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

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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

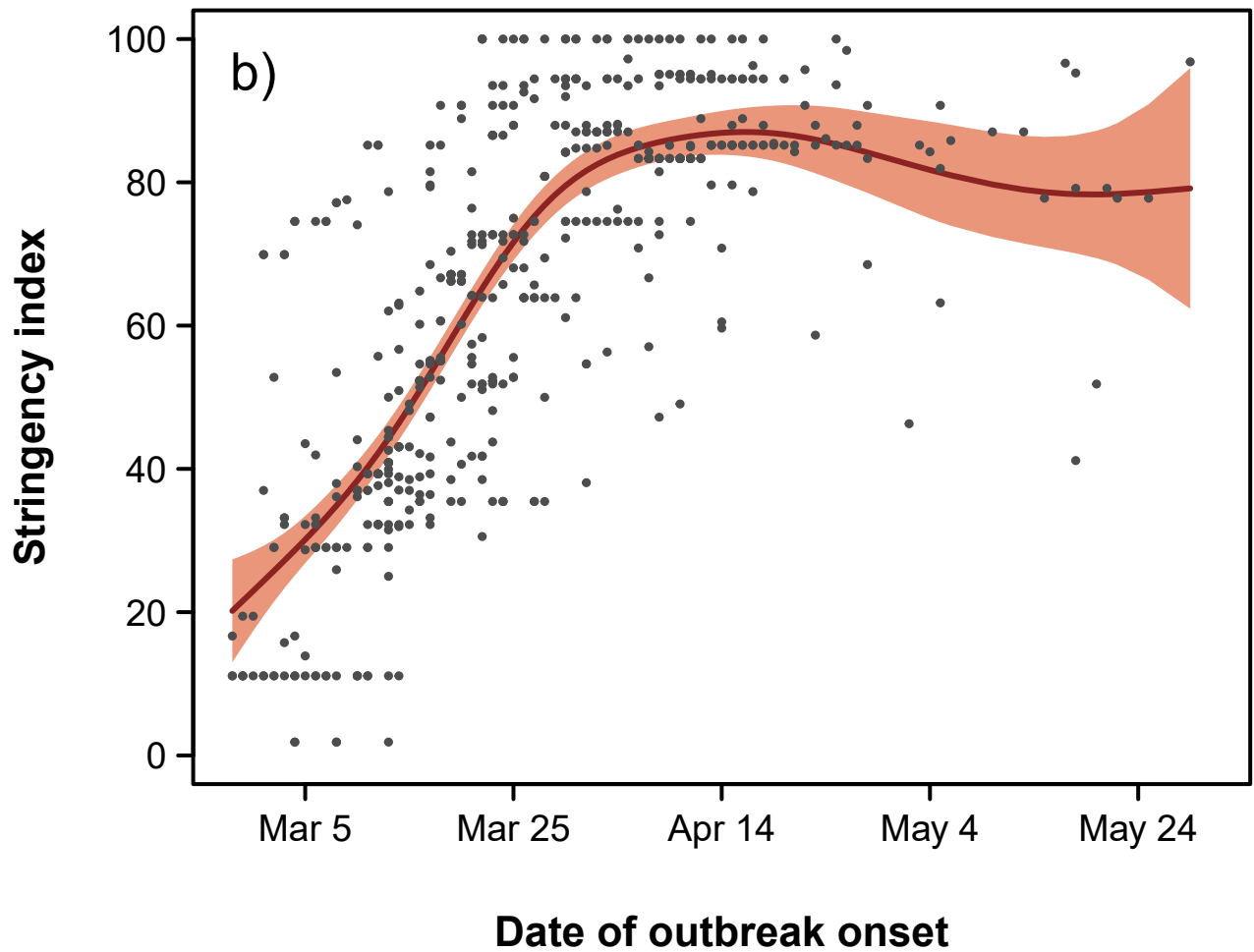
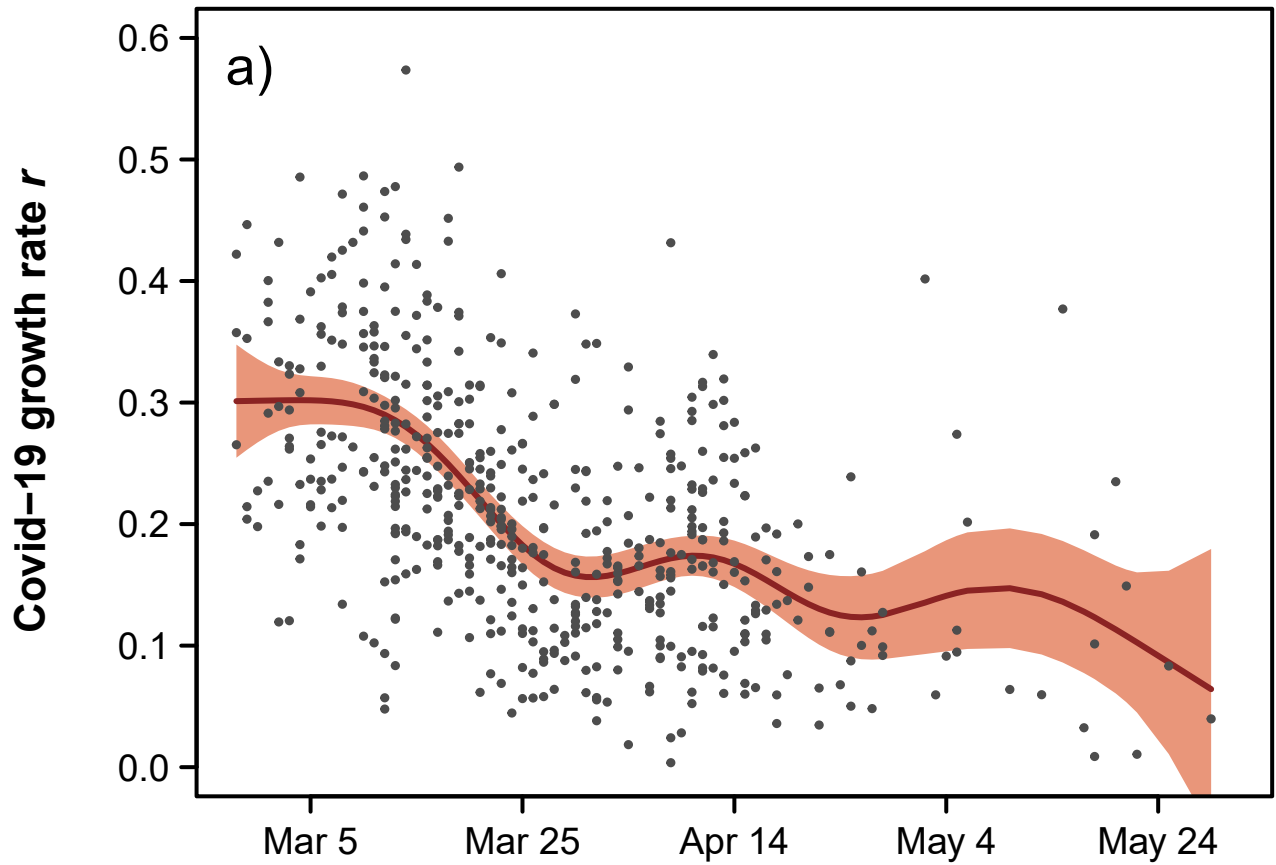
114 throughout the experiments using Bruker Vertex 70 (pathlength: 303 m) and Nicolet 5700 Magna
115 (pathlength: 143 m) Fourier-transform infrared spectrometers coupled with white-type multipass
116 optics for HELIOS and the 7.3 m³ chamber respectively.

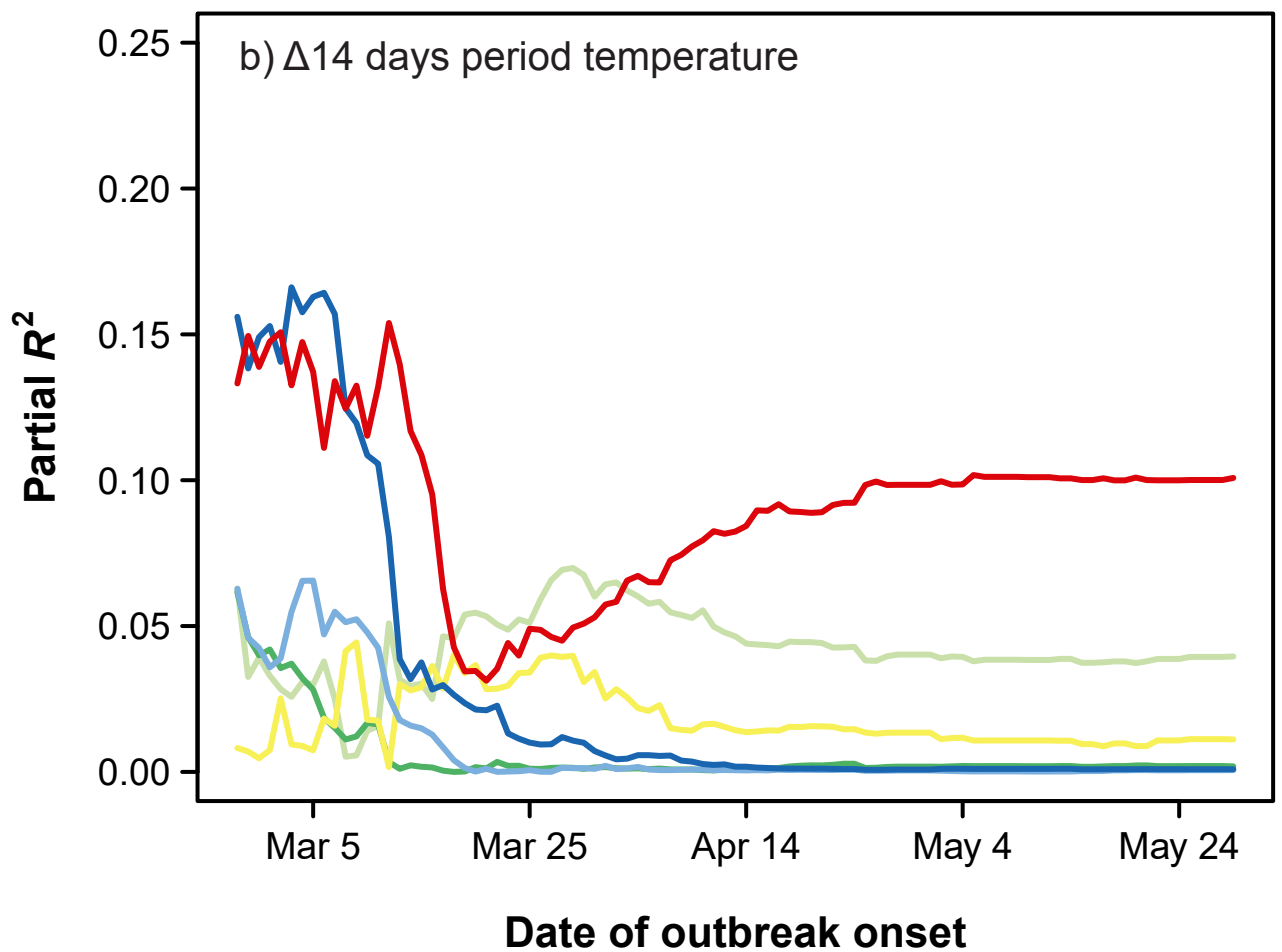
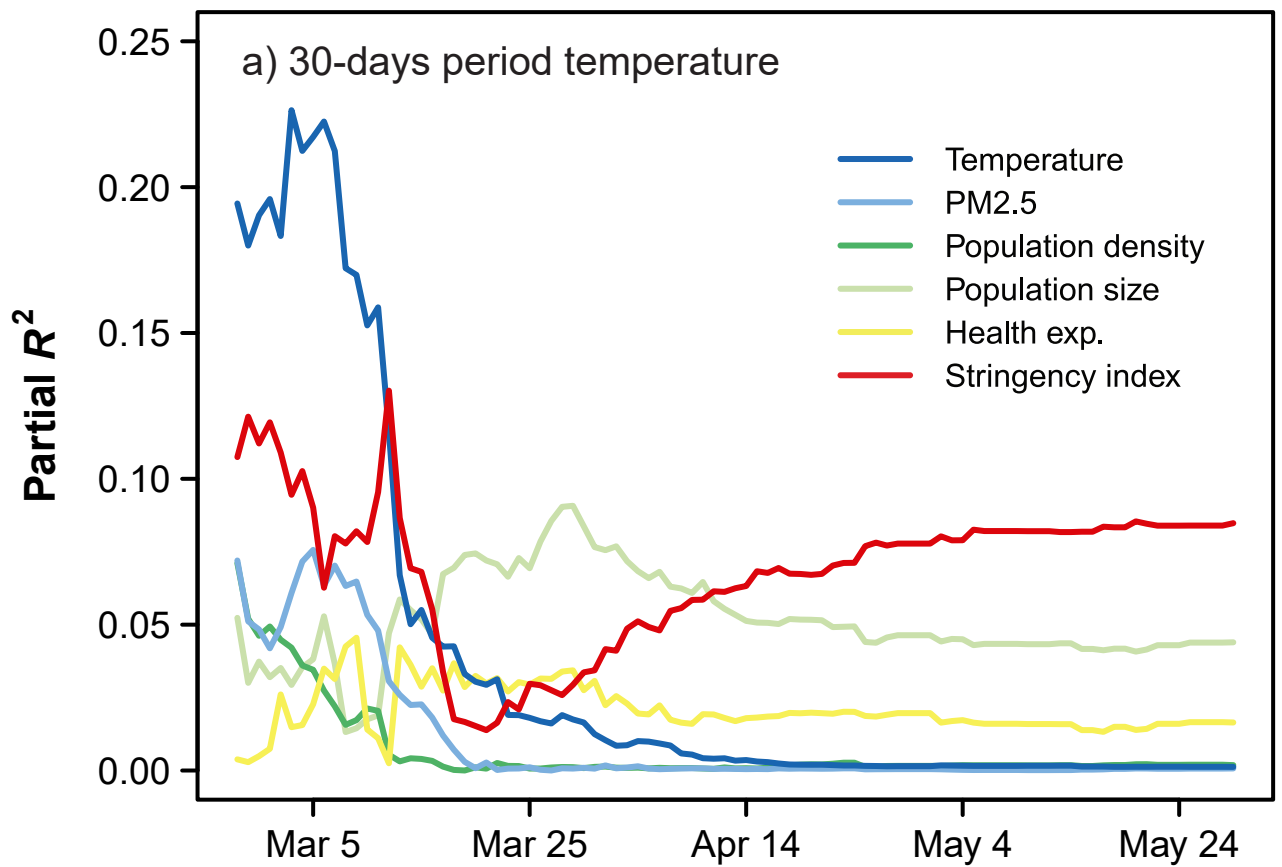
117 **2.2 Organic compound analysis in the gas and particle phases, and aerosol measurements:**

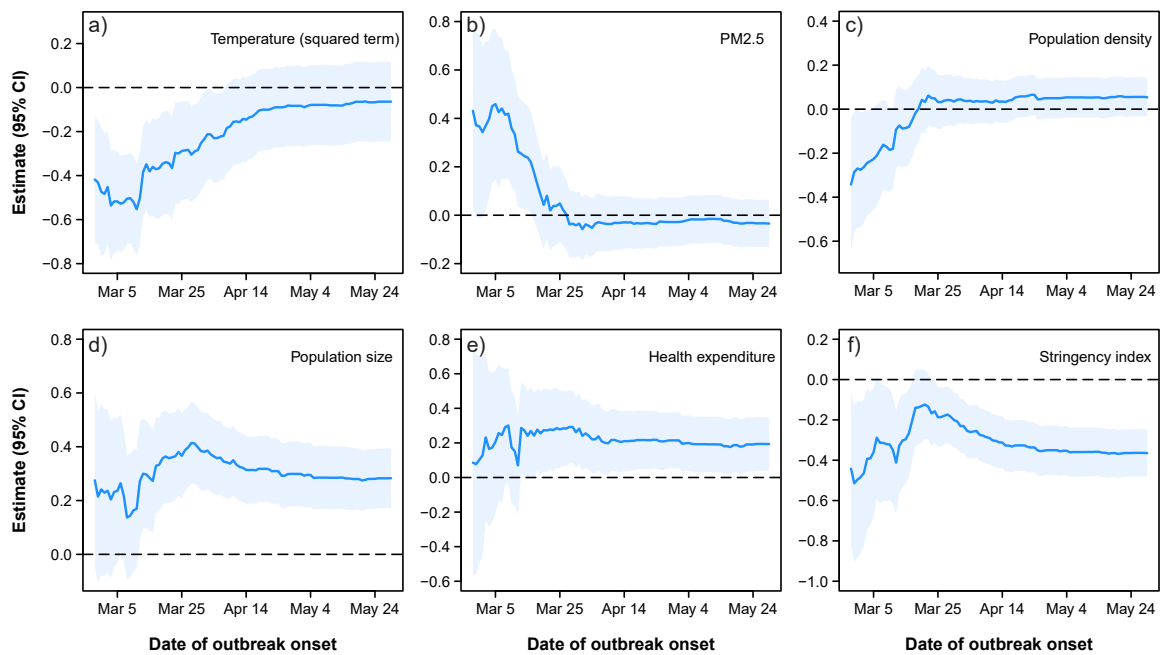
118 Gas-phase MeSA together with several other organic compounds were monitored using a high-
119 resolution proton transfer reaction time-of-flight mass spectrometer (Ionicon Analytik, PTR-ToF-MS
120 8000) with a hydronium ion (H₃O⁺) detection scheme. The pressure and voltage in the PTR-ToF-MS
121 drift 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, Zefluor™ 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:**

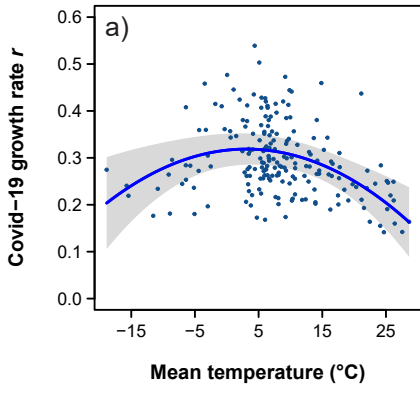
137 Because of the low vapor pressure of MeSA, 0.086 Torr at 298 K (Yaws, 2015), it is difficult to
138 introduce into the chamber using the conventional method of impinging a liquid sample into a



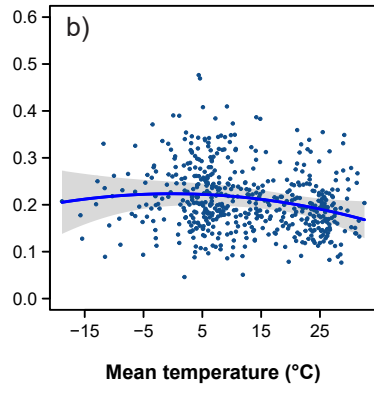




15 March dataset



15 April dataset



15 May dataset

