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1	Photochemical formation of C ₁ -C ₅ alkyl nitrates in
2	suburban Hong Kong and over South China Sea
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12 ABSTRACT: Alkyl nitrates (RONO₂) are important reservoirs of atmospheric nitrogen, regulating nitrogen cycling and ozone (O₃) formation. In this study, we found that propane and 13 *n*-butane were significantly lower at the offshore site (WSI) in Hong Kong (p < 0.05), whereas C₃-14 C_4 RONO₂ were comparable to the suburban site (TC) (p>0.05). Stronger oxidative capacity at 15 WSI led to more efficient RONO₂ formation. Relative incremental reactivity (RIR) was for the 16 first time used to evaluate RONO₂-precursors relationships. In contrast to consistently volatile 17 organic compounds (VOCs)-limited regime at TC, RONO₂ formation at WSI switched from 18 VOCs-limited regime during O_3 episodes to VOCs and nitrogen oxides (NO_x) co-limited regime 19 20 during non-episodes. Furthermore, unlike the predominant contributions of parent hydrocarbons to C_4 - C_5 RONO₂, the productions of C_1 - C_3 RONO₂ were more sensitive to other VOCs like 21 aromatics and carbonyls, which accounted for ~40-90% of the productions of C_1 - C_3 alkylperoxy 22 23 (RO_2) and alkoxy radicals (RO) at both sites. This resulted from the decomposition of larger RO₂/RO and the change of OH abundance under the photochemistry of other VOCs. This study 24 advanced our understandings on the photochemical formation of RONO₂, particularly the 25 relationships between RONO₂ and their precursors which were not confined to the parent 26 hydrocarbons. 27

28

29 1 Introduction

Alkyl nitrates (RONO₂) comprise a critical fraction of reactive nitrogen (NO_y) in the atmosphere.^{1,2} Most RONO₂ are formed as byproducts in the process of O₃ formation, derived from reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x = NO + NO₂) in the presence of sunlight, thus influencing the tropospheric O₃ formation. They also act as nitrogen reservoir due to their relatively long lifetimes,^{3,4} hence affecting air pollutants profile in remote regions. Therefore, they have significant impact on local, regional and global atmospheric chemistry.

 C_1 - C_5 RONO₂ generally dwell in gas phase and involve in homogeneous reactions in the 37 atmosphere. Previous studies on RONO₂ spanned from the oceans to the continents and from 38 rural areas to urban regions. The mixing ratios of individual RONO₂ vary from several to 39 hundreds pptv.^{5,6,7,8,9} In continental air plumes, such as in rural Ontario,¹⁰ in rural and urban 40 Karachi⁵ and in urban China, ⁶ C₃-C₄ RONO₂ were generally the most abundant RONO₂ (15-80 41 pptv), due to the combined effect of the abundance of parent hydrocarbons, and the branching 42 ratios and the lifetimes of RONO₂.^{11,12} The cruise studies over the equatorial Pacific Ocean 43 revealed higher concentrations of C₁-C₃ RONO₂.¹³ For example, C₁ RONO₂ observed over the 44 Pacific Ocean could reach 50 pptv.¹⁴ Under the influence of oceanic emissions, C₁ RONO₂ also 45 ranked the first (5-20 pptv) among all the RONO₂ in coastal England.⁸ In Hong Kong, C₃-C₄ 46 RONO₂ generally dominated, but high mixing ratio of C_1 RONO₂ was also reported (~20 pptv at 47 a mountainous site and ~15 pptv at a coastal site), likely indicating the characteristics of both 48 continental and marine origins.^{15,16} 49

Similar to O_3 , Observed RONO₂ usually showed a peak at midday, reflecting the dominance of photochemical reactions.^{4,17} Besides, studies have confirmed that RONO₂ are also directly emitted from the oceans, particularly for light (<C₂) RONO₂.^{13,18} Biomass burning is also a source of RONO₂, which are quickly formed through the pathway of "RO + NO₂".^{15,19} The source contributions may vary in different locations and/or under the influence of different origins of air masses.^{16,17}

Text S1 shows the chemical production and destruction of RONO₂. The oxidations of 56 hydrocarbons (Alk) by OH lead to the formation of RO2 and RO, which further react with NO 57 and NO₂, respectively, producing RONO₂.²⁰ Reactions between RO₂ and NO can also result in 58 O₃ formation through another branch reaction.²¹ Generally, with carbon number increasing, the 59 possibility of RONO₂ formation from the reaction of RO₂+NO increases. OH oxidation and 60 photolysis are the major sinks of RONO₂. While photolysis plays a more important role in 61 destruction of C₁-C₃ RONO₂, the larger (\geq C₄) RONO₂ are more degraded through OH initiated 62 oxidation. ^{3,22} Besides, dry deposition is another sink of the airborne RONO₂.¹¹ 63

VOCs and NO_x play roles in RONO₂ formation by acting as the precursors^{23,24} and also regulating the atmospheric oxidative capacity.²⁵ Although a handful of studies investigated the relationship between RONO₂ and their precursors, the effects of VOCs other than the parent hydrocarbons on RONO₂ formation were not well documented. In fact, the possible decomposition of larger molecular hydrocarbons was ever speculated as the sources of RONO₂.^{1,8,26} However, the mechanisms and the extents of other VOCs regulating RONO₂ formation still remain unknown.

Despite increased concerns on the photochemical pollution in Hong Kong and adjacent Pearl
 River Delta (PRD) region, only few studies focused on RONO₂ in this region which put the

4

emphasis on continental areas strongly affected by local emissions and lacked insight into
RONO₂-precursor relationships.^{7,15,16,27} This work was the first attempt to investigate RONO₂
formation over the South China Sea (SCS). Moreover, in-depth analysis was given to the
relationships between RONO₂ and their precursors.

77 2 Methodology

78 **2.1 Data source**

In this study, concurrent field measurements were conducted in suburban Hong Kong (TC) and 79 over SCS (WSI) from 10th Aug. to 21st Nov., 2013. Figure S1 shows the geographical locations 80 of the sampling sites (TC: 22.28°N, 113.94°E; WSI: 22.04°N, 113.93°E). The TC site was 81 82 located in southwestern Hong Kong, surrounded by newly-developed residential town and close to the Hong Kong International Airport (~ 3 km to the northwest). The sampling was carried out 83 on the rooftop of a six-storey building, approximately 20 m above ground level. It has been 84 recognized that the air pollution at TC was attributable to both local emissions and regional 85 transport.²⁸⁻³⁰ For example, an increase of O_3 was often observed in autumn, when dirty air 86 87 masses were brought by dominant northerly winds from PRD region in mainland China to Hong Kong and weather conditions were favorable for secondary pollutants formation.^{31,32} The WSI 88 site was located on a hillside (with a height of 65 m above ground level) on Wan Shan Island 89 (area of $\sim 8.1 \text{ km}^2$) over the SCS. It was $\sim 64 \text{ km}$ southwest of Hong Kong urban center, and ~ 40 90 km southeast of Zhuhai, a rapidly developing city in PRD. Since WSI is nearly free of 91 anthropogenic emissions, the air pollution at this site reflected the interferences of continental air 92 masses from mainland China and Hong Kong on the marine air quality. 93

94 Hourly whole air samples were collected using 2-L stainless steel canisters every two hours from 07:00 to 19:00. In total, 311 whole air samples were collected at the two sites. The samples 95 were then analyzed by Guangzhou Institute of Geochemistry (GIG), Chinese Academy of 96 Sciences, with the quantification of 84 VOCs, including 7 C₁-C₅ RONO₂. Full names and 97 abbreviations of RONO₂ are listed in Table S1. Text S1 described the analytical system and 98 quality control/assurance in details. Briefly, the accuracy and detection limit for the analysis of 99 C₁-C₅ RONO₂ were 2-10% and 0.02 pptv, respectively. In addition, carbonyl samples, online 100 trace gas data and meteorological parameters were all collected during the sampling period, 101 102 which were also described in Text S2.

2.2 Simulation of secondary RONO₂ formation

The PBM-MCM model is a photochemical box model incorporating master chemical 104 mechanism. and has been successfully applied to simulate the photochemistry of O₃ and RONO₂ 105 in the study region.^{15,40} As an observation-based model, field measurement data, *i.e.*, VOCs, NO, 106 NO₂, SO₂, CO, temperature and relative humidity were input to construct the model from 07:00 107 108 to 19:00. CH₄ is the parent hydrocarbon of methyl nitrate (MeONO₂), which however was not analyzed in this study. Since it has a lifetime for years, we here applied the past 10-year average 109 CH₄ mixing ratios in Hong Kong as model input (Table S2). The RONO₂ module in PBM-MCM 110 used in this study was developed by our group, and has been repeatedly testified through RONO₂ 111 simulations in Hong Kong.^{15,27} 112

Since primary emissions and regional transport of RONO₂ are not fully considered in the model, there may be discrepancies between the simulated and observed RONO₂. However, big differences are not expected in view of the dominant contributions of photochemical formation to RONO₂ in Hong Kong.^{15,27} Therefore, the index of agreement (IOA) is used to evaluate the model performance in modelling RONO₂. Equation 1 describes the calculation of IOA,⁴⁰ according to which higher IOA (0<IOA<1) represents better agreement between the simulated (S_i) and observed values (O_i) .

120
$$IOA = 1 - \frac{\sum_{i=1}^{n} (O_i - S_i)^2}{\sum_{i=1}^{n} (|O_i - \bar{O}| + |S_i - \bar{O}|)^2}$$
(Eq. 1)

121 where \overline{O} refers to the mean observed value averaged over *n* samples.

122 2.3 Scenario analysis

The reactions " $RO_2 + NO$ " and " $RO + NO_2$ " are the main formation pathways of RONO₂ 123 considered in PBM-MCM. The pathway contributions to RONO₂ were simulated with the 124 method used by Lyu et al.^{15,27} The contribution of " $RO_2 + NO$ " to RONO₂ was derived from the 125 difference of the simulated RONO₂ between the base run with the two pathways open and the 126 constrained run with "RO2 + NO" closed (Scenario A), and vice versa. Moreover, the 127 contributions of specific species/group of VOC(s) to the secondary RONO₂ formation and 128 related radicals (e.g. RO₂ and RO) concentrations were determined through subtracting the 129 simulated RONO₂ (or radicals) in the constrained runs without the input of the specific 130 species/group of VOC(s) (Scenario B1) from those simulated in the base run. Furthermore, 131 VOCs can directly generate RO₂ and RO radicals (factor 1) or regulate the production of these 132 radicals through changing OH concentration (factor 2). To distinguish these effects, another 133 array of constrained scenarios was designed, in which OH simulated in base run was input to 134 constrain the OH concentration in the constrained runs (Scenario B2). The difference of the 135 simulated RO2 and RO between base run and Scenario B1 reflected the combined effect of 136 factors 1 and 2, while the effect of factor 1 was obtained from the difference between base run 137 and Scenario B2. More information on the scenarios was provided in Text S3 and Table S3. 138

139 **2.4 Relative incremental reactivity**

The RONO₂-precursors relationship can be evaluated using relative incremental reactivity (RIR), which is defined as the change of RONO₂ formation according to the change of mixing ratio of its precursors (NO, NO₂, parent hydrocarbons and other VOCs) during both episodes and non-episodes. The RIR values are calculated using Equation 2:⁴¹

144
$$RIR(X) = \frac{[P_{RONO_2}(X) - P_{RONO_2}(X - \Delta X)]/P_{RONO_2}(X)}{\Delta S(X)/S(X)}$$
(Eq. 2)

where X represents a specific precursor, e.g. NO, NO₂, parent hydrocarbons or other VOCs; S(X) is the observed hourly average mixing ratio of species X (in pptv) at the site; ΔX is the change in the mixing ratio of X caused by a hypothetical change in S(X), $\Delta S(X)$; P_{RONO_2} is the production rate of RONO₂ in unit of pptv/h. In this study, the hourly production was defined as the difference in RONO₂ mixing ratio between two adjacent hours. The change in the mixing ratio of X was assumed to be 10% of the measured data.

151 **3 Results and discussion**

152 **3.1 General characteristics**

Table 1 presents the descriptive statistics of RONO₂, their parent hydrocarbons, total VOCs (TVOCs) and O₃. 2-BuONO₂ and 2-PrONO₂ were the most abundant species at both sites, consistent with previous studies in Hong Kong.^{7,15,16} This feature was associated with the balance between the increased branching ratio for RONO₂ formation and reduced abundances of their parent hydrocarbons in the atmosphere, as well as the decreased lifetime of RONO₂ with the increase of carbon number.^{7,42} Further, the formation possibility (α_1 =0.74) of secondary RO₂ from propane is higher than primary RO₂ (α_1 = 0.26), so was the formation of RONO₂ from the

primary (α_2 =0.02) and secondary C₃ RO₂ (α_2 =0.04). Thus, 2-PrONO₂ was much more abundant 160 than 1-PrONO₂.⁹ We also found that the compositions of RONO₂ at the two sites were similar, 161 both having largest abundance for 2-BuONO₂ (36.7±3.4-37.5±3.5%) followed by 2-PrONO₂ 162 $(22.4\pm2.1-22.9\pm2.8\%)$, and lowest for 1-PrONO₂ $(1.8\pm0.3-2.1\pm0.3\%)$, likely due to the influence 163 164 of the same air masses and/or interactions between the two sites. In addition, there was no significant difference in levels of C₂-C₅ RONO₂ between TC and WSI despite higher propane 165 and *n*-butane at TC, suggesting the different sources/source contributions to RONO₂ and/or 166 167 different production efficiencies of secondary RONO₂. It is noteworthy that ship emission would not be the cause of the comparable C₂-C₅ RONO₂ at the two sites though we observed some 168 ships passing by during the sampling period. In addition, Lyu et al.²⁷ found that the impacts of 169 170 dry deposition on RONO₂ abundances were minor with the deposition velocities of 0.13/HMIX 171 (HMIX: height of mixing layer) for C₁-C₄ RONO₂ in continental area of Hong Kong. Therefore, dry deposition did not play a significant role in redistribution of RONO₂ at TC and WSI. 172

MeONO₂, however, was more abundant at TC. MeONO₂ at both sites were higher than those 173 measured over open seas.^{8,12,43} However, the proportion of MeONO₂ in C₁-C₄ RONO₂ (12.8±0.1-174 175 16.9±0.2%) were much lower than those in oceanic atmosphere (20.6-71.0%), comparable to that in continental air shed (9.9-14.9%) instead.^{6,11} This indicated that $RONO_2$ in the study area, even 176 at the offshore site (WSI), was more influenced by the continental air flow. Therefore, higher 177 TVOCs (35.1 \pm 8.0 ppbv) and NO_x (44.1 \pm 4.14 ppbv), precursors of MeONO₂, at TC than at WSI 178 (TVOC: 16.8 ± 2.9 ppbv; NO_x: 5.32 ± 1.25 ppbv), might partially explain higher MeONO₂ at TC. 179 On the other hand, MeONO₂ in the continental area might also be elevated by emissions from 180 biomass burning. 181

Table 1. Descriptive statistics of RONO₂, parent hydrocarbons, TVOCs (ppbv) and O₃ (ppbv) at

183 TC and WSI (pptv, unless otherwise specified).

Snecies	TC		WSI			
species _	Mean ¹	Min.	Max.	Mean ¹	Min.	Max.
MeONO ₂	17.7±2.71	0.30	84.1	12.5±1.51	1.80	49.4
EtONO ₂ ²	6.81±1.01	0.50	28.6	6.92±0.91	0.30	24.0
2-PrONO ₂ ³	29.9±2.61	7.90	81.4	28.3±2.12	4.60	66.6
1-PrONO ₂ ⁴	2.43±0.31	0.50	8.9	2.74±0.31	0.30	10.1
2-BuONO ₂ ⁵	47.9±4.13	10.9	158.1	47.3±3.8	3.70	117
2-PeONO ₂ ⁶	15.1±2.12	1.33	86.3	15.7±1.8	1.32	63.7
3-PeONO ₂ ⁷	10.7±1.5	0.79	49.4	12.9±1.7	0.22	65.9
Ethane	1979±205	305	5700	1719±149	141	5610
Propane	1719±179	122	6199	1224±136	112	5247
<i>n</i> -Butane	1456±144	115	5354	823±125	24.2	2983
<i>n</i> -Pentane	406±108	24.4	6666	335±55.5	17.4	1866
TVOCs	35.1±8.00	6.23	131.8	16.8±2.91	2.94	5.63
O ₃	42.3±4.44	1.53	121.2	68.6±5.03	6.52	152

¹ Average level with 95% confidence interval; ² Ethyl nitrate (EtONO₂); ³*iso*-Propyl nitrate (2-PrONO₂);
 ⁴ *n*-Propyl nitrate (1-PrONO₂); ⁵ 2-Butyl nitrate (2-BuONO₂); ⁶ 2-Pentyl nitrate (2-PeONO₂); ⁷ 3-Pentyl nitrate (3-PeONO₂).

Figure 1 shows temporal variations of total RONO₂, TVOCs, NO_x, O₃ and meteorological parameters at both sites. RONO₂ generally correlated well ($R^2=0.55$) with O₃ as the photochemical formation of RONO₂ shares the same formation pathways with O₃. In total, 5 and 190 8 out of 21 canister sampling days were identified as O₃ episodes at TC and WSI, respectively. The total C₁-C₅ RONO₂ during O₃ episodes (TC: 172±12.2 pptv; WSI: 142±7.55 pptv) were 191 significantly higher (p < 0.01) than those during non-episodes (TC: 120 ± 8.35 pptv; WSI: 192 107±7.55 pptv), same as their precursors, i.e. VOCs and NO_x (Table S4). Similarly, individual 193 RONO₂ was higher (p < 0.01) during episodes except for MeONO₂ and EtONO₂ (p > 0.1) which 194 195 were comparable between episodes and non-episodes at both sites (Figure S2), likely due to the fact that MeONO₂ and EtONO₂ have sources of oceanic emission and biomass burning, apart 196 from photochemical formation. 197

198 Generally, the high levels of RONO₂ were accompanied with strong solar radiation and low relative humidity at both sites. It was reasonable as the photochemical reactions could be 199 enhanced under these conditions. In addition, northerly winds prevailed when RONO₂ were 200 201 elevated during O₃ episodes, with the frequency of 40% at TC and 72% at WSI. This implied the regional transport of RONO₂ and/or their precursors to both sites, in view of the severer air 202 pollution in PRD. To further understand the impact of regional transport on RONO₂ abundances, 203 the average backward trajectories during O₃ episodes and non-episodes in the sampling period 204 are shown in Figure S3. It was found that 91% of air masses passed along the coastline of South 205 China 24 hours before arriving in Hong Kong during non-episodes. These air masses were 206 expected to be relatively clean, thus diluting or at least not aggravating air pollution in the study 207 area. In contrast, during O_3 episodes, Hong Kong received nearly all the air masses originated 208 from and passed over the inland cities of China, which might deliver RONO2 and/or their 209 210 precursors from the polluted regions to Hong Kong. In summary, apart from meteorological impact, polluted continental air masses aggravated air pollution at TC and WSI on O₃ episodes, 211 212 while this adverse influence was lessened during non-episodes. Further insight into the backward

trajectories in the last 12 hours (Figure S4) found that the air masses reaching the two sites were

in parallel during non-episodes. However, the air passed over TC before reaching WSI on O₃

episode days, implying the interactions between the two sites in some cases.



Figure 1. Temporal variations of meteorological parameters together with mixing ratios of TVOCs, total alkyl nitrates (TAN), NO_x and O_3 at TC and WSI sites (O₃-episodes are highlighted in yellow)

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3.2 Potential sources and photochemical formation of RONO₂

As aforementioned, regional transport might partially explain the redistribution of RONO₂ at both sites, indicated by the RONO₂ variations against wind fields. In addition, the different patterns of RONO₂ and their parent hydrocarbons might be caused by the sources other than photochemical formation (e.g. oceanic emission and biomass burning). The ratio between RONO₂ and the parent hydrocarbon was used to preliminarily understand the photochemical evolution and potential sources of RONO₂. Figure 2 shows the observed RONO₂/Alk ratio versus 3-PeONO₂/n-pentane ratio, and the predicted BIR and PP curves (detailed explanations are provided in Text S4).

At the initial stage of evolution, BIR curve was positioned far above PP curve, which was 230 231 caused by the background RONO₂ and Alks. However, the gaps narrowed with the increase of evolution time, indicating weakened impacts of the background concentrations. This feature was 232 more pronounced for C₂-C₃ RONO₂ due to the longer atmospheric lifetimes of C₂-C₃ RONO₂ 233 than C₄-C₅ RONO₂.^{6,11,16} Even taking the background concentrations into consideration, the 234 observed ratios of $\frac{[RONO_2]}{[Alk]}$ were generally located above the BIR curves for C₂-C₃ RONO₂ at 235 both sites, suggesting that the observed RONO₂ could not only be explained by the 236 photochemical formation (specifically RO_2 + NO, see section 2.3) and background 237 238 concentrations. The direct emissions of RONO₂ from biomass burning and oceans might be partially responsible for this discrepancy.^{12,18,19} Further, RONO₂ formed from the oxidation of 239 VOCs other than the parent hydrocarbons and through pathways other than RO₂+NO could also 240 be important reasons.^{26,46} In contrast, the observed ratios of $\frac{[RONO_2]}{[Alk]}$ were close to and even 241 overlapped with the BIR curves for C₄ and C₅ RONO₂, indicating that photochemical formation 242 through the reactions between RO₂ (derived from the oxidation of parent hydrocarbons) and NO 243 dominated the sources of C_4 - C_5 RONO₂. 244

Moreover, as indicated by the evolution time (triangles on the curves), air masses at both sites experienced evolution time between 6 hours and 10 days, while WSI had more aged air masses as indicated by the upper-right symbols in Figure 2.²⁶ This is reasonable because WSI was
farther from the sources.



Figure 2. Predicted and observed relationships between C_2 - C_5 RONO₂/Alk and 3-PeONO₂/*n*-pentane at TC and WSI. The triangles and times on PP curve (red) and BIR curve (TC: yellow; WSI: grey) denote the evolution times. The figures are plotted according to the method introduced in Text S4.

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254 **3.3** Evaluation of oxidative capacity at TC and WSI

255 To understand the impact of oxidative capacity on secondary RONO₂ formation, PBM-MCM 256 model was used to simulate RONO₂ with the settings consistent with those detailed by Lyu et al.²⁷ It is noteworthy that the model validations were only carried out for O₃ episodes when the 257 in-situ photochemical processes were intensive, as the PBM-MCM model does not fully consider 258 259 the physical processes which may be stronger during non-episodes. Figure S5 shows the simulated and observed RONO₂ at TC and WSI. Generally, the simulated RONO₂ captured the 260 diurnal variations of RONO₂ with IOA ranging from 0.45 to 0.97 at TC and from 0.52 to 0.79 at 261 262 WSI (Table S5). The differences between the simulated and observed RONO₂ were attributable to the primary emissions, as well as the lack of full consideration of physical processes in PBM-263 MCM. Hereafter, simulations were conducted for all canister sampling days to investigate the 264 local photochemical processes of RONO₂. 265

Given the comparable or even lower levels of VOCs including parent hydrocarbons at WSI, 266 267 the higher simulated RONO₂ implied higher oxidation efficiency of the parent hydrocarbons and/or other VOCs which could also be precursors of RONO₂, such as carbonyls and aromatics 268 (see section 3.3.2). Figure 3 presents the average diurnal patterns of the simulated OH, HO₂, 269 270 CH₃O₂ and CH₃O. CH₃O₂ and CH₃O are shown as an example of C₁-C₅ RO₂ and RO, respectively (see Figure S6 for details of the simulated concentrations of these radicals). 271 Noticeably, WSI featured more abundant radicals than TC. The higher OH and HO₂ indicated the 272 stronger oxidative capacity of the atmosphere at WSI, causing more efficient oxidation of VOCs 273 and production of intermediates and other radicals, such as RO₂ and RO. As a result, RONO₂ 274 could be more efficiently formed. In fact, the similar phenomenon was also reported by Lyu et 275 al.²⁷ who found that RONO₂ at a mountainous site were comparable to or even higher than those 276

at an adjacent urban site due to the higher atmospheric oxidative capacity. Consistent with the previous study,²⁷ the much lower level of NO_x (the main scavenger of oxidative radicals) at WSI than at TC might be the reason of more abundant oxidative radicals at this offshore site.



Figure 3. Simulated concentrations of (a) OH and HO₂, and (b) CH₃O₂ and CH₃O at TC and WSI.

282 **3.4 RONO₂ – precursors relationship**

Figure 4 presents the average RIRs of RONO₂ precursors at TC. It was found that VOCs 283 including parent hydrocarbons and other VOCs had positive RIR values, while RIRs of NO and 284 NO₂ were negative except for the positive RIR of NO₂ in the formation of MeONO₂. This 285 indicated that RONO₂ production was limited by VOCs at TC. However, NO₂ also facilitated 286 MeONO₂ formation, which was due to the considerable production of MeONO₂ through the 287 pathway of CH₃O+NO₂. Both Simpson et al.⁷ and Lyu et al.²⁷ reported this finding in Hong 288 Kong, and Archibald et al.⁴⁷ revealed that MeONO₂ production through this route was strongly 289 NO₂ dependent. Text S5 and Table S6 in the supplement discussed the contributions of RO₂+NO 290 291 and RO+NO₂ to RONO₂ production at TC and WSI. It was found that RO+NO₂ greatly contributed to MeONO₂ at TC, while negligible to the formation of other RONO₂, which explained the positive RIR of NO₂ in MeONO₂ formation. Furthermore, in contrast to the exclusively positive contribution of the parent hydrocarbons to C₄-C₅ RONO₂, RIRs of other VOCs were even higher than those of parent hydrocarbons for C₁-C₃ RONO₂. This implied that VOCs other than parent hydrocarbons were important precursors of C₁-C₃ RONO₂, which however made minor contributions to C₄-C₅ RONO₂.



Figure 4. Average RIRs of RONO₂ precursors during the canister sampling period at TC.

Consistently, the RIRs of VOCs including parent hydrocarbons and other VOCs were positive at WSI, regardless of O₃ episodes or non-episodes (Figure 5). During O₃ episodes, NO_x inhibited RONO₂ formation (RIR<0) except for the positive effect of NO₂ on MeONO₂ production, which was discussed above. However, NO_x made positive contribution to RONO₂ production (RIR>0) during non-episodes at this site, indicating that cutting either NO or NO₂ would lead to decrease of RONO₂ production during non-episodes at WSI. This phenomenon was not identified at TC where NO_x level was much higher (45.78±3.33 ppbv at TC versus 6.11±0.96 ppbv at WSI). In fact, the dual role of NO_x in RONO₂ formation has been documented in Lyu et al.,²⁷ who found that low level of NO_x stimulated while high level of NO_x inhibited RONO₂ formation. This explained the positive RIR of NO_x at WSI during non-episodes when NO_x (1.97 \pm 0.76 ppbv) was significantly lower than that during episodes (9.57 \pm 1.19 ppbv) and at TC (45.78 \pm 3.33 ppbv). It therefore can be concluded that RONO₂ formation was limited by VOCs during O₃ episodes and co-limited by VOCs and NO_x during non-episodes at WSI.



Figure 5. Average RIRs of RONO₂ precursors during (a) O₃ episodes and (b) non-episodes of the canister
sampling period at WSI.

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317 **3.5 Sources of RO₂ and RO radicals**

Since " RO_2 +NO" and "RO+ NO_2 " were the main pathways leading to $RONO_2$ formation, the contributions of parent hydrocarbons and other VOCs to the production of RO_2 and RO radicals were identified. As introduced in section 2.5.2, the effects of factors 1 (oxidation and/or direct decomposition) and factor 2 (indirect effect through regulation on OH concentration) on the production of both radicals were distinguished for different species/group of VOC(s), as shown in Figures 6-7. C_2 - C_5 RO are not displayed due to the negligible contributions of the pathway "RO+NO₂" to C_2 - C_5 RONO₂ (see Text S5 in the supplement).

325 It was found that in addition to the parent hydrocarbon, other VOCs also made considerable contributions to RO₂ and CH₃O at TC (Figure 6), such as aromatics, BVOCs and carbonyls for 326 C₁-C₅ RO₂ and CH₃O, and C₄-C₅ hydrocarbons for C₂-C₃ RO₂. Noticeably, the parent 327 328 hydrocarbons played important roles in the production of larger molecular (C₄-C₅) RO₂ through oxidation (factor 1), with the contribution of 97-100%. However, less than 60% of C_1 - C_3 RO₂ 329 and CH₃O (as low as 6% for C₂H₅O₂) could be attributable to the parent hydrocarbons, with the 330 remainder attributable to the other VOCs. Specifically, aromatics, carbonyls and BVOCs were 331 responsible for 36-38%, 18-20% and 12% of CH₃O₂/CH₃O, respectively. C₂H₅O₂ were largely 332 contributed by C₄-C₆ hydrocarbons (75%) and aromatics (13%), while 27-36% of $1-/2-C_3H_7O_2$ 333 were derived from C₄-C₆ hydrocarbons. One possible pathway of MeONO₂ formation through 334 the oxidation of *p*-xylene and the decomposition of the oxidation products is shown in Figure S7 335 as an example. Furthermore, the other VOCs produced RO₂ and CH₃O not only through 336 oxidation/decomposition (factor 1) but also through regulating the OH concentration (factor 2). 337 Particularly, aromatics, BVOCs and carbonyls all had largest influence on facilitating the 338 339 production of the aforementioned radicals through building up OH concentration in the atmosphere. Namely, OH was elevated by these VOCs, which further enhanced the production of 340 RO₂ and RO radicals. In fact, as shown in Figure S8, aromatics, BVOCs and carbonyls did lead 341 to the increase of OH at TC, likely associating with their contributions to O₃ (an important 342

source of primary OH).⁴⁸⁻⁵¹ Figure S9 shows the decreases of the simulated O₃ with the removal 343 of BVOCs or aromatics from the model input. Correspondingly, the OH cycling was also 344 weakened without BVOCs or aromatics, as presented in Figure S10. As an important source of 345 primary OH, O₃ photolysis reduced from 1.92×10^6 molecules cm⁻¹ s⁻¹ with the inclusion of both 346 BVOCs and aromatics to 1.79×10^6 and 1.78×10^6 molecules cm⁻¹ s⁻¹ with the removal of BVOCs 347 and aromatics, respectively. In addition to this effect, the high contribution of carbonyls to OH 348 349 also resulted from the production of HO₂ from their photolysis and further reaction between HO₂ and NO.⁵² The dominance of parent hydrocarbons rather than other VOCs in the sources of C₄-350 C₅ RONO₂ was due to the fact that the large RO₂ radicals cannot be generated from the 351 decomposition of other radicals. This was also confirmed by the negligible contribution of other 352 VOCs to C_4 - C_5 RONO₂ through factor 1 (see Figure 6). 353



354

Figure 6. Average contributions of specific species/group of VOC(s) to C_1 - C_5 RO₂ and CH₃O at TC. Factor 1 and factor 2 are shown with blue and red bars, respectively. Please refer to Table S7 for details of the species in each group of VOCs.

Similarly, the parent hydrocarbons only accounted for 9-60% of C_1 - C_3 RO₂ and CH₃O, while the contribution increased to 96-100% for C_4 - C_5 RO₂ at WSI (Figure 7). However, aromatics and BVOCs generally inhibited the formations of C_1 - C_5 RO₂ and CH₃O through regulating the OH concentration (factor 2). Insight into the impacts of these compounds on OH production also found that they presented net destruction to OH (see Figure S8). The negative contributions of

aromatics, BVOCs and carbonyls to OH production at WSI might be due to the consumption of 363 OH at the initial oxidation of these compounds, which could not be as efficiently recycled from 364 the reactions between RO₂ and NO as that ,at TC because NO was much lower at WSI than at 365 TC. Wang et al. also identified this mechanism at the same site.³² For carbonyls, they still 366 enhanced OH production in the early morning and late afternoon at WSI, when the OH 367 concentration was low (Figure 3). The positive contributions were likely caused by the 368 photolysis of carbonyls (a pathway of OH production), which overrode the OH consumption in 369 the oxidation of carbonyls. Therefore, we conclude that other VOCs contributed to the 370 production of C₁-C₃ RO₂ and CH₃O mainly through the decomposition of larger radicals in the 371 low NO_x environment. 372



Figure 7. Average contributions of specific species/group of VOC(s) to C_1 - C_5 RO₂, CH₃O at WSI. Factor 1 and factor 2 are shown with blue and red bars, respectively. Please refer to Table S7 for details of the species in each group of VOCs.

377 4 IMPLICATION

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Previous studies on RONO₂ were generally based on the observations and kinetic calculations, which considered the parent hydrocarbons as the sole precursors of RONO₂. The photochemical evolution curves of RONO₂ proposed by Bertman et al.²⁶ also started from this premise. 381 However, this study revealed that confining RONO₂ precursors to the parent hydrocarbons would underestimate RONO₂ production to a great extent, particularly for the C_1 - C_3 RONO₂. 382 This may explain why the observed short-chain RONO₂ were always higher than the kinetic 383 calculations. We also recommend including more VOCs as the precursors of RONO₂ when 384 applying Bertman's curves. To our best knowledge, the photochemical reactions in chemical 385 transport models (CTMs) are generally group based, deficient in explicit description of radical 386 reactions, which may have higher uncertainty on estimating RONO₂ production. Moreover, with 387 the lumped mechanisms, it is difficult to study the impacts of individual VOCs on RONO₂ 388 chemistry, particularly in the regions where these analyses are necessary, e.g. in forest with high 389 isoprene emissions and over the southern ocean where methane and methyl nitrate are abundant. 390 The results in this study are actually benefitted from the application of the MCM, a near-explicit 391 392 chemical mechanism describing the photochemical degradations of individual VOCs. To more comprehensively understand the RONO₂ chemistry in larger (regional, national or even global) 393 scales, it is of high necessity to update the species-based RONO₂ photochemistry in CTMs. 394

395

396 ASSOCIATED CONTENT

397 Supporting Information

Production and destruction of RONO₂ (Text S1); Description of sample collection and
chemical analysis (Text S2); Description of scenario analysis (Text S3); Methodology of
photochemical evolution of RONO₂ (Text S4); Description of reaction pathways to RONO₂
formation (Text S5); Figures S1-S10; Tables S1-S7; Reactions R1-R6; Equations S1-S2.

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