# 1 Influence of temperature, relative humidity, and water

## 2 saturation on airborne emissions from cigarette butts

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## 7 Abstract

8 With five trillion generated per year, cigarette butts are some of the most common litter worldwide. 9 However, despite the potential environmental and human health risks from cigarette butts, little 10 effort has been made to understand airborne emissions from cigarette butts. This study examined 11 the influence of temperature, relative humidity and water saturation on airborne chemical 12 emissions from cigarette butts. Experiments were conducted to measure the emitted chemical 13 masses from butts using headspace analysis after the butts were conditioned in a controlled chamber under four conditions (30 °C and 25 % RH, 30 °C and 50 % RH, 40 °C and 25 % RH, 14 15 40 °C and 50 % RH) and in an outdoor environment (two sets of experiments in both summer and 16 winter). The measured target chemicals included furfural, styrene, ethylbenzene, 2-methyl-2-17 cyclopenten-1-one, limonene, naphthalene, triacetin, and nicotine. Results indicate that increased 18 temperature increased the emission rates of all target chemicals from the butts conditioned in both 19 chambers and outdoors. In addition, water has considerable influence on the emission rates from 20 the butts. Seven of the eight chemicals were emitted faster from butts at 50 % RH compared to 21 25 % RH. During water saturation, chemicals with high water solubility and partition coefficient 22 between water and air ( $K_{wa}$ ), e.g., triacetin and nicotine, mainly migrate into the surrounding 23 environment via aqueous rather than airborne routes. This highlights the importance of rainfall 24 events on airborne emission variability for triacetin and nicotine. Other less soluble chemicals are 25 more likely to be emitted from saturated butts into air as  $K_{wa}$  increases. For these chemicals, the 26 ratios of initial emitted mass for both wet butts to dry butts and wet filters to dry filters increase 27 with increasing  $K_{wa}$ . Water saturation increased the decay rate (decreased the decay time) of 28 emitted mass measured in headspace analysis for the two carbonyl chemicals: furfural and 2-29 methyl-2-cyclopenten-1-one, while it decreased the decay rate (increased the decay time) for the 30 three hydrocarbons (styrene, limonene, and naphthalene).

### 31 Keywords:

32 Cigarette butt, nicotine, triacetin, emission, air

### 33 **1. Introduction**

34 An environmental consequence of the use of tobacco products is the disposal of discarded 35 cigarette butts. Over five trillion cigarette butts are generated per year, (Novotny and Zhao 1999, 36 Chapman 2006, Healton et al. 2011, Bonanomi et al. 2015) with each butt potentially persisting in 37 the environment over a year (Novotny and Zhao 1999). Cigarette butts are often the most prevalent 38 litter on beaches (Claereboudt 2004, Smith et al. 2014), near streams, night clubs (Becherucci and 39 Pon 2014), bus stops (Wilson et al. 2014), roads and streets (Healton et al. 2011, Patel et al. 2013). 40 They have been found at densities averaging more than 4 butts per square meter in urban 41 environments (Seco Pon and Becherucci 2012). Cigarette butts may result in health risk to humans 42 and wildlife (Kadir and Sarani 2015). Cigarette butts have been consumed by small children 43 (Novotny et al. 2011), leach chemicals into water (Zhao et al. 2010a, Zhao et al. 2010b, Green et 44 al. 2014, Kadir and Sarani 2015) and alter wildlife reproduction habits and mortality rates (Dieng 45 et al. 2013, Suarez-Rodriguez et al. 2013, Waters 2013, Dieng et al. 2014, Booth et al. 2015, Wright 46 et al. 2015).

47 Despite these potential risks from cigarette butts, little effort has been done to characterize 48 airborne emissions from cigarette butts. Four studies have measured the emissions from cigarette 49 butts into the air of headspace of test vials (Fukuhara et al. 1985, Huang et al. 2014, You et al. 50 2014, Ji et al. 2015). Fukuhara et al. (1985) detected a range of volatile components (e.g., carbonyls, 51 hydrocarbons, pyrroles and terpenes) in the headspace of vessels that contained cigarette butts, and 52 found that these compounds were also found in mainstream smoke. They also indicated that the 53 tar-like odors in butts may result from 2,3-pentanedione, N-methyl pyrrole, 3-methyl pyrrole, 54 isocapronitrile, pyrrole, and 2-methyl pyrrole. You et al. (2014) developed a static headspace gas 55 chromatography-flame ionization detector (GC-FID) method for quantifying menthol 56 concentrations in the cigarette filter and cigarette papers in a mentholated cigarette. The samples 57 were first heated at 100 °C for 30 min in a headspace sampler, and then measured by GC-FID. The menthol concentration in the cigarette papers ranged from 3.0 mg g<sup>-1</sup> paper to 4.1 mg g<sup>-1</sup> paper, 58 while the menthol concentration in the cigarette filter was 13.7 mg  $g^{-1}$  paper to 27.2 mg  $g^{-1}$  paper. 59 60 Huang et al. (2014) measured the emissions from cigarette tipping paper (which attaches the filter

61 to the tobacco column) into the headspace of vials. The samples were first incubated at 80 °C for 62 45 min, and then 20 volatile organic compounds (VOCs) were quantified using gas 63 chromatography-mass spectrometry (GC-MS). Among the 20 target VOCs, methanol, ethanol, 64 isopropanol, ethyl acetate, 1-methoxy-2-propanol, and n-propyl acetate were the most abundant, with concentrations ranging from below detection to 20.7 mg m<sup>-2</sup> paper. A recent study developed 65 66 a static headspace GC-MS method to quantify benzene, toluene, m-xylene, p-xylene, o-xylene, styrene and ethylbenzene concentrations in cigarette filters (Ji et al. 2015). The method heated the 67 cigarette filters at 120 °C for 30 min in the headspace vials. The measured concentrations for 68 69 benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, and styrene ranged from 70 0.4  $\mu$ g/filter to 5.7  $\mu$ g/filter.

71 These four studies provide some basis for understanding the potential airborne emissions 72 into indoor and outdoor environments. However, the study reported by Fukuhara et al. (1985) was 73 limited in the number of cigarette butts tested and did not quantify the identified chemicals. For 74 the three more recent studies (Huang et al. 2014, You et al. 2014, Ji et al. 2015), the types of 75 chemicals detected were limited and only cigarette filters or tipping papers were studied. These 76 studies did not include the unburned tobacco or ash of cigarette butts, which may emit different 77 chemicals from the filters and tipping papers. In addition, the high incubation temperatures 78  $(> 80 \,^{\circ}\text{C})$  would enhance the emission of some non-volatile chemicals that may not be emitted to 79 a significant degree at more typical indoor and outdoor temperatures. Finally, all these studies only 80 measured freshly generated cigarette butts, or part of the unburned cigarette, and didn't examine 81 the influence of environmental factors that could impact the emissions from cigarette butts, such 82 as temperature, relative humidity, and water saturation.

This study aims to examine the influence of temperature, relative humidity and water saturation on airborne chemical emissions from cigarette butts conditioned in a controlled chamber and in a real outdoor environment. This paper is a partial summary of the interagency report from the United States National Institutes of Standards and Technology to the United States Food and Drug Administration, which is available online (https://doi.org/10.6028/NIST.IR.8256) (Poppendieck and Gong 2019).

#### 89 **2. Methods**

90 Cigarettes butts were generated using a custom-built system for this study. The cigarette 91 butts were placed in different conditioning environments for up to one week. After conditioning, 92 airborne chemicals emitted from each cigarette butt were measured by headspace analysis. The 93 goal of the headspace analysis was not to fully extract all chemicals remaining on the cigarette 94 butt, but to provide a consistent basis to compare chemical emissions into the air after the cigarette 95 butts had been conditioned in different environments.

#### 96 2.1 Generation of cigarette butts

97 A smoking apparatus was specially designed to consistently produce cigarette butts in this 98 study. The cigarette used was a leading cigarette brand in the United States market (United States 99 Center for Disease Control and Prevention 2017). Two cigarettes at a time were smoked with puff 100 sequence similar to ISO 3308 (ISO3308 2012). The smoking apparatus and procedures are 101 described in detail in Poppendieck and Gong (2019). In brief, each cigarette was smoked for 6 102 puffs, while each puff lasted 2.7 s with a flow rate of 1.0 L min<sup>-1</sup>. The time interval between each 103 puff was 60 s. After the last puff, butts were extinguished by placing it in a sand ashtray for 60 s. 104 Butts were then immediately placed in a pre-weighed 20 mL headspace vial. The vial with butts 105 in it was then weighed to determine the butt weight via difference. To ensure emission consistency, 106 only butts that weighed between 0.370 g and 0.442 g were used for experiments in this study.

## 107 2.2 Conditioning of cigarette butts

To examine the influence of temperature, relative humidity and water saturation on airborne emissions from cigarette butts, cigarette butts were conditioned in two types of environments, i.e., a controlled environmental chamber and a rooftop outdoor environment. In total, ten sets of experiments have been conducted. The measured temperatures, relative humidities and chamber airflow rates or wind velocities for each experiment are summarized in Table 1.

115	Table 1. Summary of conditioning experiments. Standard deviations appear in parenthesis. Each experimental condition was
116	tested for a range of durations (typically nine tests: 2 h to 144 h.). For Experiments 1 through 6, the standard deviations shown
117	in parenthesis are for the average values over the varying duration experiments.

	Condition environment	Temperature (°C)	Relative humidity (%)	Airflow rate or wind speed	Rainfall (mm min <sup>-1</sup> )		
1	chamber	31.1 (±0.2)	50 (±1)	350 mL/min <sup>a</sup>	N/A		
2	chamber	40.3 (±0.2)	51 (±2)	344.7 (±14.0) mL/min	N/A		
3	chamber	30.8 (±0.2)	25 (±1)	357.3 (±5.2) mL/min	N/A		
4	chamber	40.3 (±0.2)	25 (±1)	347.3 (±14.9) mL/min	N/A		
5	chamber	30.9 (±0.2)	52 (±4)	357.8 (±8.2) mL/min	wet <sup>b</sup>		
6	chamber	30.6 (±0.2)	51 (±1)	359.8 (±6.3) mL/min	dry <sup>b</sup>		
7	rooftop summer	25.1 (±3.0)	73 (±14)	1.8 (±1.1) m s <sup>-1</sup>	0.001 (±0.01)		
8	rooftop summer	24.4 (±3.3)	73 (±12)	2.1 (±1.1) m s <sup>-1</sup>	0.001 (±0.03)		
9	rooftop winter	3.7 (±2.7)	65 (±14)	3.2 (±1.9) m s <sup>-1</sup>	0.002 (±0.01) <sup>c</sup>		
10	rooftop winter	3.5 (±4.2)	65 (±17)	3.7 (±2.9) m s <sup>-1</sup>	0.001 (±0.008)		
aCotn	Astroint value. A stual values were not recorded for this experiment						

Setpoint value. Actual values were not recorded for this experiment.

<sup>b</sup>Cigarette butts that were soaked in a petri dish with artificial rainwater before being placed into the dark chamber were considered "wet", while cigarette butts that were placed in an empty petri dish before placed into the dark chamber were considered "dry".

<sup>c</sup>Value may be elevated due to snow on the sensor for over 24 h.

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#### 119 2.2.1 Conditioning in chambers

120 Cigarette butts were conditioned under four settings in three rectangular cuboid chambers 121 (Figure 1 (b)) with an airflow rate of 350 mL min<sup>-1</sup> but different temperature and relative humidity 122 combinations: 30 °C and 50 %, 40 °C and 50 %, 30 °C and 25 %, and 40 °C and 25 % 123 (experiments 1 through 4 in Table 1). The volume of each chamber is 590 mL. The temperature 124 and relative humidity were recorded automatically every minute, while the airflow rates were 125 checked at the beginning and end of each experiment with a bubble flow meter. For each test, three 126 freshly smoked, non-smoldering cigarette butts were placed in the chamber with a specially 127 designed holder (Figure 1 (a)) for eight different time durations (2 h, 5 h, 18 h, 24 h, 48 h, 72 h, 128 96 h, 120 h and 144 h). The filter holder had 1.7 mm diameter pegs to mount the butts onto the 129 vertical butt holder. The pegs made two holes in the filter area of each butt that were present for 130 the headspace analysis.



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Figure 1 (a) Cigarette butt holder for conditioning in chamber; (b) Cigarette butts conditioned in a chamber.

134 To study the influence of rainwater saturation on emissions from cigarette butts, freshly 135 smoked cigarette butts were first preconditioned before being placed into the chambers. However, 136 preliminary experiments showed that once the cigarette butts were saturated, the paper surrounding 137 the ash and tobacco could disintegrate erratically when handled and placed in chambers. In 138 addition, butts exposed to heavy rain events on the roof had similar fates, and it was challenging 139 to recover the entire cigarette butt intact. In contrast to the degradation of the ash and tobacco when 140 exposed to water, cigarette filters typically contain plasticized cellulose acetate fibers that show 141 minimal degradation after two years of outdoor exposure (Bonanomi et al. 2015). In addition, 142 experiments demonstrated that the emitted masses of the target chemicals from cigarette filters 143 were comparable to the emitted mass from the entire cigarette butts for most of the target chemicals 144 (Poppendieck and Gong 2019). Therefore, two sets of water saturation experiments were 145 conducted, one with the entire cigarette butt and one with just the cigarette filter.

146 In the first set of experiments, seven pairs of cigarette butts and three pairs of cigarette 147 filters were preconditioned using the procedure below and then directly placed in the headspace 148 vials for analysis to determine the impact of rainwater saturation on the initial emitted mass into 149 headspace. An artificial rainwater solution was prepared by dissolving the following components 150 in 1 L of distilled water: NaCl (3.24 g), KCl (0.36 g), CaCl<sub>2</sub>·2H<sub>2</sub>O (1.65 g), (NH<sub>4</sub>)2SO<sub>4</sub> (3.41 g), 151 MgSO<sub>4</sub>·7H<sub>2</sub>O (2.98 g), and NaNO<sub>3</sub> (4.08 g) and then diluting the solution by a factor of 1 000 as 152 previously used for cigarette butt aqueous leaching experiments (Chevalier et al. 2018). For each 153 pair of freshly smoked cigarette butts or cigarette filters, one was placed in a dry petri dish while 154 the other was soaked in 30 mL rainwater solution in another petri dish for 3 min (Figure 3 (a) -155 (d)). After 3 min of conditioning, the butts were transferred onto a wire mesh rack using tweezers.

156 Each butt was left on the rack for 30 s to remove any residual water that wasn't absorbed by the 157 cigarette butt, and then placed into a pre-weighed 20 mL vial using tweezers for analysis.

158 In the second set of experiments, dry and wet cigarette filters were conditioned in chambers 159 to investigate the impact of water saturation on the decay rate of the emitted masses after 160 conditioning for different times. Cigarette butts were first cut using the apparatus described in 161 Supplementary Information Section S.1. The ash and unburned tobacco were discarded. After 162 cutting, three cigarette filters were wet following the same procedure as above, while three other 163 filters were handled in the same manner but kept dry (Figure 3 (c) and (d)). The dry and wet filters 164 were then conditioned in chambers at 30 °C and 50 % RH (Experiment 5 and 6 in Table 1). The 165 dry filters were analyzed after five different conditioning times, i.e., 2 h, 5 h, 18 h, 24 h and 120 h, 166 while the wet filters were analyzed after four different conditioning times, i.e., 5 h, 18 h, 24 h and 167 120 h.







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### 175 2.2.1 Conditioning on rooftop

176 Cigarette butts were conditioned on the roof of a five-story laboratory building (Figure 3) 177 on the NIST campus to study the influence of environmental conditions, including temperature, 178 relative humidity and water saturation, on the airborne emissions from cigarette butts. The roof 179 consists of a melted asphalt membrane covered by a layer of pebbles. This environment was chosen 180 to keep the butts safe from the interference of people and animals other than birds. In addition, the 181 roof hosts an existing solar PV panel logging and weather station (Figure 3); more information on 182 this system can be found in Boyd (2016). The cigarette butts were placed on concrete blocks to 183 mimic the thermal properties of a butt discarded on a street or in a parking lot. Two sets of 184 experiments were conducted in summer (August 2018, Experiments 7 and 8 in Table 1) and two 185 sets of experiments were conducted in winter (November 2018, Experiments 9 and 10 in Table 1). 186 Rain occurred during each sampling event. The butts were placed beneath wires to pin them to a 187 concrete block. In addition, a wire mesh was placed on top of the blocks to limit interference from 188 birds (Figure 3). For each test, 27 freshly smoked cigarette butts were placed on the roof at the 189 same time and 3 cigarette butts were removed after 9 different time durations, ranging from 2 h to 190 144 h. The solar radiation, precipitation, temperature, relative humidity, wind speed, and 191 atmospheric pressure were recorded every minute during the experiments. Those data are shown 192 in Figure S.2 through Figure S.7.



Figure 3 Cigarette butts conditioned on the roof of the NIST laboratory building. Solar tracking system on left, weather station in center, and protective mesh cover shown on right.

#### 196 2.3 Headspace analysis of conditioned cigarette butts

197 All the fresh and conditioned cigarette butt samples were placed in 20 mL vials and 198 analyzed with headspace analysis to determine the mass emitted from the butts into the headspace 199 air of the vial. Each sample was placed in a 20 mL vial and conditioned for 10 min at 30 °C. After 200 conditioning, a Tenax tube was used to sample the headspace air from the vial at a flow rate of 100 201 mL/min for 1 min. The Tenax tube was then automatically transported to a thermal desorption unit 202 (TD). The thermal desorption started at 40 °C for 0.5 min, ramped up to 300 °C at a rate of 12 °C 203 s<sup>-1</sup> and held for 8 min, while the desorbed chemicals were captured by a cooled injection system 204 (CIS) at -120 °C. After desorption, the CIS temperature ramped up to 280 °C at a rate of 12 °C s<sup>-1</sup> 205 and held for 3 min, and the desorbed chemicals were transferred to a gas chromatograph (GC) 206 column with a split ratio of 15:1. The transfer temperature to the gas chromatograph was 280 °C. 207 The gas chromatograph used a 30 m, 0.25 mm ID, and 0.25 µm film thickness column with a flow of 1 mL min<sup>-1</sup> of helium. The column oven temperature started at 30 °C for 1 min, ramped up at 208 10 °C min<sup>-1</sup> to 200 °C, then ramped up at 20 °C min<sup>-1</sup> to 300 °C and held for 2 min. The mass 209 210 spectrometer (MS) was operated in full scan mode.

211 Target chemicals were determined based on criteria including representativeness of 212 chemicals, response area abundance and repeatability, chamber background concentrations, and 213 whether it is listed in the Food and Drug Administration (FDA) Harmful and Potentially Harmful 214 Constituents (HPHC) list (2012) for tobacco products and tobacco smoke or not (Poppendieck and 215 Gong 2019). Eight chemicals (furfural, styrene, 2-methyl-2-cyclopenten-1-one, limonene, 216 naphthalene, triacetin, and nicotine) were analyzed for this study. The mass-to-charge ratios for 217 quantification of the target chemicals (quantification ion) and their chemical properties are listed 218 in Table 2.

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CAS No.	Chemical name	Molecular mass, g mol <sup>-1</sup>	Quantification ion	Boiling point °C	Vapor pressure log(atm)	Water solubility mg L <sup>-1</sup>	Log K <sub>wa</sub> [-] <sup>b</sup>
98-01-1	furfural	96	96	214	-3.1	64,400	4.3
100-41-4	ethylbenzene	106	91	140	-1.8	160	0.4
100-42-5	styrene	104	104	149	-2.1	205	0.8
1120-73-6	2-methyl-2- cyclopenten -1-one	96	67	173	-2.4	43,900	3.4
138-86-3	limonene	136	68	179	-2.6	4	-0.6
91-20-3	naphthalene	128	128	205	-3.7	47	1.6
102-76-1	triacetin	218	103	258	-4.7	64,600	5.5
54-11-5	nicotine	162	84	244	-4.7	86,800	5.8

a: Chemicals listed in order of TD-GC-MS retention time. Chemical properties were calculated at 25 °C using sparc online calculator (http://archemcalc.com/sparc-web/calc) on 11/7/2018.

b: Calculated using  $\text{Log}K_{wa} = \text{Log}H + \text{Log}(RT)$ , H is the Henry's law constant, M atm<sup>-1</sup>, R is the universal constant, 0.0821 atm  $M^{-1}K^{-1}$ , T is the temperature, 298 K.

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Standards curves were made by spiking 0.2  $\mu$ L to 4  $\mu$ L of standard solutions of the eight target chemicals in methanol, with 1  $\mu$ L of ethylbenzene-d<sub>8</sub> as an internal standard (quantification ion: 116) directly onto the bottom of the glass frit of the sorption tube. Each sample tube was also spiked with 1  $\mu$ L of ethylbenzene-d<sub>8</sub> in methanol onto the bottom of the glass frit of the sorption tube prior to being used for sampling the headspace vial. Nitrogen gas was passed from the bottom to the top of the sorption tube for 2 min prior to analysis to remove the methanol after spiking either the standard or internal standard.

## 230 2.4 Quality assurance/quality control

Six quality assurance and quality control (QA/QC) issues were addressed during the headspace analysis. Detailed information can be found in Poppendieck and Gong (2019). Briefly, (1) To ensure reliability of the TD-GC-MS analysis, standard curves were run in each sequence, and only data from sequences where the standard curves had linear R<sup>2</sup> values larger than 0.98 were 235 used; (2) The instrument detection limits for each target chemical were determined following the 236 method described in Code of Federal Regulations (2003). The quantification limits were 237 determined by multiplying the instrument detection limit by 3.3. The instrument detection limits 238 and quantification limits for headspace analysis are shown in Table S.1; (3) Six sets of at least 12 239 cigarette butts were analyzed to investigate the consistency of the initial emitted mass from freshly 240 smoked cigarette butts. The overall average emitted masses from the 78 cigarette butts is shown 241 in Table S.2. The relative standard deviations (RSDs) within each set of data are within 25 %, 242 except ethylbenzene (28 %) and nicotine (27 %) in one set of data, while the RSDs between 243 different sets are within 25 % except naphthalene (33 %) and nicotine (34 %); (4) Loss of 244 chemicals while butts were in the 20 mL analysis vial waiting to be analyzed by the TD-GC-MS 245 was investigated. Most of the butts (n = 349 out of 497) were analyzed during a period ranging 246 from 5 h to 35 h, and the emitted mass analyzed during that period was relatively consistent, with 247 relative standard deviation of less than 25 % for those samples, except for triacetin (27 %) and 248 nicotine (41 %); (5) Consistency of chemical emissions from the butts before they were placed in 249 the conditioning environments was examined by analyzing the influence of relative humidity in 250 the fume hood during cigarette burning and transportation time between extinguishing of cigarette 251 butt and placement into the conditioning environment. The relative humidity in the burning 252 environment had moderate influence on the measured mass from cigarette butts for nicotine but 253 no significant influence on other target chemicals (Pearson correlation, p > 0.05). The 254 transportation time didn't influence the emitted mass within the first 4 h (Pearson correlation, p > 255 (0.05). Placing the cigarette butts in the transport vials for less than 4 h prior to placing in the 256 conditioning environment had minimal impact on the emitted mass; (6) Measures were taken to 257 ensure the consistency of the conditioning environments. Tests were repeated in Experiment 1 258 though Experiment 6 if the relative standard deviation of the temperature during the conditioning 259 period was greater than 1 %, or the relative standard deviation of relative humidity and flow were 260 greater than 5 %.

#### 261 2.5 Data analysis

To mathematically characterize the emission of each chemical, an empirical two-stage emission model was used to fit the measured mass emitted from butts conditioned in chamber for examining influence of temperature and relative humidity (data in Figure 4) and rooftop exposure (data in Figure 8) :

$$M = M_0 (F \cdot e^{-k_1 t} + (1 - F) \cdot e^{-k_2 t})$$
<sup>(1)</sup>

In this model, the decay of measured mass (*M*) is partitioned into two components: a fast emitting fraction (*F*) that emits at a rate of  $k_1$ , and a slow emitting fraction (*1-F*) that emits at a rate of  $k_2$ (Hawthorne et al. 2001).  $M_0$  is the initial measured mass emitted before conditioning.

270 Although empirical, the two-stage model has some physical basis given the composition 271 of the butts. As shown in our previous experiments (Poppendieck and Gong 2019), the target 272 chemicals are distributed in the butts between the filter and the ash/unburned tobacco. The 273 chemical emission rate from each component of a butt may be different for each chemical. Hence, 274 conceptually a two-stage model is a reasonable approach to characterize the emission of the target 275 chemicals from these two portions of the butt. The average values of measured initial masses from 276 78 cigarette butts were used as  $M_0$ , shown in Table S.2. The three fitting parameters were F,  $k_1$ , 277 and  $k_2$ . Boundary conditions were set for the parameters with  $0 \le F \le 1$ ,  $k_1 \ge 0$ , and  $k_2 \ge 0$ . The 278 non-linear model in equation (6) was fitted using the Levenberg Marquardt method in OriginPro (2017). The  $R^2$  values of the curve fits averaged 0.89 with a range of 0.62 to 1.0. 279

280 The cigarette butt samples were tested using headspace analysis after they were 281 conditioned for one of nine durations (2 h, 5 h, 18 h, 24 h, 48 h, 72 h, 96 h, 120 h and 144 h). For 282 each designated time, if there are no data points for the chemical in Figure 4or Figure 8, it means 283 that the emitted mass for the chemical was below the quantification limit. Under some conditions, 284 e.g. the ethylbenzene mass from cigarette butts conditioned at 30 °C and 50 % RH, the number of 285 time points that have masses greater than the quantification limit were fewer than three. Curve 286 fitting was not conducted when the number of time points was fewer than three. In addition, in 287 some cases the curve fits resulted in a  $k_2$  value of zero, which makes the last term of equation (6) 288 a constant.

Since only cigarette filters were placed in the chambers for the second set of experiments examining the influence of water saturation and the filter is a relatively uniform media, the physical reason for using a two-stage model was no longer valid. Hence, a simple exponential decay model was used when curve fitting to data in Figure 6 that examine the influence of water saturation:

$$M = M_0 \cdot e^{-kt} \tag{2}$$

During the fitting,  $M_0$  was fixed as the average value of the measured masses from the unconditioned filters (4<sup>th</sup> and 5<sup>th</sup> column in Table 3) so that the only fitting parameter was *k* (rate constant). The boundary condition set for the parameter *k* was  $k \ge 0$ . The non-linear model in equation (2) was also fitted using the Levenberg Marquardt method in OriginPro (2017).

298 The curve fitting to equation (1) resulted in three parameters that did not consistently reveal 299 trends in the data for the varying exposure conditions. This may be due to the scatter in the data or 300 that the two-stage non-linear model is over-parameterized for the data collected. Regardless, the 301 curve fits do allow comparison of the impacts of the binary levels (e.g., 30 °C and 40 °C) that were 302 tested for each conditioned environment. For six of the target chemicals (furfural, ethylbenzene, 303 styrene, 2-methyl-2-cyclopenten-1-one, limonene, naphthalene), the curve fits were used to 304 determine the amount of exposure time in the conditioned environment required for the mass 305 emitted into the headspace vial to be 5 % of the initial emitted mass. This was defined as the decay 306 time. Triacetin and nicotine did not always reach 5 % of the initial mass within the experimental 307 period, so a 25 % decay time was used for these two chemicals. A longer decay time indicates a 308 smaller emission rate in the conditioned environment. These decay times were compared for the 309 upper and lower levels of the experimental conditions. Using a single parameter decay time allows 310 for more direct comparisons of data sets than the three-parameter values in the fitted curve.

#### 311 **3. Results and discussion**

#### 312 3.1 Conditioning in chambers

Experiment 1 through Experiment 6 investigated how environmental conditions in a controlled chamber (temperature, relative humidity, and water saturation) impacted the emitted mass.

#### 316 3.1.1 Influence of temperature and relative humidity

The measured masses of the eight target chemicals from cigarette butts conditioned in chambers under four different conditions (Experiment 1 through Experiment 4 in Table 1: 30 °C and 25 % RH, 30 °C and 50 % RH, 40 °C and 25 % RH, 40 °C and 50 % RH) and their curve fits are shown in Figure 4 (a) through (h). The relative standard deviations (RSDs) of each triplicate data set for 90 % of the time points in Figure 4 are within 30 %, while the RSDs for the other 10 % range from 31 % to 51 %. By 48 h the emitted masses decayed to less than 5 % of the initial emitted 323 masses for all chemicals except triacetin and nicotine. In contrast, the emitted masses of nicotine 324 and triacetin decayed more slowly with the measured mass at 48 h being 18 % to 51 % of the initial mass for all conditions. The  $R^2$  values of the curve fits are higher than 0.92 for furfural, 325 ethylbenzene, styrene, 2-methyl-2-cyclopenten-1-one, and limonene. However, the R<sup>2</sup> values for 326 327 the other three chemicals, i.e., naphthalene, triacetin, and nicotine, are all lower, ranging from 0.62 328 to 0.90. The RSDs of each triplicate data set at a given sampling time for these three chemicals are 329 similar to the RSDs for the other five chemicals. But the data for these three chemicals tend to 330 exhibit more scatter, e.g., the emitted masses can be higher than the emitted mass at an earlier time 331 point. For example, the average mass of triacetin emitted at 120 h was 1.6 times higher than the mass emitted at 96 h under the condition of 30 °C and 25 % RH. The cause of the erratic data for 332 333 these three chemicals is unknown at this time.



334335

(a)



(b)













SC, T=30°C, RH=50%

SC, T=40°C, RH=50%

SC, T=30°C, RH=25% C = 19.5\*e<sup>-0.076t</sup>, R<sup>2</sup> = 0.82 SC, T=40°C, RH=25%

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40

80

Time (h)

 $C = 19.5*(0.82e^{-0.49t} + 0.18e^{-0.069t}), R^2 = 0.85$ 

 $C = 19.5*(0.83e^{-0.49t} + 0.17e^{-0.088t}), R^2 = 0.86$ 

100

120

140

160

 $C = 19.5*(0.67e^{-148t} + 0.33e^{-0.67t}), R^2 = 0.81$ 

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Measured mass of Naphthalene (ng)









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350Figure 4. Measured emitted masses and curve fits for target chemicals from cigarette butts conditioned in chambers at different<br/>temperature (T) and relative humidity (RH).

(h)

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353 To examine the influence of a 10 °C temperature change and a 25 % RH change, decay 354 times were calculated using the curve fits shown in Figure 4. Only one of the four conditioning 355 environments resulted in a curve fit for ethylbenzene. Styrene only had curve fits for the 25 % RH 356 environments. Hence, ethylbenzene and styrene are not included in this analysis. The decay times 357 for the other six target chemicals are shown in Figure 5 (a) through (f). The decay time changes 358 due to a 10 °C temperature change show similar trends. The 10 °C increase decreased the decay 359 time by 21 % to 92 % at 25 % RH and by 48 % to 82 % at 50 % RH. The trend for decay time is 360 consistent with the fact that the measured emitted mass at higher temperature is generally lower 361 than the mass emitted at lower temperature at the same time point and same relative humidity 362 (Figure 4). A decrease of the decay time indicates that more mass has been emitted during the 363 conditioning phase prior to headspace analysis. This is consistent with the fact that as the 364 temperature increases, the vapor pressures of the target chemicals increase so that the chemical 365 concentrations at the surface of the cigarette butts increases, and the chemical emission rates 366 increase. For reference, increasing the temperature from 30 °C to 40 °C increases the vapor

pressures of the chemicals by 51 % to 163 % (vapor pressures were calculated using the sparc
online calculator, http://archemcalc.com/sparc-web/calc).

369 In general, the change in decay times for an increase of relative humidity from 25 % to 50 %370 was similar to the change in decay times for a 10 °C temperature increase. For furfural, limonene, 371 naphthalene, and nicotine, the influence of increasing relative humidity from 25 % to 50 % showed 372 similar trends, decreasing the decay time by 33 % to 71 % at 30 °C and 32 % to 90 % at 40 °C. 373 This trend in decay time is consistent with the fact that the measured masses emitted at higher 374 relative humidity were lower than the masses emitted at the same time point and same temperature 375 (Figure 4). Changes in relative humidity would impact the adsorbed water layer in the cigarette 376 butts. When conditioning the cigarette butts in the chamber with relative humidity of 50 %, more 377 water would be adsorbed onto the porous surface of the butts compared to a relative humidity of 378 25 %. More adsorbed water at 50 % RH can result in fewer adsorption sites for other chemicals, 379 enhancing the target chemical emissions from the butts to air. To our knowledge, no other studies 380 have examined the influence of relative humidity on airborne emissions from cigarette butts. But, 381 a similar influence of increase in relative humidity increasing emissions have been observed for 382 volatile organic chemical (VOC) emissions from a variety of materials. Markowicz and Larsson 383 (2015) indicated that VOC emissions from gypsum, wood, and concrete were higher when the 384 relative humidity in the chamber was 85 % compared to 45 %. Specifically, that study showed 385 limonene and styrene concentrations increased from below detection at 40 % RH to quantifiable 386 at 85 % RH. Laskar et al. (2019) demonstrated a faster breakthrough of 2-propanol in activated 387 carbon adsorbed at 95 % RH compared to 50 % RH, attributing the difference to the competitive 388 adsorption of water vapor with 2-propanol.

389 Triacetin and 2-methyl-2-cyclopenten-1-one did not follow the trend of decreasing decay 390 time with increasing relative humidity. For 2-methyl-2-cyclopenten-1-one, even though the decay 391 time decreased by 66 % at 30 °C with an increase from 25 % RH to 50 % RH, the decay time 392 increased by 45 % at 40 °C. For triacetin an increase from 25 % RH to 50 % RH resulted in the 393 decay time increasing 24 % at 30 °C and 21 % at 40 °C. The relatively small number of points (n 394 = 5) for curve fitting for 2-methyl-2-cyclopenten-1-one at 40 °C and 50 % RH may result in an inaccurate estimate of the decay time. In addition, curve fits with low R<sup>2</sup> values (0.77 to 0.90) may 395 396 contribute to the increasing decay time with increasing relative humidity for triacetin. Another 397 possibility is that since these chemicals are two of the most water soluble (Table 2) among the 398 target chemicals, they may be more amenable to positively interacting with an increased water 399 layer than the other target chemicals. More experiments need to be conducted to understand the 400 influence of relative humidity on emissions of these two chemicals.





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#### 410 3.1.2 Influence of water saturation

#### 411 3.1.2.1 Initial emitted mass

Table 3 reports the initial emitted masses for the target chemicals from the tested butts and filters (dry and wet). The chemical masses emitted from the wet samples are smaller than the dry samples except triacetin from the wet butt and furfural from wet filter. These differences indicate that either 1) during the 3 min when the butts or filters were in the petri dishes, more chemicals were emitted from the wet filter and butts (either to the air or the water solution) than the dry filter and butts, or 2) less chemicals were emitted from the wet filters and butts into the headspace vials during analysis due to more partitioning into the water phase in the wet samples.

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421	Table 3. Measured initial mass for				
	Chamical	dry butt	wet butt	dı	
	Chemicai	( <b>n</b> = 7)	(n = 7)	(	

Table 3. Measured initial mass for dry and wet butts and filters (mean  $\pm$  SD, ng) and dry-to-wet ratios

ry filter wet filter wet butt/ wet filter/ filter ratio/ (n=3)(n = 3)dry butt dry filter butt ratio  $542\pm71$  $420\pm72$  $777\pm63$ 0.8 1.1 1.4 Furfural  $689\pm31$ Ethylbenzene  $140 \pm 29$  $93 \pm 17$  $301 \pm 43$  $191 \pm 7$ 0.7 0.6 1.0  $294\pm52$  $182\pm26$  $402 \pm 37$  $291 \pm 15$ 0.6 0.7 1.1 Styrene 2-methyl-2- $368\pm68$  $210\pm28$  $358\pm20$  $301 \pm 39$ 0.6 0.8 1.4 cyclopenten-1-one Limonene  $1380\pm350$  $699\pm86$  $2320 \pm 55$  $1450\pm63$ 0.5 0.6 1.3  $12 \pm 1.3$ Naphthalene  $16 \pm 1.9$  $14 \pm 0.4$  $12\pm0.3$ 0.8 0.9 1.1 Triacetin  $166 \pm 84$  $242 \pm 80$  $373 \pm 50$  $159 \pm 18$ 0.4 1.4 0.3 Nicotine  $175 \pm 75$  $52 \pm 25$  $146 \pm 77$  $13 \pm 3$ 0.3 0.1 0.3

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423 Structurally, furfural and 2-methyl-2-cyclopenten-1-one both have a polar carbonyl group, 424 corresponding to their higher water solubility than other chemicals except triacetin and nicotine 425 (Table 2). Triacetin has three polar carboxylic ester groups, which contributes to its high water 426 solubility. Nicotine is an amine (a weak base), also making it relatively soluble. In contrast, the 427 other four target chemicals (ethylbenzene, styrene, limonene, and naphthalene), which are non-428 polar hydrocarbons, have much lower water solubilities. For the four non-polar hydrocarbons, the 429 ratio of the wet to dry emitted mass (wet-to-dry ratio) for the butts and filters positively correlates with the water/air partition coefficient ( $K_{wa}$ , butt R<sup>2</sup> value = 0.77, filter R<sup>2</sup> value = 0.77, Figure 430 431 S.8). These correlations indicate that these four hydrocarbons in the wet butts and filter mainly 432 migrated into the air above the petri dish, not the water solution during the saturation process. 433 Otherwise, if these four hydrocarbons were mainly emitted into the water during saturation, then 434 more mass would emit into the petri dish water for chemicals with higher  $K_{wa}$ . This case would 435 result in the wet-to-dry ratio decreasing with  $K_{wa}$  increasing, opposite of the observed trend in 436 Figure S.8.

The two carbonyl chemicals (furfural and 2-methyl-2-cyclopenten-1-one) followed the same correlation trends as the hydrocarbons (negative with  $K_{wa}$ ). Due to its higher  $K_{wa}$  value, the wet-to-dry ratios for furfural were larger than the ratios for 2-methyl-2-cyclopenten-1-one. However, the carbonyls didn't fall on the same curve fits as the hydrocarbons, as the structural differences result in  $K_{wa}$  values at least two orders of magnitude higher than the hydrocarbons. 442 Given there are only two carbonyl target chemicals, no  $\mathbb{R}^2$  values for the correlation with  $K_{wa}$  could 443 be calculated.

444 In general, the wet-to-dry ratios for filters are greater than the ratios for butts indicating 445 that the removal of the ash and unburned tobacco impacts the relative partitioning between the 446 air/water/solid phases of cigarette filter. Interestingly, the two carbonyl containing chemicals both 447 had a filter ratio/butt ratio of 1.4, indicating that cutting and removing the ash/tobacco had a 448 consistent positive impact on the ratios. The four non-polar hydrocarbons were not impacted as 449 much by the presence of ash/tobacco with an average filter ratio/butt ratio of 1.1. A reason that 450 furfural and 2-methyl-2-cyclopenten-1-one were impacted more is likely because furfural and 2-451 methyl-2-cyclopenten-1-one have high water solubility and the cellulose acetate filters are more 452 hydrophilic than the butts. The filters therefore gained relatively more water than the butts. The 453 masses of the wet filters after conditioning in petri dishes increased by an average of 420  $\% \pm 80 \%$ 454 (n = 9). The masses of the wet butts after conditioning in petri dishes increased by an average of 455  $273 \% \pm 54 \%$  (n = 7). The filter ratio/butt ratio was negatively impacted for both triacetin and 456 nicotine (average value 3.4) by the removal of ash and tobacco.

457 Triacetin is the only ester among the target chemicals. More triacetin was emitted from the 458 wet butts than the dry butts. In contrast, more triacetin was emitted from the dry filters than the 459 wet filters. Given the large  $K_{wa}$ , large  $K_{oa}$ , low vapor pressure, and high-water solubility, triacetin 460 emissions from the wet filters may be due to dissolution into the water solution in the petri dish, 461 not emissions into air. The high dissolution of triacetin in the wet filters into water solution in the 462 petri dish would decrease triacetin's mass in the headspace vial for the wet filters. This difference 463 is consistent with the visual migration of the chemicals seen on the saturated roof butts (discussion 464 in Section 3.2.2). The reason that the relative magnitude of triacetin mass in wet and dry butts is 465 opposite to the relative magnitude of triacetin mass in wet and dry filter is not clear. However, the 466 relative standard deviations on the triacetin butt data (33 % wet and 50 % dry) could limit the 467 ability to make accurate conclusions.

For nicotine, the wet-to-dry ratios (3 for butts and 11 for filters) were much lower than the ratios for the other chemicals (0.5 to 1.4 for butts, 0.4 to 1.1 for filters). Nicotine is the only target chemical that can protonate, meaning it can add a proton to the molecule. Also, nicotine can exist in three forms: 1) a diprotonated molecule that exists when in contact with envrionments with pH

472 < 3, 2) a monoprotonated molecule that can exist in a tobacco filter (where 5 < pH < 6), and 3) a 473 free-base molecule (deprotanted conjugate base) (Liang and Pankow 1996, Ishizu and Ishizu 2013). 474 Only the free-base species is volatile (Liang and Pankow 1996). Free-base nicotine is the dominant 475 form of nicotine on the cigarette filter when freshly smoked, although the pH and nicotine species 476 can change with environmental exposures. The artificial rainwater solution has been measured by 477 Chevalier et al. (2018) to have a pH of 5.2, indicating that most of the nicotine in the aqueous 478 phase may be in the non-volatile monopronated form. Nicotine is also fairly water soluble, so a 479 significant amount of nicotine in the wet filters and butts would likely disolve into the aqueous 480 phase and then protonate, making it non-volatile so that less mass was emitted during headspace 481 analysis. In addition, some of the nicotine could have migrated into the water in the petri dish, also 482 contributing to its low mass in the wet filters and butts.

### 483 **3.1.2.2** *Emitted mass after conditioning wet and dry filters*

484 The measured emitted masses of the eight target chemicals emitted from the cigarette filters 485 conditioned in the chamber (Experiment 5 and 6 in Table 1) and their curve fits are shown in Figure 486 6 (a) through (b). The curves for the drying wet filter were similar to the dry filters, with all 487 chemicals other than triacetin and nicotine decaying to less than 5 % of the initial masses within 488 10 h. During conditioning in the chamber, the saturated filters dried. The 5 h wet filters averaged 489 a 9 %  $\pm$  21 % (average  $\pm$  standard deviation, n = 3) mass increase from their pre-saturation mass 490 (decreasing from 420 %  $\pm$  80 % when saturated). The 24 h wet filters averaged a -3 %  $\pm$  5 % mass 491 change from their pre-saturation mass (n = 3). These wet filters may initially experience conditions 492 where pore spaces were saturated with water, and then after five hours in the conditioning chamber 493 water may be mainly adsorbed on the porous surface layers and competed for sorption sites with 494 the target chemicals. The limited number of samples prevents a full understanding of the rate of 495 drying. However, it seems that the wetting/drying process enhances the emission of furfural and 496 2-methyl-2-cyclopenten-1-one from the filter so that the decay times were lower for the wet filters as compared to the dry filters for these two chemicals, as shown in Figure 7. In contrast, the 497 498 wetting/drying process may retard the emission of the hydrocarbons from filters so that the decay 499 time was higher for the wet filter compared to the dry filter for the three hydrocarbons (styrene, 500 limonene, and naphthalene). For triacetin and nicotine, the emitted mass from the wet filters 501 increased for the 5 h and 18 h samples and then decayed. In the saturated butts, nicotine was likely 502 present primarily in the non-volatile, monoprotonated form. As the butts dried in the dark chamber,

nicotine likely reverted to the free-base form. Hence, more nicotine was emitted into the headspace
vial at the 5 h sample than the initial sample. The reason triacetin also increased from the 5 h and

so i viar at the 5 it sumple than the initial sample. The reason tracetin also increased from the 5 if all

505 18 h samples compared to the initial sample is unknown.



(a)

506 507



508 509

(b)



(c)



(d)



(e)







*Figure 6. Measured emitted masses of target chemicals from dry and wet cigarette filters conditioned in chambers.* 



#### 523

Figure 7. Amount of exposure time required for the masses emitted into the headspace vial to be 5 % of the initial emitted masses for dry and wet filters. The decay time was not calculated for triacetin and nicotine, since their mass change with time didn't follow an exponential decay.

#### 527 3.2 Conditioning on rooftop

#### 528 3.2.1 Influence of temperature and relative humidity

529 Unlike the chamber datasets (Figure 4), the emitted masses for samples on the roof 530 (Experiment 7 through experiment 10) did not always decay to less than 5 % of the initial masses 531 by 48 h (Figure 8). The masses from summer samples typically decayed faster than the masses 532 from winter samples. As noted in Section 3.1.1, a 10 °C increase in temperature and an increase 533 from 25 % RH to 50 % RH resulted in roughly the same increase in emitted mass for most of the 534 target chemicals under controlled chamber conditions. There was roughly a 20 °C difference 535 between the seasonal experiments. The overall average temperatures were nearly the same for the two summer experiments (25.1 °C  $\pm$  3.0 °C and 24.4 °C  $\pm$  3.3 °C, Table 1) and two winter 536 experiments (3.7 °C  $\pm$  2.7 °C and 3.5 °C  $\pm$  4.2 °C, Table 1). The overall average relative humidity 537 538 was nearly the same for the two summer experiments (72.6  $\% \pm 14.1 \%$  and 72.8  $\% \pm 12.1 \%$ ) and 539 two winter experiments (64.6  $\% \pm 14.1 \%$  and 64.5  $\% \pm 17.1 \%$ ). The temperature change between 540 summer and winter experiments was twice as big as in the chamber experiments.

Even though the overall averages for temperature and relative humidity were similar for the two summer events and for the two winter events, the daily values were different. Specifically, the temperatures during the first 48 h were different for the two winter events. The average temperature during the first 48 h of the first winter experiment was 2.8 °C  $\pm$  2.5 °C, while in the

545 second experiment it was -0.2 °C  $\pm$  1.4 °C. In addition, the maximum relative humidity in the first 546 48 h was 87% for Winter 1 and 60% for Winter 2 (91% for Summer 1, 87% for Summer 2). 547 Together, these factors (higher temperature and higher relative humidity) indicate, as seen in 548 Section 3.1.1, that for most of the target chemicals the emitted mass during the first 48 h should 549 reduce faster for the Winter 1 experiment as compared to the Winter 2 experiment. This was seen 550 for furfural, ethylbenzene, styrene, 2- methyl-2-cyclopenten-1-one, limonene and naphthalene 551 (Figure 8 (a) through (f)). Only data for these six chemicals were curve fitted, with decay times 552 being faster for the Winter 1 experiment for five of these six chemicals (Figure S.10). The 553 variability in the triacetin and nicotine data are discussed in section 3.2.2.



(a)



(b)











 (e)



(f)



(g)



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570

571 Figure 8. Measured emitted masses of target chemicals from cigarette butts conditioned on roof of a NIST building in both summer 572 and winter.

#### 573 3.2.2 Influence of water saturation

574 The data from triacetin and nicotine are more erratic than other chemicals, with emitted 575 masses at several time points after 72 h being higher than the masses between 2 h and 72 h (Figure 576 9 (g)-(h)), which may be partly resulted from the precipitation events described below. Water 577 solubility of triacetin and nicotine are three orders of magnitude larger than four of the six other 578 chemicals and their  $K_{wa}$  values are one to six orders of magnitude higher than the other chemicals 579 (Table 2). In addition, as noted in Section 3.1.2.2, nicotine protonates in the presence of acidic 580 water. Hence, it would be expected that the emitted masses of triacetin and nicotine would be more 581 dependent upon water saturation of butts due to precipitation than other chemicals. The timing of 582 water saturation can be deduced from precipitation data (Figure S.6). For each experiment a major rainfall event (0.01 mm min<sup>-1</sup> for longer than 30 min) or major snow event (0.01 mm min<sup>-1</sup> 583 584 intermittently for more than 1 h) was correlated with an increase in butt mass between placement 585 on the roof and removal from the roof (Figure 9, colored vertical bars show the approximate 586 timeframes of the precipitation events). The emitted masses for triacetin and nicotine from samples 587 taken after these precipitation events were significantly higher than the masses from samples taken

immediately before these precipitation events (Figure 8 (g) and (h)): Summer 1, 122 h to 124 h;
Summer 2, 72 h to 85 h; Winter 1, 46 h to 62 h; and Winter 2, 96 h to 116 h).



590

591 Figure 9. Percentage change in cigarette butt mass between placement on roof and removal from roof. No data for Roof Summer
592 2 or Roof Winter 1 at 48 h. Vertical bars shows major rain and snow events. The pink bar is for the Summer 1 sample. The green
593 bar for the Summer 2 sample. The blue bar is for the Winter 1 sample. The yellow bar is for the Winter 2 sample.

594 For the 15 butts sampled after the first major precipitation event in each experiment 595 (samples with mass change above 100 % in Figure 9), the average butt mass increase was 185 % 596 (standard deviation of 60 %). The average mass change of the butts removed prior to each major 597 rainfall/snow event was 0 % (standard deviation 11 %, n = 72). Hence, the precipitation events 598 likely saturated the butts (as opposed to adsorbing water from the high relative humidity that 599 occurred throughout the experiments). The mass data for butts conditioned on the rooftop were 600 more variable than the mass data for the 179 butts conditioned in chambers for roughly the same time periods which had a standard deviation = 1 % (average change = -1 %). For chemicals other 601 602 than triacetin and nicotine, most of the major precipitation events (vertical bars in Figure 9)

occurred after the calculated 5 % decay times (Figure S.10). Exceptions included the data for
furfural and 2- methyl-2-cyclopenten-1-one in Winter 2, and naphthalene datasets for both Winter
1 and Winter 2.

606 Not only were the butts gaining mass from precipitation, their physical appearance after 607 major precipitation events also changed. Figure S.9 shows butts collected after a major rainfall 608 event during a preliminary experiment. Noticeable discoloration occurred to the butts, indicating 609 that water soluble chemicals had migrated from the interior of the butts to the exterior paper or the 610 concrete below. Some butts were more discolored than others, and some of the concrete below the 611 butts was also more stained than others. Most of the discoloration was on the paper wrapping the 612 unburned tobacco and ash as opposed to the filter. Given the solubility of triacetin and nicotine in 613 water, it is likely that some of these chemicals initially present inside the butts migrated to the 614 surface of the butts during saturation with water, which enhanced the emission during headspace 615 analysis. Other researchers have demonstrated that aqueous emission of nicotine from cigarette 616 butts into water can be a relatively fast process. Standardized cigarette butts produced with a 617 smoking machine leached 7.3 mg of nicotine per g of butts into 1 L of purified water, of which 618 50 % was released in the first 27 min during the experiment (Green et al. 2014). The same study 619 also found that the cumulative nicotine release from fifteen consecutive rainfall events each with 620 1.4 mm of precipitation was 3.8 mg of nicotine per g of cigarette butt, of which 47 % was released 621 during the first event (Green et al. 2014).

622 In contrast to triacetin and nicotine, masses of furfural and 2-methyl-2-cyclopenten-1-one 623 are less erratic even though they also have high solubility in water (Table 2). The 2- methyl-2-624 cyclopenten-1-one mass emitted was at or near detection limits by the time the major precipitation 625 events occurred during all experiments. The only experiment where there was significant furfural 626 mass remaining prior to a major precipitation event was conducted during Winter 2. The furfural 627 mass emitted immediately fell after the major precipitation event (96 h to 116 h) (Figure 8 (a)). 628 The fact that furfural fell after a major precipitation event while triacetin and nicotine increased is 629 likely because the  $K_{wa}$  of furfural is 1.5 orders of magnitude lower than triacetin and nicotine. The 630 precipitation event mobilized all three chemicals, but furfural volatilized faster than triacetin and 631 nicotine during the winter sampling events.

#### 632 **4. Conclusions**

633 Experiments have been conducted to determine the influence of temperature, relative 634 humidity and water saturation on the emitted masses of airborne chemicals from cigarette butts for 635 the first time. The cigarette butts have been conditioned in both a controlled chamber and in a real 636 environment (rooftop). Results in this study indicate that increased temperature increased the rate 637 at which all target chemicals were emitted from the butts in both chamber and outdoor experiments. 638 In addition, water exposure has considerable influence on the emission rates from butts. Seven of the eight chemicals were emitted faster from butts at a 50 % RH compared to a 25 % RH. For butts 639 640 discarded in dry environments, increasing the relative humidity can result in water competition for 641 sorption sites with the target chemicals, which would enhance the emission rate of target chemicals. 642 During the saturation process under conditions of exposure to liquid water, the chemicals with 643 high water solubility and  $K_{wa}$ , e.g., triacetin and nicotine, can migrate into the surrounding 644 environment via aqueous rather than airborne routes. Other less soluble chemicals are more likely 645 to be emitted from saturated butts into air as  $K_{wa}$  increases. For these chemicals, the ratios of initial 646 emitted mass for both wet butts to dry butts and wet filters to dry filters increase with increasing 647  $K_{\rm wa}$ . Water saturation increased the decay rate (decreased the decay time) of emitted mass 648 measured in headspace analysis for the two carbonyl chemicals: furfural and 2-methyl-2-649 cyclopenten-1-one, while it decreased the decay rate (increased the decay time) for the three 650 hydrocarbons (styrene, limonene, and naphthalene).

651 This study has several limitations and additional work remains to be done to more 652 completely understand airborne emissions from cigarette butts. Given only butts from one brand 653 of cigarette was tested, this study was not a comprehensive survey of cigarette butt airborne 654 emissions, which limits the generalizability of the present study. The cigarette butts were produced 655 using a custom-built smoking apparatus at one target length. Thus, the cigarette butts tested in this 656 study may be different from the varied butts produced by human smoking. Studies comparing 657 different brands and characterizing differences between smoking by human and smoking apparatus 658 would be valuable. The environmental conditions tested in this study (two each for temperature, 659 relative humidity, and water saturation) are limited. More tests under a wider range of conditions 660 are needed to more fully understand the environmental impacts on butt emissions. In addition, 661 when examining the influence of various factors, the emitted masses into headspace of a vial were

662 measured, not the actual emission rates. More studies directly examining the influence of 663 environmental conditions on emission rates would help us gain a better quantitative understanding 664 of the influence of environmental conditions on airborne cigarette butt emissions.

665

## 666 **5. Disclaimer**

667 Certain commercial equipment, instruments, or materials are identified in this paper in 668 order to specify the experimental procedure adequately. Such identification is not intended to 669 imply recommendation or endorsement by the National Institute of Standards and Technology, nor 670 is it intended to imply that the materials or equipment identified are necessarily the best available 671 for the purpose.

672

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