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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, NO₃, Cl and
27 O₃; photolysis rates; and deposition rates of gas-phase MeSA onto organic aerosols. Room
28 temperature rate coefficients are determined (in units of cm³ molecule⁻¹ s⁻¹) to be (3.20±0.46)×10⁻¹²,
29 (4.19±0.92)×10⁻¹⁵, (1.65±0.44)×10⁻¹² and (3.33±2.01)×10⁻¹⁹ for the reactions with OH, NO₃, Cl and O₃
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

41

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 m³ hemispherical FEP Teflon foil chamber equipped with two Teflon fans installed at
97 the base, which generate flow velocities of 14 m s⁻¹ 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⁻¹) 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 m³ 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⁻¹). This led to gradual
113 dilution of the chamber contents. This was quantified using SF₆ 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 m³ 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 (H₃O⁺) 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⁻¹, 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⁻ 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⁻ 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⁻¹ onto a
129 PTFE filter (SKC, ZefluorTM 25 mm, 2 µm) for 20 mins, and were volatilized by slowly ramping the
130 temperature of a 2 L min⁻¹ carrier flow of N₂ 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, NO₃, Cl and O₃ were determined in the 7.3 m³ 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_{ref}), k_{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 NO_3 experiments, NO_2 was slowly and continuously introduced into the chamber, maintaining
173 $[\text{NO}_2]$ at $\sim 1 \times 10^{12}$ molecule cm^{-3} , under an excess of O_3 (2.5×10^{13} molecule cm^{-3}), producing NO_3
174 through the following reaction:



176 In the Cl experiments, Cl_2 was photolyzed at 365 nm, yielding two chlorine atoms:



178 In the O_3 experiments, O_3 was generated from pure 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 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_{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_{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), O₂ (99.999%, Air-Liquide), N₂ (99.999%, Air-Liquide), chlorine (99.6%, Air-Liquide), NO₂ (1%
203 in N₂, Air-Liquide), methanol (99.98%, Biosolve), sodium nitrite (>97%, Sigma-Aldrich), nitric acid

204 (70%, Sigma-Aldrich), sulphuric acid (95%, Prolabo) and P₂O₅ (≥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 N₂, to remove water soluble impurities such as HONO, then through a drying tube containing
209 P₂O₅, 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 O₃ was tested by exposing MeSA to 200 ppb of O₃ 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_{SF_6} is the dilution rate as defined by SF_6 loss, and k_{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_{chamber} and V_{chamber} are the surface area and volume of the chamber, 108 m^2 and 90 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 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 :

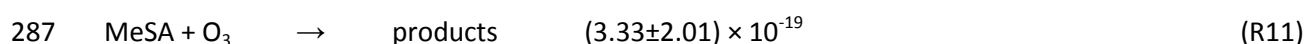
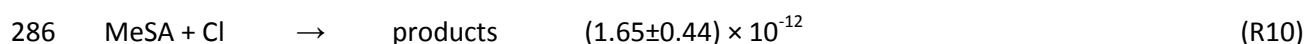
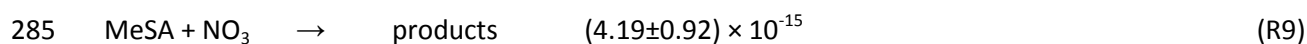
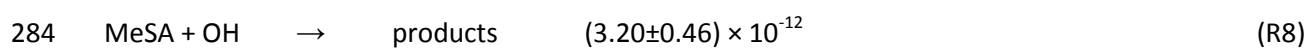
$$261 \quad F = \frac{\int_0^t \text{SOA}_{\text{MeSA}} - \int_0^t \text{SOA}}{[\text{MeSA}]^{\#}} \quad (11)$$

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 $1\text{--}50 \mu\text{g m}^{-3}$,²⁶ 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, NO₃, Cl and O₃ 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 cm³ molecule⁻¹ s⁻¹:



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 × 10⁻¹² cm³
291 molecule⁻¹ s⁻¹ was obtained, which is higher than our value of (1.65±0.44) × 10⁻¹². The same study
292 determined R11 to be >4.1 × 10⁻²², based on a relative rate with respect to the reaction of O₃ +
293 toluene (Atkinson, 1994), and also provided a rough estimate of ~4 × 10⁻²¹ cm³ molecule⁻¹ s⁻¹ using an
294 absolute method. In our case, we find the rate coefficient of R11 to be (3.33±2.01) × 10⁻¹⁹ cm³
295 molecule⁻¹ s⁻¹, 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 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 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 OH + phenol (McGillen et al., 2020), $k = 2.80 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, k_{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_{R9} that much larger rate
310 coefficients were observed at higher $[\text{NO}_2]$ (where N_2O_5 was used as the NO_3 source). This is similar
311 to previous findings on NO_3 + 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 NO_2 . For this reason, $[\text{NO}_2]$ was kept at a minimum by maintaining R4 under a large
314 excess of O_3 . This suggests that similar precautions should be taken when measuring NO_3 rate
315 coefficients with other aromatic species.

316 k_{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 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_{ox} is the rate coefficient of the reaction of MeSA with respect to that oxidant in cm^3
 354 molecule $^{-1} \text{s}^{-1}$, and τ_{ox} is the lifetime in seconds.

355 The lifetime with respect to photolysis, τ_{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} 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 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 NO₃ 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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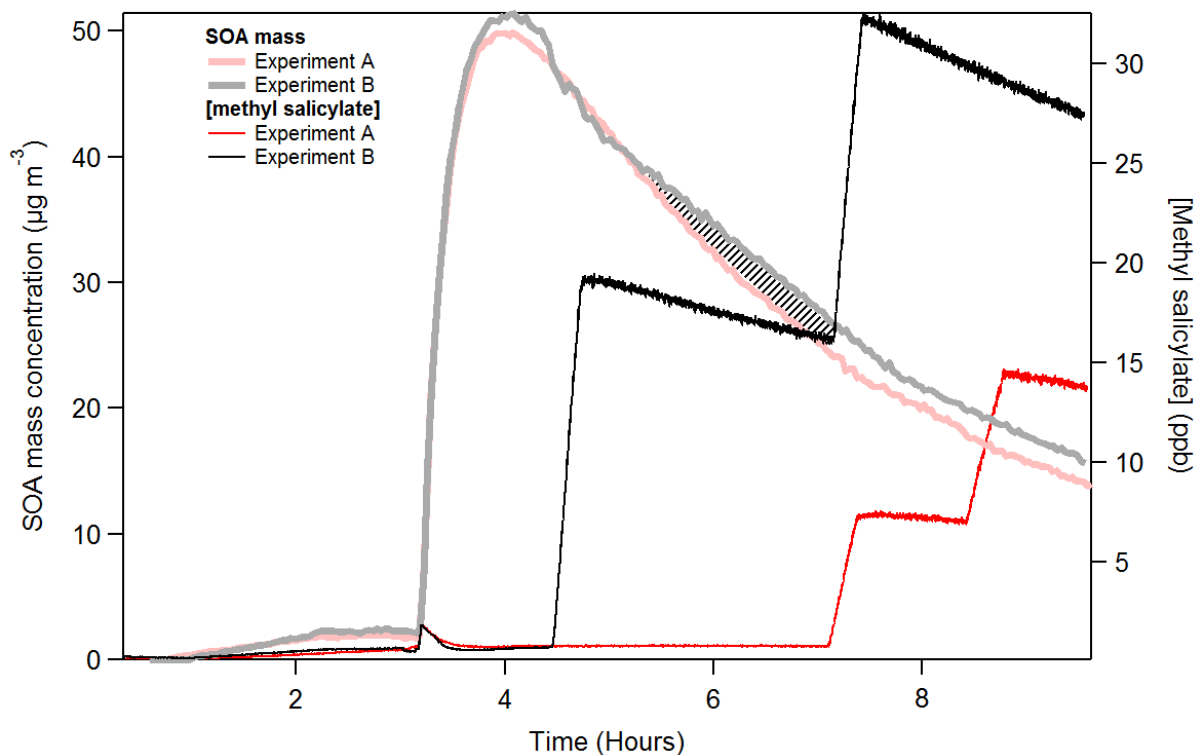
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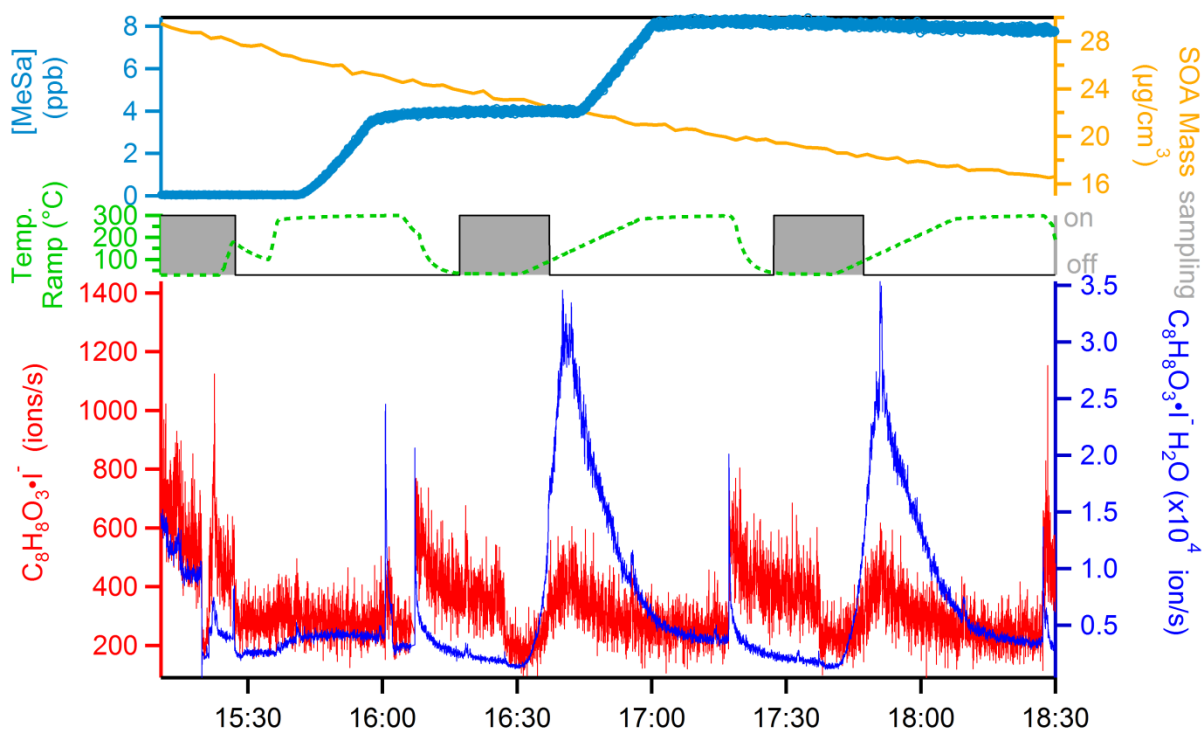
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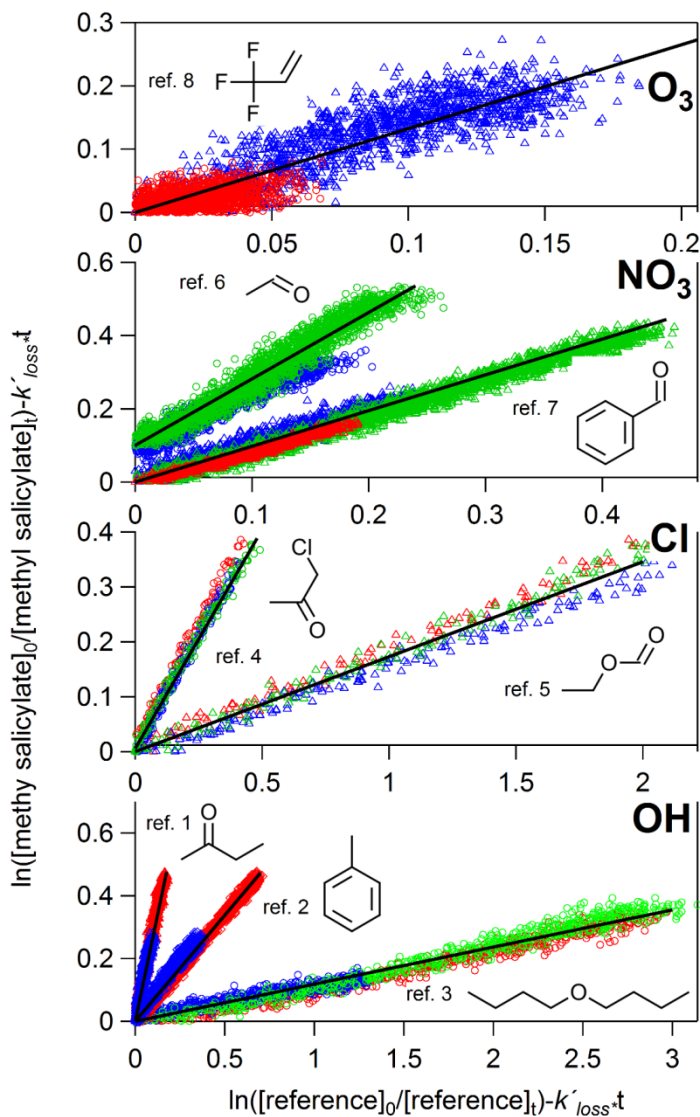
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582 **Figure 1.** Time profile of secondary organic aerosol (SOA) mass concentration in the absence /
 583 presence of MeSA under the condition of RH ca 50%. Experiment A: MeSA introduced when SOA
 584 mass concentration ca. $45 \mu\text{g m}^{-3}$; 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, NO₃ and O₃ 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; NO₃ references: ref. 6
 600 acetaldehyde and ref. 7 benzaldehyde; O₃ references: ref. 8 3,3,3-trifluoropropene. Ref. 6 was offset
 601 0.1 on the y-axis for clarity.

602

