Influence of temperature, relative humidity, and water saturation on airborne emissions from cigarette butts

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Abstract

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

1. Introduction

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

Despite these potential risks from cigarette butts, little effort has been done to characterize airborne emissions from cigarette butts. Four studies have measured the emissions from cigarette butts into the air of headspace of test vials (Fukuhara et al. 1985, Huang et al. 2014, You et al. 2014, Ji et al. 2015). Fukuhara et al. (1985) detected a range of volatile components (e.g., carbonyls, hydrocarbons, pyrroles and terpenes) in the headspace of vessels that contained cigarette butts, and found that these compounds were also found in mainstream smoke. They also indicated that the tar-like odors in butts may result from 2,3-pentanedione, N-methyl pyrrole, 3-methyl pyrrole, isocapronitrile, pyrrole, and 2-methyl pyrrole. You et al. (2014) developed a static headspace gas chromatography-flame ionization detector (GC-FID) method for quantifying menthol concentrations in the cigarette filter and cigarette papers in a mentholated cigarette. The samples 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⁻¹ paper to 4.1 mg g⁻¹ paper, while the menthol concentration in the cigarette filter was 13.7 mg g⁻¹ paper to 27.2 mg g⁻¹ paper. Huang et al. (2014) measured the emissions from cigarette tipping paper (which attaches the filter
to the tobacco column) into the headspace of vials. The samples were first incubated at 80 °C for
45 min, and then 20 volatile organic compounds (VOCs) were quantified using gas
chromatography-mass spectrometry (GC-MS). Among the 20 target VOCs, methanol, ethanol,
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\(^{-2}\) paper. A recent study developed
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
cigarette filters at 120 °C for 30 min in the headspace vials. The measured concentrations for
benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, and styrene ranged from
0.4 μg/filter to 5.7 μg/filter.

These four studies provide some basis for understanding the potential airborne emissions
into indoor and outdoor environments. However, the study reported by Fukuhara et al. (1985) was
limited in the number of cigarette butts tested and did not quantify the identified chemicals. For
the three more recent studies (Huang et al. 2014, You et al. 2014, Ji et al. 2015), the types of
chemicals detected were limited and only cigarette filters or tipping papers were studied. These
studies did not include the unburned tobacco or ash of cigarette butts, which may emit different
chemicals from the filters and tipping papers. In addition, the high incubation temperatures
(> 80 °C) would enhance the emission of some non-volatile chemicals that may not be emitted to
a significant degree at more typical indoor and outdoor temperatures. Finally, all these studies only
measured freshly generated cigarette butts, or part of the unburned cigarette, and didn’t examine
the influence of environmental factors that could impact the emissions from cigarette butts, such
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).
2. Methods

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

2.1 Generation of cigarette butts

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

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

<table>
<thead>
<tr>
<th>Condition environment</th>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Airflow rate or wind speed</th>
<th>Rainfall (mm min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 chamber</td>
<td>31.1 (±0.2)</td>
<td>50 (±1)</td>
<td>350 mL/min⁴</td>
<td>N/A</td>
</tr>
<tr>
<td>2 chamber</td>
<td>40.3 (±0.2)</td>
<td>51 (±2)</td>
<td>344.7 (±14.0) mL/min</td>
<td>N/A</td>
</tr>
<tr>
<td>3 chamber</td>
<td>30.8 (±0.2)</td>
<td>25 (±1)</td>
<td>357.3 (±5.2) mL/min</td>
<td>N/A</td>
</tr>
<tr>
<td>4 chamber</td>
<td>40.3 (±0.2)</td>
<td>25 (±1)</td>
<td>347.3 (±14.9) mL/min</td>
<td>N/A</td>
</tr>
<tr>
<td>5 chamber</td>
<td>30.9 (±0.2)</td>
<td>52 (±4)</td>
<td>357.8 (±8.2) mL/min</td>
<td>wetᵇ</td>
</tr>
<tr>
<td>6 chamber</td>
<td>30.6 (±0.2)</td>
<td>51 (±1)</td>
<td>359.8 (±6.3) mL/min</td>
<td>dryᵇ</td>
</tr>
<tr>
<td>7 rooftop summer</td>
<td>25.1 (±3.0)</td>
<td>73 (±14)</td>
<td>1.8 (±1.1) m s⁻¹</td>
<td>0.001 (±0.01)</td>
</tr>
<tr>
<td>8 rooftop summer</td>
<td>24.4 (±3.3)</td>
<td>73 (±12)</td>
<td>2.1 (±1.1) m s⁻¹</td>
<td>0.001 (±0.03)</td>
</tr>
<tr>
<td>9 rooftop winter</td>
<td>3.7 (±2.7)</td>
<td>65 (±14)</td>
<td>3.2 (±1.9) m s⁻¹</td>
<td>0.002 (±0.01)ᶜ</td>
</tr>
<tr>
<td>10 rooftop winter</td>
<td>3.5 (±4.2)</td>
<td>65 (±17)</td>
<td>3.7 (±2.9) m s⁻¹</td>
<td>0.001 (±0.008)</td>
</tr>
</tbody>
</table>

ᵃSetpoint value. Actual values were not recorded for this experiment.
ᵇCigarette 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”.
ᶜValue may be elevated due to snow on the sensor for over 24 h.

2.2.1 Conditioning in chambers

Cigarette butts were conditioned under four settings in three rectangular cuboid chambers (Figure 1 (b)) with an airflow rate of 350 mL min⁻¹ but different temperature and relative humidity combinations: 30 °C and 50 %, 40 °C and 50 %, 30 °C and 25 %, and 40 °C and 25 % (experiments 1 through 4 in Table 1). The volume of each chamber is 590 mL. The temperature and relative humidity were recorded automatically every minute, while the airflow rates were checked at the beginning and end of each experiment with a bubble flow meter. For each test, three freshly smoked, non-smoldering cigarette butts were placed in the chamber with a specially designed holder (Figure 1 (a)) for eight different time durations (2 h, 5 h, 18 h, 24 h, 48 h, 72 h, 96 h, 120 h and 144 h). The filter holder had 1.7 mm diameter pegs to mount the butts onto the vertical butt holder. The pegs made two holes in the filter area of each butt that were present for the headspace analysis.
To study the influence of rainwater saturation on emissions from cigarette butts, freshly smoked cigarette butts were first preconditioned before being placed into the chambers. However, preliminary experiments showed that once the cigarette butts were saturated, the paper surrounding the ash and tobacco could disintegrate erratically when handled and placed in chambers. In addition, butts exposed to heavy rain events on the roof had similar fates, and it was challenging to recover the entire cigarette butt intact. In contrast to the degradation of the ash and tobacco when exposed to water, cigarette filters typically contain plasticized cellulose acetate fibers that show minimal degradation after two years of outdoor exposure (Bonanomi et al. 2015). In addition, experiments demonstrated that the emitted masses of the target chemicals from cigarette filters were comparable to the emitted mass from the entire cigarette butts for most of the target chemicals (Poppendieck and Gong 2019). Therefore, two sets of water saturation experiments were conducted, one with the entire cigarette butt and one with just the cigarette filter.

In the first set of experiments, seven pairs of cigarette butts and three pairs of cigarette filters were preconditioned using the procedure below and then directly placed in the headspace vials for analysis to determine the impact of rainwater saturation on the initial emitted mass into headspace. An artificial rainwater solution was prepared by dissolving the following components in 1 L of distilled water: NaCl (3.24 g), KCl (0.36 g), CaCl$_2$·2H$_2$O (1.65 g), (NH$_4$)$_2$SO$_4$ (3.41 g), MgSO$_4$·7H$_2$O (2.98 g), and NaNO$_3$ (4.08 g) and then diluting the solution by a factor of 1 000 as previously used for cigarette butt aqueous leaching experiments (Chevalier et al. 2018). For each pair of freshly smoked cigarette butts or cigarette filters, one was placed in a dry petri dish while the other was soaked in 30 mL rainwater solution in another petri dish for 3 min (Figure 3 (a) - (d)). After 3 min of conditioning, the butts were transferred onto a wire mesh rack using tweezers.
Each butt was left on the rack for 30 s to remove any residual water that wasn’t absorbed by the cigarette butt, and then placed into a pre-weighed 20 mL vial using tweezers for analysis.

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

Figure 2. Condition of (a) cigarette butt in a dry petri dish; (b) cigarette butt in a wet petri dish with 2 mm deep simulated rainwater; (c) cigarette filter in a dry petri dish; (d) cigarette filter in a wet petri dish with 2 mm deep simulated rainwater.
2.2.1 Conditioning on rooftop

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

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

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

<table>
<thead>
<tr>
<th>CAS No.</th>
<th>Chemical name</th>
<th>Molecular mass, g mol$^{-1}$</th>
<th>Quantification ion</th>
<th>Boiling point $^\circ$C</th>
<th>Vapor pressure log(atm)</th>
<th>Water solubility mg L$^{-1}$</th>
<th>Log $K_{wa}$ [-]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-01-1</td>
<td>furfural</td>
<td>96</td>
<td>96</td>
<td>214</td>
<td>-3.1</td>
<td>64,400</td>
<td>4.3</td>
</tr>
<tr>
<td>100-41-4</td>
<td>ethylbenzene</td>
<td>106</td>
<td>91</td>
<td>140</td>
<td>-1.8</td>
<td>160</td>
<td>0.4</td>
</tr>
<tr>
<td>100-42-5</td>
<td>styrene</td>
<td>104</td>
<td>104</td>
<td>149</td>
<td>-2.1</td>
<td>205</td>
<td>0.8</td>
</tr>
<tr>
<td>1120-73-6</td>
<td>2-methyl-2-cyclopenten-1-one</td>
<td>96</td>
<td>67</td>
<td>173</td>
<td>-2.4</td>
<td>43,900</td>
<td>3.4</td>
</tr>
<tr>
<td>138-85-3</td>
<td>limonene</td>
<td>136</td>
<td>68</td>
<td>179</td>
<td>-2.6</td>
<td>4</td>
<td>-0.6</td>
</tr>
<tr>
<td>91-20-3</td>
<td>naphthalene</td>
<td>128</td>
<td>128</td>
<td>205</td>
<td>-3.7</td>
<td>47</td>
<td>1.6</td>
</tr>
<tr>
<td>102-76-1</td>
<td>triacetin</td>
<td>218</td>
<td>103</td>
<td>258</td>
<td>-4.7</td>
<td>64,600</td>
<td>5.5</td>
</tr>
<tr>
<td>54-11-5</td>
<td>nicotine</td>
<td>162</td>
<td>84</td>
<td>244</td>
<td>-4.7</td>
<td>86,800</td>
<td>5.8</td>
</tr>
</tbody>
</table>

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 $\log K_{wa} = \log H + \log (RT)$, H is the Henry’s law constant, M atm$^{-1}$, R is the universal constant, 0.0821 atm M$^{-1}$K$^{-1}$, T is the temperature, 298 K.

Standards curves were made by spiking 0.2 µL to 4 µL of standard solutions of the eight target chemicals in methanol, with 1 µL of ethylbenzene-d$_8$ 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 µL of ethylbenzene-d$_8$ 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.

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$^2$ values larger than 0.98 were
used; (2) The instrument detection limits for each target chemical were determined following the
method described in Code of Federal Regulations (2003). The quantification limits were
determined by multiplying the instrument detection limit by 3.3. The instrument detection limits
and quantification limits for headspace analysis are shown in Table S.1; (3) Six sets of at least 12
cigarette butts were analyzed to investigate the consistency of the initial emitted mass from freshly
smoked cigarette butts. The overall average emitted masses from the 78 cigarette butts is shown
in Table S.2. The relative standard deviations (RSDs) within each set of data are within 25 %, except ethylbenzene (28 %) and nicotine (27 %) in one set of data, while the RSDs between
different sets are within 25 % except naphthalene (33 %) and nicotine (34 %); (4) Loss of
chemicals while butts were in the 20 mL analysis vial waiting to be analyzed by the TD-GC-MS
was investigated. Most of the butts (n = 349 out of 497) were analyzed during a period ranging
from 5 h to 35 h, and the emitted mass analyzed during that period was relatively consistent, with
relative standard deviation of less than 25 % for those samples, except for triacetin (27 %) and
nicotine (41 %); (5) Consistency of chemical emissions from the butts before they were placed in
the conditioning environments was examined by analyzing the influence of relative humidity in
the fume hood during cigarette burning and transportation time between extinguishing of cigarette
butt and placement into the conditioning environment. The relative humidity in the burning
environment had moderate influence on the measured mass from cigarette butts for nicotine but
no significant influence on other target chemicals (Pearson correlation, p > 0.05). The
transportation time didn’t influence the emitted mass within the first 4 h (Pearson correlation, p >
0.05). Placing the cigarette butts in the transport vials for less than 4 h prior to placing in the
conditioning environment had minimal impact on the emitted mass; (6) Measures were taken to
ensure the consistency of the conditioning environments. Tests were repeated in Experiment 1
though Experiment 6 if the relative standard deviation of the temperature during the conditioning
period was greater than 1 %, or the relative standard deviation of relative humidity and flow were
greater than 5 %.

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) :
\[
M = M_0(F \cdot e^{-k_1t} + (1 - F) \cdot e^{-k_2t})
\]  

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.

Although empirical, the two-stage model has some physical basis given the composition of the butts. As shown in our previous experiments (Poppendieck and Gong 2019), the target chemicals are distributed in the butts between the filter and the ash/unburned tobacco. The chemical emission rate from each component of a butt may be different for each chemical. Hence, conceptually a two-stage model is a reasonable approach to characterize the emission of the target chemicals from these two portions of the butt. The average values of measured initial masses from 78 cigarette butts were used as \(M_0\), shown in Table S.2. The three fitting parameters were \(F, k_1, \) and \(k_2\). Boundary conditions were set for the parameters with \(0 \leq F \leq 1, k_1 \geq 0, \) and \(k_2 \geq 0\). The 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.

The cigarette butt samples were tested using headspace analysis after they were 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 each designated time, if there are no data points for the chemical in Figure 4 or Figure 8, it means that the emitted mass for the chemical was below the quantification limit. Under some conditions, e.g. the ethylbenzene mass from cigarette butts conditioned at 30 °C and 50 % RH, the number of time points that have masses greater than the quantification limit were fewer than three. Curve fitting was not conducted when the number of time points was fewer than three. In addition, in some cases the curve fits resulted in a \(k_2\) value of zero, which makes the last term of equation (6) 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:

\[
M = M_0 \cdot e^{-kt}
\]
During the fitting, $M_0$ was fixed as the average value of the measured masses from the unconditioned filters (4th and 5th column in Table 3) so that the only fitting parameter was $k$ (rate constant). The boundary condition set for the parameter $k$ was $k \geq 0$. The non-linear model in equation (2) was also fitted using the Levenberg Marquardt method in OriginPro (2017).

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

3. Results and discussion

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.

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...
masses for all chemicals except triacetin and nicotine. In contrast, the emitted masses of nicotine 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, ethylbenzene, styrene, 2-methyl-2-cyclopenten-1-one, and limonene. However, the $R^2$ values for the other three chemicals, i.e., naphthalene, triacetin, and nicotine, are all lower, ranging from 0.62 to 0.90. The RSDs of each triplicate data set at a given sampling time for these three chemicals are similar to the RSDs for the other five chemicals. But the data for these three chemicals tend to exhibit more scatter, e.g., the emitted masses can be higher than the emitted mass at an earlier time 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 these three chemicals is unknown at this time.

(a)
(b) Measured mass of Ethylbenzene (ng)

(c) Measured mass of Styrene (ng)

\[ C = 227 \times (0.91e^{-1.4t} + 0.09e^{-0.087t}), \quad R^2 = 0.95 \]

\[ C = 344 \times (0.90e^{-1.5t} + 0.10e^{-0.056t}), \quad R^2 = 0.94 \]
To examine the influence of a 10 °C temperature change and a 25 % RH change, decay times were calculated using the curve fits shown in Figure 4. Only one of the four conditioning environments resulted in a curve fit for ethylbenzene. Styrene only had curve fits for the 25 % RH environments. Hence, ethylbenzene and styrene are not included in this analysis. The decay times for the other six target chemicals are shown in Figure 5 (a) through (f). The decay time changes due to a 10 °C temperature change show similar trends. The 10 °C increase decreased the decay time by 21 % to 92 % at 25 % RH and by 48 % to 82 % at 50 % RH. The trend for decay time is consistent with the fact that the measured emitted mass at higher temperature is generally lower than the mass emitted at lower temperature at the same time point and same relative humidity (Figure 4). A decrease of the decay time indicates that more mass has been emitted during the conditioning phase prior to headspace analysis. This is consistent with the fact that as the temperature increases, the vapor pressures of the target chemicals increase so that the chemical concentrations at the surface of the cigarette butts increases, and the chemical emission rates 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 sparcalc online calculator, http://archemcalc.com/sparc-web/calc).

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

Triacetin and 2-methyl-2-cyclopenten-1-one did not follow the trend of decreasing decay time with increasing relative humidity. For 2-methyl-2-cyclopenten-1-one, even though the decay time decreased by 66% at 30°C with an increase from 25% RH to 50% RH, the decay time increased by 45% at 40°C. For triacetin an increase from 25% RH to 50% RH resulted in the decay time increasing 24% at 30°C and 21% at 40°C. The relatively small number of points (n = 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 R² values (0.77 to 0.90) may contribute to the increasing decay time with increasing relative humidity for triacetin. Another possibility is that since these chemicals are two of the most water soluble (Table 2) among the
target chemicals, they may be more amenable to positively interacting with an increased water layer than the other target chemicals. More experiments need to be conducted to understand the influence of relative humidity on emissions of these two chemicals.
3.1.2 Influence of water saturation

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.

Figure 5. Amount of exposure time required for the mass emitted into the headspace vial to be 5% or 25% of the initial emitted mass. Left-side values demonstrate the impacts of a temperature change in the conditioning chamber. Right-side values demonstrate the impact of a relative humidity change in the conditioning chamber.
Table 3. Measured initial mass for dry and wet butts and filters (mean ± SD, ng) and dry-to-wet ratios

<table>
<thead>
<tr>
<th>Chemical</th>
<th>dry butt (n = 7)</th>
<th>wet butt (n = 7)</th>
<th>dry filter (n = 3)</th>
<th>wet filter (n = 3)</th>
<th>wet butt/ dry butt</th>
<th>wet filter/ dry filter</th>
<th>filter ratio/ butt ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>542 ± 71</td>
<td>420 ± 72</td>
<td>689 ± 31</td>
<td>777 ± 63</td>
<td>0.8</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>140 ± 29</td>
<td>93 ± 17</td>
<td>301 ± 43</td>
<td>191 ± 7</td>
<td>0.7</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>294 ± 52</td>
<td>182 ± 26</td>
<td>402 ± 37</td>
<td>291 ± 15</td>
<td>0.6</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>2-methyl-2-cyclopenten-1-one</td>
<td>368 ± 68</td>
<td>210 ± 28</td>
<td>358 ± 20</td>
<td>301 ± 39</td>
<td>0.6</td>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Limonene</td>
<td>1380 ± 350</td>
<td>699 ± 86</td>
<td>2320 ± 55</td>
<td>1450 ± 63</td>
<td>0.5</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>16 ± 1.9</td>
<td>12 ± 1.3</td>
<td>14 ± 0.4</td>
<td>12 ± 0.3</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Triacetin</td>
<td>166 ± 84</td>
<td>242 ± 80</td>
<td>373 ± 50</td>
<td>159 ± 18</td>
<td>1.4</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Nicotine</td>
<td>175 ± 75</td>
<td>52 ± 25</td>
<td>146 ± 77</td>
<td>13 ± 3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Structurally, furfural and 2-methyl-2-cyclopenten-1-one both have a polar carbonyl group, corresponding to their higher water solubility than other chemicals except triacetin and nicotine (Table 2). Triacetin has three polar carboxylic ester groups, which contributes to its high water solubility. Nicotine is an amine (a weak base), also making it relatively soluble. In contrast, the other four target chemicals (ethylbenzene, styrene, limonene, and naphthalene), which are non-polar hydrocarbons, have much lower water solubilities. For the four non-polar hydrocarbons, the 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 $R^2$ value = 0.77, filter $R^2$ value = 0.77, Figure S.8). These correlations indicate that these four hydrocarbons in the wet butts and filter mainly migrated into the air above the petri dish, not the water solution during the saturation process. Otherwise, if these four hydrocarbons were mainly emitted into the water during saturation, then more mass would emit into the petri dish water for chemicals with higher $K_{wa}$. This case would result in the wet-to-dry ratio decreasing with $K_{wa}$ increasing, opposite of the observed trend in 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.
Given there are only two carbonyl target chemicals, no $R^2$ values for the correlation with $K_{wa}$ could be calculated.

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

Triacetin is the only ester among the target chemicals. More triacetin was emitted from the wet butts than the dry butts. In contrast, more triacetin was emitted from the dry filters than the wet filters. Given the large $K_{wa}$, large $K_{oa}$, low vapor pressure, and high-water solubility, triacetin emissions from the wet filters may be due to dissolution into the water solution in the petri dish, not emissions into air. The high dissolution of triacetin in the wet filters into water solution in the petri dish would decrease triacetin’s mass in the headspace vial for the wet filters. This difference is consistent with the visual migration of the chemicals seen on the saturated roof butts (discussion in Section 3.2.2). The reason that the relative magnitude of triacetin mass in wet and dry butts is opposite to the relative magnitude of triacetin mass in wet and dry filter is not clear. However, the relative standard deviations on the triacetin butt data (33% wet and 50% dry) could limit the 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
< 3, 2) a monoprotonated molecule that can exist in a tobacco filter (where $5 < \text{pH} < 6$), and 3) a free-base molecule (deprotonated conjugate base) (Liang and Pankow 1996, Ishizu and Ishizu 2013). Only the free-base species is volatile (Liang and Pankow 1996). Free-base nicotine is the dominant form of nicotine on the cigarette filter when freshly smoked, although the pH and nicotine species can change with environmental exposures. The artificial rainwater solution has been measured by Chevalier et al. (2018) to have a pH of 5.2, indicating that most of the nicotine in the aqueous phase may be in the non-volatile monopronated form. Nicotine is also fairly water soluble, so a significant amount of nicotine in the wet filters and butts would likely dissolve into the aqueous phase and then protonate, making it non-volatile so that less mass was emitted during headspace analysis. In addition, some of the nicotine could have migrated into the water in the petri dish, also contributing to its low mass in the wet filters and butts.

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

The measured emitted masses of the eight target chemicals emitted from the cigarette filters conditioned in the chamber (Experiment 5 and 6 in Table 1) and their curve fits are shown in Figure 6 (a) through (h). The curves for the drying wet filter were similar to the dry filters, with all chemicals other than triacetin and nicotine decaying to less than 5% of the initial masses within 10 h. During conditioning in the chamber, the saturated filters dried. The 5 h wet filters averaged a 9% ± 21% (average ± standard deviation, n = 3) mass increase from their pre-saturation mass (decreasing from 420% ± 80% when saturated). The 24 h wet filters averaged a -3% ± 5% mass change from their pre-saturation mass (n = 3). These wet filters may initially experience conditions where pore spaces were saturated with water, and then after five hours in the conditioning chamber water may be mainly adsorbed on the porous surface layers and competed for sorption sites with the target chemicals. The limited number of samples prevents a full understanding of the rate of drying. However, it seems that the wetting/drying process enhances the emission of furfural and 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 wetting/drying process may retard the emission of the hydrocarbons from filters so that the decay time was higher for the wet filter compared to the dry filter for the three hydrocarbons (styrene, limonene, and naphthalene). For triacetin and nicotine, the emitted mass from the wet filters increased for the 5 h and 18 h samples and then decayed. In the saturated butts, nicotine was likely 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 18 h samples compared to the initial sample is unknown.
(c)

(d)
(e)

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

3.2 Conditioning on rooftop

3.2.1 Influence of temperature and relative humidity

Unlike the chamber datasets (Figure 4), the emitted masses for samples on the roof (Experiment 7 through experiment 10) did not always decay to less than 5% of the initial masses by 48 h (Figure 8). The masses from summer samples typically decayed faster than the masses from winter samples. As noted in Section 3.1.1, a 10 °C increase in temperature and an increase from 25% RH to 50% RH resulted in roughly the same increase in emitted mass for most of the target chemicals under controlled chamber conditions. There was roughly a 20 °C difference between the seasonal experiments. The overall average temperatures were nearly the same for the two summer experiments (25.1 °C ± 3.0 °C and 24.4 °C ± 3.3 °C, Table 1) and two winter experiments (3.7 °C ± 2.7 °C and 3.5 °C ± 4.2 °C, Table 1). The overall average relative humidity was nearly the same for the two summer experiments (72.6% ± 14.1% and 72.8% ± 12.1%) and two winter experiments (64.6% ± 14.1% and 64.5% ± 17.1%). The temperature change between 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 ± 2.5 °C, while in the
second experiment it was -0.2 °C ± 1.4 °C. In addition, the maximum relative humidity in the first
48 h was 87% for Winter 1 and 60% for Winter 2 (91% for Summer 1, 87 % for Summer 2). Together, these factors (higher temperature and higher relative humidity) indicate, as seen in
Section 3.1.1, that for most of the target chemicals the emitted mass during the first 48 h should
reduce faster for the Winter 1 experiment as compared to the Winter 2 experiment. This was seen
for furfural, ethylbenzene, styrene, 2- methyl-2-cyclopenten-1-one, limonene and naphthalene
(Figure 8 (a) through (f)). Only data for these six chemicals were curve fitted, with decay times
being faster for the Winter 1 experiment for five of these six chemicals (Figure S.10). The
variability in the triacetin and nicotine data are discussed in section 3.2.2.
(b) Measured mass of Ethylbenzene (ng) vs. Time (h)

- Roof Summer 1
  - \( C = 227(0.93e^{1.2t} + 0.069e^{-0.02t}) \), \( R^2 = 0.94 \)
- Roof Winter 1
  - \( C = 227(0.91e^{1.3t} + 0.09e^{-0.08t}) \), \( R^2 = 0.96 \)
- Roof Winter 2
  - \( C = 227(0.70e^{1.0t} + 0.30e^{-0.019t}) \), \( R^2 = 0.95 \)

(c) Measured mass of Styrene (ng) vs. Time (h)

- Roof Summer 1
  - \( C = 344(0.95e^{-0.076t} + 0.056e^{-0.044t}) \), \( R^2 = 0.92 \)
- Roof Winter 1
  - \( C = 344(0.89e^{-1.2t} + 0.11e^{-0.98t}) \), \( R^2 = 0.94 \)
- Roof Winter 2
  - \( C = 344(0.63e^{-1.3t} + 0.37e^{-0.026t}) \), \( R^2 = 0.91 \)
(d) Measured mass of 2-Cyclopropen-1-one, 2-methyl (ng)

(e) Measured mass of limonene (ng)
Figure 8. Measured emitted masses of target chemicals from cigarette butts conditioned on roof of a NIST building in both summer and winter.

3.2.2 Influence of water saturation

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

![Figure 9](image)

**Figure 9.** Percentage change in cigarette butt mass between placement on roof and removal from roof. No data for Roof Summer 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 bar for the Summer 2 sample. The blue bar is for the Winter 1 sample. The yellow bar is for the Winter 2 sample.

For the 15 butts sampled after the first major precipitation event in each experiment (samples with mass change above 100 % in Figure 9), the average butt mass increase was 185 % (standard deviation of 60 %). The average mass change of the butts removed prior to each major rainfall/snow event was 0 % (standard deviation 11 %, n = 72). Hence, the precipitation events likely saturated the butts (as opposed to adsorbing water from the high relative humidity that occurred throughout the experiments). The mass data for butts conditioned on the rooftop were 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 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.

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

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

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

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

5. Disclaimer

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

6. Acknowledgements

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