Impact of HO₂ aerosol uptake on radical levels and O₃ production during summertime in Beijing

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56 **Abstract** The impact of heterogeneous uptake of HO_2 onto aerosol surfaces on radical

57 concentrations and the O_3 production regime in Beijing summertime was investigated. The

58 uptake coefficient of HO_2 onto aerosol surfaces, γ_{HO_2}, was calculated for the AIRPRO

59 campaign in Beijing, Summer 2017, as a function of measured aerosol soluble copper

60 concentration, $[Cu^{2+}]_{eff}$, aerosol liquid water content, $[ALWC]$, and particulate matter

61 concentration, $[PM]$. An average γ_{HO_2} across the entire campaign of 0.070 ± 0.035 was

62 calculated, with values ranging from 0.002 to 0.15, and found to be significantly lower than

63 the value of $\gamma_{HO_2} = 0.2$, commonly used in modelling studies. Using the calculated γ_{HO_2} values

64 for the Summer AIRPRO campaign, OH, HO_2 and RO_2 radical concentrations were modelled

65 using a box-model incorporating the Master Chemical Mechanism (v3.3.1), with and without

66 the addition of γ_{HO_2}, and compared to the measured radical concentrations. Rate of destruction

67 analysis showed the dominant HO_2 loss pathway to be $HO_2 + NO$ for all NO concentrations

68 across the Summer Beijing campaign with HO_2 uptake contributing < 0.3 % to the total loss of

69 HO_2 on average. This result for Beijing summertime would suggest that under most conditions

70 encountered, HO_2 uptake onto aerosol surfaces is not important to consider when investigating

71 increasing O_3 production with decreasing $[PM]$ across the North China Plain. At low $[NO]$,

72 however, i.e. < 0.1 ppb, which was often encountered in the afternoons, up to 29% of modelled

73 HO_2 loss was due to HO_2 uptake on aerosols when calculated γ_{HO_2} was included, even with the

74 much lower γ_{HO_2} values compared to $\gamma_{HO_2} = 0.2$, a results which agrees with the aerosol-

75 inhibited O_3 regime recently proposed by Ivatt et al., 2022. As such it can be concluded that in

76 cleaner environments, away from polluted urban centres where HO_2 loss chemistry is not

77 dominated by NO but where aerosol surface area is high still, changes in PM concentration and

78 hence aerosol surface area could still have a significant effect on both overall HO_2

79 concentration and the O_3 production regime.

80 Using modelled radical concentrations, the absolute O_3 sensitivity to NO_x and VOC showed

81 that, on average across the summer AIRPRO campaign, the O_3 production regime remained

82 VOC-limited, with the exception of a few days in the afternoon when the NO mixing ratio

83 dropped low enough for the O_3 regime to shift towards NO_x-limited. The O_3 sensitivity to VOC,

84 the dominant regime during the summer AIRPRO campaign, was observed to decrease and

85 shift towards a NO_x sensitive regime both when NO mixing ratio decreased and with the

86 addition of aerosol uptake. This suggests that if $[NO_x]$ continues to decrease in the future, ozone

87 reduction policies focussing solely on NO_x reductions may not be as efficient as expected if

88　[PM] and, hence, HO$_2$ uptake to aerosol surfaces, continues to decrease. The addition of aerosol

89　uptake into the model, for both the γ_{HO_2} calculated from measured data and when using a fixed

90　value of γ_{HO_2} = 0.2, did not have a significant effect on the overall O$_3$ production regime across

91　the campaign. While not important for this campaign, aerosol uptake could be important for

92　areas of lower NO concentration that are already in a NO$_x$-sensitive regime.

1　Introduction

94　Climate change and air quality are two significant environmental issues faced by society today

95　with the drive to net zero emissions by 2050 becoming increasingly important to remain

96　consistent with the long-term anthropogenic temperature warming outcome of below 1.5 ℃ as

97　set out by the Paris Agreement in 2016. Increasing anthropogenic emissions have caused not

98　only an increase in atmospheric warming, but also a deterioration in atmospheric air quality: a

99　concern due to both short and long term negative health effects seen as a product of poor air

100　quality such as respiratory and cardiovascular diseases and cancer (Brauer et al., 2016; Gakidou

101　et al., 2017), in addition to a variety of negative effects on the environment such as increased

102　soil acidification and the ensuing damage to vegetation and crop yield as a by-product of

103　increasing acidity of rain (Forster et al., 2007).

104　Ambient air pollution has become a serious issue globally, specifically in large urban areas

105　effected by anthropogenic emission sources. Due to rapid industrialisation, Chinese megacities

106　in particular face significant environmental and health challenges from the decline in air quality

107　following urbanisation, with areas such as the Beijing-Tianjin-Hebei area in the North China

108　Plain (NCP) suffering from seasonal extreme pollution episodes as a consequence (Wang,

109　2021; Jin et al., 2016). In terms of human health, the most important pollutants in many regions

110　are ground level O$_3$, NO$_x$ (NO$_2$ and NO) and particulate matter. Nitrogen dioxide (NO$_2$) can be

111　directly emitted into the atmosphere from high temperature combustion sources or can be

112　formed via the reaction of nitrogen monoxide (NO) with an oxidising species in the

113　troposphere, such as HO$_2$, leading to the formation of hydroxyl radical (OH) (Ye et al., 2017).

114　Ozone, while vital in the stratosphere to protect the earth from harmful UV radiation and

115　excessive planetary heating, is toxic to both plant and human life at ground level and can react

116　with NO to form NO$_2$. Particulate matter is emitted anthropogenically and biogenically and can

117　play a role in the warming and cooling of the atmosphere due to the ability of aerosols to absorb

118　or scatter IR radiation depending on their composition. High levels of particulate matter, NO$_x$

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119 and tropospheric O_3 in areas of low atmospheric mixing lead to photochemical smog and the
120 reduction of visibility characteristic of extreme pollution episodes.

121 The concentration of pollutants and trace gases in the troposphere is controlled not only by
122 emission levels but also by the oxidation capacity of the atmosphere which is determined
123 largely by the concentration of the hydroxyl radical (OH) and the closely coupled hydroperoxyl
124 (HO_2) radical, referred to collectively as HO_x radicals. Known for their role in chemical
125 oxidation processes in the atmosphere, OH and HO_2 are vital species when considering climate
126 change and air pollution. The OH radical is the main daytime tropospheric oxidant, with a
127 major role as a source of ground level ozone (O_3) (Levy, 1971) and as a sink for both
128 atmospheric pollutants, such as methane, and other radical species. The OH radical also has a
129 role in the formation of secondary pollutants including secondary organic aerosols (SOAs)
130 formed via the oxidation of volatile organic compounds (VOCs). OH and HO_2 radicals are
131 closely linked, due to the recycling of HO_2 to give OH, either via the reaction with NO or CO,
132 with the dominant loss pathway of HO_2 in polluted regions being the reaction with NO to form
133 OH (for example, as shown in Beijing by Slater et al., 2020; Whalley et al., 2021). As such,
134 understanding the sources and sinks of both OH and HO_2 within the troposphere is crucial to
135 fully understand the concentration and distribution of trace atmospheric species associated with
136 climate change and poor air quality.

137 Observed HO_2 concentrations from field measurements frequently can-not be fully explained
138 by atmospheric chemistry models which often have a tendency to over-predict HO_2 in low NO_x
139 conditions (Kanaya et al., 2007; Commane et al., 2010; Whalley et al., 2010; Whalley et al.,
140 2021; Slater et al., 2020; Sommariva et al., 2004). Following the ClearfLo campaign in London
141 2012, zero-dimensional modelling showed an over-prediction of HO_2 by up to a factor of 10 at
142 low NO_x which was attributed to uncertainties in the degradation mechanism of complex
143 biogenic and diesel-related VOC species at low NO_x (Whalley et al., 2018). Over-prediction of
144 HO_2 is also commonly thought to be due, in part, to lack of understanding of HO_2 uptake onto
145 aerosol surfaces. A 2014 modelling study by Xue et al., 2014 focussing on the transport,
146 heterogeneous chemistry and precursors of ground level ozone in Beijing, Shanghai,
147 Guangzhou and Lanzhou, identified HO_2 uptake as a source of uncertainty when considering
148 ozone production, with uptake onto aerosols having the largest effect on HO_2 concentration in
149 Beijing where aerosol loadings were the highest.

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While the impact of HO_2 uptake on HO_x concentrations has been calculated to vary from ~10-40 % (Jacob, 2000; Whalley et al., 2010; Whalley et al., 2021; Slater et al., 2020; Mao et al., 2010; Li et al., 2019; Li et al., 2018) globally, often a single value of $\gamma_{HO_2} = 0.2$ is used within models, as recommended by Jacob, 2000. Previous experimental studies report uptake coefficients which span several orders of magnitude, however, and vary largely based on the state of the aerosol and whether transition metal ion catalysis is involved. For dry inorganic salt aerosols values as low as $\gamma_{HO_2} < 0.002$ have been reported (Cooper and Abbatt, 1996; Taketani et al., 2008; George et al., 2013) increasing to up to $\gamma_{HO_2} = 0.2$ for aqueous aerosols (Thornton and Abbatt, 2005; Taketani et al., 2008; George et al., 2013). Previous experimental studies report much higher $\gamma_{HO_2} > 0.4$ for Cu-dopped aqueous aerosols (Thornton and Abbatt, 2005; Mozurkewich et al., 1987; Taketani et al., 2008; George et al., 2013; Lakey et al., 2016). Recently, larger values of γ_{HO_2} have been measured experimentally from samples taken offline at Mt. Tai (0.13-0.34) and Mt. Mang (0.09-0.40) in China by Taketani et al., 2012, while another study in Kyoto, Japan, directly measured γ_{HO_2} values under ambient conditions from 0.08 to 0.36 (Zhou et al., 2020). With $\gamma_{HO_2} > 0.1$, HO_2 concentrations can be significantly influenced particularly in areas of low [NO] and/or high aerosol loadings (Lakey et al., 2015; Matthews et al., 2014; Mao et al., 2013; Zhou et al., 2021; Martinez et al., 2003).

Following multiple policies implemented across China in response to the poor air quality "crisis", a number of studies have reported a decrease in NO_x and $PM_{2.5}$ emissions in China (Jin et al., 2016). Liu et al., 2017 reported NO_x (NO_2 + NO) emissions over 48 Chinese cities to have decreased by 21 % in the period of 2011-2015, supported by observed declines in NO_x emissions reported by other studies (Krotkov et al., 2016; Liu et al., 2016; Miyazaki et al., 2017; Van Der A et al., 2017). Ma et al., 2016b reported a mean annual decrease in $PM_{2.5}$ of 0.46 µg m^{-3} between 2008-2013, while Lin et al., 2018 reported an average decrease of 0.65 µg m^{-3} yr^{-1} between 2006-2010 increasing to a decline of 2.33 µg m^{-3} yr^{-1} for the period of 2011-2015. In contrast to the observed decrease in NO_x and $PM_{2.5}$ emissions, several studies have reported increasing O_3 levels. Ma et al., 2016a reported a maximum daily average 8h mean (MDA8) increase in O_3 concentrations of 1.13 ppb yr^{-1} for the period between 2003-2015 at a rural site north of Beijing while satellite observations suggested ground level ozone had increased ~7% for the period between 2005-2010 (Verstraeten et al., 2015). A recent study by Silver et al., 2018 also observed a significant increase in O_3 concentrations with median MDA8 increasing at a rate of 4.6 µg m^{-3} yr^{-1} across China.

182 A 2018 modelling study using the regional model GEOS-Chem by Li et al., 2018 suggested
183 the increase in O_3 across China between 2013-2017 could be attributed to the decrease in $PM_{2.5}$,
184 with changes in $PM_{2.5}$ being a more important driver of increasing O_3 trends than NO_x and
185 VOC emissions for the period studied. It was proposed that a decrease in $PM_{2.5}$ emissions had
186 led to a decrease in loss of HO_2 via aerosol uptake resulting in an increase in HO_2 concentration,
187 and a proportional increase in the loss of HO_2 via NO leading to NO_2 which, when photolyzed,
188 forms O_3 leading to an increase in O_3 (Li et al., 2018). However, analysis of measured radical
189 budget from a field campaign in the North China Plain in Summer 2014 with a calculated γ_{HO_2}
190 of 0.08 ± 0.13, showed no evidence for a significant impact of HO_2 heterogeneous chemistry
191 on radical concentrations in North China Plain, concluding that reduced HO_2 uptake was
192 unlikely to therefore be the cause of increasing O_3 levels in the North China Plain (Tan et al.,
193 2020). Using a novel parameterisation developed by Song et al., 2020 in the framework of the
194 resistor model to take into account the influence of aerosol soluble copper, aerosol liquid water
195 content and particulate matter concentration on HO_2 uptake, and the Multiphase Chemical
196 Kinetic box model (PKU-MARK) to assess the impact of HO_2 uptake on the O_3 budget for
197 Wangdu Campaign in 2014, Song et al., 2022 concluded that HO_2 heterogeneous processes
198 could decrease the O_3 production rates by up to 6 ppbv hr^{-1}, particularly in the morning VOC-
199 limited regime.

200 In this study, the new parameterisation introduced by Song et al., 2021, hereafter referred to
201 solely as the Song parameterisation, coupled with measured data from the Summer AIRPRO
202 campaign in Beijing 2017 was used to calculate a time series of the HO_2 uptake coefficient,
203 which was then used to investigate the impact of heterogeneous uptake of HO_2 onto aerosol
204 surfaces on the HO_2 radical budget in Summertime Beijing using the Master Chemical
205 Mechanism and the impact on the O_3 regime. We will test the hypothesis that reduced HO_2
206 uptake due to a reduction in $PM_{2.5}$ concentration is a significant driver of the recent increase in
207 ozone concentrations in China.

208 2   Experimental

209 2.1   Campaign overview and site description

210 As part of the Atmospheric Pollution and Human Health (APHH) in a Chinese Megacity
211 programme, the University of Leeds took simultaneous measurements of OH, HO_2, RO_2 and
212 OH reactivity (k_{OH}), in addition to measurements of HCHO and photolysis rates, during two

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field campaigns at an urban site in Winter 2016 and Summer 2017 in Beijing, with the aim to study the chemical and physical processes governing gas and particle pollution and meteorological dynamics in the Beijing region and the links between the two (Shi et al., 2019; Slater et al., 2020; Whalley et al., 2021). The two field campaigns in Beijing were part of the AIRPRO (The integrated study of AIR pollution PROcesses in Beijing) project within the APHH programme, described fully by Shi et al., 2019.

For the summer AIRPRO campaign, the official science period was from 23rd May 2017 to the 22nd June 2017, with observations taking place at the Institute of Atmospheric Physics (IAP) within the Chinese Academy of Sciences, located between the third and fourth ring roads in central Beijing within 100 m of a major road, making local traffic emission sources an important source of pollution during measurement period. All instrumentation for the campaign was located at this site, housed within nine shipping containers surrounding a meteorological tower. Further details of the instrumentation and measurement site can be found in Shi et al., 2019.

2.2 FAGE instrumentation description

The University of Leeds Fluorescence Assay by Gas Expansion (FAGE) instrument made measurements of OH, HO_2 and RO_2 radicals and OH reactivity (k_{OH}). The FAGE instrument set up is described fully in Whalley et al., 2018 while the OH reactivity instrument set up is described fully in Whalley et al., 2016. Both instruments are also described fully in Slater et al., 2020 and so only a brief description is given here.

Two cells, a HO_x cell and a RO_x cell connected together with a side arm, were used to take radical measurements from the roof of the Leeds FAGE lab container. A RO_xLIF flow reactor was also coupled to the RO_x cell to allow for detection of RO_2 (total, complex and simple) as described by Fuchs et al., 2008. The HO_x cell took sequential measurements of OH and the sum of OH and HO_2, by the addition of NO (Messer, 99.5 %), which titrated HO_2 to OH for detection by Laser Induced Fluorescence (LIF) at 308 nm.

The RO_xLIF reactor operated in 2 modes: a 'HO_x mode' where a flow of CO (10 % in N_2) was added to ambient sampled air close to the pin hole to convert all ambient OH to HO_2; and a 'RO_x mode' where NO (500 ppmv in N_2) was added in addition to the CO flow to convert all RO_2 into OH was then rapidly converted by CO into HO_2. The air from the RO_xLIF reactor was then drawn into the FAGE low pressure fluorescence cell, whereupon pure

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2.3 2.2 Determination of aerosol soluble copper concentration through ICP-MS Analysis

The soluble copper ion concentration was determined by analysing the effluent extracted from quartz filter samples taken daily for the entire campaign using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A 6 cm² punch from each large quartz filter PM$_{2.5}$ sample was cut and put in a 15 mL extraction tube and extracted with 10 mL ultrapure water (18.2 MΩ cm) under ultrasonication for 60 minutes at below 35 ℃. The sample was then shaken by a temperature-controlled shaker at 4 ℃ for 3 hours at approximately 60 cycles min^{-1}. After filtering through a filter syringe, 8 mL of effluent was transferred to a new 15 mL metal free tube, and 2 mL of 10% HNO₃ was added to make a 10 mL 2% HNO₃ extract solution which was then analysed to determine the soluble copper ion concentration using ICP-MS.

2.4 2.3 MCM v3.3.1 box model description

The Master Chemical Mechanism (MCMv3.3.1) is a near-explicit mechanism which describes the gas-phase degradation of a series of primary emitted VOC's in the troposphere. The mechanism considers the degradation of 143 VOC's and contains ~17000 elementary reactions of 6700 species (Whalley et al., 2013).

275 The model was constrained to measurements of NO, NO$_2$, O$_3$, CO, HCHO, HNO$_3$, HONO,
276 PAN, H$_2$O vapour, temperature, pressure, j(O^{1}D), j(HONO), j(NO$_2$), j(ClNO$_2$), j(HOCl),
277 j(ClONO$_2$) and specific VOC species measured using GC-FID (gas chromatography with
278 flame ionisation) and PTR-ToF-MS (proton-transfer reaction time of flight mass
279 spectrometry). The measured species were input into the model at a time resolution of 15
280 minutes, with species measured at a higher time resolution averaged up to 15 minutes and those
281 measured at a lower time resolution interpolated to give a value every 15 minutes. The full list
282 of all species constrained in the model is shown in Table 1Table 1.

Type	Species
Gas-phase inorganic species	NO, NO$_2$, O$_3$, CO, HNO$_3$, HONO, H$_2$O, SO$_2$, ClNO$_2$, HOCl
Gas-phase organic species	HCHO, PAN, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$, C$_3$H$_6$, isobutane, butane, C$_2$H$_2$, trans-but-2-ene, but-1ene, Isobutene, cis-but-2-ene, 2-Methylbutane, pentane, acetone, 1,3-butadiene, trans-2-pentene, cis-2- pentene, 2-methylpetane, 3-methypetane, hexane, isoprene, heptane, benzene, toluene, nonane, decane, undecane, dodecane, o-xylene, CH$_3$OH, CH$_3$OCH$_3$, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, ethylbenzene, CH$_3$CHO, C$_2$H$_5$OH, α-pinene, limonene, isopropylbenzene, propylbenzene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene.
Photolysis rates	j(O^{1}D), j(HONO), j(NO$_2$), j(ClNO$_2$), j(HOCl), j(ClONO$_2$)
Other	Mixing height, aerosol surface area

283 **Table 1.** Full description of measured species during Summer AIRPRO campaign constrained within the model

284 The different model scenarios referred to in this study are described in full below:

285   1. **MCM_base:** The base model run constrained to species described in Table 1Table
286   1.
287   2. **MCM_gamma:** The base model including heterogeneous HO$_2$ uptake onto
288   aerosols with γ_{HO_2} calculated from parameterisation developed by Song et al., 2020.
289   3. **MCM_SA:** The base model including heterogeneous HO$_2$ uptake, this time with
290   γ_{HO_2} fixed at 0.2, as commonly used within models and recommended by Jacob,
291   2000.

2.4 Calculation of L_N/Q and absolute O_3 sensitivity

First introduced by Kleinman et al., 1997, L_N/Q is the ratio of radical loss via NO_x to total primary radical production and is used as a means of determining O_3 production sensitivity to VOCs and NO_x (Kleinman, 2000; Kleinman et al., 1997; Kleinman et al., 2001). This method was then built on by Sakamoto et al., 2019 who included loss of peroxy radicals ($XO_2 = HO_2 + RO_2$) onto aerosol surfaces within the calculation of O_3 sensitivity.

The only source of tropospheric O_3 is by the reaction of peroxy radicals with NO, while the main source of XO_2 species is via the reaction of OH with VOCs.

$$XO_2 + NO \rightarrow XO + NO_2 \tag{R 1}$$

$$OH + VOC + O_2 \rightarrow XO_2 + products \tag{R 2}$$

The O_3 production rate in the troposphere is therefore:

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + k_{RO_2+NO}[RO_2][NO] \tag{1}$$

where k_{HO_2+NO} and k_{RO_2+NO} are the bimolecular rate constants for the reaction of HO_2 and RO_2 with NO.

The production rate of OH, HO_2 and RO_2 radicals, Q, must equal the loss rate:

$$Q = L_P + L_N + L_R \tag{2}$$

where L_P is the loss rate of radicals onto aerosol particles, L_N is the loss rate of radicals via reaction with NO_x species and L_R is the loss rate of radicals via radical-radical reactions to give peroxides.

$$L_P = k_{HO_2\ uptake}[HO_2] + k_{RO_2\ uptake}[RO_2] = k_P[XO_2] \tag{4}$$

$$L_N \approx k_{NO_2+OH}[NO_2][OH] \tag{5}$$

$$L_R = 2(k_{HO_2+HO_2}[HO_2]^2 + k_{RO_2+HO_2}[HO_2][RO_2]) \tag{6}$$

where $k_{HO_2\ uptake}$ is the rate constant for the loss of HO_2 onto aerosol surfaces, $k_{RO_2\ uptake}$ is the rate constant for the loss of RO_2 onto aerosol surfaces, k_{NO_2+OH} is the bimolecular rate constant for the reaction of NO_2 with OH, $k_{HO_2+HO_2}$ is the bimolecular rate constant for the self-reaction of HO_2 and $k_{RO_2+HO_2}$ is the bimolecular rate constant for the reaction of RO_2 with HO_2.

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312 For radical loss onto aerosol surfaces, the rate constant is given as a function of the reactive
313 uptake coefficient, γ_{XO_2}, aerosol particle surface area (cm^2 cm^{-3}) and mean thermal velocity
314 (cm s^{-1}), given by $\nu = \sqrt{8RT/\pi M}$ with R, T and M as the gas constant, the absolute temperature
315 and the molar mass of species respectively.

$$k_{radical\ uptake} = \frac{\gamma_{XO_2} \times SA \times \nu}{4} \tag{67}$$

316 According to the method described in Sakamoto et al., 2019, the ratio of radical loss to NO_x to
317 primary O_3 production including radical loss via aerosol uptake, $\frac{L_N}{Q}$ is defined as follows:

$$\frac{L_N}{Q} = \frac{1}{1 + \left(\frac{(2k_R[XO_2] + k_P)k_{OH+VOC}[VOC]}{(1-\alpha)k_{HO_2+NO}[NO]k_{NO_2+OH}[NO_2]} \right)} \tag{78}$$

318 where k_{OH+VOC} is the bimolecular rate constant for the loss of OH via reaction with VOCs and
319 $(1-\alpha)$ is the fraction of XO_2 that is HO_2.

320 The relative sensitivity of O_3 production to NO_x and VOCs is described by:

$$\frac{\delta lnP(O_3)}{\delta \ln [NO_x]} = (1-\chi)\left(\frac{1 - \frac{3}{2}\frac{L_N}{Q}}{1 - \frac{1}{2}\frac{L_N}{Q}} \right) + \chi(1 - 2\frac{L_N}{Q}) \tag{89}$$

$$\frac{\delta lnP(O_3)}{\delta \ln [VOC]} = (1-\chi)\left(\frac{\frac{1}{2}\frac{L_N}{Q}}{1 - \frac{1}{2}\frac{L_N}{Q}} \right) + \chi\frac{L_N}{Q} \tag{910}$$

321 where $\chi = \frac{L_P}{L_P+L_R}$. The O_3 regime transition point, where $\frac{\delta lnP(O_3)}{\delta \ln [NO_x]} = \frac{\delta lnP(O_3)}{\delta \ln [VOC]}$, is given by $\frac{L_N}{Q_{trans}}$.

$$\frac{L_N}{Q_{trans}} = \frac{1}{2}(1-\chi) + \frac{1}{3}\chi \tag{101}$$

322 Absolute O_3 sensitivity was introduced by Sakamoto et al., 2019, and allows for the assessment
323 of how reduction in O_3 precursors could contribute to reduction in $P(O_3)$ by integrating over
324 time and area. The absolute sensitivity of O_3 production to VOC and NO_x is then described by:

$$Absolute\ P(O_3) = \frac{\delta P(O_3)}{\delta \ln [X]} = P(O_3)\frac{\delta P(O_3)}{\delta \ln [X]} \tag{112}$$

325 where is $[X]$ is NO_x or VOC.

326 **2.5**

327 **2.52.6Description of the "Song parameterisation"**

328 A large uncertainty in determining the effect of HO$_2$ uptake onto the surface of aerosol particles

329 is the lack of understanding of the dependence of γ_{HO_2} on Cu (II)/transition metal ion

330 concentration within aerosols. Experimentally this dependence is quite well known from

331 laboratory studies (Mozurkewich et al., 1987; Thornton and Abbatt, 2005; George et al., 2013;

332 Mao et al., 2013), however the effective concentrations in ambient aerosols and the impact on

333 γ_{HO_2} of aerosol liquid water concentration, [ALWC], has not been incorporated into models

334 before. A novel parameterisation was developed by Song et al., 2020 in the framework of the

335 resistor model to include the influence of aerosol soluble copper on the uptake of HO$_2$. The

336 new parameterisation for the uptake coefficient of HO$_2$ onto aerosols, as given in Song et al.,

337 2020, is as follows:

$$\frac{1}{\gamma_{HO_2}} = \frac{1}{\alpha_{HO_2}} + \frac{3 \times \nu_{HO_2}}{(4 \times 10^6) \times R_d H_{eff} RT \times \left(5.87 + 3.2ln\left(\frac{ALWC}{[PM] + 0.067}\right)\right) \times [PM]^{-0.2} \times [Cu^{2+}]_{eff}^{0.65}} \quad (12)$$

338 where γ_{HO_2} is the uptake coefficient of HO$_2$ onto aerosols, α_{HO_2} is the mass accommodation

339 coefficient of HO$_2$, ν_{HO_2} is the mean molecular speed in cm s^{-1}, R_d is the count median radius

340 of the aerosol in cm, H_{eff} is the effective Henry's Law constant calculated from $H_{eff} =$

341 $H_{HO_2}\left(1 + \frac{K_{eq}}{[H+]}\right)$ where H_{HO_2} is the physical Henry's Law constant for HO$_2$ (i.e. 3900

342 (Thornton et al., 2008)) in M atm^{-1}, K_{eq} is the equilibrium constant for HO$_2$ dissociation (M),

343 and $[H^+]$ is the hydrogen ion concentration within the aerosol calculated from the pH (M), R

344 is the gas constant in cm^3 atm K^{-1} mol^{-1} (i.e. 82.05), T is the temperature in K, $[ALWC]$ is the

345 aerosol liquid water content in μg m^{-3} (which is related to the ambient relative humidity), $[PM]$

346 is the mass concentration of PM$_{2.5}$ in μg m^{-3} and $[Cu^{2+}]_{eff}$ is the effective aerosol condensed-

347 phase soluble copper (II) ion concentration in mol L^{-1}.

348 The Song parameterisation can reportedly be used for urban environmental conditions of

349 aerosol mass concentrations between 10-300 μg m^{-3}; aqueous copper (II) concentrations of

350 10^{-5}–1 mol L^{-1}; and relative humidity between 40-90 %. However, for the Summer AIRPRO

351 campaign data, the minimum [ALWC] supported by the parameterisation was 14 μg m^{-3}, below

352 which the parameterisation returned negative values for γ_{HO_2}. As such, despite the average

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353 calculated [ALWC] for the campaign being 6.9 ± 10 µg m^{-3}, a fixed value of 14 µg m^{-3} was
354 used to calculate γ_{HO_2} across the entire campaign.

3 Results and Discussion

3.1 Overview of field observations during summer AIRPRO campaign

357 Radical concentration measurements were taken throughout the official science period of the
358 summer campaign, from 23/05/2017 to 22/06/2017, using the Fluorescence Assay by Gas
359 Expansion technique. Alongside the radical observations and photolysis rate measurements
360 made by the University of Leeds, there was a varied suite of supporting measurements operated
361 by several universities and institutions. The supporting measurements used for the analysis and
362 discussion in this study were provided chiefly by the Universities of York, Birmingham and
363 Cambridge as detailed in Table 2Table 2.

Instrument	Species measured	University	Reference
FAGE	OH, HO$_2$, RO$_2$	Leeds	Whalley et al., 2010; Whalley et al., 2021; Slater et al., 2020
OH reactivity	OH reactivity	Leeds	Stone et al., 2016; Whalley et al., 2021; Slater et al., 2020
Spectral Radiometer	Photolysis rates	Leeds	Bohn et al., 2016
Filter Radiometer	j(O^{1}D)	Leeds	Whalley et al., 2010
Teledyne CAPS	NO$_2$	York	Smith et al., 2017
TEI 42c	Total NO$_y$	York	Smith et al., 2017
TEI 49i	O$_3$	York	Smith et al., 2017
Sensor box	CO	York	Smith et al., 2017
DC-GC_FID	C$_2$-C$_7$ VOCs and oVOCs	York	Hopkins et al., 2011
GCxGC-FID	C$_6$-C$_{13}$ VOCs and oVOCs	York	Dunmore et al., 2015
BBCEAS	HONO	Cambridge	Le Breton et al., 2014
TEI 42i	NO	Birmingham	-
LOPAP	HONO	Birmingham	Crilley et al., 2016
SMPS	Particle Size distribution	Birmingham	Wiedensohler et al., 2012
High volume sampler	PM$_{2.5}$ filter samples, Aerosol copper	IAP	-

Table 2. Measurements taken by universities and institutions during the Beijing Summer AIRPRO campaign. These species are directly referred to in this chapter: full description of every instrument and measurement taken can be found in Slater, 2020. IAP: Institute of Atmospheric Physics, Beijing. Time resolution of all instruments was averaged up to or interpolated down to 15 minutes for modelling purposes with the exception of the PM$_{2.5}$ filter samples, of which there was only 1 sample taken a day.

The median average diurnals for important gas phase species (ppb) and j(O^{1}D) (s^{-1}) measured during the summer campaign are shown in Figure 1~~Figure 1~~. j(O^{1}D) showed a maximum at solar noon peaking at 2.5×10^{-5} s^{-1}. The diurnal variation in both NO and NO$_2$ was very distinct, with a peak in NO at rush hour (~08:00) of ~ 8 ppb. NO decreased into the afternoon following this morning peak to a minimum of 0.3 ppb. The low values of NO mixing ratio observed in the afternoon were a result of high levels of O$_3$, peaking at 89 ppb at ~15:30, leading to increased titration of NO + O$_3$ to give NO$_2$, the diurnal of which can be seen to peak in the morning at   ~ 32 ppb at 06:30, coinciding with peak in traffic emissions. Conversely

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O$_3$ mixing ratio was at a minimum of ~14 ppb during the morning traffic peak in NO. Due to the expected accumulation of HONO overnight, HONO mixing ratio is highest in the morning, peaking before 07:30 at ~ 7 ppb, after which HONO is lost rapidly via photolysis to give OH + NO. This study will use these measured observations to compare modelled and measured concentrations of OH, HO$_2$ and RO$_2$ radicals and investigate the effect of HO$_2$ uptake on radical concentrations.
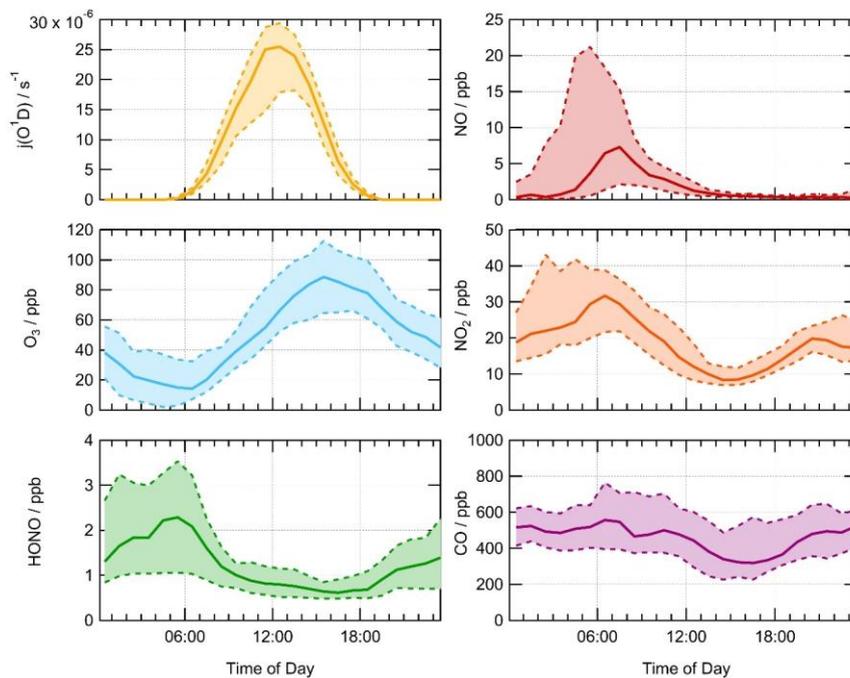

Figure 1. Average median diurnal profile for measured j(O^{1}D) (s^{-1}), O$_3$ (ppb), HONO (ppb), NO (ppb), NO$_2$ (ppb) and CO (ppb) for the Summer AIRPRO campaign. The dashed lines with shaded regions represent the 25th/75th percentiles. Diurnals show 60 minute averages, taken over the entire measurement period.

The majority of the Summer Beijing campaign occurred during a non-haze period, meaning PM$_{2.5}$ concentrations remained below 75 µg m^{-3}, only exceeding this on the 28/05, 31/05, 05/06, 07/06, 17/06 and 18/06/2017. The average median diurnal of PM$_{2.5}$ surface area (cm^2 cm^{-3}) is shown in Figure 2Figure 2. PM$_{2.5}$ surface area concentration was available at a higher resolution due to use of online particle sizers compared to filter samples taken daily to give PM$_{2.5}$ mass concentration. PM$_{2.5}$ surface area was then averaged up to a time resolution of 15 minutes to be used in the model. Online particle sizers were run without a drying inlet to

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406 ensure aerosol measurements were as close to real ambient size distributions as possible, and
407 therefore correction for hygroscopic growth was not necessary. No strong diurnal trend was
408 seen, with an average across the campaign of 5.5×10^{-6} cm^2 cm^{-3}, with a maximum surface
409 area of 2.5×10^{-5} cm^2 cm^{-3}.

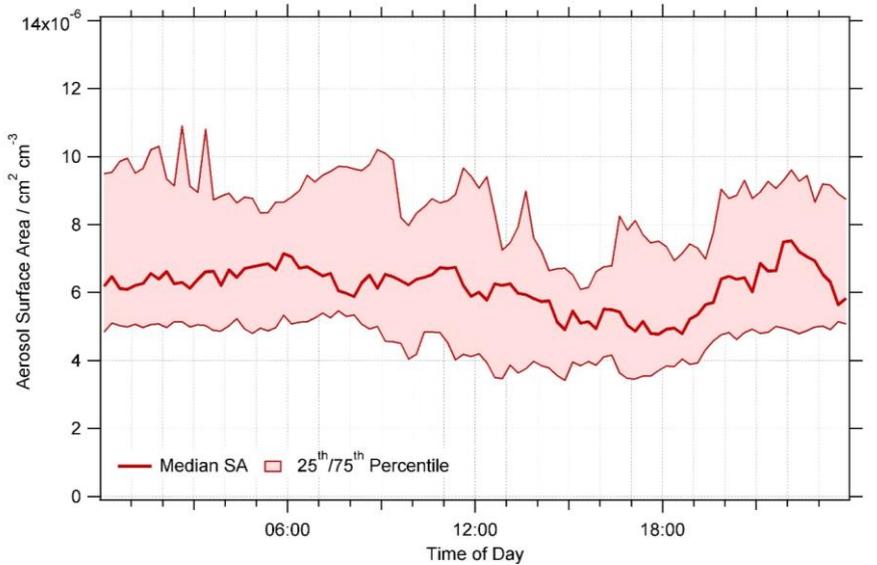**Figure 2.** Average median diurnal of PM$_{2.5}$ aerosol surface area (cm^2 cm^{-3}) for Summer AIRPRO campaign. Data averaged up to 15 mins time resolution. The dashed lines with shaded regions represent the 25th/75th percentiles.

410 During haze periods in Beijing, it is expected that a strong correlation would exist between
411 PM$_{2.5}$ and NO$_x$, as seen in Winter Beijing AIRPRO campaign in 2016 (Slater et al., 2020).
412 However, during the Summer campaign, no strong correlation between PM$_{2.5}$ and NO$_x$ was
413 seen. The time series of NO (ppb) and PM$_{2.5}$ (cm^2 cm^{-3}) is shown in Figure 3Figure 3. A
414 correlation plot of PM$_{2.5}$ aerosol surface area (cm^2 cm^{-3}) versus NO and NO$_2$ mixing ratio (ppb)
415 is shown in Figure 1 of Supplementary Information.

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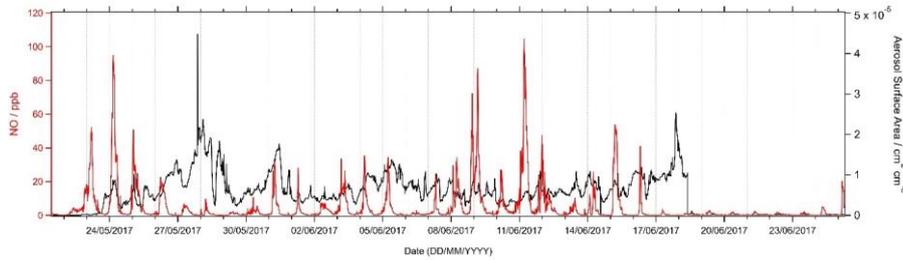Formatted: Font: 12 pt, Not Bold, Not Italic

Figure 3. Time series of measured NO / ppb and PM$_{2.5}$ / cm^2 cm^{-3} across entire summer AIRPRO campaign in Beijing.

3.2 Calculated γ_{HO_2} for summer AIRPRO campaign

Measured values of [PM], copper (II) ion concentration and aerosol pH (used to calculate H_{eff} in equation 12), and values of [ALWC] estimated using the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) were input into the parameterisation at a time resolution of 1 day. PM$_{2.5}$ mass concentration and Cu (II) ion concentration values were measured by extracting from filter samples offline with one filter sample taken every day. As such all measured values input into the parameterisation were averaged up to this time resolution. R_d was calculated from the measured aerosol size distribution across the entire campaign. A value of 0.5 was chosen for the mass accommodation coefficient, a_{HO_2} , to reflect values previously measured for copper doped inorganic salts (Thornton and Abbatt, 2005; George et al., 2013; Taketani et al., 2008) and to allow better comparison with results from Song et al., 2020. For summer AIRPRO campaign, the soluble copper ion concentration was measured by extracting Cu (II) ions from filter samples and analysing the effluent using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). As in Song et al., 2020, the total copper (II) mass concentration (ng m^{-3} converted to g m^{-3}) was divided by the aerosol volume concentration (nm^3 cm^{-3} converted to dm^3 m^{-3}) and the molar mass of copper (g mol^{-1}) to give the total copper molar concentration in the aerosol, [Cu^{2+}]$_{eff}$ (mol L^{-1}), which was then used in equation 12. The average values across summer AIRPRO campaign for parameters used in equation 12 are shown in Table 3Table 3.

Parameter	Average value across campaign
Temperature (K)	300
Relative humidity (%)	43
Aerosol pH	3

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Count median radius (cm)	2.3×10^{-6}
ALWC (µg m^{-3})^a	14
[PM] (µg m^{-3})	38.3
[Cu^{2+}]$_{eff}$ (mol L^{-1})	0.0008
[Cu^{2+}]$_{eff}$ (ng m^{-3})	4
$\boldsymbol{a_{HO_2}}$	0.5 (fixed)

435 **Table 3.** Average values for summer AIRPRO campaign in Beijing, 2017 for parameters in equation 12. ^{a}This
436 was a fixed minimum value of ALWC for the parameterisation to be used for this data set, fully explained in
437 Section 3.4. Cu (II) ion concentration is given in both mol L^{-1} and ng m^{-3}, due to mol L^{-1} being used in equation
438 12 but ng m^{-3} being the more atmospherically relevant unit.

439 For the Beijing summer AIRPRO campaign, an average value of $\gamma_{HO_2} = 0.07 \pm 0.035$ (1σ) was
440 calculated across the entire campaign, with values ranging from 0.002 to 0.15. The time series
441 for the calculated γ_{HO_2}, R_d (cm), [PM] (µg m^{-3}), [ALWC] (µg m^{-3}) and [Cu^{2+}]$_{eff}$ (mol L^{-1}) is
442 shown in Figure 4Figure 4.

443 As fully described in Song et al., 2020 supplementary information, the uncertainty in the
444 calculation of γ_{HO_2} using equation 12 comes mainly from the uncertainty in [ALWC] (~10-20
445 %, calculated using ISORROPIA-II (Fountoukis and Nenes, 2007)), the uncertainty in the mass
446 accommodation coefficient (varying a_{HO_2} within the parameterisation from 0.1 to 1, increased
447 the calculated γ_{HO_2} from 0.042 to 0.077. However, by $a_{HO_2} = 0.5$ this dependence has begun to
448 plateau with $\gamma_{HO_2} = 0.070$ when $a_{HO_2} = 0.5$), and the uncertainty of the model calculations used
449 to formulate the parameterisation (~40 % as explained in Song et al., 2020). Uncertainties in
450 measured parameters i.e. temperature, [PM], [Cu^{2+}] and count median radius are due to
451 associated instrumental error which are assumed small in comparison.
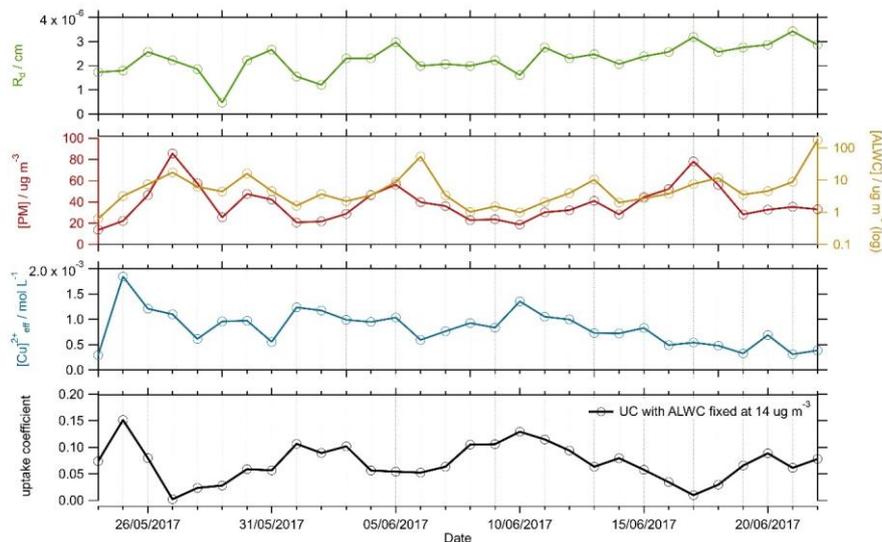
Figure 4. Time series of R_d (cm, orange), [PM] (µg m^{-3}, red), [ALWC] (µg m^{-3}, yellow) and [Cu^{2+}]$_{eff}$ (mol L^{-1}, blue), parameters used in equation 1~~2~~ to calculate γ_{HO_2} (bottom panel). Each parameter has been averaged up to a time resolution of 1 day to match the lowest resolution measurement. The calculated γ_{HO_2} is shown in the bottom panel, for a fixed [ALWC] = 14 ug m^{-3} (solid black line).

To examine the effect within the Song parameterisation of [PM] and [ALWC] on γ_{HO_2} as a function of copper molarity, the uptake coefficient was calculated by varying the [Cu^{2+}]$_{eff}$ concentration within the parameterisation with alternatively fixed values of [PM] or [ALWC]. For a given value of [Cu^{2+}]$_{eff}$, at fixed [ALWC] an increase in [PM] causes a decrease in the curvature of γ_{HO_2} vs [Cu^{2+}]$_{eff}$, whereas at a fixed [PM], an increase in [ALWC] leads to an increase in γ_{HO_2} for a given [Cu^{2+}]$_{eff}$. As shown in Figure 5~~Figure 5~~, [AWLC] and [PM] have the greatest effect on γ_{HO_2} between [Cu^{2+}]$_{eff}$= 10^{-5}-10^{-1}M before the curve levels off towards the mass accommodation coefficient of 0.5, as input into the model. For context within the Beijing campaign, the curve of γ_{HO_2} vs [Cu^{2+}]$_{eff}$ was plotted in Figure 5~~Figure 5~~ using the average values for the AIRPRO summer campaign fixed at [ALWC] = 14 ug m^{-3} and [PM] = 38.3 ug m^{-3}. For the average AIRPRO summer campaign values, an increase [Cu^{2+}]$_{eff}$ has the most effect on γ_{HO_2} between [Cu^{2+}]$_{eff}$ ~10^{-3} -10^{-1} M, with the average [Cu^{2+}]$_{eff}$ for the campaign being 8×10^{-4} M (values ranged from 3×10^{-4} to 2×10^{-3} M across campaign).
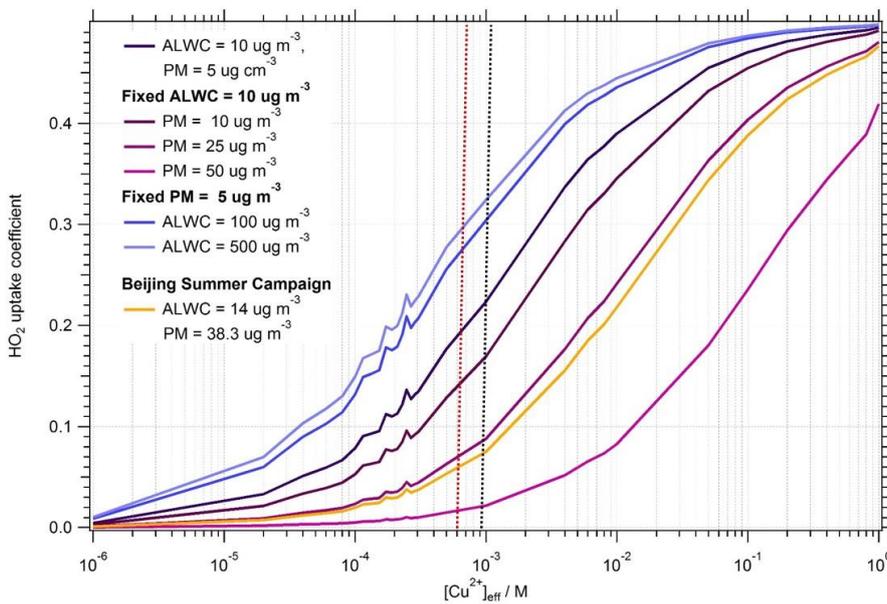
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Figure 5. Dependence of uptake coefficient, γ_{HO_2} on aerosol copper concentration, $[Cu^{2+}]_{eff}$ (M), showing the effect of varying [PM] with fixed [ALWC] and vice versa. Pink to purple lines show the effect on uptake coefficient of varying [PM] from 5-50 µg m^{-3} with a fixed [ALWC] of 10 g cm^{-3}. Blue to dark blue lines show the effect on γ_{HO_2} of varying [ALWC] from 10-500 ug m^{-3} (much higher than typically seen atmospherically) with a fixed [PM] of 5 µg m^{-3}. The yellow line shows the effect on the γ_{HO_2} of varying $[Cu^{2+}]_{eff}$, with [ALWC] and [PM] taken as the averages from the Beijing campaign, i.e. [ALWC] = 14 ug m^{-3} and [PM] = 38.8 ug m^{-3}. Black dashed line indicates the average $[Cu^{2+}]_{eff}$ for Beijing summer campaign. Red dashed line indicates the average $[Cu^{2+}]_{eff}$ for the Wangdu campaign. Note that the [PM] and [ALWC] are both higher for Wangdu campaign compared to the Beijing campaign.

3.3   Box modelling results

3.3.1   Effect of calculated γ_{HO_2} on modelled AIRPRO Summer radical concentrations

As reported in Whalley et al., 2021, radical concentrations were high during the AIRPRO summer campaign with maximum measured concentrations of OH, HO$_2$ and RO$_2$ of 2.8×10^7 molecule cm^{-3}, 1×10^9 molecule cm^{-3} and 5.5×10^9 molecule cm^{-3} on the afternoons of the 30th May, 9th June and 15th June respectively. The time series of measured OH, HO$_2$ and RO$_2$ for the entire summer campaign as measured by the Leeds FAGE instrument with MCM_base model outputs for OH, HO$_2$ and RO$_2$ can be found in Whalley et al., 2021. Using the MCM and the γ_{HO_2} calculated for the Summer Beijing campaign with the Song parameterisation, the effect of HO$_2$ uptake on the concentration of OH, HO$_2$ and RO$_2$ radicals was investigated and compared to the base model.

The MCM_base model predicted radical concentrations are shown as average diurnal profiles compared to both the measured diurnals and the MCM_gamma model in Figure 6Figure 6. A detailed description of the diurnal variation in measured and modelled OH, HO$_2$ and RO$_2$ radicals for the summer Beijing campaign is given in Whalley et al., 2021, so only a brief summary will be given here.

The average diurnal profiles show that the MCM_base model can re-produce the measured OH concentrations relatively well, however the modelled peak in OH is shifted to the afternoon with a peak at ~14:00 compared to the midday peak in the observations. In comparison, HO$_2$ is over-predicted, particularly during the day with the exception being when NO was high from 9-12th June. Day-time HO$_2$ is over-predicted on average by MCM_base by up to a factor of ~2.9 with a peak in the diurnal at ~ 14:30. In-comparison, daytime RO$_2$ concentration is under-predicted on average by MCM_base by up to a factor of ~7.5, with a larger under-prediction in the morning between ~6:30-10:30 when NO levels were highest. At the peak of the RO$_2$ diurnal, on average the concentration was under-predicted by MCM_base by a factor of ~2.7. While the MCM_base model is able to reproduce measured OH concentrations reasonably well, the inability of this model to reproduce HO$_2$ and RO$_2$ suggests missing key reactions. In Whalley et al., 2021, budget analysis highlighted a missing source of OH, in addition to a missing RO$_2$ production reaction which could partially explain the under-prediction of RO$_2$ by the MCM_base model. It was also suggested that the over-prediction of HO$_2$ could be due, in part, to an under-prediction in the rate of reaction of RO$_2$ with NO to produce a different RO$_2$ species, i.e. RO$_2$+NO →RO$_2$', which would lead to propagation of RO$_2$ to different, more

22

504 ~~oxidised RO₂ species, competing with the recycling of RO₂ via RO to give HO₂, or due to lack~~
505 ~~of RO₂ autoxidation pathways within the model which could lead to the formation of highly~~
506 ~~oxygenated molecules as opposed to HO₂. The higher measured RO₂ concentrations could,~~
507 ~~therefore, suggest that the lifetime of total RO₂ is longer than currently considered in the model.~~
508 the over-prediction of HO_2 could be due, in part, to the propagation rate of RO_2 to HO_2 being
509 significantly slower than currently included in the model. This could be due to a lack of
510 understanding of the rate of reaction of RO_2 with NO to produce different RO_2 species, i.e.
511 $RO_2 + NO \rightarrow RO_2$', which would lead to propagation of RO_2 to different, more oxidised RO_2
512 species, competing with the recycling of RO_2 via RO_2 to give HO_2. It is also possible, that the
513 overestimation in the propagation rate of RO_2 to HO_2 could be due to a lack of RO_2 autoxidation
514 pathways included within the model which could lead to the formation of highly oxygenated
515 molecules as opposed to HO_2. The higher, measured RO_2 concentrations could, therefore,
516 suggest that the lifetime of total RO_2 is longer than currently considered within the model.

517 As stated in Section 3.3, for the Beijing summer AIRPRO campaign, values of calculated γ_{HO_2}
518 varied ranging from 0.002 to 0.15, giving an average value of $\gamma_{HO_2} = 0.07 \pm 0.035$ (1σ) across
519 the campaign. These γ_{HO_2} values calculated on a daily time resolution, were added into the
520 MCM_base model to give the MCM_gamma model. The average median diurnals of modelled
521 OH, HO₂ and RO₂ (molecule cm⁻³) for MCM_base, MCM_gamma (with γ_{HO_2} ranging from
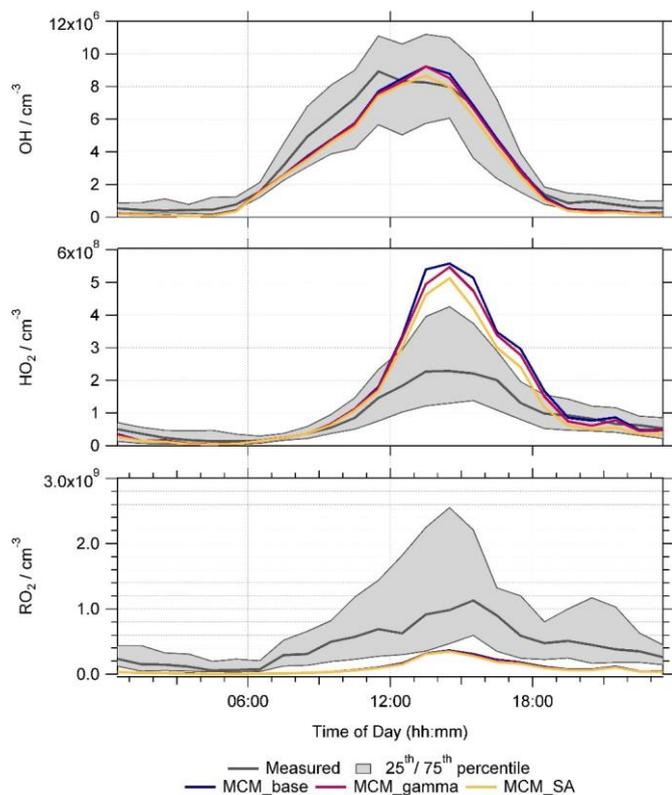522 0.002-0.15) and MCM_SA (with γ_{HO_2} fixed at 0.2) are shown in Figure 6~~Figure 6~~.

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Figure 6. Average median diurnals for measured radical concentrations (grey) and modelled OH, HO_2 and total RO_2 radical concentrations in molecule cm^{-3} for MCM_base (blue), MCM_gamma (dark pink) and MCM_SA (yellow) model runs. All diurnal's are 60 minute averages, taken over the entire measurement period. Shaded grey regions represent the $25^{th}/75^{th}$ percentiles of measured radical data.

523   Due to a combination of the calculated uptake coefficient being smaller, on average, than
524   usually used within models (i.e < 0.2), and the high NO_x levels, little effect on average radical
525   diurnals was seen by adding in HO_2 aerosol uptake into the model. Figure 6Figure 6 shows that
526   the OH and RO_2 radical concentrations were not significantly affected on average across the
527   campaign by the addition of aerosol uptake. The average median diurnal of HO_2 can be seen
528   as slightly decreased, i.e. the over-prediction of HO_2 is slightly less for MCM_gamma
529   compared to MCM_base, with the over-prediction decreasing from a factor of ~2.9 to ~2.4 at
530   the 14:30 peak in the diurnal.

531   Due to the recycling of RO_2 to HO_2 and then back to OH by NO, it is important to consider the
532   dependency of radicals on NO and whether the addition of the HO_2 uptake coefficient has an

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533 effect on the model's ability to predict the dependency of radical concentrations on NO. The

534 dependency of measured/modelled OH, HO_2 and RO_2 on NO mixing ratio is discussed fully

535 for the MCM_base model in Whalley et al., 2021, and is compared to MCM_gamma in Figure

536 2 of Supplementary Information. Figure 7 shows the ratio of measured to modelled OH, HO₂

537 and RO₂ radical concentrations binned against NO mixing ratio (ppb) for MCM_gamma,
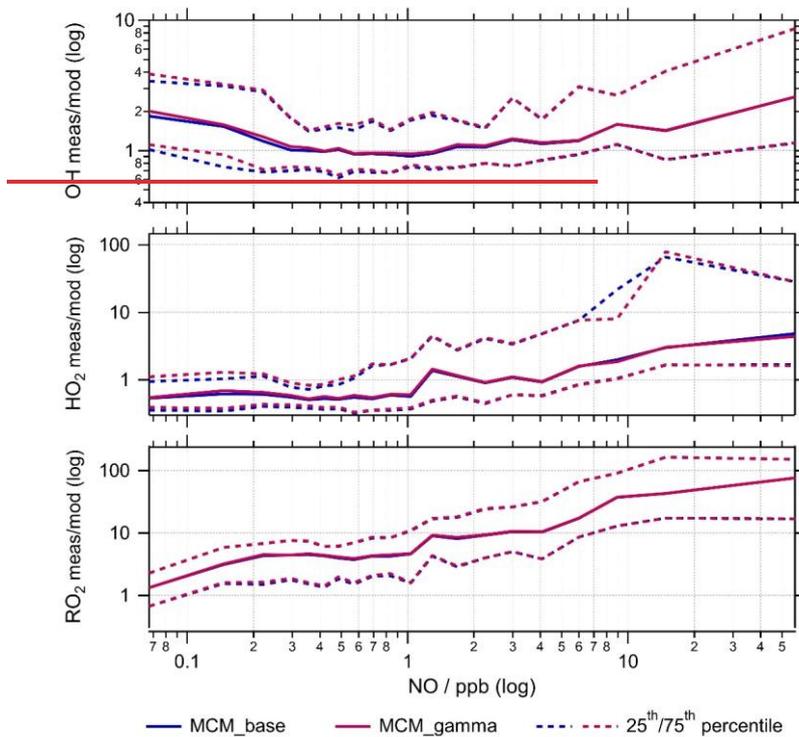
538 compared to MCM_base.

Figure 7. Ratio of measured to modelled OH, HO₂ and RO₂ radical concentrations using the MCM_base (blue)
and MCM_gamma (dark pink) model binned over the range of NO mixing ratios (ppb) for the summer AIRPRO
campaign. Solid lines show the median average measured to modelled radical concentration. Dashed lines show
the 25ᵗʰ/75ᵗʰ percentiles.

539 For the range of NO mixing ratios observed across the summer AIRPRO campaign, the OH

540 measured to modelled ratio is close to 1 between ~0.3 and 2 ppb NO with the MCM_base

541 model beginning to under-predict OH slightly both below 0.3 ppb NO and above 2 ppb NO.

542 Both HO₂ and RO₂ radical concentrations were strongly dependent on NO mixing ratio, with

543 the model over-predicting HO₂ below ~1 ppb NO. For the entire campaign the average NO

544 was 4.7 ppb with 45% of NO measurements taken across campaign being less than or equal to
545 1 ppb. Across all NO mixing ratios the measured to modelled ratio for RO_2 shows a large
546 under-prediction, with the largest under-prediction at the highest NO mixing ratios. This is
547 likely contributing to the underprediction of HO_2 at higher NO mixing ratios. From Figure 7 it
548 can be seen that the addition of the calculated HO_2 uptake coefficient has had little effect across
549 the range of NO mixing ratios measured during the summer AIRPRO campaign.

550 To showcase any effect adding HO_2 aerosol uptake would have on HO_2 loss pathways as a
551 whole, and thereby make a judgement on the effect of decreased $PM_{2.5}$ and hence HO_2 loss via
552 aerosol surfaces on the O_3 production within Beijing, a rate of destruction analysis (RODA)
553 was done for MCM_gamma. The loss pathways of HO_2 within MCM_gamma are shown in
554 Figure 7Figure 8 as an average median diurnal and as a function of NO mixing ratio (ppb), in
555 addition to the percentage contribution of HO_2 uptake to the overall loss of HO_2 within the
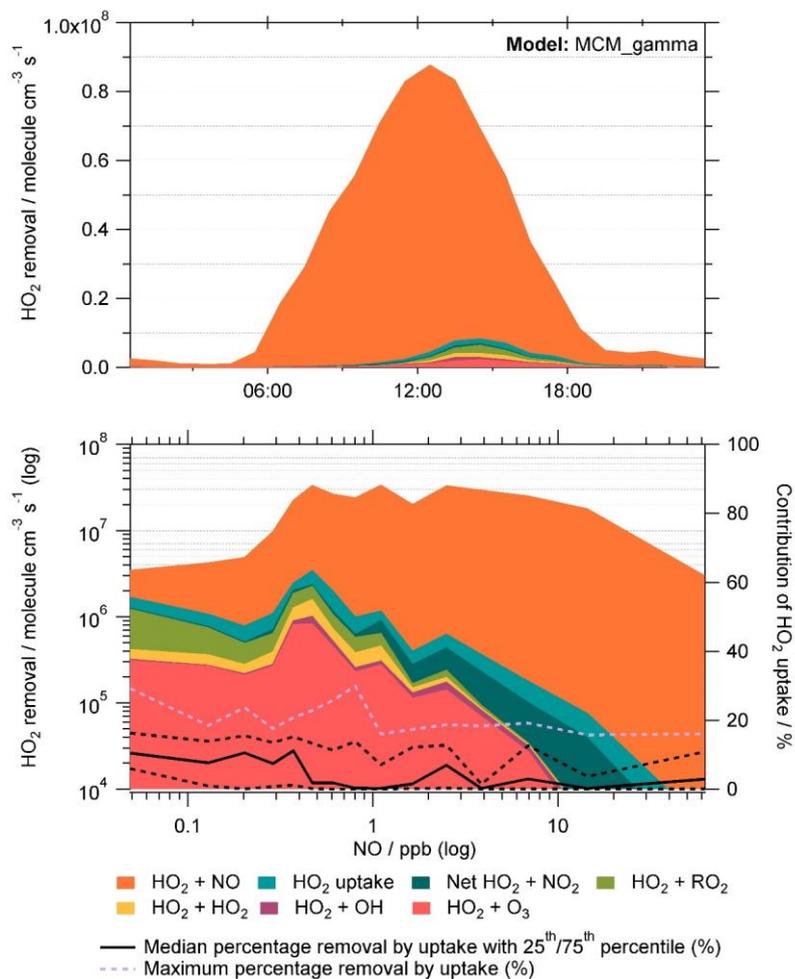556 model.

557

Figure 78. Rate of destruction analysis (RODA) showing the dominant loss pathways of HO_2 within MCM_gamma shown as (a) a diurnal variation and (b) as a function of NO mixing ratio (ppb). Median removal of HO_2 by uptake (%) as a function of NO (ppb) is shown as solid black line in (b), with $25^{th}/75^{th}$ percentile shown as the black dashed lines. Maximum percentage removal by uptake for a given NO mixing ratio is shown as a lilac dashed line.

558 As shown in the RODA, the dominant loss pathway of HO_2 is HO_2 + NO across the entire
559 campaign (90 ± 14 % of total loss), followed by HO_2 + RO_2 (3.5 ± 8.1 % of total loss). This is
560 expected due to high levels of NO_x in Beijing, especially during the day. As seen in the RODA
561 diurnal, the HO_2 + NO loss pathway peaks at midday following the morning peak in NO mixing
562 ratio due to rush hour traffic. As NO mixing ratio decreases, the relative importance of other

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loss pathways of HO_2 increases. At the lowest NO mixing ratio, i.e. < 0.1 ppb NO, the loss pathways of HO_2 within MCM_gamma with the largest contribution to total loss were HO_2 + NO (55 ± 19 %), HO_2 + RO_2 (23 ± 17 %) and HO_2 + O_3 (9.3 ± 4.1 %). It is worth noting that as the NO mixing ratio decreases the relative importance of HO_2 removal by O_3 increases presumably due to the titration reaction of O_3 with NO decreasing (and hence higher observed $[O_3]$). This could be important when considering policy changes with NO_x pollution in China decreasing in recent years. The contribution of the various loss pathways of HO_2 to total HO_2 loss within MCM_gamma under low (< 0.1 ppb) and high (>0.1 ppb) NO are compared in Table 4Table 4.

	HO_2+O_3	HO_2+OH	HO_2+HO_2	HO_2+RO_2	Net HO_2+NO_2	HO_2+NO	uptake
Low NO (< 0.1 ppb)	9.3 ± 4.1	0.1 ± 0.1	3.0 ± 1.8	23 ± 17	2.4 ± 3.0	55 ± 19	7.3 ± 7.3
High NO (> 0.1 ppb)	1.8 ± 2.3	0.2 ± 0.3	0.8 ± 1.3	2.0 ± 4.4	0.4 ± 1.2	93 ± 9.0	1.9 ± <0.01

Table 4. Average relative percentage contribution of individual HO_2 loss pathways to the total loss of HO_2 within MCM_gamma, averaged for days when NO was low, (< 0.1 ppb) and high (> 0.1 ppb). Net HO_2+NO_2 refers to HO_2+NO_2→HO_2NO_2 minus HO_2NO_2→HO_2+NO_2.

Though there is not a strong dependence of HO_2 aerosol uptake loss pathway on NO mixing ratio for the calculated γ_{HO_2} (av. 0.07 ± 0.035) within MCM_gamma, it can be seen that at the lowest NO mixing ratios an average of ~7 % of total HO_2 loss is due to uptake, with a maximum at the lowest NO of ~29% (shown as lilac dashed line in Figure 7Figure 8). This is a significant loss of HO_2, especially on days where the NO mixing ratio is low and the aerosol surface area is high, highlighting that the uptake of HO_2 onto aerosols could be important, and will be increasingly so at lower NO.

3.3.2 Comparison to γ_{HO_2} fixed at 0.2

While the maximum γ_{HO_2} calculated using the Song parameterisation for the summer AIRPRO campaign was 0.15, to provide context with previous modelling studies, the commonly used fixed value of γ_{HO_2}= 0.2 was added into the MCM_base model to give the MCM_SA model. The average median diurnals of modelled OH, HO_2 and RO_2 (molecule cm^{-3}) for MCM_base, MCM_gamma and MCM_SA are shown in Figure 6Figure 6.

In comparison to calculated γ_{HO_2} in MCM_gamma, a fixed γ_{HO_2}= 0.2 had a more significant effect on radical concentrations. While the median diurnal shows that the RO_2 concentration was not significantly affected by the addition of HO_2 uptake, the over-prediction seen in the average median HO_2 concentration compared to the measurements at the 14:30 peak decreased

592   from a factor of ~2.9 in MCM_base to ~2.3. A plot of measured to modelled ratio of HO2 as a

593   function of aerosol surface are is shown in Figure 4 of Supplementary Information for both

594   MCM_gamma and MCM_SA. OH radical concentrations were still relatively well reproduced

595   with early afternoon OH concentrations predicted better though this is due to a shift in the

596   modelled peak compared to the measured concentration peaking at midday. The ability of the

597   model to reproduce the NO dependence of radical concentrations with the addition of

598   ~~As seen in Figure 9, the addition of~~ γ_{HO_2} = 0.2 is discussed in Section 1.3 of Supplementary

599   Information.

600   ~~affected the ability of the model to reproduce the NO dependence of radical concentrations.~~

601   ~~While MCM_base over-predicts HO₂ below ~ 1 ppb NO, the over-prediction of HO₂ decreases~~

602   ~~below 1 ppb NO for MCM_SA with HO₂ being well reproduced at the lowest NO mixing ratios~~

603   ~~(i.e. < 0.1 ppb) due to the relative increase in the importance of HO₂ uptake as a sink of HO₂.~~

604   ~~Modelled RO₂ is not significantly affected by the addition of HO₂ uptake at any NO mixing~~

605   ~~ratio. The modelled concentration of OH is under-predicted for the entire range of NO mixing~~

606   ~~ratios compared to measured values, though only slightly between ~ 1 and 6 ppb NO. Below ~~~

607   ~~4 ppb NO, the underprediction of OH by MCM_SA increases compared to MCM_base due~~

608   ~~most likely to loss of HO₂ onto aerosols competing with loss via NO to give OH. Budget~~

609   ~~analysis done by Whalley et al., 2021, showcases that with a reduction in over-prediction of~~

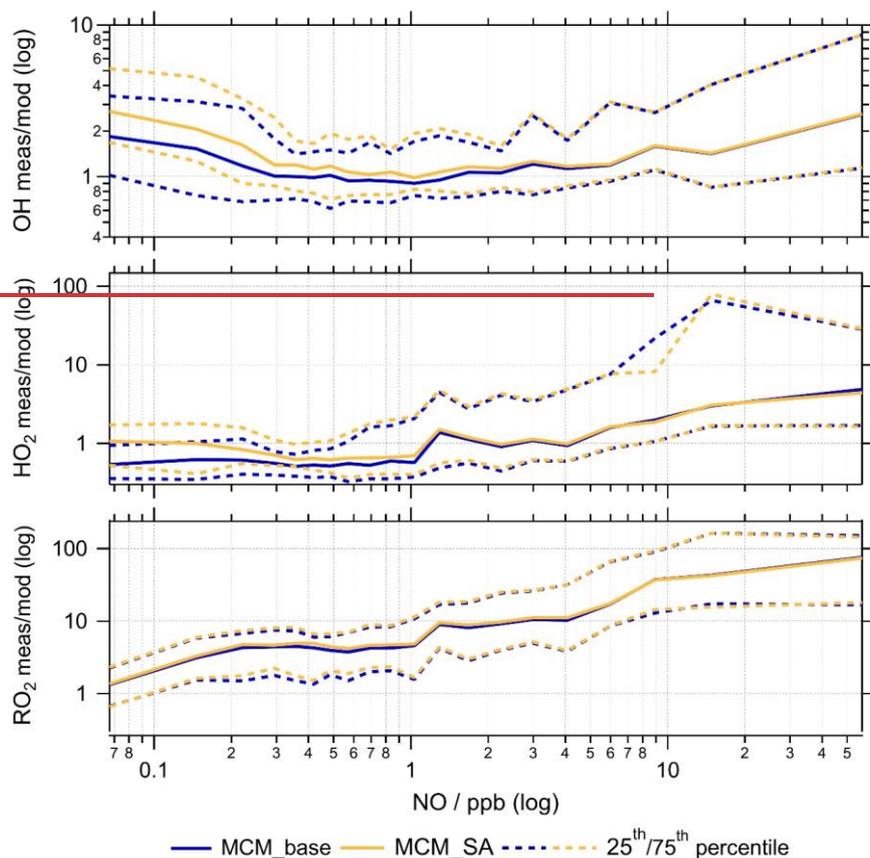610   ~~modelled HO₂, OH is under-predicted revealing a missing OH source.~~

Analysis of the RODA for MCM_SA shows that with γ_{HO_2} = 0.2 HO₂ aerosol uptake is a significant contributor to total loss of HO₂ (8.1 ± 13 %, averaged for all NO mixing ratios). However, for all NO mixing ratios HO₂ + NO is still the dominant loss pathway (86 ± 18 %), as expected. At the lowest NO mixing ratios (i.e. < 0.1 ppb) an average of ~29 % of total HO₂ loss is due to uptake, with a maximum at the lowest NO of ~78%, shown in Figure 8Figure 10. The contribution of the various loss pathways of HO₂ to total HO₂ loss within MCM_gamma under low (< 0.1 ppb) and high (>0.1 ppb) NO are compared in Table 5Table 5. The comparison

618 of percentage contribution of HO$_2$ uptake to total HO$_2$ removal binned against NO mixing ratio
619 (ppb) for MCM_gamma and MCM_SA RODA is shown in Figure 8Figure 10.

	HO$_2$+O$_3$	HO$_2$+OH	HO$_2$+HO$_2$	HO$_2$+RO$_2$	Net HO$_2$+NO$_2$	HO$_2$+NO	uptake
Low NO (< 0.1 ppb)	6.9 ± 3.5	0.1 ± 0.1	1.7 ± 1.4	17 ± 14	1.6 ± 2.2	44 ± 24	29 ± 24
High NO (> 0.1 ppb)	1.8 ± 2.1	0.2 ± 0.2	0.6 ± 1.0	1.7 ± 3.8	0.4 ± 1.0	89 ± 13	6.5 ± 9.7

620 **Table 5.** Average relative percentage contribution of individual HO$_2$ loss pathways to the total loss of HO$_2$ within
621 MCM_SA (fixed γ_{HO_2} = 0.2), averaged for days when NO was low, (< 0.1 ppb) and high (> 0.1 ppb). Net
622 HO$_2$+NO$_2$ refers to HO$_2$+NO$_2$→HO$_2$NO$_2$ minus HO$_2$NO$_2$→HO$_2$+NO$_2$.
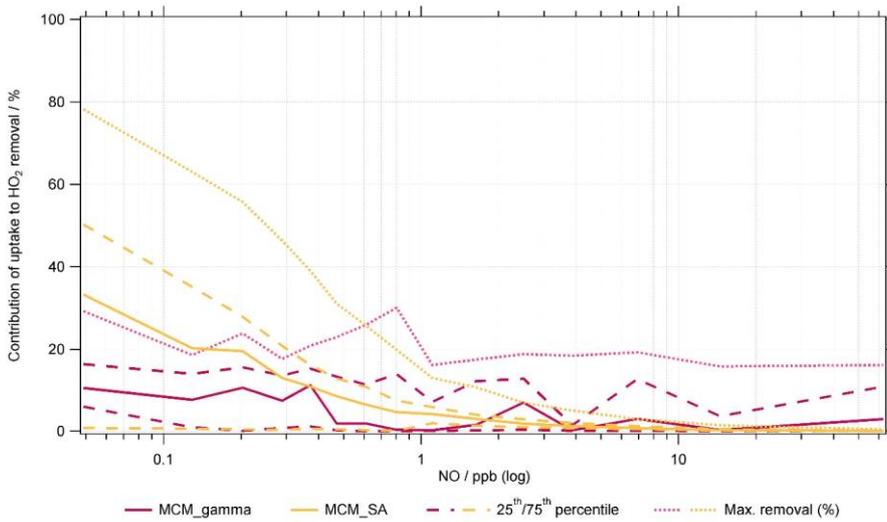

Figure 810. Average percentage contribution of HO$_2$ uptake to total HO$_2$ removal within MCM_gamma (pink
line, γ_{HO_2}= 0.070 ± 0.035) and MCM_SA model (yellow line, γ_{HO_2} = 0.2) for Summer AIRPRO campaign
plotted as a function of NO mixing ratio (ppb). Dashed lines represent the 25th/75th percentiles. Dotted lines
represent maximum removal.

623 ### 3.3.3 Effect of γ_{HO_2} on the O$_3$ regime

624 3.3.3.11.1.1.1 Calculation of L$_N$/Q and absolute O$_3$ sensitivity
625 First introduced by Kleinman et al., 1997, L$_N$/Q is the ratio of radical loss via NO$_x$ to total
626 primary radical production and is used as a means of determining O$_3$ production sensitivity to
627 VOCs and NO$_x$ (Kleinman, 2000; Kleinman et al., 1997; Kleinman et al., 2001). This method
628 was then built on by Sakamoto et al., 2019 who included loss of peroxy radicals
629 (XO$_2$=HO$_2$+RO$_2$) onto aerosol surfaces within the calculation of O$_3$ sensitivity.

The only source of tropospheric O_3 is by the reaction of peroxy radicals with NO, while the main source of XO_2 species is via the reaction of OH with VOCs.

$$XO_2 + NO \rightarrow XO + NO_2 \tag{R 1}$$

$$OH + VOC + O_2 \rightarrow XO_2 + products \tag{R 2}$$

The O_3 production rate in the troposphere is therefore:

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + k_{RO_2+NO}[RO_2][NO] \tag{2}$$

where k_{HO_2+NO} and k_{RO_2+NO} are the bimolecular rate constants for the reaction of HO_2 and RO_2 with NO.

The production rate of OH, HO_2 and RO_2 radicals, Q, must equal the loss rate:

$$Q = L_P + L_N + L_R \tag{3}$$

where L_P is the loss rate of radicals onto aerosol particles, L_N is the loss rate of radicals via reaction with NO_x species and L_R is the loss rate of radicals via radical-radical reactions to give peroxides.

$$L_P = k_{HO_2 \ uptake}[HO_2] + k_{RO_2 \ uptake}[RO_2] = k_P[XO_2] \tag{4}$$

$$L_N \sim k_{NO_2+OH}[NO_2][OH] \tag{5}$$

$$L_R = 2(k_{HO_2+HO_2}[HO_2]^2 + k_{RO_2+HO_2}[HO_2][RO_2]) \tag{6}$$

where $k_{HO_2 \ uptake}$ is the rate constant for the loss of HO_2 onto aerosol surfaces, $k_{RO_2 \ uptake}$ is the rate constant for the loss of RO_2 onto aerosol surfaces, k_{NO_2+OH} is the bimolecular rate constant for the reaction of NO_2 with OH, $k_{HO_2+HO_2}$ is the bimolecular rate constant for the self-reaction of HO_2 and $k_{RO_2+HO_2}$ is the bimolecular rate constant for the reaction of RO_2 with HO_2.

For radical loss onto aerosol surfaces, the rate constant is given as a function of the reactive uptake coefficient, γ_{XO_2}, aerosol particle surface area (cm^2 cm^{-3}) and mean thermal velocity (cm s^{-1}), given by $\nu = \sqrt{8RT/\pi M}$ with R, T and M as the gas constant, the absolute temperature and the molar mass of species respectively.

$$k_{radical \ uptake} = \frac{\gamma_{XO_2} \times SA \times \nu}{4} \tag{7}$$

According to the method described in Sakamoto et al., 2019, the ratio of radical loss to NO_x to primary O_3 production including radical loss via aerosol uptake, $\frac{L_N}{Q}$ is defined as follows:

$$\frac{L_N}{Q} = \frac{1}{1 + \left(\frac{(2k_R[XO_2] + k_P)k_{OH+VOC}[VOC]}{(1-\alpha)k_{HO_2+NO}[NO]k_{NO_2+OH}[NO_2]} \right)} \tag{8}$$

where k_{OH+VOC} is the bimolecular rate constant for the loss of OH via reaction with VOCs and $(1-\alpha)$ is the fraction of XO_2 that is HO_2.

The relative sensitivity of O_3 production to NO_x and VOCs is described by:

$$\frac{\delta lnP(O_3)}{\delta ln\,[NO_x]} = (1-\chi)\left(\frac{1 - \frac{3}{2}\frac{L_N}{Q}}{1 + \frac{1}{2}\frac{L_N}{Q}} \right) + \chi(1 - 2\frac{L_N}{Q}) \tag{9}$$

$$\frac{\delta lnP(O_3)}{\delta ln\,[VOC]} = (1-\chi)\left(\frac{\frac{1}{2}\frac{L_N}{Q}}{1 + \frac{1}{2}\frac{L_N}{Q}} \right) + \chi\frac{L_N}{Q} \tag{10}$$

where $\chi = \frac{L_P}{L_P + L_N}$. The O_3 regime transition point, where $\frac{\delta lnP(O_3)}{\delta ln\,[NO_x]} = \frac{\delta lnP(O_3)}{\delta ln\,[VOC]}$, is given by $\frac{L_N}{Q_{trans}}$.

$$\frac{L_N}{Q_{trans}} = \frac{1}{2}(1-\chi) + \frac{1}{3}\chi \tag{11}$$

Absolute O_3 sensitivity was introduced by Sakamoto et al., 2019, and allows for the assessment of how reduction in O_3 precursors could contribute to reduction in $P(O_3)$ by integrating over time and area. The absolute sensitivity of O_3 production to VOC and NO_x is then described by:

$$Absolute\,P(O_3) = \frac{\delta P(O_3)}{\delta ln\,[X]} = P(O_3)\frac{\delta P(O_3)}{\delta ln\,[X]} \tag{12}$$

where is $[X]$ is NO_x or VOC.

$\frac{L_N}{Q}$ was calculated for all model runs, MCM_base, MCM_gamma and MCM_SA using modelled [HO$_2$] and [RO$_2$] concentrations but measured values of [NO] and [NO$_2$], to investigate the effect on the O_3 regime of adding HO$_2$ aerosol uptake into the model. The time series of calculated $\frac{L_N}{Q}$ for all models, in addition to the regime transition point, $\frac{L_N}{Q_{trans}}$ for the entire campaign is shown in Figure 9Figure 11.

When $\frac{L_N}{Q} < \frac{L_N}{Q_{trans}}$, this is defined as a NO$_x$-sensitive regime, meaning that small changes in NO$_x$ will affect the rate of in situ O$_3$ production. This can be seen on a few days across the campaign, specifically in the afternoon, due to NO$_x$ peaking in the morning due to traffic emissions before rapidly decreasing in the afternoon which pushes the O$_3$ regime on certain days from VOC-

667 limited to NO$_x$-limited. However, for the majority of the campaign, the O$_3$ production regime

668 is VOC-limited, for all models, meaning that O$_3$ production rates will not be significantly

669 affected by small changes in NO$_x$.

670 Binning $\frac{L_N}{Q}$ against NO mixing ratio (ppb), in Figure 10~~Figure 12~~, shows the change from VOC

671 to NO$_x$-limited regime at very low NO mixing ratios for MCM_base, MCM_gamma and

672 MCM_SA. As aerosol uptake is added the transition to NO$_x$-limited regime occurs at higher

673 NO, with average median transition point occurring at ~ 0.2 ppb NO for MCM_gamma

674 (average γ_{HO_2} = 0.070 ± 0.035) and at ~0.5 ppb NO for MCM_SA (fixed γ_{HO_2} = 0.2). This

675 suggests that a reduction in PM (and therefore uptake of HO$_2$ onto aerosols) would delay the

676 transition to a NO$_x$-sensitive regime until lower NO$_x$ levels are reached. Therefore, any

677 emissions policy aimed at reduced NO$_x$ to decrease O$_3$ levels would not be as effective if PM
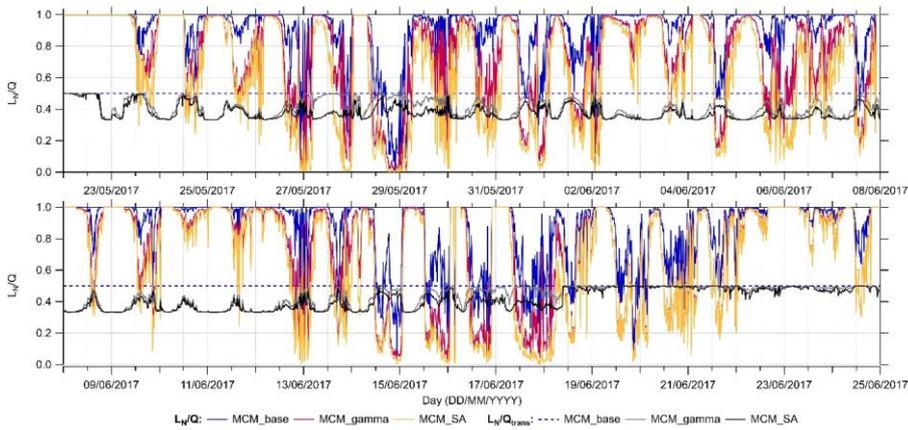
678 is decreasing at the same time.

Figure 9~~11~~. Time series of calculated $\frac{L_N}{Q}$ and $\frac{L_N}{Q_{trans}}$ values for MCM_base (blue), MCM_gamma (pink) and MCM_SA (yellow) models across the entire summer AIRPRO campaign. $\frac{L_N}{Q_{trans}}$ for MCM_gamma is shown as grey line, while $\frac{L_N}{Q_{trans}}$ for MCM_SA is the black line.
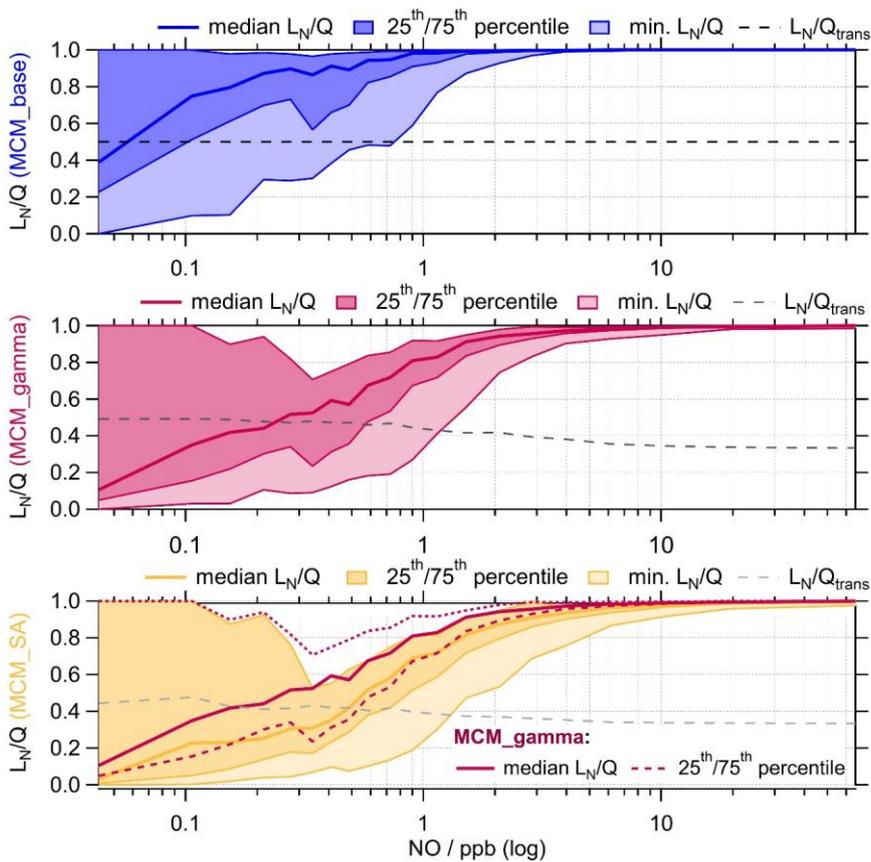
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Figure 10̶1̶2. $\frac{L_N}{Q}$ for MCM_base (blue, top panel), MCM_gamma (pink, middle panel) and MCM_SA (yellow, bottom panel) binned against the log of measured NO mixing ratio for the entire summer AIRPRO campaign. $\frac{L_N}{Q_{trans}}$ for MCM_base (black dashed line) taken as 0.5 for entire range of NO mixing ratios. $\frac{L_N}{Q_{trans}}$ for MCM_gamma (dark grey dashed line) and MCM_SA (light grey dashed line) calculated using equation 1̶10. 25th/75th percentiles and minimum $\frac{L_N}{Q}$ are plotted to show full spread of data for each model scenario.

680   The average median diurnal of absolute P(O$_3$), $\frac{\delta P(O_3)}{\delta \ln [X]}$, for the MCM_gamma and MCM_SA

681   over the entire campaign is shown in Figure 11Figure 13. The time series of absolute P(O$_3$),

682   averaged up to a daily time resolution, across the entire measurement period can be found in

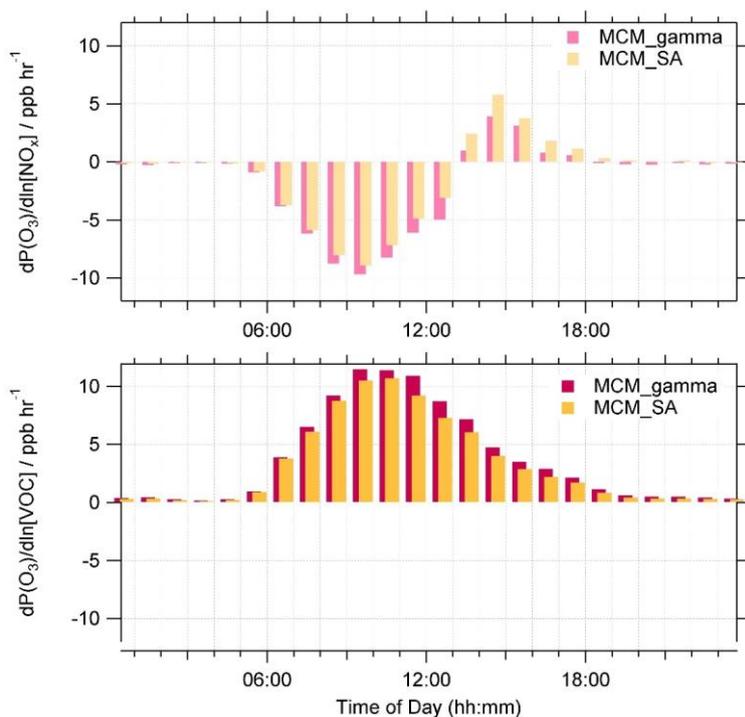683   Supplementary Information as SI Figure 5̶2.

Figure 1113. Average median diurnal of absolute O_3 sensitivity to NO_x (top panel) and VOC (bottom panel) in ppbV h^{-1} for MCM_gamma (pink) and MCM_SA (yellow) across the entire summer AIRPRO campaign. MCM_gamma includes γ_{HO_2} calculated using the Song parameterisation (av. 0.070 ± 0.035) while MCM_SA includes γ_{HO_2} at a fixed value of 0.2. All diurnals are 60 minute averages.

684   As expected from $\frac{L_N}{Q}$ calculations, calculations of absolute O_3 production sensitivity showcase

685   that for both MCM_gamma and MCM_SA, on average, the O_3 regime was VOC sensitive

686   throughout the day with NO_x sensitivity increasing in the afternoons. On a few days, when low

687   NO mixing ratio coincided with high SA, the O_3 regime can be seen shifting from VOC to NO_x

688   limited. An example of this can be found in SI Figure 63, for the 17/06/2017 and 18/06/2017

689   when the average NO mixing ratio was 0.41 ± 0.50 ppb and the average SA was $(8.4 \pm 6.2) \times$

690   10^{-6} cm^2 cm^{-3}. With an increase in γ_{HO_2} between MCM_gamma and MCM_SA, the sensitivity

691   of O_3 regime to VOC decreased but sensitivity to NO_x increased. This effect could be important

692   for areas where O_3 production regime is NO_x sensitive or less strongly VOC sensitive. With

693   NO_x levels reportedly decreasing across China in recent years (Krotkov et al., 2016; Liu et al.,

694   2016; Miyazaki et al., 2017; Van Der A et al., 2017), O_3 production regimes would be expected

695   to move more towards NO_x-sensitive regimes in urban China. However, with concomitant

36

696   reduction in PM (Ma et al., 2016b; Lin et al., 2018), this transition to a NO_x-sensitive regime

697   may be delayed until lower NO_x levels are reached.

698   Our result for the Beijing campaign are consistent with the results of Song et al., 2022 which

699   concluded that for the conditions of the Wangdu campaign the addition of HO_2 uptake does not

700   change the overall O_3 sensitivity regime throughout the campaign. However, the shift in O_3

701   sensitivity regime from VOC-limited to NO_x-limited from the consideration of HO_2 uptake

702   could be important for areas with lower NO_x and high aerosol particle loading.

4   Conclusions

704   Using the Song parameterisation, the heterogeneous uptake coefficient of HO_2, γ_{HO_2}, was

705   calculated for the summer AIRPRO campaign in Beijing, 2017 as a function of measured

706    $[Cu^{2+}]_{eff}$, [ALWC] and [PM]. The calculated average $\gamma_{HO_2} = 0.070 \pm 0.035$ (ranging from 0.002

707   to 0.15 across the campaign) was significantly lower than the fixed value of $\gamma_{HO_2} = 0.2$

708   commonly used in modelling studies. This calculated value was similar, however, to values

709   calculated for the Wangdu 2014 summer campaign in China (Tan et al., 2020; Song et al.,

710   2020). Using the calculated γ_{HO_2}, the OH, HO_2 and RO_2 radical concentrations were modelled

711   using the Master Chemical Mechanism, and compared to the measured campaign values, with

712   and without the addition of HO_2 aerosol uptake. Due to the low calculated value of γ_{HO_2}, and

713   the high levels of NO, rate of destruction analysis showed the dominant HO_2 loss pathway to

714   be HO_2 + NO for all NO mixing ratios with HO_2 uptake not contributing significantly to the

715   loss of HO_2 (< 2 %). However, at the lowest NO mixing ratios (i.e. < 0.1 ppb) HO_2 loss onto

716   aerosols contributed up to a maximum of 29 % of the total HO_2 loss. Using the modelled HO_2

717   and RO_2 radical concentrations for model scenarios with and without HO_2 uptake, showed that

718   on average the O_3 production regime was VOC-limited across the entire campaign with the

719   exception of several days with low NO mixing ratio where the regime tended towards NO_x-

720   limited, meaning that small changes in NO_x would not have a large effect on the O_3 production

721   for this summer period in Beijing, however changes in HO_2 uptake could. While the addition

722   of the calculated uptake coefficient did not change the overall O_3 regime across the campaign,

723   with the O_3 production regime remaining strongly VOC-limited, the transition from a VOC-

724   sensitive to NO_x-sensitive O_3 regime occurs at higher NO_x. This means that for Beijing, where

725   the O_3 production regime is strongly VOC-sensitive and NO_x levels are high, any policy

726   looking to reduce O_3 via the reduction of NO_x needs to consider concurrent PM reduction

727   policies which may affect HO_2 uptake. In cleaner environments, where NO_x levels are lower,

but aerosol surface area is still high, lower values of γ_{HO_2}, i.e. less than 0.2, could have a more significant effect on both overall HO_2 concentration and the O_3 production regime.

Author contributions. LKW, EJS, RWM, CY and DEH carried out the radical measurements. LKW and EJS developed the model and JED performed the calculations. JDL, FS, JRH, RED, MS, JFH, ACL, AM, SDW, AB, TJB, HC, BO, CJP, CNH, RLJ, LRC, LJK, WJFA, WJB, SS, JX, TV, ZS, RMH, SK, SG, YS, WX, SY, LW, PF and XW provided logistical support and supporting data to constrain the model. JED prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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