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# 1       **The fate of methyl salicylate in the environment and its role as** 2   **signal in multitrophic interactions**

3

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21 **Abstract**

22 Phytohormones emitted into the atmosphere perform many functions relating to the defence,  
23 pollination and competitiveness of plants. To be effective, their atmospheric lifetimes must be  
24 sufficient that these signals can be delivered to their numerous recipients.

25 We investigate the atmospheric loss processes for methyl salicylate (MeSA), a widely emitted plant  
26 volatile. Simulation chambers were used to determine gas-phase reaction rates with OH, NO<sub>3</sub>, Cl and  
27 O<sub>3</sub>; photolysis rates; and deposition rates of gas-phase MeSA onto organic aerosols. Room  
28 temperature rate coefficients are determined (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) to be (3.20±0.46)×10<sup>-12</sup>,  
29 (4.19±0.92)×10<sup>-15</sup>, (1.65±0.44)×10<sup>-12</sup> and (3.33±2.01)×10<sup>-19</sup> for the reactions with OH, NO<sub>3</sub>, Cl and O<sub>3</sub>  
30 respectively. Photolysis is negligible in the actinic range, despite having a large reported near-UV  
31 chromophore. Conversely, aerosol uptake can be competitive with oxidation under humid  
32 conditions, suggesting that this compound has a high affinity for hydrated surfaces. A total lifetime  
33 of gas-phase MeSA of 1–4 days was estimated based on all these loss processes.

34 The competing sinks of MeSA demonstrate the need to assess lifetimes of semiochemicals  
35 holistically, and we gain understanding of how atmospheric sinks influence natural communication  
36 channels within complex multitrophic interactions. This approach can be extended to other  
37 compounds that play vital roles in ecosystems, such as insect pheromones, which may be similarly  
38 affected during atmospheric transport.

39 **Keywords:** methyl salicylate (MeSA), atmospheric chemistry, kinetics, simulation chamber, odor  
40 aerosol transport, multitrophic interactions, phytohormones

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## 42 1. Introduction

43 The emission of biogenic volatile compounds (BVOCs) into the atmosphere by vegetation carries a  
44 metabolic cost, but also concomitant benefits. Methyl salicylate (MeSA, methyl 2-hydroxybenzoate)  
45 is an example of a phytohormone that is emitted from a broad variety of species. For example, in  
46 their review on floral scents, Knudsen et al. (2006) listed 51 families of flowering plants that have  
47 been identified as MeSA emitters in the literature, encompassing many of the world's most  
48 economically important crops (such as apples, peaches, almonds and strawberries) in addition to  
49 many of the floral constituents of natural ecosystems. There are several proposed strategies by  
50 which plants can be advantaged through MeSA emission, as defence mechanisms, as an attractant  
51 for pollinators and as a method for reducing the local density of competing plants. MeSA has been  
52 observed to be involved in the following interactions:

53 1. Plant-herbivore interactions: MeSA can stimulate systemic acquired resistance (SAR) responses in  
54 healthy plant tissues (Park et al., 2007). This triggers salicylic acid production in the healthy tissues of  
55 a plant or in neighbouring plants, which primes plant defences against future herbivorous attacks  
56 (Thulke and Conrath, 1998). Furthermore, MeSA may act as a repellent towards certain herbivores  
57 (Hardie et al., 1994), although it may be difficult to decouple this effect from other deterrents such  
58 as SAR.

59 2. Plant-predator interactions: Several beneficial arthropods, that are known to predate upon  
60 herbivorous pests have been found to use the MeSA emissions of herbivore-infested plants in  
61 locating their prey (De Boer and Dicke, 2004; James, 2003; James and Price, 2004), thus reducing  
62 herbivorous attacks indirectly.

63 3. Plant-pollinator interactions: MeSA is a common floral scent that can attract pollinating insects  
64 (Dudareva et al., 1998; Knudsen et al., 2006; Loughrin et al., 1991), and is therefore an important  
65 component of the reproductive cycle in many flowering plants.

66 4. Plant-plant interactions: MeSA has been found to exhibit allelopathic effects (Bi et al., 2007),  
67 which may interfere with other species growth processes and reduce the root growth of  
68 neighbouring plants, favouring the emitter in a competition for soil nutrients.

69 For each of these four strategies, there is an apparent target for the MeSA emission, and efficient  
70 transport between the emitter and the recipient is required in order for these signalling chemicals to  
71 perform their function, particularly for cases where transport over long distances is necessary. It is  
72 therefore logical that the atmospheric lifetime of MeSA is sufficiently long that transport can occur  
73 prior to any chemical transformation in the atmosphere.

74 Enhanced emissions of MeSA may also occur as a consequence of biotic stress factors such as  
75 pathogen infection (Jansen et al., 2011; Martini et al., 2016), or abiotic stresses such as wounding,  
76 drought, temperature changes or ozone exposure (Chalal et al., 2015; Heiden et al., 1999; Karl et al.,  
77 2008). In these cases, there may be no obvious target for the emission of MeSA and this may be an  
78 immune response of wounded or diseased plants. Under these circumstances, MeSA emissions can  
79 represent a large flux, which can be comparable or even exceed that of monoterpenes (Karl et al.,  
80 2008). If these emissions are a response to abiotic stress factors such as drought or temperature  
81 swings, then these fluxes could be occurring across the scale of an ecosystem, which, depending on  
82 the atmospheric chemistry of MeSA, could have a major impact upon regional air quality.

83 Besides the biogenic emissions, which are expected to represent the dominant fluxes of MeSA into  
84 the atmosphere, several anthropogenic sources of MeSA exist, which could come from washing and  
85 cleaning products, disinfectants, air fresheners, polishes, waxes, cosmetics, personal care products  
86 and perfumes (European Chemicals Agency, 2020). Such emissions could impact indoor air quality,  
87 and knowledge of the oxidation reactions of MeSA is therefore important in assessing this.

88 The aim of this work is therefore to assess the various ways in which MeSA can interact with the  
89 atmospheric environment, which will allow a first assessment of the sensitivity of MeSA as a

90 phytohormonal signal towards transport in the atmosphere. Furthermore, these data will provide  
91 insight into the role that a large MeSA emission could play in regional air pollution.

## 92 **2. Experimental methods**

### 93 **2.1 Chamber systems:**

94 Two simulation chamber systems were employed in this work. For particle uptake experiments, the  
95 HELIOS chamber was used, which has been described elsewhere (Ren et al., 2019, 2017). In brief,  
96 HELIOS is a 90 m<sup>3</sup> hemispherical FEP Teflon foil chamber equipped with two Teflon fans installed at  
97 the base, which generate flow velocities of 14 m s<sup>-1</sup> and induce rapid mixing of reactants in  
98 approximately 90 seconds. A three-axis ultrasonic anemometer (Delta Ohm, HD 2003) installed in  
99 the centre of the chamber was used to determine pressure, temperature and wind speed/ direction.  
100 Relative humidity (RH) was controlled using a water spray system, and was monitored using a  
101 humidity probe (Vaisala, HMT333). The chamber was cleaned overnight after each experiment with  
102 a fast flow (800 L min<sup>-1</sup>) of zero air supplied by a pure air generation system (AADCO Instruments,  
103 Inc., 737 series).

104 Kinetic and photolysis measurements were conducted in the 7.3 m<sup>3</sup> ICARE-CNRS chamber, described  
105 previously (Bernard et al., 2010). This is a FEP Teflon foil chamber of a cuboidal design, equipped  
106 with Teflon fans that promote mixing within 1–2 mins. Illumination was provided artificially from  
107 lamp output centred at 254 nm (14 × UV-C T-40 L, Viber Lourmat); at 365 nm (24 × UV-A T-40 L,  
108 Viber Lourmat); and broad emissions, >300 nm, from sunlight simulating lamps (12 × Ultra-Vitalux  
109 300 W, Osram). A thermocouple (PT-100) and a humidity probe (Vaisala HMT330) measured the  
110 temperature and RH.

111 Both chambers were operated at a slight overpressure to compensate for sample flows and small  
112 leaks, which was achieved using a continuous flow of zero air (5–60 L min<sup>-1</sup>). This led to gradual  
113 dilution of the chamber contents. This was quantified using SF<sub>6</sub> as a tracer, which was monitored

114 throughout the experiments using Bruker Vertex 70 (pathlength: 303 m) and Nicolet 5700 Magna  
115 (pathlength: 143 m) Fourier-transform infrared spectrometers coupled with white-type multipass  
116 optics for HELIOS and the 7.3 m<sup>3</sup> chamber respectively.

## 117 **2.2 Organic compound analysis in the gas and particle phases, and aerosol measurements:**

118 Gas-phase MeSA together with several other organic compounds were monitored using a high-  
119 resolution proton transfer reaction time-of-flight mass spectrometer (Ionicon Analytik, PTR-ToF-MS  
120 8000) with a hydronium ion (H<sub>3</sub>O<sup>+</sup>) detection scheme. The pressure and voltage in the PTR-ToF-MS  
121 drift tube was maintained at 2.4 mbar and 480 V affording an electric field strength of 99 Td. The  
122 sampling flow was 0.1 L min<sup>-1</sup>, through a 1 m long, ¼ inch OD PEEK tube heated to 333 K. A high-  
123 resolution time-of-flight FIGAERO-ToF-CIMS instrument (Aerodyne Research Inc. and ToFwerk) with  
124 an I<sup>-</sup> ionization scheme, similar to instruments described elsewhere (Lee et al., 2014; Lopez-Hilfiker  
125 et al., 2014), was used to determine concentrations of MeSA in the gas and particle phases. Voltages  
126 affecting ion transmission and declustering were optimized to maximize MeSA.I<sup>-</sup> signal using the  
127 Thuner software (ToFwerk). The sampling protocol was as follows: aerosol samples were collected  
128 through a 1 m long, ¼ inch OD straight length of stainless steel tube at a flow rate of 2 L min<sup>-1</sup> onto a  
129 PTFE filter (SKC, Zefluor™ 25 mm, 2 µm) for 20 mins, and were volatilized by slowly ramping the  
130 temperature of a 2 L min<sup>-1</sup> carrier flow of N<sub>2</sub> from 298 to 573 K over 30 mins, which was held at 573 K  
131 for 20 mins subsequently, to ensure that the all particulate-phase MeSA had been thoroughly  
132 desorbed. Gas-phase samples were taken during the aerosol collection phase, through a 1 m long, ¼  
133 inch OD PFA tube, also at a flow of 2 SLM. Aerosol size distributions were monitored using a single  
134 mobility particle sizer and differential mobility analyzer (3080, 3081 and 3085, TSI) coupled with a  
135 condensation particle counter (3788, TSI).

## 136 **2.3 MeSA introduction system:**

137 Because of the low vapor pressure of MeSA, 0.086 Torr at 298 K (Yaws, 2015), it is difficult to  
138 introduce into the chamber using the conventional method of impinging a liquid sample into a  
139 carrier gas flow, which would require excessive heating of the liquid sample, and could result in  
140 pyrolysis and/ or condensation of the sample in transfer lines. Accordingly, the sample was  
141 introduced by nebulizing an aqueous MeSA solution with a commercial nebulizer (TSI, Model 3076)  
142 and subsequently volatilizing the nebulized droplets in a 1 m long, ¼ inch OD stainless steel tube  
143 held at ~373 K. MeSA is only sparingly soluble in water and the aqueous solution was prepared by  
144 introducing 250 mg of MeSA into 500 ml of deionized water (18.2 MΩ·cm at 298 K) and continuously  
145 stirring the sample at 333 K for 12 hours. The quantity of MeSA introduced into the chamber was  
146 calibrated by nebulizing an aqueous MeSA solution containing known concentrations of internal  
147 standards (acetone and cyclohexanone) and analysing all three with the PTR-ToF-MS. The major ions  
148 attributed to these standards were found to correlate strongly ( $R^2 = 0.99$ ) with the protonated mass  
149 of MeSA [ $m/z$  153.0551,  $C_6H_4(OH)(C(O)OCH_3)H^+$ ] over the course of several nebulizing steps (see  
150 Figure S1) demonstrating that MeSA volatilization is both complete and reproducible. Subsequently,  
151 the intensities of these major ions were compared, yielding slopes and conversion factors (CFs),  
152 which were used in the following equation to obtain the gas-phase [MeSA].

$$153 \quad [MeSA]_{gas} = [internal\ standard]_{gas} \times CF \quad (1)$$

154 The concentrations of internal standards in the gas phase were quantified by expanding known  
155 volumes of pure sample into the HELIOS chamber.

## 156 **2.4 Kinetic studies**

157 The rate coefficients of MeSA + OH, NO<sub>3</sub>, Cl and O<sub>3</sub> were determined in the 7.3 m<sup>3</sup> chamber through  
158 the relative rate method. In these experiments, the temporal decay of MeSA was monitored in the  
159 presence of a reference compound for which the absolute rate coefficient is known. By comparing  
160 these decays and accounting for other loss process such as dilution and wall loss ( $k_d$ ), the rate



161 coefficient ( $k$ ) can be determined using the following equation (Finlayson-Pitts and Pitts, 2000; Ren  
162 et al., 2020):

$$163 \quad \ln\left(\frac{[\text{MeSA}]_0}{[\text{MeSA}]_t}\right) - k_d t = \frac{k_{\text{MeSA}}}{k_{\text{ref}}} \ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) - k_d t \quad (2)$$

164 where  $[\text{MeSA}]_0$ ,  $[\text{MeSA}]_t$  and  $[\text{ref}]_0$ ,  $[\text{ref}]_t$  are the concentrations of MeSA and reference compounds  
165 initially and at time  $t$ . Therefore, plots of  $\ln\left(\frac{[\text{MeSA}]_0}{[\text{MeSA}]_t}\right) - k_d t$  vs.  $\ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) - k_d t$  yields  $\frac{k_{\text{MeSA}}}{k_{\text{ref}}}$ , and  
166 with knowledge of the reference rate coefficient ( $k_{\text{ref}}$ ),  $k_{\text{MeSA}}$  can be placed on the absolute scale.

167 In the OH experiments, OH radicals were produced using the methyl nitrite precursor through the  
168 following sequence of reactions:



172 In the  $\text{NO}_3$  experiments,  $\text{NO}_2$  was slowly and continuously introduced into the chamber, maintaining  
173  $[\text{NO}_2]$  at  $\sim 1 \times 10^{12}$  molecule  $\text{cm}^{-3}$ , under an excess of  $\text{O}_3$  ( $2.5 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ), producing  $\text{NO}_3$   
174 through the following reaction:



176 In the Cl experiments,  $\text{Cl}_2$  was photolyzed at 365 nm, yielding two chlorine atoms:

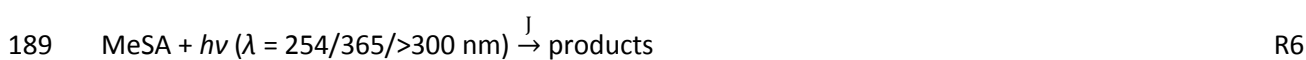


178 In the  $\text{O}_3$  experiments,  $\text{O}_3$  was generated from pure  $\text{O}_2$  in a discharge ozone generator (Trailgaz).

## 179 **2.5 Photolysis studies**

180 Photolysis experiments were conducted at atmospheric pressure and 298 K using artificial light  
181 sources in the 7.3  $\text{m}^3$  chamber. In these experiments, MeSA was first introduced into the chamber

182 and left in the dark for two hours to quantify wall loss and dilution, following this the >300 nm lamps  
183 were switched on (see Figure S2). Subsequently, the 365 nm lamps were switched on, and then the  
184 254 nm lamps. To minimize temperature fluctuations induced by the lamps, which may perturb wall  
185 loss processes, room air was circulated around the chamber walls using fans. Cyclohexane was  
186 added to the chamber as a radical scavenger, to minimize the effects of enhanced radical production  
187 either from the chamber walls or the photolysis of MeSA itself. Under chamber conditions, loss  
188 processes for MeSA were considered as the following:



191 where J is the photolysis rate and  $k_d$  is the combined dark loss (wall loss and dilution rate), with the  
192 sum of J and  $k_d$  representing  $k_{\text{total}}$ , the overall loss of MeSA with time. Under irradiation, the total  
193 decay of MeSA can be formulated as follows:

$$194 \ln \left( \frac{[\text{MeSA}]_0}{[\text{MeSA}]_t} \right) = k_{\text{total}} t \quad (3)$$

195 and J is obtained by subtracting the dark loss  $k_d$ , obtained at the beginning of the experiment, from  
196  $k_{\text{total}}$ :

$$197 J = k_{\text{total}} - k_d \quad (4)$$

## 198 2.6 Materials:

199 Methyl salicylate (>99%, TCI), methyl ethyl ketone (99%, Sigma-Aldrich), di-*n*-butyl ether (99.3%,  
200 Sigma-aldrich), toluene (>99.5%, TCI), chloroacetone (95%, Alfa Aesar), acetaldehyde (>99.5%,  
201 Sigma-Aldrich), benzaldehyde (>99%, Sigma-Aldrich) and 3,3,3-trifluoropropene (99%, Sigma-  
202 Aldrich), O<sub>2</sub> (99.999%, Air-Liquide), N<sub>2</sub> (99.999%, Air-Liquide), chlorine (99.6%, Air-Liquide), NO<sub>2</sub> (1%  
203 in N<sub>2</sub>, Air-Liquide), methanol (99.98%, Biosolve), sodium nitrite (>97%, Sigma-Aldrich), nitric acid

204 (70%, Sigma-Aldrich), sulphuric acid (95%, Prolabo) and P<sub>2</sub>O<sub>5</sub> (≥98%, Fluka) were used as supplied,  
205 without further purification. Methyl nitrite was synthesized by adding sulphuric acid (50% in water)  
206 dropwise to a saturated solution of sodium nitrite in methanol that was stirred continuously and  
207 held at 273 K in a 3-necked flask, the effluent was swept through a water bubbler using a small flow  
208 of N<sub>2</sub>, to remove water soluble impurities such as HONO, then through a drying tube containing  
209 P<sub>2</sub>O<sub>5</sub>, before entering a cold trap maintained at 77 K. The sample was then purified under vacuum.

### 210 3. Results and discussion

#### 211 3.1 Surface uptake of MeSA

212 Four types of experiments were conducted in the HELIOS chamber to evaluate the uptake of MeSA  
213 under a variety of conditions (see Table 1):

- 214 A. Dry (<1%) with no secondary organic aerosol (SOA) present.
- 215 B. Dry (<1%) with SOA produced from limonene ozonolysis.
- 216 C. Humid (~40–60%) with no SOA present.
- 217 D. Humid (~40–60%) with limonene SOA.

218 Figure S3 presents a typical experimental time profile of MeSA in the presence of humid SOA. The  
219 possible loss of MeSA through reaction with O<sub>3</sub> was tested by exposing MeSA to 200 ppb of O<sub>3</sub> over  
220 the course of 90–120 minutes. Loss of MeSA was indistinguishable from dilution and can therefore  
221 be neglected. Hence, particle deposition rates on SOA and chamber surfaces were determined as  
222 follows. Firstly, first-order losses of gas-phase MeSA with respect to SOA and chamber surfaces were  
223 calculated thus:

$$224 \quad k'_{\text{dry}} = k_{\text{totalA}} - k_{\text{SF}_6} = 1.0 \pm 0.1 \times 10^{-6} \text{ s}^{-1} \quad (5)$$

$$225 \quad k'_{\text{dry SOA}} = k_{\text{totalB}} - k_{\text{SF}_6} - k'_{\text{dry}} = 0.4 \pm 0.1 \times 10^{-6} \text{ s}^{-1} \quad (6)$$

$$226 \quad k'_{\text{humid}} = k_{\text{totalC}} - k_{\text{SF}_6} = 4.8 \pm 0.1 \times 10^{-6} \text{ s}^{-1} \quad (7)$$

227  $k'_{\text{humid SOA}} = k_{\text{totalD}} - k_{\text{SF}_6} - k'_{\text{humid}} = 2.1 \pm 0.1 \times 10^{-6} \text{s}^{-1}$  (8)

228 where  $k'_x$  represent first-order decays of MeSA with respect to dry chamber, humid chamber, dry  
 229 SOA and humid SOA surfaces (see Figure S4);  $k_{\text{SF}_6}$  is the dilution rate as defined by  $\text{SF}_6$  loss, and  $k_{\text{total}}$   
 230 represents the total first-order loss of MeSA observed during the experiment, corresponding to  
 231 conditions A, B, C and D respectively.

232 Using these first-order decays, deposition rates can be calculated for chamber and SOA surfaces as  
 233 follows:

234  $k_{\text{chamber}} = \frac{k'_{\text{dry or humid}}}{\frac{S_{\text{chamber}}}{V_{\text{chamber}}}}$  and  $k_{\text{SOA}} = \frac{k'_{\text{dry SOA or humid SOA}}}{\frac{S_a}{V}}$  (9)

235 where  $S_{\text{chamber}}$  and  $V_{\text{chamber}}$  are the surface area and volume of the chamber,  $108 \text{ m}^2$  and  $90 \text{ m}^3$   
 236 respectively;  $S_a/V$  represents the particle surface density calculated from the particle size  
 237 distribution measured by the SMPS between 3 and 500 nm and assuming a spherical shape (see  
 238 Figure S3). Deposition rates were ordered as follows,  $k_{\text{dry chamber}} (8.3 \times 10^{-7}) < k_{\text{humid chamber}} (4.0 \times 10^{-6}) <$   
 239  $k_{\text{dry SOA}} (3.0 \times 10^{-4}) < k_{\text{humid SOA}} (1.8 \times 10^{-3})$ , with calculated values in parentheses in units of  $\text{m s}^{-1}$ .

240 Further experimental details are provided in Table 1. Ultimately, condition D is expected to be the  
 241 most realistic, since MeSA is emitted from the terrestrial biosphere, likely in the presence of  
 242 moisture and other BVOCs. However, it was necessary to study the other conditions in order to  
 243 isolate the effects of humidity and SOA surfaces and chamber surfaces. Different analytical  
 244 approaches were employed to investigate deposition processes, resulting in three key findings:

- 245 1. SMPS measurements show that introduction of gas-phase MeSA slows the decrease of SOA mass  
 246 concentration over time, indicating that gas-phase MeSA partitions to SOA (see Figure 1).
- 247 2. PTR-ToF-MS measurements demonstrate that first-order losses of gas-phase MeSA are  
 248 enhanced by SOA and humidity (see Table 1), showing that gas-phase MeSA is being lost to  
 249 surfaces, especially humid surfaces.

250 3. SOA particles sampled by the CIMS FIGAERO inlet were found to contain MeSA (see Figure 2),  
251 corroborating points 1 and 2.

252 The partitioning fraction of gas-phase MeSA onto SOA ( $F$ ) was defined based on the reference of  
253 Pankow (1994) and estimated in two ways of this work. Firstly, the concentration of MeSA lost to  
254 SOA surfaces  $[\text{MeSA}]_{\text{lost}}$  was quantified using the first-order loss rate for  $k'_{\text{dry SOA}}$  and  $k'_{\text{humid SOA}}$  derived  
255 from Eqs. 6 and 8 respectively, divided by the concentration of MeSA in the chamber in the presence  
256 of SOA particles,  $[\text{MeSA}]^{\#}$ :

$$257 \quad F = \frac{[\text{MeSA}]_{\text{lost}}}{[\text{MeSA}]^{\#}} = \frac{[\text{MeSA}]_0 \left( 1 - \exp(-k'_{\text{dry SOA}} \text{ or } -k'_{\text{humid SOA}} \times t) \right)}{[\text{MeSA}]^{\#}} \quad (10)$$

258 Secondly, the mass of SOA mass in the presence and absence of gas-phase MeSA was integrated  
259 over a time period of ~3 hours as shaded area in Figure 1 ( $\int_0^t \text{SOA}_{\text{MeSA}}$  and  $\int_0^t \text{SOA}$ , respectively),  
260 providing an alternative calculation of  $F$ :

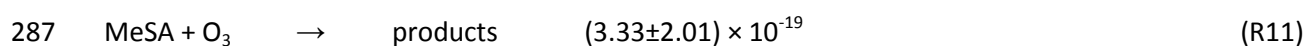
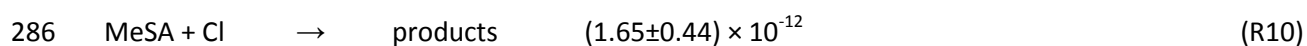
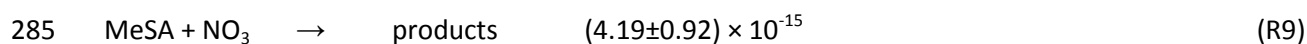
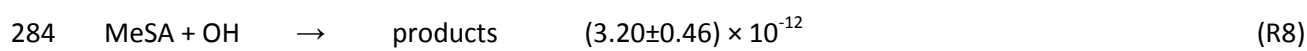
$$261 \quad F = \frac{\int_0^t \text{SOA}_{\text{MeSA}} - \int_0^t \text{SOA}}{[\text{MeSA}]^{\#}} \quad (11)$$

262 Equation 10 yielded values for  $F$  of 0.2–4.6% under dry and humid conditions respectively, whereas  
263 Equation 11 was only employed under humid conditions and resulted in  $F = 10.9\%$ . These findings  
264 are therefore in general accordance with previous suggestions that, as a result of its low vapour  
265 pressure (Yaws, 2015), under typical aerosol mass loadings of  $1\text{--}50 \mu\text{g m}^{-3}$ ,<sup>26</sup> 0.4–18% of MeSA is  
266 expected to partition to the particle phase (Karl et al., 2008), based on partition modelling (Pankow,  
267 1994). It is noted that on the timescales of our experiments, there is insufficient time for equilibrium  
268 of gas-phase MeSA with SOA surfaces to be established, which may be a contributory factor in the  
269 spread of values provided by Eqs. 10 and 11, and our estimates of partitioning may also be slightly  
270 lower than previous estimates would indicate. Furthermore, we find that there is an enhancement  
271 of MeSA uptake at humid condition (see Table 1), suggesting that the activity towards MeSA on  
272 humid surfaces is higher than that of dry ones, which is an inference that would not emerge from

273 simple partition models. Molecular modelling work(Liyana-Arachchi et al., 2013) has demonstrated  
 274 the intuitive result that the oxygenated sites of MeSA have a high affinity for water, which may  
 275 explain this enhancement, and also shows that once MeSA has entered the particle phase, it will  
 276 accumulate primarily at the air-water interface.

### 277 **3.2 Atmospheric oxidation of MeSA**

278 Rate coefficients for the reactions of MeSA with OH, NO<sub>3</sub>, Cl and O<sub>3</sub> were determined at room  
 279 temperature (296±2 K) using the relative rate method. Figure 3 presents the plots of  $\ln\left(\frac{[\text{MeSA}]_0}{[\text{MeSA}]_t}\right) -$   
 280  $k_d t$  vs.  $\ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) - k_d t$  yields  $\frac{k_{\text{MeSA}}}{k_{\text{ref}}}$  and the obtained  $\frac{k_{\text{MeSA}}}{k_{\text{ref}}}$  according to the experiment conditions  
 281 are shown in Table 2. Reference compound rate coefficients were taken from the recent evaluated  
 282 database of McGillen et al. (2020) (see Table 2), and were used to place these reactions on the  
 283 absolute scale. These are as follows, in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>:



288 There is one previous experimental study of the kinetics of MeSA oxidation (Canosa-Mas et al.,  
 289 2002), where the reactions of R10 and R11 were measured. For R10, adjusting for re-evaluation of  
 290 the reference rate coefficient, Cl + acetone (McGillen et al., 2020), a value of 2.5±0.3 × 10<sup>-12</sup> cm<sup>3</sup>  
 291 molecule<sup>-1</sup> s<sup>-1</sup> was obtained, which is higher than our value of (1.65±0.44) × 10<sup>-12</sup>. The same study  
 292 determined R11 to be >4.1 × 10<sup>-22</sup>, based on a relative rate with respect to the reaction of O<sub>3</sub> +  
 293 toluene (Atkinson, 1994), and also provided a rough estimate of ~4 × 10<sup>-21</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> using an  
 294 absolute method. In our case, we find the rate coefficient of R11 to be (3.33±2.01) × 10<sup>-19</sup> cm<sup>3</sup>  
 295 molecule<sup>-1</sup> s<sup>-1</sup>, using the relative method, which is considerably larger than the previous

296 determination. The reasons for these discrepancies are unclear, although it is noted that the  
297 chamber employed in the previous experiments is substantially smaller ( $0.05 \text{ m}^3$ ) than that of this  
298 study, and for a compound of low vapour pressure such as MeSA, any wall effects are likely to be  
299 exacerbated by a greatly increased surface-area to volume ratio. In relation to R11, it is further  
300 noted that the reactivity of  $\text{O}_3$  with other closely related oxygenated aromatic compounds such as  
301 guaiacol has been found to be quite similar to our determination (Zein et al., 2015),  $k = (4.0 \pm 3.1) \times$   
302  $10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and suggests that phenolic compounds such as these have an enhanced  
303 reactivity compared with other aromatics.

304 We present the first determinations for the rate coefficient of R8 and R9. Compared with the  
305 reaction of  $\text{OH} + \text{phenol}$  (McGillen et al., 2020),  $k = 2.80 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{\text{R8}}$  is almost an  
306 order of magnitude smaller, suggesting that the acetate group *ortho* with respect to a hydroxyl  
307 group has an electron-withdrawing effect on the aromatic ring. This hypothesis is supported by the  
308 slow rate of R9 and R10, since each of these reactions is expected to be dominated by electrophilic  
309 addition to the ring system. It was observed during test experiments on  $k_{\text{R9}}$  that much larger rate  
310 coefficients were observed at higher  $[\text{NO}_2]$  (where  $\text{N}_2\text{O}_5$  was used as the  $\text{NO}_3$  source). This is similar  
311 to previous findings on  $\text{NO}_3 + \text{alkylnaphthalenes}$  (Phouongphouang and Arey, 2002). This  
312 phenomenon can be attributed to an equilibrium complex formed in R9, which may undergo a fast  
313 reaction with  $\text{NO}_2$ . For this reason,  $[\text{NO}_2]$  was kept at a minimum by maintaining R4 under a large  
314 excess of  $\text{O}_3$ . This suggests that similar precautions should be taken when measuring  $\text{NO}_3$  rate  
315 coefficients with other aromatic species.

316  $k_{\text{R8}}$  can also be compared with structure-activity relationship predictions. Taking the approach of  
317 Kwok and Atkinson (1995), a value of  $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is predicted, which is considerably  
318 larger than our measured value. The likely reason for this is because of the paucity of data regarding  
319 aromatics that contain an acetate group. Unfortunately, it appears that the recent technique of  
320 Jenkin et al.(2018) is optimized based solely on this estimated value, which is probably unintentional,

321 and yields an identical value to Kwok and Atkinson.(1995) This comparison highlights the need to  
322 study the kinetics of more compounds of this type, which are currently poorly represented in the  
323 experimental database (McGillen et al., 2020). Given the large variety of hormonal compounds that  
324 are emitted by the biosphere (Herrmann, 2010), and the small number of these compounds whose  
325 atmospheric chemical behaviour has been determined experimentally, it is crucial that estimation  
326 methods such as these are improved, so that the impact of the environment on semiochemicals can  
327 be better assessed.

### 328 **3.3 Atmospheric photolysis of MeSA**

329 The potential for several UV wavelengths (254/ 365/ >300 nm) to photolyze MeSA was investigated.  
330 In the case of the 365 and >300 nm lamps, photolytic loss of MeSA was found to be statistically  
331 indistinguishable from the dark losses (see Figure S5, Table S1). For the 254 nm lamps, the photolysis  
332 rate was significant ( $2.82 \pm 0.26 \times 10^{-5} \text{ s}^{-1}$ ), although this wavelength is not important in the  
333 troposphere (Finlayson-Pitts and Pitts, 2000), and is presented here only for completeness.

334 A previous study determined the UV absorption cross section of MeSA (Canosa-Mas et al., 2002),  
335 and found a strong chromophore with a peak of  $\sim 1.5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  at 310 nm. Assuming  
336 that this measurement is correct, and that the quantum yield of photolysis is unity, this would lead  
337 to very significant losses of MeSA in the troposphere and would dominate its overall loss in the  
338 atmosphere. However, our measurements suggest the opposite. The reasons for this discrepancy  
339 cannot be known with certainty, but two possibilities are considered. Firstly, the cross section could  
340 be inaccurate – this was determined by measuring absorbance in the saturated headspace above a  
341 pure sample of MeSA. There are several pitfalls to this approach, most notably, that under saturated  
342 conditions, it is expected that MeSA could deposit on the absorption cell windows, which could  
343 strongly influence the retrieved cross section. Secondly, even with a large absorbance, the photolysis  
344 quantum yield could be very low, leading to no measurable transformation of MeSA within the



345 actinic range. Either way, we conclude that photolysis is not a major sink for MeSA under  
 346 tropospheric conditions.

### 347 **3.4 Atmospheric lifetime of MeSA**

348 A practical approach to estimating the importance of atmospheric loss processes is to calculate the  
 349 lifetime of MeSA with respect to each loss process. Oxidation lifetimes are calculated thus:

$$350 \quad \tau_{\text{ox}} = \frac{1}{[\text{ox}] \cdot k_{\text{ox}}} \quad (12)$$

351 where [ox] is a globally representative concentration of a given oxidant in molecule  $\text{cm}^{-3}$  (see Table 3  
 352 for the selected values (Atkinson, 1991; Monks et al., 2009; Spivakovsky et al., 2000; Wingenter et  
 353 al., 1996)),  $k_{\text{ox}}$  is the rate coefficient of the reaction of MeSA with respect to that oxidant in  $\text{cm}^3$   
 354 molecule $^{-1} \text{s}^{-1}$ , and  $\tau_{\text{ox}}$  is the lifetime in seconds.

355 The lifetime with respect to photolysis,  $\tau_{\text{phot}}$ , is provided using an analogous equation:

$$356 \quad \tau_{\text{phot}} = \frac{1}{J} \quad (13)$$

357 The lifetime with respect to heterogeneous loss is considered as follows (Jacob, 1999):

$$358 \quad \tau_{\text{heterogeneous}} = \left( \frac{1}{\frac{S_a}{V} \cdot k_{\text{dry SOA}}} + \frac{1}{\frac{S_a}{V} \cdot k_{\text{humid SOA}}} + \frac{1}{\frac{S}{V} \cdot k_{\text{dry surface}}} + \frac{1}{\frac{S}{V} \cdot k_{\text{humid surface}}} \right)^{-1} \quad (14)$$

359 where  $S_a$  represents the SOA surface area  $S$  represents the various ground and vegetation surfaces.  
 360 Typical  $S_a/V$  ratios for rural and urban areas range from  $10^{-4}$  to  $10^{-3} \text{ m}^{-1}$  (Li et al., 2012; Wang et al.,  
 361 2016), which result in lifetimes between 1 and 190 days and are therefore comparable to gas-phase  
 362 oxidation.

363 Once all loss processes have been accounted for, the overall lifetime can be assessed through  
 364 Equation (15):

$$365 \quad \frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} + \frac{1}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{phot}}} + \frac{1}{\tau_{\text{heterogeneous}}} \quad (15)$$

366 which leads to an estimated total lifetime of gas-phase MeSA of 1–4 days.

367 It should be emphasized that globally averaged values of [ox], J values and  $S/V$  employed in Eq. 15  
368 will not always be applicable in understanding the fate of emissions from a terrestrial ecosystem. For  
369 example, recent work shows that  $\text{NO}_3$  (which is considered on a global scale to be an exclusively  
370 night-time oxidant) plays an important role even during the day in some forested environments  
371 (Liebmann et al., 2019). Similar caveats are offered regarding the heterogeneous losses described in  
372 Eq. 14, where local factors such as the amount and type of vegetation surfaces and the season in  
373 which the emission occurred could have a profound effect on the uptake of MeSA and analogous  
374 compounds. However, such further, more detailed analyses of these points are beyond the scope of  
375 the present study.

376 A further consideration is that the loss of gas-phase MeSA onto SOA surfaces is not necessarily a  
377 permanent sink for this compound. The affinity for MeSA towards the air-water interface (Liyana-  
378 Arachchi et al., 2013), and our FIGAERO-CIMS measurements, demonstrates the reversibility of  
379 MeSA uptake and suggests that MeSA may subsequently re-enter the gas phase under field  
380 conditions. It is therefore logical, given that in the absence of surfaces MeSA emissions would be  
381 rapidly advected and diluted, that the presence of surfaces – whether they are leaf or aerosol  
382 surfaces – could actually slow the removal of MeSA from a local environment. Accordingly, these  
383 loss processes are not considered within the lifetime assessment.

#### 384 **4. Atmospheric and ecological implications**

385 Our analysis may help to assess the plausibility of some of the proposed ecological roles of MeSA.  
386 For example, its lifetime with respect to oxidation is sufficiently long under field conditions that  
387 transport from the point of emission would be possible over 10s of kilometres, which is more than  
388 necessary in most cases. Of course, an emission from a single plant would be highly dispersed over  
389 this distance, however, a collective emission from an ecosystem, such as that observed by Karl et

390 al.(2008) could influence the semiochemistry of the air over this region, and may be able to affect  
391 the response of an ensemble of plants towards herbivory, systematic acquired resistance or in  
392 attracting pollinators and herbivore predators.

393 By investigating the many diverse sinks of MeSA, it is apparent that both OH and NO<sub>3</sub> represent the  
394 dominant permanent sinks, and that losses during the night-time are lower. Given that MeSA along  
395 with several other floral scents possess a circadian emission profile, with higher emissions during the  
396 night (Loughrin et al., 1991), it is possible to hypothesize that some plants may have adapted their  
397 emissions to account for the atmospheric reactivity of MeSA or perhaps other phytohormones.  
398 Given that sufficient kinetic information is available for relatively few phytohormones, this  
399 hypothesis remains speculative.

400 The observation that a substantial fraction of MeSA can partition to aerosol particles is consistent  
401 with previous studies (Karl et al., 2008; Liyana-Arachchi et al., 2013), and should be an important  
402 focus when investigating signalling among biotic entities. Indeed, MeSA is perceived at the same  
403 time and location as many other semiochemicals within an odorscape, by a variety of organisms  
404 (Conchou et al., 2019; Xu and Turlings, 2018). Here, MeSA can serve the dual role of a synergetic  
405 compound with insect pheromones, for example in facilitating the orientation to a sexual partner  
406 (Xu and Turlings, 2018), or antagonistically, by hampering this orientation (Rouyar et al., 2015),  
407 depending on the volatile, plant and insect species. The efficiency of transport within the  
408 atmosphere and the sensory mechanisms by which these compounds operate are so far unknown,  
409 but they have already been exploited in pest management programs, for example in combining a  
410 crop species with repelling or masking plants (Mofikoya et al., 2019). Like MeSA, other  
411 semiochemicals (especially pheromones) with similar physicochemical properties may partition to  
412 SOA, which could be instrumental in their atmospheric transport. It is clear that further work is  
413 needed, particularly regarding how semiochemicals that are absorbed onto surfaces are perceived  
414 by the biota of interest.

415

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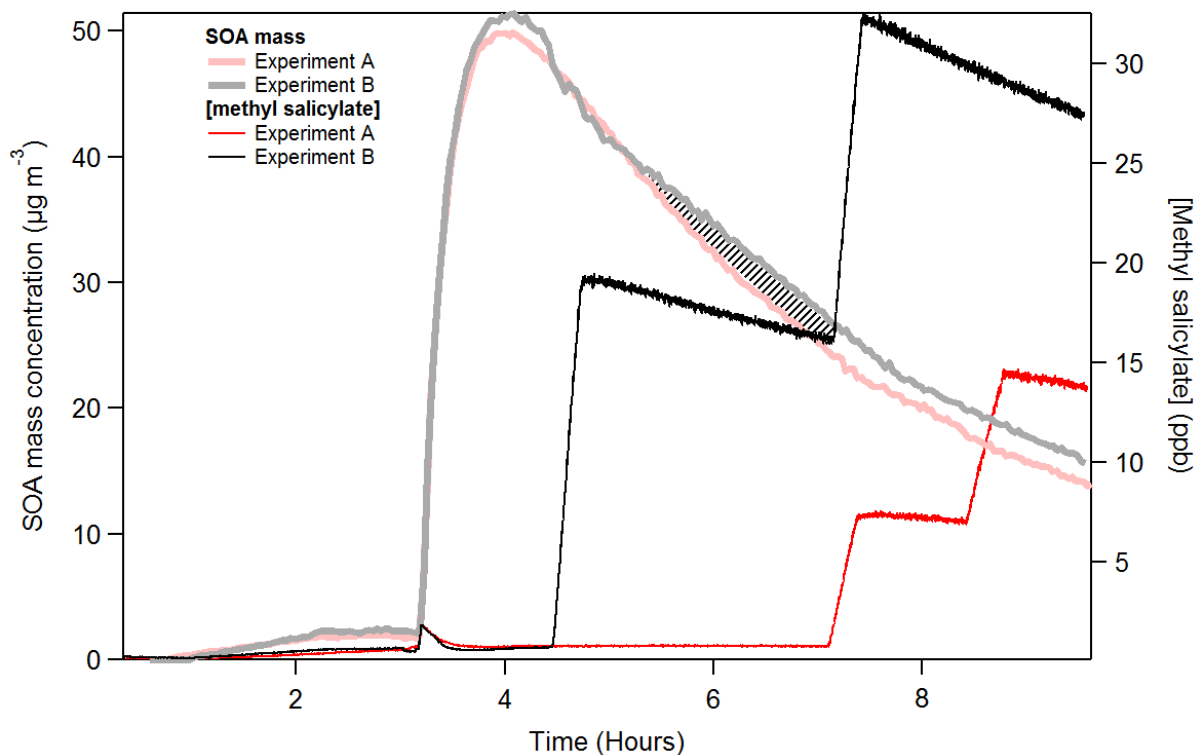
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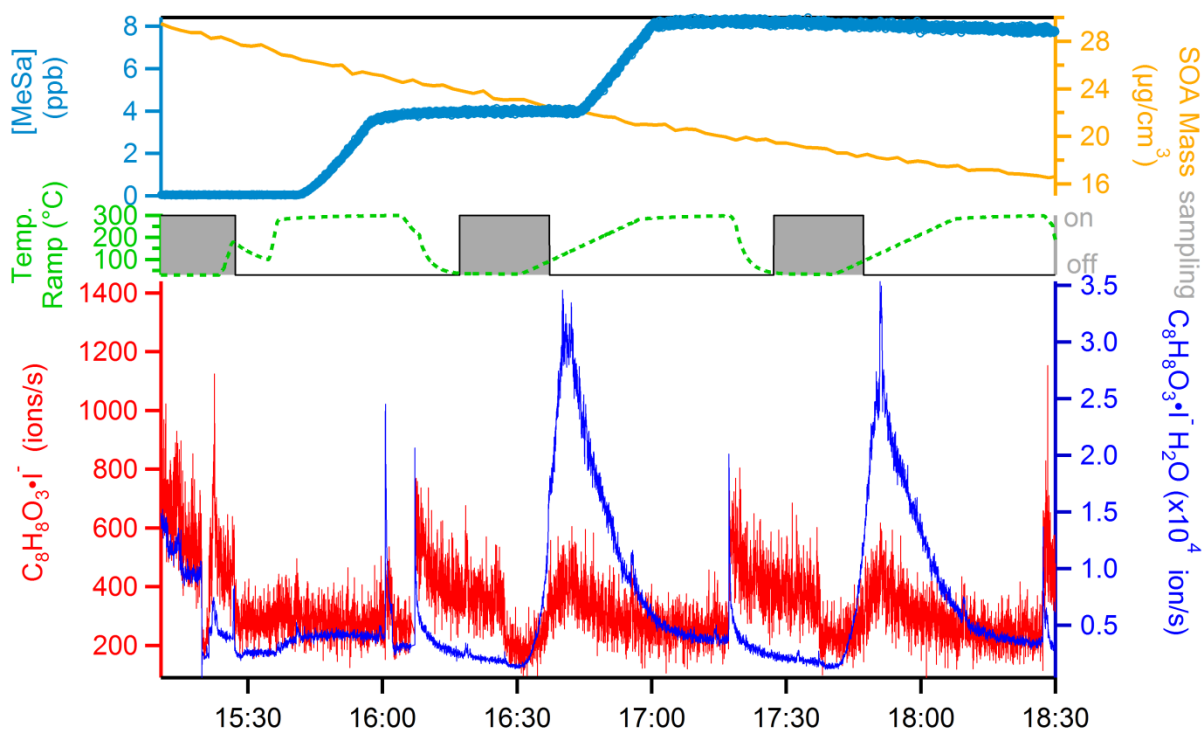
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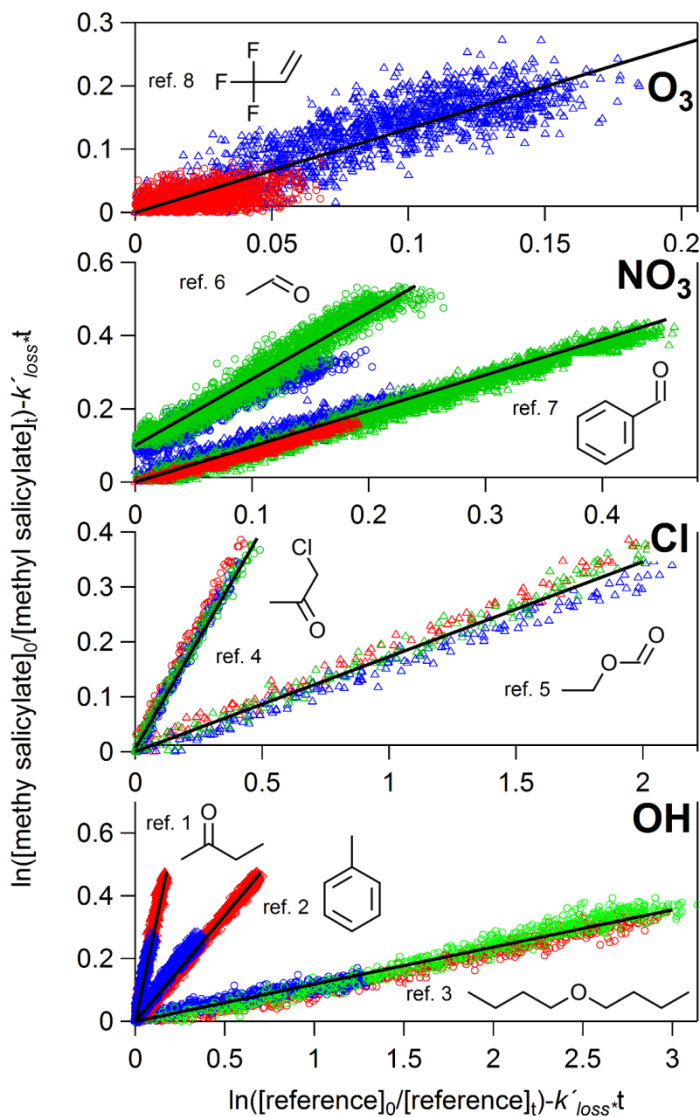
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582 **Figure 1.** Time profile of secondary organic aerosol (SOA) mass concentration in the absence /  
 583 presence of MeSA under the condition of RH ca 50%. Experiment A: MeSA introduced when SOA  
 584 mass concentration ca.  $45 \mu\text{g m}^{-3}$ ; Experiment B: MeSA introduced when SOA mass concentration ca.  
 585  $25 \mu\text{g m}^{-3}$ . A reduction in the rate of SOA mass decrease is observed upon introduction of MeSA,  
 586 indicating uptake from the gas phase. The shaded area presents the calculation of partitioning  
 587 fraction of gas-phase MeSA onto SOA ( $F$ ) in Equation 12.



588

589 **Figure 2.** Time series of MeSA under humid conditions (~40-60%) with SOA in HELIOS. Upper Panel:  
 590 MeSA concentration was quantified using PTR-ToF-MS and SOA mass concentration was calculated  
 591 from size distribution in the SMPS. Middle Panel: Temperature ramp of on-line SOA composition  
 592 analysis in FIGAERO-CIMS, the grey-shaded area indicates the gas-phase analysis and SOA sampling  
 593 in the same time; Lower Panel: the MeSA signal ( $C_8H_8O_3I^-$ ,  $m/z$  278.952 and  $C_8H_8O_3I^- \cdot H_2O$ ,  $m/z$   
 594 278.952) in FIGAERO-CIMS.



595

596 **Figure 3:** Plots of relative rate kinetic data obtained for the OH, Cl, NO<sub>3</sub> and O<sub>3</sub> reactions with MeSA.  
 597 Note that each color (blue, green and red) represents individual experiments using the same  
 598 reference compound. OH references: ref. 1 methyl ethyl ketone, ref. 2 toluene and ref. 3 di-*n*-butyl  
 599 ether; Cl references: ref. 4 chloroacetone and ref. 5 ethyl formate; NO<sub>3</sub> references: ref. 6  
 600 acetaldehyde and ref. 7 benzaldehyde; O<sub>3</sub> references: ref. 8 3,3,3-trifluoropropene. Ref. 6 was offset  
 601 0.1 on the y-axis for clarity.

602

