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Measurements of the HO₂ uptake coefficients onto single component organic aerosols

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1 Abstract

2

3 Measurements of HO₂ uptake coefficients (γ) were made onto a variety of organic aerosols derived
4 from glutaric acid, glyoxal, malonic acid, stearic acid, oleic acid, squalene, mono ethanol amine
5 sulphate, mono-methyl amine sulphate and two sources of humic acid, for an initial HO₂
6 concentration of 1×10^9 molecule cm⁻³, room temperature and at atmospheric pressure. Values in the
7 range of $\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$ were measured for all of the aerosols apart from the aerosols
8 from the two sources of humic acid. For humic acid aerosols, uptake coefficients in the range of $\gamma =$
9 0.007 ± 0.002 to $\gamma = 0.09 \pm 0.03$ were measured. Elevated concentrations of copper (16 ± 1 and $380 \pm$
10 20 ppb) and iron (600 ± 30 and 51000 ± 3000 ppb) ions were measured in the humic acid atomiser
11 solutions compared to the other organics that can explain the higher uptake values measured. A strong
12 dependence upon relative humidity was also observed for uptake onto humic acid, with larger uptake
13 coefficients seen at higher humidities. Possible hypothesises for the humidity dependence include the
14 changing liquid water content of the aerosol, a change in the mass accommodation coefficient or in
15 the Henry's law constant.

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18

19

20 **Introduction**

21

22 The HO₂ radical is important in the troposphere as it is closely coupled with OH, which initiates the
23 removal of many trace gases via oxidation. However, a combination of field measurements of HO₂
24 and comparison with calculations from box modelling has indicated that the heterogeneous uptake of
25 HO₂ by aerosols has the potential to be an important loss pathway of HO₂.¹⁻¹⁷ Global tropospheric
26 models have also shown that in areas of high aerosol loadings, heterogeneous uptake can have a
27 significant impact on gaseous HO₂ concentrations.^{9, 18-22} Therefore, it is important to accurately
28 measure the HO₂ uptake coefficient onto different aerosols and under different conditions in order
29 provide data to constrain both box and global models. There are currently relatively few laboratory
30 measurements of the HO₂ uptake coefficient onto aerosols and surfaces and these have concentrated
31 on effloresced and deliquesced salts, dicarboxylic acids, levoglucosan, soot, copper doped aerosols
32 ammonium sulphate and Arizona Test Dust.²³⁻³⁷

33

34 Organic aerosols are ubiquitous in the troposphere with 20 – 90 % of submicron particulate mass
35 being attributable to organics.^{38, 39} Many different organics have been observed or are predicted to be
36 present in tropospheric aerosols, including both water insoluble organics (e.g. *n*-alkanes, *n*-alkanoic
37 and *n*-alkenoic acids, diterpenoid acids, aromatic polycarboxylic acids, polycyclic aromatic
38 hydrocarbons and oxygenated polyaromatic hydrocarbons) and water soluble organics (e.g.
39 dicarboxylic acids, glyoxal, ketoacids, polyols, hydroxyamines, amino acids and nitrophenol).⁴⁰⁻⁴²
40 Humic-like substances have also been identified as a major component of aerosols and have been
41 measured in different aerosol types including marine aerosols, dust from soil and biomass burning
42 aerosols.⁴³⁻⁴⁸ Although there are high mass fractions of organics and many different types of organics
43 present in tropospheric aerosols, only a few measurements of the HO₂ uptake coefficient have been
44 made in the laboratory onto single component organic aerosols, and these have focused on
45 dicarboxylic acids and levoglucosan.^{32, 35} Therefore, the aim of this study was to extend the
46 measurements to a variety of different single component organic aerosols that are representative of
47 tropospheric aerosol components including both water insoluble (stearic acid, oleic acid and squalene)
48 and water soluble organics (glutaric acid, glyoxal and malonic acid and two sources of humic acid).
49 The first HO₂ uptake measurements were also made onto two aerosols containing amines, mono-
50 methyl amine sulphate aerosols (MMS) and mono ethanol amine sulphate-H₂SO₄ (MEA-H₂SO₄). It
51 should be noted that amines have previously been measured in the atmosphere.⁴⁹ MEA-H₂SO₄ has
52 previously been suggested as suitable for carbon capture and would reduce the medium term CO₂
53 emissions into the troposphere.⁵⁰ If amines were to be used for carbon capture, it is likely that some of

54 these amines would be released into the atmosphere where they could partition to the aerosol phase. It
 55 would therefore be important to understand the impact that these amines would have upon the
 56 concentrations of different species in the atmosphere, including HO₂ concentrations.

57

58 **Experimental**

59

60 An identical experimental setup was used in this work as described in detail by George et al. ,²⁶ and is
 61 therefore only briefly summarised below. An glass aerosol flow tube (coated in halocarbon wax, 107
 62 cm length, 5.9 cm inner diameter) coupled with a sensitive Fluorescence Assay by Gas Expansion
 63 (FAGE) instrument, capable of measuring HO₂ concentrations at ambient levels, which enabled HO₂
 64 uptake coefficients to be measured at room temperature (293 ± 2 K), atmospheric pressure, and at an
 65 initial HO₂ concentration of 1 × 10⁹ molecule cm⁻³. By moving an injector (110 cm length, 1.9 cm
 66 outer diameter, 1.6 cm inner diameter) which released the HO₂ into the flow of aerosols along the
 67 flow tube, pseudo-first order decays of HO₂ were measured at different aerosol surface area
 68 concentrations. Experiments were performed over a range of relative humidities (32 - 80%) which
 69 was varied by using mass flow controllers that controlled the ratio of a dry flow and a humidified flow
 70 from a bubbler. Prior to entering the aerosol flow tube the aerosols were conditioned for ~ 5 seconds
 71 within a conditioning flow tube at the chosen relative humidity.

72

73 **HO₂ production and detection**

74

75 HO₂ radicals were formed through Reactions 1 – 2 by passing humidified nitrogen containing trace
 76 levels of O₂ over a mercury lamp that was placed at the end of the injector furthest away from the
 77 flow tube in order to avoid any local heating in the flow tube:



80 The total flow exiting the injector was 1.32 ± 0.05 lpm that mixed into a 4.0 ± 0.3 lpm humidified
 81 flow containing aerosols. A sensitive FAGE cell enabled the HO₂ to be measured by firstly converting
 82 it to OH by reaction with added NO, and subsequently detected by utilising laser induced fluorescence
 83 from the Q₁(2) transition of the OH (A²Σ⁺ - X²Π_i; v''=0 - v''=0) band at ~308 nm.^{14, 51} The FAGE cell
 84 was kept at a low pressure (0.85 Torr) using a rotary pump (Edwards, model E1M80) and roots
 85 blower (EH1200) combination to ensure a high flow velocity through the FAGE cell. There was no
 86 change in the LIF signal when the NO added to the fluorescence cell (to convert HO₂ to OH) was

87 switched off. In addition when the NO is switched off there is no difference in signal when the
88 mercury lamp was either switched on or off. These results indicate that any OH radicals formed in the
89 injector alongside HO₂ following the photolysis of water vapour were removed within the injector.

90

91 **Aerosol production and detection**

92

93 Aerosols were produced using two different methodologies. For soluble organics (glutaric acid
94 (Aldrich, 99%), glyoxal (Acros organics, 99%), malonic acid (Acros organics, 99%) and humic acid
95 (Acros organics, 50 – 60%, sodium salt and Leonardite) 5 grams were dissolved into 500 ml milli-Q
96 (mQ) water (only 1 gram in 500 ml for Leonardite humic acid, 1S104H). The solutions containing the
97 humic acid were then filtered to remove insoluble particles, and an atomiser (TSI, 3076) was then
98 used to produce aerosols. For experiments with mono ethanol amine sulphate-H₂SO₄ (MEA-H₂SO₄)
99 and mono-methyl amine sulphate (MMS) aerosols, the amine MEA (Sigma Aldrich, > 99.5 %) and
100 methyl amine (Sigma Aldrich, 40 % w/v) were added into 500 ml mQ water which had been acidified
101 with sulphuric acid. The pH measured to be 8.1 and 8.5 for MEA-H₂SO₄ and MMS solutions,
102 respectively. However, for insoluble organics (stearic acid (Sigma Aldrich, 99%), oleic acid (Sigma
103 Aldrich, 99%) and squalene (Aldrich, 99%)) the aerosols were generated by homogeneous nucleation.
104 Homogeneous nucleation involved placing the organic compound into a steel tube (21 cm length, 1.2
105 cm outer diameter, 1.0 cm inner diameter) and passing a 0.5 lpm flow over the organic whilst heating
106 the tube to 106 - 111°C for stearic acid, 137 - 143°C for oleic acid and 139 - 140°C for squalene. For
107 all experiments the aerosol concentration was varied using a HEPA filter and a bypass. The aerosol
108 surface area was then measured using a Scanning Mobility Particle Sizer, which assumed a spherical
109 geometry, (SMPS, TSI, 3080) at the end of the flow tube. Checks were made to ensure that the
110 aerosol concentration did not change along the flow tube during the HO₂ decays for both experiments
111 using the atomiser and during homogeneous nucleation experiments. and that the aqueous aerosols
112 (glutaric acid, glyoxal, malonic acid, humic acid, MEA-H₂SO₄ and MMS) were never exposed to
113 relative humidities below their efflorescence points.⁵²⁻⁵⁵ The diameters of the aerosols contributing to
114 the surface area weighted size distribution were measured as being between ~ 30 nm - ~ 400 nm. By
115 decreasing the relative humidity (RH) in the flow tube a downwards shift in the aerosol size
116 distribution was also observed for deliquesced aerosols but no change in the size distribution was
117 observed for the effloresced aerosols. For example, with an Leonardite humic acid aerosol number
118 concentration of $5.7 \times 10^5 \text{ cm}^{-3}$ the total aerosol surface area was measured as $9.5 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ at
119 75 % RH but decreased to $8.6 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ at 33 % RH. Information about the aerosol size
120 distributions and the aerosol concentrations used is summarised in the Supplementary Information.

121

122 Data analysis

123

124 The observed decays followed pseudo first-order kinetics as given in Equation 1 when the injector
125 was moved along the flow tube in both the presence and absence of aerosols:

$$126 \ln \frac{[HO_2]_t}{[HO_2]_0} = -k_{obs}t \quad (E1)$$

127 where $[HO_2]_t$ is the HO_2 concentration at time t , $[HO_2]_0$ is the initial HO_2 concentration and k_{obs} is the
128 observed pseudo-first order rate constant. Therefore, as shown in Figure 1, the natural log of the
129 background-subtracted signal was plotted against the reaction time (calculated from the dimensions of
130 the flow tube, the flow rate and the injector position) in the flow tube. Measurements were made
131 between ~ 11 and 20 seconds in order to ensure well mixed flows, with a mixing time of ~ 7 seconds
132 having been previously calculated.²⁶ The k_{obs} values were then corrected (to k') for the non-plug flow
133 conditions within the flow tube using the method described by Brown⁵⁶ which also subtracted the
134 wall loss and increased the rate constants on average by 15 % compared to $k_{obs} - k_{wall}$. On average wall
135 losses were measured as 0.04 s^{-1} with slightly higher wall losses measured at higher relative
136 humidities (indicating a reaction limited wall loss). There was no change in the wall loss when the
137 atomiser solution was swapped from pure water to the solutions containing organics suggesting
138 negligible gas phase reactions between HO_2 and volatile or semi-volatile organics. The k' rate
constants are related to γ_{obs} , the observed uptake coefficient, by Equation 2:

$$139 k' = \frac{\gamma_{obs} w_{HO_2} S}{4} \quad (E2)$$

140 where w_{HO_2} is the molecular thermal speed of HO_2 , and S is the total aerosol surface area. Therefore,
141 k' was plotted against the total aerosol surface area, as shown in Figure 2, which enabled γ_{obs} to be
142 obtained. A correction was made to correct for gas phase diffusion using the methodology described
143 by Fuchs and Sutagin.⁵⁷ The change in the uptake coefficient due to this diffusion correction was less
144 than 1 %. Initial HO_2 concentrations were determined by propagating back the wall loss decay back to
time ($t = 0$ seconds) equaling $1 \times 10^9 \text{ molecule cm}^{-3}$.

145

146 Results and discussion

147

148 The HO_2 uptake coefficients measured onto the different organic aerosols in this work are summarised
149 in Table 1, and displayed in Figure 3. The measured HO_2 uptake coefficients were small ($\gamma < 0.004$ to
150 $\gamma = 0.008 \pm 0.004$) for all of the organic aerosols (including the amine species) apart from the two
151 brands of humic acid, where the uptake coefficient ranged from $\gamma = 0.007 \pm 0.002$ to $\gamma = 0.06 \pm 0.01$

152 for the Acros organics humic acid, and from $\gamma = 0.043 \pm 0.009$ to $\gamma = 0.09 \pm 0.03$ for the Leonardite
153 humic acid over a range of humidities. Due to the much higher HO₂ uptake coefficients measured for
154 the humic acids, the atomiser solutions were tested for the presence of metal ions using Inductively-
155 coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer Elan DRCE, sensitivity 1 ppt) to test for
156 copper and iron ions. The HO₂ radical is catalytically destroyed in the presence of copper and iron
157 forming either hydrogen peroxide or water.^{58, 59} The results of the ICP-MS analysis for the atomiser
158 solutions is shown in Table 2. The copper and iron ion concentrations in the Acros organics humic
159 acid aerosols at 50% RH were estimated as $(5.5 \pm 0.3) \times 10^{-4}$ M and $(8.3 \pm 0.5) \times 10^{-2}$ M, respectively,
160 whereas the copper and iron ion concentrations of Leonardite humic acid were estimated as $(1.2 \pm$
161 $0.1) \times 10^{-4}$ M and $(4.8 \pm 0.3) \times 10^{-3}$ M respectively. These estimations were based upon the change in
162 the humic acid mass fraction within the atomiser solution (assuming no filtration had occurred) and
163 the mass fraction of humic acid within the aerosols based upon the growth factors of humic acid
164 measured by Badger et al.⁶⁰ However, it should be noted that Badger et al.⁶⁰ used a different humic
165 acid to that used in this work and so the growth factors may be slightly different. Also, as the humic
166 acid solutions were filtered there would have been less than one gram of Leonardite humic acid and
167 less than 5 grams of Acros organics humic acid in the 500 ml of water and hence the mass fractions of
168 humic acid within the atomiser solutions were overestimated. Therefore, it is likely that the molarity
169 of iron and copper ions in the aerosols would be much higher than the concentrations calculated
170 above. Mozurkewich et al.³¹ showed that at copper (II) ion concentrations greater than 10^{-4} M, the
171 HO₂ uptake coefficient starts to increase until it reaches the mass accommodation value at a copper
172 ion concentration of 10^{-2} M. Therefore, it seems likely that the high HO₂ uptake coefficients observed
173 for the two humic acids was due to the presence of elevated copper ion concentrations, and perhaps
174 also the elevated iron ion concentrations, within the aerosols. However, it should be noted that
175 aerosols containing humic like substances in the troposphere do not necessarily contain elevated
176 transition metal ion concentrations and that therefore the HO₂ uptake coefficients onto those aerosols
177 may deviate from the measurements in this work.⁴⁸

178

179 In the absence of metals, the HO₂ uptake coefficients measured onto organic aerosols were similar to
180 the uptake coefficients that have previously been measured onto effloresced and deliquesced salt
181 aerosols using the same experimental setup,²⁶ suggesting that the rate of the HO₂ self-reaction within
182 the aerosols determines the HO₂ uptake coefficient rather than the aerosol composition and hence the
183 reaction of HO₂ with an organic. Another trend that can be observed in Table 1 is that the HO₂ uptake
184 coefficients for the deliquesced aerosols tend to be larger than for the effloresced aerosols. For solid
185 organic aerosols only an upper limit could be calculated ($\gamma < 0.004$), however, as these particles are
186 non-spherical the HO₂ uptake coefficients are likely to be significantly lower than this upper limit.
187 Larger HO₂ uptake coefficients have previously been measured onto deliquesced salts than onto

188 effloresced salts and this trend has also been observed by Taketani et al.³⁵ for deliquesced
189 dicarboxylic acid particles compared to effloresced dicarboxylic acid particles. The impact of organic
190 aerosols on atmospheric HO₂ concentrations is likely to be small (a few % maximum) unless aerosols
191 contain a concentration of copper ions of at least 10⁻⁴ M. A similar effect was observed with inorganic
192 salt aerosols.²⁶ The exact effect upon tropospheric HO₂ concentrations would depend on the total
193 aerosol surface concentration as well as the aerosol phase, the relative humidity and the aerosol liquid
194 water content. However, given the magnitude of the uptake coefficients measured in this work, it
195 seems unlikely that uptake of HO₂ to organic aerosols can explain the discrepancy that has sometimes
196 been seen between measurements made in the field and predictions made by box models. In previous
197 work the uptake coefficient measured onto salt ($\gamma = 0.01$) and dust ($\gamma = 0.031$) aerosols have been
198 included into a box model but the impact on gaseous HO₂ concentrations has been small, ~ 2% and
199 0.3 - 6.5% (depending on the aerosol surface area), respectively.^{26,30} The first HO₂ uptake coefficient
200 measurements onto aerosols containing MEA-H₂SO₄ and MMS which have been suggested for carbon
201 capture were made. It was shown that these would also not have a large impact upon the HO₂ uptake
202 coefficient if these amines were to partition to the aerosol phase.

203

204 Although HO₂ uptake coefficients have not previously been measured and published in the literature
205 for most of the organic aerosols chosen in this work, Taketani et al.³⁵ measured the HO₂ uptake
206 coefficient onto aqueous glutaric acid aerosols. In this work, as shown in Table 1, the HO₂ uptake
207 coefficient onto aqueous glutaric acid aerosols was measured as ranging from $\gamma < 0.004$ to $\gamma = 0.006 \pm$
208 0.002 in the relative humidity range of 23 – 76 %. In contrast, Taketani et al.³⁵ measured a HO₂ uptake
209 coefficient of 0.15 ± 0.04 onto glutaric acid aerosols at a relative humidity of 68 % RH. In general
210 Taketani et al. (2013) also measured high HO₂ uptake coefficients onto deliquesced aerosols ($\gamma = 0.13$
211 ± 0.04 to $\gamma = 0.18 \pm 0.07$) and effloresced aerosols ($\gamma = 0.02 \pm 0.01$ to 0.07 ± 0.03) compared to lower
212 HO₂ uptake coefficients measured in this work onto deliquesced aerosols containing low transition
213 metal ion concentrations ($\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$) and effloresced aerosols ($\gamma < 0.004$). The
214 discrepancy between the uptake coefficients measured with the experimental setup used in this work
215 and measured by Taketani et al.³³ has previously been discussed by George et al.²⁶ for aqueous
216 sodium chloride and ammonium sulphate aerosols, where Taketani et al.³³ measured uptake
217 coefficients that were also at least an order of magnitude larger than with the experimental setup used
218 in this work. Possible reasons for the difference between this work and literature values^{33,35} include
219 differences in the reaction time, the HO₂ concentration that was used, and the trace metal ion content
220 of the aerosols. Taketani et al.³⁵ measured HO₂ uptake with reaction times of approximately five to
221 eleven seconds, whereas in this work the reaction times were between approximately eleven and
222 twenty seconds. Taketani et al.³⁵ also worked at initial HO₂ concentrations of ~ 10⁸ molecule cm⁻³
223 compared to an initial HO₂ concentration of 1 × 10⁹ molecule cm⁻³ in this work. George et al.²⁶

224 measured larger uptake coefficients at shorter reaction times and at smaller HO₂ concentrations for
 225 aqueous inorganic salt aerosols, consistent with the observed difference for organics in the two
 226 studies. Potential explanations given by George et al. for the time and HO₂ concentration dependence
 227 included a saturation mechanism or a trace reactant being used up over time. Future work will likely
 228 include the interpretation time and HO₂ concentration dependences for γ observed by George et al.
 229 (2013)²⁶ within the framework of the kinetic multi-layer model of aerosol surface and bulk chemistry
 230 (KM-SUB), described by Shiraiwa et al.⁶¹.

231

232 **The humidity dependence of the HO₂ uptake coefficient onto humic acid aerosols**

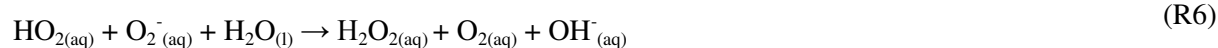
233

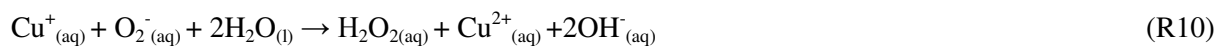
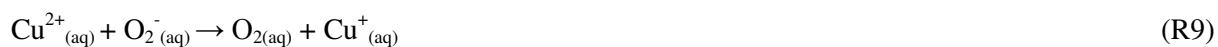
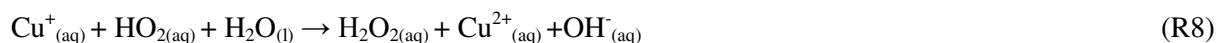
234 In this work a large humidity dependence was observed for HO₂ uptake onto humic acid aerosols. The
 235 HO₂ uptake coefficient increased from 0.007 ± 0.002 to 0.06 ± 0.01 between 32 and 76 % RH for the
 236 Acros organics humic acid, and from 0.043 ± 0.009 to 0.09 ± 0.03 between 33 and 75 % RH for the
 237 Leonardite humic acid. If the HO₂ uptake coefficient was solely controlled by the copper and iron ion
 238 concentrations within the aerosols, a decrease in the HO₂ uptake coefficient would have been
 239 expected with increasing humidity as the aerosols absorb more water, and become more dilute in
 240 metal ions at higher humidities. Therefore, although the presence of copper and iron ions within the
 241 aerosol has the potential to explain the magnitude of the uptake coefficients, it cannot explain the
 242 humidity trend.

243

244 Badger et al.⁶² observed a similar uptake trend onto humic acid aerosols for N₂O₅, with the N₂O₅
 245 uptake coefficient increasing from 2×10^{-4} to 9×10^{-4} between 25 and 75 % RH. The mechanism that
 246 was suggested for N₂O₅ uptake within aerosols involved the presence of water. However, at relative
 247 humidities of less than 40 % the uptake coefficient was limited by the liquid water content of the
 248 aerosols. Similarly, it is expected that the HO₂ uptake mechanism would be dependent upon the liquid
 249 water content of the aerosols. The mechanism in the aerosols with the low concentrations of copper
 250 ion present in the aerosols is expected to be given by:⁵⁸

251





252

253 Therefore, as can be seen from the reaction scheme above, Reactions 6, 8 and 10 are dependent upon
 254 the liquid water content within the aerosols that may limit the HO₂ uptake coefficient at low relative
 255 humidities. The liquid water content of the aerosols could also explain the slightly lower HO₂ uptake
 256 coefficient measured for glyoxal aerosols at 33 % RH compared to 80 % RH and for humic acid
 257 aerosols over a range of humidities, although the viscosity of these aerosols could affect the uptake if
 258 the aerosols were much more viscous at lower humidity.^{63, 64} The same mechanism would be expected
 259 to occur in the presence of iron ions although the rate constants between HO₂/ O₂⁻ and iron ions are
 260 significantly lower (~ 2 orders of magnitude) than with copper ions.⁵⁸

261

262 However, there are other possible explanations for the relative humidity dependence of the HO₂
 263 uptake coefficient at higher humidities. Humic acid is known to have surfactant properties and several
 264 studies have shown that it can form micelles at the surface of aqueous solutions.^{65, 66} Badger et al.⁶²
 265 suggested that the humic acid surfactant could cause a diffusion barrier to an incoming species
 266 thereby reducing the mass accommodation coefficient. As the humidity increases there would be a
 267 greater probability of water being present at the surface of the aerosol and therefore the mass
 268 accommodation would increase. Alternatively, the humic acid at the surface of the aerosol could
 269 cause a decrease in the Henry's law coefficient for HO₂ leading to a slower initial solvation of the
 270 HO₂ into the aerosol. However, in this work, accurate concentrations of copper and iron ions within
 271 the humic acid aerosols are not known with only a lower limit having been calculated in the first
 272 paragraph of the 'Results and discussion' section, so that it is currently difficult to determine whether
 273 it is a change in the mass accommodation or the Henry's law coefficient that is causing the HO₂
 274 uptake coefficient dependence upon relative humidity. Finally, it should be noted that if atmospheric
 275 aerosols were to contain high concentrations of copper (> 10⁻² M), the uptake coefficient would not
 276 necessarily be equal to the mass accommodation coefficient if humic acid was also present within the
 277 aerosol. However, more investigation is required to determine at what humic acid concentration the
 278 uptake coefficient deviates from the mass accommodation.

279

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281

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515 **Tables**

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517 **Table 1:** Summary of the HO₂ uptake coefficients measured in this work for organic aerosols at 293 ±
 518 2 K and at an initial HO₂ concentration of 1 × 10⁹ molecule cm⁻³. The error represents two standard
 519 deviations.

520 * Determined by the efflorescence and deliquescence points of the organics.

521 + The magnitude of these uptake coefficients was influenced by the presence of copper and iron ions
 522 within the aerosol.

Compound	RH/ %	Aqueous or Solid *	Uptake coefficient (γ)
Stearic acid	32 - 75	Solid	< 0.004
Oleic acid	32	Solid	< 0.004
Squalene	32	Solid	< 0.004
Glutaric acid	32	Aqueous	< 0.004
	54	Aqueous	0.006 ± 0.002
	76	Aqueous	< 0.004
Glyoxal	33	Aqueous	0.003 ± 0.003
	80	Aqueous	0.008 ± 0.004
Malonic acid	55 - 76	Aqueous	< 0.004
Mono ethanol amine sulphate- H ₂ SO ₄	32	Aqueous	< 0.004
Mono-methyl amine sulphate	36	Aqueous	0.005 ± 0.004
Humic acid (Acros organics)	32	Aqueous	0.007 ± 0.002 ⁺
	54	Aqueous	0.017 ± 0.003 ⁺
	65	Aqueous	0.031 ± 0.009 ⁺
	76	Aqueous	0.06 ± 0.01 ⁺
Humic acid (Leonardite)	33	Aqueous	0.043 ± 0.009 ⁺
	51	Aqueous	0.07 ± 0.02 ⁺
	75	Aqueous	0.09 ± 0.03 ⁺

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534 **Table 2:** The copper and iron ion concentrations measured by ICP-MS within the atomiser solutions
535 and the estimated copper and iron ion molarities within the aerosols. Atomiser solutions were made
536 by dissolving 5.0 grams of an organic into 500 ml of milliQ water with the exception of Leonardite
537 humic acid where 1.0 gram was dissolved into 500 ml of mQ water. Both of the humic acid solutions
538 were then filtered before being used for experiments. The range of molarities given for the glyoxal,
539 glutaric acid and malonic acid aerosols is due to the range of humidities to which the aerosols were
540 exposed. For humic acid aerosols only a lower limit of the molarity could be calculated as the ratio of
541 humic acid to the transition metal ions was unknown due to the filtration of the atomiser solutions.

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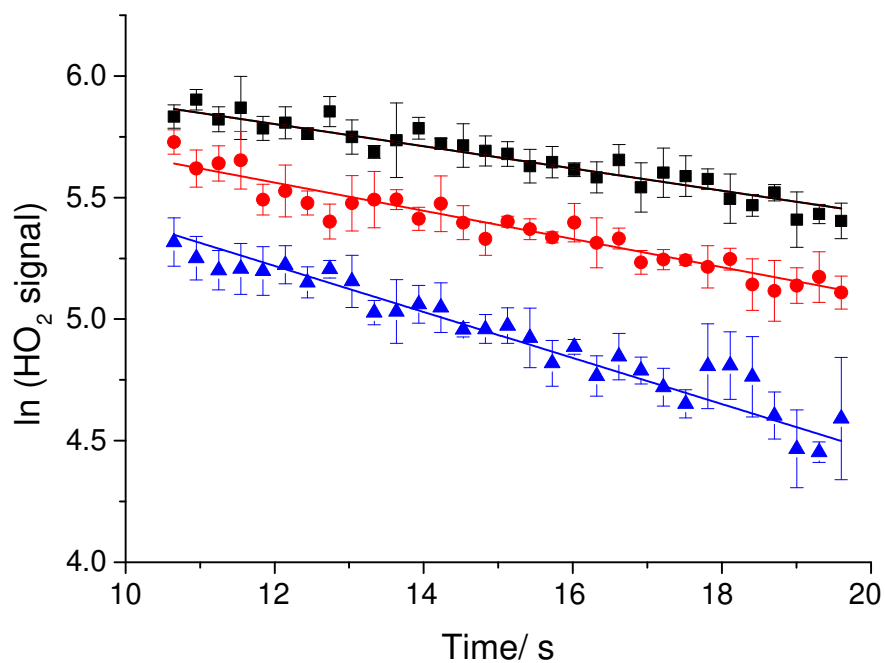
Compound	Iron concentration in 500 ml mQ water / ppb	Estimated iron molarity within the aerosols/ M	Copper concentration in 500 ml mQ water / ppb	Estimated copper molarity within the aerosols/ M
Humic acid (Acros organics)	51000 ± 3000	$> 8.3 \times 10^{-2}$	380 ± 20	$> 5.5 \times 10^{-4}$
Humic acid (Leonardite)	600 ± 30	$> 4.8 \times 10^{-3}$	16 ± 1	$> 1.2 \times 10^{-4}$
Glyoxal	12 ± 2	$\sim (1.1 - 2.5) \times 10^{-5}$	5 ± 1	$\sim (4.2 - 9.4) \times 10^{-6}$
Glutaric acid	1620 ± 70	$\sim (1.7 - 3.4) \times 10^{-3}$	0.7 ± 0.1	$\sim (0.7 - 1.3) \times 10^{-7}$
Malonic acid	46 ± 3	$\sim (4.8 - 7.2) \times 10^{-5}$	5 ± 1	$\sim (4.7 - 7.0) \times 10^{-6}$

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546 **Figures**

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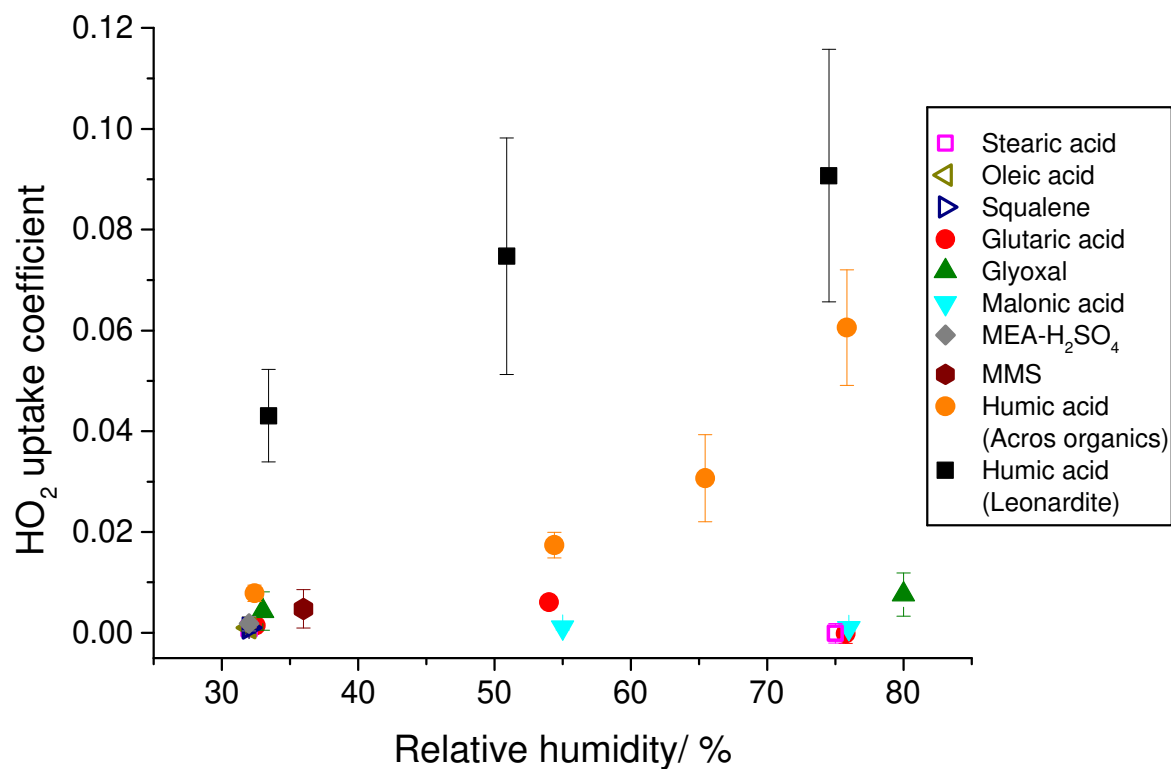
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549 **Figure 1:** Examples of the HO₂ wall loss along the flow tube (black squares) and HO₂ loss in the
 550 presence of Leonardite humic acid aerosols with a surface area of $5.3 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ (red circles) and
 551 $8.9 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ (blue triangles) at a relative humidity of 33 %, an initial HO₂ concentration of $1 \times$
 552 $10^9 \text{ molecule cm}^{-3}$ and a temperature of $293 \pm 2 \text{ K}$. The gradient of the lines represent k_{obs} as given by
 553 Equation 1. The error bars represent one standard deviation.

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566 **Figure 3:** HO₂ uptake coefficients measured in this work for organic aerosols at 293 ± 2 K and at an
 567 initial HO₂ concentration of 1×10^9 molecule cm⁻³. At 32 % relative humidity there are points for
 568 MEA-H₂SO₄, oleic acid, squalene, stearic acid and glutaric acid all plotted over each other. Open
 569 symbols represent solid phase aerosols. The error represents two standard deviations of the
 570 propagated error in the gradients of the k' against aerosol surface area graphs. The magnitude of the
 571 HO₂ uptake coefficients measured onto humic acid aerosols was influenced by the presence of copper
 572 and iron ions.

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