NISTIR 8147

Measuring Airborne Emissions from Cigarette Butts: Literature Review and Experimental Plan

Final Report to U.S. Food and Drug Administration under Interagency Agreement #244-15-9012

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This publication is available free of charge from:
http://dx.doi.org/10.6028/NIST.IR.8147

National Institute of Standards and Technology
U.S. Department of Commerce

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October 2016
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U.S. Department of Commerce
Penny Pritzker, Secretary

National Institute of Standards and Technology
Willie May, Under Secretary of Commerce for Standards and Technology and Director

Abstract

Under an interagency agreement with the Food and Drug Administration (FDA), a comprehensive literature review was conducted to gather and analyze existing research related to airborne emissions from non-smoldering cigarette butts. Based on the results from the literature review, an experimental plan was developed to measure the airborne emissions from non-smoldering cigarette butts. The literature review found that: 1) Non-smoldering cigarette butts can contain many of the same chemicals found in mainstream and sidestream smoke, and they are a potential source of these chemicals in both indoor and outdoor environments; 2) A number of studies have investigated the chemicals found in cigarette butts and chemicals leached? from cigarette butts into water. However, there are very limited data on the emissions from cigarette butts into air; 3) The emission rates from cigarette butts into air may be minimal for some heavy chemicals (e.g., metals, tobacco-specific nitrosamines), but may be significant for more volatile chemicals (e.g., nicotine, pyridine, benzene); 4) The airborne emissions of cigarette butts may be influenced by the cigarette brand, filter material, butt length, environmental temperature, airflow around the cigarette, number of puffs during smoking, degradation of the butt, and smoking method; 5) Much more data are needed on the airborne emission rates under different conditions. Based on the information from the literature review, the proposed experimental plan aims to fill the data gaps by using a screening tool (e.g. headspace analysis) to examine the airborne emission from non-smoldering cigarette butts under various environmental conditions. Steps in the proposed investigation include development of headspace analysis methods, selection of cigarette brand, determination of butt length, generation of cigarette butts, and determination of the target compounds. The proposed experiments will be conducted under four exposure environments, including small chamber, large chamber (to mimic indoor conditions), Simulation Photo-degradation via High Energy Radiation Emission chamber (SPHERE), with ultra violet radiation to simulate accelerated aging in outdoor environments, and outdoor rooftop (to represent aging in an outdoor environment).

Contents

Glossary

Airborne emission: Release of pollutants into air from a solid or liquid source as it burns or volatilizes.

Automated headspace analysis: Measurement of compounds of interest from the vapor phase around a sample placed in a closed system instead of directly from the sample matrix. Automation allows for enhanced precision and sample throughput.

Chemical: A form of matter that is composed of a particular set of elements and has characteristic properties. A chemical cannot be separated into the elements it is comprised of by physical separation methods, i.e., without breaking chemical bonds.

Cigarette butt: Defined in this document as the cigarette remaining at the conclusion of the smoldering phase following smoking. The conclusion of the smoldering phase is defined as when the entire cigarette butt reaches the ambient temperature of the environment in which it is located. Typically, the cigarette butt has three major parts: ash, unburnt tobacco, and filtration material. The cigarette butt includes any remaining paper (wrapping paper, tipping paper, and plug wrap paper).

Cigarette filter: Includes the filtration material, tipping paper, plug wrap paper, and adhesive. The filtration material is usually made of cellulose acetate, the cigarette filter is intended to trap less desirable components of mainstream smoke.

Cigarette tip: A term used to refer to cigarette filters, especially for cigarettes that people roll themselves.

Compendex Engineering Village: Database of patents and journals across disciplines. Disciplines include: electrical, civil, chemical, mechanical, mining, and general engineering in addition to applied science. This database covers engineering to a greater depth than the Web of Science database.

Compounds: A form of matter that is composed of two or more elements and has characteristic properties. A compound cannot be separated into the elements it is comprised of by physical separation methods, i.e., without breaking chemical bonds.

Constituents: Compounds present in a cigarette after it has been smoked.

Cross flow: Ambient air flow surrounding the cigarette.

Ingredients: Compounds or additives added to cigarettes during the manufacturing process.

ISI Web of Science Databases of journals across disciplines. The disciplines include agricultural, biological, and environmental sciences, engineering, technology, applied science, medical and life sciences, and physical and chemical sciences. This database covers biological, medical, and environmental sciences to a greater depth than the Compendex Engineering Village database.

Mainstream smoke: All smoke that leaves the butt end of a cigarette during the smoking process **(ISO3308 2012)**.

Non-smoldering: The non-smoldering phase starts when the entire cigarette butt reaches the ambient temperature of the environment in which it is located and particles are no longer emitted from the combustion process.

Rooftop experiments: Experiments that will be conducted on the rooftop of building 226 on the NIST-Gaithersburg campus to measure the effect of aging in the outdoor environment on airborne emissions from cigarette butts. Several instruments are located on this rooftop to measure environmental conditions such as solar irradiance, wind speed, rain, etc.

Sidestream smoke: All smoke which leaves a cigarette during the smoking process other than from the butt end **(ISO3308 2012)**.

SPHERE experiments: Experiments that will be conducted in the Simulation Photo-degradation via High Energy Radiation Emission chamber (SPHERE), with ultra violet radiation to simulate accelerated aging of cigarette butts in outdoor environments.

Tenax-TA tubes: Porous polymer adsorbent used for collecting airborne organic contaminants. For analysis the tubes are thermally desorbed into the inlet of a gas chromatography system.

Tobacco filter: A term used to refer to cigarette filters.

Ventilation: Air flow though the cigarette.

1 Background

The Family Smoking Prevention and Tobacco Control Act (Tobacco Control Act) was signed into law on June 22, 2009, amending the Food, Drug and Cosmetic Act and providing the Food and Drug Administration (FDA) the authority to regulate the manufacturing, distribution, and marketing of tobacco products. More specifically, the Tobacco Control Act gives FDA the authority to, among other things, establish science and research programs to inform the development of tobacco product regulations and better understand the risks associated with tobacco use.

FDA considers the environmental impacts of its actions as an integral part of its regulatory process. The National Environmental Policy Act (NEPA) of 1969, as amended (42 U.S.C. § 4321 et seq.), directs that all agencies of the Federal Government include a detailed assessment of the environmental effects of a major Federal action significantly affecting the quality of the human environment. To comply with NEPA, according to 21 CFR 25, FDA follows guidance from the Council for Environmental Quality (CEQ) in assessing the environmental effects of any proposed action. Under 21 CFR 25.40(a), the environmental assessment shall focus on relevant issues relating to the use and disposal of FDA regulated articles. Included in the environmental considerations of tobacco product applications, FDA considers, among other factors, the environmental effects of waste generated as a result of disposal after use.

A major existing environmental consequence of the use of tobacco products, such as conventional and roll-your-own cigarettes, is the waste disposal of discarded cigarette filters or butts, which can persist in the environment for more than 10 years **(Novotny and Zhao 1999)**. Globally, around 5 trillion cigarette butts are generated per year **(Novotny and Zhao 1999, Chapman 2006, Healton et al. 2011, Bonanomi et al. 2015)**. Cigarette butts are some of the most common forms of litter found 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)**. Cigarette butts have been found at densities averaging more than four cigarette butts m^{-2} in urban environments **(Seco Pon and Becherucci 2012)**.

The environmental toxicity of cigarette butts due to air emissions is not well studied. FDA is seeking to gather more information regarding air emissions from cigarette butts and to assess the cumulative environmental impact of filtered tobacco products.

2 Purpose

This report summarizes activities under an interagency agreement (#244-15-9012) between the Food and Drug Administration (FDA) and the National Institute of Standards and Technology (NIST). The objective of that agreement was: 1) to conduct a literature review to gather and analyze existing research related to airborne emissions from non-smoldering cigarette butts, and 2) to develop an experimental plan to measure the airborne emissions from non-smoldering cigarette butts.

3 Literature Review on Cigarette Butt Emissions

A literature search, as described below, was conducted to evaluate existing literature that assessed emissions from non-smoldering cigarette butts

3.1 Literature Search

A literature search of papers published prior to January 20th of 2016 was carried out using the ISI Web of Science and Compendex Engineering Village databases. As shown in Table 1 , the search keywords used were “Cigarette butt*”, “Cigarette filter*”, “Cigarette tip*” and “Tobacco filter*”. The “*” wildcard character allowed for plural words to be searched simultaneously. A total of 1 793 papers were identified from ISI Web of Science, while 1 101 papers were identified from Compendex Engineering Village. Combining the papers from the two search results and removing the duplicate papers resulted in a database with 2 381 papers. Of those 2 381 papers, 2 186 papers were excluded since the studies performed were not related to the topics discussed in this document. Specifically, those excluded papers focused on subjects such as the act of smoking, diseases caused by the act of smoking, how to make cigarettes, experiments on rats or mice smoking, and indoor air filters to remove cigarette smoke.

Table 1. Summary of literature searches.

Search database	Search keywords	No. of papers	Search date
Web of Science	Cigarette butt* or Cigarette filter* or Cigarette tip* or Tobacco filter*	1 793	01-20-16
Compendex Engineering Village	Cigarette butt* or Cigarette filter* or Cigarette tip* or Tobacco filter*	1 101	01-20-16

None of the remaining reviewed 195 articles directly studied airborne emission from non-smoldering cigarette butts in indoor or outdoor environmental conditions. Four articles reported the emission from cigarette butts into the headspace of sample vials at elevated temperatures. The detailed summary of these four papers is described in section 3.3.1. As a result of the limited data set on airborne emission, the focus of the literature review was widened to investigate all possible emissions from cigarette butts to provide context to the experimental plan. Consequently, the 195 papers were scrutinized for this report. Of those 195 papers, 121 relevant articles which discussed the definition of cigarette butts, chemical composition of cigarette butts, factors that potentially influence cigarette butt airborne emissions, impacts of cigarette butts on human health and environment, and alternative uses for cigarette butts, have been cited in this document.

3.2 Definition of Cigarette Butt

A definition of a cigarette butt is needed to accurately discuss emissions from cigarette butts. ISO 3308 **(2012)** (Routine analytical cigarette-smoking machine - Definitions and standard conditions) defines a butt length as the “length of unburnt cigarette remaining at the moment when smoking is stopped.” For the purpose of this document, this definition of a cigarette butt will be the cigarette remaining at the conclusion of the smoldering phase following smoking (i.e. the remaining cigarette butt has reached the temperature of the environment it is in). For the remainder of this document the term cigarette butt will refer to a non-smoldering cigarette butt.

A cigarette butt has three major components: 1) ash, 2) unburned tobacco and 3) filtration material (Figure 1). These three major components are wrapped by three types of paper (wrapping paper, tipping paper, and plug wrap paper).

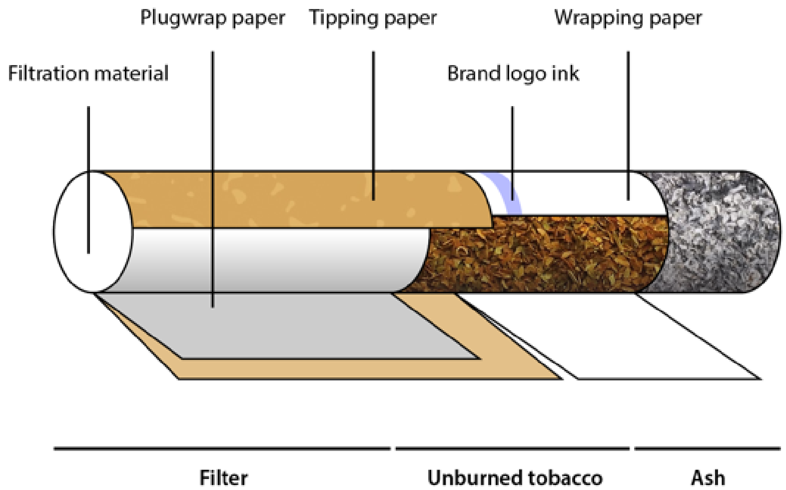

Figure 1: Components of cigarette butt.

3.3 Chemical Composition of Cigarette Butts

Since there are limited data on airborne emissions from cigarette butts, it is important to characterize the chemical composition of cigarette butts in order to assess their potential airborne emissions. The chemicals in cigarette butts can be the original chemicals in the unsmoked cigarettes or the pyrolysis and distillation products deposited in the cigarette butts. Each component of a cigarette butt (e.g., ash, unburned tobacco, filter and paper) can contain different chemicals that could possibly emit as the cigarette butt ages.

The chemical composition of the ash and the unburned tobacco depends on the types of tobacco, how the cigarette was smoked, and the mass transfer behavior of combustion products along the cigarette. The diameter of the cigarette **(Coggins et al. 2013)** and the permeability of the wrapping paper will influence the burned condition **(Xia et al. 2012)**. Depending on the burning conditions, the combustion temperature in a cigarette can reach up to 800 °C **(Hertz et al. 2012)**. Different chemicals are produced at different temperatures and times during the burning process. Hydrocarbons (e.g., benzene and naphthalene) are formed by pyrolysis above 600 °C, while phenols are generated at 400 °C. In contrast, nicotine is released by distillation at temperatures below 300 °C **(Baker 1987)**.

Chemicals found in cigarette filters will depend on the filter design. Filters are designed to capture various less desirable components of mainstream smoke, with each cigarette brand using different strategies. The type of filter material will influence the initial chemicals present in the cigarette butt that can potentially be emitted. Most filters are made of cellulose acetate. However, researchers have examined the performance of filters consisting of activated carbon, tert-butylhydroquinone (TBHQ), vitamin C, carotene, grape seed extract, Ginkgo biloba extract, dried hemoglobin, and polyurethane foam/aluminum hydroxide hybrid **(Smith et al. 1997, Valavanidis and Haralambous 2001, Masoudi Soltani and Kazemi Yazdi 2012, Liu et al. 2013, Petraru et al. 2013, Salman et al. 2014, Soltani et al. 2015)**.

It should be noted that some additives may be added to the unburned tobacco to improve their sensory properties and increase attractiveness to smokers. These additives include single compounds such as glycerol, propylene glycol, menthol, vanillin, diammonium hydrogenphosphate, and n-propyl-p-hydroxybenzoate, as well as complex additive mixtures such as cocoa, licorice, and mint oil **(Merckel and Pragst 2007, Huang et al. 2014)**. Some of the additives may remain in the cigarette butt. Similar to other original chemicals, the additive transfer behavior to the cigarette butt is dependent on the molecular weight and boiling point of the additive, the configuration of the cigarette, and other factors such as the chemical polarity of the additive **(Huang et al. 2014)**.

Regardless of the different composition of different cigarette butts, even for cigarette butts from the same pack, different chemicals can be detected when the butt is exposed to different environments or measured using different methods. The following sections (3.3.1 to 3.3.4) summarize the studies that have reported chemicals related to cigarette butts or related to individual components of cigarette butts (e.g. filter, unburned tobacco, ash and paper), including: 1) emissions from cigarette butts or individual butt components into air, 2) emissions from cigarette butts or individual butt components into water, 3) extraction of cigarette butts and direct analysis of cigarette butts or individual butt components, and 4) components in mainstream or sidestream smoke that potentially exist in cigarette butts. Table 2 summarizes the chemicals reported to be directly associated with cigarette butts and the analytical methods used in the first three groups of studies. The fourth group of studies are excluded from Table 2, since the experiments did not positively associate the measured chemicals with cigarette butts.

Table 2. Summary of detected chemicals reported in cigarette butt emission and extraction studies. Acronyms are defined in Table 3. Chemicals highlighted in bold and marked using asterisk are on the United States Food and Drug Administrations' Harmful and Potentially Harmful Constituents in Tobacco Products and Tobacco Smoke: Established List

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Alcohols	Ethanol	64-17-5	46.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Alcohols	2-Furfuryl Alcohol	98-00-0	98.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Alcohols	Isopropanol	67-63-0	60.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Alcohols	Methanol	67-56-1	32.0	Cigarette Filter	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-FID	**(You et al. 2014)**
Alcohols	1-methoxy-2-propanol	107-98-2	90.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Alcohols	1-ethoxy-2-propanol	1569-02-4	104.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Alkaloids	7-Carbaldehyde camptothecin	80758-83-4	376.4	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Aromatic amines	**Nicotine***	22083-74-5	162.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**, **(Zhao et al. 2010b)**
Aromatic amines	**Nicotine***	22083-74-5	162.2	Cigarette butt	Water	Leach into purified water and simulated rainwater, analyze the leachate by LC-MS-MS	**(Green et al. 2014)**
Aromatic amines	Hexaconazole	79983-71-4	314.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Aromatic amines	Imidocarb	27885-92-3	348.4	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Aromatic amines	Cotinine	486-56-6	176.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010b)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Aromatic amines	2-(Pyridin-3-yl) Pyrrolidine-1-Carbaldehyde	3000-81-5	176.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Aromatic amines	Sulfadoxine	2447-57-6	310.3	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Aromatic amines	5-(4,6-Dichloropyridin-3-yl)-Pyridine-1(2H)-Carboxamide[a]		270	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010b)**
Carbonyls	Acetol	116-09-6	74.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	**Acetone***	67-64-1	58.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	**Acetone***	67-64-1	58.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	Butyl acetate	123-86-4	116.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	Cyclohexanone	108-94-1	98.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	2-Pentanone	107-87-9	86.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	n-propanol	71-23-8	60.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	n-propyl acetate	109-60-4	102.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	Cyclopentanone	120-92-3	84.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Carbonyls	2-Cyclopentenone	930-30-3	82.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	2-Methylcyclo pentenone	1120-73-6	96.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	4-methyl-2-pentanone	108-10-1	100.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	Methyl n-Butyl Ketone	591-78-6	100.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	n-butyl alcohol	71-36-3	74.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	Ethyl acetate	141-78-6	88.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	3-Furaldehyde	498-60-2	96.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	2-Furaldehyde	98-01-1	96.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	**Formaldehyde***	50-00-0	30	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	Isopropyl acetate	108-21-4	102.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Carbonyls	**Acetaldehyde***	75-07-0	44.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	**Acrolein***	107-02-8	56.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Carbonyls	**Propionaldehyde***	123-38-6	58.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	Protoanemonin	108-28-1	96.08	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	**Crotonaldehyde***	4170-30-3	70.09	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	2-Butanone	78-93-3	72.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	Butyraldehyde	123-72-8	72.1	Cigarette filter	Extract solution	Extract with acetonitrile aqueous solution, analyze the extract by LC-MS-MS	**(Yu et al. 2013)**
Carbonyls	Acetol Formate	116-09-6	74.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	3-Methyl-2-Cyclopentenone	2758-18-1	96.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	2,3-Pentanedione	600-14-6	100.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Carbonyls	5-(4-Hydroxy Pyridin-3-yl)-Pyridine-1(2H)-Carboxamide		217	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Carbonyls	7-Keto-Benzo(a)pyrene		272	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Hydrocarbons	**Ethyl Benzene***	100-41-4	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	**Ethyl benzene***	100-41-4	106.2	Tipping	Air	Incubate a cigarette butt in a headspace vial, analyze	**(Huang et al. 2014)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
				paper		the air in the headspace by GC-MS	
Hydrocarbons	**Ethyl Benzene***	100-41-4	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	**Benzene***	71-43-2	78.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Hydrocarbons	**Benzene***	71-43-2	78.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	3,3-Dimethyl-1-Butene	558-37-2	84.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	Pyridine	110-86-1	79.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	Cyanobenzene	100-47-0	103.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	Cyclooctatetraene	629-20-9	104.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	Isocapronitrile	542-54-1	97.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Hydrocarbons	**Toluene***	108-88-3	92.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	**Toluene***	108-88-3	92.1	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Hydrocarbons	**Toluene***	108-88-6	92.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Hydrocarbons	p-Xylene	106-42-3	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	m-Xylene	108-38-3	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	m-Xylene	108-38-3	106.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Hydrocarbons	o-Xylene	95-47-6	106.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Hydrocarbons	o-Xylene	95-47-6	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	**Styrene***	100-42-5	104.2	Tipping paper	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Huang et al. 2014)**
Hydrocarbons	**Styrene***	100-42-5	104.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, analyze the air in the headspace by GC-MS	**(Ji et al. 2015)**
Hydrocarbons	Xylene	1330-20-7	106.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Insecticides	Maleic Hydrazide	123-33-1	112.1	Cigarette butt	Extract solution	Extract with methanol, dissolve the extract in DMF and silylate with BSTFA, analyze the silylated extract by GC-MS	**(Zhang et al. 2012)**
Insecticides	Chlorantraniliprole	500008-45-7	483.2	Cigarette butt	Extract solution	Extract with acetonitrile, radioassay the extract by LSC	**(Gaddamidi et al. 2011)**
Insecticides	Imidacloprid	138261-41-3	255.7	Cigarette butt	Extract solution	Extract with acetone, radioassay the extract by LSC	**(Clark et al. 1998)**
Metals	Aluminum (Al)	7429-90-5	27	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	Antimony (Sb)	7440-36-0	121.8	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper)	**(Wu et al. 1997)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
						directly by INNA	
Metals	**Arsenic (As)***	7440-38-2	74.9	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**
Metals	**Arsenic (As)***	7440-38-2	74.9	Cigarette filter	Extract solution	Extract with HNO_3 and H_2O_2 by heating in water bath, analyze the extract by HG-AFS	**(Wang et al. 2007)**
Metals	Barium (Ba)*	7440-39-3	137.3	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Cigarette butt	Extract solution	Extract with HNO_3-$HClO_4$ by wet ashing technique, analyze the extract by FAAS	**(Pelit et al. 2013)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Cigarette butt	Extract solution	Extract with 69 % HNO_3 and 36 % HCl using a microwave system, analyze the extract by FAAS	**(Galazyn-Sidorczuk et al. 2008)**
Metals	**Cadmium (Cd)***	7440-43-9	112.4	Unburned tobacco	Extract solution	Extract with HCl, analyze the extract by solid surface fluorescence using nylon membranes coated with carbon nanotubes	**(Carolina Talio et al. 2013)**
Metals	**Chromium (Cr)***	7440-47-3	52	Cigarette butt	Extract solution	Extract with HNO_3, analyze the extract by ICP-AES	**(Wang and Finlayson-Pitts 2003)**
Metals	**Cobalt (Co)***	7440-48-4	58.9	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Metals	Copper (Cu)	7440-50-8	63.6	Cigarette butt	Extract solution	Extract with HNO_3-$HClO_4$ by wet ashing technique, analyze the extract by FAAS	**(Pelit et al. 2013)**
Metals	**Mercury (Hg)***	7439-97-6	200.6	Cigarette filter	Extract solution	Extract with HNO_3 and H_2O_2 by heating in water bath, analyze the extract by HG-AFS	**(Wang et al. 2007)**
Metals	**Mercury (Hg)***	7439-97-6	200.6	Cigarette butt	Cigarette butt	Analyze the cigarette butt directly by mercury analyzer AMA-254	**(Kowalski and Wiercinski 2009)**
Metals	Iron (Fe)	7439-89-6	55.9	Cigarette butt	Extract solution	Extract with HNO3, analyze the extract by ICP-AES	**(Wang and Finlayson-Pitts 2003)**
Metals	**Lead (Pb)***	7439-92-1	207.2	Cigarette butt	Extract solution	Extract with 69% HNO3 and 36% HCl using a microwave system, analyze the extract by FAAS	**(Galazyn-Sidorczuk et al. 2008)**
Metals	**Lead (Pb)***	7439-92-1	207.2	Cigarette filter	Extract solution	Extract with solvent using a microwave system, analyze the extract by FAAS	**(Huang et al. 2013)**
Metals	**Lead (Pb)***	7439-92-1	207.2	Cigarette paper	Extract solution	Ash the cigarette paper with microwave ashing at 450 °C, extract the ash with nitric acid, analyze the extract by FAAS	**(Wu et al. 2012)**
Metals	**Lead (Pb)***	7439-92-1	207.2	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	Manganese (Mn)	7439-96-5	54.9	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	Manganese (Mn)	7439-96-5	54.9	Cigarette butt	Extract solution	Extract with HNO_3-$HClO_4$ by wet ashing technique, analyze the extract by FAAS	**(Pelit et al. 2013)**
Metals	**Nickel (Ni)***	7440-02-0	58.7	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	Potassium (K)	7440-09-7	39.1	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**
Metals	Strontium (Sr)	7440-24-6	87.6	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Metals	Titanium (Ti)	7440-32-6	47.9	Cigarette butt	Water	Leach into aqueous solution, analyze the leachate by ICP-OES	**(Moerman and Potts 2011)**
Metals	Zinc (Zn)	7440-66-6	65.4	Cigarette butt	Extract solution	Extract with HNO_3, analyze the extract by ICP-AES	**(Wang and Finlayson-Pitts 2003)**
Metals	Zinc (Zn)	7440-66-6	65.4	Cigarette butt	Extract solution	Extract with HNO3-HClO4 by wet ashing technique, analyze the extract by FAAS	**(Pelit et al. 2013)**
Metals	Zinc (Zn)	7440-66-6	65.4	Cigarette butt	Cigarette butt	Analyze different components of cigarette butt (unburned tobacco, ash, filter, cigarette paper) directly by INNA	**(Wu et al. 1997)**
Nitrosamines	**N-Nitrosonornicotine (NNN)***	16543-55-8	177	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a, Zhao et al. 2010b)**
Nitrosamines	TSNAs[c]			Cigarette filter	Extract solution	Extracting the filter with mixture of deuterated water/dimethyl sulfoxide, analyze the extract by NMR	**(Verdolotti et al. 2012)**
NPAHs	1,3-dinitronaphthalene			Cigarette filter	Extract solution	Extract with toluene, analyze the extract by EM-MS	**(John Dane et al. 2002)**
NPAHs	9-nitroanthracene			Cigarette filter	Extract solution	Extract with toluene, analyze the extract by EM-MS	**(John Dane et al. 2002)**
NPAHs	**Nitrobenzene***			Cigarette filter	Extract solution	Extract with toluene, analyze the extract by EM-MS	**(John Dane et al. 2002)**
PAHs	Anthracene	120-12-7	178.2	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
PAHs	**Benzo(a)pyrene***	50-32-8	252.3	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
PAHs	**Benzo[a]pyrene***	50-32-8	252.3	Cigarette filter	Extract solution	Strip the wrapping paper, extract with acetone, clean up by solid phase extraction, analyze the extract by HPLC-FLD	**(Ding et al. 2014)**
PAHs	**Benzo[a]pyrene***	50-32-8	252.3	Cigarette filter	Extract solution	Extract with acetonitrile, analyze the extract by LC-MS-MS	**(Zhang et al. 2014)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
PAHs	**Benzo[a]pyrene***	50-32-8	252.3	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
PAHs	**Benz[a]anthracene***	56-55-3	228.3	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
PAHs	**Benzo[b]fluoranthene***	205-99-2	252.3	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
PAHs	Fluoranthene	206-44-0	202.3	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
PAHs	Pyrene	129-00-0	202.3	Cigarette filter	Extract solution	Extract with acetonitrile and water, analyze the extract using SPME and HPLC	**(Demirci 2014)**
Phenols	**Catechol***	120-80-9	110.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	Hydroquinone	123-31-9	110.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	**m-cresol***	108-39-4	108.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	**o-cresol***	95-48-7	108.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	**p-cresol***	106-44-5	108.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	**Phenol***	108-39-4	108.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	Resorcinol	108-95-2	94.1	Cigarette filter	Extract solution	Extract with mix solution of acetic acid, methanol water, analyze the extract by HPLC	**(Hu et al. 2015)**
Phenols	Rutin	153-18-4	610.5	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a, Zhao et al. 2010b)**
Phenols	Rutin	153-18-4	610.5	Cigarette filter	Extract solution	Extract with methanol, analyze the extract with HPLC-UV	**(Sun et al. 2012)**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
Phenols	2,2-Dimethyl-2,3-Dihydrobenzofuran-7-ol	1563-38-8	164.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010b)**
Phenols	1,5-Dihydroxy-Anthraquinon	117-12-4	240.2	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010b)**
Phthalates	Dibutyl Phthalate	84-74-2	278.3	Cigarette filter	Extract solution	Ultrasonic extract with water and ethanol mixture, analyze the extract by GC-MS	**(Zhang et al. 2012)**
Phthalates	Diisobutyl Phthalate	84-69-5	278.3	Cigarette filter	Extract solution	Ultrasonic extract with water and ethanol mixture, analyze the extract by GC-MS	**(Zhang et al. 2012)**
Phthalates	Di(2-ethylhexyl) phthalate	117-81-7	390.6	Cigarette filter	Extract solution	Ultrasonic extract with water and ethanol mixture, analyze the extract by GC-MS	**(Zhang et al. 2012)**
Pyrazines	Pyrazine	290-37-9	80.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Pyrazines	2-Methylpyrazine	109-08-0	94.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Pyrroles	N-Methylpyrrole	96-54-8	81.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Pyrroles	Pyrrole	109-97-7	67.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Pyrroles	3-Methylpyrrole	616-43-3	81.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Pyrroles	2-Methylpyrrole	636-41-9	81.1	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Terpenes	Beta-Carotene-4,4'-Dione	472-61-7	596.8	Cigarette	Water	Leach into distilled water, analyze the leachate by LC-	**(Zhao et al. 2010a,**

Class	Chemical	CAS	MW[a] (g/mol)	Component	Media[b]	Summary of method	Reference
				butt		MS	**Zhao et al. 2010b)**
Terpenes	Xanthophylls	127-40-2	568.9	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010a)**
Terpenes	Limonene	5989-27-5	136.2	Cigarette butt	Air	Incubate a cigarette butt in a headspace vial, collect the sample with Tenax GC, analyze the sample by GC-FID	**(Fukuhara et al. 1985)**
Terpenoids	Solanesol	13190-97-1	631.1	Cigarette filter	Extract solution	Extract with hexane, analyze the extract by LC-MS	**(Watson et al. 2004, Polzin et al. 2009, Ashley et al. 2010, Brinkman et al. 2012)**
Terpenoids	Solanesol	13190-97-1	631.1	Cigarette filter	Extract solution	Extract with KOH, analyze the extract with LC-MS-MS	**(Watson et al. 2004)**
Unknown	6-(2,6-Dichlorophenoxy) Pyrimidine-2,4-Diamiine[d]		271	Cigarette butt	Water	Leach into distilled water, analyze the leachate by LC-MS	**(Zhao et al. 2010b)**

[a]MW: molecular weight

[b]Media: media describes the environment the detected chemicals were analyzed in (air, water, extract solution, cigarette filter, cigarette butt).

[c]The specific chemicals of tobacco specific nitrosamines (TSNAs) are not available in the cited paper **(Verdolotti et al. 2012)**

[d]CAS number can't be found based on the name and the structure reported in the reference **(Zhao et al. 2010b),** so it is classified as unknown chemical.

Table 3. Analytical technique acronyms

Acronym	Method	Description
EM-MS	electron monochromatic-mass spectrometry	Chemical species are ionized with electron ionization, and then sorted based on their mass-to-charge ratio. The ion signal as a function of the mass-to-charge ratio is characteristic of different chemicals.
FAAS	flame atomic absorption spectrometry	A flame heats a sample, causing the atoms in the sample to undergo a transition from the ground state to an excited state. In the excited state the atoms absorb the light passed through the sample. The elements in the sample are identified based on the absorption of light by free atoms in a gaseous state.
GC-MS	gas chromatography-mass spectrometry	A sample is forced by a gas through a column that is lined with a stationary phase which causes the components to separate. A mass spectrometer ionizes the chemical compounds to generate charged molecules which are separated according to their mass-to-charge ratio by electromagnetic fields. The ion signal detected is then processed into mass spectra.
GC-FID	gas chromatography-flame ionization detector	A sample is forced by a gas through a column that is lined with a stationary phase which causes the components to separate. A flame ionization detector ionizes the chemical compounds producing a signal in proportion to the concentration of organic species in a gas stream.
HG-AFS	hydride generation-atomic fluorescence spectrometry	A technique for speciation studies of hydride forming elements (e.g. Arsenic) and Mercury. A hydride is a compound that generally contains one or more hydrogens with reducing properties. Atomic fluorescence spectrometry is based on absorption of radiation by an atomic vapor and subsequent emission of radiation at wavelengths that are characteristic of the atomic species present.
HPLC-FLD	high performance liquid chromatography-fluorescence detector	A sample is forced by a liquid through a column that is packed with a stationary phase which causes the components to separate. Different components will adsorb to the column at different rates, thereby separating the components as they flow out of the column. Components fluoresce in proportion to the concentration of the component.
HPLC-UV	high performance liquid chromatography-UV detector	A sample is forced by a liquid through a column that is packed with a stationary phase which causes the components to separate. Different components will adsorb to the column at different rates, thereby separating the

		components as they flow out of the column. Components absorb UV spectra in proportion to the concentration of the component.
ICP-AES	inductively coupled plasma-atomic emission spectroscopy	A technique for elemental analysis that uses a plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. As they return to their ground state, they emit photons of a characteristic wavelength depending on the element present. This light can be recorded with an optical spectrometer.
ICP-OES	inductively coupled plasma-optical emission spectroscopy	A technique for elemental analysis that uses a plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. As they return to their ground state, they emit photons of a characteristic wavelength depending on the element present. This light can be recorded with an optical spectrometer.
INAA:	instrumental neutron activation analysis	A technique for elemental analysis that bombards the sample with neutrons, causing the elements to form radioactive isotopes. Based on the known radioactive emissions of different elements, the emissions from the sample can be analyzed to determine the concentration of elements in it.
LC-MS	liquid chromatography-mass spectrometry	A sample is forced by a liquid through a column that is packed with a stationary phase which causes the components to separate. Different components will adsorb to the column at different rates, thereby separating the components as they flow out of the column. A mass spectrometer ionizes the chemical compounds to generate charged molecules which are separated according to their mass-to-charge ratio by electromagnetic fields. The ion signal detected is then processed into mass spectra.
LC-MS-MS	liquid chromatography-mass spectrometry-mass spectrometry	A sample is forced by a liquid through a column that is packed with a stationary phase which causes the components to separate. Different components will adsorb to the column at different rates, thereby separating the components as they flow out of the column. In a mass spectrometer, ions are produced and separated by their mass-to-charge ratio. However, in mass spectrometry-mass spectrometry (MS/MS), ions of particular mass-to-charge ratios are further dissociated into fragment ions. These fragment ions are then separated and detected in a second stage of mass spectrometry.
LSC	liquid scintillation counter	A technique for detection and quantification of radioactivity. A scintillation fluid is added to the sample

		which interacts with the beta particles released from the sample. The energized molecules of the scintillation fluid emit photons of light at intensities that are proportional to the energy of the beta particle. The emitted spectra are unique for different-energy beta emitters.
NMR	nuclear magnetic resonance	An analytical technique used to determine the structure of organic compounds. Nuclear magnetic resonance is based on the absorption of electromagnetic radiation by a nucleus having a magnetic moment when placed in an external magnetic field. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, which provides details of the electronic structure of a molecule.
SPME	solid phase microextraction	A sampling technique that involves the use of a fiber coated with a material which extracts both volatile and non-volatile compounds from different kinds of media (liquid or gas phase).

3.3.1 Chemicals Emitted from Cigarette Butts into Air

As mentioned before, no study has investigated the airborne emissions from cigarette butts in indoor or outdoor environmental conditions. However, there are four studies that measured the emissions from cigarette butts into the airborne headspace of test vials. In this section, we summarize the four studies. Both the measured chemicals and a brief description of the analytical methods are summarized in Table 2 and Table 3, respectively.

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 not different from those found in mainstream smoke. They also found 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 (tipping and wrapping papers together) in a mentholated cigarette. The samples were first heated at 100 ^{o}C for 30 minutes in a headspace sampler, and then measured by GC-FID. The methanol concentration in the cigarette papers ranged from 3.0 mg/g paper to 4.1 mg/g paper, while the methanol concentration in the cigarette filter was 13.7 mg/g paper to 27.2 mg/g paper. Huang et al. **(2014)** measured the emissions of cigarette tipping paper into the headspace of vials. The samples were first incubated at 80 ^{o}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 concentration ranging from 0.01 mg/m^2 paper to 3.3 mg/m^2 paper, 1.0 mg/m^2 paper to 13.2 mg/m^2 paper, 0.0 mg/m^2 paper to 8.9 mg/m^2 paper, 0.03 mg/m^2 paper to 1.33 mg/m^2 paper, 0.0 mg/m^2 paper to 3.0 mg/m^2 paper, and 0.02 mg/m^2 paper to 20.7 mg/m^2 paper, respectively. 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 were from 0.4 µg/filter to 1.1 µg/filter, 1.1 µg/filter to 4.7 µg/filter, 0.4 µg/filter to 1.7 µg/filter, 0.3 µg/filter to 1.4 µg/filter, 0.8 µg/filter to 3.3 µg/filter, 0.4 µg/filter to 1.4 µg/filter, and 2.0 µg/filter to 5.7 µg/filter, respectively.

These four studies provide some basis for understanding the potential airborne emissions into indoor or outdoor environments. However, the study reported by Fukuhara et al. **(1985)** was limited in the number of cigarette butts tested and quantification of 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 are very limited and only cigarette filters or tipping papers were measured. These studies did not include the unburned tobacco or ash of cigarette butts, which likely emit different chemicals from the filters and tipping papers. In addition, the high incubation temperatures (> 80 °C) will enhance the emission of some non-volatile chemicals that may not emit to a significant degree at normal indoor and outdoor temperatures. These testing conditions could result in overloading the GC-MS if the unburned tobacco and ash were included. Finally, all of these studies only measured freshly generated cigarette butts, or part of the unburned cigarette, and didn't examine the influence of several factors that could impact the emission of cigarette butts, such as the exposed temperature, relative humidity, aging, and ultra-violet (UV) radiation.

3.3.2 Chemicals Emitted from Cigarette Butts into Water

In this section, we summarize the chemicals found in studies on emissions from cigarette butts or their components into water. Both the chemicals detected and more detailed information on the measurement methods are shown in in Table 2 and Table 3, respectively.

Compounds within cigarette butts can leach out into water, potentially threatening human health and the environment, especially marine ecosystems **(Kadir and Sarani 2015)**. Zhao et al. **(2010a)** measured the chemicals in both aerobic and anaerobic cigarette butt water extracts. They found that the main chemicals in both water extracts were aromatic amines, e.g., nicotine and N-nitroso-nornicotine (NNN). More types of compounds were found in aerobic water extracts than anaerobic water extracts, which may be because of the oxidization of amine compounds in aerobic water. Another study published by Zhao et al **(2010b)** also primarily detected amines in water, but also found different chemicals than the first Zhao et al. **(2010a)** study, e.g., cotinine.

Emissions from cigarette butts into water can be a 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 minutes during the experiment **(Green et al. 2014)**. The same study also found that the cumulative nicotine release from fifteen consecutive rainfall events with 1.4 mm of precipitation for each event was 3.8 mg of nicotine per g butt, of which 47 % was released during the first event **(Green et al. 2014)**. A study of metals (aluminum, barium, chromium, cadmium, copper, iron, lead, manganese, nickel, strontium, tin and zinc) showed that more than half the mass was leached within one day from the cigarette butts into acidic aqueous solution **(Moerman and Potts 2011)**.

Interestingly, cigarette butts can not only emit chemicals into water, but also absorb chemicals from water. Chen et al. **(2012)** used cigarette filters as adsorbents for pre-concentration of fluoroquinolones antibacterial agent. Hence, it is possible that not all chemicals present in the cigarette butt as it ages are from the original cigarette or the result of the smoking process.

3.3.3 Chemicals Measured in Cigarette Butts

Since there are limited data on chemicals emitted from cigarette butts into air or water, we examined the literature for information on chemicals that are present in cigarette butts.

In this section, we summarize the chemicals from studies on extraction of cigarette butts or individual butt components by solvents. We also examine studies that directly analyzed the cigarette butts or individual butt components via their radioactivity. Chemicals detected in cigarette butts and more detailed information on the measurement methods are included in Table 2 and Table 3, respectively.

3.3.3.1 Metals

Metals are commonly detected within cigarette butts or individual butt components **(Wu et al. 1997, Huang et al. 2013)**. Cadmium, copper, manganese and zinc were measured in cigarette butts at concentrations up to 104 μg/g butt **(Pelit et al. 2013)**. Mercury and arsenic concentrations in cigarette filters have been measured between 0.002 mg/kg to 0.051 mg/kg and 0.025 mg/kg to 0.651 mg/kg, respectively **(Wang et al. 2007)**. Zinc and iron have been detected in the cigarette tobacco, filter and ash **(Wang and Finlayson-Pitts 2003)**. After smoking, 15 % to 50 % of heavy metals (lead, arsenic, cobalt, cadmium, potassium, antimony and zinc) originally in cigarettes is retained in cigarette butts **(Galazyn-Sidorczuk et al. 2008, Wu et al. 2012, Carolina Talio et al. 2013)**. However, despite the detection of mercury in the cigarette butts, a majority of mercury that is initially present in the cigarette was released into the air during smoking and not trapped on cellulose acetate filters **(Kowalski and Wiercinski 2009)**.

3.3.3.2 Polycyclic Aromatic Hydrocarbons (PAHs) and Terpenoids

Since cigarette butt samples can be collected easily and noninvasively, levels of some chemicals in cigarette butts are often used to estimate mouth-level intake of the chemicals for smokers. Benzo[a]pyrene (B[a]P) levels in used cigarette filters have been measured and demonstrated to be highly correlated with B[a]P measured in mainstream smoke. This correlation allows B[a]P concentrations in cigarette butts to be used as an estimate of mouth-level B[a]P exposure of smokers **(Ding et al. 2014, Zhang et al. 2014)**. PAHs in cigarette filters have been studied using solid-phase microextraction (SPME) and high performance liquid chromatography (HPLC) **(Demirci 2014)**. The sum all of the studied PAHs found in the filter tar of three brands of cigarettes were 17.9 ng, 66.7 ng and 320.2 ng per cigarette.

Solanesol is a chemical found in tobacco leaves. The concentration solanesol deposited in cigarette filters has been shown to be stable for over four weeks after smoking **(Watson et al. 2004)**. As a result, solanesol extracted from cigarette filters may be used as an indicator chemical to assess smokers' mainstream smoke exposure to tobacco specific nitrosamines (TSNAs) **(Polzin et al. 2009)**, tar **(Watson et al. 2004)** and nicotine **(Watson et al. 2004, Polzin et al. 2009)**. The concentrations of solanesol in cigarette filters were used to estimate the mouth-level intake of 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) **(Ashley et al. 2010, Brinkman et al. 2012)**, which was found to be significantly associated with urinary concentrations of its major metabolite 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol (NNAL) **(Ashley et al. 2010)**.

3.3.3.3 Insecticides and Plant Growth Regulators

Different chemicals are often used to protect tobacco plants prior to harvest. These chemicals can be in the unburned tobacco of a cigarette butt or potentially transferred to other parts of the cigarette butt and detected in the extract of cigarette butts. Maleic hydrazide (1,2-dihydro-3,6-pyridazinedione), a plant growth regulator that inhibits the growth of suckers on tobacco plants, is often present in cigarettes, ranging from 1 µg/g cigarette to 100 µg/g cigarette **(Zhang et al. 2012)**. Zhang et al. **(2012)** found that maleic hydrazide can be transferred to the cigarette butt in the range from 1.1 % to 1.9 % of the initial mass present in the cigarette. Chlorantraniliprole is the active ingredient in the insecticide used to control budworm and hornworm in tobacco plants. A study on pyrolysis of ^{14}C chlorantraniliprole in a cigarette showed that about 17 % of spiked ^{14}C chlorantraniliprole was found in extracts of cigarette butts after smoking **(Gaddamidi et al. 2011)**. Of the spiked radio-labelled insecticide imidacloprid [1-(6-chloropyridin-3-ylmethyl)-N-nitro-imidazolidin-2-ylideneamine] in tobacco leaves, 39 % of the radioactivity was found in cigarette butts after the smoking of cigarettes made of the spiked leaves **(Clark et al. 1998)**.

3.3.3.4 Other Organics

In addition to the aforementioned chemicals, phenolic compounds, tobacco specific nitrosamines (TSNAs), carbonyls, phthalates and nitropolycylic aromatic hydrocarbons (NPAHs) have also been detected in cigarette butts.

Sonication solvent extraction of cigarette filters followed by HPLC analysis has been used to measure seven major phenolic compounds (hydroquinol, resorcinol, catechol, phenol, p-cresol, m-cresol and o-cresol) on cigarette filters in a comparative study run between six laboratories **(Hu et al. 2015)**. Rutin, a kind of phenolic compound, was found in cigarette filters at a mass of 0.1 µg/filter to 0.3 µg/filter **(Sun et al. 2012)**. However, the rutin mass in the cigarette filter was two orders of magnitude lower than in the tobacco part of the cigarette **(Sun et al. 2012)**, and rutin is likely not volatile enough (molecular mass 610.5 g mol^{-1}, boiling point 956^{o}C) to be emitted into the air at significant levels from extinguished butts.

TSNAs have been detected in cigarette filters by extracting the filters with a mixture of deuterated water/dimethyl sulfoxide and then analyzing with nuclear magnetic resonance (NMR) **(Verdolotti et al. 2012)**.

Yu et al. **(2013)** extracted carbonyls (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, 2-butanone and butyraldehyde) from cigarette filters and determined that the filtration efficiencies of four different types of cigarette filters (i.e. cellulose acetate filter, activated carbon filter, polypropylene fiber filter, and paper filter) were roughly 5 % for the total content of the eight carbonyls.

Phthalate esters were extracted with water and ethanol from 45 cigarette filters and analyzed using GC-MS **(Zhang et al. 2012)**. Among the 17 targeted phthalate esters, only dibutyl phthalate (DBP), diisobutyl phthalate (DIBP) and di(2-ethylhexyl)phthalate (DEHP) were found in the cigarette filters with detection frequency for each phthalate less than 20 % **(Zhang et al. 2012)**.

NPAHs in cigarette filters have been measured using toluene extraction followed by electron monochromator-mass spectrometry (EM-MS) **(John Dane et al. 2002)**.

3.3.4 Mainstream and Sidestream Smoke Chemicals Potentially in Cigarette Butts

The previous sections of this report reviewed chemicals that were present in a cigarette butt or emitted into air or water from a cigarette butt. In addition to the chemicals identified in cigarette butts (Table 2), chemicals found in cigarette smoke may also be present in cigarette butts despite not having been identified as such in a previous study. Hence, the literature on chemicals in cigarette smoke was reviewed to guide the planning process for investigating airborne emissions from cigarette butts by (1) more broadly identifying the types of compounds that may be emitted from cigarette butts into the air, and (2) identifying a wider range of the analytical tools available. Preliminary experiments (section 4.2.5) show that many of the components in cigarette smoke are similar to the components measured in air above a freshly-smoked, extinguished cigarette butt and an aged cigarette butt.

Cigarette smoke is a complex mixture of 40 000 to 100 000 compounds **(Dalluge et al. 2002)** including metals, hydrocarbons, phenols, quinones, alcohols, phytosterols, aldehydes, ketones, carboxylic acids, ethers, carbohydrates, esters, anhydrides, amines, amides, nitriles, inorganic gases (e.g. CO_2, CO, NO_x), free radicals and other compounds. Most of the organic compounds are in the range of n-heptane to n-dodecane. Cigarette smoke is comprised of mainstream and sidestream smoke. Mainstream smoke is the term used for smoke drawn through “the butt end of the cigarette during the smoking process” **(ISO3308 2012)** and can also be applied to the smoke that a smoker exhales. Sidestream smoke refers to the smoke that wafts off the lit end of the cigarette during the smoking process **(ISO3308 2012)**. Sidestream smoke makes up about 85 % of environmental tobacco smoke **(Pieraccini et al. 2008)**. Mainstream smoke includes several chemicals classified by the International Agency Research On Cancer (IARC) as Group 1 Human Carcinogens: benzene, cadmium, arsenic, nickel, chromium, 2-naphthyl-amine, vinyl chloride, 4-aminobiphenyl and beryllium **(Smith et al. 1997)**. Sidestream smoke contains higher concentrations of some chemicals than mainstream smoke due to incomplete combustion. The chemical composition of sidestream and mainstream smoke is also different, because the combustion temperature of a smoldering cigarette is much lower than the temperature during a puff. For instance, aromatic amines **(Luceri et al. 1993)** and PAHs **(Lodovici et al. 2004)** are found at higher levels in sidestream smoke than in mainstream smoke as a result of incomplete combustion as cigarettes smolder.

The sample collection methods for chemicals in cigarette smoke are based on their inherent stability or some aspect of their chemical reactivity **(Liu et al. 2011)**. There is greater diversity in the trapping and analysis techniques used for volatile compounds in smoke than in the extraction techniques of cigarette butts presented in the previous section. Compounds such as tar, nicotine, phenols, tobacco-specific nitrosamines (TSNA) and benzo[a]pyrene are typically collected onto glass fiber filters. Aromatic amines, hydrogen cyanide, ammonia, certain semi-volatiles, and certain carbonyls and volatile compounds are often trapped using impingers or glass fiber filters. Other trapping techniques include sorbent tubes (for certain semi-volatiles), activated silica gel (for hydrogen cyanide and certain carbonyls) and DNPH treated filters (for certain carbonyls). Solid sorbent trapping and thermal desorption-gas chromatography has been used extensively over the last few decades to measure gas phase and particulate matter components in cigarette smoke **(Higgins et al. 1984)**. Inorganic gases, such as carbon monoxide and nitric oxide, are sampled using gas collection bags.

Real-time smoke analytical techniques have highlighted the dynamic and reactive nature of some of the compounds in cigarette smoke **(Liu et al. 2011)**. Boldridge and Ingebrethsen **(1986)** developed a model to predict the changes in cigarette smoke aerosol as it travels through a length of tobacco-filled rod.

Compounds in cigarette smoke that can readily volatilize are more likely to appear in airborne emissions from cigarette butts. Compounds with high boiling points (e.g. metals, compounds with high molecular weights) are unlikely to get volatilized from cigarette butts. Sections 3.3.4.1 and 3.3.4.2 categorize compounds in cigarette smoke into these two classes and discuss the analytical techniques used to measure these compounds. These sections do not attempt to be an authoritative or exhaustive analysis of compounds in mainstream or sidestream smoke. Rather, they provide a background on analytical techniques in order to support the discussions of experimental investigations described in Section 4.

3.3.4.1 Chemicals in Cigarette Smoke Unlikely to be Present in Airborne Emissions from Cigarette Butts

Only some compounds from cigarette smoke that are retained on the discarded cigarette butt are likely to emit into the air. Some compounds can be too volatile to get fully retained in the cigarette filter, and others can get retained but are very unlikely to be emitted from cigarette butts because they are not volatile enough. Petraru et al. **(2013)** examined the ability of 29 different cigarette filters to retain chemicals, showing that lower molecular weight chemicals breakthrough filters faster. These lower molecular weight chemicals included methane, ethane, propane, 2-methylpropane, ethene, acetylene, 1-butene, 1,3 -butadiene, 2-butene, cis-2-butene, 2-methyl-2-butene, benzene, toluene, furan, 2-methylfuran, 2,5 meththylfuran, acetaldehyde, acrolein, propionaldehyde, 2-methylpropanal, crotonaldehyde, acetone, methyl vinyl ketone, methyl ethyl ketone, acetonitrile, propionitrile, methyl acrylate, methanol and chloromethane. Other compounds may get retained in cigarette butts but are unlikely to volatilize from cigarette butts at significant rates if their boiling points are high. These compounds can, however, leach out of the discarded cigarette butt into water, soil, and other media, as described in section 3.3.2. Analytical techniques and measurements of these compounds in cigarette smoke is described below.

3.3.4.1.1 Metals

Most particulate phase compounds emitted in cigarette smoke are collected with glass fiber filters (Cambridge Filter Pads) and analyzed using a range of extraction solvents and analytical techniques **(Liu et al. 2011)**. Metals present in cigarette smoke are typically associated with particles. Hence, most airborne metal studies collect particulate matter on filters and measure metals on the filter using inductively-coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GFAAS). Wagner et al. **(2001)** measured arsenic, cadmium and lead in this manner. Due to the association with particles, it is unlikely that metals will emit into the air from cigarette butts.

Although most metal emissions are typically associated with particles, there is some potential for organometallic compounds to be present and volatilize. The emission of nickel tetracarbonyl from cigarettes was investigated by Torjussen et al. **(2003)**. Nickel tetracarbonyl has a boiling point of 43 °C, and hence it could be emitted from a butt if present.

3.3.4.1.2 Tobacco-Specific Nitrosamines

Tobacco-specific nitrosamines (TSNAs) are carcinogens **(Sleiman et al. 2009, Verdolotti et al. 2012)**, and TSNA urinary metabolites can be detected after secondhand smoke exposure **(Schick et al. 2013)**. TSNAs are typically associated with particles and sorbed to indoor surfaces **(Schick et al. 2014)**. TSNAs have been analyzed by trapping particles on glass fiber filters and extracting them using various methods including supercritical fluid extraction (carbon dioxide with 10 % methanol) **(Brunnemann et al. 1996, Sleiman**

et al. 2009). The elution is then analyzed using gas chromatography–ion-trap tandem mass spectrometry.

Emission of TSNAs vary over an order of magnitude between different cigarettes. Analyzing secondhand smoke particles, Brunnemann et al. **(1996)** found N-nitrosonornicotine (NNN) from 28 ng to 730 ng per cigarette, and for 4-(methylnitrosamino)-1-(3-pyridyl-1-butanone (NNK) from 16 ng to 369 ng per cigarette depending on the cigarette composistion. The TSNA concentrations correlated with nicotine concentrations. Haorah et al. **(2001)** measured N-nitroso compounds and their precursors in cigarette smoke using sampling filters to collect the smoke. The method employed measured the total amount of N-nitroso compounds present, not individual species, as is possible with GC-MS methods. The total amount of N-nitroso compounds was found to be more than an order of magnitude higher than previously published values of TSNAs, including NNN and NNK, indicating that most of the N-nitroso compounds do not consist of these nitrosamines. The concentrations of precursors of N-nitroso compounds correlated with particulate and tar concentrations.

All known TSNAs methods require the TSNA to be located in a solid phase (on particles or filters). Hence, since TSNAs are primarily seen associated with particles, they are unlikely to be present when no particles are generated, as with cigarette butts.

3.3.4.1.3 Carbon Monoxide

Yang et al. **(2015)** analyzed carbon monoxide in mainstream cigarette smoke from four different types of cigarettes using tunable diode laser absorption spectroscopy (TDLAS) with a modified single port smoking machine. Carbon monoxide is a very volatile gas that is generated due to incomplete combustion. It is therefore not expected to persist at significant concentrations in cigarette butts.

3.3.4.2 Chemicals in Cigarette Smoke that may be Present in Airborne Emissions from Cigarette Butts

Compounds with moderate volatility in cigarette smoke that do get retained in the cigarette butt can potentially be emitted from a cigarette butt after it is disposed, depending on the environmental conditions (temperature, relative humidity, UV intensity, etc.) to which it was exposed. Analytical techniques and measurements of these types of compounds are described below.

3.3.4.2.1 Nicotine

Nicotine is more volatile than most TSNAs, making a wider range of analytical methods available, in addition to extraction from particles on particle collection filters. Ishizu et al. **(2013)** used a passive XAD-4/PDMS (styrene-divinylbenzene copolymer with polydimethylsiloxane) coated glass fiber filter (extracted and analyzed using GC-MS) to show that the ratio of nicotine to 3-ethenylpyridine decreased as the secondhand smoke aged. Watson et al. **(2004)** analyzed nicotine concentrations using SPME followed by GC-MS. Fu et al. **(2013)** measured nicotine in secondhand smoke using sodium bisulphate-treated filters and GC-MS.

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 < pH < 6), and 3) the free-base molecule **(Liang and Pankow 1996, Ishizu and Ishizu 2013)**. Only the free-base species is volatile **(Liang and Pankow 1996)**. Free-base nicotine is thought to be the dominant species in cigarette smoke because cigarette smoke is generally alkaline. Adding ammonia-releasing chemicals to the tobacco can ensure the alkaline nature of the smoke, pushing more of the nicotine into the free-base form **(Liang and Pankow 1996)**. Free-base nicotine is also the dominant form of nicotine on the cigarette filter when freshly smoked, although the pH and nicotine species can change with environmental exposures. Free-base nicotine is lipophilic and more readily absorbed across membranes, increasing its bioavailability. Watson et al. **(2004)** showed that fewer ventilation holes blocked in the filter resulted in a greater fraction of free-based nicotine in the mainstream smoke particulate matter.

3.3.4.2.2 PAHs

Several studies have measured PAHs in cigarette smoke. The sampling technique used most often is to collect sidestream smoke onto glass fiber filters, extract the samples with a solvent, and analyze the extracts using HPLC or GC-MS. Two- and three-ring PAHs are relatively volatile, which makes them likely to desorb from discarded cigarette butts and be emitted to the surrounding air. Five and six-ring PAHs (benzo[a]pyrene) are less volatile and less likely to be emitted to the surrounding air at measurable rates.

Endo et al. **(2000)** analyzed seven PAHs (including benzo[a]pyrene) collected on filters, which were extracted with ethanol/benzene and analyzed on HPLC. Demirci and Alver **(2013)** analyzed PAHs using hollow, fiber-liquid-phase microextraction and HPLC-UV. Lodovici et al. **(2004)** measured PAHs in mainstream and sidestream smoke from 14 commercial brands of cigarettes using HPLC. PAH concentrations in mainstream smoke varied by three-fold for the different brands, and were ten times higher in sidestream smoke compared to mainstream. They also found that most tobacco-related PAHs occurred in the particulate phase.

Daher et al. **(2010)** captured particulate PAHs from sidestream smoke on glass fiber filters and analyzed them using GC-MS. Xie et al. **(2012)** analyzed 14 PAHs that were collected on filters, extracted, cleaned with a silicon cartridge, concentrated, and finally injected into a GC-MS. Liang et al. **(1996)** captured secondhand smoke particles on filters and measured the partitioning coefficient between particle phase and gas phase for PAHs (fluorene, phenathrene, flouranthene, pyrene and chrysene) and nitrogen-containing PAHs (quinoline and isoquinoline) using thermal desorption tubes and GC-MS. This study highlights that lighter PAHs will likely be present in the air phase near cigarette butts.

Schick et al. **(2014)** studied the effects of aging on the concentration of 16 PAHs, nicotine, cotinine and TSNAs in cigarette smoke as it was passed through a flow reactor at 1 air change per hour to simulate residential air change rates when a mechanical ventilation system is on. Measurements were made with GC-MS and showed that the levels of PAHs, nicotine and TSNAs were reduced by 60 % to 80 % over a 60-minute period, but the levels of cotinine did not decrease over this period. Other studies in controlled indoor environments have also shown that nicotine is removed faster than gas-phase hydrocarbons and some particulate species **(Eatough 1990)**. Schick et al. also measured sorption and deposition of nicotine, cotinine and TSNAs on materials placed in a flow reactor. They concluded that the majority of these compounds deposit on room surfaces when cigarettes are smoked in indoor environments, which can lead to the accumulation of carcinogens on indoor surfaces. Gradual desorption of these chemicals and their reaction with common indoor pollutants leads to chemical being present for extended periods of time after a cigarette has been smoked.

3.3.4.2.3 Other Organics

Other organic gases have been studied using unique analytical techniques. Zheng et al. **(2014)** identified 67 gas-phase components in mainstream cigarette smoke using sorption tubes containing 3 beds of adsorbents (Carbopack C, Carbopack B and Carboxen III) analyzed using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Hertz-Schunemann et al. **(2015)** studied the evolution of organic gases during a two-second cigarette puff using a novel microprobe to extract gases from inside a burning cigarette and analyzed them with a photoionization mass spectrometer. The concentrations of various pyrolysis and combustion products such as 1,3-butadiene, toluene, acetaldehyde and phenol were monitored at different sampling locations within cigarettes. The measurements were combined to generate time-resolved concentration maps, showing the formation and destruction zones of the investigated compounds in the burning cigarette.

Reactive oxygenated species (ROS) are a broad class of chemicals that are reactive and contain oxygen. Cigarette filters have been shown to remove 26 % of the gas-phase ROS and 17 % of particle phase ROS **(Zhao and Hopke 2012)**. However, gas-phase ROS is only a small fraction of total ROS **(Zhao and Hopke 2012)**. Hence, volatile ROS may be present in cigarette butts, but likely not in large quantities.

3.3.4.2.4 Hydrogen Cyanide

Hydrogen cyanide has been measured in cigarette smoke using continuous flow analysis **(Guo et al. 2015)**. Liu et al. **(2014)** noted that nitrogen oxides in cigarette smoke can dissolve in the alkaline solution used for the measurement of hydrogen cyanide in cigarette smoke, and can produce nitrates and nitrites, which further react with cyanide and result in underestimating the yield of hydrogen cyanide. They improved upon this method by collecting hydrogen cyanide on a Cambridge filter pad treated with a solution of sodium hydroxide and then analyzing it with a continuous flow analyzer containing isonicotinic acid and 1,3-dimethylbarbituric acid. Compared to the conventional method, this method was shown to be simpler, and the collected hydrogen cyanide had greater stability.

3.4 Factors that Potentially Influence Airborne Emissions from Cigarette Butts

There are a wide range of factors that can impact the airborne chemical emissions from cigarette butts. These include the brand of the cigarette, the length of the cigarette butt, the temperature during the aging process, the airflow around the butt, the airflow through the butt, the number of puffs taken while the cigarette was being smoked, the degradation of the cigarette butt, and if the butt was smoked by a machine or human. The following section highlights the studies that have looked at these factors.

3.4.1 Brand

The chemical content of cigarettes varies with the cigarette brand and the source of the tobacco, and each cigarette brand is engineered to have different performance. As a result, cigarette butts from various brands will have different emission characteristics. Demirci et al. **(2013)** was able to differentiate between brands by extracting cellulose acetate cigarette filters (with acetonitrile/n-hexane) and analyzing them with HPLC-UV.

In a 2008 study, tar yield data were collected for 172 cigarettes sold in the United States, Canada, Australia, and the United Kingdom. A total of 11 cigarette design parameters were measured, including filter ventilation, cigarette pressure drop, filter pressure drop, tobacco rod length, filter length, cigarette diameter, tipping paper length, tobacco weight, filter weight, rod density and filter density. Filter ventilation was found to be the main design parameter that accounted for the tar yield differences among different brands **(O'Connor et al. 2008)**.

Cigarettes of different brands use different types of tobacco. Ding et al. **(2008)** demonstrated nitrate contents are different in different types of tobacco, which can influence the levels of nicotine, TSNAs and PAHs in mainstream smoke.

Jenkins et al. **(1979a, 1979b)** showed that the tar, nicotine and carbon monoxide content of smoke varies between samples of a given brand of cigarettes, depending on the nation in which they are purchased. Djordjevic et al. **(1991)** compared cigarettes from the former Union of Soviet Socialist Republics (USSR) with those from the United States and Western Europe, and found that the nicotine level and the total alkaloid content of the cigarettes from the western countries were slightly higher than in the cigarettes from the former USSR. They observed that non-filter and filter cigarettes from the former USSR had slower burning rates and yielded 14 to 16.7 puffs per cigarette, while cigarettes in the western countries yielded 11 puffs per cigarette. Tar, benzo[a)pyrene and nitrosamines yields were reported to be especially high in the smoke of cigarettes with filters.

However, not all studies have shown a large difference between cigarette brands. Pieraccini et al. **(2008)** developed a SPME-GC-MS method to determine the components of mainstream and sidestream smoke for 15 different cigarette brands. The quantitative compositions of mainstream and sidestream smoke for all brands of cigarettes were similar, with 67 chemicals identified. For the quantified chemicals (benzene, toluene, p-xylene, m-xylene, pyridine, o-xylene, limonene, naphthalene, phenol and nicotine), the concentration difference among different brands was within an order of magnitude for both mainstream and sidestream smoke.

3.4.2 Filter Material

Cigarette filters are typically constructed from cellulose acetate, but the filter can be designed in each brand to enhance flavor properties and reduce toxic compounds in the mainstream smoke. While filter additives can reduce chemical concentrations in mainstream smoke (i.e., nitric oxide, carbon monoxide, hydrogen peroxide, aldehydes, vinyl chloride, 1,3-butadiene, isoprene, acrylonitrile, benzene, toluene and nitroso-compounds) **(Smith et al. 1997, Valavanidis and Haralambous 2001, Liu et al. 2013, Awji et al. 2015)**, they can also increase the chemicals present in the filter that can emit later from the cigarette butt.

Each chemical may behave differently in the cigarette filter. Qin et al. **(2014)** studied the retention of crotonaldehyde in cigarette filters. Longitudinal concentration distribution of crotonaldehyde in the cigarette filter was found to be different from the distribution of nicotine, phenol and other smoke components.

Several studies have been conducted on reducing compounds in cigarette smoke by making modifications to cigarette filters **(Dittrich et al. 2014, Duan et al. 2014, Chen et al. 2015, Marcilla et al. 2015)**. The filter modification can be engineered from a chemical or mechanical perspective. For instance, a study on the effect of cellulose acetate and polypropylene filter materials on semi volatiles in smoke indicated that the polar cellulose acetate filter selectively retains polar compounds, such as phenols and furans, while the non-polar polypropylene filter shows a non-selective retention behavior **(Formella et al. 1992)**. Grooves can be added to cigarette filters to change the inertial impaction of particles and diffusion of chemicals. Duan et al. **(2014)** studied the effects of 35 kinds of grooved filters on the yield of particles, tar, nicotine and carbon monoxide in mainstream cigarette smoke. They found that increasing the length of the grooved section in the filter reduced the yields (up to a length of 20 mm after which filtration efficiency of particles and nicotine decreased), while the position of the grooved section did not influence the yields.

3.4.3 Butt Length

The length of the cigarette butt has been shown to impact the chemicals present in the cigarette butt. A longer cigarette butt will have more unburned tobacco and greater tobacco associated emissions than a shorter cigarette butt. Green et al **(2014)** reported that nicotine released into water increases as the butt length increases, as more nicotine is retained in tobacco than in the filter of cigarette butts. In contrast, the shorter cigarette butt will have a greater proportion of pyrolysis products and metals present.

Cigarettes can either be extinguished by the smoker or be self-extinguished. . There is no defined standard cigarette butt length for testing emissions. However, Watson et al. **(2004)** used a butt length of 23 mm or the length of the filter overlap plus 3 mm, whichever was longer, for their research.

3.4.4 Temperature

Cigarette butts discarded outdoors are in a dynamic environment with a changing temperature, which can impact the chemicals present in the butt over time. Clayton et al. **(2010)** showed that nitrosamines levels in cigarette butts decreased after three weeks of storage at 22 ^{o}C, especially for 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK). However, the nitrosamines levels in cigarette butts were relatively consistent over four weeks of storage at -17 ^{o}C and 4 ^{o}C.

3.4.5 Cross flow

The cigarette burning process can be influenced by environmental conditions, which in turn can influence the components retained in the cigarette butt post-smoking. Modeling of combustion of a cigarette has indicated that increasing the ambient cross flow surrounding the cigarette increases the burn rate and temperature in the cigarette column **(Saidi et al. 2006, Saidi et al. 2007)**. Different combustion temperatures will result in the formation of different pyrolysis products that can eventually deposit in the cigarette butt.

3.4.6 Ventilation

Ventilation through the cigarette during smoking can also influence the chemicals present. The burn rate, temperature and delivery of chemicals through a burning cigarette to the cigarette filter increases as a result of the increasing of ventilation through the cigarette **(Saidi et al. 2006, Saidi et al. 2007)**. The change to these parameters can then result in the formation of different pyrolysis products. Dittrich et al. **(2014)** placed a band of porous paper in the center of the filter to minimize the loss of filter ventilation that occurs at the high flow rates encountered during human-smoking. This “split-tipping” facilitates the diffusional loss of volatile chemicals. Mouth level exposure to tar and nicotine was also lower in low-tar split-tipped cigarettes.

3.4.7 Puff Number

The number of puffs that a smoker draws through a cigarette has been shown to impact the chemicals present. Li et al. **(2002)** found that formaldehyde concentrations in mainstream smoke were higher in the first puff compared to subsequent puffs. The authors concluded that the heat exposure of the tobacco from previous puffs was the largest factor in differing formaldehyde concentrations. Li et al. **(2002)** also showed that heat treatment of cigarettes (200 ^{o}C to 250 ^{o}C) prior to lighting reduced formaldehyde concentration by 20 % to 90 %. This was attributed to the conversion of cellulose to other products at temperatures below 500 ^{o}C.

3.4.8 Degradation

Cigarette butts will eventually degrade due to microbial degradation, photo-oxidation, mechanical abrasion and chemical degradation. However, not all components of cigarette butts are readily biologically degradable or photo-oxidized. Filters typically contain plasticized cellulose acetate fibers that are slow to degrade **(Puls et al. 2011)**. Cellulose can be degraded by organisms with cellulose enzymes, but the acetyl groups in cellulose acetate first need to be removed to a certain extent (via the action of esterases or by chemical hydrolysis) for biodegradation of the cellulose backbone to initiate. Cellulose acetate can be photochemically degraded by UV wavelengths shorter than 280 nm, but has limited photo-degradability in sunlight due to the lack of chromophores for absorbing UV light **(Puls et al. 2011)**. Cellulose acetate cigarette butts tend to linger in the environment for extended periods of time for these reasons. After two years of outdoor decomposition, ^{13}C -cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy analysis indicated minimal microbial degradation of cigarette filters **(Bonanomi et al. 2015)**. This stability may be due to the nitrogen limitations in the butts. Studies have been conducted to develop methods to accelerate the degradation of cigarette butts. Honso et al. **(2007)** found that radical reactions of cellulose acetate by photo-irradiation can lead to oxidation and random cleavage of cellulose acetate. In addition, the authors found benzophenone additives effectively accelerated the degradation of cellulose acetate under ambient environment conditions.

Some states have considered legislation that would require filters to degrade faster **(Robertson et al. 2012)**. One method to meet this requirement is to alter filters so they start degrading once they have been impacted by water. Robertson et al. **(2012)** showed that hydrolysis can be accelerated by adding weak acids encapsulated in sulfate/phosphate esters. When in contact with water, the encapsulation breaks down and releases weak acids that attack the cellulose acetate.

3.4.9 Smoking Method

The demand for data regarding the health impacts of mainstream and sidestream smoke led to the development of complex smoking machines. The operation of these machines is guided by ISO 3308:2012: Routine analytical cigarette-smoking machine - Definitions and standard conditions, details of which are summarized in Section 4.2.4 **(ISO3308 2012)**. The standard gives a single set of operating conditions for smoking machines, while in reality smokers have a wide range of habits that can impact emissions. For instance, Purkis et al. **(2010)** demonstrated that increased puffing intensity decreased the tar, nicotine and carbon monoxide yields due to more rapid burning of the cigarette. Another study evaluated the tar and nicotine emissions from both human smoking and machine smoking across seventeen brands of cigarettes **(St Charles et al. 2010)**. The comparison of nicotine and tar yields between human smoking and machine smoking was non-linear and scattered. In addition, the relationship was not consistent across various brands. A third study found lower environmental tobacco concentrations generated by smokers compared to smoking machine-generated sidestream smoke **(P.R. Nelson 1998)**. However, the authors did not account for sorption to the smokers' clothes and skin.

Hence, there can be differences in emissions from a cigarette using a smoking machine compared to a human-smoked cigarette. If the mainstream smoke is different, it is likely that the chemical composition of a cigarette butt is also different.

3.5 Impacts of Cigarette Butts on Human Health and Environment

Cigarette butts may impact human health and the environment through direct and indirect exposure routes. Only two studies have reported direct human health effects related to the ingestion of cigarette products. Novotny et al. **(2011)** reviewed published and grey literature regarding cigarette butt waste consumption by children, pets and wildlife, and found that accidental ingestion of cigarettes and butts were not uncommon among children, especially those under 6 years of age. Significant toxicity from the ingestion of cigarette products in children has been reported to be rare, with vomiting within 20 minutes being the most common symptom **(McGee et al. 1995)**. The impacts of cigarette butts on cells and animals have been documented in a broader series of studies, as described below.

3.5.1 In Vitro Assay

In vitro assays have been used to evaluate the genotoxic potential of cigarette butts. Di Giacomo, et al., **(2015)** tested the methanol extract from cigarette butts in the bacterial reverse mutation assay (with Salmonella typhimurium TA98 and TA100 and Escherichia coli WP2uvrA strains) and found that it was mutagenic. On the other hand, some compounds can provide protection from the mutagenic effects of cigarette butts. Di Giacomo et al. **(2015)** found that natural sesquiterpenes (caryophyllene and caryophyllene oxide) can be used to inhibit the mutagenicity of cigarette butts. Such compounds may have a place in remedial strategies to decontaminate cigarette butt waste.

3.5.2 Animal Exposure

A variety of detrimental effects have been observed in animals exposed to cigarette butts directly or indirectly via leachate in water. However, no studies were found on the effects of cigarette butts in animals via airborne exposure routes. Animals reported to be affected by cigarette butts include birds, mosquitoes, snails, ragworms and fish. Birds use cellulose from smoked cigarette butts as lining material in nests, which helps to reduce ectoparasites in the nests, possibly because nicotine repels anthropods **(Suarez-Rodriguez et al. 2013, Waters 2013)**. However, signs of genotoxicity in house finches have been seen to increase with the amount of butt cellulose in their nests **(Suarez-Rodriguez and Garcia 2014)**. In addition, mosquitoes that have hatched in water environments containing cigarette butts have been shown to have shorter life spans **(Dieng et al. 2014)** and higher mortality rates during developmental stages **(Dieng et al. 2013)**. Cigarette butt leachate in seawater has also been shown to cause mortality and behavioral modifications in snails **(Booth et al. 2015)**. Ragworms experienced significant weight loss and DNA damage when exposed to levels of filtration that were over sixty times less concentrated compared to average runoff in urban settings **(Wright et al. 2015)**.

Slaughter et al. **(2011)** investigated the LC50 (concentration in water at which 50 % of test subject will die) of cigarette butt leachate in fish. Their results indicated that the toxicity of cigarette butt leachate increases from unsmoked cigarette filters (no tobacco) to smoked cigarette filters (no tobacco) to smoked cigarette butts (smoked filter + tobacco). Smoked cigarette butts had an LC50 of about one cigarette butt L^{-1} in both the marine topsmelt (Atherinops affinis) and the freshwater fathead minnow (Pimephales promelas).

3.6 Alternative Uses for Cigarette Butts

Cigarette butts are frequently randomly discarded in the urban environment. However, there can be productive uses for cigarette butts. For example, they have been used as a media for biofilm growth in anaerobic digestors **(Sabzali et al. 2012)**. Cigarette filters have also been used to store energy by heat treating them under a nitrogen atmosphere to prepare N-doped mesoporous / microporous carbon material **(Minzae et al. 2014)**. This material provides a favorable pathway for electrolyte permeation and contact probability. The latent energy in cigarette filter waste has also been harnessed to supply heat recovery units in industry **(Nagarajan 2014)**.

Another application of used cigarette filters is as a source of porous carbon material for producing activated carbon **(Masoudi Soltani and Kazemi Yazdi 2012, Salman et al. 2014, Soltani et al. 2015)**. Soltani et al. **(2015)** showed that the charred carbon from cigarette filters can remove lead from water. Chen et al. **(2015)** synthesized mesoporous carbonaceous materials on the surface of cigarette filters, and these materials exhibited enhanced performance in phenol adsorption and carbon dioxide capture.

4 Experimental Plan for Phase II

The above literature review on emissions from cigarette butts shows that airborne emissions from cigarette butts is not well understood and needs further study. The purpose of Section 4 is to describe an experimental plan intended to quantify the emissions of a selected number of chemicals emitted from cigarette butts into air under a variety of environmental conditions. The design of the experimental plan focuses on three potential exposure scenarios for discarded cigarette butts:

- **Outdoor Exposure.** In this scenario, discarded cigarette butts in a park or playground may impact children or adults. Furthermore, emissions from discarded cigarette butts in a trash or cigarette receptacle may impact people or even be drawn into a building if it is located near an outdoor air intake or other building opening.
- **Indoor Exposure.** In this scenario, discarded cigarettes butts located in an ashtray in a building may impact occupants.
- **Car Exposure**. In this scenario, occupants may be present in hot cars with discarded cigarettes butts despite not being present during the smoking event.

The experimental plan aims to be a screening analysis that can help address these potential exposure scenarios.

4.1 Screening Tool: Headspace Analysis

As discussed in the literature review, air emissions from cigarette butts can be a complex mixture of thousands of chemicals. These chemicals will interact with the environment, whether it be the photo-oxidation of the volatile chemicals or sorption to surfaces and particles of less volatile chemicals. Given there is a lack of data on what chemicals will emit from cigarette butts, it is proposed to first develop a screening tool to first determine which chemicals are important and estimate how long these chemicals are present. The screening tool to be used for this task is automated headspace analysis.

Once a cigarette butt is placed in a headspace vial, chemicals will be emitted from the butt under the given test conditions (temperature, flow rate and desorption time). While the emission rate of the chemical in the vial will not be the same emission rate of the cigarette butt in the exposed environment, the mass released during headspace analysis will allow comparison of the emission from a cigarette butt expose to different conditions. For instance, the headspace analysis would show different masses released for cigarettes stored outdoors for three months during summer and in an indoor controlled environment for three months. Further details of the headspace analysis are described in Section 4.2.1. If resources permit, the emittable mass over time generated from headspace analysis (Figure 2) will be compared with an emission experiment conducted in a large chamber.

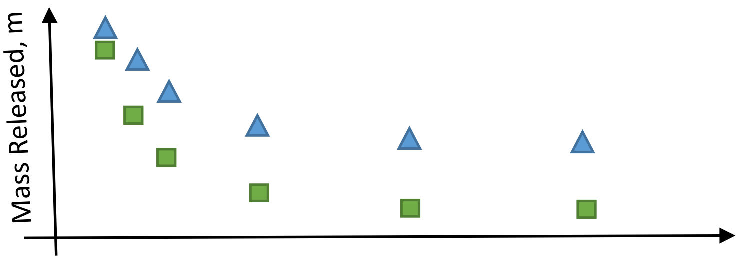

Figure 2: Illustrative data from headspace analysis of a chemical in two different experiments (e.g. squares from cigarettes in an outdoor environment versus triangles from cigarettes in an indoor environment). Each symbol represents the mass of the chemical derived from headspace analysis for a cigarette butt exposed under different, controlled environmental conditions over time.

This screening tool will be used in the tasks described below to allow comparison of how cigarette butts age under different conditions for Tasks 2 through Tasks 5.

- Task 1: Method development
- Task 2: Initial experiments
- Task 3: SPHERE experiments
- Task 4: Large chamber experiments
- Task 5: Roof top experiments

The following sections describe the proposed activities for each of the tasks.

4.2 Task 1: Method Development

There are a range of parameters that need to be determined prior to conducting the experiments in Tasks 2 through 5. The parameters include but are not limited to the following:

- Parameters for headspace analysis (temperature, flow, sample volume, split, etc.)
- Cigarette brand
- Length of cigarette butts
- Method for generation of cigarette butts
- Compounds to be quantified
- Method validation

These parameters will be determined based on experimental results and discussion with FDA. NIST First Level Hazard Reviews and standard practices for all NIST laboratory work will also be developed as part of this task.

4.2.1 Headspace Analysis

Headspace analysis will be used to determine the emittable mass of each tested cigarette butt. After exposing a cigarette but to under a specific set of environmental conditions for a defined time, the cigarette butt will be placed in a sealed headspace vial and incubated at a defined temperature (above room temperature) for a defined time (Figure 3A). A constant volume of air from the headspace of the vial will then be collected using conditioned Tenax-TA tubes (Figure 3B). The sample will be thermally desorbed (TD) and quantified using GC-MS under defined conditions. To increase the sensitivity and reduce the analysis time of the method, experiments will be conducted to optimize the parameters, including the incubation temperature, incubation time, sampling volume, and TD-GC-MS conditions.

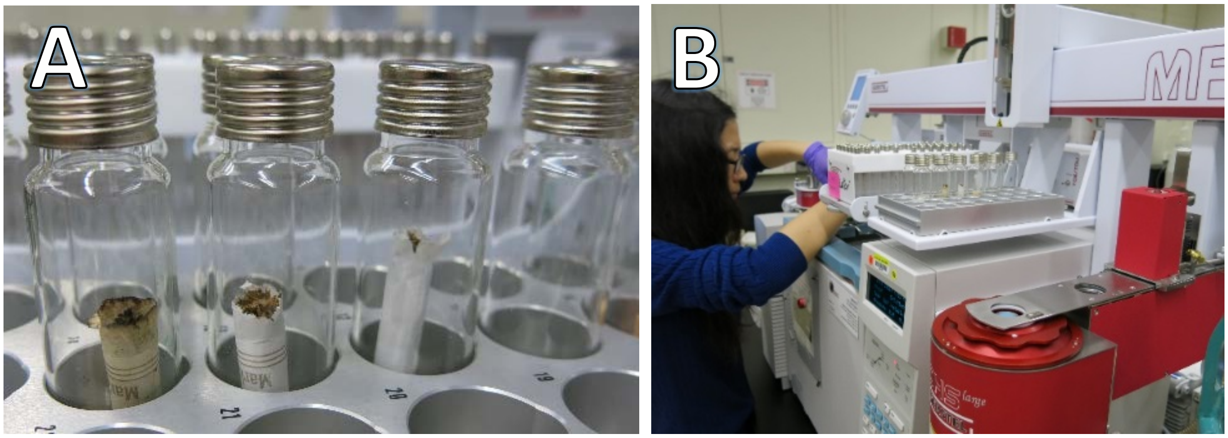

Figure 3: A) Incubation of cigarette butts in headspace vials. B) Sampling from headspace vials.

4.2.2 Selection of Cigarette Brand

Unless otherwise noted, three of the most popular cigarette brands based on FDA information will be selected for preliminary study during the method development period. One of these three brands will be selected for all other experiments based on its performance in the headspace analysis.

4.2.3 Determination of Butt Length

Roughly 50 cigarette butts will be randomly collected from a variety of public places. These cigarette butt lengths will be measured. The median value of the measured lengths will be used as the butt length for all the experiments.

4.2.4 Generation of Cigarette Butt

To make data comparable across different experiments, the generation of cigarette butts must be consistent. Hence, a smoking machine will be employed, as described below, to generate most of the cigarette butts. To determine how representative smoking machine butts are, they will be compared with butts generated by human smoking. Cigarette butts will be collected from NIST outdoor ashtrays shortly after humans complete smoking. Smokers will not be asked to smoke. Rather signs will be placed at designated smoke areas asking smokers to place cigarette butts in provided headspace vials. The signs will also ask the smokers to record the number puffs and brand on the vial. This collection method has preliminary approval from the by the NIST Institutional Review Board (IRB) and will be fully reviewed prior to conducting the research. Freshly generated cigarette butts of the same brand and similar lengths from both the smoking machine and human smoking will be measured using the headspace analysis. Both the qualitative and quantitative differences between emissions of cigarette butts by the smoking machine and human smoking will be examined to determine the representativeness of the smoking machine. Adjustments for the butts generated from the smoking machine will be made if necessary.

A smoking machine will be constructed to partially fulfill the requirements described in ISO 3308. This device will draw a fixed volume of air through the cigarette (a puff) in a sequence similar to the puff profile defined in ISO 3308 **(2012)**. As per ISO 3308:2012, the device will hold 9.0 mm of the butt end of the cigarette using labyrinth seals in a restricted smoking fashion (filter ventilation holes covered). The device will be placed in a NIST fume hood configured to allow air speeds of 170m/s to 230 m/s, temperatures of 22 °C ± 2 °C, and relative humidity of 60 % ±5 %.

The device will deviate from ISO 3308:2012 in two important ways: 1) a smoke trap will not be included in the machine, since measurement of the mainstream smoke is outside the scope of this research; and 2) the machine may not produce a bell-shaped puff profile due to technical challenges. This will likely not influence the experiments in this study as long as the puff profile is consistent for different cigarette butts.

4.2.5 Target Compound List

The above literature review shows that certain compounds with high boiling points in cigarette smoke, such as metals and TSNAs, mainly exist in the particle phase in mainstream and sidestream smoke due to their low volatility. Since, it would be difficult to detect these chemicals in the air emissions from cigarette butts, we are not selecting them as target compounds for quantification in this investigation. Compounds which have moderate boiling points and weak to moderate sorption will be the main target compounds; these include nicotine, and PAHs. Both compounds are found on the United States Food and Drug Administrations' Harmful and Potentially Harmful Constituents in Tobacco Products and Tobacco Smoke: Established List. It is unclear whether other compounds such as hydrogen cyanide will be able to be detected with the proposed experimental techniques.

Preliminary headspace analyses were conducted using two cigarette butts (one freshly smoked and one found on the ground). The results showed that cigarette butts can emit a large number of chemicals, with over 50 different peaks identified from the chromatograms shown in Figure 4.

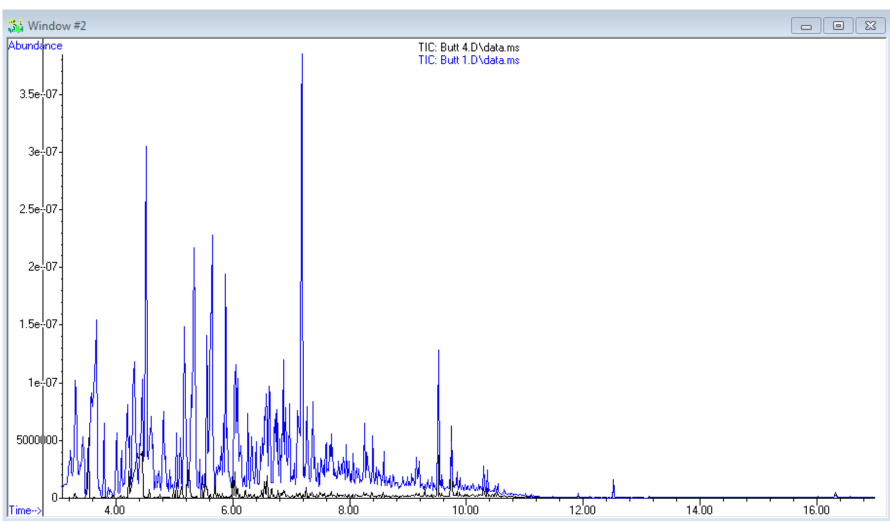

Figure 4: Illustrative data from headspace analysis for two different cigarette butts. The blue trace was from a freshly smoked cigarette; the black trace was from a cigarette found on the ground. The x-axis represents time in minutes, while the y-axis represents chemical abundance in dimensionless units.

For the freshly generated cigarette butt, the peaks with top five largest areas were identified as d-limonene, toluene, pyridine, benzene and styrene. The top five peaks for the cigarette butt found on the ground were nicotine, 3-methyl-pyridine, furfural, pyridine, and methyl-pyrazine, which is very different from the chemicals emitted from the freshly generated cigarette butt. This indicates that the target chemicals to be quantified need to be carefully chosen to ensure that the data captures both short- and long-term emissions.

For proposed experiments, the compounds will be first tentatively identified with the NIST mass spectral library and chosen as target compounds for qualitative analysis when the quality of the match is higher than 90 %. Then, the top ten identified chemicals based on response area, and being both carcinogenic and with good peak shapes, will be chosen as target compounds for quantitative analysis.

4.2.6 Method Validation

Once method parameters and target chemicals are determined method validation will be conducted. TD-GC-MS parameters for the quantitative target compounds will be determined to ensure the linear correlation coefficient of the corresponding standard curve is higher than 0.98. The recovery of quantified chemicals in the headspace vials will be determined. In addition, method detection limit and repeatability experiments will be conducted. Reported data will include combined uncertainties.

4.3 Task 2: Initial Experiments

As described in Section 3.4, there are a wide range of factors that can influence the emissions from a cigarette butt. The cigarette butt length and brand (which will dictate the filter type) will be defined during Task 1: Method Development. Task 2: Initial Experiments will examine the influence of some of the remaining factors described in Section 3.4, including: 1) smoking condition (puffing parameters); 2) temperature; and 3) moisture (to account for rain).

4.3.1 Smoking Condition

Freshly generated cigarette butts from a smoking machine with different puffing parameters (number and airflow) will be examined using headspace analysis. All butts will be analyzed after they have reached room temperature.

4.3.2 Temperature

A micro-chamber system, as shown in Figure 5, will be used for studying the cigarette butt emissions after aging at different temperatures. The butts will be placed in the micro-chambers for up to a week at different temperatures with constant flows. Then, the conditioned cigarette butts will be put into the headspace vial for analysis. The exact number of experiments will be determined based on technical complexity.

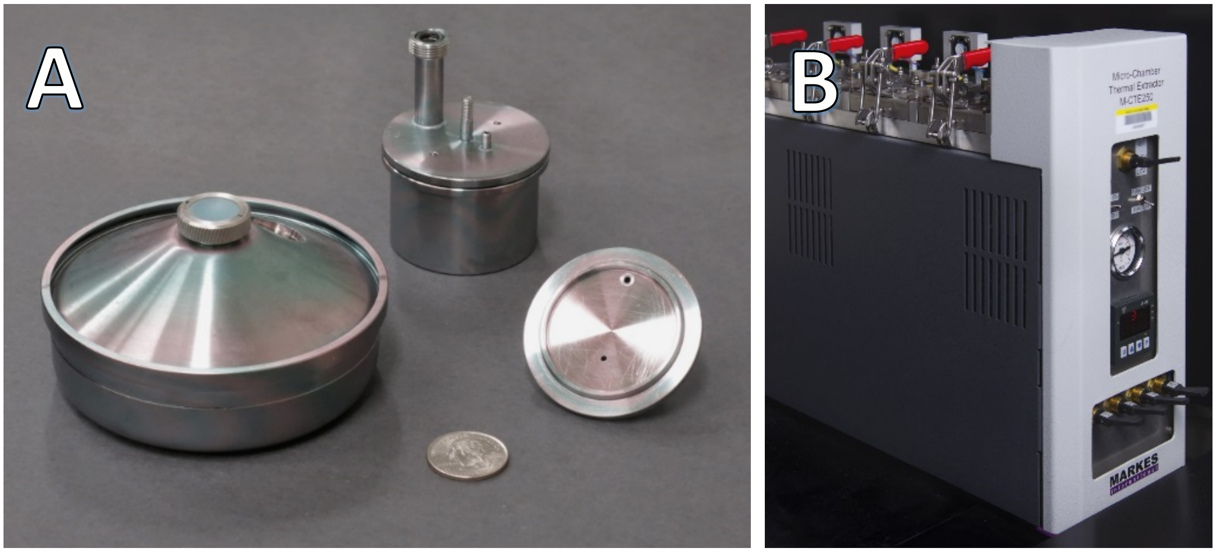

Figure 5: A) Different kinds of micro-chambers. B) Markes micro-chamber system

4.3.3 Moisture

Cigarette butts will be saturated with water to simulate a rain event. Added moisture to the cigarettes will be measured by mass change. After wetting, the butts will be placed in headspace vials for analysis. A subset of the wet butts will be placed in a micro-chamber system for up to a week to simulate a drying event prior to the headspace analysis. The exact number of experiments will be determined based on technical complexity.

4.4 Task 3: Large Chamber Experiments

To mimic indoor conditions, cigarette butts will be placed in a large stainless steel walk-in chamber, shown in **Error! Reference source not found.**, for a defined time. The chamber will be operated at typical indoor test conditions (20 °C, air change rate of 1 h^{-1}). After placement in the chamber, butts will be removed at various points in time for headspace analysis. The exact number of butts and length of aging will be determined based on technical complexity and experimental design. The emissions from the cigarette butts in the large chamber will be compared to emissions from butts in the ultra violet radiation exposure (Section 4.5) and rooftop experiments (Section 4.6) to determine the impact of exposure to radiation and outdoor conditions on emissions, respectively.

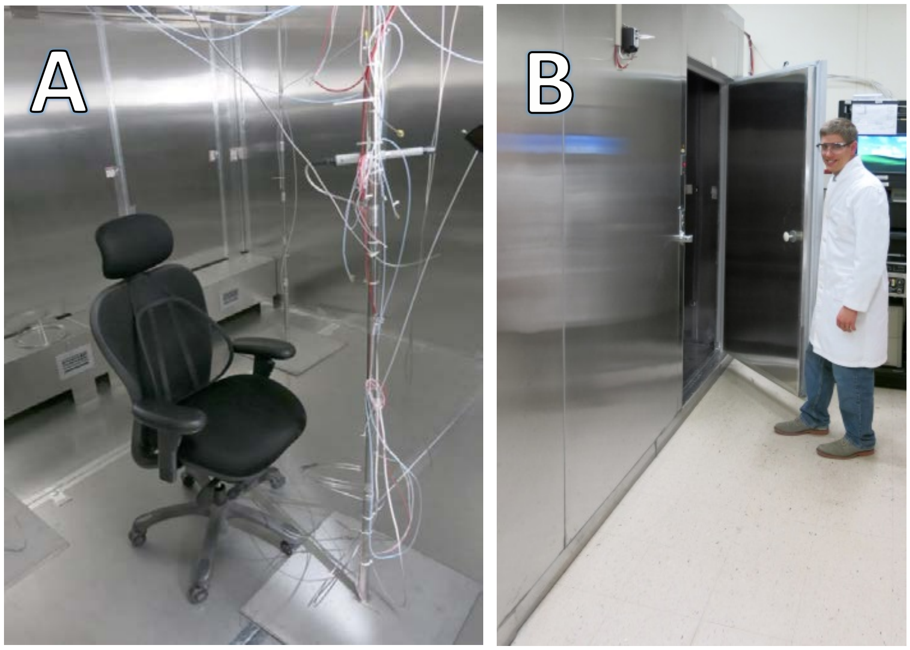

Figure 6: A) Inside of the large chamber. B) Outside of the large chamber

If there is enough time, a chamber emission study will be conducted using the large chamber. In these experiments, a large number of cigarette butts will be placed in the large chamber. The air will be sampled at regular intervals using a Tenax TA sorbent tube. At some point in time, a 100 cm^2 section of the wall will be wiped with a methanol impregnated pad. The pad will be extracted to determine the sorption rate of the chemicals to the chamber walls, which will be used to determine the average emission rate in the chamber. The chamber will be ventilated with outdoor air, which will contain particles. Particle concentrations in the chambers will be measured to allow for estimation of the chemical concentrations on particles using established methods **(Little et al. 2012Little et al. 2012)**. Once the average cigarette butt emission rate in the chamber is known, it will be compared to the screening headspace analysis to demonstrate the relevance of the screening data (**Error! Reference source not found.**).

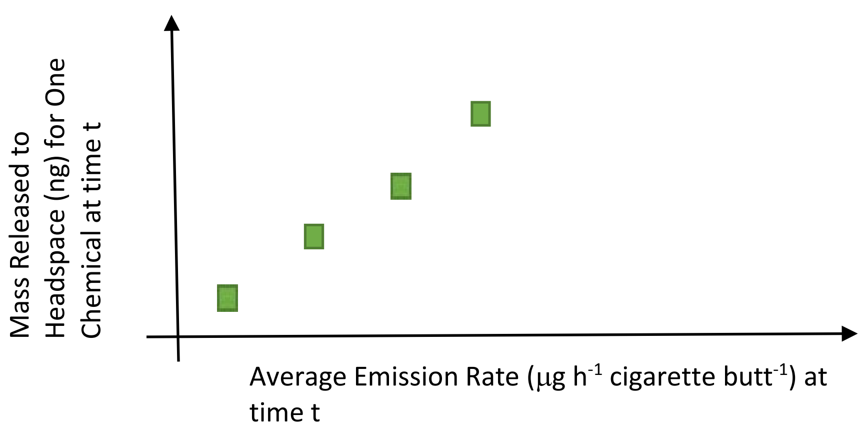

Figure 7: Illustrative data comparing mass recovered during headspace analysis to average emission rate at different times in a large chamber).

4.5 Task 4: SPHERE Experiments

Another factor that possibly can influence the emissions from the cigarette butts is radiation exposure. The NIST Simulation Photo-degradation via High Energy Radiation Emission (SPHERE) chambers, as shown in Figure 8, will be used to study cigarette butt emissions under different UV radiation conditions. Fresh cigarette butts from a smoking machine will be placed in the SPHERE chamber with different UV radiation intensities. After placement in the chamber for different aging durations, cigarette butts will be put in headspace vials for analysis.

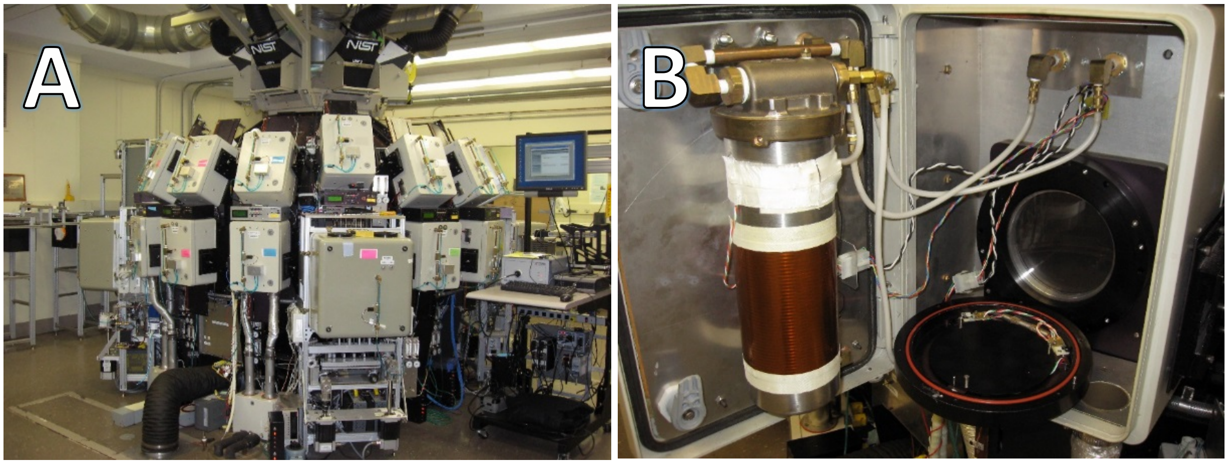

Figure 8: A) Simulation Photo-degradation via High Energy Radiation Emission (SPHERE) system. B) An individual SPHERE chamber.

4.6 Task 5: Roof Top Experiments

To understand cigarette butt emissions in the outdoor environment, this task will compare emissions from cigarette butts that have been placed on a rooftop during four different seasons. Solar irradiance, UV radiation, cloud cover, temperature, wind speed, pressure, relative humidity, rain and snow accumulations will all be recorded while the butts are exposed on the roof to determine if any of these parameters has a significant impact on the emissions. After placement on the roof for different time periods, butts will be removed for headspace analysis. Some butts may be placed on the roof under cover that limits direct sunlight and rain but maintains butts at the same temperature, humidity and wind conditions. The exact number of butts and length of aging will be determined based on technical complexity and experimental design.

Figure 9: NIST solar observation equipment. Cigarette butts aged for Task 7 would be located near this infrastructure.

4.7 Schedule

The experimental tasks are scheduled to take two years to complete. The experimental schedule will commence at the conclusion of Phase 1 of this project, which corresponds to final delivery of this document to FDA.

Table 4: Proposed Experimental schedule

Task	Purpose	Duration	Headspace Analysis
Method Development	Determine brand and length of cigarette butt, method to generate cigarette butt, and parameters for headspace analysis	6 months	N/A
Initial experiments	Examine the influence of factors on emissions, including smoking condition, temperature, and moisture	3 months	Weekly
SPHERE experiments	Examine the influence of UV radiation on emissions	12 months*	Monthly
Large Chamber Experiments	Study the emissions in a large chamber environment	6 months*	Monthly
Roof Top Experiments	Study the emissions in the outdoor environment	6 months*	Monthly
Data Evaluation/ Report	Document all project tasks	3 months	N/A

*** concurrently**

5 Summary

Cigarette butts can contain many of the same chemicals found in mainstream and sidestream smoke, making them a potential source of chemical exposure in both indoor and outdoor environments. Many studies have analyzed chemicals in cigarette butts and quantified chemicals emitted from cigarette butts into water. However, there are limited data on emissions from cigarette butts into air. The emission rates from cigarette butts to the air may be minimal for some heavy chemicals (e.g., metals, TSNAs), but could be high for more volatile chemicals (e.g., nicotine, pyridine, benzene). In addition, the airborne emissions of cigarette butts can be influenced by the cigarette brand, filter material, butt length, environmental temperature, airflow around the cigarette, number of puffs during smoking, degradation of the butt, and smoking method. Based on the results of the literature review presented in this report, more data are needed on the airborne emission rates of cigarette butts. The proposed research aims to fill this data gap by using a screening tool (e.g. headspace analysis) to examine the airborne emission of chemicals from cigarette butts under various environmental conditions (small chamber, large chamber, outdoor, and chamber with enhanced ultra violet radiation).

6 Disclaimer

Certain trade names or company products are mentioned in the text to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is the best available for the purpose.

7 Acknowledgements

This work was funded under U.S. Food and Drug Administration Interagency Agreement #244-15-9012.

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