provide years of formaldehyde column concentrations, there have been no attempts to relate them to the surface observations in Korea. To gain insight into the impact of formaldehyde on ozone production, it is necessary to analyze longer periods using many sources, including satellite observations.

This study aims to understand the observed surface ozone air quality at the two sites, Seoul and Incheon, in SMA from 2016 to 2018, and to identify the characteristics of each region by investigating the contribution of individual VOCs to ozone formation, including OVOCs, and to suggest measures to control ozone concentrations by region. To this end, we collected and analyzed observational data for aldehydes in addition to VOCs routinely monitored for photochemistry assessment at the two sites. The analysis includes a comparison of the time series evolution of formaldehyde concentrations at the two surface sites with satellite observations, and an investigation of the meteorological conditions, NOx to VOCs ratio by means of OH reactivity (OHR), and OFP of each VOC at the two sites.

2 METHODS

2.1 Surface Observation Data

The study period is from May to September every year from 2016 to 2018, focusing on the active ozone formation time (9:00–18:00). We use ozone, NO2, NOx, and VOCs monitoring data at the Seoul and Incheon sites of the National Institute of Environmental Research (NIER) (Fig. 1). Eunpyeong-gu (EP, 37.45°N, 126.72°E), Seoul is commercial area in the city and Bukhan mountain...
in the east of the site and Gwangjin-gu (GJ, 37.55°N, 127.09°E), Seoul is inside water purification facility. Incheon (37.45°N, 126.72°E) is residential area in the city.

The NIER provides hourly observations of ozone and NO₂ at 598 ambient air monitoring stations (as of the end of December 2021) across the country running by the Korean Ministry of
Table 1. List of measured VOCs and corresponding rate constant for reaction with OH (unit: cm^3 molecule^{-1} s^{-1}) and Maximum Incremental Reactivity (MIR) coefficient (unit: µg O_3 µg^{-1} VOC) used in this study.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>k_{OH}</th>
<th>MIR coefficient</th>
<th>No.</th>
<th>Name</th>
<th>k_{OH}</th>
<th>MIR coefficient</th>
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<td>1</td>
<td>Ethane</td>
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<td>n-Heptane</td>
<td>6.76E-12^b</td>
<td>1.07</td>
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<td>2.35E-12^a</td>
<td>1.23</td>
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<td>6.60E-12^b</td>
<td>1.03</td>
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<td>Toluene</td>
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<td>n-Octane</td>
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<td>1.17</td>
<td>46</td>
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<td>1.86E-11^b</td>
<td>7.39</td>
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<td>1.18E-11^b</td>
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<td>11.76</td>
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<td>2.19</td>
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<td>p-Diethylbenzene</td>
<td>–</td>
<td>4.43</td>
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<td>26</td>
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<td>0.72</td>
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<td>n-Undecane</td>
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<td>0.61</td>
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<td>Cyclohexane</td>
<td>8.48E-12^a</td>
<td>1.25</td>
<td>56</td>
<td>Formaldehyde</td>
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<td>28</td>
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<td>6.86E-12^a</td>
<td>1.19</td>
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<td>Acetaldehyde</td>
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<td>6.54</td>
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<tr>
<td>29</td>
<td>2,3-Dimethylpentane</td>
<td>-</td>
<td>1.34</td>
<td>58</td>
<td>Acetone</td>
<td>1.80E-13^a</td>
<td>0.36</td>
</tr>
</tbody>
</table>

^a Heald et al. (2020); ^b Atkinson and Arey (2003); ^c Altshuller (1991); ^d Carter (2010).
guidelines: calibration curves correlation coefficient $\geq 0.995$ for online-VOCs, and $\geq 0.98$ for carbonyl compounds; precision determined by measuring the calibration gas in duplicate seven times; and relative standard deviations for online-VOCs and carbonyl compounds $< 25\%$ and $< 10\%$, respectively. We used meteorological data from the closest Korea Meteorological Administration (KMA) monitoring station to each site (Seoul 37.57°N, 126.97°E, Incheon 37.48°N, 126.63°E) in order to see meteorological effects on the ozone formation.

2.2 Satellite Observation

Surface observations of formaldehyde were compared with formaldehyde total column observations from Ozone Mapping and Profiler Suite Nadir Mapper aboard the joint NASA/NOAA Suomi National Polar-orbiting Partnership (OMPS-NPP) launched in October 2011. The OMPS-NPP has a spectral resolution of 1 nm and spectral sampling of 0.42 nm, and measures back-scattered radiances in the ultraviolet spectral range (300–380 nm) with a nadir ground pixel size of 50 km × 50 km.

Formaldehyde vertical column densities (VCDs) were derived by the Smithsonian Astrophysical Observatory (SAO) retrieval algorithm (González Abad, 2022; Nowlan et al., 2023). Kwon et al. (2023) showed that OMPS-NPP formaldehyde products have negative biases of $-15 \pm 4\%$ in sites with formaldehyde VCDs $> 4.0 \times 10^{15}$ molecules cm$^{-3}$ in comparisons with ground-based Fourier-Transform Infrared (FTIR) observations. The monthly mean OMPS-NPP and FTIR product comparisons showed good correlation coefficients of 0.83.

The good quality pixels with the following conditions were collected: the main data quality flag of zero, the cloud fraction less than 0.4, and the solar zenith angle less than 70. We temporally oversampled OMPS-NPP formaldehyde data on a horizontal resolution of 0.1 degrees to reduce noise level and re-grid formaldehyde pixels on a finer spatial resolution. At this resolution, we were able to distinguish GJ and EP sites with insignificant noise on a monthly basis (Fig. S2).

2.3 Ozone production Regime

To determine the ozone production regime, we used a metric ($\varphi = \text{OHR}_{\text{NOx}}/\text{OHR}_{\text{ROC}}$) suggested by Kirchner et al. (2001) and Heald et al. (2020), where $\text{OHR}_{\text{NOx}}$ and $\text{OHR}_{\text{ROC}}$ is the OH reactivity of NOx and reactive organic carbon, respectively. The OHRROC is defined as $\sum (k_{\text{OH} + X_i} [X_i])$, the sum of OH reactivity of each species ($X_i$) including not only VOC species but also other gas phase species that react with OH, i.e., CO and NOx (Heald et al., 2020). The observed mixing ratios were multiplied by the number of carbons in a mole of each VOC (ppbC), and CO and NOx (ppb) were used without correction. We used reaction rate constants ($k_{\text{OH} + X_i}$) at standard temperature and pressure (298 K, 1013.25 hPa), taken from Altshuller (1991), Atkinson and Arey (2003) and Heald et al. (2020) (Table 1). Since the average temperature during our study period did not deviate much from the 298 K (Table S1), no correction was made. For $\varphi < 0.01$, the ozone production is insensitive to changes of VOC emissions, and $\varphi > 0.2$ indicates NOx-saturated conditions where reduced NOx emissions promote ozone production (Heald et al., 2020; Kirchner et al., 2001).

2.4 Ozone Formation Potential

The photochemical formation of ozone by formaldehyde and other VOCs can be quantified by their OFP. The widely used methods of OFP calculation are the Photochemical Ozone Creation Potential (POCP), which shows the relative ozone production of other VOC chemical species based on the ozone production amount of ethylene (Derwent et al., 1996), and the Maximum Incremental Reactivity (MIR) method, which calculates the maximum amount of ozone that can be generated in 1 hour for each VOCs using a box model (Carter et al., 1995). The POCP method is suitable for looking at the effect of long-range transport, assuming a residence time of 4 to 6 days for VOCs (Derwent et al., 1996), so this study used the MIR method to determine the difference between the two adjacent sites at a local scale.

$$\text{OFP (ppb) = VOCi (ppb) \times \frac{\text{molecular mass of VOCi}}{\text{molecular mass of O}_3} \times \text{MIRi} \times \text{O}_3 \mu g^{-1} \text{VOCi}}$$ (1)
The OFP of each VOC was calculated using Eq. (1), where \(i\) denotes the VOC species. We used the MIR coefficients derived from SAPRC-07 mechanism (Carter, 2010), and those are listed in Table 1.

### 3 RESULTS AND DISCUSSION

#### 3.1 Annual Variation of Mean MDA8 and Hourly Ozone Standard Violation Frequency in Warm Seasons

Although Seoul and Incheon belong to SMA and the two observation sites are only apart around 20 km, they showed a very different tendency of MDA8 ozone and the hourly ozone standard violation frequency (HOF, the number of hourly ozone standard violations, hourly ozone \(\geq\) 100 ppb) for three years (Fig. 2). MDA8 ozone in Seoul increased sharply from 2016 to 2017 and then decreased slightly from 2017 to 2018. The HOF increased significantly from 9 to 41 to 46 in three years. Meanwhile, in Incheon, MDA8 ozone showed a decreasing trend and the HOF had also decreased from 21 to 3 to 1. To understand the deriving factors for the different tendencies in the nearby urban sites, we further analyzed meteorological factors, the abundance of precursors, VOCs to NOx ratio by means of OHR, and speciated VOCs contribution to ozone formation using MIR in the following sections.

#### 3.2 Meteorological Factors

Meteorological factors of the whole period, ozone violation hours (\(\geq\) 100 ppb), and others (< 100 ppb) are compared. Fig. 3 and Table S1 summarize temperature, relative humidity (RH), solar radiation, and wind speed averaged over each period each year. The whole period averages showed insignificant differences between the two sites: temperature \(\leq\) 2.1°C, RH \(\leq\) 7.9%, solar radiation \(\leq\) 0.09 MJ m\(^{-2}\), and wind speed \(\leq\) 0.5 m s\(^{-1}\). Comparing the meteorological factors between ozone violation hours and others, the violation hours generally showed ozone formation favorable conditions.

Fig. 4 shows the wind roses and pollution roses for each site. We see that ozone is higher when the wind blows from the west side of the SMA. Incheon had a similar distribution of winds over the three years, and Seoul had a slight increase in west-northwest winds fraction in 2018, but overall, easterly winds accounted for about 20% of the winds in both regions. However, when looking only at the winds when ozone exceeds 100 ppb, there were no easterly winds, and overwhelmingly westerly and west-northwesterly winds. This suggests ozone or precursors may have come from the west. Meanwhile, calm hours (wind speed < 0.5 m s\(^{-1}\)) when \(O_3\) > 100 ppb were only about 2.3% in Seoul and 7.0% in Incheon, suggesting a relatively small contribution from local sources.

Fig. 2. MDA8 and high ozone frequency (hourly ozone exceeding 100 ppb) during warm season (May–September) daytime (9:00–18:00) from 2016 to 2018 in Seoul (EP) and Incheon.
Fig. 3. Box plot of meteorological conditions ((a) temperature, (b) relative humidity, (c) solar radiation), and (d) NO$_2$ mixing ratios for three years in Incheon and Seoul. The lower and upper boundary of the box are 25th and 75th percentile, a line within the box marks the median, and red dashed lines are for average. Whiskers are 10th and 90th percentiles and black dots are 5th and 95th percentiles.

3.3 Comparison of Formaldehyde Surface Observations with Satellite Data and Previous Studies

In the absence of additional formaldehyde surface observations, we assessed the reliability of our surface observation of formaldehyde concentration via comparison with satellite observations of formaldehyde column density although the latter has more uncertainty. We selected the surface observation sampled during 12:00–15:00 to compare with the OMPS satellite observations which has overpass time of 13:30 local time. This is the first-time comparison of formaldehyde surface observations from NIER with satellite observations. Fig. 5 shows the temporal variations of monthly mean formaldehyde during the study period from the two observation sets. They are well correlated and satellite observations are included within the margin of one standard deviation of surface observations. Therefore, we found our surface observations of formaldehyde are reliable for representing spatial and temporal variations on a monthly basis. Some of the observed differences in the monthly mean variability likely resulted from the accuracy of model profiles used in the OMPS-NPP air mass factor (AMF), which were determined using GEOS-Chem 2018 monthly climatologies at 0.5° × 0.5° resolution (Nowlan et al., 2023). This comparison could be elaborated by applying daily and/or higher-resolution model simulations of the vertical profiles of formaldehyde to the satellite observations (Zhu et al., 2017).

In order to examine the feasibility of analyzing GI’s formaldehyde surface observation with other species measured at EP, in addition to the correlation of surface observation of O$_3$ from the two
sites (Fig. S1), the correlation between formaldehyde from GJ and EP was calculated from the satellite observation (Fig. S3). We found a good correlation (slope = 0.97, correlation coefficient = 0.9358), so it is reasonable to analyze the formaldehyde surface observation of GJ together with other species measured at EP in this study. Site-specific local characteristics can be important for finer-scale temporal variation such as diurnal profiles owing to the short lifetime of formaldehyde, but not critical for monthly variation (De Smedt et al., 2015).
Table S1 lists the ground observation of formaldehyde concentrations reported in previous studies by season. In the 2000s, the highest concentrations were reported in China, > 30 ppb in Shanghai (Huang et al., 2008) and > 15 ppb in Beijing (Pang and Mu, 2006), but since the 2010s, they have decreased significantly to < 10 ppb in both Shanghai and Beijing due to strict control (Ho et al., 2015; Qian et al., 2019). The formaldehyde concentrations in measured Seoul in this study were generally similar to those in Beijing in the 2000s (Pang and Mu, 2006). Concentrations in Incheon were 2–3 ppb lower than in Seoul, but higher than those in Beijing (Qian et al., 2019), Shenzhen (Wang et al., 2017), Guangzhou or Shanghai (Ho et al., 2015). Seasonally, both Seoul and Incheon had higher concentrations in summer compared to spring and fall, implying a major contribution from secondary formaldehyde (Qian et al., 2019).

3.4 Ozone Production Regime Determined by Means of OHR

VOCs/NOx ratio is often used for policy-making purposes. Indeed, Seoul has been found to be a NOx-saturated condition based on VOCs/NOx ratio of 4 and 15 based on Dodge (1977) (e.g., Kim et al., 2018). However, we should be careful in using the ratio because the result of Dodge (1977) is based on a chamber study and used only the sum of propylene, n-butane, and aldehydes among VOCs. Here, we used \( \vartheta \) as a metric to determine the ozone production regime (Heald et al., 2020; Kirchner et al., 2001).

Fig. 6 shows the \( \vartheta \) (= OHNOx/OHROC) calculated with and without carbonyl compounds. OHRNOx, OHRROC with and without carbonyl, and their ratios are provided in Table 2. In Seoul, \( \vartheta \) values exceeded 0.2 indicating a NOx-saturated regime but with decreasing trends. OHRNOx was decreasing owing to NOx reduction policies applied in the SMA (KMA, 2013), and OHRROC remained high for VOCs without regulations. OHRROC in Incheon was similar to that of Seoul but OHRROC was larger than that of Seoul, resulting in Incheon being almost in the transition regime (\( \vartheta \approx 0.2 \)). In the NOx-saturated regime, the reduction of NOx can lead to an increase in ozone, and in the VOC-saturated regime, the reduction of NOx directly leads to the reduction of ozone, but in the transition regime, neither of them is dominant enough, so the chemical reaction changes of NOx and VOC are very sensitive. Therefore, in an environment where NOx is steadily decreasing, such as in SMA, it is important to understand the composition of VOCs and their speciated contribution to ozone production to set the reduction target properly.

Due to COVID-19, South Korea was an anomaly from 2020 to 2022, so starting in 2023, we will again be able to interpret air pollution data as a continuation of 2018. However, judging the ozone production regime without including carbonyls can lead to the misconception that we still need active NOx reduction measures. Fig. 7 shows the speciated OHRROC in both sites. We found an important role of carbonyls in determining the ozone production regime, accounting for 23% in Seoul and 11% in Incheon of OHRROC on a 3-year average (Fig. 6). In addition to carbonyls, the
Table 2. Annual OH reactivities (OHR) and their ratios in Seoul and Incheon. ϑ > 0.2: NOx saturated regime, ϑ < 0.01: VOC saturated regime (Details in text).

<table>
<thead>
<tr>
<th>site</th>
<th>OHR (unit: s⁻¹)</th>
<th>2016</th>
<th>2017</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seoul</td>
<td>(a) OHRNOx</td>
<td>12.39</td>
<td>8.91</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>(b) OHRROC with Carbonyl</td>
<td>29.33</td>
<td>34.53</td>
<td>27.74</td>
</tr>
<tr>
<td></td>
<td>(c) OHRROC without Carbonyl</td>
<td>23.39</td>
<td>31.02</td>
<td>24.09</td>
</tr>
<tr>
<td></td>
<td>ϑ_w_carbonyl = (a)/(b)</td>
<td>0.47</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>ϑ_wo_carbonyl = (a)/(c)</td>
<td>0.61</td>
<td>0.32</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Number of data</td>
<td>289</td>
<td>213</td>
<td>184</td>
</tr>
<tr>
<td>Incheon</td>
<td>(a) OHRNOx</td>
<td>9.18</td>
<td>9.20</td>
<td>8.02</td>
</tr>
<tr>
<td></td>
<td>(b) OHRROC with Carbonyl</td>
<td>37.01</td>
<td>53.82</td>
<td>43.16</td>
</tr>
<tr>
<td></td>
<td>(c) OHRROC without Carbonyl</td>
<td>32.00</td>
<td>50.65</td>
<td>40.66</td>
</tr>
<tr>
<td></td>
<td>ϑ_w_carbonyl = (a)/(b)</td>
<td>0.27</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>ϑ_wo_carbonyl = (a)/(c)</td>
<td>0.32</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Number of data</td>
<td>281</td>
<td>194</td>
<td>255</td>
</tr>
</tbody>
</table>

Fig. 7. Speciated OHRROC in Seoul and Incheon (carbonyl compounds are marked with * in legend).

largest contributors were m,p-xylene (10%), toluene (8%), and styrene (5%) in Incheon and isoprene (8%), m,p-xylene (7%), and toluene (7%) in Seoul. Xylene, toluene, and styrene come from anthropogenic sources such as the use of petroleum, gasoline, solvent, and plastics (Chen et al., 2006; McDonald et al., 2018), but isoprene is emitted from natural sources, indicating the importance of natural sources in Seoul’s atmosphere.

3.5 Speciated Ozone Formation Potential of VOCs and Carbonyl Compounds

Fig. 8 shows the concentration and OFP of each VOC in each year in Seoul and Incheon. Three-year average OFP (carbonyl compounds fraction) was 171 ppb (61%) in Seoul and 200 ppb (41%) in Incheon (graphical abstract). In 2016, the order of total OFP and VOC abundancies was similar in the two sites. However, in 2017, total OFP decreased by 6% in Seoul and increased by 27% in Incheon resulting in about 42% higher OFP than in Seoul. Then in 2018, the total OFP decreased by 24% in Seoul and 35% in Incheon, but it was still 20% higher in Incheon than in Seoul.

Formaldehyde accounted for the largest OFP among VOCs in both sites in all years. Formaldehyde was also the most abundant species in Seoul in all years and in Incheon in 2016. Toluene and n-butane were the most abundant species in Incheon in 2017 and 2018, respectively. Previously, toluene has been found to be the most abundant VOC in Seoul when carbonyl compounds were not considered and is a major management target for ozone reduction (Shin et al., 2013b; Simpson et al., 2020). Our result showed that formaldehyde had a higher mixing ratio and larger OFP than toluene in Seoul. In Incheon, for the mixing ratio, formaldehyde, toluene, and n-butane were the highest each year from 2016 to 2018, but for the OFP, it was the largest for formaldehyde in all three years.
Fig. 8. Annual mean daytime (9:00–18:00) mixing ratio of measured VOCs and calculated daytime ozone formation potential (OFP) from May to September in Seoul and Incheon from 2016 to 2018. (Formaldehyde*, Acetaldehyde*, and Acetone* are measured in Gwangjin, and other VOCs are measured in Eunpyeong.)
Formaldehyde showed the highest OFP followed by toluene in an urban site in South China (Wang et al., 2017). However, in a suburban site in North India, where automobiles are the predominant source of VOC emissions, the OFP of toluene was greater than that of formaldehyde (Kumari et al., 2021). According to the National Air Emission Inventory and Research Center (www.air.go.kr), solvent use (accounting for > 81%) is the largest emission source category of VOCs in Seoul, while solvent use (48%) and industry (28%) are the largest source categories in Incheon (Fig. S4).

4 SUMMARY AND CONCLUSIONS

In this study, we identified the opposite tendencies in national 1-hour ozone standard violation frequencies from two sites in SMA, Seoul and Incheon, from 2016 to 2018 and investigated factors deriving the difference. In the 2016–2018 period examined in this study, ozone inflow from the west and its dilution by locally emitted NOx, rather than the local formation of O3, appears to have been the main factor determining ozone concentrations in the SMA, consistent with the results of previous studies (Colombi et al., 2022; Lee and Park, 2022).

However, an essential finding of this multi-year study is that Seoul and Incheon are changing toward the transition regime in ozone production with a large contribution of carbonyl compounds. Thus, the question will be how to balance NOx and VOC concentrations to minimize ozone production, and the contribution of VOCs to ozone formation needs to be closely understood. We found a significant fraction of carbonyl compounds, accounting for 51% and 37% of the total VOCs in Seoul and Incheon, respectively. The carbonyl compounds contributions to OHR and OFP are 23% and 61% in Seoul, and 11% and 41% in Incheon, on a three-year average. Among the carbonyl compounds, formaldehyde showed the highest OFP in both sites during the three years.

In the previous studies that did not consider aldehyde compounds, it has been found that toluene was the most responsible for ozone air quality in Seoul (Shin et al., 2013a). Our analysis using MIR suggested 4 times and 2 times higher OFP of formaldehyde than toluene in Seoul and Incheon, respectively. Currently, as much effort is being given to reducing NOx emissions in SMA (KME, 2021), and the contribution of VOCs to ozone will be more important as the ozone formation regime is expected to change to a transition regime in the coming years. Because of its widespread presence and its role in O3 and radical photochemistry (Lei et al., 2009), formaldehyde has to be continuously observed. Our study used a combination of GC-FID and DNPH cartridge methods in formaldehyde measurement which is easy to maintain for the sake of monitoring but has a 3-hr time resolution. However, formaldehyde's lifetime is 2 hours or less (Anderson et al., 2017; Jones et al., 2009; Vigouroux et al., 2009). For a better understanding and control of ozone in SMA, it is desirable to observe formaldehyde with finer time resolution at the ozone measurement stations collocated with other VOCs. This will also help clarify the formaldehyde's primary and secondary sources in SMA.

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SUPPLEMENTARY MATERIAL

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