Unexplored VOC emitted from petrochemical facilities: implications for ozone production and atmospheric chemistry

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29 Abstract

30 A compound was observed using airborne PTR-TOF-MS measurements in the emission plumes

31 from Daesan petrochemical facility in South Korea. The compound was detected at m/z 43.018 on 32 the PTR-TOF-MS and was tentatively identified as Ketene, a rarely measured reactive VOC. 33 Estimated Ketene mixing ratios as high as ~ 50 ppb were observed in the emission plumes. 34 Emission rates of ketene from the facility were estimated using a horizontal advective flux approach and ranged from 84 - 316 kg h⁻¹. These emission rates were compared to the emission 35 36 rates of major known VOCs such as benzene, toluene, and acetaldehyde. Significant correlations 37 $(r^2 > 0.7)$ of ketene with methanol, acetaldehyde, benzene, and toluene were observed for the peak 38 emissions, indicating commonality of emission sources. The calculated average ketene OH 39 reactivity for the emission plumes over Daesan ranged from 3.33 - 7.75 s⁻¹, indicating the 40 importance of the quantification of ketene to address missing OH reactivity in the polluted 41 environment. The calculated average O_3 production potential for ketene ranged from 2.98 - 6.91ppb h^{-1} . Our study suggests that ketene, or any possible VOC species detected at m/z 43.018, has 42 43 the potential to significantly influence local photochemistry and therefore, further studies focusing 44 on the photooxidation and atmospheric fate of ketene through chamber studies is required to

45 improve our current understanding of VOC OH reactivity and hence, tropospheric O₃ production.

46 **1. Introduction**

47 Reactive volatile organic compounds (VOCs) can have atmospheric lifetimes ranging from 48 minutes to days (Atkinson, 2000) and have significant influence on regional air quality as they 49 participate in atmospheric chemical reactions that leads to the formation of secondary pollutants 50 such as tropospheric ozone (O_3) and secondary organic aerosol (SOA). Both tropospheric O_3 and 51 SOA are important from the standpoint of air quality and human health and have impact on the 52 radiative forcing of the atmosphere (IPCC, 2013). In addition, through chemical reactions with the 53 hydroxyl radicals (major oxidant of the atmosphere; Lelieveld et al. (2004)), photodissociation and 54 radical recycling reactions, VOCs strongly influence the HO_x (OH, HO₂) radical budget that 55 controls the removal rates of gaseous pollutants from the atmosphere, including most greenhouse 56 gases (such as CH₄).

57 Ketene (ethenone; CAS: 674-82-8; H₂C=C=O) is a highly reactive oxygenated VOC. Recent 58 studies have revealed that gaseous ketene has very high pulmonary toxicity and can be lethal at 59 high concentrations (Wu and O'Shea, 2020). Ketene is formed due to pyrolysis reactions of 60 furfural derivatives and furans emitted during thermal cracking of cellulose and lignin in biomass material (Kahan et al., 2013). Pyrolysis of acetic anhydride is also reported to be a potential source 61 62 of ketene in the atmosphere (Atkinson et al., 2016). Ozonolysis of propene and oxidation of 63 heterocyclic oxepin (benzene oxide) also produce ketene in the atmosphere (Klotz et al., 64 1997;McNelis et al., 1975). Due to the presence of both double bond and carbonyl functional 65 groups, ketene is highly reactive and can play a significant role in ambient OH reactivity and hence

OH recycling processes (Lelieveld et al., 2016). Kahan et al. (2013) has demonstrated that 66 67 hydration reaction of ketene can form acetic acid under ambient conditions. Therefore, ketene has 68 the potential to explain acetic acid chemistry in the troposphere, notably near the biomass burning plumes (Akagi et al., 2012; Yokelson et al., 2009). A recent theoretical study proposed that 69 70 hydrolysis of ketene produces acetic acid at a much faster rate in the atmosphere in presence of 71 formic acid (Louie et al., 2015). This mechanism pathway can facilitate hydrolysis of ketene if it 72 is adsorbed into the interface of SOA, and therefore can contribute to rapid growth of aerosols 73 even in the absence of a proper aqueous environment. A quantum chemical study recently showed 74 that ammonolysis (addition of NH₃) of ketene has the potential to produce acetamide (CH₃CONH₂) 75 in the troposphere (Sarkar et al., 2018). Photooxidation of this acetamide can produce isocyanic 76 acid (HNCO) that has potential health impacts such as cataracts, cardiovascular diseases, and 77 rheumatoid arthritis as it undergoes protein carbamylation (Wang et al., 2007;Roberts et al., 78 2014;Sarkar et al., 2016).

79 In this study, we present results from an aircraft measurement campaign conducted in the summer

80 (May-June) and fall (October) of 2019 that shows that a compound emitted from a petrochemical

81 facility in South Korea, was detected at m/z 43.018 by a high sensitivity proton transfer reaction

82 time-of-flight mass spectrometry (PTR-TOF-MS) technique and tentatively identified as ketene.

83 Emission rate estimation of ketene using a horizontal advective flux approach adapted from the 84 top-down emission rate retrieval algorithm (TERRA) (Gordon et al., 2015) with in-situ chemical

85 and meteorological observations is presented. Finally, an estimation of the OH reactivity and

tropospheric O_3 production potential of ketene in the emission plumes is provided and their

87 importance is discussed.

88 **2. Methods**

89 **2.1 Aircraft campaign**

90 Airborne VOC measurements were carried out during seven research flights of typically 3-4 hour 91 duration, conducted in the summer (May-June) and fall (October) of 2019, to characterize 92 emissions from large industrial facilities (coal power plants, steel mills and petrochemical facilities) 93 in the Taean Peninsula, located approximately 50 km south of Seoul metropolitan. A PTR-TOF-94 MS (model 8000; Ionicon Analytic GmbH, Innsbruck, Austria) was deployed on the Hanseo 95 University research aircraft (Beechcraft 1900D, HL 5238) for VOC measurements along with a 96 fast-meteorological sensor (AIMMS 30; Aventech Research Inc.) that is capable of quantifying 97 aviation such as global positioning information, heading, angle of attack and meteorological data 98 such as water vapor, temperature, pressure, three-dimensional wind field at 10 Hz resolution. To 99 capture real time emission activity, the research aircraft encircled individual industrial facilities at 100 a flight altitude of 300-1000 m above ground level. Table 1 provides details of the research flights 101 with VOC measurements during summer and fall aircraft campaigns while Figure 1 shows 102 locations of the industrial facilities and research flight tracks.

103 **2.2 VOC measurements**

104 VOC measurements were performed over major point and area sources (Daesan petrochemical 105 facility, Dangjin and Boryoung thermal power plants, Hyundai steel mills and Taean coal power 106 plants) using a high-sensitivity PTR-TOF-MS that enables high mass resolution with a detection 107 limit of low ppb to ppt using H₃O⁺ as reagent ion (Lindinger et al., 1998; Jordan et al., 2009; Sarkar 108 et al., 2016;Sarkar et al., 2020). The PTR-TOF-MS was operated over the mass range of 21-210 109 amu at a drift tube pressure of 2.2 mbar and temperature of 60° C (E/N ~ 136 Td) that enabled 110 collection of VOC data at 1 Hz resolution. Ambient air was sampled continuously through a Teflon 111 inlet line (OD = 3/8''; length = 3 m) at an inlet flow rate of 100 sccm. To avoid any condensation 112 effect, inlet line was well insulated and heated to 40°C. Instrumental backgrounds were performed 113 using ambient air through a VOC scrubber catalyst heated to 350°C (GCU-s 0703, Ionimed 114 Analytik GmbH, Innsbruck, Austria).

115 The mixing ratio calculations for methanol, acetaldehyde, benzene and toluene reported in this 116 study were done by using the sensitivity factors (in ncps ppb⁻¹) obtained from the PTR-TOF-MS 117 calibrations performed using a gravimetric mixture of a 14-component VOC gas standard 118 ((Ionimed Analytik GmbH, Austria at ~ 1 ppm; stated accuracy better than 6% and NIST traceable) 119 containing methanol, acetonitrile, acetaldehyde, ethanol, acrolein, acetone, isoprene, methyl vinyl 120 ketone, methyl ethyl ketone, benzene, toluene, o-xylene, chlorobenzene, α-pinene and 1,2-121 dichlorobenzene. Calibrations were performed in the range of 2-10 ppb. In order to establish the 122 instrumental background, VOC-free zero air was generated by passing the ambient air through a 123 catalytic converter (stainless steel tube filled with platinum-coated glass wool) heated at 350°C. 124 The measured ion signals were normalized to the primary ion (H_3O^+ , m/z = 19) as follows (Sarkar 125 et al., 2016;Sarkar et al., 2020):

$$ncps = \frac{I(RH^{+}) \times 10^{6}}{I(H_{3}O^{+})} \times \frac{2}{P_{drift}} \times \frac{T_{drift}}{298.15} \qquad \dots (1)$$

127 The VOC sensitivities did not show any significant change during the calibrations performed as 128 the instrumental operating conditions remained constant, which is in agreement to several previous 129 studies (de Gouw and Warneke, 2007). Table S1 of the supplement lists the sensitivity factors for 130 methanol, acetaldehyde, benzene and toluene and their estimated limit of detection (LOD), 131 calculated as the 2σ value while measuring VOC free zero air at 1 Hz resolution (Sarkar et al., 132 2016). VOCs for which we do not have any sensitivity factors from the calibrations (e. g. ketene), 133 concentrations were estimated based on the reaction rate constants as described by de Gouw and Warneke (2007). A proton transfer reaction rate coefficient of 2.21×10^{-9} cm³ s⁻¹ was used (Zhao 134 135 and Zhang, 2004) to calculate ketene concentrations. The estimated limit-of-detection (LOD) for 136 ketene was 0.58 ppb. Data acquisition and analysis of the PTR-TOF raw mass spectra was 137 accomplished using TofDaq (version 1.89; Tofwerk AG, Switzerland) and PTR-MS-viewer 138 (version 3.2; Ionicon Analytic GmbH, Innsbruck, Austria) softwares, respectively.

3. Results and Discussions

140 **3.1 Detection of ketene using PTR-TOF-MS**

141 For the identification of VOCs in the raw mass spectra, we followed the protocol described by 142 Sarkar et al. (2016) and attributed the ion peak detected at m/z 43.018 in the mass scan spectra to 143 monoisotopic mass of protonated ketene. Absence of any competing shoulder ion peaks between 42.968-43.068 amu (mass width bin of 0.05 amu) indicated no contribution from other ions in this 144 145 mass window as shown in Figure S1 of the supplement. The major advantage of using a PTR-146 TOF-MS over a conventional PTR-Q-MS (with a quadrupole mass analyzer; Sarkar et al. (2013)) 147 for VOC measurements is the ability of PTR-TOF-MS to separate the isobaric species such as 148 ketene (measured at m/z 43.018) and propene (measured at m/z 43.054) based on their 149 monoisotopic masses, allowing us to characterize more VOC species and thus minimize interfering 150 compounds. With the conventional PTR-Q-MS, both ketene and propene appear at a nominal mass 151 of m/z 43 and therefore, individual contribution of propene and ketene at m/z 43 remains unknown. 152 PTR-TOF-MS overcomes this limitation of PTR-O-MS due to its high sensitivity and a mass 153 resolution of m/ Δ m > 4000, enabling separate detection of ketene (at m/z 43.018) and propene 154 (m/z 43.054). Detection of propene at m/z 43.054 using a PTR-TOF-MS is well established and 155 have been reported in several previous studies (Stockwell et al., 2015;Sarkar et al., 2016;Koss et 156 al., 2018). On the other hand, Ketene has been quantified only recently at m/z 43.018 using PTR-157 TOF-MS in the ambient air (Jordan et al., 2009) and in laboratory biomass smoke (Stockwell et 158 al., 2015). Therefore, propene does not interfere in the detection of ketene using PTR-TOF-MS as 159 they show separate peaks in the raw mass spectra (Figure S2 of the supplement). Fragmentation 160 of propanol also results in propene which is detected at m/z 43.054 by PTR-TOF-MS and therefore, propanol fragmentation does not interfere in the detection of ketene at m/z 43.018. Figure S3 of 161 the supplement shows the timeseries plot of the corrected ketene measured at m/z = 43.018 (in red) 162 163 and propene measured at m/z = 43.054 (in blue) during the research flight conducted on 29 May morning. It can be seen from the timeseries that we detected propene as well in the emission plumes 164 165 from the petrochemical industries. A list of all the VOCs detected in the emission plumes from 166 petrochemical industries and other industrial facilities during our campaigns will be provided in a 167 companion paper (in preparation).

168 Although PTR-TOF-MS signal at m/z 43.018 could potentially originate from several other VOC 169 species (e. g. acetic acid, glycolaldehyde, vinyl acetate etc.) due to the fragmentation process, our 170 results suggest that ketene is the most probable species detected at this mass during this study. 171 Accurate quantification of ketene with PTR-MS technique depends on the fragmentation of acetic 172 acid (CH₃COOH) and glycolaldehyde (C₂H₄O₂) (Karl et al., 2007), parent ion of which is 173 measured at m/z 61.027 by PTR-TOF-MS (Stockwell et al., 2015; Sarkar et al., 2016). It is not 174 possible to differentiate structural isomers acetic acid and glycolaldehyde using PTR-TOF-MS, 175 however, ~ 82% of acetic acid is reported to contribute to the m/z 61.027 signal (Karl et al., 2007). 176 Fragmentation of this ion can significantly contribute to ketene signal (m/z = 43.018) in the mass

spectra. During our study, the measured ratio between m/z 61.027 and 43.018 outside of the peak

- emission cases (Figure 2) was ~ 0.9, which is consistent with the ratio reported in previous studies
- 179 at a similar E/N ratio (Hartungen et al., 2004;Haase et al., 2012). This indicates that the
- 180 fragmentation of acetic acid and glycolaldehyde results in about half at m/z 61.027 and the
- 181 remaining half at m/z 43.018, which is an interference for ketene signal and was subtracted to
- 182 obtain the corrected ketene concentrations. Henceforth, we refer to the m/z 43.018 signal, corrected
- 183 for the contribution of acetic acid and glycolaldehyde fragments, as ketene in this manuscript.
- 184 Fragmentation of vinyl acetate (detected at m/z 87.044) could also potentially contribute to the 185 signal at m/z 43.018. However, during our airborne measurements, m/z 87.044 did not show any 186 high peaks that we observed in m/z 43.018 (attributed to ketene). In addition, no significant 187 correlations were observed between m/z 43.018 and m/z 87.044 when data corresponding to the 188 plume episodes were utilized. The signal-to-noise (S/N) ratio for m43.018 and m87.044 were 6 189 ppt and 2 ppt, respectively which indicates that the instrument sensitivity was good enough to 190 observe the linearity between m43.018 and m87.044. This indicates that high peaks of m/z 43.018 191 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different 192 source. Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-193 butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are 194 reported to be emitted from incomplete combustion/biomass burning sources. We have carried out 195 laboratory experiments with these two VOC standards and found that similar to vinyl acetate, these 196 two VOCs were unlikely to be contributing to the m/z 43.018 peaks observed during our airborne 197 measurements over Daesan. Ketene has a proton affinity of 196 kCal/mol which is much higher 198 than that of water (166 kCal/mol) and therefore, it is possible to detect protonated ketene using 199 PTR-TOF-MS. The direct protonation of ketene can result in three different structural 200 conformations and the most stable structure of protonated ketene is the acylium ion (Vogt et al., 201 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005) which is detected at m/z 202 43.018 using PTR-TOF-MS. Therefore, even we have detected the same acylium ion (at m/z43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl 203 204 acetate/methyl acrylate/2,3-butanedione, our results suggest that the origin of the acylium ion 205 detected during our field campaign is the protonation of directly emitted ketene and not the 206 fragmentation of vinyl acetate.
- 207 Figures 2a and 2b show timeseries plots for the mixing ratios of acetic acid and glycolaldehyde 208 parent ion (m/z = 61.027; in green), ketene fragment (m/z = 43.018; in brown) and the corrected 209 ketene (in red) during research flights conducted on 29 May morning and 1 June afternoon. It can 210 be seen from Figure 2a that there were several high peaks of ketene over the Daesan petrochemical 211 facility on 29 May. Such high peaks of ketene were observed over Daesan during all flights 212 conducted in the summer and fall (Figures 2b and S4 of the supplement). These high ketene peaks 213 are entirely absent in the timeseries of m/z 61.027, indicating that acetic acid and glycolaldehyde 214 fragmentation made a relatively small contribution to the signal detected in the emission plumes 215 over Daesan. Some peaks were also observed for both m/z 61.027 and m/z 43.018 over Dangjin

- 216 coal power plants and Hyundai steel mills during the flights conducted on 29 May and 23 October
- 217 (Figures 2a and S4 of the supplement). However, in most cases, these peaks of m/z 43.018
- 218 originated from the fragmentation of m/z 61.027, and so they do not contribute to the corrected
- 219 ketene signals. This further demonstrates that ketene has fresh emission sources in the plumes over
- 220 Daesan petrochemical facility. Since the measured ketene outside the plume was always < 2 ppb
- 221 (Figures 2 and S4 of the supplement), contribution from photochemically produced ketene would
- 222 be negligible, further indicating direct emission of ketene from the facility.
- 223 VOC correlation analyses were performed for the peak values to identify potential emission sources for ketene at Daesan. Ketene showed strong correlations ($r^2 > 0.7$) with acetaldehyde, 224 225 methanol, benzene, and toluene, indicating commonality of emission sources. Figure S5 represents 226 example correlation plots between these VOCs during 28 October afternoon flight. Many of these
- 227
- VOCs are emitted during high temperature production processes such as thermal cracking of
- 228 ethylene and production of polypropylene in the petrochemical industries (Cetin et al., 2003;Chen
- 229 et al., 2014; Mo et al., 2015). Daesan petrochemical facility is a major manufacturer of heat resistant
- 230 polypropylene in South Korea and therefore, ketene could potentially be produced during these
- 231 high temperature production processes. However, future studies focusing on VOC measurements
- 232 in the stacks and analysis using source apportionment models (e.g. USEPA-PMF; Sarkar et al.
- 233 (2017)) will improve our understanding of ketene emissions and chemistry at Daesan.

234 3.2 Estimation of ketene emission rate using a horizontal advective flux approach

235 Emission rates (ERs) of ketene and accompanying VOCs were estimated by integrating the 236 horizontal advective flux around Daesan petrochemical facility. A two-dimensional cylindrical 237 screen is created encompassing each facility during each flight. The mixing ratio flux through this 238 screen is then used to determine the emission rate coming from the interior of the screen. To create 239 the screen, a single horizontal path surrounding the facility is determined for flight tracks to 240 represent the horizontal component of the screen. The start of the horizontal path is approximately 241 set as the south-east corner of the ellipse and progresses in a counter-clockwise direction. The 242 horizontal path length (s) is calculated in meters and as a function of longitude (x) and latitude (y). 243 Each measurement point within 100 meters of the determined horizontal path is mapped to the 244 closest point on the horizontal path but retains its altitude (z). This creates a set of points on the 245 cylindrical screen. The measured mixing ratios of each compound, zonal wind (U), meridional 246 wind (V) and air density are interpolated to fill areas on the screen to a resolution of 40×20 meters 247 $(s \times z)$. Interpolation is performed using a radial basis function with weights estimated by linear 248 least squares. The interpolated screens of zonal wind, meridional wind, and air density are used to 249 calculate the air flux $(E_{air,H})$ through the screen as follows:

250
$$E_{air,H} = \iint \rho_{air} U_{\perp} ds dz \qquad \dots (2)$$

Air density (ρ_{air}) is calculated at each flight position from the measured temperature (*T*), pressure (*p*), and percent relative humidity (RH) as described by (Yau and Rogers, 1996):

253
$$\rho_{air} = \frac{p}{RT(1+0.6\chi_{H_20})}, \chi_{H_20} = \frac{A_d\varepsilon}{p} \exp\left(\frac{T_d}{B_d}\right) \qquad ...(3)$$

where $R = 287.1 \text{ J kg}^{-1} \text{ K}^{-1}$; χ_{H_20} is the water vapor mixing ratio; $A_d = 3.41 \times 10^9 \text{ kPa}$; $\varepsilon = 0.622$; B_d = 5420 K and T_d is the dew-point temperature calculated using the August-Roche-Magnus approximation as follows:

257
$$T_d(T, RH) = \frac{\lambda \left(\ln \left(\frac{RH}{100} \right) + \frac{\beta T}{\lambda + T} \right)}{\beta - \left(\ln \left(\frac{RH}{100} \right) + \frac{\beta T}{\lambda + T} \right)} \qquad \dots (4)$$

- 258 where $\lambda = 243.12^{\circ}$ C and $\beta = 17.62$.
- 259 The wind speed normal to the path is calculated as described by Gordon et al. (2015):

260
$$U_{\perp} = \frac{V \frac{ds}{dx} - U \frac{ds}{dy}}{\sqrt{\left(\frac{ds}{dx}\right)^2 + \left(\frac{ds}{dy}\right)^2}} \qquad \dots (5)$$

The mixing ratios of the compounds are interpolated for each point on the screen and combined with the air flux to calculate the emission rate (ER) of the compounds using the following equation:

$$ER = M_R \iint \chi_C \rho_{air} U_{\perp} ds dz \qquad \dots (6)$$

264 where χ_c = mixing ratio of VOCs and M_R = ratio between compound molar mass and the molar 265 mass of air (42.04/28.97 for ketene). The air density (ρ_{air}) from the lowest flight track altitude is approximated with a linear dependence on altitude. U_{\perp} is the normal wind vector (positive 266 267 outwards). Mixing ratios in the areas between the flight track measurements are interpolated using 268 a radial basis function with weights estimated by linear least square approximation. Interpolated 269 screens (resolution 40×20 m; horizontal \times altitude) of U, V wind and air density were then used 270 to retrieve air flux through the screens. This method is adapted from the TERRA approach 271 described by Gordon et al. (2015). The mass-balance approach was used to estimate emissions 272 through the top of the cylinder. Pressure and temperature were assumed to be constant during the 273 measurement timeframe. To determine emissions through the top of the cylinder, the following mass-balance approach was used: 274

$$E_{air,H} + E_{air,V} + E_{air,M} = 0$$
 ... (7)

where, $E_{air,H}$ is the net horizontal air flux, $E_{air,V}$ is the net air flux through the top of the cylinder, and $E_{air,M}$ is the change in air mass within the volume. We considered constant average pressure and temperature for the duration of the observations to assume no change in air mass within the volume. As a result, the air flux through the top of the cylinder can be considered $E_{air,V} = -E_{air,H}$. The average value of the mixing ratio at the top of the cylinder is multiplied by $E_{air,V}$ to retrieve emissions through the top of the cylinder.

282 Figures 3a and 3b depict mixing ratio screens for ketene for the 29 May morning and 28 October 283 afternoon flights. For both flights, highest ketene mixing ratios (χ_{ketene}) were measured near the 284 lowest flight path clearly indicating that surface emission sources caused the bulk of the ketene to be below the flight track. The estimated net ERs (kg h^{-1}) for ketene and accompanying VOCs are 285 shown in Table 2a. The net ER represents emissions only from the facility and excludes the 286 287 contribution of emissions from outside sources that are upwind of the screen. The difference 288 between the estimated net ER and the ER going out of the screen (Table S2 of the supplement) for 289 ketene were < 12% for both flights. For 29 May flight, estimated net ketene ER was similar to that 290 of toluene and ~ 3 times lower than benzene while it was ~ 4 times lower than acetaldehyde. For 291 28 October flight, estimated net ketene ER was ~ 1.3 times lower and ~ 1.5 times higher than 292 benzene and toluene, respectively while it was ~ 2 times lower than acetaldehyde. These results 293 indicate that accurate estimation of ketene emissions from petrochemical facilities could be as 294 important as some of the major VOCs and therefore, including ketene (a rarely quantified VOC) 295 to the emission inventory will be a step forward towards effective VOC mitigation strategies.

296 To address the uncertainty in the extrapolation method below the measurement heights, we have 297 used two different approaches. In the first approach, we considered the nature of emissions from 298 the petrochemical facility being mainly from evaporative sources. As a result, we assumed that the 299 mixing ratios of ketene increases as it approaches the ground. This is observed when we used the 300 radial basis function to extrapolate linearly. To quantify the uncertainty in this extrapolation, we 301 assumed a constant value for heights under the measurement height equal to the mixing ratios at 302 the lowest observed altitude and defined it as a "constant" case. We assumed that the "constant" 303 case represents a lower end estimation due to the nature of the evaporative sources from the facility. 304 Then, we estimated the uncertainty due to ground extrapolation as the percentage change in 305 emission rates calculated from the linear radial basis function and from the "constant" case. The 306 estimated uncertainties were < 20% for most cases. For example, for the 29 May morning flight, 307 the estimated uncertainty was ~ 16% (Figure 4). As expected, this uncertainty is highly dependent 308 on the vertical position of the plume, with uncertainty being higher in cases where the highest 309 mixing ratio observed is at the lowest altitude measured. The second approach is to assess the 310 accuracy of the radial basis function interpolation method, plumes resembling the observed plumes were simulated. The plumes were generated based on a Gaussian distribution of the mixing ratio: 311

312
$$\chi(s,z) = \sum_{i} \exp\left[-\frac{1}{2}\left(\left(\frac{s-s_{o,i}}{\sigma_{s,i}}\right)^2 + \left(\frac{z-z_{o,i}}{\sigma_{z,i}}\right)^2\right)\right] \qquad \dots (8)$$

where, χ is the mixing ratio, $s_{o,i}$ is the horizontal plume center, $z_{o,i}$ is the vertical plume center, 313 314 and i is the plume number. The parameters used for each date are listed in Table S3 of the 315 supplement. The flight path of each date is used to sample the simulated plume on the screen. The 316 simulated Gaussian plume is then reconstructed using the radial basis function interpolation based 317 on the points sampled from the simulated plume. Figure 5 shows the simulated plumes and radial 318 basis function-interpolated plumes for the 29 May and 28 October flights. The root-mean square 319 (RMS) and correlation coefficient (R^2) values were calculated to compare the simulated plume 320 with the radial basis function-interpolated plumes. The calculated RMS and R² values for 29 May were 0.034 and 0.983, respectively. For 28 October, calculated RMS and R² values were 0.018 321 322 and 0.991, respectively.

323 **3.3 OH reactivity and O₃ production potential**

324 The OH reactivity of ketene was calculated according to the following equation (Sinha et al., 2012):

325

Ketene OH reactivity =
$$k_{Ketene+OH}$$
 [Ketene] ... (9)

where $k_{Ketene+OH}$ = first-order rate coefficient for the reaction of ketene with OH radicals and 326 [Ketene] = measured mixing ratio of ketene. The rate coefficient of 3.38×10^{-11} cm³ molecule⁻¹ s⁻¹ 327 ¹ was used for the reaction of ketene with OH (Brown et al., 1989). For the 29 May and 1 June 328 flights (summer campaign), calculated average ketene OH reactivity for the emission plumes over 329 Daesan were 5.42 and 7.75 s⁻¹, respectively. The average OH reactivities during research flights 330 conducted in October (fall campaign) ranged from 3.33 to 7.35 s⁻¹. Table 2b shows the calculated 331 332 average and maximum OH reactivity and O₃ production potential of ketene during seven research flights. Several previous studies have reported 50% or more missing OH reactivities near industrial 333 334 areas (Kim et al., 2011; Ryerson et al., 2003) and showed large uncertainties affecting HO_x budget. 335 Ambient ketene was not quantified in these studies due to absence of PTR-TOF-MS and the 336 attribution of nominal mass of m/z 43 (detected by PTR-QMS) only to propene. With PTR-TOF-MS measurements, it is clear that both propene and ketene can contribute to the nominal mass of 337 m/z 43. While the rate coefficient of propene with OH radical is about 10% lower (3×10^{-11} and 338 3.38×10^{-11} cm³ molecule⁻¹ s⁻¹ for propene (Atkinson et al., 2006) and ketene (Brown et al., 1989), 339 340 respectively at 298 K), their chemical reactions with OH would be different since ketene contains 341 a carbonyl functional group ($H_2C=C=O$) but propene is an alkene ($H_3C-C=CH_2$). Therefore, 342 quantification of ketene will improve our estimation of the missing OH reactivity.

Tropospheric O_3 formation is significantly influenced by VOCs in polluted environments and has strong impacts on air quality (ability to form photochemical smog), climate (contribution to radiative forcing), human health (a pulmonary irritant) and can cause decreased crop yields 346 (Monks et al., 2015;Jerrett et al., 2009). The O_3 production potential of ketene was calculated 347 according to the following equation (Sinha et al., 2012):

348

 O_3 production potential = (Ketene OH reactivity) × [OH] ... (10)

Average OH radical concentration of 6.2×10^6 molecules cm⁻³, derived using a reactive plume 349 model considering NO_x photochemistry (with 255 condensed photochemical reactions) in power-350 plant plumes (Kim et al., 2017), was used for the O₃ production potential calculation. The 351 calculated atmospheric lifetime of ketene using this OH concentration was ~ 1.4 h, indicating that 352 353 the spatial scale for which ketene would be effective in photochemistry could be at least a few km (e. g. ~ 10 km assuming horizontal wind speed of 2 m s⁻¹). For the 29 May and 1 June flights, 354 calculated average O₃ production potential for ketene in the emission plumes over Daesan were 355 4.84 and 6.91 ppb h⁻¹, respectively. For research flights conducted in October (fall campaign), 356 average O₃ production potential ranged from 2.98 to 6.56 ppb h⁻¹ (Table 2b). However, maximum 357 O₃ production potential for ketene at Daesan was 45.70 ppb h⁻¹ on 1 June. Due to its fast reaction 358 rate with OH, ketene can contribute significantly to VOC OH reactivity, and hence O₃ production, 359 360 and a quantitative understanding of ketene is vital for tropospheric O₃ mitigation efforts. Therefore, 361 it is important to carry out further field and chamber studies to investigate the implications of 362 ketene photo-oxidation on HO_x chemistry and the atmospheric fate of ketene.

363 **4. Conclusions**

364 Ketene, a rare and highly reactive VOC, was tentatively identified and quantified as the major 365 species at m/z 43.018 using PTR-TOF-MS technique in the emission plumes of Daesan 366 petrochemical facility in South Korea during aircraft measurement campaigns conducted in the 367 summer (May-June) and Fall (October) of 2019. Ketene mixing ratios of as high as ~ 50 ppb were 368 measured in the emission plumes. Estimated ketene emission rates from the facility using a horizontal advective flux approach ranged from 84-316 kg h⁻¹. Ketene emission rates were 369 370 compared to the estimated emission rates of benzene, toluene, and acetaldehyde. In most cases, 371 ketene emission rates were comparable to toluene. During peak emissions, ketene also showed 372 significant correlations ($r^2 > 0.7$) with acetaldehyde, methanol, benzene, and toluene, indicating 373 emissions of these VOCs occur from common processes. The petrochemical facility at Daesan is 374 the largest producer of heat resistant polypropylene in South Korea and the high temperature 375 production processes of polypropylene could be a potential source of ketene at Daesan. However, 376 future VOC measurement studies focusing on the stack emissions at Daesan in combination with 377 source apportionment models such as USEPA-PMF will provide better insights on ketene 378 emissions and chemistry at Daesan petrochemical facility.

For the emission plumes over Daesan, calculated average OH reactivity for ketene ranged from 380 $3.33-7.75 \text{ s}^{-1}$. This indicates the importance of the quantification of ketene in the polluted 381 environment to address the puzzle of missing OH reactivity. During this study, calculated average 382 ketene O₃ production potential ranged from 2.98-6.91 ppb h⁻¹. Our study suggests that ketene can potentially influence local photochemistry. Therefore, future studies focusing on the photooxidation processes and atmospheric fate of ketene using chamber studies is required to get a better insight of ketene formation in the atmosphere. Such studies will also improve our current understanding of VOC-OH reactivity and hence secondary pollutants formation.

387 Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to

388 ketene, the possibility of the contribution from vinyl acetate and other species cannot be ruled out

389 completely and therefore, further laboratory and field studies focusing on this aspect are needed.

- 390 Since the rate coefficient of vinyl acetate with OH radical is 2.5 \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹
- 391 (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate
- 392 can be ~ 20-25% less than that of ketene. Since ketene as well as vinyl acetate can significantly 393 contribute to the OH reactivity and O_3 production, it is important to explore these new and
- 393 contribute to the OH reactivity and O_3 production, it is important to explore these new and 394 understudied oxygenated VOCs and their impact on secondary pollutants formation.

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407 Data Availability

408 The observational data will be available upon the request to the corresponding authors.

409 Author Contributions

- 410 C. S., A. G., T. L., J. A., S. B. P., and S. K. conceptualized the study; C. S., G. W., A. M., T. P., J.
- 411 B., S. K., J-S. P., D. K., H. K., J. C., B-K. S., and J-H. K. conducted the field measurements; C.S.,
- 412 S. N. and N. J. G. performed laboratory experiments; C. S., G. W. and S. K. analyzed the data; A.
- 413 G., T. L., J. A., S. B. P., and S. K. supervised and administered the project; C. S., G. W., S. K., and
- 414 A. G. wrote the original draft; All authors reviewed and edited the manuscript; All authors have
- 415 given approval to the final version of the manuscript.

416 **Conflict of Interest Disclosure**

417 The authors declare no competing financial interest.

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Table 1. Summary of research flights with VOC measurements during the summer (May-June)and fall (October) aircraft campaigns in South Korea

Date	Flight	Start	End	Facilities	Flight Design	Wind
	No.	Time	Time	Included		Direction
		(LT)	(LT)			
Summer 20.	19:					
29 May	1	09:32	12:36	Daesan, Dangjin,	Circular spirals at	Southwest
				Hyundai	6 altitudes; 300 -	
					1100 m	
1 June	2	13:42	16:13	Boryoung,	Circular spirals at	Wind data
				Daesan, Dangjin,	6 altitudes; 300 -	not available
				Hyundai	1100 m	
Fall 2019:						
23 October	3	13:30	16:45	Boryung, Taean,	Racetrack and	East
				Daesan, Dangjin,	circular spirals at	
				Hyundai	a single altitude ~	
					400 m	
28 October	4	13:38	16:48	Daesan, Hyundai	Racetrack spirals	Southwest
					and crosstrack at 2	
					altitudes; 400 -	
					600 m	
29 October	5	08:14	11:14	Daesan, Hyundai	Racetrack and	West
					circular spirals at	
					2 altitudes; 400 –	
					600 m	
30 October	6	13:32	16:48	Boryung, Taean,	Racetrack and	West
				Daesan, Dangjin,	circular spirals at	
				Hyundai	3 altitudes; 400 -	
21.0 + 1	7	12.22	15.04		1000 m	XX7' 1 1
31 October	/	13:33	15:34	Boryung, Taean,	Racetrack and	Wind data
				Daesan, Dangjin,	circular spirals at	not available
				Hyundai	3 altitudes; 400 -	
					1000 m	

Table 2. a) Net emission rates (kg h ⁻¹) of ketene, benzene, acetaldehyde and toluene over	Daesan
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612	petrochemical facility; b) calculated OH reactivity (s ⁻¹) and O ₃ production potential (ppb h ⁻¹) of
613	ketene during emission plumes measured over Daesan petrochemical facility

	a) Research Flights	Ketene (kg h ⁻¹)	Benzene (kg h ⁻¹)	e Acetaldehyde (kg h ⁻¹)	Toluene (kg h ⁻¹)	
	<u>Summer 2019:</u>	-				
	29 May Morning	312	917	1256	314	
	<u>Fall 2019:</u>					
	23 October Afternoon	286	146	-1	-43	
	28 October Afternoon	316	426	619	210	
	29 October Morning	27	241	430	103	
	30 October Afternoon	84	211	359	102	
	b) Research Flights	OH reactivity	(s ⁻¹)*	O ₃ production poten	tial (ppb h ⁻¹)*	
	<u>Summer 2019:</u>					
	29 May Morning	5.42 (33.76)		4.84 (30.10)		
	1 June Afternoon	7.75 (51.24)		6.91 (45.70)		
	<u>Fall 2019:</u>					
	23 October Afternoon	7.35 (33.33)		6.56 (29.80)		
	28 October Afternoon	5.28 (15.74)		4.71 (14.00)		
	29 October Morning	3.79 (14.77)		3.38 (13.20)		
	30 October Afternoon	3.33 (19.71)		2.98 (17.60)		
	31 October Afternoon	4.56 (8.09)		4.07 (7.22)		
614	*Values in the parentheses rep	presents maximum	n OH reacti	vity and O ₃ production	potential	
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Figure 1. Composite Google Earth images (©Google Earth) showing research flight tracks over the Daesan petrochemical facility, Dangjin and Boryoung thermal power plants, Hyundai steel mills and Taean coal power plants during the airborne study conducted in summer (May-June 2019) and fall (October 2019). The white arrow in each plot represents mean wind direction during the flight. Only those flights are shown for which wind direction measurements were available



641 **Figure 2.** Timeseries profiles for mixing ratios (1 Hz resolution) of acetic acid and glycolaldehyde 642 parent ion (m/z = 61.027), ketene fragment (m/z = 43.018) and corrected ketene (corrected for m/z643 61.027 fragmentation) during a) 29 May morning flight and b) 1 June afternoon flight. The light 644 pink, light green and light blue shaded areas represent the duration for which the flights were flying 645 over Daesan, Dangjin and Hyundai, respectively

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Figure 3. Kriging-interpolated ketene mixing ratios for a) 29 May morning and b) 28 Octoberafternoon flights. Black dots represent the flight path.



Figure 4. Estimation of uncertainty in the emission rates using approach 1 during 29 May morning flight: a) Air flux screen (green = going out of the facility; purple = into the facility); b) Case 1: Linear extrapolation using radial basis function (net emission rate from the facility = 312.36 kg h⁻¹; emission rate going out of the screen = 357.73 kg h⁻¹); c) Case 2: Linear extrapolation using the "constant case" (net emission rate from the facility = 262.44 kg h⁻¹; emission rate going out of the screen = 298.74 kg h⁻¹; exponentials are the same for both the cases; uncertainty ~ 15.5% - 16%)

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Figure 5. a) Simulated plume scenario and b) radial basis function-interpolated plume for May 29
morning flight. c) Simulated plume scenario and d) radial basis function-interpolated plume for
October 28 afternoon flight. Black dots are the flight position measurements of each flight.