WATER-SOLUBLE ORGANIC GASES IN RESIDENTIAL INDOOR AIR AND THE

POTENTIAL FOR AQUEOUS CHEMISTRY INDOORS TO ALTER EXPOSURES

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ABSTRACT OF THE DISSERTATION

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chemistry indoors to alter exposures

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Dampness occurs in 18 to 50% of homes in the United States and is associated

with negative health effects. Currently, mold and mildew only partially explain these

health outcomes (Mendell et al., 2011). Could aqueous chemistry indoors play a role?

This dissertation explores the presence of water-soluble organic gases (WSOGs) indoors.

Which WSOGs have already been reported? Which WSOGs are expected to be present

indoors? How will aqueous chemistry on surfaces, in particles, and elsewhere indoors

affect indoor chemistry?

First, the literature was searched for previously measured WSOG. Additional

WSOG likely to be present from direct emission sources indoors as well as WSOG

formed from gas-phase oxidation chemistry were proposed. Then, using knowledge of

aqueous chemistry in outdoor air and the current understanding of indoor chemistry, the

plausibility of aqueous chemistry to occur indoors was postulated.

Integrated samples of WSOGs were collected inside and directly outside thirteen

homes. WSOGs were found to be on average 15 times higher indoors than outdoors

(Duncan et al., 2018), meaning most WSOGs are emitted or formed indoors. About 50%

of this WSOG can be attributed to formic, acetic, and lactic acids. The rest consists of

67% CHO, 11% CHN, 11% CHON, and 11% sulfur-, phosphorus-, or chlorine-containing compounds.

WSOGs were also measured in real time in one home. Acetic and formic acids were found to decrease 30 – 50% at the onset of the central air conditioner cycling on. Lactic acid strongly correlated with human occupancy and cooking. Several other compounds were characterized on the molecular level that also cycled with the air conditioner. Measurements were also taken briefly outside the home which illuminated that some compounds had primarily indoor sources while others had primarily outdoor sources.

Dose estimates were calculated for WSOG and found that infants and young children will receive elevated doses compared to adults under the same conditions. Subsequent health implications were discussed. Recent advancements in the field of indoor chemistry were provided, and future directions of research proposed. Ultimately, this work furthers our understanding of indoor chemistry and therefore exposure and may provide future insights into observed negative health effects in homes.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1. Introduction

1.1 Motivation

In 2015, an estimated 6.4 million people worldwide died from causes related to air pollution exposure (Landrigan, 2017). While the majority of those deaths occurred in developing countries, exposure to air pollution in developed countries such as the United States continues to be a problem (United State Environmental Protection Agency, 2013; United States Environmental Protection Agency, 2009). While most of the studies that form the basis of these estimates focus on exposures to particulate and ozone pollution of outdoor origin, the indoor environment constitutes a key location where exposures to outdoor-generated pollution occur; exposure to air pollution of indoor origin is also substantial and comparatively understudied.

However, there are several large studies that have been conducted on indoor air pollution that shapes our understanding of these exposures. The TEAM study, conducted in several states in the early 1980s, sampled for various volatile organic compounds (VOCs). In California and Pennsylvania, of 13 compounds detected, in each case, at least 12 of those compounds had median personal air-to-outdoor air ratios over 1 (in one case this ratio was higher than 40) (Hartwell et al., 1987). The PTEAM study, conducted in 178 California homes in 1990, found indoor and outdoor $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) concentrations to be about the same (geometric mean $\sim$ 50 μg/m^3) (Clayton et al., 1993). Another large exposure study, the RIOPA study, conducted from 1999 to 2001 in homes in California, New Jersey, and Texas, found median indoor and outdoor $PM_{2.5}$ concentrations were also about the same, while median personal $PM_{2.5}$ concentrations were twice as high (Turpin et al., 2007). In addition 66-

78% of VOC exposure occurred indoors (Su et al., 2013), and all 10 carbonyls analyzed for exhibited median concentrations higher indoors than outdoors (Liu et al., 2006). Besides select compounds, such as the carbonyls reported in the RIOPA study (Liu et al., 2006), polar, oxygenated VOCs are poorly characterized indoors and their exposures remain largely unknown. Our understanding of exposures to pollutants generated/formed indoors and health effects of these materials is far from complete.

Indoor air exposures occur in homes, schools, vehicles, and workplaces. Workplace exposures vary greatly depending on occupation and vehicle exposures (such as those in a car during rush hour), can be quite high. The focus of this dissertation is on air exposures that occur in residences. People in the United States, spend almost 70% of their time in homes, on the population level (Klepeis et al., 2001). Children, the elderly, stay-at-home parents, and those working from home are likely to have the vast majority of their air exposures occur in their homes. Most exposure to air pollution occurs through inhalation into the respiratory tract, although there is increasing evidence that dermal uptake of air pollutants through the skin is also an important exposure route (Weschler & Nazaroff, 2012; Weschler & Nazaroff, 2014). It is known that exposures in damp homes lead to increased negative health effects (Mendell et al., 2011), however, causal agent remain unknown. Potentially, aqueous chemistry of oxygenated and water-soluble compounds in homes may play a role, thereby affecting indoor chemistry, exposures, and potentially health.

1.2 State of indoor chemistry
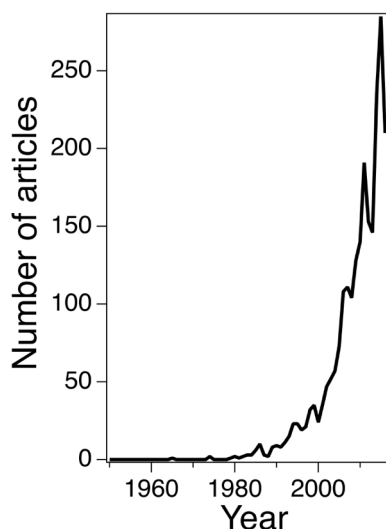
Figure 1-1. Scopus search "indoor chemistry" from 1950 to 2016.

Indoor air chemistry is relatively understudied despite the fact that people are much more likely to be exposed to indoor air than outdoor air (Klepeis et al., 2001). Between 1950 and 2016, 2,340 articles have been published that include the words "indoor chemistry" in the title, abstract, or key words of the publication (although the exact number is expected to be higher since all articles on this subject may not include the specified key words, Figure 1.1). During that time, there were about 30 times more articles written about "atmospheric chemistry." As a result of this work and EPA's regulatory authority, ambient air pollution is much better understood and concentrations have been reduced leading to demonstrated improvements in human health (United States Environmental Protection Agency, 2011). As an additional benefit, advances in fundamental atmospheric chemistry and instrumentation enabled by the funding of atmospheric chemistry research are now benefiting indoor chemistry research.

Historically (Sundell, 2017), chemical characterization of indoor air pollution has focused on inorganic particulate matter (Clayton et al., 1993) and non-polar organic gases (Hartwell et al., 1987; Lioy et al., 1991) because these compounds and compound classes have well developed analytical methods. Non-polar VOCs and semi-volatile VOCs (SVOCs) have been measured for decades by techniques such as gas chromatography

with flame ionization detection (GC-FID) and gas chromatography mass spectrometry (GC-MS) (Adgate et al., 2004; Dodson et al., 2008; Edwards et al., 2001;Weschler & Nazaroff, 2008). Non-polar VOCs have been frequently measured at much higher concentrations indoors than outdoors (Edwards et al., 2001; Hartwell et al., 1987; Paciência et al., 2016). However, some notable exceptions, such as those compounds associated with vehicle emissions, tend to be elevated outdoors compared to indoors (Edwards et al., 2001). Again, the vast majority of these measured compounds are non-polar; are polar, oxygenated VOCs also elevated indoors?

Quantifying and characterizing exposures to indoor air is challenging because of the heterogeneity of indoor spaces. Indoor air includes volatile and semi-volatile gases, particles of various sizes and compositions, and oxidants such as ozone, hydroxyl radical, and nitrate radical. The indoor air composition is different in each indoor space and is influenced by indoor emissions from sources such as cooking, cleaning, and off-gassing from building materials and furniture. It is also influenced by the infiltration of pollutants from outdoors, indoor deposition, indoor chemistry, and exfiltration (Nazaroff, 2004).

1.2.1 Indoor dampness

In the United States, twenty to fifty percent of homes are considered damp (Gunnbjörnsdóttir et al., 2006; Mudarri & Fisk, 2007). Studies utilize various techniques to measure/ determine dampness such as high relative humidity (RH), presence of mold, presence of standing water, and damp building materials. Several studies have shown associations between dampness and adverse health effects (Antova et al., 2008; Fisk, Lei-Gomez, & Mendell, 2007). Dampness is associated with microbial growths such as mold, fungus, and mildew. Exposure to these microbes is associated with adverse health

outcomes, although evidence for postulated, causal evidence remains weak (Mendell et al., 2011). Could indoor dampness be responsible for adverse health effects through other avenues besides microbial exposures? Is it possible that chemistry on damp surfaces also contributes? Polar, water-soluble gases, if present, would be expected to be taken up onto wet surfaces where they might react further. Such chemistry might plausibly alter the indoor air composition and dermal exposures in damp homes. These possibilities motivate the work contained in this dissertation.

1.2.2 New instrumentation

A major goal of this work is to characterize oxygenated VOCs (OVOCs, also called water-soluble organic gases (WSOGs)). Recent advancements have improved our ability to do this, in particular the use of chemical ionization mass spectrometry. Chemical ionization mass spectrometry (CIMS) is a valuable tool for indoor chemical characterization and for the study of indoor chemistry because of its high time resolution, lack of need for sample preparation, and its ability to measure highly functionalized and reactive compounds (Lee et al., 2014), which previously required derivatization. The CIMS can make use of several different ionization reagents that target different compound classes, and has been employed to detect oxygen- and nitrogen-containing VOCs in various outdoor environments (e.g. forests, urban air, and oil and gas fields (Jobson et al., 2017; Koss et al., 2017; Yatavelli et al., 2014; You et al., 2014). This instrument's high time resolution can aid in determining chemical dynamics, source identification, and loss rates indoors. There are three commonly used adducts for chemical ionization: acetate, iodide (I^-), and hydronium ion (H_3O^+). The acetate-CIMS has been utilized to study organic acids, their dimers, and some vicinal diol species such

as lactic acid ($C_3H_6O_3$), octanoic acid ($C_8H_{16}O_2$) (Liu et al., 2017), $C_{17}H_{26}O_8$ (consistent with a large dimer ester) (Mohr et al., 2017), methacrylic acid epoxide (MAE, $C_4H_5O_3$), and isoprene-derived epoxides (IEPOX, $C_5H_{10}O_3$) (Budisulistiorini et al., 2015). I^-CIMS detects many oxygenated compounds including organic acids, alcohols, ketones, and organic peroxides as well as nitrogen-containing compounds such as amines and organic nitrates (Lee et al., 2014; Mohr et al., 2017). The H_3O^+CIMS detects many nonpolar and relatively small, polar VOCs (Koss et al., 2017).

1.3 Mist chamber characterization

Electrospray ionization mass spectroscopy and ion chromatography are useful analytical techniques for integrated analysis of polar, organic gases. Mist chambers provide a way of collecting these gases into the aqueous phase for analysis by these methods. Mist chambers, first developed by Cofer et al., 1985 (Cofer et al., 1985), have been used extensively to collect specific water-soluble compounds such as halogens, certain carbonyls, dimethyl sulfoxide, and in many cases with derivatization prior to analysis (Jourdain & Legrand, 2001; Keene et al., 1993; Munger et al., 1995). They have also been used a few times to collect the total mix of water-soluble organic gases found in outdoor air (Hennigan et al., 2009; Sareen et al., 2016). A common mist chamber design consists of a 190 mL glass chamber containing 10 – 30 ml of water, which is introduced through an external capilary tube. Particle filtered air is pulled through the mist chamber with a pump at a relatively high flow (~25L/min). As the air moves
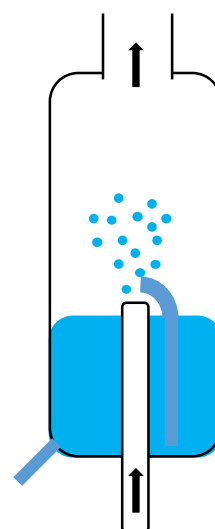
Figure 1-2. A simple diagram of a mist chamber apparatus. Air flow is indicated with black arrows.

through the device, pressure drop occurs at the top of an interal capilary tube, thereby

pulling water up through the tube. The air jet then atomizes the water creating a mist

inside the chamber. This mist provides a large air-water surface area that facilitates the

collection of water-soluble gases. Mist is continuously generated and continuously

refluxed back into the water reservoir.

A 2002 paper by Spaulding et al. aims to optimize and characterize mist chambers

for sampling WSOGs in air (Spaulding et al., 2002). If Henry's law equilibrium is

established in a sprayed water droplet during its time

$$\text{Eq 1-1: CE} = \frac{K_H RT w_L}{1 + K_H RT w_L}$$

suspended in the mist chamber (in the case of

Spaulding et al., 2002, in less than 0.36 seconds), then collection efficiency can be

calculated with equation 1-1. This is the maximum collection efficiency. Where K_H is the

Henry's law equilibrium constant (M/atm), R is the ideal gas law constant, T is the

temperature, and w_L is the liquid water content (volume of water in the mist

chamber/volume of collected air). Table 1-1 displays the theoretical collection efficency

for some compounds likely to be in indoor air using the parameters described in

Spaulding et al., 2002. The mist chambers are well suited for collection of highly water-

soluble gases.

Compounds with Henry's law constants greater than 10^3 M/atm have a maximum

collection efficiency in excess of 70%. In practice, Spaulding et al. (2002) found that

glyoxal, methylglyoxal, hydroxyactone, and glycoaldehyde, which all have Henry's law

constants over 10^3 M/atm, had collection efficiencies of >80% (Spaulding et al., 2002). In

theory, sampling for longer will reduce collection efficiencies (decrease in W_L, Equation

1), but will increase the total amount of water-soluble gas collected until the water in the reservoir is in equilibrium with the incoming gas.

Compound	Molecular formula	Henry's law constant (M/atm)	Theoretical collection efficiency (%)
Glyoxal	$C_2H_2O_2$	4,000,000	100
Formic acid	CH_2O_2	8,000	87
Acetic acid	$C_2H_4O_2$	4,000	77
Formaldehyde	CH_2O	3,000	71
Acetone	C_3H_6O	31	2.5
2-Hexanone	$C_6H_{12}O$	11	0.89
Nonanal	$C_9H_{18}O$	2	0.16

Table 1-1. Maximum mist chamber collection efficiency for Spaulding et al. 2002 mist chamber parameters: 10 mL water, 30 L/min, 10 minute collection time, 0.36 second mist droplet residence time.

1.4 Critical knowledge gaps

1.4.1 Residential water-soluble organic gases

Water-soluble organic gases are poorly characterized indoors. I hypothesize that, like non-polar VOCs, WSOG concentrations are higher indoors than outdoors. Select, WSOGs have been measured indoors and outdoors, but are more poorly understood than non-polar VOCs, due to analytical challenges. It is understood that biomass burning (e.g., acetone, phenols) and atmospheric photochemistry are important sources of outdoor WSOGs (Christian et al., 2003; Crutzen et al., 2000; Yokelson et al., 1997). Photochemical products include glyoxal and other aldehydes formed by the oxidation of alkenes (including isoprene) with hydroxyl radical and ozone and by the oxidation of fossil-fuel derived aromatics from combustion (Volkamer et al., 2001). Indoor VOCs can also undergo oxidation in the gas phase (e.g., with hydroxyl radical, nitrate radical, and ozone) or on surfaces (e.g. clothing, latex paint, and polyvinyl chloride) to form WSOGs when conditions are favorable (Gómez Alvarez et al., 2013; Nøjgaard, 2010; Rai et al.,

2014; Shu & Morrison, 2011; Weschler, 2000, 2006; Weschler et al., 1992; Weschler & Shields, 1996). While formaldehyde has been measured extensively, and several other WSOGs have been measured indoors, it is not yet known whether outdoor-to-indoor transport or indoor sources/formation is responsible for the preponderance of the total indoor WSOG burden. What are the composition and direct emission sources of indoor WSOGs? What is the dominant chemistry that forms WSOGs indoors? What are the major sinks? How do these compounds react and what are the implications to exposure? How are these processes altered in damp homes? This dissertation frames this area of research and makes major steps forward in addressing these questions.

1.4.2 Liquid water indoors

To date, most of the effort to study liquid water in building air, surfaces, and materials has been conducted by the building science community (Osanyintola & Simonson, 2006; Rode et al., 2007; Svennberg et al., 2004). The overall aim of this building science work is to understand the potential for building materials and furniture to moderate indoor humidity, as well as to understand structurally how building materials respond to absorbed water. Until now, the potential for condensed water in and on building materials and furniture to serve as a medium for indoor chemistry is largely unexplored.

I hypothesize that liquid water indoors has a substantial impact on indoor air concentrations of WSOGs and on indoor interfacial chemistry (chemistry occurring at the interface of the surface and air). Liquid water indoors can exist as thin films on building and furniture surfaces, in wet particles, as condensation from cooking and bathing, and on occupant skin as well as in the respiratory tract. It is well accepted that aqueous chemistry

in outdoor clouds, fogs, and wet aerosol alters the composition of outdoor gases and particles (Ervens et al., 2011). In fact, in many cases reaction rates are higher in the aqueous phase than in the gas phase. The impacts of aqueous chemistry on indoor air composition are not well understood. This dissertation provides new insights into the impacts of liquid water on indoor WSOG concentrations.

1.5 Hypothesis and specific aims

I hypothesize that water-soluble organic gases of indoor origin are ubiquitous and abundant in homes and their subsequent aqueous uptake and processing alters the chemical composition of indoor air.

In order to test this hypothesis and answer these questions I will:

1. a. Compile information about WSOGs measured indoors and predict the presence of additional WSOGs.

    b. Examine the potential for aqueous chemistry to occur indoors through the use of existing literature.

2. a. Make integrated measurements of total WSOG inside and outside homes.

    b. Chemically characterize the integrated indoor WSOG samples.

3. Make real-time measurements of selected WSOG in one well-described home and use the measurements to gain insights about WSOG sources and sinks.

1.6 Dissertation overview

The purpose of this research is to characterize water-soluble organic gases indoors and to explore the likelihood of aqueous processing of these gases.

Chapter 2 uses the existing literature to make the case that WSOGs and liquid water are present in homes, that WSOGs partition into liquid water, and subsequent interfacial chemistry occurs. A literature review was conducted to identify WSOGs in indoor air that have been measured prior to this research. Given measured concentrations and Henry's law constants of those compounds, potential aqueous concentrations were calculated. In addition, the literature was explored for compounds that have not been measured in indoor air, but are expected to be in indoor air due to their emission sources (e.g. human perspiration and cooking). Also, using examples from the outdoor air literature and indoor air chamber experiments, additional WSOGs were proposed to be present because they are gas phase oxidation products of common indoor VOCs. Finally, using knowledge of building science and aqueous chemistry in outdoor air (particularly in wet aerosols), the case was made for aqueous phase chemistry to occur in indoor air, especially in homes with high RHs and/or standing water. The case was made that this chemistry has the potential to substantially alter indoor air composition, thereby affecting exposure and possibly health.

Total WSOG measurements indoors and outdoors (Chapter 2) and chemical characterization of those samples (Chapter 3) (collected with the help of Dr. Kenneth Sexton) in 13 homes showed for the first time that, like VOCs, indoor WSOG are predominantly of indoor origin. Interestingly, roughly half of the WSOG mass was comprised of organic acids. WSOG were collected in an integrated fashion over four hours using mist chambers. Samples were analyzed for organic acids by ion chromatography and for aldehydes, ketones, organic peroxides, and amines by positive-

mode electrospray ionization mass spectrometry, which provided elemental formulas. Chemical structures were proposed based on likely indoor sources.

Chapter 4 describes subsequent real-time I⁻CIMS measurements inside and outside of a 14th home. The I⁻CIMS was operated by postdoctoral researcher Dr. Sophie Tomaz. This home was substantially characterized and sampled for many days under different conditions, including high occupancy, cooking, and open windows. To facilitate a comparison with the previous 13 homes, integrated WSOG measurements were also made. Substantial losses of acetic, lactic, and formic acids in the air conditioning system were documented for the first time. Several additional compounds were also identified at the molecular level. Some were primarily of indoor origin, whereas others were of primarily outdoor origin. We observed several compounds that peaked during cooking events and others that increased with an increase in occupancy. These are among the first real-time WSOG measurements in a real home.

Chapter 5 summarizes this research in its entirety and provides main conclusions from my work. Calculated average daily doses are provided for gas phase WSOG via inhalation and dermal routes and possible health effects are discussed. Then advancements in this scientific field that were published during my studies are summarized. Next, future research directions are proposed to follow up on continued characterization of WSOG indoors and ideas for chemically exploring aqueous chemistry indoors are provided. Finally, implications and broader impacts of my work to the fields of indoor air chemistry and exposure science are discussed.

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Chapter 2. Oxygenated VOCs, aqueous chemistry, and potential impacts on residential indoor air composition

Material in this chapter has been published previously as:

2.1 Abstract

Dampness affects a substantial percentage of homes and is associated with increased risk of respiratory ailments; yet the effects of dampness on indoor chemistry are largely unknown. We hypothesize that the presence of water-soluble gases and their aqueous processing alters the chemical composition of indoor air and thereby affects inhalation and dermal exposures in damp homes.

Herein, we use the existing literature and new measurements to examine the plausibility of this hypothesis, summarize existing evidence, and identify key knowledge gaps. While measurements of indoor volatile organic compounds (VOCs) are abundant, measurements of water-soluble organic gases (WSOGs) are not. We found that concentrations of total WSOGs were, on average, 15 times higher inside homes than immediately outside (N=13). We provide insights into WSOG compounds likely to be present indoors using peer-reviewed literature and insights from atmospheric chemistry. Finally, we discuss types of aqueous chemistry that may occur on indoor surfaces and speculate how this chemistry could affect indoor exposures. Liquid water quantities, identities of water-soluble compounds, the dominant chemistry, and fate of aqueous

products are poorly understood. These limitations hamper our ability to determine the effects of aqueous indoor chemistry on dermal and inhalation exposures in damp homes.

2.2 Introduction

Dampness in buildings is common in the United States, with estimates ranging from 18 to 50% of buildings affected, where buildings were defined as "damp" based on observation of standing water, water damaged materials, presence of mold and/or high measured relative humidity (RH) (Gunnbjörnsdóttir et al., 2006; Mudarri & Fisk, 2007). Dampness and high RH indoors can be caused by high humidity outdoors, water leakage into buildings, leakage of pipes, flooding, water infiltration into building materials, and moisture resulting from human activities such as cooking and bathing (Bornehag et al., 2001). Dampness can also occur as a result of water vapor condensation in the building structure or on surfaces indoors. Building dampness is associated with increased risk of respiratory symptoms such as cough, wheeze, asthma, and respiratory infections (Mendell et al., 2011). Dampness is also associated with mold exposures. Two scientific reviews report that dampness or mold exposures result in increased respiratory symptoms with a range of odds ratios from 1.30-1.75 and 1.4-2.2, respectively (Bornehag et al., 2001; Mendell et al., 2011). Mold and mildew indoors and its health effects have been studied extensively. However, to date, mold and mildew have only been able to partially explain the associations between damp buildings and adverse health outcomes, and causal linkages remain weak (Mendell et al., 2011). Certainly, there could be additional chemical, physical, or biological factors that contribute to adverse health in damp spaces.

We hypothesize that aqueous uptake and processing of water-soluble gases in damp homes alters the chemical composition of indoor air and can affect dermal and

inhalation exposure. If true, aqueous chemistry indoors could plausibly affect health in damp homes. Aqueous chemistry outdoors (in clouds, fogs, and wet particles) has been demonstrated to alter the concentrations and composition of *outdoor* gases and particles; (Blando & Turpin, 2000; Crahan et al., 2004; Ervens et al., 2013; Volkamer et al., 2007) aqueous chemistry may also occur indoors in damp buildings where the surface area for water condensation is large. In fact, the observation of HONO production in residences (Gómez Alvarez et al., 2013; Spengler et al., 1993) provides definitive evidence that indoor liquid water concentrations are sufficient, at least in certain homes/times, to drive aqueous chemistry because HONO is produced on surfaces (from NO_2 hydrolysis) only in the presence of liquid water (Finlayson-Pitts et al., 2003).

For aqueous processing indoors to be an important factor for indoor air chemical composition, liquid water and water-soluble gases must be present indoors. When dampness occurs in homes, liquid water can be present in and on indoor surfaces as well as in hygroscopic airborne particles. Knowledge about water-soluble gases indoors is limited, although nonpolar volatile organic compounds (VOCs) have been extensively measured. VOCs are frequently measured at much higher concentrations indoors than outdoors. A systematic review of indoor and outdoor VOC measurements found indoor/outdoor residential VOC ratios range from 1 to 150 (Paciência et al., 2016). One study that measured 30 VOCs using GC-FID inside and outside homes in Helsinki, Finland, found indoor/outdoor VOC ratios of measured compounds ranged from 0.25 to 55 with an average ratio of 6 (Edwards et al., 2001) (compounds with higher concentrations outside homes tended to be associated with vehicle emissions). We speculate that, similar to non-polar VOCs, polar and water-soluble VOCs are present at

higher concentrations indoors than outdoors. While measurements of formaldehyde are relatively common and other targeted polar VOCs are sometimes measured indoors (Liu et al., 2006; Reiss et al., 1995; Zhang et al., 1994), measurement of polar and water-soluble VOCs (also called *oxygenated* VOCs, OVOCs; or water-soluble organic gases, WSOGs) is, in general, more challenging.

WSOGs are emitted from indoor sources and formed through oxidation. They will be taken up into liquid water, when present, and subsequently react. Thus, aqueous chemistry could affect exposure by acting as a sink for certain water-soluble gases in indoor air and a source of other volatile products (altering inhalation exposure) and condensed phase products (altering particle inhalation and dermal exposure).

This paper provides insights into WSOGs likely to be in residential indoor air and examines the potential for aqueous chemistry indoors to alter the chemical composition of this air, with the motivation of further understanding dermal and inhalation exposure to gaseous and particulate species in homes. We demonstrate that water-soluble organic gases are elevated in residential indoor environments. We make use of the literature to document water-soluble compounds measured or likely to be present in homes. Finally, we discuss knowledge and knowledge gaps concerning indoor aqueous chemistry and its implications, and we make recommendations for future research.

2.3 Approach

First, we address the potential importance of indoor water-soluble organic gases. Because, to our knowledge, measurements of *total* WSOGs have not previously been made indoors, we conducted these measurements inside 13 homes and directly outside

for comparison. We then provide a list of water-soluble gas-phase compounds that have been measured in residential indoor air. Next, we use knowledge about emissions, non-polar VOC concentrations, and oxidation chemistry to identify additional water-soluble organic compounds that are likely to be present indoors. This is followed by a presentation of the case for indoor aqueous chemistry. We familiarize the reader with outdoor atmospheric aqueous chemistry and speculate about wet chemistry on indoor surfaces. Finally, we discuss the potential for aqueous chemistry to alter indoor exposures and summarize major knowledge gaps.

Indoor and outdoor concentrations of *total* WSOG were determined by collecting the ambient mix of water-soluble gases into water using Cofer scrubbers (Cofer et al., 1985), also called mist chambers, and measuring the total carbon collected. While it is possible to target specific water-soluble compounds by optimizing analytical methods and through the use of authentic standards, such an approach would likely only provide a small fraction of total WSOG. The goal of these measurements is to determine whether or not total WSOG is enriched indoors compared to outdoors.

For this purpose, field samples were collected from a convenience sample of 3 homes in central New Jersey and 10 homes in the Triangle region of North Carolina between June and October 2015; each home was sampled once. WSOGs were collected from particle-filtered air (particles filtered with pre-baked quartz fiber filters (Pall, 47 mm)) using 2 mist chambers (Cofer et al., 1985) in parallel sampling from a common area of the home and 2 simultaneously sampling directly outside the home. Each mist chamber scrubbed the air with an air flow rate of 25 L/min and water collection volume of 25 mL (ultra-pure deionized water, conductivity = 17.8 $\pm$ 0.5 MΩ) for a duration of

two hours, twice consecutively. Indoor and outdoor samples were composited separately for each home, analyzed for total organic carbon using a Shimadzu 5000a TOC analyzer as described previously (Perri et al., 2009; Yi Tan et al., 2009), and the remaining volume was frozen for future research.

In order to gain additional insights into WSOGs in indoor air, a literature search was performed on September 14-15, 2015 using the Scopus database. The search terms using the Boolean operators "and" and "or" were:

> One of the following: Volatile, semi-volatile, gas phase, gas-phase, organic, organic compounds, organic gases, aldehydes, aromatic hydrocarbons, terpenes, alcohols, alkanes, alkenes, epoxides, phenols, ethers, carboxylic acids, amines, pesticides, termiticides, insecticides, flame retardants, cooking emissions, cleaning, repellent, deodorant, deodorizer, PBDE, or PAH;

> And: indoor or indoors

> And: air, gas phase or gas-phase;

> And: concentration or concentrations;

> And: measured or calculated.

The search yielded 517 results. From among these, 37 articles provided concentration data on gas-phase species measured in homes in the United States. Compounds with Henry's law constants greater than 1 M/atm were considered water-soluble, as recommended by Sander (Sander, 2015). Potential aqueous phase

concentrations were calculated from typical indoor air concentrations reported in the literature and Henry's law constants. This provides a "first assessment" of *compounds* that could be important to indoor aqueous chemistry. (Note that the magnitude of the aqueous reservoir depends also on the liquid water volume.)

Although the literature search yielded an extensive list of WSOGs in indoor air, we expect that there are many more water-soluble gases present in indoor air that have not been measured, because advances in measurement methods for oxidized compounds are a recent phenomenon. Thus, we made use of chemical insights from the *outdoor* (atmospheric) chemistry literature (e.g., smog chamber studies) to propose additional types of oxidized compounds that we expect to be present indoors. Knowledge of indoor source emissions, including cooking, microbial activity, and occupant skin off-gassing provided a few additional WSOGs.

Finally, we used knowledge about outdoor aqueous chemistry and indoor spaces to speculate on how indoor aqueous chemistry may affect indoor air composition and therefore affect exposure.

2.4 Total water-soluble organic gases measured during this study

Figure 2-1 compares the concentrations of organic carbon collected concurrently in the mist chamber samples inside and immediately outside the 13 homes. Indoor samples contained 540 - 1,400 µM-C, with mean indoor WSOG concentration of 940 µM-C, standard deviation of 300 µM-C and the 95% confidence interval of 770 - 1,100 µM-C. In contrast, concurrently-collected samples from residential outdoor air contained

only 28 - 110 µM-C, with a mean of 69 µM-C, standard deviation of 25 µM-C, and 95%

confidence interval of 56 - 83 µM-C.

Indoor concentrations of WSOG were, on average, 15 times higher than outdoor

concentrations (Figure 2-1), suggesting that the vast majority of indoor WSOG is emitted

or formed indoors. A lower-bound estimate of the percentage of indoor WSOG that is of

indoor origin can be calculated by assuming that all water-soluble organic gases that

originated outdoors penetrate and persist indoors with 100% efficiency (100%

penetration, no indoor losses). Using this lower-bound assumption, the mean, median and

range of indoor-origin WSOG are 86%, 92%, and 83% to 98% respectively. Thus, the

indoor residential environment is substantially enriched in water-soluble organic gases

and this WSOG is predominantly emitted or formed indoors.
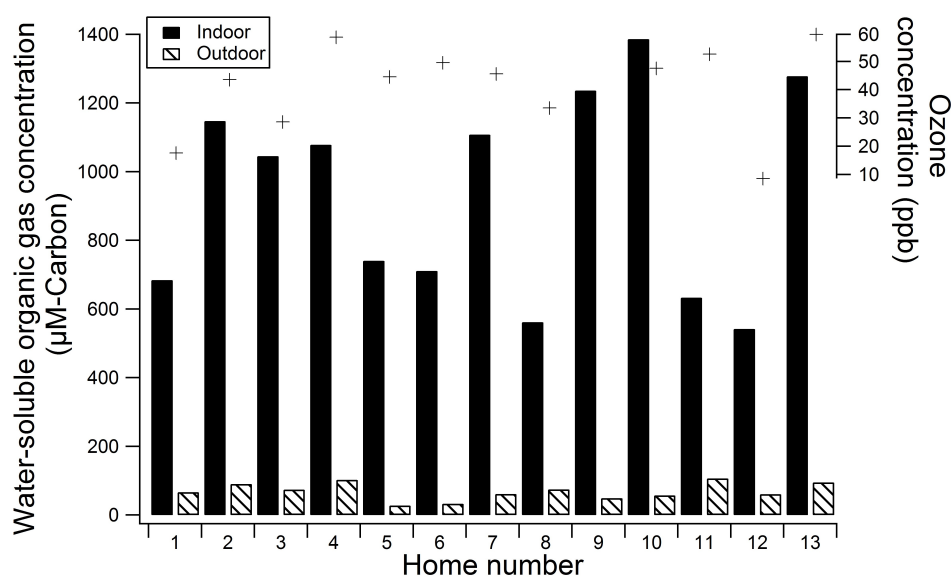
Figure 2-1. Total organic carbon (µM-C) in aqueous mist chamber samples collected concurrently from particle-filtered ambient air inside (black bars) and directly outside (striped bars) 13 New Jersey and North Carolina homes. Indoor concentrations were significantly higher (paired t-test, $\alpha=0.05$, $p<0.001$) than outdoor concentrations. (Source blanks were below the detection limit and field blanks = 7±2.5 µM-C; neither were subtracted from the sample totals) Nearby outdoor ozone concentrations for each home

are plotted directly above each pair of bars. For homes in New Jersey and North Carolina, outdoor ozone concentrations were reported from the New Jersey Department of Environmental Protection Rider University Campus and the North Carolina Department of Environmental Quality Durham Armory ambient air quality sites respectively (ozone data was not available for home 9). Indoor relative humidity ranged from 53 - 67%, indoor temperatures ranged from 20 - 26 ˚C, and the absolute difference between indoor and outdoor temperatures ranged from 0.5 - 8 ˚C.

Comparison of indoor and outdoor organic carbon concurrently collected under identical conditions enables a quantitative comparison of WSOG indoors relative to outdoors. However, to calculate gas phase WSOG concentrations (μg-C/m^3 air) rather than the concentration of WSOG in the collected aqueous samples (μg-C/L water) would require the average Henry's Law constant for the mixture. In this work, sample collection times were long to increase organic compound concentrations in aqueous samples for more detailed chemical characterization and laboratory experiments. At long collection times, mist chamber water approaches Henry's Law equilibrium with the sampled air. Thus, for long collection times, calculation of WSOG concentrations in μg-C/m^3 requires an estimate of the average Henry's Law constant of the collected WSOG mixture. To provide an example, if the average Henry's Law concentration of the mixture were 3000 M/atm (the same as formaldehyde), the average indoor WSOG concentration would be 350 ppb$_v$ (470 μg/m^3). However, Henry's Law constants vary tremendously. For example, the Henry's Law constant is 4×10^6 M/atm for glyoxal and 20 M/atm for 2-butanone (Sander, 2015), both water-soluble gases found in air. Thus since the composition of the WSOG mixture is unknown, the error in such a calculation could potentially be large. Despite this limitation, the knowledge that WSOG concentrations indoors are substantially greater than outdoors, and thus indoor WSOG
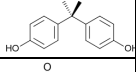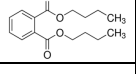
sources/production is substantial, constitutes a major step forward in understanding

indoor WSOG.

Below we use knowledge from the existing literature to infer what water-soluble

organic gases are likely to be available to participate in indoor aqueous chemistry.

2.5 Water-soluble organic gases in indoor air

2.5.1 Compounds previously measured

Table 2-1 shows *water-soluble* organic compounds identified in the literature

search that have a potential aqueous concentration equal to or greater than 10^{-3} µM,

organized by potential aqueous-phase concentrations. Concentrations are the product of

the Henry's law constant (Sander, 2015) and typical gas-phase concentration.

Compound	Structures	Henry's law constant (M/ atm)	Mean (and range) gas phase concentrations (ppb)	Mean (and range) potential aqueous concentrations (µM)	References
Glyoxal		4,000,000	1 (0.5 – 1.8)	4,300 (1,900 – 7,500)	(Dodson et al., 2008)
Formaldehyde		3,000	22 (4 – 100)	66 (10 – 300)	(Jurvelin et al., 2003; Liu et al., 2006; Reiss et al., 1995; Ross Highsmith et al., 1988; Sax et al., 2004; Zhu & Jia, 2012)
Methylglyoxal		32,000	0.9 (0.4 – 1.6)	30 (10 – 50)	(W. Liu et al., 2006)
Trichloroacetic acid (TCA)		74,000	0.07 (NA)	5.2	(Jia et al., 2008)
Bisphenol A (BPA)		25,000,000	0.00015 (BDL – 0.02)	3.8 ($\leq$ 500)	(Weschler & Nazaroff, 2008; Wilson et al., 2007)
Dibutyl phthalate (DBP)		1,000	(0.018 – 0.11)	(1.3 – 8.1)	(Weschler & Nazaroff, 2008)
Acetone		31	16 (0.4 – 280)	0.5(0.01 – 9)	(Jurvelin et al., 2003; Liu et al., 2006; Quackenboss et al., 1989; Reiss et al., 1995; Highsmith et al., 1988; Sax et al., 2004; Zhang et al., 1994)
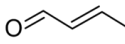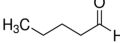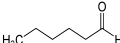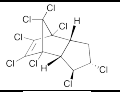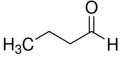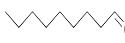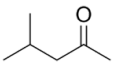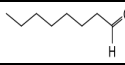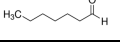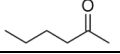
Name	Structure				Reference
Acetaldehyde		15	7.4 (0.7 – 23)	0.11 (0.01 – 0.3)	(Dodson et al., 2008; Jurvelin et al., 2003; Liu et al., 2006; Reiss et al., 1995; Sax et al., 2004; Zhang et al., 1994)
2-Butanone (methyl-ethyl-ketone)		18	2 (BDL – 8.4)	0.035 (≤ 0.15)	(Jia et al., 2008; Jurvelin et al., 2003; Reiss et al., 1995; Weisel et al., 2008)
Propionaldehyde (propanal)		13	1 (BDL – 7.3)	0.012 (≤ 0.1)	(Jurvelin et al., 2003; Liu et al., 2006; Reiss et al., 1995; Zhang et al., 1994)
Crotonaldehyde		60	0.15 (BDL – 1.1)	0.012 (≤ 0.07)	(Liu et al., 2006)
Benzaldehyde		20	0.5 (BDL – 1.4)	0.010 (≤ 0.03)	(Jurvelin et al., 2003; Liu et al., 2006; Reiss et al., 1995; Sax et al., 2004; Zhang et al., 1994)
Valeraldehyde (pentanal, pentanaldehyde)		6.1	1 (BDL – 23)	0.007 (≤ 0.14)	(Jurvelin et al., 2003; Reiss et al., 1995; Sax et al., 2004; Zhang et al., 1994)
Hexaldehyde (hexanal)		5.1	1.2 (BDL – 8.5)	0.006 (≤ 0.0078)	(Jurvelin et al., 2003; Liu et al., 2006; Reiss et al., 1995; Sax et al., 2004; Zhang et al., 1994)
Chlordane		18	0.26 (BDL – 5.7)	0.0047 (≤ 0.1)	(Weschler & Nazaroff, 2008; Zhu & Jia, 2012)
Tetrahydrofuran		10	0.44 (NA – 83)	0.0044 (≤ 0.84)	(Jia et al., 2008)
Butyraldehyde (butanal)		6.5	0.66 (BDL – 4.7)	0.0044 (≤ 0.31)	(Jurvelin et al., 2003; Reiss et al., 1995; Sax et al., 2004; Zhang et al., 1994)
Nonylaldehyde (nonanal)		2	2 (NA – 4.9)	0.0044 (≤ 0.01)	(Jurvelin et al., 2003)
Acrolein (propenal)		10	0.25 (BDL – 2.4)	0.0026 (≤ 0.024)	(Liu et al., 2006)
Methyl isobutyl ketone, 3-methyl 2-pentanone (MIBK)		7.4	0.3 (BDL – 81)	0.0024 (≤ 0.6)	(Jia et al., 2008; Weisel et al., 2008)
Octylaldehyde (octanal)		2	0.9 (NA – 2.4)	0.0018 (≤ 0.0044)	(Jurvelin et al., 2003)
Heptaldehdye (heptanal)		4	0.4 (NA – 1.1)	0.0017 (≤ 0.01)	(Jurvelin et al., 2003)
2-Hexanone		11	0.13 (NA – 0.8)	0.0014 (≤ 0.009)	(Jurvelin et al., 2003)

Table 2-1. Water-soluble organic gases measured inside homes in the United States. NA = not available, values not reported. BDL = below detection limit.

2.5.2 Compounds predicted to be present

In addition to the water-soluble gases *measured* in air, many more are expected to be present. Some of these compounds may be directly emitted while others will be formed through gas phase reactions. Table 2-2 provides examples of water-soluble gases measured in emissions from sources typical of indoor environments, specifically from building occupants, cooking, wood burning, and microbial metabolism. We also included volatile disinfection byproducts (DBPs) from drinking water because, if present in the household water supply, they can partition to indoor air as a result of activities such as showering and water boiling. Microbial VOCs (MVOCs) are released from metabolism of bacteria and fungi; the majority of MVOCs listed are emitted from other indoor sources as well (Korpi et al., 2009). Although not included here, off gassing from building materials, furniture, tobacco smoke, and consumer products can also produce a wide variety of VOCs including WSOGs (Charles et al., 2007; Hodgson et al., 2000; Salthammer, 1997; Singer et al., 2006). In most cases listed compounds were measured in controlled chamber studies using analytical techniques optimized to particular compound classes (e.g. phenols and syringols using GC-FID (Schauer et al., 2001)). We expect that as sophisticated methods for measurement of polar gases are applied to indoor air measurement, these and other WSOGs will be increasingly found in indoor spaces.

Emission source	WSOG emitted	Source
Building occupants	Acids such as: • Oxopentanoic acid (H=4,000 M/atm) • Lactic acid (H=12,000 M/atm) • Pyruvic acid (H=310,000 M/atm) Ketones, such as: • Acetone (H=31 M/atm) Alcohols, such as: • Ethanol (H=200 M/atm) • Propanol (H=150 M/atm) • Phenol (H=1,500 M/atm) Other carbonyls such as: • 4-Oxopentanal (H=430 M/atm)	(Liu et al., 2016; Liu et al., 2017)
Cooking	Aldehydes, such as: • Acetaldehyde (H=15 M/atm) • Propanal (H=10 M/atm) • Acrolein (H=10 M/atm) Ketones, such as: • 2-hexanone (H=11 M/atm) • 2-heptanone (H=6 M/atm) Alcohols, such as: • Pentanol (H=80 M/atm) • Hexanol (H=60 M/atm) • 1-octen-3-ol (H=13 M/atm)	(Katragadda et al., 2010)
Fireplace	Phenols and substituted phenols, such as: • Phenol (H=1,500 M/atm) • *o*-benzenediol (H=4,600 M/atm) • *m*- and *p*-cresol (H=1,200 M/atm) Guaiacol and substituted guaiacols, such as: • Guaiacol (H=1,000 M/atm) • Vanillin (H=470,000 M/atm) • Eugenol (H=500 M/atm) Syringols and substituted syringols, such as: • Syringol (H=NA, highly oxidized) • 4-methylsyringol (H=NA, highly oxidized) Aliphatic aldehydes, such as: • Formaldehyde (H=3,000 M/atm) • Acetaldehyde (H=15 M/atm) • Hexanal (H=5.1 M/atm) Aliphatic ketones, such as: • Acetone (H=31 M/atm) • Butanone (H=18 M/atm) Olefinic aldehdyes, such as: • Acrolein (H=10 M/atm) • Crotonaldehyde (H=50 M/atm) Aromatic carbonyls, such as: • Benzaldehyde (H=20 M/atm) • *m*- and *p*-toluadehyde (H=40 M/atm) Dicarbonyls, such as: • Glyoxal (H=4,000,000 M/atm) • Methylglyoxal (H=32,000 M/atm) • Biacetyl (H=50 M/atm)	(Schauer et al., 2001)

Disinfection byproducts in drinking water	Volatile trihalomethanes such as: • Chloroform • Bromodichloromethane • Chrolodibromomethane • Bromoform	(Nieuwenhuijsen et al., 2000)
	Volatile DBPs: • 1,1,1,2-Tetrabromo-2-chloroethane • 1,1,2,2-Tetrabromo-2-chloroethane benzyl chloride	(Richardson, 2003)
Microbial VOCs	Aldehydes, such as: • Formaldehyde (H=3,000 M/atm) • Propanol (H=150 M/atm) • Benzaldehyde (H=20 M/atm) Acids, such as: • Acetic acid (H=4,000 M/atm) • Octanoic acid (H=15 M/atm) Ethers, such as: • Anisole (H=3 M/atm) Esters, such as: • Methyl acetate (H=10 M/atm) • Ethyl acetate (H=6 M/atm) Ketones, such as: • Cyclopentanone (H=80 M/atm) • 3-hydroxy-2-butanone (H= 60M/atm)Acetone (H=25 M/atm)	(Korpi et al., 2009)

Table 2-2. Water-soluble organic compounds measured in emissions from indoor source types. These are expected to be released into indoor air and may then partition into any liquid water present. NA = not available

In addition to WSOG directly released into indoor air, WSOG will also be formed indoors from gas-phase VOC oxidation and oxidation of organic surfaces. Gas-phase oxidation has been observed to form WSOGs on time scales that are competitive with the air exchange rate, for example from d-limonene (Carslaw, 2013). Oxidation of surface materials is considered the major formation pathway for WSOGs because surface oxidation can produce indoor WSOGs even when reaction times are long relative to the time-scale for air exchange. Three oxidants are of particular importance to the formation of WSOG indoors: ozone, hydroxyl radical (OH·) and nitrate radical (NO$_3$·). Ozone infiltrates from outdoors while OH· and NO$_3$· are produced indoors (Weschler, 2000; Weschler, Brauer, et al., 1992; Weschler & Shields, 1996). Nitrogen pentoxide (N$_2$O$_5$)

and chlorine radical may also play an important role occasionally, such as in homes with natural gas combustion and ozone ($NO_2 + O_3$) or cleaning and photolysis, respectively.

Ozone oxidation of unsaturated VOCs has long been recognized as an indoor source of polar organics (e.g., gas-phase aldehydes) (Weschler, et al., 1992); the importance of ozonolysis of surface-bound organics to WSOG formation has more recently been recognized (Wang & Morrison, 2010; Wisthaler & Weschler, 2010). The predominant source of indoor residential ozone is infiltration from outdoors, yielding indoor concentrations that are typically 20-70% of those outside (Weschler, 2000). It is not uncommon for indoor ozone concentrations to range from negligible to 40 ppb, depending on outdoor levels, air exchange rate and indoor sinks (Weschler, Brauer, et al., 1992). Higher concentrations usually occur midday, during summertime, although high concentrations can also occur in wintertime under certain circumstances (Schnell et al., 2009). In addition to formation of oxidized organic gases, ozone – VOC reactions can produce indoor OH·.

Indoor hydroxyl and nitrate radical concentrations are not well constrained, but are expected to be substantial at times. Ozone - NO_2 reactions provide a source of nitrate radicals (Weschler, et al., 1992), particularly when natural gas combustion provides an indoor source of NO_2 (Yamanaka et al., 1979; Zhang et al., 2000). Because there is less photolysis indoors, $NO_3·$ can persist longer in indoor spaces than outdoors. $NO_3·$ concentrations on the order of 10^{-3} ppb (Carslaw, 2007; Nøjgaard, 2010; Weschler, 2004) can occur indoors. When ozone concentrations are elevated (e.g., through outdoor-to-indoor transport), or NO_2 is elevated indoors, OH· can be produced through VOC oxidation reactions (Weschler & Shields, 1996) or with adequate infiltrated sunlight,

through HONO photolysis (Gómez Alvarez et al., 2013). New evidence suggests that

indoor OH· can reach concentrations comparable to daytime outdoor concentrations

through HONO photolysis (Gómez Alvarez et al., 2013) (10^{-5} to 10^{-6} ppb). However,

indoor OH· concentrations are probably frequently lower than peak daytime outdoor

levels. Given that indoor oxidants co-exist with elevated indoor VOCs and organic-rich

surface materials, formation of water-soluble organic compounds in indoors spaces is

inevitable.

To provide insights into secondary oxidized compounds expected from gas phase

or surface oxidation chemistry in indoor air, Table 2-3 shows compounds identified

indoors and their oxidation products gleaned from the atmospheric and indoor chemistry

literature. Smog chamber studies designed to better understand atmospheric chemistry

and indoor literature examining oxidation products of cleaning agents and human skin

lipids provide the bulk of the insights provided in Table 2-3. Several examples of non-

polar VOC precursors and soluble oxidation products are given. However, this list is not

exhaustive.

VOC	Oxidant	Water-soluble product	Source
C_5-C_8 *n*-alkanes (from attached garages)	OH·	Hydroxycarbonyls, such as: • 5-hydroxy-2-pentanone (H=NA, highly oxidized) • 4-hydroxypentanal (H=NA, highly oxidized)	(Reisen et al., 2005)
Monoterpenes (from cleaning products, wood floors, e.g. α-pinene, β-pinene, limonene)	Ozone	Aldehydes and acids, such as: • Pinonaldehyde (H=9,000 M/atm) • Succinic semialdehyde (H=NA, highly oxidized) • Glyoxal (H=4,000,000 M/atm) • Pinic acid (H=NA, highly oxidized)	(Atkinson & Arey, 2003; Yu et al., 1998)
	OH·	Aldehydes and ketones, such as: • Pinonaldehyde (H=9,000 M/atm) • Acetone (H=30 M/atm) • Formaldehyde (H=3,000 M/atm) Organic nitrates, such as:	(Atkinson & Arey, 2003; Capouet et al., 2004;

		Peroxyacyl nitrates (H=NA, highly oxidized)	Larsen et al., 2001)
Alkylbenzenes (building materials, furniture, attached garages)	OH·	Quinones, such as: • Benzoquinone (H=2 M/atm) Hydroxyl dicarbonyls	(Yu et al., 1997)
Squalene (human skin lipid)	Ozone	• Acetone (H=30 M/atm) • Hydroxyacetone (H=7,700 M/atm) • 1,4-butanediol (H=800,000 M/atm) • Levulinic acid (H=3,900 M/atm) • 4-oxobutanoic acid (H=4,900 M/atm)	(Wisthaler & Weschler, 2010)
Isoprene (indoor plants, people)	OH·	Carbonyls, such as: • Acetaldehyde (H=13 M/atm) • Acetone (H=30 M/atm) • Butanone (H=18 M/atm) Hydroperoxides, such as: • Isoprene hydroxyl hydroperoxide ISOPOOH (H=NA, highly oxidized) • Methylhydroperoxide (H=NA, highly oxidized) • Hydroxymethyl hydroperoxide (H=NA, highly oxidized) Epoxides, such as: • Isoprene epoxide (H=30,000,000 M/atm)	(Crutzen et al., 2000; Paulot et al., 2009; Reeves & Penkett, 2003)
	NO₃·	Alkyl nitrates (H is dependent on exact compound, expected to be high) Hydroxycarbonyls (H is dependent on exact compound, expected to be high)	(Rollins et al., 2009)

Table 2-3. VOCs identified indoors and water-soluble gas-phase oxidation products expected to be found indoors based on knowledge from atmospheric (smog chamber) and indoor chemistry studies. NA = not available

As shown in Table 2-3, oxidation of organics leads to the formation of water-soluble gases, such as ketones, acids, alcohols, organic nitrates, peroxides, and epoxides. Some of these have been measured indoors and more are likely to be present. These water-soluble organic gases, have the potential to play a key role in aqueous chemistry indoors when liquid water is present.

2.6 Aqueous chemistry in outdoor air

Since water-soluble organic gases are plentiful indoors and liquid water is expected to be present in a substantial fraction of homes, it is plausible that aqueous chemistry could alter the concentrations of gas and condensed phase compounds indoors, like it does outdoors. In outdoor air, aqueous chemistry occurs because WSOGs partition into clouds, fog and wet aerosols and react through radical and non-radical reactions (Jacob, 1986). This reactive uptake is a substantial sink for some atmospheric WSOGs (Volkamer et al., 2007). Low-volatility products of atmospheric chemistry in clouds, fog, and wet aerosol remain in the particle phase even after water evaporation; thus aqueous organic chemistry is a source of secondary atmospheric organic particulate matter (secondary organic aerosol; SOA; (Blando & Turpin, 2000; Ervens et al., 2011; McNeill, 2015; Nozière et al., 2015)). Aqueous chemistry also alters the gas phase composition via volatile products (Jacob, 1986).

There is substantial atmospheric evidence for the importance of aqueous atmospheric chemistry. Perhaps the most well-established and best-known example is aqueous oxidation of SO_2 by H_2O_2. Dramatic co-depletion of SO_2 and H_2O_2 has been documented with cloud on-set, for example at Whiteface Mountain, NY (Mohnen & Kadlecek, 1989). Aqueous SO_2 oxidation is much more rapid than gas phase oxidation, and forms the majority of particulate sulfate and acid rain (Aleksic et al., 2009; Mohnen & Kadlecek, 1989; Munger et al., 1983). Additionally, aqueous processing (heterogeneous hydrolysis of NO_2) is a major source of HONO (Heikes & Thompson, 1983). Global modeling suggests that SOA formation via OH· oxidation of aldehydes and acetic acid in clouds is comparable in magnitude to SOA formation via gas phase

chemistry and vapor pressure driven partitioning (Liu et al., 2012), and this chemistry largely explains the global atmospheric loading of oxalate, the most abundant dicarboxylic acid in the atmosphere (Myriokefalitakis et al., 2011). Isoprene-derived epoxides and peroxides are known to react in wet acidic sulfate aerosol; the products of these reactions are substantial contributors to organic aerosol in the southeastern U.S. (Budisulistiorini et al., 2016). Likewise, a variety of compelling atmospheric evidence suggests that aqueous uptake can be a major sink for WSOGs, such as formic and acetic acids (Chebbi & Carlier, 1996), formaldehyde and acetaldehyde (Grosjean & Wright, 1983), and glyoxal (Hodas et al., 2014; Volkamer et al., 2007).

In the atmosphere, liquid water is found in the form of clouds, fog, and wet aerosols. Interestingly, liquid water is the largest component of fine particulate matter (PM$_{2.5}$) in the atmosphere, globally, (Liao & Seinfeld, 2005) and the largest summertime component of PM$_{2.5}$ in the eastern United States (Carlton & Turpin, 2013). Additionally, water-soluble gases are ubiquitous and abundant outdoors, (Carlton & Turpin, 2013; Goldstein & Galbally, 2007) mostly due to atmospheric oxidation of VOCs. For example, glyoxal and other aldehydes are formed from the hydroxyl radical oxidation of isoprene and 2-methyl-3-buten-2-ol (MBO) emitted from trees (Spaulding, 2003) and from the oxidation of aromatics emitted from fossil fuel combustion (Volkamer et al., 2001). There are also primary sources of water-soluble gases such as acetone, formaldehyde, acetic acid, and phenols from biomass burning (Christian et al., 2003; Yokelson et al., 1997).

Once in the atmosphere, water-soluble gases can partition into liquid water (Blando & Turpin, 2000) and hydrate, dissociate, undergo hydrolysis, nucleophilic or

other acid-base and catalytic reactions, or be oxidized by ozone, H_2O_2, OH or NO_3

radicals (Ervens et al., 2011; McNeill, 2015; Seinfeld & Pandis, 2006) dissolved from the

gas phase or formed in the aqueous phase (e.g. aqueous OH· formation though Fenton

reaction, or HONO, nitrate, or peroxide photolysis). Lifetimes with respect to OH· are

frequently shorter in the aqueous phase than in the gas phase. For example, for OH· in

equilibrium between the gas phase and aqueous phase (i.e., for [OH·] = 10^6

molecules/cm^3 in the gas phase and [OH·] = 10^{-12} M in the aqueous phase), the lifetimes

of glyoxal, formaldehyde and phenol are 1.2 days, 1.4 days and 10 hours, respectively, in

the gas phase (Atkinson, 1997) and 15 min, 40 s, and 3 min., respectively, in the aqueous

phase (Doussin & Monod, 2013). OH radicals are so reactive, that their uptake or

aqueous formation rate controls product formation rates (Ervens et al., 2014), and

concentrations will be lower than equilibrium values unless aqueous OH· formation is

substantial. In clouds and fogs, where solute concentrations are low, OH radicals

dominate daytime aqueous organic chemistry due to their abundance, high reactivity and

water solubility (Ervens et al., 2003; Faust & Allen, 1993). NO_3· and Fenton reactions are

more important contributors at night (Atkinson et al., 1986; Moonshine et al., 2008).

Formaldehyde, for example, partitions into the aqueous-phase (H = 3,000 M/atm

(Betterton & Hoffmann, 1988)), hydrates and reacts with OH· to make formic acid, HO_2

radicals and water (Bothe & Schulte-Frohlinde, 1980; Chameides & Davis, 1983).

Nucleophilic addition to formaldehyde is also possible; for example, addition of bisulfite

leads to the formation of hydroxymethanesulfonate (Munger et al., 1986).

Aqueous-phase reaction can form different products than gas-phase reaction. For

example, gas-phase glyoxal oxidation produces formaldehyde (Atkinson, 1990; Ervens et

al., 2004), whereas aqueous-phase glyoxal oxidation makes glyoxylic and oxalic acids (Carlton et al., 2007; Karpel Vel Leitner & Doré, 1997); subsequent neutralization (e.g., by ammonium) can produce low volatility salts (e.g., ammonium oxalate) that remain in the condensed phase (in particles or on surfaces) even after water evaporation (Häkkinen et al., 2014; Ortiz-Montalvo et al., 2012). This difference in chemistry occurs because glyoxal is doubly hydrated in the aqueous phase (exists as a tetrol) (Carlton et al., 2007).

Chemistry in wet aerosols differs from that in clouds and fogs because aerosol liquid water is highly concentrated with solutes. Non-radical reactions can compete with radical reactions in wet aerosols because high solute concentrations make up for their lower rate constants (Dziedzic & Co, 2009). For example, acid-catalyzed ring opening and nucleophilic ammonium reaction with isoprene epoxydiols lead to the formation of oligomers and organosulfates in wet atmospheric particles (Nguyen et al., 2014; Surratt et al., 2010). The process of water evaporation (i.e. in evaporating fogs and clouds) speeds otherwise slow reactions, e.g., between aldehydes and amines, (De Haan et al., 2011) facilitating chemical transformation. Further, photosensitized radical reactions involving humic-like substances that are found in wet aerosols and at air-sea interfaces have been shown to produce oxygenated organic gases (Fu et al., 2015). Thus, aqueous chemistry can be both a sink for water-soluble gases and a source of both gases and condensed phase species in airborne particles and on surfaces (Blando & Turpin, 2000; Ervens et al., 2011; Liu et al., 2012).

The now substantial body of research being conducted to understand *atmospheric* aqueous chemistry provides insights into the potential for aqueous chemistry to alter concentrations and exposures indoors.

2.7 The case for aqueous chemistry in indoor air

Surfaces play an important role in indoor chemistry. Indoor surface area-to-volume (S/V) ratios are greater than 3 m^2/m^3, and much greater when internal surface areas are considered for materials such as carpets and upholstery (Morrison & Nazaroff, 2000; Singer et al., 2007). This is orders of magnitude greater than the <0.01 m^2/m^3 typical of ambient outdoor air. Even a 1 nm water film on indoor surfaces, a film consistent with simple water adsorption, will provide more than 1000 times the volume of liquid water as is found in aerosols in outdoor air (assuming 3 $\mu g/m^3$ of liquid water in aerosol). Combined with the knowledge that WSOGs are present at much higher concentrations indoors than outdoors, the potential for aqueous chemistry to play an important role indoors, as it does outdoors, is substantial.

The measurement of HONO indoors provides clear evidence that there is sufficient liquid water to drive aqueous chemistry in residences, and that aqueous chemistry can alter the composition of indoor air. HONO is produced from the heterogeneous hydrolysis of NO_2. HONO has been measured in many homes over the last few decades, including the early study of 10 homes by Spengler and Brauer, who found HONO concentrations ranging from 2 to 8 ppb (Spengler et al., 1993). Recently, measured indoor OH· concentrations of 1.8 x 10^6 molecules/m^3 were linked to HONO photolysis on surfaces (Gómez Alvarez et al., 2013). Interestingly, this suggests that OH radicals can be produced through photolysis in indoor liquid water films on windows. Those OH radicals can then go on to oxidize aldehydes (e.g., glyoxal), organic acids (e.g., acetic, lactic) and phenols (e.g., guaiacol, phenol) in the aqueous phase to produce oxalic acid, oligomers and other products (Docherty et al., 2005; Tan et al., 2012; Yu et

al., 2014). Aqueous OH· oxidation of formaldehyde will be a source of gas-phase formic acid (Jacob, 1986). We also expect that ammonia/amines, which have varying water-solubilities and could also be elevated indoors (Ongwandee et al., 2005), will react with aldehydes as water evaporates from indoor surfaces.These reactions will form brown surface films (De Haan et al., 2009). Other likely chemistry is described below.

One important knowledge gap pertains to indoor liquid water. The hygroscopicity of indoor surfaces, indoor liquid water quantities and chemical characteristics of aqueous solutions are not well understood. Evidence for the presence of water has been documented in a substantial percentage of buildings (Gunnbjörnsdóttir et al., 2006; Mudarri & Fisk, 2007), and water can be present indoors for a variety of reasons. Some indoor locations are constantly wet, like toilet bowl and sink traps, but have limited interfacial surface areas for chemical mass transport. Other locations are seasonally wet, such as air conditioning coils (summer) and windows/exterior walls (winter) that are colder than the indoor air and thus condense moisture from that air. Still other locations are subject to regular condensation/ evaporation cycles such as sinks, showers and bathroom mirrors. Liquid water can also be found indoors due to snow melt, rain water, leaks and faulty plumbing (Bornehag et al., 2001). Building occupants themselves have liquid water in their respiratory tract and hygroscopic salts on human skin also take up water when the RH exceeds the deliquescence point (Finlayson-Pitts & Pitts, 2000). Finally, a wide variety of hygroscopic materials (e.g., clothing, furniture, building materials, aerosols and surface grime) absorb water vapor,(Baergen et al., 2015; Hill et al., 2009; Künzel et al., 2004; Saxena & Hildemann, 1996; Straube et al., 2002; Svennberg et al., 2004) creating highly concentrated aqueous solutions where reactions

can take place. For example, a room with walls consisting of lime–gypsum interior plaster can reduce the RH by 10% (Künzel et al., 2004). This accounts for a water uptake of 3 mL per square meter of plaster (equivalent to a water layer 3 μm thick, were it all to exist as a surface film). Airborne particles are also hygroscopic, increasing their water content with increasing RH. While the hygroscopicity of indoor-generated particles is not well known, roughly half of indoor fine particle mass is of outdoor origin. Globally, ambient fine particles are 70% water, on average (Liao & Seinfeld, 2005). At particularly high RH, ambient particle mass can increase by a factor of five due to water uptake (Nguyen et al., 2016). Indoor surfaces are known to accumulate surface films 1-14 nm thick (Gao et al., 2016; Huo et al., 2016; Li et al., 2010; Liu et al., 2003; Weschler & Nazaroff, 2017). Although polar compounds have been measured in surface films (Liu et al., 2003), the hygroscopicity of these films is not known. Based on aerosol hygroscopicity, it is not unreasonable to think that the film thickness could double or triple at high RH, due to hygroscopic growth, leading to highly concentrated aqueous mixtures.

The extent of WSOG uptake to wet surfaces depends on the volume of liquid water indoors, which is poorly understood, the Henry's law constant, and on subsequent reactions in the aqueous phase. For example, assuming aqueous uptake to reach Henry's Law equilibrium but no subsequent aqueous reaction, 20 ppb_v of formaldehyde (a typical indoor concentration) would decrease by 1% in a 40 m^3 room that has a liquid water film 1 nm thick (surface water adsorption only) and 15% if the liquid water film were 30 nm thick. Once taken up, formaldehyde will hydrate and reactions in liquid water will enhance uptake to reestablish Henry's law equilibrium.

Unfortunately, little work has been done to characterize the quantity and the physical and chemical properties of liquid water on indoor surfaces. Many factors may affect the aqueous chemistry that could occur indoors including, but not limited to:

- The hygroscopicity of surface materials. If the hygroscopicity is high (e.g. fabric furniture, unpainted walls, salty skin, infiltrated outdoor particles), then water vapor can be taken up into the material, sometimes even at modest humidities (Svennberg et al., 2004), forming highly concentrated aqueous solutions (Simonson et al., 2004)

- The surface area and volume of liquid water films. The capacity to remove water-soluble gases depends on the water volume but also on compound removal through aqueous reaction; the (reactive) uptake rate can depend on the water surface area or on the rate of reaction after uptake (Ervens et al., 2014).

- The features of the aqueous solution such as pH, water activity, presence of salts (which can change Henry's law constants and affect hygroscopicity) (Waxman et al., 2015), production of oxidants (Lim & Turpin, 2015), photosensitizers (Aregahegn et al., 2013), nucleophiles (Nguyen et al., 2014), transition metals (Vidrio et al., 2008), and other reactants.

- The chemical composition of the surface. Indoor surfaces can become soiled with semi-volatile organic compounds that partition and continuously re-partition between the gas and adsorbed phases, particles released by occupant activities, and occupant skin flakes (Weschler,

2016). Soiled surfaces can also become oxidized, e.g., by ozone transported from outdoors (Wang & Morrison, 2010; Wisthaler & Weschler, 2010). The properties of the soiled surfaces will affect hygroscopicity (Duplissy et al., 2011) and aqueous reactivity.

Chemical composition affects surface water uptake. While some atmospheric aerosol constituents (i.e., sulfuric acid) take up water even at 10% RH, others do not deliquesce until high RH (e.g., 85% RH, many common salts). Non-polar hydrocarbons are not hygroscopic, but some aerosol organics do retain water even as low as 10% RH (Man et al., 2008; Peng et al., 2001) (e.g., malonic, citric, tartaric acids). We expect that indoor surface films will be comprised of complex mixtures. Aerosol particles comprised of complex mixtures take up water at lower RH values than single component particles (Svenningsson et al., 2006). For example, a particle mixture of ammonium sulfate, ammonium nitrate, levoglucosan, fulvic acid and succinic acid experiences deliquescence behavior at relative humidities from 55 to 70%. Independently, the inorganic salts would not be in solution until an RH of 85% (Seinfeld & Pandis, 2006; Svenningsson et al., 2006). Also, because of the presence of ammonia and amines indoors and atmospheric aerosol studies of their effect on hygroscopicity, we anticipate that reaction of indoor organic surface films with ammonia and amines will increase water uptake by indoor surfaces (Ongwandee et al., 2005; Smith et al., 2010). Additionally, as surfaces age, they become oxidized leading to carbonyl, alcohol, and carboxylic acid functional groups (Wang & Morrison, 2010). Methods to predict atmospheric aerosol water uptake as a function of RH and surface composition (oxygen-to-carbon ratio or functional group

contributions) (Duplissy et al., 2011) have the potential to predict the hygroscopicity of indoor surfaces, if they are chemically-characterized.

Once partitioned in the aqueous phase, water-soluble compounds could undergo several types of reactions including radical reactions, acid-base, nucleophilic and hydrolysis reactions. We expect that aqueous surface films will contain high concentrations of solutes, and thus the chemistry will be more similar to the chemistry in wet aerosols rather than clouds. Compounds taken up from the gas phase may react with carbonyl, alcohol, and carboxylic acid functional groups present in surface films (Wang & Morrison, 2010) or with compounds taken up from the gas phase. Since ammonia and amines are water soluble, they are likely to be taken up from the gas phase and to participate in aqueous chemistry. TiO_2, present in most paints, is a photosensitizer (Fujishima et al., 2000) and thus can initiate radical reactions in aqueous solutions in the presence of light, as can humic-like organics (Ciuraru et al., 2015; Fu et al., 2015). Because solar radiation penetrates through windows, photosensitized reactions could yield volatile products, as has been observed previously for photosensitizers at air-ocean interfaces (Fu et al., 2015) and could be a major pathway for OH· formation in water films. This is especially true when condensation forms on windows. When window condensate evaporates, it will release volatile products to the gas phase (De Haan et al., 2009, 2011). Aqueous photolysis (Faust & Allen, 1993) of HONO (Gómez Alvarez et al., 2013), HOCl (Wong et al., 2017), organic peroxides (Lim & Turpin, 2015) and nitrate are also likely sources of OH in indoor water films. While OH radicals can also be taken up from the gas phase, they are so reactive that diffusion would be the rate limiting step to product formation in the absence of aqueous phase sources. Even though reaction rate

constants are much smaller, non-radical reactions are competitive with OH· reactions in wet aerosols because solute concentrations are so high (e.g., molar). We expect the same to be true in indoor water films. Note also that, unlike gas phase reactions, surface reactions do not have to be faster than air exchange in order to be important, because molecules sorbed to surfaces have much longer residence times indoors.

pH is likely to affect the types of chemical reactions that occur in liquid water. Wet airborne particles are frequently acidic, while thin aqueous films on indoor surfaces may be basic or acidic depending on the composition of the surface and adsorbed gases. For example, indoor carbon dioxide concentrations are quite high due to the presence of occupants; dissolved carbon dioxide will lead to the formation of carbonic acid making the aqueous film acidic. Or ammonia may dominate pH since it can be present in high quantities indoors (Šišović et al., 1987) leading to more basic conditions. The presence of salts, for example on skin, can also affect uptake and reactions. Compounds that may undergo hydrolysis in liquid water partitioned onto surfaces include phthalates from plasticizers and organophosphates from pesticides (Weschler, 2011) as well other compounds that can be easily protonated or deprotonated, such as alcohols and amines. OH radicals (H=30 M/atm), ozone (H=10^{-2} M/atm) and peroxides (H=varies, high) will also be taken up into liquid water, and can react with WSOG in the aqueous phase to form volatile and low volatility products.

Some reactions will produce products that remain in the condensed phase (e.g. on surfaces) even after water evaporation. For example, OH· oxidation of acetic acid and glyoxal may occur in indoor water films. In dilute solution these reactions produce oxalic acid, which remains in the condensed phase as an ammonium salt (Lim et al., 2010; Tan

et al., 2012). In concentrated aqueous solution low volatility oligomers form (Lim et al., 2010; Tan et al., 2012). Evaporation of water films containing aldehydes and amines or amino acids, also found indoors, enables the formation of low-volatility imidazoles and other nitrogen containing oligomers (De Haan et al., 2009, 2011). Oligomers are also expected from nucleophilic reaction of organic epoxides, e.g. in the presence of ammonium (Nguyen et al., 2014). Organic hydroperoxides are very water soluble and very reactive in the condensed phase. If present, we expect that they will react with aldehydes or carbonyl functionalities in indoor surface films to form peroxyhemiacetals (Docherty et al., 2005).

Chemistry in liquid water indoors may also be a source of volatile compounds that will be released into the gas phase upon formation or undergo additional chemistry before they are released. For example, aqueous OH· oxidation of phenols emitted from wood combustion forms formic and acetic acids that will evaporate when the surface dries (and oxidized aromatic oligomers that remain in the condensed phase) (Li et al., 2014). Formaldehyde oxidation by OH radicals also produces formic acid (Jacob, 1986). The fate of oxalic acid, an aqueous oxidation product of phenol, glyoxal, and acetic acid (Carlton et al., 2007; Li et al., 2014; Tan et al., 2012), depends on whether it remains a volatile acid or is neutralized and present as a low volatility salt (Häkkinen et al., 2014).

Human skin contains hygroscopic salts that take up water as relative humidity increases, therefore building occupants themselves are expected to be a medium for aqueous chemistry. In addition to the types of reactions discussed above, indoors, these salts may participate in displacement reactions such as those observed in wet marine aerosols. Chlorine present in marine aerosol, is displaced by organic acids and is released

into the atmosphere as HCl (Laskin et al., 2012). This could happen on wet skin with organic acids such as acetic acid (which has been measured indoors) (Laskin et al., 2012). Damp skin may be a source of reactive halogen gases such as Cl_2 and Br_2 as well as nitrate especially if there is sufficient sunlight indoors (Richards-Henderson et al., 2013). These halogens can then drive further gas phase chemistry. Also, there is evidence that NO_2 and HCl forms ClNO and $ClNO_2$ in the presence of water molecules at air-surface interfaces. These products are highly volatile and reactive and can further drive indoor chemistry (Raff et al., 2009).

Lung fluid, a saline aqueous solution, is also a probable location for aqueous chemistry of indoor water-soluble gases. Formaldehyde, is known to dissolve in lung fluid and produce reactive oxygenated species (Jung et al., 2007). Water-soluble organic peroxides and quinones found in atmospheric particles have been shown to produce strong oxidants in synthetic lung fluid (Charrier et al., 2014; Lin et al., 2016). Chemically similar WSOGs may also be expected to do so. However, little is known about the potential health effects of inhalation exposures to most WSOG and how their aqueous products that are released from lung fluid may affect indoor chemistry.

2.8 Conclusions and future work

Aqueous chemistry has been found to be an important factor in the atmospheric processing of organic compounds. Because the indoor surface area to volume ratios are so much higher than the outdoor values, even a thin water surface coating would provide more water per unit volume than found outdoors. Since the concentrations of WSOGs and several other potential reactants are also much higher indoors than out, we argue that

aqueous chemistry is likely to affect indoor air composition and affect inhalation and dermal exposures in damp homes.

Oxygenated, polar, water-soluble organic compounds are poorly characterized because methods for their gas-phase measurement are less developed than measurement methods for non-polar VOCs. Thus, herein we report measurements of total water-soluble organic gases in 13 real homes, and find for the first time that WSOG concentrations are substantially higher indoors than outdoors where photochemistry is known to make WSOG ubiquitous and abundant (Carlton & Turpin, 2013). Literature-based evidence suggests that indoor WSOG includes carbonyl compounds, carboxylic acids, epoxides, organic peroxides, organic nitrates, amines, and phenols. When liquid water is present as indoor surface films, on skin and in wet particles (i.e., at elevated RH), we expect that WSOG will partition into that water and react further. This chemistry is likely to remove some compounds from the gas phase, while introducing others to the gas phase, thereby altering indoor air composition and inhalation exposure. When reactions occur on damp skin, dermal exposures could also be altered.

While we argue that aqueous chemistry will alter exposures in damp indoor spaces, the following are critically needed to assess the magnitude of this effect and are poorly understood:

- The composition of indoor WSOG
- The hygroscopicity of indoor surfaces
- The chemical and physical properties of indoor aqueous surface films

- The relative importance of radical and non-radical chemistry and thermodynamic properties of the products

Ultimately we wish to know the degree to which "dampness" alters indoor air composition, inhalation and dermal exposures through indoor aqueous chemistry, and whether this chemistry helps to explain adverse health effects in damp homes.

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Chapter 3: Characterization of water-soluble organic gas collection using mist chambers and composition of water-soluble organic gases in 13 homes in the eastern United States

In preparation for journal submission

3.1 Abstract

People spend considerable time in their homes. Thus, characterization of residential indoor air is important for understanding exposures to airborne chemicals. While it is well known that non-polar VOCs are elevated indoors, polar VOCs remain poorly characterized. Recent measurements showed that concentrations of total polar water-soluble organic gases (WSOG) are much higher indoors than directly outdoors (on average 15x greater at 13 homes, on a carbon-mass basis). This work aims to chemically characterize these WSOG mixtures. Acetic, lactic, and formic acids account for up to 50%, by mass, of the total WSOG-carbon collected inside each home. Remaining WSOG was characterized by elemental composition via positive mode electrospray ionization mass spectrometry. 98 individual molecular formulas were detected. On average 67% were CHO, 11% were CHN, 11% were CHON, and 11% were sulfur-, phosphorus-, or chlorine-containing. Some molecular formulas are consistent with compounds having known indoor sources such as diethylene glycol (m/z$^+$ 117.091, $C_4H_{10}O_3$), methylmelamine (m/z$^+$ 141.113, $C_6H_{12}N_4$), and methacrylamide (m/z$^+$ 86.060, C_4H_7NO). Identification and quantification of WSOG indoors as well as understanding sources and sinks of these compounds, will provide a more complete picture of indoor exposures.

3.2 Introduction

Residential indoor environments are critical locations for exposure to pollutants of indoor and outdoor origin. Despite this, indoor air composition remains poorly characterized. It is well known that non-polar volatile organic compounds (VOCs) concentrations are higher indoors than outdoors (Wallace et al., 1987). Recent measurements indicate that polar VOCs, measured as total water-soluble organic gases (WSOGs), are also much higher indoors than outdoors. Specifically, concentrations of WSOG were measured on average 15 times higher (by mass) inside 13 homes in New Jersey and North Carolina than directly outside them (Duncan et al., 2018). Duncan et al. (2018) speculate that multiphase (aqueous) chemistry on wet surfaces is an important sink, and possible source, of WSOGs in damp homes. Roughly 18-50% of homes in the United States are considered to be damp (Mendell et al., 2011). While several polar VOCs (WSOGs) are commonly measured (e.g., formaldehyde, acetaldehyde) (Dodson et al., 2008) and measurements of additional compounds are becoming more numerous (Liu et al., 2016; Liu et al., 2017), polar VOCs are poorly characterized due to analytical challenges. In this work, we aim to chemically characterize the WSOG collected in the 13 New Jersey and North Carolina homes.

3.3 Methods

Water-soluble organic gases were collected into liquid water from a convenience sample of 13 homes in New Jersey and North Carolina from June to October 2015. These gases were sampled using Cofer scrubbers, or mist chambers, for two hours twice consecutively in each home. Technician surveys and participant questionnaires were

conducted to characterize each home while samples were collected. Samples were then analyzed for total organic carbon, organic acids, and elemental composition.

3.3.1 Sampling

Two mist chambers sampled inside the main living area of the home (such as the living or dining room) for two hours twice sequentially from approximately 10:00 am to 2:00 pm (Cofer et al., 1985; Duncan et al., 2018; Hennigan et al., 2009; Sareen et al., 2016). Sampling inlets were placed about 1.5 meters from the floor and at least one meter from the edge of the room. Each mist chamber sampled particle filtered air using pre-baked quartz filters (QFF) (Pall, 47mm) at 25 L/min into a mist created from the spray of 25 mL of 17.8±0.5 MQ ultra-pure bulk water that then refluxed back down into the chamber; water lost by evaporation during sampling was replaced periodically during sampling. For each home, samples were composited in analysis sized aliquots. Prior to sampling, field water blanks and 2-minute "dynamic" blanks (conducted by placing Pall activated carbon filters in line before the mist chambers) were collected each day.

3.3.2 Characterization of the sampling environment

Before sampling began, sample participants were asked to verbally answer a questionnaire with the aim of characterizing the sampling environment (Rutgers IRB #15-636M and UNC IRB #15-1611, see Appendix A1 for complete questionnaire and table of accompanying answers). Questions included: "Do you have a gas or electric stove?" and "What food have you cooked, in the past 24 hours?" and "Do you have an attached garage?" House dimensions and floor/building height were measured using a laser tape measure (Bosch GLM 15, Robert Bosch Tool Corporation, Mount Prospect,

Illinois). Information about home age, type of flooring, food cooked during sampling, and number of people present during sampling were recorded (Table 3-1). Indoor temperature, relative humidity and CO_2 concentrations were recorded hourly with an Extech SD800 CO_2/ humidity/ temperature data logger (Extech, Nashua, New Hampshire). Outdoor ozone and temperature data were recorded from nearby monitoring sites.

Some of this information (e.g., home age, indoor-outdoor temperature difference) was collected because it is predictive of air exchange rates which will likely impact indoor WSOG concentrations. Since air exchange rate was calculated with these parameters rather than measured (see next paragraph), a step-wise multiple linear regression was conducted to determine predictors of WSOG concentration. Indoor WSOG concentrations were regressed against outdoor WSOG concentration, indoor temperature, outdoor temperature, delta temperature, indoor RH, outdoor ozone, indoor carbon dioxide, number of occupants, year home built, and home area. At a p-value of <0.05, year home built was the only predictor included in the model with an R^2 of 0.61. This may be because newer homes are often more air tight leading towards less air exchange to the outdoors resulting in higher indoor WSOG concentrations. Air exchange rates were calculated using equation 11 from Chan et al. (Chan et al., 2005). Estimated air exchange rate was given by:

$$Eq\ 3-1: AER\ [h^{-1}] = 48 \left(\frac{2.5\ m}{H}\right)^{0.3} \frac{NL}{H \times F}$$

where H = building height (m), NL = normalized leakage (function of year built and floor area), F = scaling factor = 16. Since all homes were above the poverty line, NL (derived from Chan et al. (Chan et al., 2005; Hodas et al., 2014)) was calculated as:

$$Eq\ 3-2: NL = \ e^{11.1-(1.07\times10^{-2}\times\ year\ built)-(2.20\times10^{-3}\times\ floor\ area)}$$

In general, air exchange rate was negatively correlated with WSOG concentration, but calculated air exchange rate was not a strong predictor (R^2=0.34).

Home #	Home built (year)	Home area (m^2)	Building height (m)	Calculated AER	T (indoors, average, °C)	Collected WSOG (μM-C)	WSOG (gas phase (μg-C/m^3)	Acetic acid (gas phase (μg/m^3)	Formic acid (μg/m^3)
1	1960-1979	>200	5-6	0.4	22	680	106	55	14
2	1980-1989	<100	5-6	0.5	26	1150	178	58	11
3	1980-1989	100-200	5-6	0.4	23	1050	162	61	7
4	1990-2015	<100	5-6	0.3	23	1080	167	78	13
5	1930-1950	<100	3-5	0.8	24	740	115	42	6
6	1980-1989	-	-	-	26	710	110	56	9
7	1990-2015	>200	6-8	0.3	25	1110	172	87	16
8	1930-1950	>200	3-5	0.5	22	560	87	37	8
9	1960-1979	<100	3-5	0.5	21	1240	192	87	16
10	1980-1989	>200	5-6	0.3	23	1380	215	37	8
11	1930-1950	<100	5-6	0.8	25	630	98	48	8
12	1930-1950	100-200	6-8	0.6	20	540	84	34	8
13	1960-1979	-	-	-	25	1280	198	66	12

Table 3-1 (part 1 of 2).

Home #	RH (indoors, average, %)	CO_2 (indoors, average, ppm)	Occupancy (Weighted)	T (outdoors, average, °C)	Outdoor ozone (ppb)
1	57	1000	4	23	17
2	56	620	2	30	43
3	60	850	3	27	28
4	55	1010	3	30	58
5	61	750	3	25	44
6	58	750	4	25	49
7	59	950	2.25	32	45
8	55	870	4.25	20	33
9	67	1390	2.75	21	no data
10	60	970	2.56	27	47
11	62	1130	2.13	33	52
12	58	690	2.81	15	8
13	53	1120	2.69	29	59

Table 3-1 (part 2 of 2). Characteristics of sampled homes and the indoor/outdoor environments during sampling. Occupancy was weighted by multiplying the number of occupants by the time they were present divided by the total sample time. Home 6 and 13 house areas and building height were highly irregular, preventing air exchange rates from being calculated. Outdoor temperature was obtained from Weather Underground Linden, New Jersey, and Morrisville, North Carolina sites. Outdoor ozone was obtained from New Jersey Department of Environmental Protection Rider University Campus and North Carolina Department of Environmental Quality Durham Armory ambient air quality site.

3.3.3 Analyses

Aqueous samples and blanks were analyzed for total organic carbon (TOC) with a Shimadzu TOC 5000A (Shimadzu Corporation, Kyoto, Japan), for organic acids by ion chromatography (IC) using a Dionex ICS 3000 (Thermo Fisher Scientific, Waltham, Massachusetts) and for aldehydes, ketones, organic peroxides, epoxides and reduced nitrogen compounds by accurate-mass Quadrupole Time-of-Flight Liquid Chromatography/Mass Spectrometry with an Electrospray Ion Source (ESI-QTOF-LC/MS, Agilent 6520, Agilent Technologies, Santa Clara, California). For TOC, the analytical accuracy of the standard TOC concentrations was 2%, field blanks averaged 7 ± 2.5 µM (not subtracted from samples), and the analytical precision (calculated as the pooled coefficient of variation of duplicate analyses of the same samples) was 10%. Organic acids were measured by IC using an IonPac AS11-HC column and guard column with conductivity detection at 35°C. Milli-Q water was the eluent (flow rate = 0.4 mL/min) and a gradient of potassium hydroxide was the buffer. The analytical accuracies of the standards for acetic and formic acids were 27 and 12.5% respectively; the analytical precisions for acetic and formic acids (calculated as the pooled coefficient of variation of duplicate analyses of the same samples) were 5 and 1%, respectively; and the method precisions for acetic and formic acid (calculated as the pooled coefficient of variation of the same bulk sample analyzed on different days) was 26 and 10%, respectively. Samples were directly injected into the ESI-QTOF-LC/MS for positive mode analysis, which detects the above compound classes with 5 ppm mass resolution. The ESI-QTOF-LC/MS was operated over a mass range of 50-1000 amu. The mobile phase was 50% methanol and 50% Milli-Q water with 0.05% formic acid and flowed at

0.2 mL/min. The fragmentor voltage was set to 40 V and the capillary voltage was set to

3700 V. The nitrogen drying gas was operated at 350°C at 11 l/min, and a nebulizer

voltage of 25 psig. HP-921 (m/z$^+$ 921) and purine (m/z$^+$ 121) were used as mass

calibrants. m/z$^+$ were considered real signals if they were not present in the blank or their

abundances in the samples were more than mean + 3σ of the blank.

3.4 Mist chamber characterization

Mist chambers have been used extensively to collect specific water-soluble

compounds. They have also been used occasionally to collect the total mix of water-

soluble gases found in outdoor air (Hennigan et al., 2009; Sareen et al., 2016), including

with chemical characterization (Sareen et al., 2016). In theory, sampling for 10 minutes

with Cofer mist chambers will collect compounds with Henry's law constants >10^3

M/atm with 100% efficiency (Spaulding et al., 2002). In practice, Spaulding et al (2002)

found that glyoxal, methylglyoxal, hydroxyactone, and glycoaldehyde, which all have

Henry's law constants over 10^3 M/atm, had collection efficiencies of >80% (Spaulding et

al., 2002). Since mist chamber water refluxes continuously during collection, longer

collection times will result in higher concentrations of sampled compounds in the mist

chamber water. Theoretically, if collection times are long enough, the concentrations of

all compounds present in the mist chamber water will reach Henry's law equilibrium with

their concentrations in the sampled air. At equilibrium, the proportion of a compound

collected is determined by its Henry's law constant; an increasing fraction will be

collected with increasing Henry's law constant (increasing water solubility). Once

equilibrium is achieved, additional net collection is zero. In this work, we aim to collect

the ambient mix of WSOGs at high enough concentrations for analysis.

To characterize mist chamber collection of WSOG as a function of sampling time, we sampled the same air with different sample collection times (Figure 3-1). First, four mist chambers sampled for a total of 1 hour, concurrently (25 mL of DI water; air flow rate of 25 L min^{-1}). The first mist chamber collected 8 – 7.5 min samples, which were composited; the second collected 4 – 15 min samples, the third collected 2 – 30 min samples; and the fourth collected 1 – 1 hour sample. Immediately after, the four mist chambers sampled for a total of 8 hours, concurrently. The first mist chamber collected 8 – 1 hour samples, the second 4 – 2 hour samples, the third 2 – 4 hour samples and the fourth 1 – 8 hour sample. Each mist chamber's
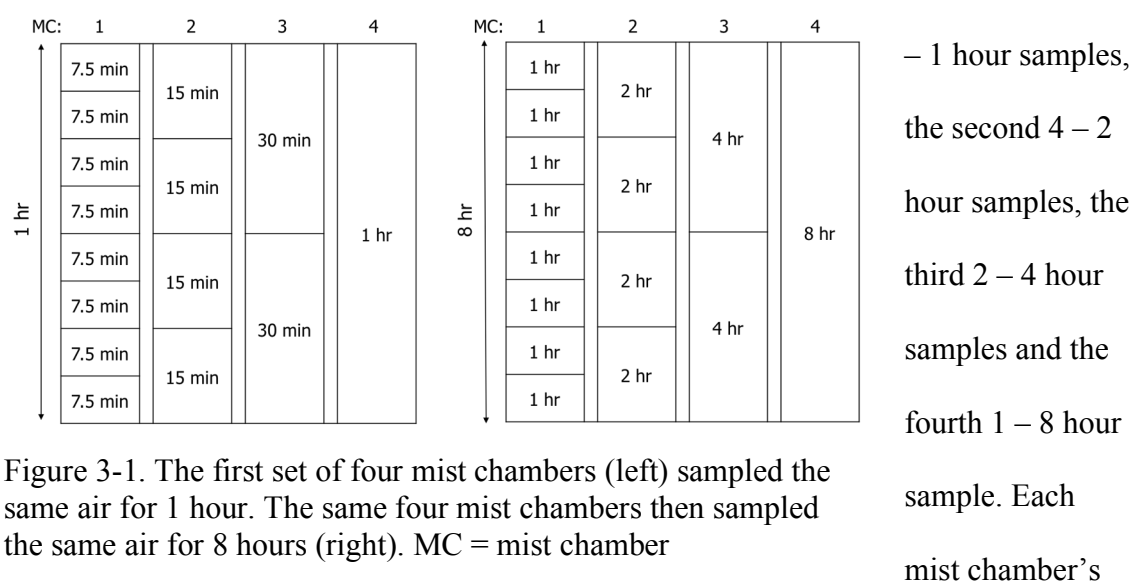
Figure 3-1. The first set of four mist chambers (left) sampled the same air for 1 hour. The same four mist chambers then sampled the same air for 8 hours (right). MC = mist chamber

samples were composited for analysis. Thus, in Figure 3-2, mist chamber total WSOG concentrations with collection times from 7.5 min to 1-hour were collected concurrently and concentrations with collection times from 1-hour to 8-hours were collected concurrently immediately after. This complete set of measurements was conducted three times over three days.

Concentrations of collected acetic (H = 4,000 M/atm) and formic (H = 9,000

M/atm) acids increased similarly (Figure 3-2b.). Note that lactic acid (H=12,000 M/atm)

eludes so close to acetic acid that the peaks were not integrated/quantified separately. It

appears that acetic acid is the dominant peak, however, lactic acid is observed as a small shoulder on the acetic acid peak (see figure A4-2 in Appendix A). Thus, the acetic + lactic acid peak was quantified as acetic acid and will be referred to below as acetic (rather than acetic + lactic) acid. The contributions of acetic and formic acids relative to the total mixture are smaller with shorter collection times and larger with longer collection times (Figure 3-2c.). This may be because more water-soluble compounds approach equilibrium faster (such as
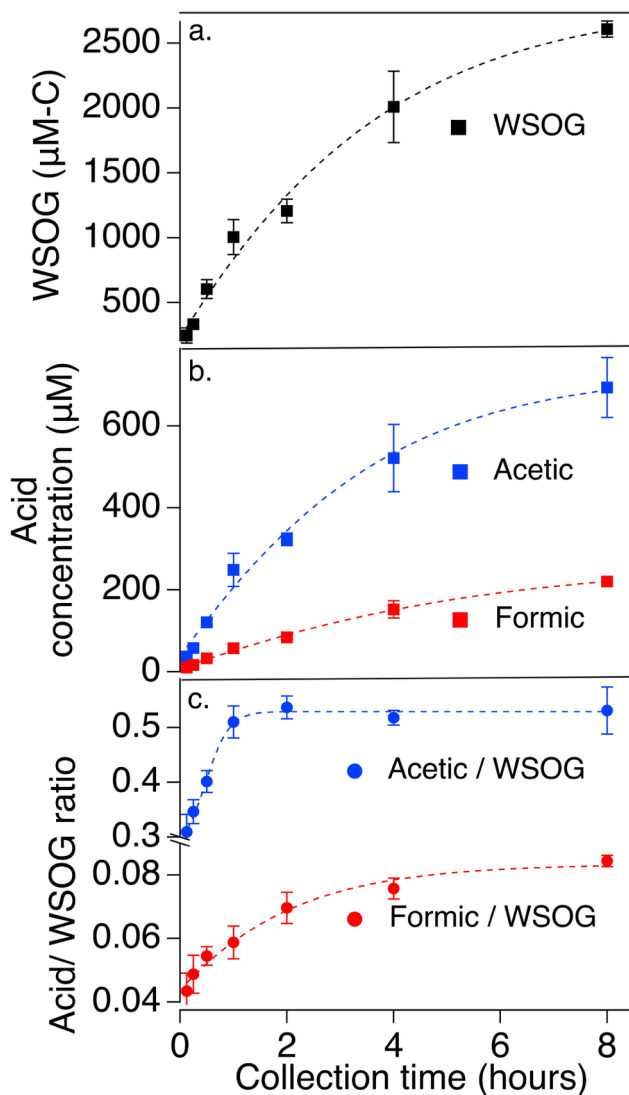

Figure 3-2. a) Total water-soluble organic gas concentration (WSOG in μM – carbon) in mist chamber water versus collection time. The mixture is approaching Henry's law equilibrium after 8 hours. b) Acetic and formic acids also increase with sample time. c) Acetic and formic acids as a ratio to WSOG concentration related to sample time. Note: acetic acid has two organic carbons so it's collected concentration is multiplied by two giving it a higher percentage of the total mixture.

glyoxal (H=4,000,000 M/atm)) than less water-soluble compounds (Spaulding et al.,

2002). Ultimately, we chose a 2-hour sampling time to balance competing considerations.

Longer times provide higher concentration samples and mixtures weighted by water

solubility. Shorter samples provide higher collection efficiencies and more composited

sample volume for replicate analyses.

Collection efficiency was determined for 2-hour

sampling times by placing two sets of paired mist

$$Eq\ 3-3\!: CE = 1 - \frac{C_2}{C_1}$$

chambers in series (four mist chambers total, 10 repetitions, order of mist chambers

switched after each test). Collection efficiency was calculated by Equation 3-3 as derived

in the SI of Spaulding et al. 2002 and takes into consideration breakthrough through the backup mist chamber as well as through the first one in series
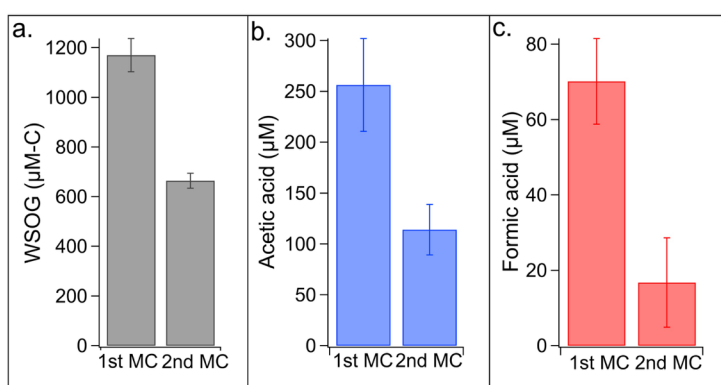
Figure 3-3. "MC" = mist chamber a) WSOG concentrations in first and second mist chamber in series. b) Acetic acid concentrations in first and second mist chamber in series. c) Formic acid concentration in first and second mist chamber in series.

(Spaulding et al., 2002). For these mist chambers, the collection efficiency was 43

± 10% for WSOG, 55 ± 4% for acetic acid, and 76 ± 5% for formic acid (Figure 3-3 a-c).

Once the collection efficiency of the mist chambers is known, the gas phase carbon

concentration can be calculated. Concentrations are provided below and in Table 3-1.

3.5 Results

Figure 3-4. Contribution of acetic and formic acids (on a carbon basis) to total organic carbon collected.

Organic acids account on average (and range) for 49% (21 - 65%) of the WSOG, on a carbon basis, across all homes. Acetic acid contributed on average (and 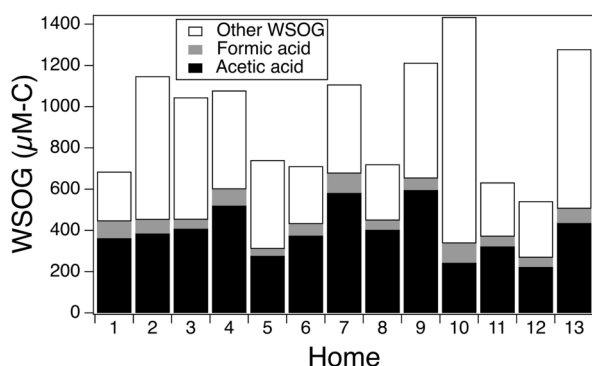range) 42% (18 - 53%) of total water-soluble organic carbon; formic acid contributed on average (and range) 7% (3 - 12%) (Figure 3-4). Despite the fact that lactic acid was difficult to quantify with ion chromatography, the molecular weight of lactic acid was detected in negative mode ESI-MS, which aligns with other evidence of the prevalence of lactic acid indoors from human sources (Liu et al., 2017). Also sulfate peaks were quantified and chlorine peaks were detected in each sample, but where not highlighted in this work since they do not add to the organic carbon mass. Using the determined collection efficiencies, the average gas-phase WSOG concentration (and range) for all homes is 145 µg - C/m^3 (84 – 215 µg - C/m^3), while the average gas phase (and range) of acetic acid and formic acid concentrations are 57 µg/m^3 (34 – 87 µg/m^3) and 10 µg/m^3 (6 – 16 µg/m^3), respectively. These concentrations are within previously measured ranges (Liu et al., 2017 and references therein).

Because our IC analysis was designed to detect organic acids, we used positive mode ESI-MS to characterize the remaining mass. In negative mode ESI-MS, negative ions are generated by H-atom abstraction, which preferentially identifies organic acids. In

the positive mode, alcohols, carbonyls, peroxides and reduced nitrogen species are ionized by addition of a hydrogen or sodium ion.

Figure 3-5a, shows a number balance of elemental formulas detected via positive mode ESI-MS in each home. A total of 13 – 40 elemental formulas were detected in any given home, with a mean of 27 and median of 28. The majority of the detected ions were CHO compounds (67%). In addition, on average, 22% of the detected ions were nitrogen-containing (11% CHN and 11% CHNO). Since these were detected in the positive mode, these

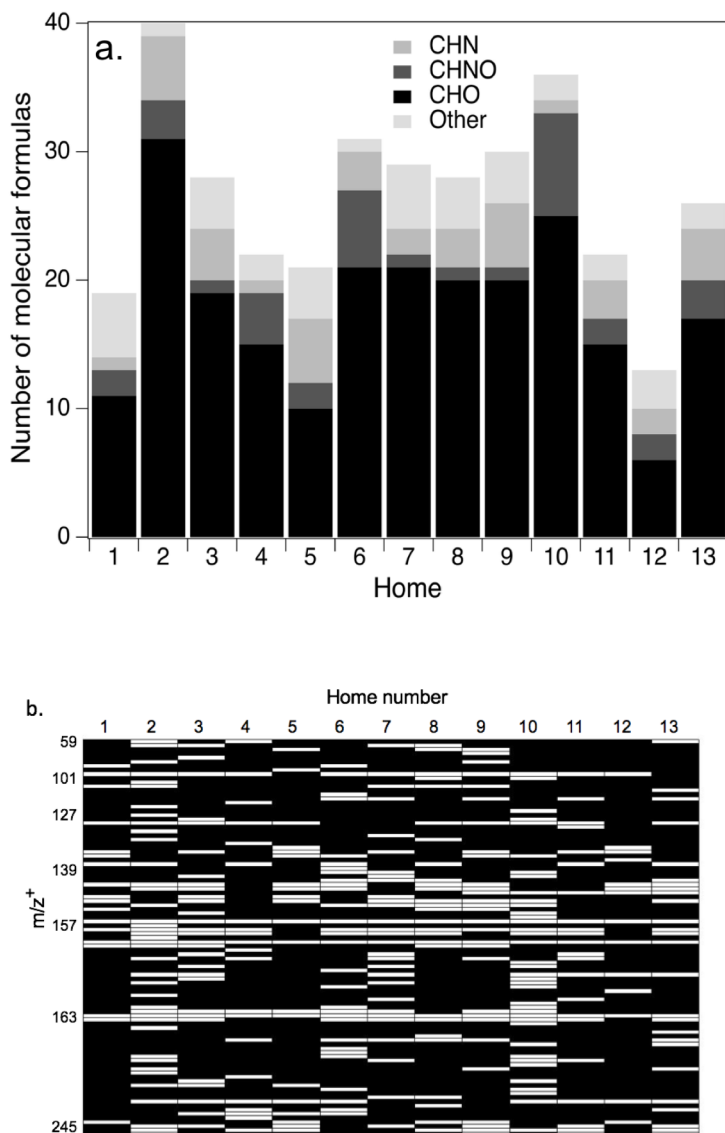Figure 3-5. a) Number of ions detected by home and by compound class: CHO, CHN, CHNO and "other." Other includes chlorine, phosphorous and sulfur-containing ions. b) Individual ions (m/z+) detected by home shown in white, from m/z+ 59 to m/z+ 245. In some cases, two to four ions represent a single compound ionized in one case with H$^+$ and the other with Na$^+$ and/or ionized as isotopes of the same compound (see Table 4-2).

are presumably reduced nitrogen compounds. Ions containing chlorine, phosphorus, and/or sulfur were also detected (11%, labeled "other" in Figure 3-5a). The average nitrogen-to-carbon ratio and oxygen-to-carbon ratio for the all homes was 0.25 and 0.31, for ions detected via positive mode ESI-MS, respectively.

Figure 3-5b shows that there was considerable variability across homes. A total of 98 distinct ions were detected across all homes across the m/z^+ range of 59.049 to 245.079. Some ions represent the same molecular formula as compounds may be ionized by either H^+ or Na^+ and can be isotopes (see table 3-2). Only 3 ions were detected in every home: m/z+ 157.084 ($C_6H_{14}O_3 + Na^+$, consistent with: diproplyene glycol, $H=1.8x10^5$ M/atm), 163.133 ($C_8H_{18}O_3 + H^+$), and 185.115 ($C_8H_{18}O_3 + Na^+$), both consistent with: diethylene glycol monobutyl ether (H = 15 M/atm).

Table 3-2, lists all elemental formulas detected via positive mode ESI-MS. It is quite possible that multiple water-soluble compounds with the same elemental formula could exist in the indoor environment. It is also likely that some compounds (aldehydes) are present in their hydrated form. Since there was methanol in the mobile phase, they could be hydrated either with H_2O or CH_3OH. In addition, although the ESI fragmentor voltage was optimized to avoid this, some molecular formulas may be adducts. For example, $C_{12}H_{22}O_2$ is not likely exist in the gas phase or to be water-soluble and is more likely to be an adduct of two smaller ions. In many cases, a detected elemental formula corresponds with a compound that is likely to be found indoors from reasonable sources; in those cases, the probable compound was listed.

Subgroup	Formula	m/z+	Ionization ion	n	DBE	Reasonable compound
	C_3H_6O	59.049	H^+	3	1	Acetone
	$C_3H_6O_3$	113.021	Na^+	1	1	
	$C_3H_8O_2$	99.042	Na^+	11	0	Propylene glycol
	$C_4H_6O_2$	87.044	H^+	1	2	
	$C_4H_6O_4$	141.016	Na^+	3	2	
	C_4H_8O	73.065	H^+	4	1	2-Butanone
	$C_4H_8O_2$	89.060	H^+	2	1	Ethyl acetate
	$C_4H_8O_3$	127.037	Na^+	2	1	Methyl lactate
	$C_4H_{10}O_3$	129.053	Na^+	10	0	Diethylene glycol
	$C_4H_{10}O_2$	113.058	Na^+	5	0	1,4-Butanediol
	$C_4H_{10}O_3$	107.070	H^+	5	0	Diethylene glycol
	$C_5H_8O_2$	101.060	H^+	3	2	4-Oxopentanal
	$C_5H_8O_3$	139.037	Na^+	1	2	
	$C_5H_{10}O_3$	119.070	H^+	3	1	Ethyl lactate
		141.053	Na^+			
	$C_5H_{12}O_3$	143.068	Na^+	5	1	Trimethylolethane
	$C_6H_{12}O$	101.097	H^+	1	1	2-Hexanone
	$C_6H_{12}O_2$	117.091	H^+	1	1	Ethyl butyrate
	$C_6H_{12}O_3$	155.068	Na^+	2	1	
	$C_6H_{12}O_4$	171.063	Na^+	3	1	
	$C_6H_{14}O_2$	141.089	Na^+	4	0	2-Butoxyethanol
	$C_6H_{14}O_3$	135.102	H^+	13	0	Dipropylene glycol
		157.084	Na^+			
		158.087	Na^+			
	$C_6H_{14}O_4$	173.078	Na^+	2	0	Triethylene glycol
	$C_7H_{14}O_2$	131.107	H^+	2	1	Amyl acetate
	$C_7H_{12}O_4$	161.081	H^+	3	1	Diethyl malonate
		183.063	Na^+			
CHO	$C_7H_{16}O_3$	149.117	H^+	10	0	Di(propylene glycol) methyl ether
		171.099	Na^+			
		172.103	Na^+			
	$C_8H_{14}O_4$	175.096	H^+	3	2	Diethyl succinate
		197.078	Na^+			
	$C_8H_{16}O$	129.127	H^+	1	1	Octanal
	$C_8H_{16}O_2$	167.104	Na^+	3	1	Hexyl acetate
	$C_8H_{16}O_3$	183.099	Na^+	8	1	
	$C_8H_{18}O_3$	163.133	H^+	13	0	Diethylene glycol butyl ether
		164.136	H^+			
		185.115	Na^+			
		186.118	Na^+			
		187.120	Na^+			
	$C_9H_{18}O_4$	191.128	H^+	2	1	
		213.110	Na^+			
		214.114	Na^+			
	$C_9H_{20}O_3$	199.131	Na^+	1	0	
	$C_{10}H_8O_3$	177.054	H^+	2	7	
	$C_{10}H_{18}O_2$	171.139	H^+	2	2	γ-Decanolactone
	$C_{10}H_{22}O_3$	191.164	H^+	12	0	Diethylene glycol hexyl ether
		213.146	Na^+			
		214.149	Na^+			
		215.151	Na^+			
	$C_{10}H_{22}O_4$	207.159	H^+	3	0	

	$C_{11}H_{22}O_3$	203.164	H$^+$	1	1	
	$C_{12}H_{22}O_2$	199.168	H$^+$	3	2	
		200.172	H$^+$			
CHN	$C_3H_8N_6$	129.088	H$^+$	1	3	Cyclic amine
	$C_4H_6N_2$	83.060	H$^+$	3	3	Methylimidazole
	$C_5H_8N_2$	97.076	H$^+$	1	3	
	$C_5H_{12}N_6$	157.12	H$^+$	1	2	
	$C_6H_{12}N_4$	141.113	H$^+$	9	4	Hexamethylenetetramine
		142.116	H$^+$			
	$C_6H_{12}N_6$	169.120	H$^+$	5	4	
	$C_7H_8N_4$	171.064	Na$^+$	1	6	
	$C_8H_{10}N_6$	191.104	H$^+$	1	6	
	$C_9H_{18}N_4$	205.143	Na$^+$	2	3	
	$C_{11}H_{12}N_4$	223.096	Na$^+$	7	8	
CHNO	C_3H_7NO	96.042	Na$^+$	2	1	Dimethylformamide
	$C_3H_8N_2O$	111.053	Na$^+$	1	1	Dimethylurea
	$C_4H_4N_6O_2$	169.047	H$^+$	1	6	
	C_4H_7NO	86.060	H$^+$	1	2	Methacrylamide
	C_5H_9NO	123.061	Na$^+$	1	2	N-Methyl-2-pyrrolidone
	$C_5H_{10}N_6O_2$	187.094	H$^+$	1	4	
	$C_6H_6N_6O_2$	195.063	H$^+$	1	7	
	$C_6H_8N_6O$	181.084	H$^+$	1	6	
	$C_6H_{11}NO$	114.092	H$^+$	7	2	Caprolactam
		136.074	Na$^+$			
	$C_6H_{13}NO_2$	132.102	H$^+$	1	1	Leucine
	$C_6H_{15}NO_2$	134.117	H$^+$	2	0	Diisopropanolamine
	$C_7H_{10}N_6O$	195.100	H$^+$	1	6	
	$C_7H_{10}N_6O_2$	211.094	H$^+$	1	5	
	$C_7H_{12}N_6O$	197.115	H$^+$	4	5	
	$C_7H_{14}N_6O_2$	215.126	H$^+$	4	4	
	$C_8H_{12}N_6O$	209.114	H$^+$	2	6	
	$C_9H_{19}NO_2$	174.149	H$^+$	1	1	
	$C_{12}H_{17}NO$	192.138	H$^+$	2	5	Diethyltoluamide (DEET)
Other	$C_2H_3Cl_3O_2$	164.927	Na$^+$	1	0	
	$C_3H_5O_2PS$	158.964	Na$^+$	9		Organophosphate
	$C_4H_3ClN_2O$	131.001	H$^+$	1	4	
	C_5H_5OP	134.997	H$^+$	7	4	Formylphosphole
		136.000	H$^+$			
	C_6H_5OP	146.997	Na$^+$	4	5	Oxo(phenyl)phosphine
	C_6H_7OP	149.012	Na$^+$	8	4	
		150.016	Na$^+$			
	$C_7H_{11}N_2O_4P$	219.054	H$^+$	5	5	

Table 3-2. lists all formulas that were identified within 5 ppm using ESI-MS. Some compounds appeared multiple times due to detection of C_{13} and C_{14} isotopes and their ionization with hydrogen and nitrogen ions. n depicts the number of homes a molecule was detected in and DBE shows the number of double bond equivalents that that molecule has. If that molecular formula corresponded to a compound or compound class that is likely to be indoors, it was listed (note, many of these have yet to be measured indoors, (Duncan et al., 2018)).

3.6 Discussion

Like non-polar VOCs, recent measurements suggest that polar VOCs (WSOGs) are elevated inside homes compared to outside homes (Duncan et al., 2018). Currently, little is known about the chemical makeup and gas-phase concentrations of WSOG indoors. These compounds are of particular interest because their fates will be different from that of non-polar VOCs. In particular, they will likely participate in aqueous chemistry indoors. Indoors, RH can be quite high (see table 3-1) allowing liquid water to condense as thin films on surfaces, in wet particles, on occupant skin, and also as condensed water in air conditioning systems, toilet bowls, in kitchens during cooking, and bathrooms during bathing (Duncan et al., 2018). Oxygenated VOCs tend to be "stickier" due to their functional groups, so their loss rates to surfaces, especially at increasingly high RHs will likely increase. The first step in understanding the sources, sinks, and significance of WSOG indoors is identifying what they are. To our knowledge, this research is the first effort to conduct a mass balance on WSOG-carbon in homes.

Organic acids (acetic, lactic, and formic acids) accounted for on average 49% (range = 21 – 65%) of the total WSOG, on a carbon basis, collected in each home. These acids are quite water-soluble (acetic acid: H = 4,000 M/atm, formic acid: H = 8,000 M/atm, lactic acid: H = 12,000 M/atm (Sander, 2015)) and are ubiquitous indoors. Acetic and formic acids, released from off-gassing of household products, building materials, and candle burning, as well as formed from ozone oxidation reactions at carbon-carbon double bonds, have been measured extensively indoors using analytical techniques such as HPLC in the range of 8.8 to 216 $\mu g/m^3$ and 3.0 to 62 $\mu g/m^3$ respectively (Destaillats et al., 2006; Reiss et al., 1995; Zhang et al., 1994). Lactic acid, released from human

perspiration, was recently measured in a university classroom at concentrations of 0.92 -
27 $\mu g/m^3$ (Liu et al., 2017).

Substantially more chemical complexity was found via ESI-QTOF-LC/MS
analysis, which provided elemental formulas for detected masses. Some detected masses
were consistent with the molecular formulas of compounds likely to be found in indoor
air. For example, some compounds such as acetone (C_3H_6O), ethyl acetate ($C_4H_8O_2$), and
dipropylene glycol ($C_4H_{10}O_3$, Table 3-2) diethylene glycol butyl ether ($C_8H_{18}O_3$) are
common solvents (California Air Resources Board) and caprolactam ($C_6H_{11}NO$) is a
known plastic degradation product (Tokiwa et al., 2009). Additional compounds are
known microbial VOCs (MVOCs) such as 2-butanone (C_4H_8O), 2-hexanone ($C_6H_{12}O$),
and octanal ($C_8H_{16}O$) (Korpi et al., 2009). Some are present in foods such as flavorings
and additives such as ethyl butyrate ($C_6H_{12}O_2$), and amyl acetate ($C_7H_{14}O_2$) (Jenner et al.,
1964; United States Food and Drug Administration, 2014) or are formed from Maillard
chemistry in food such as methylimidazole ($C_4H_6N_2$) (Moon & Shibamoto, 2011). Also,
the molecular formulas consistent with pesticides and insect repellents such as DEET
($C_{12}H_{17}NO$) were detected in some homes. Finally, 4-oxopentanal ($C_5H_8O_2$) is a major
skin lipid decomposition product (Wisthaler & Weschler, 2010).

Thirty individual molecular formulas, or about 30% of those detected contained
nitrogen. Since they were detected in the positive mode of ESI-QTOF-LC/MS, they are
reduced nitrogen species, likely amines. You et al. detected C1-C6 amines indoors at the
pptv level, much higher than levels in outdoor air (You et al., 2014). Indoors, ammonia is
released from human sweat and breath, as well as from house pets and cleaning products
(Sutton et al., 2000); other amines are emitted from sources such as tobacco smoke,

kitchen and human waste, and cooking (Ge et al., 2011) or secondarily formed from ammonia reactions (Seinfeld & Pandis, 2006). The presence of reduced nitrogen species indoors (amines and imidazoles) are likely to be a key difference in gas phase and interfacial chemistry than that of outdoor air.

This work supports the hypothesis that WSOGs are abundant indoors and that their presence likely participates in indoor chemistry (Duncan et al., 2018). Some molecular formulas and organic acids are associated with compounds that have been measured indoors, (acetic acid and formic acid), while some are associated with compounds from likely emission sources (octanal, acetone, ethyl acetate), and some are likely to be formed indoors through secondary gas phase chemistry (butanone, 2-butoxyethanol) (Duncan et al., 2018).

Future work needs to be conducted to further identify these compounds, their concentrations, and their sources and fates. Additional method development utilizing HPLC to separate small oxygenated organic molecules that can then be measured in the ESI positive mode would be helpful in identifying some of these compounds. Also targeted methods utilizing derivatization of mist chamber samples could be utilized. As these compounds are oxygenated and water-soluble, their fate indoors will be different than those of non-polar VOCs. They will likely be taken up into liquid water indoors in thin aqueous films on surfaces and in wet particles (especially in damp homes), into condensate from cooking, bathing, and air conditioning systems, into bulk water in toilets and sink traps, as well as onto skin and in the respiratory tract of occupants (Duncan et al., 2018). In liquid water indoors, these compounds will likely react and form new products, some of which may be released back into the gas phase. Ultimately,

identification and quantification of these WSOGs as well as knowledge of their

subsequent aqueous chemistry products will improve our understanding of inhalation and

dermal exposures indoors.

3.7 Limitations

While WSOG inherently must be oxygenated in order to be water-soluble and

therefore be collected by the mist chambers, additional oxidation could occur during

collection if oxidants are scrubbed into the mist chambers as well. While hydroxyl radical

is too reactive to make it into the mist chamber (Ingham et al., 2009), some ozone will be

collected. Ozone will react with unsaturated compounds in the aqueous phase at the

carbon-carbon double bond (Yao & Haag, 1991) and may form hydroxyl radicals to

further aqueous oxidation of collected compounds (Hoigné & Bader, 1976, 1983). It is

possible that acetic and formic acid is produced during collection from ozone or hydroxyl

radical oxidation (when ozone is present), but this will only happen if a larger unsaturated

water-soluble organic compound is scrubbed in addition to ozone. The magnitude of

aqueous phase oxidation of WSOG is unknown, but likely to be minimal.

Electrospray ionization efficiency is compound class dependent. For example,

amines are easily ionized while aromatic alcohols are not as easily ionized. Thus, relative

abundance does not indicate relative contribution to total WSOG, and some compounds

(such as amines) will be detected at lower concentrations than others. Additionally, while

we can separate by exact mass and thus know the elemental composition of the ion,

several compounds may have the same elemental composition. Further, a single

compound may be observed as several ions. For example, glyoxal (MW: 58 g/mol)

appears ionized with Na^+ and hydrated twice with water and/or methanol (m/z^+ 117, 131,

and 145). Also, some compounds may exhibit evidence of isotope ionization, such as the detection of $C_6H_{14}O_3$ leading to m/z$^+$ 157 and 158 (see table 3-2).

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Chapter 4. Dynamics of residential oxidized organic gases: Insights into sources and sinks

In preparation for journal submission

4.1 Abstract

United States residents spend on average 70% of their time in their homes, and recent results suggest that water-soluble organic gases are elevated in homes. However, the sources, sinks and concentration dynamics of indoor polar, (and often water-soluble) volatile organic compounds (oxygenated VOCs, OVOCs) are quite limited. We used an iodide chemical ionization mass spectrometer (I^-CIMS) to measure OVOCs in a North Carolina home over the course of several days. Integrated and supporting measurements collected in this and 13 additional homes suggested that this home was not unusual. Acetic, formic and lactic acid concentrations measured by I^-CIMS ranged from 30-125, 15-50 and 2.5 to 13.5 $\mu g/m^3$, respectively, daily. Each time the central air conditioner (AC) began cooling the home, acetic and formic acid concentrations decreased 30-50%, suggesting substantial losses to wet surfaces in the AC system. The AC uptake rate for acetic acid was 1.0 - 1.5 hr^{-1} and for formic acid was 1.5 - 2.0 hr^{-1}. Lactic acid concentrations appeared to be mostly impacted by human activity and cooking. On the molecular level, 11 other compounds were detected that cycle with AC operation. Several OVOCs were observed that had primarily outdoor sources while others had primarily indoor sources. OVOCs and possible sources are discussed.

4.2 Introduction

Recent integrated measurements of 13 homes demonstrated that water soluble

organic gases are higher inside homes than directly outside those homes (15 times higher,

on average) (Duncan et al., 2018). Approximately one-half of this material (on a carbon

basis) was comprised of organic acids – specifically acetic, lactic and formic acids.

According to the National Human Activity Pattern Survey, on the population level in the

United States, people spend almost 70% of their time in their residences (Klepeis et al.,

2001). It is known that concentrations of non-polar volatile organic compounds (VOCs)

are also much higher indoors than outdoors (Wallace et al., 1987). However, there is little

real-time data on indoor air composition, especially data for oxygenated and water-

soluble VOCs (OVOCs). Real-time OVOC concentration dynamics can provide valuable

insights into the sources, sinks, chemical processing of and exposures to indoor OVOCs.

Only recently have real-time mass spectrometric methods been applied to

measurement of indoor polar organic gases. Liu et al. (2016) detected masses (elemental

formulas) consistent with formaldehyde, methanol, acetaldehyde, ethanol, acetone, and

propanol in a university classroom using proton-transfer-reaction mass spectrometry

(PTR-MS, also known as H_3O^+ chemical ionization mass spectrometry (CIMS)) (Liu et

al., 2016). Concurrently, the same group measured organic acids using acetate chemical

ionization mass spectrometry (acetate-CIMS) in the same classroom setting. They found

that lactic and formic acids indoors were 5 to 10 times outdoor concentrations (Liu et al.,

2017). Tang et al. 2016 also used PTR-MS to measure VOCs in another university

classroom and found humans to be the dominant source of VOCs (Tang et al., 2016).

PTR-MS has also been used to study real time emissions in an occupied movie theatre

(Williams et al., 2016) and an amine-CIMS detected amines in a field trailer during an outdoor sampling campaign (You et al., 2014).

In this work, we examine the concentration dynamics of OVOCs in indoor air using an I⁻ CIMS deployed in one home during the humid southeastern US summer. We compare this home with 13 others through the use of integrated samples and supplemental measurements. We perturbed the indoor environment during sampling, i.e., through cooking, cleaning, opening windows, increasing occupancy, and increasing human activity. Outdoor measurements were also made for comparison. The resulting data provide quantitative insights into residential sources and sinks for several prominent OVOCs. Resulting loss rate coefficients may prove useful for indoor modeling.

4.3 Methods

4.3.1 Field sampling and site characterization

Sampling occurred at a two-story single-family home in Chapel Hill, North Carolina from 8:00 am to 5:00 pm on July 18 – 23, 2017. The home (built in 1999) had a floor area of 180 m^2, air volume of 490 m^3, and surface area to volume ratio of 1.6 m^2/m^3 (neglecting furniture). The home was in a planned residential community with trees and far from industrial emissions sources. The flooring in the home consisted of hard wood with area throw rugs. A new area rug was placed in the sampling area to protect the homeowner's floors (which was allowed to off-gas near the laboratory for two weeks prior to sampling). The house was heated with natural gas (although not used during sampling), while the stove was electric. There was an exhaust fan that vented inside of the house that was used approximately one-third of the time when cooking on the stove. There were two house cats present in the house during sampling. Insecticide roach baits

were present under the kitchen sink and typical consumer products such as scented cat litter, chlorine-based dishwashing detergent, and ammonia-based glass cleaner were used in the home regularly.

Table 4-1 displays the daily activities that took place during sampling. During the first day, referred to as a "background" day, technicians were present but care was taken to avoid activities with VOC emissions. The second was a no occupancy day, with the exception of occasions of instrument servicing. A substantial portion (5 hours) of the next day was high occupancy, followed by a day when the windows were open and the central air conditioner (AC) was off for 2.5 hours. On subsequent days (7/22/17 and 7/23/17), cleaning and cooking were performed three times at equal intervals during the day. Table 4-1 also provides measured air exchange rates for each day. The average air exchange rate for all sampling days (except for the period in which the windows were open) was 0.3 ± 0.08 h^{-1}. The air exchange rate when the windows were open was 2.2 h^{-1}.

Date	Perturbation	Activities	Measured air exchange rate (h^{-1})
7/18/17	Background (no purposeful perturbations)	3 people in home during the day, no food cooked, personal care or cleaning products used	0.19
7/19/17	No occupancy	Approximately every 30 minutes, one or two technicians entered the home to manage equipment and sampling	0.37
7/20/17	High occupancy (7-8 people)	Time - Occupancy 8:00 – 11:00 am 2 11:00 am – 1:00 pm 8 1:00 – 4:00 pm 7 4:00 – 5:00 pm 2 Periods of high physical activity (running, jumping, dancing): 12:38 - 12:42 pm, 2:06 - 2:12 pm, 3:32 - 3:38 pm	0.4

			0.23 before windows open (2.2 when windows open)
7/21/17	Windows open/ AC off	Windows open and AC off: 11:30 am - 2:00 pm (outdoor sampling one hour later)	
7/22/17	Cleaning (Windex to clean front face of kitchen appliances, then Pledge to clean front face of kitchen cabinents, then Chlorox to clean kitchen countertops)	Episode 1: 9:09 - 9:11am window cleaner 9:11 - 9:13 am wood polish 9:20 - 9:22 am bleach Episode 2: 12:23 - 12:28 pm window cleaner 12:33 - 12:38 pm wood polish 12:43 - 12:47 pm bleach Episode 3: 3:06 - 3:12 pm window cleaner 3:17 - 3:21 pm wood polish 3:26 - 3:31 pm bleach	0.34
7/23/17	Cooking (four strips of bacon then 1 quarter of medium yellow onion cooked in remaining bacon grease)	Episode 1: 9:13 - 9:28 am bacon frying 9:28 - 9:33 am onion frying Episode 2: 12:03 - 12:14 pm bacon frying 12:14 - 12:18 pm onion frying Episode 3: 3:03 - 3:17 pm bacon frying 3:17 - 3:20 pm onion frying	n/a

Table 4-1. Perturbations/ activities during sampling days. Air exchange rates are also provided (air exchange rate for 7/23/17 not available).

All sampling was conducted at 0.5 to 1 m away from the wall in the eat-in-kitchen in the main living area of the home. Auxiliary measurements were taken approximately 3 m away in the adjacent living room which was not separated from the eat-in-kitchen by any walls. Bulk room temperature and relative humidity (RH) were recorded in minute intervals by an Extech SD800 CO_2/ humidity/ temperature data logger (Extech, Nashua, New Hampshire). In order to better understand the cycling on and off of the AC system, a HOBO UX100-023 external temperature/RH data logger (Onset Computer Corporation,

Borne, MA) was placed in an air supply vent in the living room (10 cm from the exterior wall) and measured temperature and RH in minute intervals. When the AC system cycled on, the temperature dropped and the RH rose. When the AC system cycled off, the temperature rose and the RH dropped. Therefore, these temperature and RH measurements provided a surrogate indicator for the cycling of the AC syst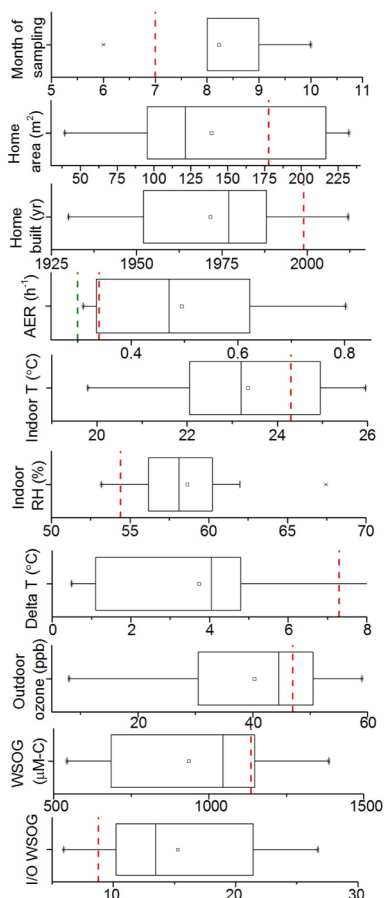em. Ozone was also measured every minute with a Model 202 Ozone Monitor (2B Technologies, Boulder, Colorado). Outdoor temperature and RH were reported from nearby Chapel Hill Williams Airport, Chapel Hill, NC. NOAA Climatological data station and 8-hour max outdoor ozone were from Durham Armory, Durham, NC. Figure 4-1 depicts the indoor temperature, RH, and indoor ozone for one day during sampling.

Figure 4-1. Indoor and outdoor temperature, RH, and indoor ozone on a typical sampling day (7/19/17). The 8-hour max outdoor ozone concentration for this day was 51 ppb.

Air exchange was measured using carbon dioxide as a tracer using the same Extech SD800 CO_2/ humidity/ temperature data logger (American Society for Testing and Materials International, 2011). Carbon dioxide was released into the return air vent of the home until the concentration at the Extech meter reached approximately 3000 ppm. The CO_2 concentration was allowed to decay for several hours and then more CO_2 was released. This was repeated two or three times each day (except for 7/23/17 when CO_2

Figure 4-2. Box plots depicting the maximum, minimum, interquartile range, and mean of all respective parameters reported from the first 13 sampled homes. The dashed red lines display where the parameters for this home fall within the range of the other homes. For air exchange rate, the measured value is depicted in green (for other homes, air exchange rate was only calculated). For this home, all parameters measured and calculated values fell within the range of those respective values from the prior 13 homes. Six out of ten values fell within the interquartile range.

was not available). Air exchange rate was determined by regressing the natural log of the concentration ($C(t)$) minus the background concentration (C_{back}) over the initial concentration (C_0) minus the background concentration against time (Equation 4-1) (American Society for Testing and Materials International, 2011). Air exchange rates ranged from 0.19 to 0.4 h^{-1} during sampling (except for 7/21/17 when windows were open during sampling and the air exchange rate increased to 2.2 h^{-1}, Table 4-1).

$$\text{Eq } 4-1: \; -\ln\left(\frac{C(t)-C_{back}}{C_0-C_{back}}\right) = \lambda t$$

In order to ensure that this sampled home is reasonably representative of other homes, the home was compared with 13 other homes in which we previously measured integrated samples of total water soluble organic gases (WSOG) (Duncan et al., 2018) (Figure 4-2). The red dashed lines represent the home sampled in this study on 7/18/17; the box plots describe the range of values for the 13 homes sampled previously. Parameters included month of sampling, calculated home area, and calculated air exchange rate using the method of Chan et al. (Chan et al., 2005; Hodas et al., 2014), indoor temperature,

RH, the difference in indoor to outdoor temperature, and outdoor ozone. Since air exchange rate was *measured* in this home (in addition to being calculated), the green dashed line represents the measured value. Based on this comparison, we conclude that the home environment sampled and discussed herein is reasonably comparable (with respect to the WSOG, AER and other properties) to this larger set of east coast (summertime) home environments. Home area, calculated air exchange rate, indoor temperature, outdoor ozone, and WSOG concentration were all within the interquartile range (25 – 75%) of all values. The month of sampling, indoor RH, indoor/ outdoor change in temperature, and indoor/ outdoor WSOG ratio were all within the total range of the other homes, but were outside of the interquartile range.

4.3.2 Integrated sampling

Water soluble organic gases (WSOGs) were collected in an integrated fashion with mist chambers as described in detail previously (Duncan et al. 2018). Briefly, water-soluble organic gases were scrubbed out of the air at 25 L/min into a refluxing water mist produced from 25 mL of bulk water. Samples were collected inside and directly outside the homes. They were analyzed for organic compounds with exact mass resolution using accurate-mass Quadrupole Time-of-Flight Liquid Chromatography/Mass Spectrometry with an Electrospray Ion Source (ESI-QTOF-LC/MS, Agilent 6520, Agilent Technologies, Santa Clara, California). This data was used to provide additional validation of OVOC compound detection. Negative-mode ESI-QTOF-LC/MS indicates the presence of on organic acid group, while positive-mode ESI-QTOF-LC/MS indicates the presents of alcohols, carbonyls, peroxides, and amine compounds. Detailed ESI-QTOF-LC/MS method parameters are provided in chapter 3. Briefly, samples were

directly injected into the instrument at 0.2 mL/min and underwent soft ionization

(fragmentor voltage = 40 V)

4.3.3 Real time sampling

A high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-

CIMS, (Tofwerk AG, Thun, Switzerland)) was operated in negative mode at two second

intervals to measure OVOCs. The HR-TOF-MS was operated in V mode with a mass

resolution of $m/\Delta m \sim 4000$. Ultra-high purity N_2 (Airgas) was used to flush (2 L/min)

through a heated (40 °C) permeation tube containing methyl iodide (CH_3I, Sigma

Aldrich). CH_3I was then ionized in a ^{210}Po source and introduce in the ionization region

set at a pressure of 80 mbar. The instrument was placed on a sturdy table inside the main

living area of the home and used without inlet tubing, so that air could be pulled directly

into the instrument at 2 L/min. For 20 minutes at approximately 8:00 am and 2:00 pm

each day, a 2 m length ¼ in (O.D.) polytetrafluoroethylene (PTFE) inlet (residence time <

1s) was connected and run directly outside the nearest window to sample outside. For

comparison and to understand inlet tubing losses, indoor sampling was also conducted for

an additional 20 min with identical inlet tubing. Then the tubing was removed and

sampling continued directly into the CIMS with no inlet tubing. (No significant signal

differences were detected indoors with or without the inlet tubing). After instrument set

up in the field and prior to sampling, single ion area tuning and m/z calibrations were

performed. Daily, the baseline and threshold were maintained in order to ensure

instrument performance. The CIMS was calibrated for formic, acetic, and lactic acids,

and imidazole before, during, and after sampling. An ultra-high purity N_2 (Airgas) field

blank was conducted twice during sampling for a duration of 20 minutes each. Data was

analyzed in TOFware Igor Pro software, Version 7.04 (TOFwerk, AG, Thun,

Switzerland; WaveMetrics, Portland, Oregon).

4.4 Results

On a typical ("background") day with no purposeful perturbations (Table 4-1), real-time acetic and formic acid concentrations
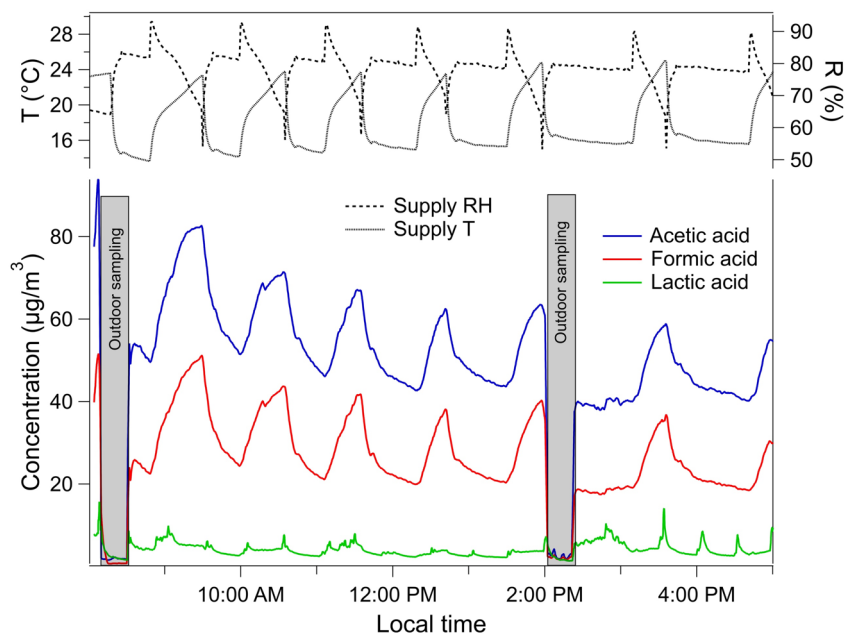
Figure 4-3. Acetic, formic, and lactic acids concentrations and temperature and RH at the central air supply vent during one sampling day (7/19). When the temperature decreased and RH increased abruptly, acetic and formic decreased drastically as well indicating organic acid uptake into the air conditioning system.

concentrations fluctuated in a cyclic fashion

approximately hourly (Figure 4-3), dropping to 30-40% and 40-50% of their peak values,

respectively. The precipitous drops in supply vent temperature and simultaneous

increases in supply vent RH indicate that the AC system turned on, introducing cold air at

the supply vents and pulling room air into AC ducts at the return vents. When the AC

turned off, temperature gradually increased leading to a decrease in RH. The steep drops

in acetic and formic acid concentration correspond to steep drops in the AC supply

temperature (and increase in supply RH), once the AC turned on and began scrubbing

these acids out of the air. To our knowledge, this is the first definitive evidence of OVOC

losses in an AC system. We expect that these highly water-soluble compounds (H =

4,000 M/atm for acetic acid, 8,000 M/atm for formic acid, and 12,000 M/atm for lactic

acid (Sander, 2015)) are taken up by water condensed in the AC ducts and/or in the AC

condensate. There is a suggestion of similar cycling in the lactic acid signal, but lactic

acid appeared to be more influenced by nearby human emissions than air conditioning

cycles. Indoor concentrations of acetic and formic acids for all sampling days varied

greatly from 30 – 125 $\mu g/m^3$ and 15 – 50 $\mu g/m^3$, respectively (Appendix B, Figure B2-

1). Lactic acid typically fluctuated between 3 and 5 $\mu g/m^3$ and peaked as high as 25

$\mu g/m^3$ with increased occupancy, increased occupant physical activity, and technician

proximity to the sampling inlet. During cooking events, lactic acid reached 360 $\mu g/m^3$

(Figure 4-6). Comparatively, outdoor concentrations of these acids were 1 to 6 $\mu g/m^3$ for

acetic acid, 0.8 to 2.2 $\mu g/m^3$ for formic acid, and 0.5 to 2.5 $\mu g/m^3$ for lactic acid,

suggesting that these acids are dominated by indoor sources. (Limits of detection for

acetic, formic, and lactic acids are 0.15 $\mu g/m^3$, 0.025 $\mu g/m^3$, and 0.14 $\mu g/m^3$,

respectively, calculated as the mean + 3σ of the blank.)

     With reasonable assumptions, indoor source and AC uptake rates were estimated

for acetic and formic acids using the mass balance equation in Equation 4-2,

$$Eq\ 4-2: \frac{dc}{dt} = C_{out}p\lambda - C_{in}\lambda + S/V - C_{in}u$$

where V is the volume of the house, $\frac{dc}{dt}$ is the change in indoor concentration over the

change in time, C_{out} is the outdoor concentration, C_{in} is the indoor concentration, p is the

penetration efficiency, λ is the air exchange rate, S is the source strength, u is the uptake

rate coefficient for loss to the AC system plus other losses. If one assumes that acetic and

formic acids have leveled off at the top of the first peak daily (e.g. at 9:28 am on 7/19/17

when the AC is off, Figure 4-3), the system can be assumed to be at steady state. When

the AC is off, u is 0. P can be assumed to be 1 since the outdoor concentration is small

compared to the indoor concentration and thus the term containing P is small (Figure 4-

3). Assuming u is also 0, Equation 2 simplifies to Equation 3 to solve for the source

strength:

$$Eq\ 4-3\colon S = (C_{in} - C_{out})\lambda V$$

The source strength for acetic and formic acid is 12.5 ± 3.7 mg/h and 5.8 ± 1.2 mg/h

respectively. These values for S represent a lower bound, as u likely isn't 0.

Using these source strengths, Equation 4-2 can be solved analytically to Equation

4-4 to estimate the AC uptake rate (u).

$$Eq\ 4-4\colon C_t = \frac{S}{V(\lambda + u)} + \frac{P\lambda}{(\lambda + u)} \times C_{out} + \left(C_0 - \frac{S}{V(\lambda + u)} - \frac{P\lambda}{(\lambda + u)}\right)^{-(\lambda+u)\times t}$$

Here, we assumed that the majority of u can be attributed to AC uptake. With this

method, u is approximately 0.2/h for both acetic and formic acids (see Appendix B,

Figure B3-1). Given the lower bound values for S, u is also minimized. Table 4-2

provides values for u as S is doubled and doubled again.

Acetic acid		Formic acid	
S (mg/h)	u (/h)	S (mg/h)	u (/h)
12.5	0.2	5.8	0.2
25	0.7	11.6	0.6
50	1.6	23.2	1.4

Table 4-2. Values for u for acetic and formic acid as S increases.

In addition to acetic, formic, and lactic acids, 20 additional elemental formulas were measured. Eleven additional compounds (elemental formulas) were characterized on the molecular level with signals that also cycled with the air conditioner (Figure 4-4a). These compounds are all oxidized with at least two oxygen atoms with oxygen-to-carbon (O:C) ratios between 0.3 and
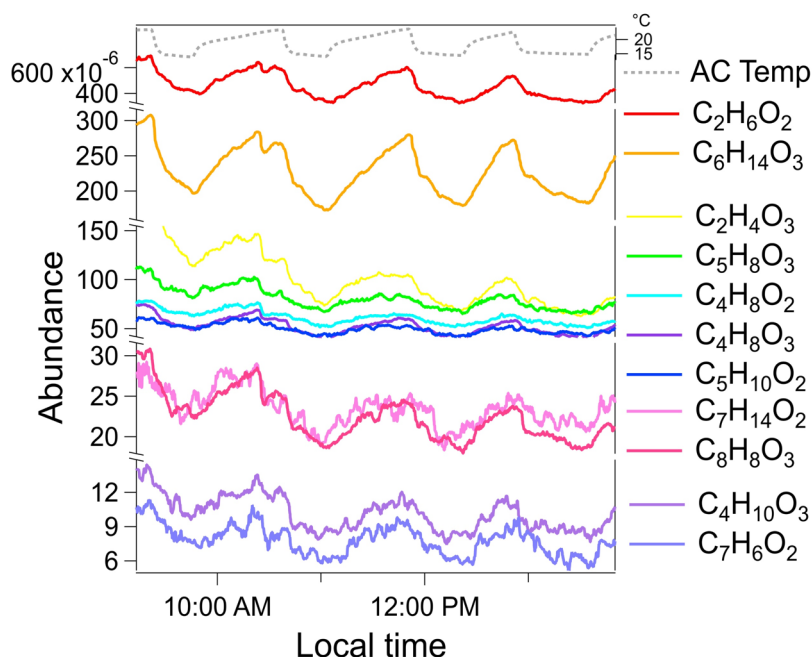
Figure 4-4 a. Additional molecular formulas fluctuate with the air conditioning cycle (7/18/17). Here, CIMS signals are shown as 2 min rolling average
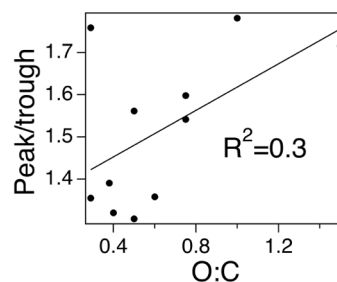
b. In general ratio of the maximum intensities to their subsequent minimum intensities of each cycle positively correlated with the O:C ratios of each of the detected

1.5. Thus, they are highly likely to be water-soluble, with high Henry's law constants. Their O:C ratios are weakly positively correlated with the drop in signal intensity when the AC turns on (Figure 4-4b, ratio of signal intensity immediately before the AC turns on (e.g. 9:45 am on 7/18/17) to signal intensity immediately before the AC turns off (e.g. 10:23 am, see Table 4-3)). We expect that compounds that are more water-soluble will be

preferentially taken up by the AC system condensate. (Possible identities for these compounds are discussed further in the discussion.)
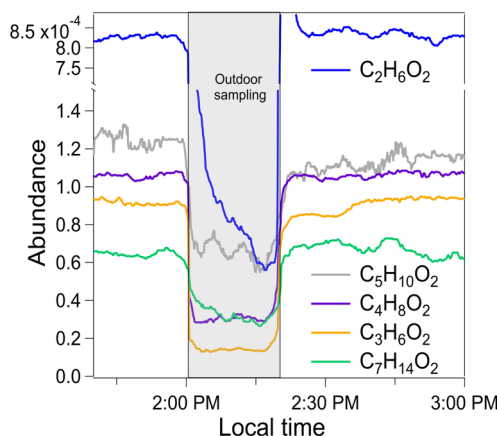
Figure 4-5 a. (7/23/17) Molecular formulas of compounds that are higher in concentration indoors than outdoors.
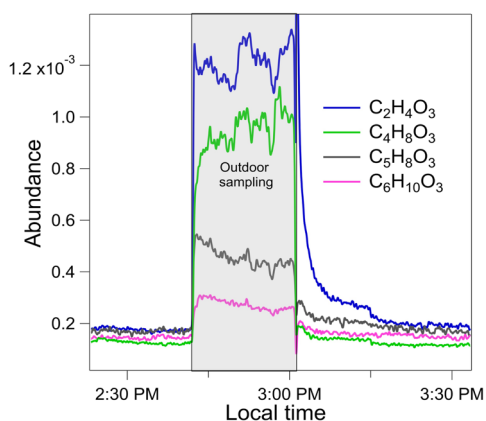
b. (7/20) Molecular formulas of compounds that are higher in concentration outdoors than indoors.

Some compounds were dominated by indoor sources (Figure 4-5a), while other compounds had primarily outdoor sources (Figure 4-5b). In Figure 4-5a, when outdoor sampling was conducted, the signal for these compounds dropped substantially. Indoor-to-outdoor ratios (I/O) are reported for these compounds in Table 4-3. I/O ratios ranged from 1.8 to 6.6 for compounds dominated by indoor sources. In general, lower carbon numbers and higher O:C ratios corresponded to higher I/O ratios (C3 and C4 at 6.6 and 3.5 respectively), while higher carbon numbers corresponded to lower I/O ratios (C5-C8, about 2). This may be because smaller oxidized compounds are being formed indoors

through surface or gas phase oxidation of larger compounds in addition to being emitted directly.

For compounds dominated by outdoor sources (Figure 4-5b) indoor-to-outdoor ratios (I/O) spanned from 0.12 to 0.56 (Table 4-3). For these compounds, lower carbon

numbers and higher O:C ratios tended to have higher O/I ratios (C2 and C4, 6.1 and 8.1

respectively) than higher carbon numbers with lower O:C ratios (C5 and C6, about 2). In

part, this might reflect higher losses with outdoor-to-indoor transport (lower P values) for

more oxidized VOCs predominately formed/emitted outdoors. While there are some

primary sources of OVOCs outdoors (e.g. wood burning), outdoor OVOCs are generally

formed in the atmosphere through gas phase photochemical reactions. Note that

compounds identified with higher concentrations outdoors have three oxygen atoms

while compounds with higher concentrations indoors have two oxygen atoms (Figures 4-

5 a and b). This is likely because of higher oxidant concentrations and longer residence

times in outdoor air led to a greater degree of VOC oxidation (Figure 4-1). (These

compounds also increased in abundance during the "open windows event" (see SI

Molecular formula	O:C	Context	Peak/ trough	Indoor/ outdoor
$C_2H_4O_3$	1.5	AC cycle, outdoor elevated	1.7	0.16
$C_2H_6O_2$	1	AC cycle, indoor elevated	1.8	9.8
$C_3H_6O_2$	0.67	Indoor elevated	-	11.5
$C_4H_8O_2$	0.5	AC cycle, indoor elevated	1.3	4.2
$C_4H_8O_3$	0.75	AC cycle, outdoor elevated	1.5	0.12
$C_4H_{10}O_3$	0.75	AC cycle	1.6	-
$C_5H_8O_3$	0.6	AC cycle, outdoor elevated	1.4	0.39
$C_5H_{10}O_2$	0.4	AC cycle, indoor elevated	1.3	8.5
$C_6H_{10}O_3$	0.5	Outdoor elevated	-	0.56
$C_6H_{14}O_3$	0.5	AC cycle	1.6	-
$C_7H_6O_2$	0.29	AC cycle	1.8	-
$C_7H_{14}O_2$	0.29	AC cycle, indoor elevated	1.4	2.1
$C_8H_8O_3$	0.38	AC cycle	1.4	-

Table 4-3. Molecular formulas of compounds detected by I⁻CIMS, oxygen-to-carbon ratios, context of identified molecular formulas, peak-to-trough ratios of compounds that cycle with the AC (Figures 4-4 a and b), indoor-to-outdoor ratios for figures 4-5 a and b. Compounds elevated outdoors are shaded in orange, while compounds elevated indoors are shaded in blue.

On one sampling day, the indoor environment was perturbed by cooking a meal of bacon and onions three times during the day. Seventeen molecular formulas were detected

Figure 4-6. Compounds emitted during cooking events.
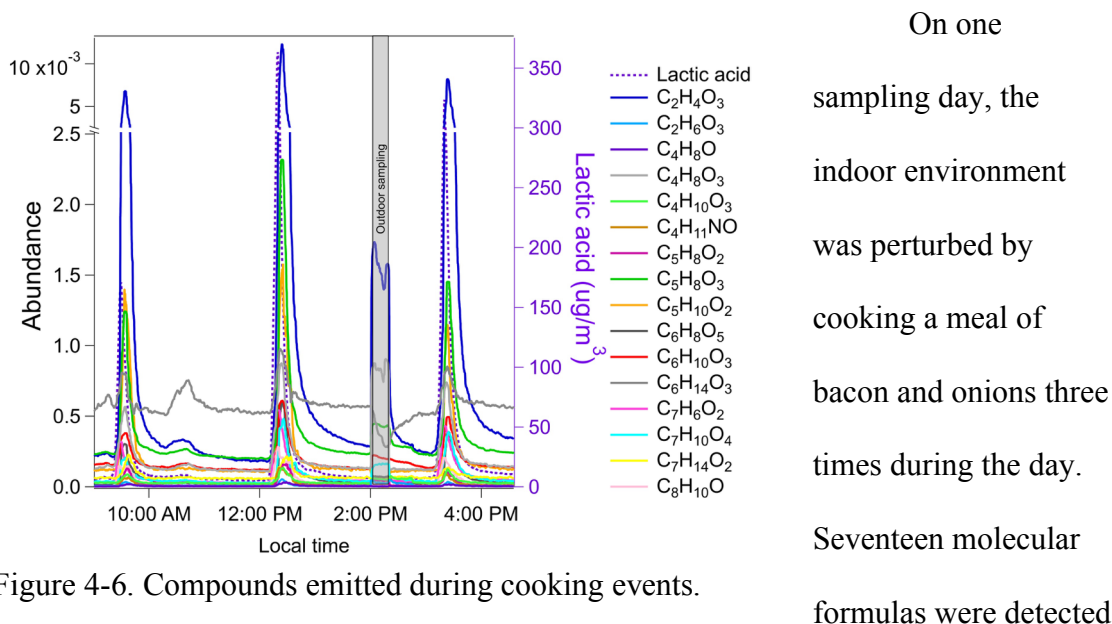
that peaked with the cooking of the meal, suggesting substantial emissions of those compounds during cooking (Figure 4-6). (AC influences were minimal compared to cooking influences). Lactic acid, $C_7H_6O_2$, and $C_8H_{10}O$ all peaked first, while there was a slight lag in the peak time for some compounds (e.g., C_4H_8O, $C_5H_8O_2$, $C_7H_{14}O_2$) which might occur because the onions were fried after the bacon. Alternatively, the lag could occur if these compounds were products of secondary chemistry. Note that some of these molecular formulas (i.e., $C_5H_{10}O_2$ and $C_7H_{14}O_2$ from Figure 5a; $C_2H_4O_3$ and $C_4H_8O_3$ from Figure 4-5b) are also emitted or formed via other sources indoors or penetrate from outdoors (Figures 4-5a and b). During cleaning events, many chlorinated compounds were detected (supplementary information, Figure 6). These results support the results published in Wong et al, 2017 (Wong et al., 2017).

4.5 Discussion

This paper provides new insights into OVOCs in homes in real time. First acetic, formic, and lactic acids were quantified, and their concentration dynamics provided insights into sources and sinks under realistic conditions in a home in the southeast during the summertime. Many other compounds (elemental formulas) were detected; sources and losses were similarly explored. The AC system was identified as a substantial loss mechanism for OVOCs in homes, presumably through uptake into wet ductwork and the AC condensate.

4.5.1 Quantification of organic acids

Acetic acid and formic acid concentrations measured here (30 – 125 $\mu g/m^3$ and 15 – 50 $\mu g/m^3$, respectively, see Appendix B, Figure B2-1) are within the range of integrated concentrations measured previously in other indoor locations (9 – 200 $\mu g/m^3$ and 3 – 60 $\mu g/m^3$, respectively; Liu et al. 2017 and references therein). Liu et al. (2017) measured formic acid in a university classroom in real time, but detected much lower concentrations (0.4 to 6.5 $\mu g/m^3$) (Liu et al., 2017). However, until now, highly time resolved measurements of acetic acid has not been conducted indoors. Concentrations of acetic and formic acids exhibited an approximately one hour cycle, dropping by 30 - 40% and 40 - 50%, respectively, (Figure 4-3) with the cycling of the AC system on. The rapid drop in concentration corresponded precisely with the drop in AC supply temperature, indicating initiation of AC cooling. In addition to acetic and formic acids, 11 other compounds also exhibited cycling with the AC. To our knowledge, this is the first time this behavior has been reported.

In the summertime in the southeastern United States the air is particularly hot and humid. Many homes utilize central air conditioning to cool their homes and when the AC system turns on, heat is exchanged from the warm, moist air to the refrigerant in the evaporator coils, thereby cooling the air. This cooling results in the condensation of substantial amounts of water. In this home, about 2.2 ± 0.2 L of water vapor was condensed in the air conditioning system during one cooling cycle (calculated from temperature-dependent saturation vapor pressures). While most of this water will be present in the condensate tray, water is also likely to be sorbed to duct surfaces. Because dramatic acetic and formic acid losses correspond precisely with the onset of AC cooling, it appears that liquid water present in the air conditioning system is the major sink for these water-soluble acids; these losses are substantially larger than exfiltration (indoor-to-outdoor air exchange). While we did not see definitive evidence to support this, it is possible that aqueous chemistry could take place in water sorbed to AC ducts and present in the condensate pan. If so, volatile products would be released, in part, with subsequent water evaporation. Thus, the AC system could be a source as well as a sink of indoor OVOCs.

Lactic acid, which is a human effluent (Yokoyama et al. 1991), ranged from between 2.5 to 13.5 $\mu g/m^3$ on a typical day with low occupancy and increased up to 25 $\mu g/m^3$ with higher occupancy and increased activity (7-8 people, Appendix B, Figure B2-2). Lactic acid concentrations are quite sensitive to human activity, resulting in spikes when a technician approached the sampling area. Lactic acid concentrations were highest during cooking. During the three cooking events of bacon, onions, and eggs lactic acid increased from 5 - 6 $\mu g/m^3$ to 170, 360, and 320 $\mu g/m^3$ during the three events,

respectively (Figure 4-6). Although, to our knowledge, this is the first time that lactic acid concentrations have been measured in indoor air during cooking events, these spikes are not surprising since lactic acid is a major component of red meat (Egan, 1983).

4.5.2 Characterization on the molecular level

Since I⁻CIMS is capable of detecting a wide range of polar organic gases, we expected to measure compounds not previously detected in homes. These compounds were characterized by exact mass (elemental composition) and were confirmed by concurrent collection in mist chambers and analysis by ESI-MS (positive and negative modes) or were proposed by Liu et al., 2017) (Using acetate-CIMS to measure acids in a university classroom).

Several compounds were dominated by indoor sources rather than outdoor, as evidenced by a substantial drop in ion abundance when measuring outdoors. They are $C_3H_6O_2$, $C_4H_8O_2$, $C_5H_{10}O_2$, $C_7H_{14}O_2$, $C_8H_8O_3$ (Figure 4-5a). $C_3H_6O_2$ was also measured in the negative mode of ESI-MS, which is selective for organic acids, and is likely propionic acid. It has a primarily indoor source with an I/O ratio of about 7. $C_3H_6O_2$ was also detected in real time by Liu et al., 2017 and reported to be propionic acid, although indoor concentrations for this compound were not reported there or elsewhere in the literature, to our knowledge. $C_4H_8O_2$, also detected in ESI negative mode, is likely butyric acid and is also a constituent of total monoacids reported in Liu et al., 2017. $C_5H_{10}O_2$ is also elevated indoors. It is present in the ESI negative mode, so is likely 3-methybutanoic acid, which is produced naturally from humans (Lee et al., 1997). $C_7H_{14}O_2$ is detected in both the positive and negative mode in ESI-MS and therefore may be heptanoic acid or an acetate with an ester group. Finally, $C_8H_8O_3$ was detected in the

ESI negative mode. Given that it has a double bond equivalent of 4, it is likely a benzene ring with acid and alcohol functional groups, such as an anisic acid.

Other detected compounds had higher outdoor concentrations and therefore concentrations of these compounds in this home were predominately of outdoor origin. Four molecular formulas meeting this criteria were: $C_2H_4O_3$, $C_4H_8O_3$, $C_5H_8O_3$, $C_6H_{10}O_3$ (Figure 4-5b). $C_2H_4O_3$, very likely to be glycolic acid (Warneck, 2003), has an outdoor to indoor ratio of 6. $C_4H_8O_3$ was detected in positive mode ESI and may be methyl lactate. $C_5H_8O_3$, consistent with oxopentanoic acid, may be an oxidation product of isoprene since it has five carbon atoms. Liu et al., 2017 detected $C_5H_8O_3$ in a university classroom and reported it as oxopentanoic acid with

concentrations of 30 to 90 ppt. $C_6H_{10}O_3$ was also detected in Liu et al., 2017, and quantified as oxohexanoic acid with concentrations reported between 0.027 to 0.12 $\mu g/m^3$.

Given that these compounds are elevated outdoors compared to indoors, assuming the source strength indoors is negligible and the penetration efficiency is 1, the decay rate coefficient can be determined by rearranging equation 2 to equation 4-5. However, given that these compounds are more oxygenated and "sticky" their penetration efficiencies may be less than one and equation 4-5 should be expanded to include p as in equation 4-6. The decay rate coefficients for $C_2H_4O_3$, $C_4H_8O_3$, $C_5H_8O_3$, $C_6H_{10}O_3$ with p=1, 0.8, and 0.5 are provided in Table 4-4. Depending on the compound, for p=0.8, the value of k decreases by $0.1 - 0.5$ hr $^{-1}$ from p=1, and for p=0.5, the value of k decreases by $0.3 - 1.6$

hr $^{-1}$ from p=1. Further work needs to be conducted to determine penetration efficiencies

small oxidized organic compounds.

Molecular formula	p	k
$C_2H_4O_3$	1	2.1
	0.8	1.6
	0.5	0.8
$C_5H_8O_3$	1	0.6
	0.8	0.4
	0.5	0.1
$C_6H_{10}O_3$	1	0.3
	0.8	0.2
	0.5	<0
$C_6H_{10}O_3$	1	2.8
	0.8	2.2
	0.5	1.2

$$Eq\ 4-5: \frac{C_{in}}{C_{out}} = \frac{\lambda}{\lambda + k}$$

$$Eq\ 4-6: \frac{C_{in}}{C_{out} \times p} = \frac{\lambda}{\lambda + k}$$

During the three cooking events of bacon, sweet onion, and eggs, 15 definitive peaks increased substantially and then decayed quickly with time after cooking. The molecular formulas for those peaks were: $C_3H_6O_3$ (lactic acid), $C_2H_4O_3$, $C_2H_6O_3$, C_4H_8O, $C_4H_8O_3$,

Table 4-4. Influences of penetration efficiencies (p) on reaction rate constants (k) of compounds with outdoor elevated concentrations.

$C_4H_{10}O_3$, $C_4H_{11}NO$, $C_5H_8O_2$, $C_5H_8O_3$, $C_5H_{10}O_2$,

$C_6H_8O_5$, $C_6H_{10}O_3$, $C_6H_{14}O_3$, $C_7H_6O_2$, $C_7H_{10}O_4$, $C_7H_{14}O_2$,

$C_8H_{10}O$. Glycolic acid ($C_2H_4O_3$) is a byproduct of

photosynthesis (Benson and Calvin, 1950), and may be released during the cooking of the

onions.

C_4H_8O, $C_4H_8O_3$, $C_4H_{10}O_3$, $C_4H_{11}NO$, $C_5H_8O_2$ and $C_8H_{10}O$ were all detected in

the ESI-MS positive mode, so are therefore likely to be alcohols, aldehydes, or amines.

$C_5H_8O_3$ and $C_6H_{10}O_3$ are likely oxopentanoic and oxohexanoic acids, respectively (these

are also measured outdoors). Oxopentanoic acid is likely formed from the degradation of

cellulose while cooking onions (Girisuta et al., 2007), while oxohexanoic acid may be a

byproduct from the degradation of larger fatty acids produced in meat cooking (Zhao et

al., 2007). $C_5H_8O_2$ and $C_6H_8O_5$, both detected in the ESI-MS negative mode, are acids

and may be other byproducts of metabolism. $C_7H_6O_2$, $C_7H_{10}O_4$ and $C_7H_{14}O_2$ also peaked during the cooking events, although their exact structures remains speculative at this point.

4.6 Conclusion

This research provides new insights into OVOCs in residential indoor air. The central air conditioning unit was found to have a significant impact on concentrations of many of these OVOCs. While many OVOCs had primarily indoor sources, some had primarily outdoor sources. Cooking and higher occupancy increased concentrations of several compounds. These compounds are likely to participate in aqueous chemistry in air conditioning condensate and/ or aqueous chemistry on damp surfaces, such as walls, carpeting, and human skin and the respiratory tract. Loss rate coefficients estimated herein may be useful inputs to indoor air models that will help to further explore indoor chemistry and determine indoor exposures.

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Chapter 5: Discussion

5.1 Summary of research

Oxidized volatile organic compounds (OVOCs) and specifically water-soluble organic gases (WSOG) indoors have been largely understudied despite their likely prevalence (Duncan et al., 2018; Weschler, 2011). The following information, while important, was previously unknown:

1. The concentrations and composition of indoor WSOG.

2. The relative contributions of outdoor and indoor sources to indoor WSOG.

3. The sources and fate of WSOGs indoors, including in damp homes.

The results herein represent a major step forward in our understanding of WSOGs indoors.

Chapter 2 makes use of the existing literature to provide insights into WSOGs (Henry's law constants greater than 1 M/atm) measured or likely to be present in U.S. residences. This work included a literature review of 517 articles conducted in Scopus that yielded residential measurements of 23 water-soluble organic compounds. To this, WSOGs from common emission sources such as cooking, human effluents, and mold and mildew were added. Finally, additional WSOGs were proposed to be formed indoors as a result of oxidation chemistry, based on smog chamber and indoor chemistry studies.

Chapter 2 documents, for the first time, the substantial enhancement of total WSOG inside homes relative to concentrations immediately outside, suggesting that there are major sources of WSOGs in homes. I measured total WSOG on an organic carbon basis in 13 real homes. On average, total WSOG was 15 times higher indoors than outdoors in sampled homes (Figure 2-1). If one assumes that all WSOG originating

outdoors comes indoors, then 85% of WSOG indoors is of indoor origin (Duncan et al., 2018). This is a lower bound estimate, since WSOG are oxidized and "sticky," so therefore unlikely to penetrate indoors with 100% efficiency.

Subsequently, Chapter 2 elucidates the case for WSOGs to participate in aqueous chemistry on indoor surfaces in damp homes. Considering 20 – 50% of homes in the United States are considered damp, liquid water is likely to be present in homes, especially homes in the southeastern U.S. in the summer. Surface area-to-volume ratios are much higher in homes than outdoors (>3 m^2/m^3 and ~ 0.01 m^2/m^3, respectively) and even a 1 nm aqueous film would provide about a 1000 times as much liquid water per volume indoors as there is in a typical outdoor environment (Duncan et al., 2018). It is known that aqueous chemistry alters outdoor air composition (Ervens et al., 2011). While indoor liquid water concentrations are uncertain, the large surface-to-volume ratios, high indoor humidities and demonstrated examples of relevant chemistry suggest that aqueous chemistry is also likely to alter indoor air composition. Chapter 2 provides the motivation to explore WSOG and aqueous chemistry indoors further.

Chapter 3 documents the chemical characterization of WSOG samples collected in the same 13 real homes. To my knowledge, this is the first effort to close the mass balance on indoor WSOG. Using ion chromatography, I found that organic acids (acetic, lactic, and formic) accounted for about half of the WSOG carbon mass. In order to characterize the remainder, I used positive mode ESI-MS. In total, 98 additional molecular formulas were identified across all homes. 67% of the molecular formulas represented CHO compounds, 22% were either CHON or CHN, and 11% contained other atoms including chlorine, phosphorus, and/or sulfur. The number of molecular formulas

detected in each home ranged from 13 – 40, with a large inter-home variability among molecular formulas detected (Figure 3-5b). When molecular formulas matched compounds previously measured or expected indoors, those possible identifications were provided. Some molecular formulas match with common solvents, flavorings and food additives, plasticizers, insecticides and insect repellents, and skin lipid decomposition products.

Chapter 4 details the real-time measurement of several OVOCs (and many WSOG) in a real home using iodide chemical ionization mass spectrometry (I⁻CIMS). Sampling was conducted under different conditions such as "background," "no occupancy," "high occupancy," "open windows," "cooking," and "cleaning." A main finding from this study was the dramatic effect of the air conditioner (AC) system on WSOG concentrations. Acetic and formic acid concentrations decreased by 30 – 50% from their peak concentrations at the onset of air conditioning. Once the AC cycled off, these acids were either emitted back into the home air and/or concentrations resumed their increase as their sources stayed the same and this major sink turned off. Several other compounds also exhibited this cycling in time with the AC. Since it was summer in the southeast, the weather was hot and humid leading to many cycles of the AC and much water condensation upon bulk air cooling. As a result of this work, I was able to provide the first estimated loss rates for acetic and formic acids into the AC system (i.e. AC condensate and ducts). Once scrubbed into liquid water in the AC system, these compounds will likely undergo reactions similar to "dark" reactions in atmospheric water at night such as acid-catalyzed chemistry involving nucleophilic attack of protonated carbonyl and epoxide groups (McNeill, 2015). Some of the products of these reactions

may volatilize back into the gas phase upon liquid water evaporation, some will remain in the condensed phase and form organic films on the interior of the AC system and duct work, while others will be removed entirely through condensate drainage.

Some measured compounds were found to have dominant indoor sources while others had dominant outdoor sources (as illuminated by short periods of outdoor air sampling). Also, many compounds were released during cooking and cleaning events. Lactic acid, a human effluent (Yokoyama et al., 1991), spiked when a technician approached the instrument and also increased when occupancy and occupant physical activity increased. Indoor/outdoor ratios, and loss rate coefficients were calculated whenever requisite data was available.

5.2 Influences on WSOG concentrations and makeup

A common question when presenting this work was "How is indoor WSOG affected by x, y, or z?" The sample size of thirteen homes during the first field campaign is too small to statistically determine many of these influences such as location, season, time of day, and occupant activities. During the second field campaign, only one home was sampled, but under different conditions such as high occupancy and cooking which provides some insight into the impact of certain occupant activities on WSOG. Despite the statistical limitations of this work, inferences can be made on how various factors can affect WSOG concentration, chemical makeup, and aqueous chemistry indoors.

One major factor is season. In this work, WSOGs were solely sampled during the summer and early fall seasons in the eastern part of the United States (June 2015 in New Jersey and August to early October 2015 in North Carolina). In general, ozone concentrations are higher during the summer (Fishman et al., 2003), resulting in

increased oxidation chemistry and thereby the formation of WSOGs indoors. Conversely, in the winter, ozone concentrations are generally lower (Fishman et al., 2003), so the potential for oxidation chemistry is decreased. On the east coast of the United States, absolute and relative humidities will also be affected by season. In the summer, warmer air has a higher saturation vapor pressure than cool air leading to absolute increases in the amount of condensed water upon indoor air conditioning. During cool months, homes with water vapor sources such as occupants and steam radiators can lead to condensation in cooler areas of the home such as windows.

In the case of this work, sampling during both field campaigns was only conducted during daylight hours, however air properties and occupant activity is likely to change at night. Ozone often peaks in the late afternoon to evening before steadily decreasing overnight (Zhang et al., 2004) while NO_2 peaks after sunset (Mayer, 1999) leading to more WSOG formation. Cooking and other occupant activities generally increase after typical working hours before significantly decreasing during sleeping hours. Due to these factors and others, WSOG concentrations in homes are likely to be highly variable throughout the day and highly variable between different households.

Occupant activities will have a large influence on WSOGs. During the second field campaign impacts of some typical activities were explored (Chapter 4), such as cooking, cleaning, increase in occupancy, and opening windows. Frying bacon and onions was demonstrated to be a substantial source of WSOGs, however there are many different cuisines and cooking methods that will likely alter WSOG emissions. Using PTR-MS, Klein et al. (2016) identified many molecular formulas corresponding with carbonyls from a variety of different meats, fish, vegetables, and cooking oils (Klein et

al., 2016). Many people use various personal care products and cleaning compounds that

directly release WSOGs such as acetaldehyde and glycol ethers and form WSOG from

the oxidation of many released terpenes (Nazaroff & Weschler, 2004; Steinemann et al.,

2010). Finally, a huge influence on WSOG makeup that was not addressed in this work is

tobacco smoke emissions from cigarettes and e-cigarettes. Smoking of cigarettes and e-

cigarettes releases many WSOGs into the air such as carbonyls, glycols, and carcinogenic

nitrosamines (McAuley et al., 2012). Other factors may affect indoor WSOG

concentration and chemical makeup such as home type (apartment, duplex, or single-

family), socio-economic status (Chan et al., 2005), and climate region.

5.3 Exposure and health implications of WSOGs

With a median WSOG concentration of 170 µg/m^3 average daily doses for

inhalation and dermal pathways were calculated (Figure 5-1). These doses are maximum

doses since the assumptions consider that the person spends all of his or her time spent in

the home (24 hours/ day, 365 days/ year) and is exposed to a constant concentration of

170 µg/m^3 for the three age ranges considered: 70 years, 10 years, and 0.5 years. The

elderly, children, and infants are likely to be most susceptible to negative effects of

WSOG exposure.

Average daily doses (ADD) via the inhalation and dermal routes are calculated

using Equations 5-1 and 5-2 obtained from the United States Environmental Protection

$$Eq\ 5-1:\ ADD_i = \frac{C \times InhR \times EF \times ED}{BW \times AT}$$

$$Eq\ 5-2:\ ADD_d = \frac{DA \times SA \times EF \times ED}{BW \times AT}$$

$$Eq\ 5-3:\ DA = k_p \times C \times t$$

Agency's ExpoBox (United States Environmental Protection Agency, 2017). C is the

WSOG concentration in the air, *InhR* is the inhalation rate, *DA* is the adsorbed dose, *SA* is

the body surface area (assumed to be the entire body as these gases likely permeate

clothing (Weschler & Nazaroff, 2014)), *EF* is the exposure factor, *ED* is the exposure

duration, *BW* is the body weight, and *AT* is the averaging time. Adsorbed dose is

calculated in equation 5-3. k_p is the permeability coefficient, and *t* is time of exposure.

Values for these inputs are displayed in table C1-1 in Appendix C.

Dose calculation results are presented in Figure 5-1 for adults, children, and

infants exposed to 170 $\mu g/m^3$ of WSOG at three reasonable permeability coefficients: diethyl phthalate (DEP), $k_p = 3.4$ m/h; 4-oxopentanal (4-OPA), $k_p = 0.56$ m/h; and butanol, $k_p = 0.053$ m/h) (permeability coefficients retrieved from the SI of Charles J Weschler & Nazaroff, 2014). For the inhalation pathway, the average daily dose was higher the younger the
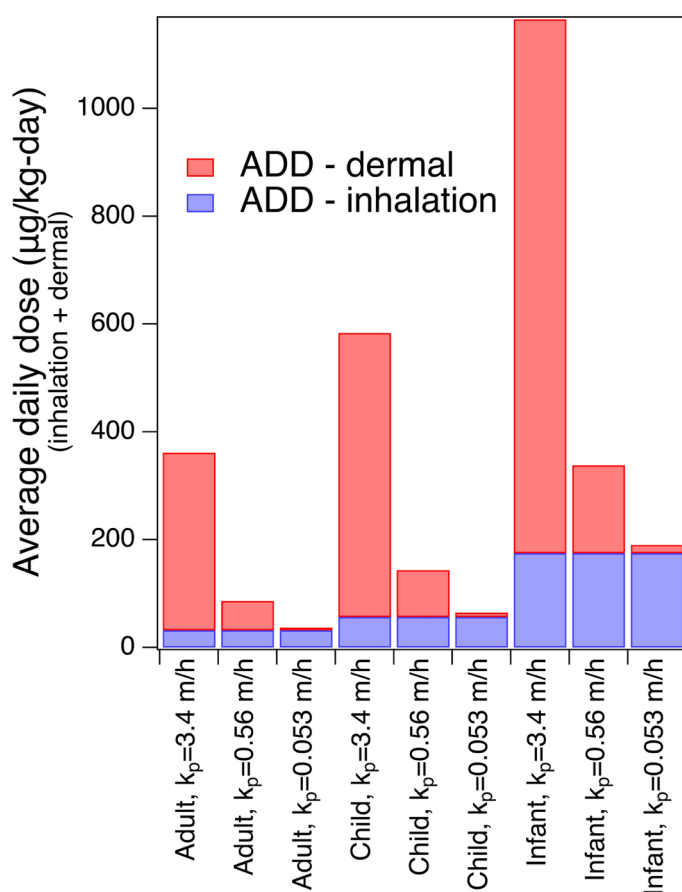
Figure 5-1 Average daily doses via the inhalation and dermal routes for three age groups.

occupant (32 µg/kg-day for 70-year-old adults, 57 µg/kg-day for 10-year-old children, and 175 µg/kg-day for 6-month-old infants). However, for the dermal pathway, the average daily dose was largely impacted by the permeability coefficient which thereby drove the overall magnitude of dose for each age group. For 70-year-old adults, total average daily dose was increased by 330 µg/kg-day when K_p = 3.4 m/h, while the dose was only 5 µg/kg-day when K_p = 0.053 m/h; for 10-year-old children, total average daily dose was increased by 530 µg/kg-day when K_p = 3.4 m/h, while only 8 µg/kg-day when K_p = 0.053 m/h; and for six-month old infants, total average daily dose was increased by 990 µg/kg-day when K_p = 3.4 m/h, while only 15 µg/kg-day when K_p = 0.053 m/h. Compounds which make up WSOG likely constitute a large range of permeability coefficients, therefore total average daily dose of WSOG is substantially dependent on K_p of each WSOG compound.

Although exact health implications of these WSOG mixtures are speculative at this point, health impacts from certain oxidized organic compounds that have been tentatively identified in this work have been studied. Health effects of carbonyls in particular are well known. Dicarbonyls and aldehydes, such as diacetyl, glyoxal, methyl glyoxal, 4-oxopentanoic acid, and glutaraldehyde have been found to increase cytokine levels in pulmonary epithelial cells and increase respiratory and dermal sensitivity in models (Anderson et al., 2007; Anderson et al., 2010). Due to their high water-solubilities (e.g. methyl glyoxal, an aldehyde), these compounds can dissolve in fluid in the respiratory tract, damp skin, and onto eyes. A study on microbial VOCs (many of which are water-soluble) reported prevalence of mucus symptoms of occupants in homes with elevated levels of 1-octen-3-ol (also preliminarily detected in this work, see Chapter 3)

(Araki et al., 2010). In addition to organic aldehydes and acids, water-soluble phthalates have been measured in high concentrations in indoor air and dust (Rudel et al., 2003) and are known endocrine disrupters which can easily cross the epidermis and enter the blood stream (Weschler & Nazaroff, 2012; Weschler & Nazaroff, 2014). Exposure to WSOGs will occur in aggregate. The potential health effects from exposures to WSOG are currently unknown and need to be explored to consider potential additive or synergistic effects.

5.4 Recent advancements in the field

Only quite recently has it become clear that human occupants have a major influence on indoor air chemistry (Weschler, 2016). It is now known that occupants are important sources of OVOCs indoors. Chemical ion mass spectrometry has recently become a common tool for the real-time study of atmospheric chemistry. During the course of this work, it has begun to be applied to the study of indoor air chemistry as well. Many compounds detected are associated with human emissions. For example, two recently published papers report measurements of many VOCs in a university classroom using PTR-MS (H_3O^+CIMS) and acetate-CIMS (Liu et al., 2016; Liu et al., 2017). In Liu et al., 2016, the authors used a PTR-MS to measure non-polar and slightly polar compounds of human influence. During the same study and in a subsequent paper, they reported concentrations of several organic acids measured with acetate-CIMS and their relationship to occupancy. They found that lactic acid as well as pyruvic acid, oxopentanoic acid, and other carboxylic acids increased in concentration with increased classroom occupancy (Liu et al., 2017). In another study of a university classroom (Tang et al., 2016), increased occupancy was associated with increases in isoprene (a reactive

terpene), acetone, 4-OPA, 6-MHO, and less so, but still significantly, geranyl acetone, hydroxyacetone (or propionic acid), 1,4-butanedial, and 5-hydroxy-4-oxopenanal. The authors found that 57% of total quantified VOC mass could be apportioned to human sources.

Evidence of how VOCs emitted by occupants affect ozone concentrations and form subsequent VOC – ozone oxidation products has also been documented. In a modeling study, where two occupants were sleeping in a bedroom, increases in air exchange rate (and therefore increases in infiltrated ozone) predicted increased concentrations of nonanal, decanal, and 4-OPA by 0.4, 0.6, and 0.6 ppb respectively (Kruza et al., 2017). Additional evidence has been provided for the scrubbing of ozone by occupants and the subsequent production of 6-methyl-5-hepten-2-one, acetone, geranyl acetone, 4-oxopentanal, and 1,4-butanedial (Lakey et al., 2017).

While previously thought to be insignificant, there is now substantial evidence that photolysis and radical chemistry play a key role in indoor chemistry. The most illuminating study is from Gómez Alvarez et al. who showed large increases in OH radicals with increases in nitrous acid (HONO, (Gómez Alvarez et al., 2013)) and indoor sunlight. They first showed that photolysis of HONO (during infiltrated sunlight events) is an important source of OH radicals indoors. They measured OH radicals up to 1.8 x 10^6 molecules/cm^3 (similar to outdoor urban air concentrations) during periods of direct sunlight through windows, while prior studies have only indirectly measured indoor concentrations up to an order of magnitude lower (Weschler & Shields, 1997; White et al., 2010). Recent models of OH radical chemistry indoors have shown OH radical concentrations increase from 0.2 – 2.1 x 10^5 molecules/cm^3 with no direct sunlight to 1.1

– 1.4 x 10^6 molecules/cm^3 during periods of open windows and then closed windows with direct sunlight (Mendez et al., 2017). HO$_2$ radicals also exhibited a similar time pattern, although they sometimes peaked after OH and with lower magnitude. The reported maximum HONO photolysis rate constant was 1.3×10^{-4}/s. Another recent study provided evidence for HO$_x$ radical production at the onset of surface cleaning in a computer classroom (Carslaw et al., 2017). Chlorine and OH radicals have also been shown to be produced during floor cleaning with bleach and infiltrated sunlight (Wong et al., 2017).

Additional work has recently been conducted that has provided insights into how these oxidants affect indoor chemistry, particularly by producing oxygenated VOCs (OVOCs) through surface and gas-phase oxidation. Waring and Wells performed indoor air chemistry simulations using various concentrations of ozone, OH radicals, NO$_3$ radicals and common VOCs. In these simulations, ozone and NO$_3$ radicals react mostly with terpenes and terpenoids at their carbon-carbon double bond, while OH reacts with a larger suite of VOCs forming carbonyls such as formaldehyde, acetone, acetaldehyde, and propanal; carboxylic acids such as acetic acid; hydroxyperoxyl and peroxy radicals; and other oxidized species (Waring & Wells, 2015). Some of these species will form secondary organic aerosol and partition to surfaces, while others will remain in the gas phase as OVOCs. New indoor air chemistry models are now coming online that will take into account HO$_x$ radicals, HONO, photolysis, OVOCs, surface chemistry, in addition to emissions and ventilation (Carslaw et al., 2017; Mendez et al., 2015).

Scientists are now more aware that surfaces indoors are crucial locations for indoor air chemistry. Even outdoors, interfacial chemistry happens on aerosol surfaces

despite the overall low relative surface area (<0.01 m^2/m^3), and it significantly alters the chemical makeup of outdoor air. Indoors, the surface area is much higher (greater than 3 m^2/m^3, (Morrison & Nazaroff, 2000; Singer et al., 2007)) suggesting that interfacial chemistry is much more important. Kruza et al. recently modelled C_6-C_{10} aldehyde production from surfaces as the result of ozone deposition. They concluded that wooden floors, hard furniture, countertops, and soft furniture are significant sources of these aldehydes. Their models showed that surface chemistry and subsequent volatilization of aldehydes will increase production of acetyl peroxy radicals through gas phase oxidation with OH radical. Reactions of acetyl peroxy radicals with NO and NO_2 will produce organic nitrates and PAN-type species (Kruza et al., 2017).

My work generally supports and furthers these new insights. Many indoor compounds have been newly detected with CIMS (Liu et al., 2016; Liu et al., 2017; Tang et al., 2016), but my work is the first to utilize I-CIMS to non-selectively detect oxygen- and nitrogen- containing compounds. With this method, I also identified some of the same compounds such as lactic and oxopentanoic acids, but also additional ones such as methyl lactate and glycolic acid. Some of the compounds that I measured in Chapters 3 and 4 also are likely to be directly emitted by occupants, or formed secondarily from occupant emissions (e.g. lactic and oxopentanoic acids). The substantial evidence of elevated WSOG/OVOCs that my work demonstrates supports the recent developments that OH radical is likely a key species in indoor gas-phase (and possibly interfacial) oxidization reactions. And finally, recent simulations have supported my speculations in Chapter 2 that interfacial and aqueous phase chemistry likely influences the indoor air chemical makeup.

5.5 Future research directions

Many molecular formulas of WSOGs were measured and some suggested

structures were provided in this work. However, future steps can be taken to more

confidently identify and quantify many of these compounds through LC pre-separation,

MS-MS fragmentation and use of authentic standards with positive mode QTOF-ESI-

MS. In addition, mist chamber collection efficiencies can be determined for these

compounds. Ultimately, such work would enable calculation of gas phase concentrations

for these compounds by collection with mist chambers. In addition, derivatization could

be used during sampling to collect and analyze particular compound classes (Spaulding et

al., 2002).

As for compounds analyzed by I⁻CIMS in the second field campaign, confident

identification is a bit more difficult for some compounds since this instrument does not

allow for pre-separation of compounds; therefore, compounds with the same molecular

weight cannot be distinguished. However, I have high confidence in the identification in

some compounds such as glycolic acid ($C_2H_4O_3$), propionic acid ($C_3H_6O_2$), and

oxopentanoic acid ($C_5H_8O_3$). Calibration for these compounds would allow

quantification.

Ultimately, a major motivation in characterizing WSOG indoors, is to study

surface chemistry in damp homes (i.e. the uptake of WSOGs by wet indoor surfaces and

subsequent reactions) and potential exposure and health effects to home occupants.

Upcoming work in the Turpin lab will delve into this topic through controlled studies of

water and WSOG uptake on common indoor surfaces and observation of surface

chemistry using simple reactors. Eventually, insights into chemistry occurring in sorbed water as well as the production of volatile products will be gained.

A major finding from my work is that the aqueous condensate in the duct work and air conditioning system in a home provides an important sink and possible source for WSOGs. Although aqueous chemistry on surfaces is likely to play an important role in indoor chemistry, depending on the season and the climate, the magnitude of liquid water condensed inside the air handling system may be more than liquid water on surface films in the living area of the house. I estimated the volume of water condensed with one air conditioning cycle to be about 2.2 L (see Chapter 4). This condensed water could be collected and measured directly from the condensate pan. Also, the chemistry in this water will be relatively easier to explore than aqueous surface chemistry. Total organic carbon, organic gases, and anions as well as cations using ion chromatography could be used to measure the condensate concentrations at various time points. Aqueous samples could be collected and measured offline as well by these methods in addition to analysis such as molecular formula identification using ESI-MS.

Overall, insights from my work provide the basis for future experimentation and analysis such as further characterizing WSOG, understanding the impacts of RH on surface chemistry, and exploring chemistry occurring in bulk water indoors.

5.6 Implications and broader impacts

Although my Ph.D. work directly used chemical knowledge in order to explore and expand upon our understanding of indoor air chemistry and, therefore, indoor air quality, this work is fundamentally motivated by health concerns and can also have implications for indoor corrosion, the performance of electronic equipment, and the

degradation of cultural artifacts. I showed that WSOG concentrations indoors are much

higher than outdoors. I collected and analyzed WSOG and demonstrated its chemical

composition represents a wide variety of oxygen- and nitrogen-containing compounds. I

also measured WSOGs/OVOCs in real time. Exposure to these compounds will occur in

mixtures that might have additive or synergistic effects even though individual compound

concentrations are small.

I provide theoretical evidence in Chapter 2 and empirical evidence in Chapter 4

for how aqueous chemistry is likely to impact indoor air chemistry. This chemistry is

likely to remove some compounds from the gas phase while releasing others back into the

gas phase. Although it is still too early to confidently determine if this chemistry affects

health especially in damp homes, due to high surface area-to-volume ratios and the

evidence for liquid water indoors, I can confidently say that aqueous uptake and possibly

subsequent chemistry can affect indoor air composition, and therefore exposure, and thus

it warrants further exploration.

5.7 References

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Appendix A (Supporting information for chapter 3)

A1. Participant questionnaire
This questionnaire was provided to participants who volunteered for the indoor sampling campaign. Questions were asked and answered verbally. Answers are provided in table A1-1.

How do you heat your home? Natural gas furnace, Oil furnace, Wood/ pellet stove, Electric heating, Other:

Do you have a gas or electric stove? Gas, Electric

Do you have an exhaust fan above your stove? Yes, No
        If yes, do you use it when you use the stove? Yes, No, Sometimes. When? _____
        If yes, does it vent outside or inside above the stove? Outside, Inside

What food have you cooked or heated up in the past twenty-four hours and how did you cook it? _____

Do you use candles, incense or air fresheners in the home? Yes, candles, Yes, incense, Yes, candles, No
        If yes, how frequently do you use them and where? _____

Have you done any remodeling to the home or are you aware of any remodeling since it was built? Yes, No
        If yes, what has been done and when? _____

Have any of the interior rooms in the home been painted in the last year? Yes, No
        If yes, when, where, and what type of paint was used? _____

Have you installed any new carpeting in the past year? Yes, No
        If yes, where and when? _____

Have you installed any new wood flooring in the past year? Yes, No
        If yes, where and when? _____

Have you brought in any new furniture in the past year (such as couches, ottomans, tables, chairs, etc)? Yes, No
        If yes, what pieces of furniture and where? _____

Do you have any hobbies that release "smelly" compounds such as painting, wood working, nail painting, kids' crafts, etc.? Yes, No
        If yes, which hobbies and when was the last time they were done? _____

Are there any office appliances such as printers, copiers, or scanners in the home? Yes, No
        If so, what are they and where are they located? _____

Are there any pets in the home? Yes, No

If yes, what type and how many of each? _____

Are there any plants in the home? Yes, No
        If yes, what type, where, and how many? _____

Do you have any dry-cleaned clothes in the home? Yes, No
        If yes, when was the last time you brought dry cleaning into the home? _____

Have you or a professional used any pesticides, termiticides, or insecticides in the past year in the home? Yes, myself, Yes, professional, No

        If yes, what was used, where, and when? _____

Do you have an attached garage? Yes, No

        If yes, do you park your car in it or do you have other gasoline burning engines in it such as lawn mowers, weed wackers, or leaf blowers? Yes, car (gasoline/ diesel (circle one)), Yes, other two stroke engines: _____, No

        If yes, do you store gasoline in containers in the garage? Yes, No

Do you use any air purifiers such as HEPA filters, ozone generators, or ionizers? Yes, HEPA filter, Yes, ozone generator, Yes, ionizer, Yes, other type of air purifier. Please specify: _____, No

When was the last time any cleaning agents were used in the home such as Pinesol, bleach, Windex, etc.? _____

        What exactly were the cleaning agents? Feel free to go and check if you can't remember. _____

When was the last time the main area of the house was vacuumed? _____

        Does your vacuum have a HEPA filter? Yes, No, Don't know

Are you aware of any mold or mildew in the house (including bathrooms and basements)? Yes, No

        If yes, where? _____

Are you currently using central air conditioning or air conditioning window units? Yes, central air conditioning,

Yes, air conditioning window units, No

Do you currently have any windows open? Yes, No

        If yes, where? _____

        If yes, are you using window fans? Yes, No

Has anyone smoked anything in the home in the last year? (for example: cigarettes, hooka, marijuana, e-cigarettes) Yes, No

        If yes, how often and when was the last time? _____

For calculation purposes, what is the gross annual income for all family members in the household? Less than or equal to $23,850, More than $23,850, Don't know, Wish not to answer

Home #	Stove type	If stove exhaust fan present, is it used? Vented?	Food cooked passed 24hrs	Candles, incense, or air freshener use in last	Remodeling or new furniture installed in the past year?	"Smelly" hobbies?	Pets?	Plants?	Pesticides, termiticides, insecticides used inside/ directly outside?
1	gas	Sometimes, outside	eggs, red meat, pasta	no	yes	no	dogs and bird	leafy plant, kitchen herb garden	yes
2	electric	Sometimes, inside	eggs	soy candles	yes	painting furniture	no	no	no
3	electric	Sometimes, outside	Mexican food	no	yes	nail painting, glue	cats, fish	cut flowers	yes
4	electric	Yes, inside	n/a	no	yes	no	dogs	leafy plants	no
5	electric	no	pasta, bread, coffee	incense, candles	yes	nail painting	dog	yes	no
6	gas	Yes, outside	chicken, pasta, vegetables, oatmeal, coffee	no	no	no	fish	cacti, leafy plants, flowering plants, succulents	yes
7	gas	Yes, inside	n/a	no	yes	no	no	kitchen herb garden	no
8	gas	Yes, inside	red meat, coffee	air fresheners	yes	no	dog	cactus, leafy plants	no
9	electric	Yes, inside	eggs, chicken, vegetables	no	yes	Wood-working	dogs	no	yes
10	gas and electric	Yes, outside	bread	air fresheners	yes	no	dog, cats	flowering plants	no
11	electric	no	n/a	no	no	no	dog	no	no
12	gas	Yes, outside	bread, pasta, vegetables, chocolate dessert, coffee	no	yes	no	cats	cacti	yes
13	electric	Sometimes, inside	Chinese food, Indian food	no	yes	no	no	flowering plants	yes

Table A-1, part 1.

Home #	Attached garage?	Car, two-stroke engines, or gasoline storage inside?	Office appliances?	Air purifiers?	Cleaning agents used in last 24hrs?	Vacuum in last 24hrs? HEPA filter?	Mold or mildew in house?	AC?	Windows open?
1	yes	yes	printer	no	Pine-sol	yes, yes	basement	central	no
2	no	n/a	no	AC filter	natural all-purpose cleaning agent	no	no	window unit	yes
3	yes	yes	laser printer	no	no	no	bedroom, kitchen	central	no
4	no	n/a	laser printer	no	Windex	no	no	central	no
5	no	n/a	No	no	-	no	no	central	yes
6	yes	yes	Laser printer	no	Windex	no	bathroom, basement	no	no
7	yes	yes	printer and scanner	no	-	no	no	central	no
8	yes	yes	inkjet printer, scanner, copier unit	HEPA filter	natural antibacterial cleaner	yes, yes	basement	no	no
9	no	n/a	printer, copier, scanner unit	no	-	yes, yes	no	no	no
10	yes	yes	front sitting room/ office	no	table wipes	yes, no	no	no	no
11	no	n/a	printer, office	no	-	no	no	central	no
12	no	n/a	upstairs	no	Windex, bleach	no	no	no	no
13	no	n/a	Printer, scanner unit	HEPA filter	bleach	yes, no	bedroom	central	no

Table A1-1, part 2. Houses were all non-smoking and no participants brought dry cleaning in their homes within a week prior to sampling.

A2. Predictors of WSOG concentration

A2.1 Multiple linear regression results for several parameters vs indoor WSOG as the dependent variable

```
REGRESSION
 /DESCRIPTIVES MEAN STDDEV CORR SIG N
 /MISSING LISTWISE
 /STATISTICS COEFF OUTS CI(95) R ANOVA COLLIN TOL ZPP
 /CRITERIA=PIN(.05) POUT(.10)
 /NOORIGIN
 /DEPENDENT Indoor_conc
 /METHOD=STEPWISE Outdoor_conc T_in T_out RH_in O3_out CO2_in Occupants Year Area deltaT
 /SCATTERPLOT=(*ZRESID ,*ZPRED)
 /RESIDUALS HISTOGRAM(ZRESID) NORMPROB(ZRESID).
```

Regression

Notes		
Output Created		19-JAN-2018 11:52:13
Comments		
Input	Data	/Users/saraduncan/Dropbox/Paper 2/IA data.sav
	Active Dataset	DataSet1
	Filter	<none>
	Weight	<none>
	Split File	<none>
	N of Rows in Working Data File	13
Missing Value Handling	Definition of Missing	User-defined missing values are treated as missing.
	Cases Used	Statistics are based on cases with no missing values for any variable used.
Syntax		REGRESSION /DESCRIPTIVES MEAN STDDEV CORR SIG N /MISSING LISTWISE /STATISTICS COEFF OUTS CI(95) R ANOVA COLLIN TOL ZPP /CRITERIA=PIN(.05) POUT(.10) /NOORIGIN /DEPENDENT Indoor_conc /METHOD=STEPWISE Outdoor_conc T_in T_out RH_in O3_out CO2_in Occupants Year Area deltaT /SCATTERPLOT=(*ZRESID ,*ZPRED) /RESIDUALS HISTOGRAM(ZRESID) NORMPROB(ZRESID).
Resources	Processor Time	00:00:00.73
	Elapsed Time	00:00:00.00
	Memory Required	10480 bytes
	Additional Memory Required for Residual Plots	752 bytes

		Indoor_conc	Outdoor_conc	T_in	T_out	RH_in	O3_out	CO2_in	Occupants	Year	Area	delta T
Pearson Correlation	Indoor_conc	1.000	.052	.434	.564	.025	.511	-.486	.778	.027	.248	.248
	Outdoor_conc	.052	1.000	.288	.456	-.333	.338	-.216	.343	-.390	.641	.641
	T_in	.434	.288	1.000	.882	.232	.764	-.639	.141	-.436	.356	.356
	T_out	.564	.456	.882	1.000	.278	.831	-.623	.409	-.329	.585	.585
	RH_in	.025	-.333	.232	.278	1.000	.124	-.454	-.401	-.155	.163	.163
	O3_out	.511	.338	.764	.831	.124	1.000	-.457	.301	-.290	.481	.481
	CO2_in	.026	.387	.102	.459	.184	.401	.088	.212	.301	.437	.437
	Occupants	-.486	-.216	-.639	-.623	-.454	-.457	1.000	-.139	.530	-.675	-.675
	Year	.778	.343	.141	.409	-.401	.301	-.139	1.000	.166	.321	.321
	Area	.027	-.390	-.436	-.329	-.155	-.290	.530	.166	1.000	-.279	-.279
	delta T	.248	.641	.356	.585	.163	.481	-.675	.321	-.279	1.000	1.000
Sig. (1-tailed)	Indoor_conc	.	.443	.105	.045	.473	.065	.077	.004	.471	.245	.245
	Outdoor_conc	.443	.	.210	.092	.174	.170	.274	.166	.133	.023	.023
	T_in	.105	.210	.	.000	.259	.005	.023	.349	.104	.156	.156
	T_out	.045	.092	.000	.	.218	.001	.027	.120	.176	.038	.038
	RH_in	.473	.174	.259	.218	.	.366	.094	.125	.335	.326	.326
	O3_out	.065	.170	.005	.001	.366	.	.092	.199	.208	.080	.080
	CO2_in	.471	.135	.389	.091	.305	.126	.404	.279	.199	.103	.103
	Occupants	.077	.274	.023	.027	.094	.092	.	.351	.057	.016	.016
	Year	.004	.166	.349	.120	.125	.199	.351	.	.324	.183	.183
	Area	.471	.133	.104	.176	.335	.208	.057	.324	.	.217	.217
	delta T	.245	.023	.156	.038	.326	.080	.016	.183	.217	.	.

Correlations, N=10 for all variables

	Mean	Std. Deviation	N
Indoor_conc	893.0625	294.26026	10
Outdoor_conc	72.4261	23.42125	10
T_in	23.2275	1.84163	10
T_out	26.1667	5.65619	10
RH_in	58.3733	2.57269	10
O3_out	37.5000	15.81315	10
CO2_in	886.4750	159.05954	10
Occupants	2.9000	.74664	10
Year	1970.2000	26.83613	10
Area	146.5152	70.86647	10
delta T	4.3092	2.44423	10

Descriptive statistics

Variables Entered/Removed[a]			
Model	Variables Entered	Variables Removed	Method
1	Year	.	Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).

a. Dependent Variable: Indoor_conc

Model Summary[b]				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.778[a]	.605	.555	196.24697

a. Predictors: (Constant), Year

b. Dependent Variable: Indoor_conc

ANOVA[a]						
Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	471198.887	1	471198.887	12.235	.008[b]
	Residual	308102.998	8	38512.875		
	Total	779301.886	9			

a. Dependent Variable: Indoor_conc

b. Predictors: (Constant), Year

Coefficients[a]								
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
		B	Std. Error	Beta			Lower Bound	Upper Bound
1	(Constant)	-15905.469	4802.954		-3.312	.011	-26981.101	-4829.838
	Year	8.526	2.438	.778	3.498	.008	2.905	14.147

Coefficients[a]						
Model		Correlations			Collinearity Statistics	
		Zero-order	Partial	Part	Tolerance	VIF
1	(Constant)					
	Year	.778	.778	.778	1.000	1.000

a. Dependent Variable: Indoor_conc

Excluded Variables[a]

Model		Beta In	t	Sig.	Partial Correlation	Collinearity Statistics		
						Tolerance	VIF	Minimum Tolerance
1	Outdoor_conc	-.243[b]	-1.032	.337	-.363	.882	1.133	.882
	T_in	.331[b]	1.619	.150	.522	.980	1.020	.980
	T_out	.296[b]	1.256	.249	.429	.833	1.201	.833
	RH_in	.401[b]	1.905	.098	.584	.839	1.192	.839
	O3_out	.305[b]	1.379	.210	.462	.909	1.100	.909
	CO2_in	-.145[b]	-.610	.561	-.225	.955	1.047	.955
	Occupants	-.385[b]	-2.019	.083	-.607	.981	1.020	.981
	Area	-.105[b]	-.442	.672	-.165	.973	1.028	.973
	delta T	-.001[b]	-.004	.997	-.002	.897	1.115	.897

a. Dependent Variable: Indoor_conc

b. Predictors in the Model: (Constant), Year

Collinearity Diagnostics[a]

Model	Dimension	Eigenvalue	Condition Index	Variance Proportions	
				(Constant)	Year
1	1	2.000	1.000	.00	.00
	2	8.348E-5	154.781	1.00	1.00

a. Dependent Variable: Indoor_conc

Residuals Statistics[a]

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	550.3049	1249.4622	904.4747	201.54743	13
Residual	-299.27811	412.96930	30.75020	230.53428	13
Std. Predicted Value	-1.498	1.558	.050	.881	13
Std. Residual	-1.525	2.104	.157	1.175	13

a. Dependent Variable: Indoor_conc

Figure A2.1-1. SPSS generated charts for the dependent variable: Indoor concentration
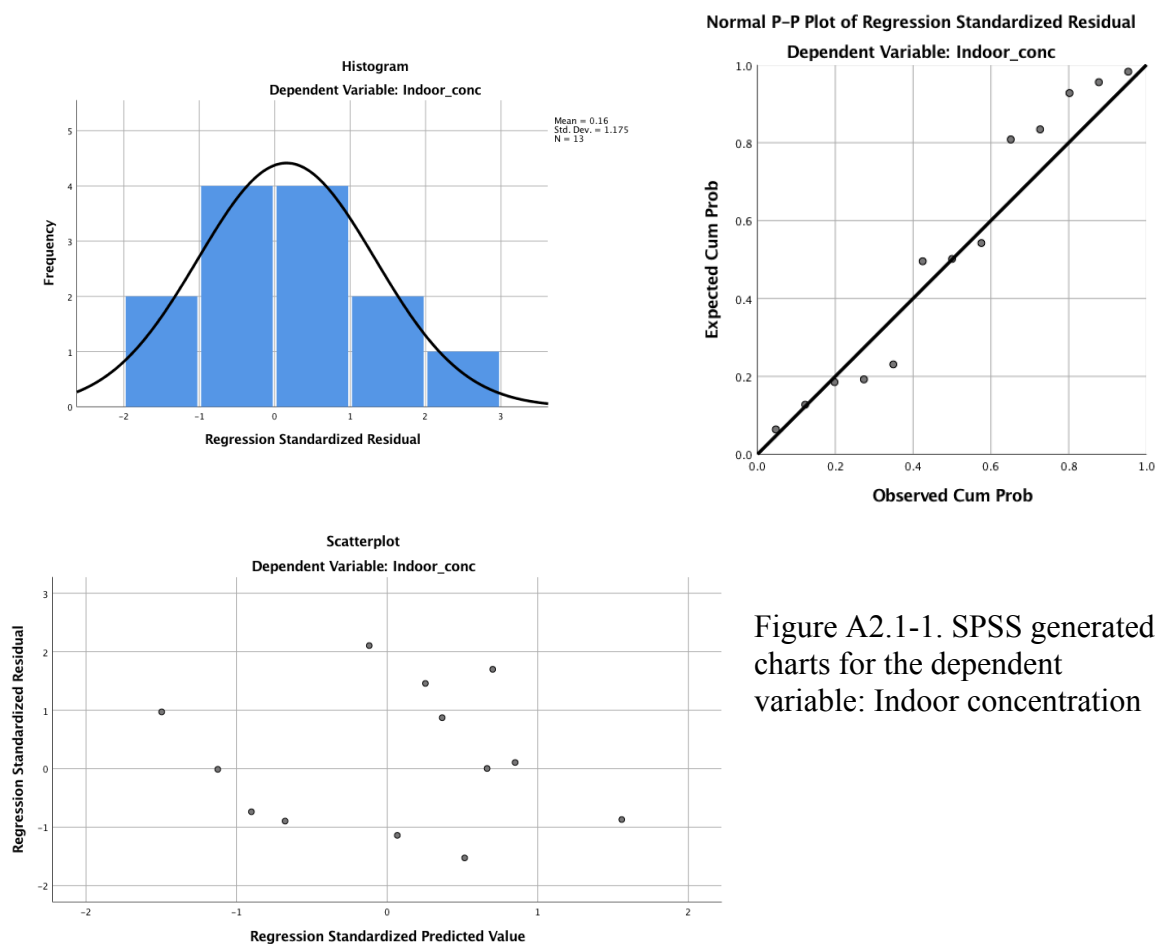
A2.2. Select individual regressions of measured and calculated data from 13 sampled homes
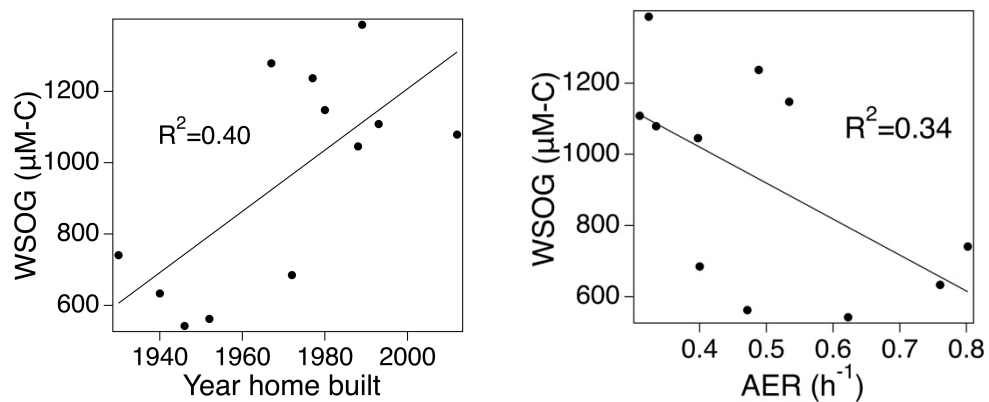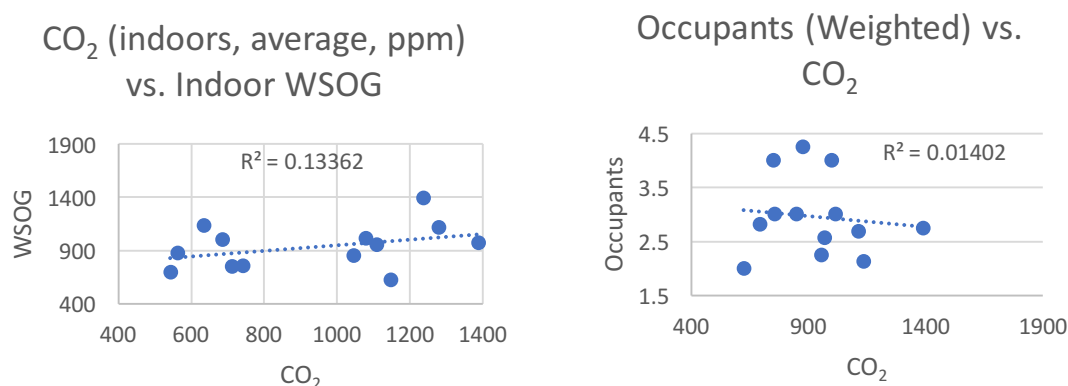
Figure A2.2-1

A3. Theoretical collection efficiencies for mist chamber experiments

Spaulding et al. (2002) determined theoretical mist chamber collection efficiency for various compounds to be calculated using equation A3-1 (Spaulding, Talbot, & Charles, 2002).

$$A3\ Eq\ 1: CE = \frac{K_H RT w_L}{1 + K_H RT w_L}$$

CE is the collection efficiency, K_H is the Henry's law constant, R is the ideal gas constant, T is the sampling temperature, and W_L is the liquid water content (volume of water in mist chamber/ volume of sampled air). Theoretical collection efficiencies for select compounds are provided below in table A3-1. Both collection efficiencies for the mist chamber sampling parameters that Spaulding et al. (2002) used and that I used are provided.

Compound	Molecular formula	Henry's law constant (M/atm)	Theoretical collection efficiency (%)	
			Spaulding (10mL water, 30L/min, 10 min)	**Duncan (25mL water, 25 L/min, 2 hours)**
Glyoxal	$C_2H_2O_2$	4,000,000	100	**100**
Formic acid	CH_2O_2	8,000	87	**62**
Acetic acid	$C_2H_4O_2$	4,000	77	**45**
Formaldehyde	CH_2O	3,000	71	**38**
Acetone	C_3H_6O	31	2.5	**0.63**
2-Hexanone	$C_6H_{12}O$	11	0.89	**0.22**
Nonanal	$C_9H_{18}O$	2	0.16	**0.04**

Table A3-1 Theoretical collection efficiencies

Empirical collection efficiencies were determined for total WSOG, acetic acid, and formic acid (chapter 2, figure 3 and equation 3). Since theoretical collection efficiencies for acetic and formic acids can be calculated using their Henry's law constants, percent differences for their empirical and theoretical collection efficiencies were determined. Since these values were about the same for both acetic and formic acids (~ 20%), I assumed that the percent difference between the empirical and theoretical collection efficiency for WSOG was also 20%. I then back calculated the theoretical efficiency for total WSOG. I then used both the empirical and theoretical collection efficiencies for WSOG to back calculate an average range of Henry's law constants for the collected WSOG mixture (table A3-2).

		Total WSOG	Acetic acid	Formic acid
H (M/atm)		2500 - 4000	4000	8000
Collection efficiency (%)	Empirical	43%	56%	76%
	Theoretical	34%	45%	62%
Percent difference		20%	20%	18%

Table A3-2 Collection efficiencies

Using empirical collection efficiencies, gas phase concentrations of WSOG, acetic acid, and formic acid were determined for each home in table A3-3

Home	Gas phase concentration		
	WSOG (μg-C/m^3)	Acetic acid (μg/m^3)	Formic acid (μg/m^3)
1	106	42	18
2	178	44	15
3	162	47	10
4	167	60	17
5	115	32	7
6	110	43	12
7	172	67	21
8	87	28	10
9	192	67	21
10	215	28	10
11	98	37	10
12	84	26	10
13	198	50	15

Table A3-3. Calculated gas phase concentrations of WSOG, acetic acid, and formic acid

A4. Supporting analytical figures
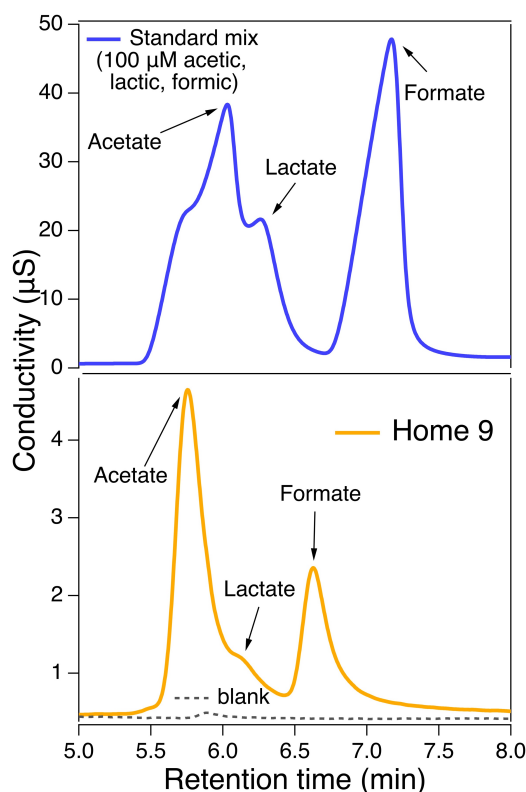
Figure A4-1: IC chromatogram of home 9 between 5 and 8 minutes
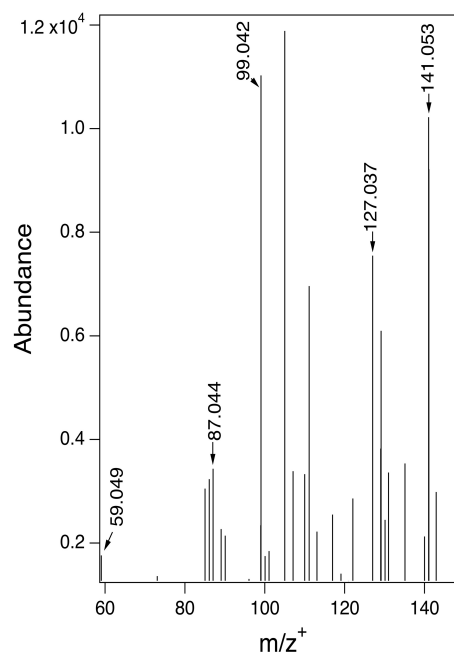
Figure A4-2. Example spectra from QTOF-ESI-MS

A5. OH radical oxidation experiments

Similar to previous work conducted in the Turpin lab (Sareen et al., 2016), mist chamber samples from the first sampling campaign, mist chamber samples were reacted with OH radicals in a custom-made cuvette chamber. OH radicals were produced by the photolysis of 500 µM H_2O_2 with 254 nm wavelength lamp (OH· production rate: =1.7 µM [OH·] s^{-1}) placed in the center of the chamber. Samples were placed in 11 - 3 mL cuvettes, H_2O_2 was added, and cuvettes were placed in chamber. Cuvettes were removed at predetermined time points until 60 minutes was reached. The controls were field blank + OH·, sample + UV, and sample + H_2O_2.

Samples were analyzed with QTOF-ESI-MS (soft-ionization) and by IC. Time series of acetic, formic, and oxalic acids are shown below (Figure A5-1). Several compounds reacted away as the experiment progressed. One such example is m/z^+ 135.102 ($C_6H_{14}O_3$) (see Figure A5-2). $C_6H_{14}O_3$ decays in all homes, but does not decay in the controls.
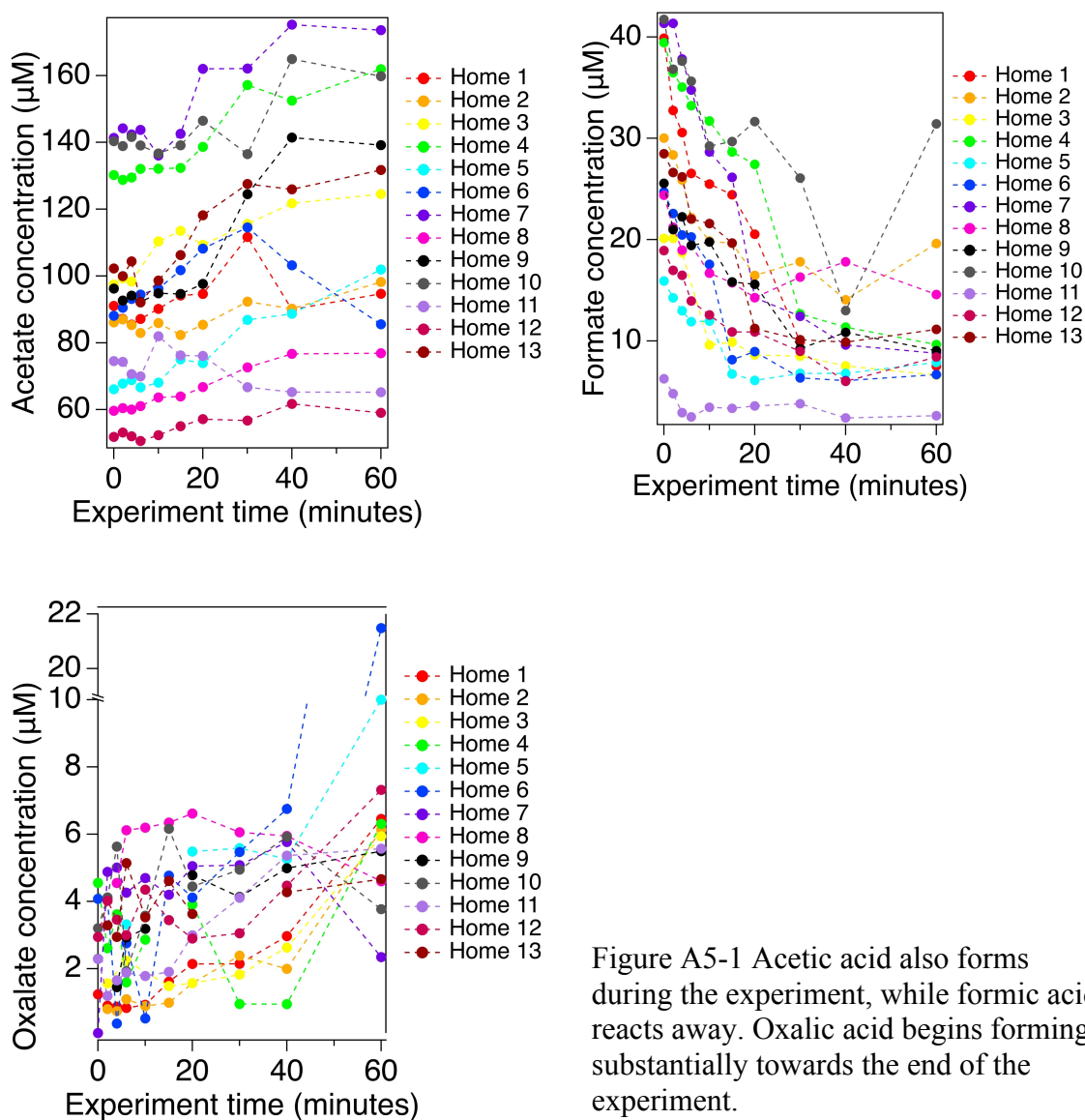
Figure A5-1 Acetic acid also forms during the experiment, while formic acid reacts away. Oxalic acid begins forming substantially towards the end of the experiment.
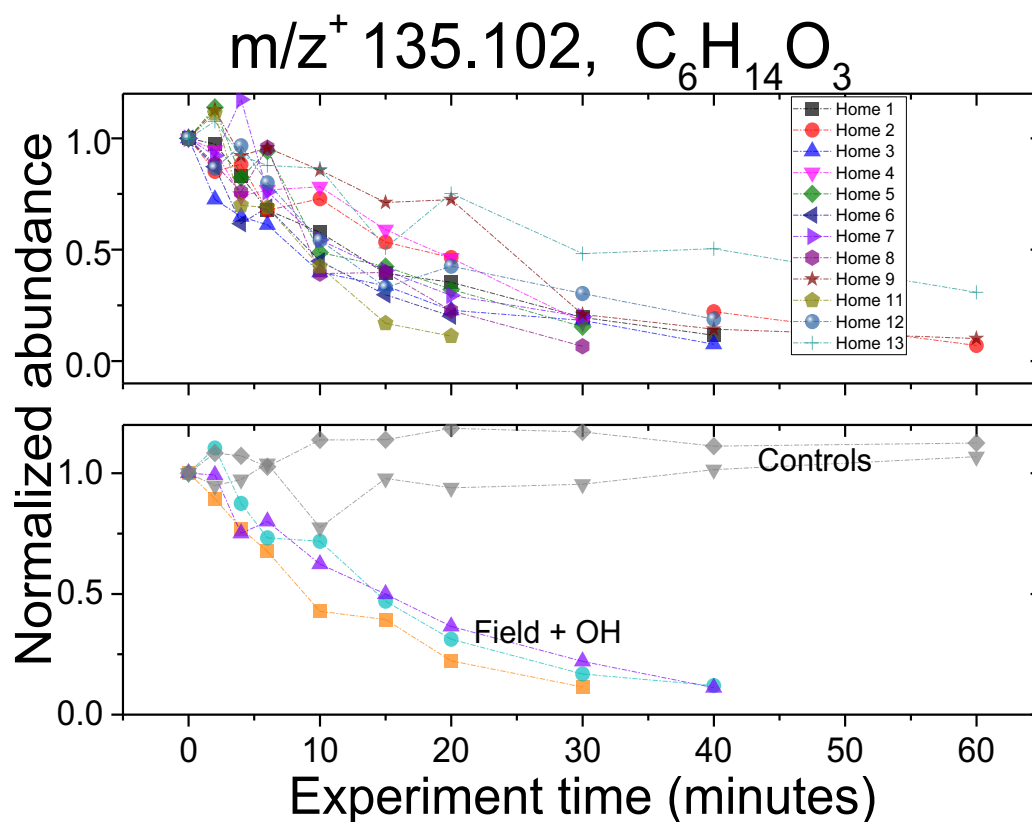
Figure A5-2. Compound $C_6H_{14}O_3$ reacting with OH over the course of the experiment

A6. References

Sareen, N., Carlton, A. G., Surratt, J. D., Gold, A., Lee, B., Lopez-Hilfiker, F. D., Mohr, C., Thornton, J. A., Zhang, Z., Lim, Y. B., & Turpin, B. J. (2016). Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign. *Atmospheric Chemistry and Physics*, *16*(22), 14409–14420. https://doi.org/10.5194/acp-16-14409-2016

Spaulding, R. S., Talbot, R. W., & Charles, M. J. (2002). Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water-Soluble Organics in Air. *Environ. Sci. Techn.*, *36*(8), 1798–1808. https://doi.org/10.1021/es011189x

Appendix B (supporting information for chapter 4)

B1. Calibration factors used for acetic and formic acids as a function of $I(H_2O)^-/I^-$ and the variation of $I(H_2O)^-/I^-$ during field measurement.
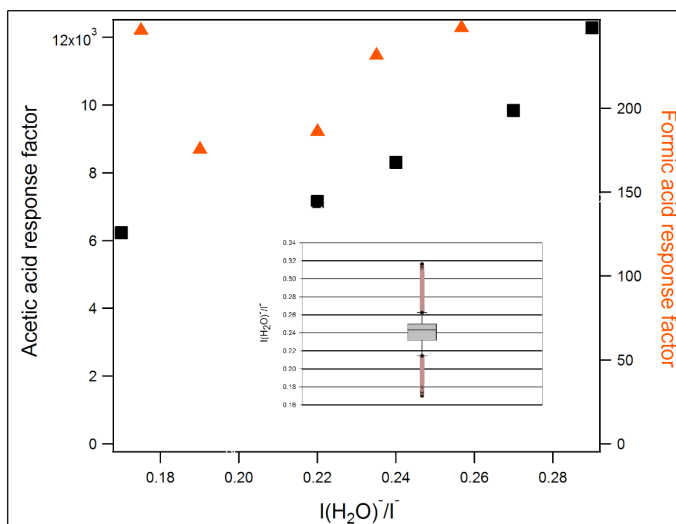
Figure B1-1.

B2: Additional CIMS figures
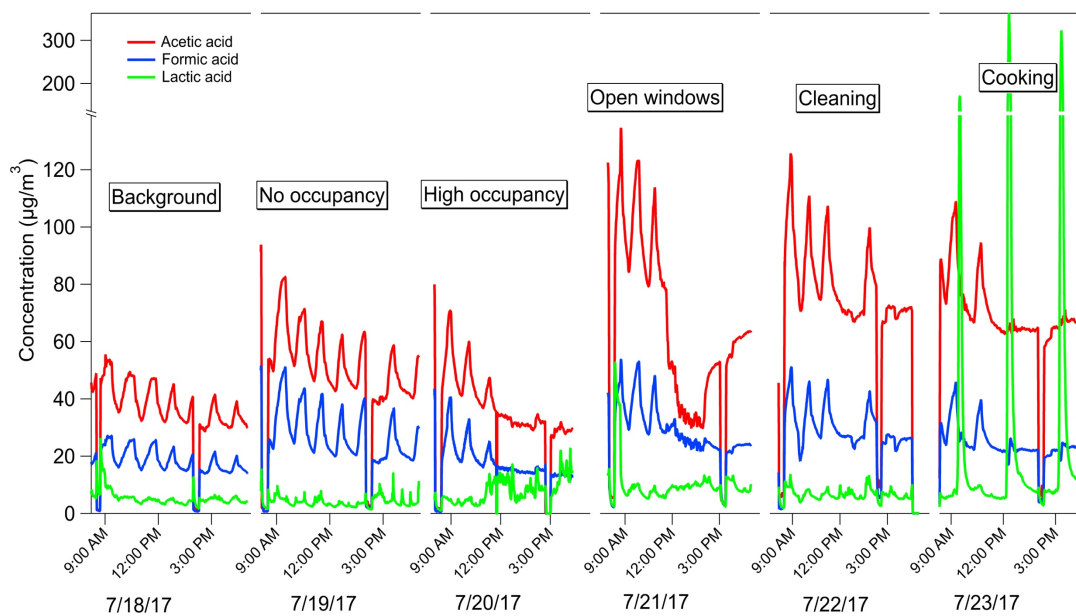
Figure B2-1 Concentrations of organic acids during field campaign
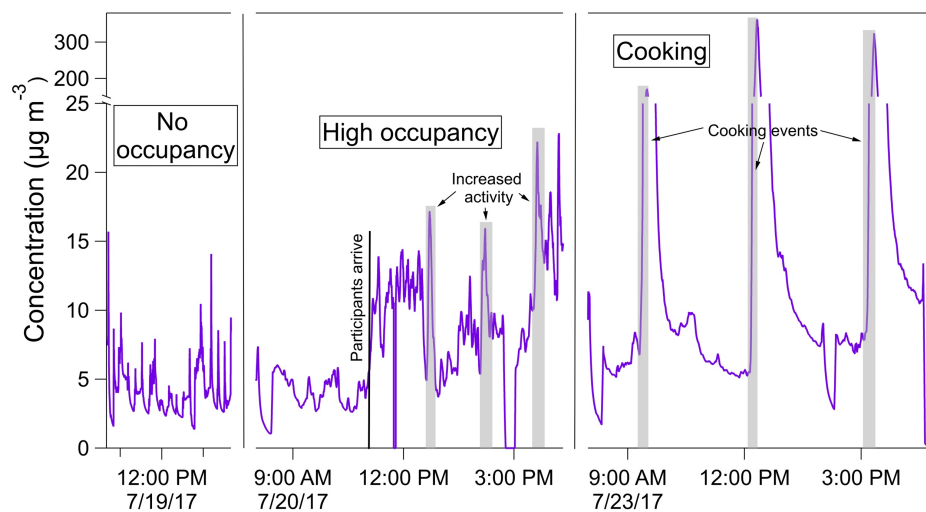
Figure B2-2 Lactic acid concentrations during "high occupancy" sampling days.
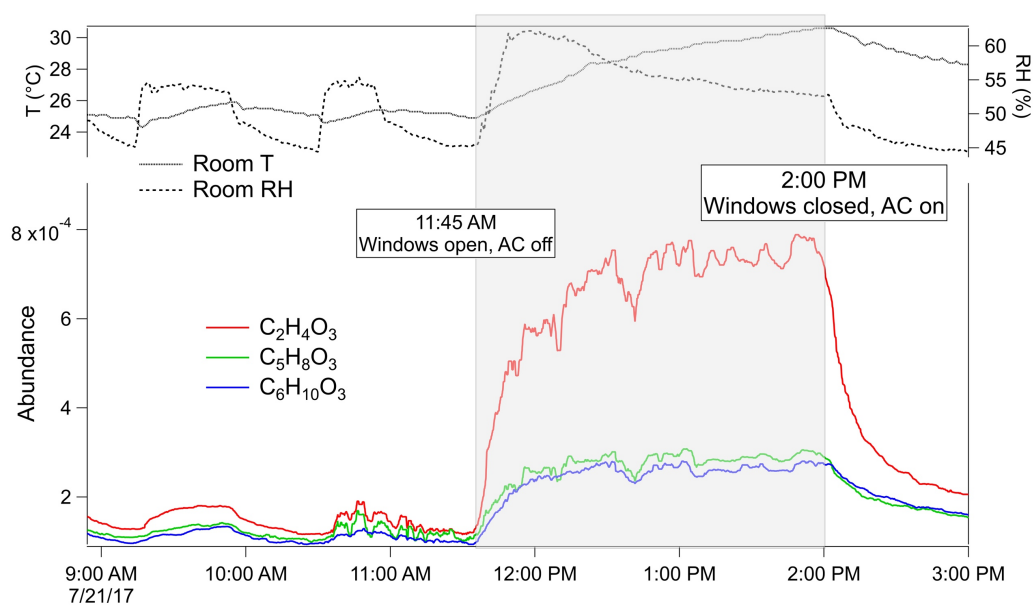
Figure B2-3 Abundances of several molecular formulas during the window opening event.
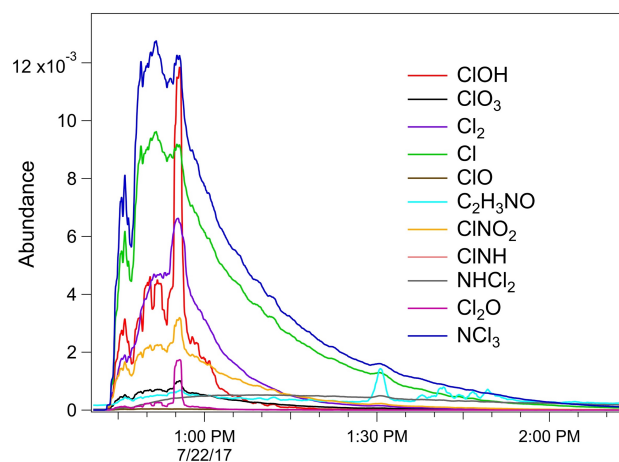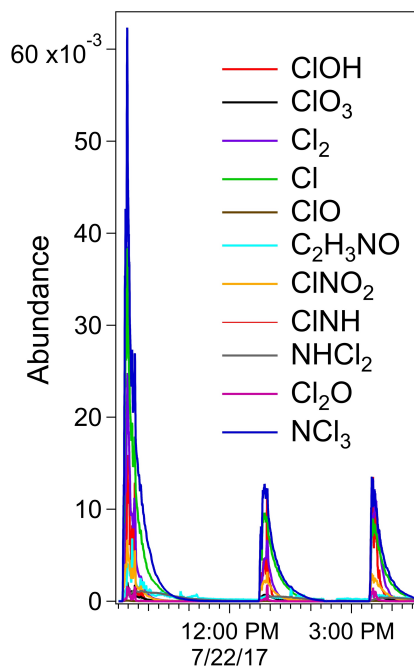
Figure B2-4 Abundances of several molecular formulas during cleaning events. These results are similar to those published in Wong et al, 2017 (Wong, Carslaw, Zhao, Zhou, & Abbatt, 2017).

B3. Modeled formic and acetic acid decays.
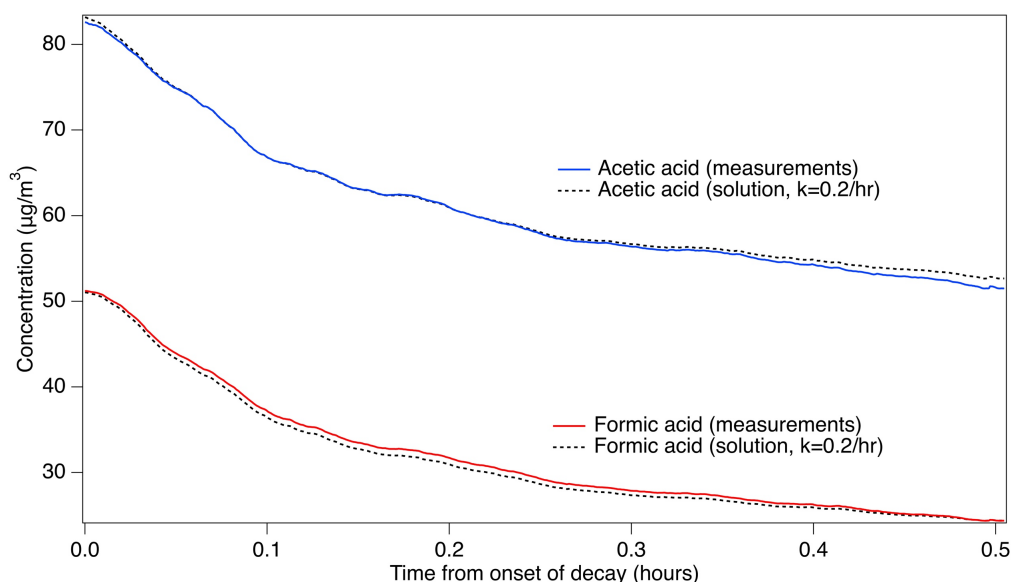
Figure B3-1

B4. Indoor loss rate coefficients for molecular formulas released during cooking events.

Indoor loss rate coefficients (k) were estimated by finding the slope ($\lambda + k$) of Equation B4-4 and subtracting the air exchange rate,

$$Eq\ B4 - 4: -\ln\left(\frac{C(t) - C_{back}}{C_{max} - C_{back}}\right) = (\lambda + k)t$$

where C(t) is the concentration at time = t, C_{back} is the background concentration indoors before cooking began C_{max} is the maximum concentration of each compound. λ is the air exchange rate, t is time in hours, and k is the indoor loss rate coefficient. This assumes steady state has been achieved and that the indoor air is well mixed. Estimated indoor loss rates are very high. It is quite possible that the well mixed/steady state assumption does not hold because these values are higher than expected.
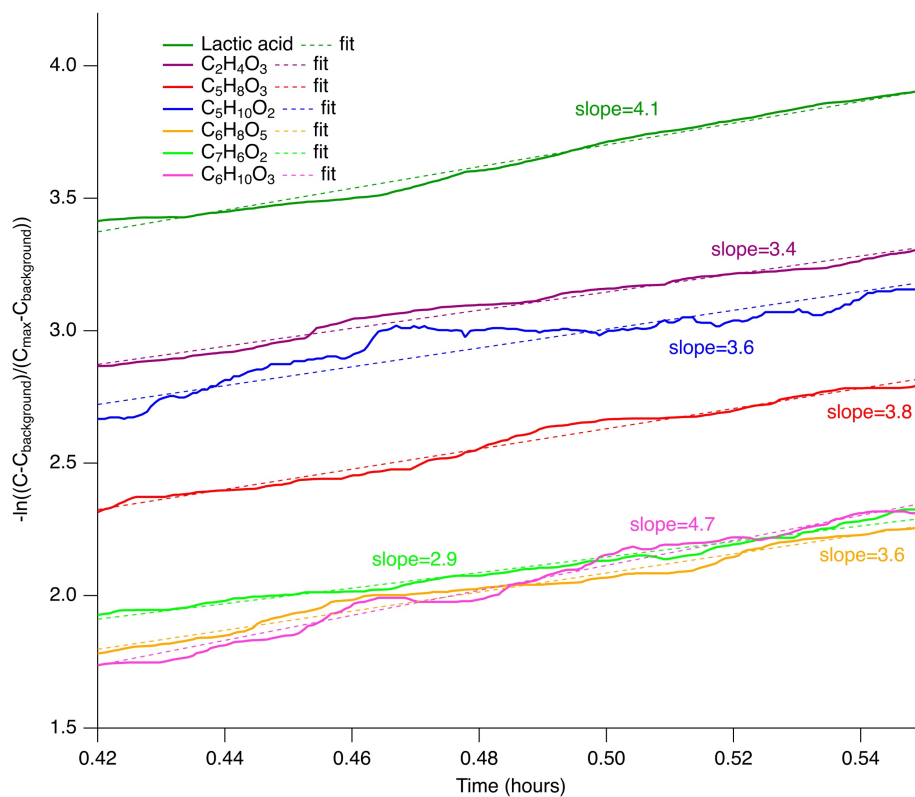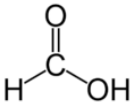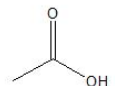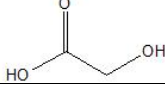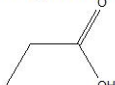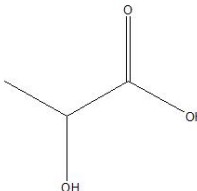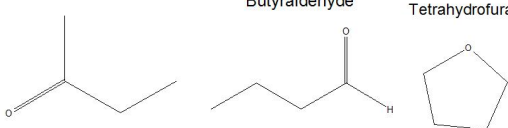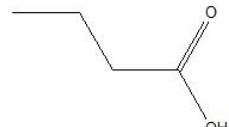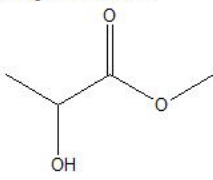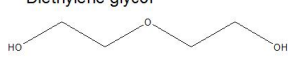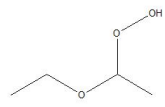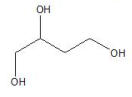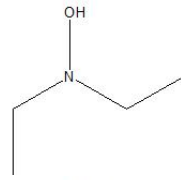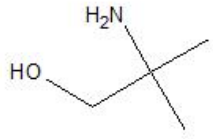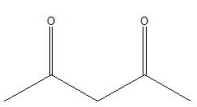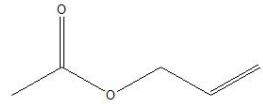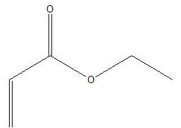
Figure B4-1. ln(concentration/max) vs time for select compounds emitted from one cooking event. Time is time from the peak of lactic acid concentration.
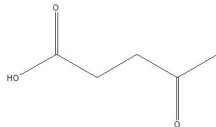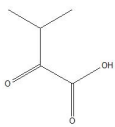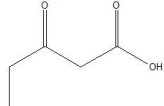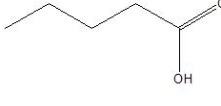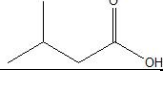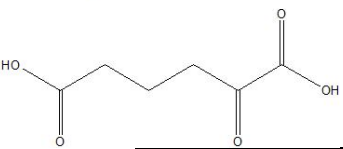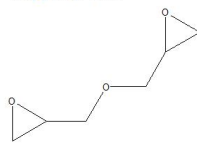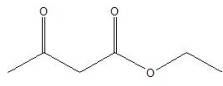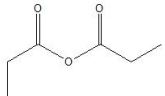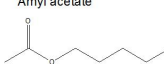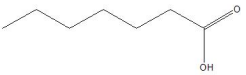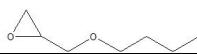
	k (h^{-1})
lactic acid	3.7
C$_2$H$_4$O$_3$	3
C$_5$H$_8$O$_3$	3.4
C$_5$H$_{10}$O$_2$	3.2
C$_6$H$_8$O$_5$	3.2
C$_7$H$_6$O$_2$	2.5
C$_6$H$_{10}$O$_3$	4.3

Table B4-1. Indoor loss rate coefficients for select compounds emitted from one cooking event.

B5. Molecular formulas detected by the iodide-CIMS

Mass + iodide (126.9)	Molecular formula	O:C	ESI ionization mode (+/-)	Possible structures/ compounds
172.925	CH_2O_2	2		formic acid
186.952	$C_2H_4O_2$	1	-	Acetic acid
202.951	$C_2H_4O_3$	1.5		Glycolic acid
200.979	$C_3H_6O_2$	0.67	-	Propionic acid
216.978	$C_3H_6O_3$	1		Lactic acid
199.006	C_4H_8O	0.25	+	Butanone Butyraldehyde Tetrahydrofuran
215.005	$C_4H_8O_2$	0.5	-	Butyric acid

231.004	C$_4$H$_8$O$_3$	0.75	+	**Methyl lactate**
233.020	C$_4$H$_{10}$O$_3$	0.75	+	Diethyl ether peroxide Diethylene glycol 1,2,4-Butanetriol
216.036	C$_4$H$_{11}$NO	0.25	+	Diethylhydroxylamine **Aminomethyl propanol**
227.016	C$_5$H$_8$O$_2$	0.4	+	Acetylacetone Allyl acetate Ethyl acrylate

243.015	$C_5H_8O_3$	0.6		Levulinic acid, alpha-Ketoisovaleric acid, Oxopentaoic acid
229.032	$C_5H_{10}O_2$	0.4	-	Valeric acid, 3-methylbutanoic acid
287.025	$C_6H_8O_5$	0.83	-	alpha-Ketoadipic acid
257.042	$C_6H_{10}O_3$	0.5		Diglycidyl ether, Ethyl acetoacetate, Propionic anhydride, add oxohexanoic acid
249.021	$C_7H_6O_2$	0.29		Benzoic acid, 1,3-Benzoidioxole, 3-Hydroxybenzaldehyde
257.085	$C_7H_{14}O_2$	0.29	+,-	Amyl acetate, Heptanoic acid, n-Butyl glycidyl ether
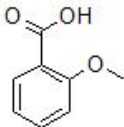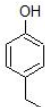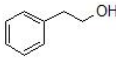
279.047	C$_8$H$_8$O$_3$	0.38	-	o-Anisic acid
249.064	C$_8$H$_{10}$O	0.13	+	4-Ethylphenol / Ethyl phenyl ether / Phenethyl alcohol / 1-Phenylethanol / 2,6-Xylenol

Table B5-1. Detected masses, molecular formulas, oxygen-to-carbon ratios, detection in ESI analysis of mist chamber samples, and possible structures for all compounds.

B6. References

Wong, J. P. S., Carslaw, N., Zhao, R., Zhou, S., & Abbatt, J. P. D. (2017). Observations and impacts of bleach washing on indoor chlorine chemistry. *Indoor Air*, *27*(6), 1082–1090. https://doi.org/10.1111/ina.12402

Appendix C (supplementary information for chapter 5)

C1: Dose calculation parameters

WSOG concentration (µg/m^3)		170
Exposure frequency (days/year)		365
time of dermal contact (hours/day)		24
permeability coefficient (m/hr)	DEP	3.4
	4-OPA	0.56
	butanol	0.053
Adult	Inhalation rate (m^3/day)	15.0
	Exposure duration (years)	70
	Body weight (kg)	80
	Skin surface area (m^2)	1.8
	Averaging time (days)	25550
Child (10 yrs)	Inhalation rate (m^3/day)	10.0
	Exposure duration (years)	10
	Body weight (kg)	30
	Skin surface area (m^2)	1.1
	Averaging time (days)	3650
Infant (0.5 yrs)	Inhalation rate (m^3/day)	3.6
	Exposure duration (years)	10
	Body weight (kg)	3.5
	Skin surface area (m^2)	0.25
	Averaging time (days)	182.5

Table C1-1 Parameters for dose calculations in section 5.3

Appendix D (additional supporting field and laboratory information)

D1. Standard Operating Procedures

D1.1. Mist Chamber Sampling SOP – field campaign 1

OVERVIEW

Mist chambers, or "Cofer scrubbers," are used to scrub water-soluble organic gases (WSOCs) from the ambient air. These devices do so by way of two GAST ½ HP vacuum pumps pulling air at 25L min^{-1} through them. Approximately 25mL of water is added into each mist chamber and upon sufficient flow a mist is created that thereby increases water to gas surface area allowing gases with a high enough affinity for the liquid phase to partition into the mist. The mist then refluxes back down into the bottom of the chamber into the bulk water where, after sufficient sample time, it is then collected for analysis. Only gases are collected into the aqueous phase; particles are filtered out by quartz fiber filters. 150301SMD

PREPARATION

1) Clean sampling equipment
   a. Clean non-metal parts (use Sonicator SOP)
   b. Bake mist chambers at 500°C
   c. Bake quartz fiber filters at 550°C
   d. Clean metal parts with kimwipes and isopropanol
   e. Acid wash 15mL vials, 50mL vials, 125mL Nalgene bottles, 250mL Nalgene bottles, 500mL Nalgene bottles, 1L Nalgene bottles, 60mL syringes, syringe tubing (use acid wash SOP)
2) Check flow meters with digital TSI flow meter calibrator kit
3) Set up mist chambers and install in cases for transport
   a. Gelman filter holds 47mm baked quartz fiber filter (fibrous side contacts incoming air first)
   b. Gelman filter holder swaged to bottom of mist chamber with Teflon tape (Teflon swagelok ½ in. pipe fitting)
   c. URG filter pack holds a 47 mm Zefluor filter (no treatment) = hydrophobic membrane
   d. Mist chamber top swaged (Teflon Swagelok ¾ in. pipe fitting) to URG filter pack plug with Teflon tape
   e. Place mist chambers in cases and secure top and bottom filter holders
   f. Carefully attach syringe tubing to capillary tube of mist chambers
   g. Connect vacuum tubing from top filter holders to bottom port of variable area flow meters

       h. Connect top port of flow meters to valves (valves should be closed)

4) Count and label vials for pipetting of experiment and analysis sized samples upon return
    a. For each day of sampling:
        i. 11 x 15mL vials
        ii. 16 x 50mL vials
    b. Label vials with sample ID stickers and unique identification codes. Record in lab notebook ID numbers, identification codes, size, and description of sample. Add a column for volume of water ultimately added and a column to denote what each sample is ultimately used for.
        i. ID example: IA-MC-150201SMD-DB-I
        ii. <u>Indoor Air – Mist Chamber – 150201SMD – Dynamic Blank – Indoors</u>

5) Label Nalgene bottles
    a. 1 x 125mL bottle for field blank: "date, field blank"
    b. 2 x 125mL bottles for indoor and outdoor dynamic blanks: "date, dynamic blank, indoors/ outdoors"
    c. 2 x 250mL bottles for indoor and outdoor samples: "date, indoor/ outdoor sample"
    d. Use larger bottles if smaller ones run out

6) Prepare equipment to take to field:
    a. Large "outdoor case" to leave outside residence. Contents:
        i. ½ inch thick vacuum tubing to connect pumps to mist chambers
        ii. Two heavy gauge extension cords
        iii. Two hepa filters
        iv. Two wooden boards to place pumps on
    b. Smaller "indoor case" to bring inside home. Contents:
        i. ¼ inch vacuum tubing to connect mist chambers to pumps
        ii. Tubing connectors and Y connectors
        iii. Two power strips
        iv. Painters tape
        v. Duct tape
        vi. Scissors and tube cutters
        vii. 12 or 16 60mL syringes (12 if mist chambers have been baked before sampling, 16 if not)
        viii. Clothespins
        ix. 250mL and 125mL Nalgene bottles filled with clean DI for composite sample and blanks
        x. 1 1L Nalgene bottle filled with clean DI for field water
        xi. 1 500mL Nalgene bottle filled with clean DI for backup

       xii.   2 1L empty Nalgene bottles for waste
      xiii.   Trash bag
      xiv.   4 activated carbon filters with tubing attached
      xv.   Hygrometer
      xvi.   Laser tape measure
      xvii.   Several pairs of gloves
     xviii.   Four nylon bug screens
      xix.   Zip ties
      xx.   4 lengths of ½ inch Teflon tubing with Swagelok fittings to screw on to mist chambers
      xxi.   A box of large and small Kimwipes
      xxii.   Extra quartz and Zefluor filters, forceps
     xxiii.   Timer
     xxiv.   Two tripods
     xxv.   Lab notebook, field data sheet, participant survey, technician checklist
- c. Two GAST ½ HP vacuum pumps (oil-less rocking piston pumps)
- d. Two pump covers
- e. Cooler with ice packs
- f. Two mist chamber cases with mist chamber set-up prebuilt and installed before going to the field
- g. Folding chair(s)
- h. Folding table

IN FIELD
1) Knock on door and enter home upon invitation inside residence
2) Do a quick walk through and determine location of sampling. This should be in main living area of house (living room) on the first floor next to a window so tubing and electrical cords can be fed outside
3) Outdoors
   - a. Find a flat ground surface to place pumps outside window closest to where the mist chambers are going to be sampling
   - b. Bring outdoor case, pumps, and pump covers to chosen pump location
   - c. Place pumps on wooden boards to protect pumps and participant property
   - d. Attach ½ inch vacuum tubing to the inlet of each pump and run through window
   - e. Plug pump power cords into extension cords and run through window
     - i. Place duct tape around attachment of extension cords if precipitation is predicted
   - f. Attach HEPA filters to outlet of pumps

g. Place cover over pumps (if it is a hot day and no precipitation is predicted, consider not using pump covers to prevent overheating)

4) Indoors

a. Bring indoor case, mist chamber cases, folding chair(s), folding table, and cooler inside and place in sampling area

b. Attach tripods to base of mist chamber cases. Legs should be extended one length by loosening the largest silicone grip lock on each leg, extending the legs out and tightening the lock again. Leg angle should be increased one "click" using adjustments located near the head of each leg

c. Once tripods are in place, place mist chamber cases with mist chambers installed near window to allow easy access to tubing and electrical cords. Determine which set of two mist chambers will sample outdoor air and which will sample indoor air

d. Attach ¼ inch vacuum tubing to valves at backs of mist chamber cases and use y connectors and straight vacuum connectors to connect mist chamber two pumps. Each pump will be pulling two mist chambers

e. Plug power cords into switched off power strip and plug into wall. (Upon turning on pumps at a later step, power strip may trip. If this happens, use additional power strip for other power cord and plug into an outlet on a different circuit)

f. Attach activated carbon filters to bottom filter pack of each mist chamber (under bottom of each case)

g. Fill four syringes with 25mL of DI water. Slowly add water to mist chambers

h. Turn on power strip(s) to turn on pump. Slowly open valves until a flow rate of 25 L/min is reached

i. Run mist chambers for 5 minutes as a "water wash"

j. While waiting for the water wash to complete, fill out data sheet and fill four more syringes with 25mL of DI and eight more syringes with 35mL of DI. Turn on hygrometer and place on table

k. After 5 minutes, turn off pumps, extract water and dump in waste container

l. Connect syringes filled with 25mL of DI to mist chambers and add all the water. Turn on pumps for 2 minutes. This is the "dynamic blank"

m. Dump DI water from dynamic blank bottles while dynamic blank is being collected

n. Turn off pumps and extract water. Add sample to corresponding bottles and put in cooler with blue ice

o. Unscrew tubing from activated carbon filters and screw on ½ Teflon tubing to bottom filter packs. Attach bug screens to end of tubing with zip

ties. Guide "outdoor" mist chamber tubing outside window and attach "indoor" mist chamber tubing to top of mist chamber cases

p. Connect syringes filled with 35mL of DI to mist chambers and add about 25mL. Use clothespins to pinch the syringe tubing closed

q. Turn on pumps, adjust valves as needed and start timer

r. Note clock time, flows, temperature, and humidity. Fill in subsequent sample times

s. Run mist chambers for 120 minutes periodically checking on mist chambers at intervals noted on data sheet. Add water from syringes to mist chamber as needed

t. During sampling, add approximately 100mL of field water to field water bottle

u. During sampling, complete technician checklist and ask participants survey questions. Record data

v. Take home dimensions using laser tape measure and record on data sheet

w. Towards end of sampling, empty sample bottles of DI water

x. After 120 minutes, turn off mist chambers, extract water from mist chambers and add sample to corresponding bottles. Place bottles in cooler

y. Sample again for another 120 minutes. Add sample to same corresponding bottles and place back in cooler

z. After sampling is complete, take down mist chamber set up, pumps, tubing, table, and chair, and other supplies. Thank participant and leave home

IN LABORATORY

1. Bring all supplies back into the lab
2. Once back in lab, pipet sample into appropriate labeled vials
   a. Water blank
      i. 1 x 15mL tube filled with at least 3.5mL for TOC analysis
      ii. 1 x 15mL tube filled with at least 1mL for ESI-MS analysis
      iii. 2 x 50mL tube filled with at least 33mL for experiments
   b. Dynamic blank – indoors and outdoors
      i. 1 x 15mL tube filled with at least 3.5mL for TOC analysis
      ii. 1 x 15mL tube filled with at least 1mL for ESI-MS analysis
      iii. 5 x 50mL tube filled with at least 17mL for experiments
   c. Samples – indoors and outdoors
      i. 1 x 15mL tube filled with at least 3.5mL for TOC analysis
      ii. 1 x 15mL tube filled with at least 1mL for ESI-MS analysis
      iii. 5 x 50mL tube filled with at least 17mL for experiments
3. Clean and organize sampling equipment for future sampling

D1.2. Mist Chamber Sampling SOP – field campaign 2

OVERVIEW

Mist chambers, or "Cofer scrubbers," are used to scrub water-soluble organic gases (WSOCs) from the ambient air. These devices do so by way of two GAST ½ HP vacuum pumps pulling air at 25 L min^{-1} through them. Approximately 25 mL of water is added into each mist chamber and upon sufficient flow a mist is created that thereby increases water to gas surface area allowing gases with a high enough affinity for the liquid phase to partition into the mist. The mist then refluxes back down into the bottom of the chamber into the bulk water where, after sufficient sample time, it is then collected for analysis. Only gases are collected into the aqueous phase; particles are filtered out by quartz fiber filters.

PREPARATION

7) Clean sampling equipment
   a. Clean non-metal parts (use Sonicator SOP)
   b. Bake mist chambers at 500°C
   c. Bake quartz fiber filters at 550°C
   d. Clean metal parts with kimwipes and isopropanol
   e. Acid wash 15 mL vials, 50 mL vials, 125 mL Nalgene bottles, 250 mL Nalgene bottles, 500 mL Nalgene bottles, 1L Nalgene bottles, 60 mL syringes, syringe tubing (use acid wash SOP)
8) Check flow meters with digital TSI flow meter calibrator kit
9) Set up mist chambers and install in cases for transport
   a. Gelman filter holds 47mm baked quartz fiber filter (fibrous side contacts incoming air first)
   b. Gelman filter holder swaged to bottom of mist chamber with Teflon tape (Teflon swagelok ½ in. pipe fitting)
   c. URG filter pack holds a 47 mm Zefluor filter (no treatment) = hydrophobic membrane
   d. Mist chamber top swaged (Teflon Swagelok ¾ in. pipe fitting) to URG filter pack plug with Teflon tape
   e. Place mist chambers in cases and secure top and bottom filter holders
   f. Carefully attach syringe tubing to capillary tube of mist chambers
   g. Connect vacuum tubing from top filter holders to bottom port of variable area flow meters
   h. Connect top port of flow meters to valves (valves should be closed)

10) Count and label vials for pipetting of experiment and analysis sized samples upon return
    a. For each sampling period:
        i. 9 x 15mL vials
        ii. 9 x 50mL vials
    b. Label vials with sample ID stickers and unique identification codes. Record in lab notebook ID numbers, identification codes, size, and description of sample. Add a column for volume of water ultimately added and a column to denote what each sample is ultimately used for.
        i. ID example: IA-MC-170712-SMD-DB-I
        ii. <u>Indoor Air – Mist Chamber – 170712-SMD – Dynamic Blank – Indoors</u>

IN FIELD

5) Outside on patio
    a. Place pumps on wooden boards to protect pumps and floors
    b. Attach ½ inch vacuum tubing to the inlet of each pump and run under door through window
    c. Plug pump power cords into power strip and plug into outlet
    d. Attach HEPA filters to outlet of pumps and attach vacuum tubing to HEPA filters. Run line under door and out window.

6) Indoors in kitchen nook
    a. Attach tripods to base of mist chamber cases. Legs should be extended one length by loosening the largest silicone grip lock on each leg, extending the legs out and tightening the lock again
    b. Place mist chambers near kitchen counter lining wall
    c. Attach ¼ inch vacuum tubing to valves at backs of mist chamber cases and use y connectors and straight vacuum connectors to connect mist chamber two pumps.
    d. Plug power cords into switched off power strip and plug into wall. (Upon turning on pumps at a later step, power strip may trip. If this happens, use additional power strip for other power cord and plug into an outlet on a different circuit)
    e. Attach activated carbon filters to bottom filter pack of each mist chamber (under bottom of each case)
    f. Fill 4 syringes with 25mL of DI water. Slowly add water to mist chambers
    g. Turn on power strip to turn on pumps. Slowly open valves until a flow rate of 25 L/min is reached
    h. Run mist chambers for 5 minutes as a "water wash"

i. While waiting for the water wash to complete, fill out data sheet and fill four more syringes with 25mL of DI and four more syringes with 35mL of DI. Turn on hygrometer and place on table

j. After 5 minutes, turn off pumps, extract water and dump in waste container

k. Connect syringes filled with 25mL of DI to mist chambers and add all the water. Turn on pumps for 2 minutes. This is the "dynamic blank"

l. Dispose of DI water from dynamic blank bottles while dynamic blank is being collected

m. Turn off pumps and extract water. Add sample to corresponding bottles and put in cooler with blue ice

n. Unscrew tubing from activated carbon filters and screw on ½ Teflon tubing to bottom filter packs. Attach bug screens to end of tubing with zip ties. Guide "outdoor" mist chamber tubing outside window and attach "indoor" mist chamber tubing to top of mist chamber cases

o. Connect syringes filled with 35mL of DI to mist chambers and add about 25mL. Use clothespins to pinch the syringe tubing closed

p. Turn on pumps, adjust valves as needed and start timer

q. Note clock time, flows, temperature, and humidity. Fill in subsequent sample times

r. Run mist chambers for 120 minutes periodically checking on mist chambers at intervals noted on data sheet. Add water from syringes to mist chamber as needed

s. During sampling, add approximately 100mL of field water to field water bottle

t. Take home dimensions using laser tape measure and record on data sheet

u. Towards end of sampling, empty sample bottles of DI water

v. After 120 minutes, turn off mist chambers, extract water from mist chambers and composite into corresponding Nalgene bottles.

w. pipet sample into appropriate labeled vials
    i. Water blank
        1. 1 x 15mL tube filled with at least 3 mL for TOC analysis
        2. 2 x 15mL tube filled with at least 1 mL for IC and ESI-MS analysis
        3. 2 x 50mL tube filled with at least 33 mL for experiments
    ii. Dynamic blank – indoors and outdoors
        1. 1 x 15mL tube filled with at least 3 mL for TOC analysis
        2. 2 x 15mL tube filled with at least 1 mL for IC and ESI-MS analysis
        3. 2 x 50mL tube filled with at least 33 mL for experiments

      iii. Samples – indoors
1. 1 x 15mL tube filled with at least 3 mL for TOC analysis
2. 2 x 15mL tube filled with at least 1 mL for IC and ESI-MS analysis
3. 5 x 50mL tube filled with at least 14 mL for experiments

      iv. Samples – outdoors
1. 1 x 15mL tube filled with at least 3 mL for TOC analysis
2. 2 x 15mL tube filled with at least 1 mL for IC and ESI-MS analysis
3. 2 x 50mL tube filled with at least 10 mL for experiments

7) Repeat mist chamber sampling if needed
8) At end of day, remove quartz filters and put in labeled petri dishes for offline analysis

IN LABORATORY

4. Once back in lab, freeze vials in chest freezer
5. Prepare additional supplies to take back to field if needed

170612SMD

D1.3. Aqueous cuvette reaction SOP (IC and QTOF-LC/MS) for Indoor Air samples from field campaign 1

Date modified: 151119 SMD

OVERVIEW

Cuvette experiments are designed for investigating aqueous-phase reaction of water soluble organic compounds (WSOCs; e.g., glyoxol) present in the field sample with OH radical. Ten cuvettes are filled with 3mL field sample solutions and H_2O_2. Each cuvette faces directly toward a 254nm UV lamp so that the same OH radical production via H_2O_2 photolysis is allowed to occur in all cuvettes. Adequate concentrations of H_2O_2 are added to the samples in order to insure reaction with the WSOCs. Catalase, which destroys peroxides, is finally added after completion of cuvette reactions in order to remove excess amounts of H_2O_2, which may degrade organic products like glyoxylic acid or pyruvic acid before analytical analysis can occur. The cuvette treated with catalase is then analyzed by IC and/or QTOF-LC/MS.

PREPARATION

1. At least two days before tests and experiments are to begin, start up the IC. Also, ensure that you have scheduled with Wanda Bodnar to use the QTOF-LC/MS in Rosenau 153
   a. For the IC, a method should be created using a five point standard calibration curve using the organic acids that will be used in the standards during the experiment. See ICS SOP step 6 for instructions
2. Before any experiments are to be completed, total organic carbon (TOC) concentrations should be determined. 125µM H_2O_2 will be used in experiments to remain consistent with concentrations used previously.
3. Before any experiments are to be completed, the H_2O_2 photolysis test and catalase test must be performed. The H_2O_2 test should also be performed at end of experiments. For the catalase test, only the catalase volume that will be used in the experiment needs to be tested (33 µL 1% catalase)
   a. UV+H_2O_2 Photolysis test (See H_2O_2 + UV SOP)
      i. Use the same concentration of H_2O_2 as in experiments
      ii. Use the same UV lamp as that will be used in experiments (same output)
   b. Catalase Test: See D1.3.1

4. Determine experiments and instrumental analysis to be conducted. Experiments should be composed of Control Experiments (Field Sample + UV only; Field Sample + H_2O_2 only; Field Water Blank + UV + H_2O_2) and Field Sample + OH Experiments (Field Sample + H_2O_2 + UV) with 20% duplicates.
    a. Experiment set
        i. Field Sample + OH experiments (Field sample + H_2O_2 + UV)
            1. Carboxylic acid compounds: IC and QTOF-LC/MS (-mode) analysis
                a. IC
                    i. Run deionized water blank, field water blank, mixed standard, and independent standard at start and end of sequence
                        1. Mix standard: acetic, formic, pyruvic, nitric, tartaric, sulfuric, oxalic
                        2. Independent standard: oxalate, acetate, pyruvate
                    ii. 20% of samples duplicated
            2. Aldehyde and alcohol compounds: QTOF-LC/MS (+ mode) analysis
                a. QTOF-LC/MS
                    i. Run deionized water blank, field water blank, mixed standard, and independent standard at start and end of sequence
                        1. Standard: glyoxal
                    ii. 20% of sample analysis duplicated
            3. Save and freeze 1 MS vial for additional runs
        ii. Control Experiments
            1. Field Sample + UV (+ and – mode in QTOF-LC/MS)
            2. Field Sample + H_2O_2 (+ and – mode in QTOF-LC/MS)
            3. Field water blank + UV and H_2O_2 (+ and – mode in QTOF-LC/MS)

CUVETTE EXPERIMENTS
    b. Prepare cuvettes for experiment
        i. Clean cuvettes, caps, and two beakers (1L and 250mL) in the sonicator (overnight) (Refer to Sonicator SOP)
            1. Triple rinse, shake dry

      ii.   Rest upside down in triple rinsed 1 L beaker that has a kimwipe in the bottom and place parafilm on top

      iii.   Place all caps in triple rinsed 250mL beaker and triple rinse

      iv.   Rinse caps one more time and wrap all caps in one large kimwipe, let sit overnight

5. Warm up UV lamp at least 45 minutes by putting it in auxiliary immersion well wrapped in foil, prior to placement in the chamber immersion well (Wear protective gear – UV goggles/face shield, lab coat/long sleeves, pull blackout curtain around experiment set up)

    a.   During lamp warm up time – set up cuvette chamber, make solutions, set up IC (refer to IC method / SOP) – run blanks/mixed standards and prep sequence table

    b.   Label properly: Make sure sample IDs are unique, and/or documented in the comments section of the sequence table. Include collection ID/ collection date, etc

6. Melt experiment sample (pipetted in exact volumes after sample collection). See lab notebook for exact amounts

7. Set up cuvette chamber reaction vessel if not already set up

    a.   Place the immersion well inside the reaction vessel

    b.   Wrap cuvette chamber in aluminum foil

    c.   Attach tubes for WATER cooling in the following manner: Connect tubes to chiller as follows: water OUT of chiller and into TOP of reaction vessel. Water IN chiller and into BOTTOM of reaction vessel

    d.   Control flow/monitor water level inside chamber (Water level should not exceed cuvette caps, but cuvettes must be mostly submerged)

8. Connect vacuum tube to lab vacuum

9. Turn on vacuum (enough for audible air flow)

10. Place thermometer and thermometer adapter in thermometer port on top of the reaction vessel. Record temperature

11. Set up dissolved oxygen (DO) meter so that the probe can be plugged in upon start of reaction. Make sure the DO meter is calibrated before a set of experiments

12. Prepare reaction solution (UV + H_2O_2 + Field Sample) and blanks, and place the cuvettes filled with the reaction solution into the reaction vessel:

    a.   Dilute sample by half since there is not enough volume for an experiment

    b.   Make at least 33mL of field sample + H_2O_2 solution in a transfer bottle. To prepare total 33mL of field sample + H_2O_2 solution, mix 1.98 mL of 10mM H_2O_2 and 31.02mL of the field sample from 50mL tube, where the field sample was first collected using the mist chamber

    c. Fill each cuvette with 3 mL of solution mix prepared in the transfer bottle. Cap all cuvettes but one

    d. Place the dissolved oxygen probe inside the one open cuvette and parafilm it closed. This cuvette will be the last time point

    e. Place the 9 capped cuvettes and 1 DO probed cuvette (FUV facing center) in the reaction vessel. Wipe Non-frosted face of cuvette with kimwipe prior to placement. IMPORTANT! Once H_2O_2 is added, start reaction ASAP to minimize H_2O_2 oxidation (i.e., H_2O_2 + Glyoxylic Acid), which is not photooxidation

        i. The 11th cuvette containing field sample + H_2O_2 + catalase is 't = 0 mins'

13. Begin the cuvette photoreaction by inserting the lamp, which is on and previously warmed up at least for 45 minutes in the "foiled immersion well," into the reaction vessel. Make sure you are wearing UV goggles!

14. Remove a cuvette at: t = 2, 4, 6, 10a, 10b, 15, 20, 40, 60, 80 minutes. Record dissolved oxygen at each timepoint

15. Add 33 µL 1% catalase to the 3mL cuvette to quench H_2O_2. Mix catalase solution (by, for example, pumping 1mL pipette 5 times)

16. After catalase is added, measure pH with microprobe for pre-0, t=0min, t=15min, and t=80min samples

17. Split 3mL cuvette volume into 1 1mL QTOF-LC/MS vial and 2 1mL IC vials

18. Label all samples with the same experiment code and sample time. And prepare IC/QTOF-LC/MS samples in between each sampling

19. Analyze 1 IC vial and the QTOF-LC/MS vial immediately following catalase addition. Freeze additional IC vial and save for further analysis

20. Measure and record temperature after the cuvette photoreaction

21. Clean up requires the following:

    a. Turn off the lamp, vacuum, and water chiller

    b. Start the cleaning procedure for the cuvettes, caps, etc.

    c. Put the lamp back in the foiled immersion well if additional experiments are to be completed shortly afterwards or into its Styrofoam sleeve for storage

    d. Monitor the instruments to make sure fluids, etc. are sufficient to finish analyzing all the samples in the sequences

D1.3.1 – Catalase Experiment

1. Use the same concentration of H_2O_2 as in experiments (125 µM)
2. Catalase test will be performed by measuring H_2O_2 with the U-3300 Spectrophotometer
3. To measure H_2O_2 in the spectrophotometer:
   a. Solutions "A" and "B" are prepared according to Allen et. al. (1952)[1].
      i. Solution "A"
         1. 33g KI
         2. 1g NaOH
         3. 0.1 g ammonium molybdate tetrahydrate
      ii. Dilute Solution "A" to 500 mL with water. Stir the solution for ~10 minutes until the molybdate is completely dissolved. Cover Solution "A" with aluminum foil and store in the dark.
      iii. Solution "B" (pH buffer)
         1. 10g potassium hydrogen phthalate
      iv. Dilute Solution "B" to 500 ml with water.
   b. Solutions stored less than 1 month can be used for H_2O_2 measurement.
   c. From each experimental sample take a 800 µL aliquot and mix with 5 ml of Solution "A" and 5 ml of Solution "B". Transfer solution to cuvette and analyze at 351 nm with the spectrophotometer within 1 hour of sampling.
   d. For calibration use 800 µL of H_2O_2 solutions (at 5 different concentrations) mixed with Solutions "A" and "B".
4. Test Instructions:
   i. Add 1% Catalase solution to 3 mL of 125 µM H_2O_2 as follows into 1 vial each
      1. 0 µL 1% Catalase (Vial 1)
      2. 15 µL 1% Catalase (Vial 3)
      3. 33 µL 1% Catalase (Vial 4)
      4. 45 µL 1% Catalase (Vial 5)
   ii. Control vials – add 1% catalase to 3 mL of lab grade DI water
      1. 0 µL 1% Catalase (Vial 1)
      2. 15 µL 1% Catalase (Vial 3)
      3. 33 µL 1% Catalase (Vial 4)
      4. 45 µL 1% Catalase (Vial 5)
   iii. 33 µL of 1% catalase will be added to each experiment cuvette after it is removed from the reaction vessel as a precaution to prevent any additional H_2O_2 reactions that may occur. 33 µL of 1% catalase is equivalent to the amount of catalase used in

photooxidation experiments with outdoor samples. For the first catalase test of a new stock solution, several volumes of 1% catalase should be tested. In subsequent catalase tests, only the volume that will be used in experiments needs to be tested

iv. Add 5 mL of soln A and 5mL of soln B to each cuvette. Mix and analyze.

v. Note: Catalase information
1. 1 unit decomposes 1 μmol H_2O_2 /min at pH = 7 and 25 °C
2. 12,852 units/mg protein (Value from bottle)
3. 45 mg protein/mL (Value from bottle)
4. Calculate amount of 1% Catalase necessary to destroy quantity of H_2O_2 in the volume of experiment solution sampled using the following equation

$$\left(\frac{1 unit}{1 \mu mol H_2O_2}\right)\left(\frac{1 mg\, Protein}{\#units}\right)\left(\frac{1 mL(100\%)cat}{\#mg\, Protein}\right)\left(\frac{\# \mu mol H_2O_2}{3 mL Sample}\right)\left(\frac{100 mL(1\%)cat}{1 mL(100\%)cat}\right)=\left(\frac{\# mL(1\%)Catalase}{3 mL Sample(=1 Cuvette)}\right)$$

D1.4. QTOF SOP

For running mist chamber samples reacted with OH in positive mode on the Agilent 6520 Accurate-Mass QTOF (in Mass Spec Core facility Rosenau 153) to determine reactive (decaying) masses. Based off of method titled "160129_flow-inj_pos_SMD.m"

Prepared by Sara Duncan
February 2017

Instrument set up

1. Prepare tuning and reference mixes (bottles on side of QTOF). Fill tuning mix (bottle B) with "ESI-L Low Concentration Tuning Mix" from stock bottle in bottle left drawer of Isotemp refrigerator in sample prep lab. Create reference mix by filling bottle A with methanol, a dash of water and 300 µL of purine and 100 µL of compound "921" (found in hood in sample prep lab).
2. Plumb HPLC to QTOF directly (figure 1).
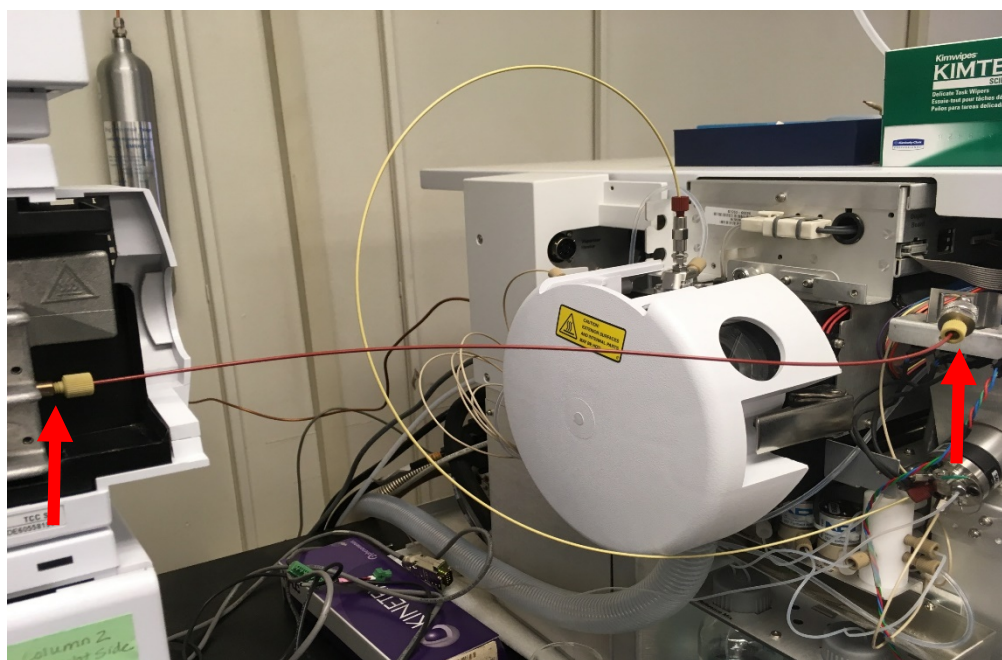
Figure 1

3. Clean out ion source from side of QTOF by wiping down entire interior with a methanol soaked kimwipe (figure 2).
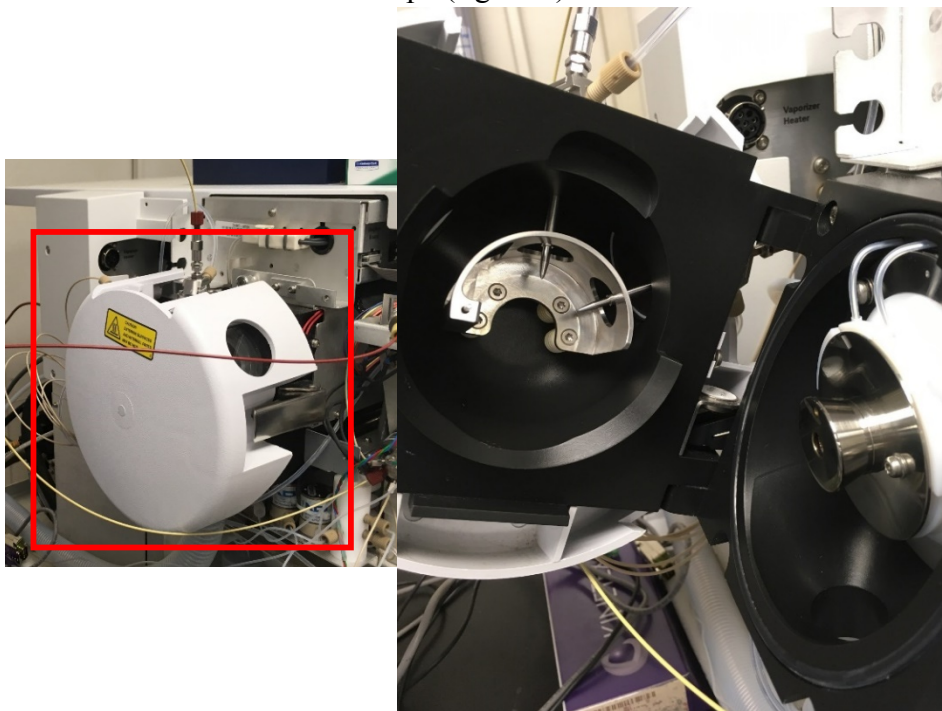
Figure 2

4. Fill two mobile phase bottles with mobile phase. One with deionized water and the other with methanol and 0.05% formic acid. Place on top of pump module and run one "A" line to water and a "B" line to methanol (see figure 3).

Figure 3

5. Open purge valve on Binary SL module by turning left until it feels loose (see figure 4)

Figure 4

Method set up
1. On QTOF computer, open Agilent Data Acquisition Software (red icon)
2. Go to method editor tab on bottom left of screen and save method with new name (or load 160129_flow-inj_pos_SMD.m to use or edit)
3. On Binary Pump tab, set flow rate to 4 mL/min and select appropriate A and B solvents. Set each at 50% (figure 5).
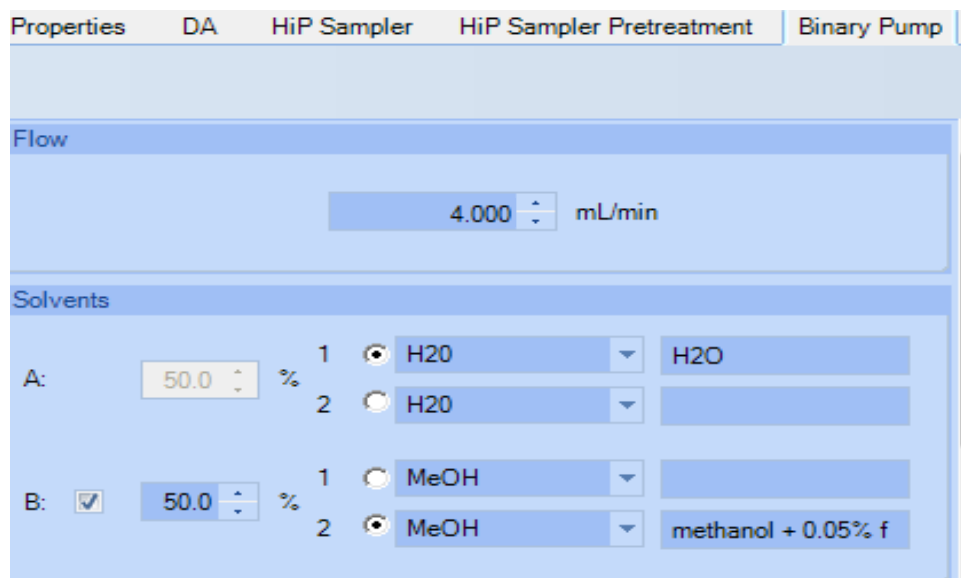
Figure 5

4. Turn on binary pump by right clicking on icon and selecting "switch on" (figure 6). Run for several minutes to purge. Right click icon and select "bottle fillings" and set actual and total volumes (figure 7)
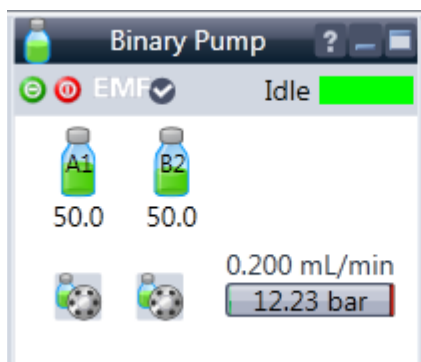
Figure 6
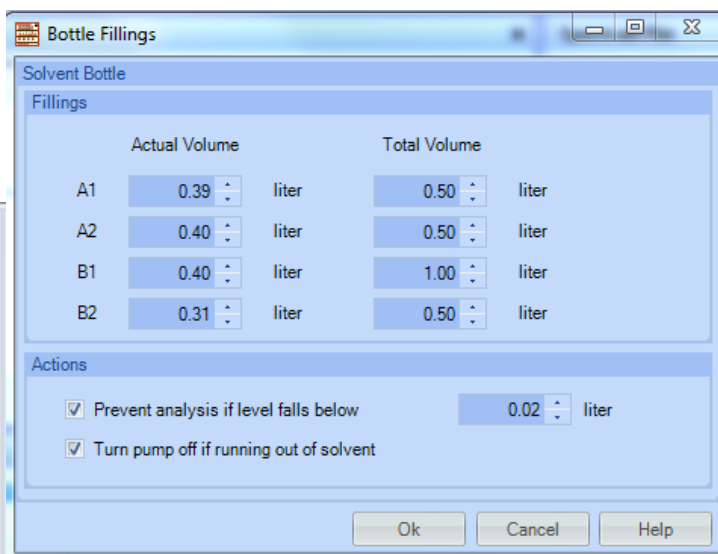
Figure 7

5. Change flow rate to 0.2 mL/min and close purge valve by turning right until tight.
6. Adjust HiP sampler parameters if needed (figure 8).
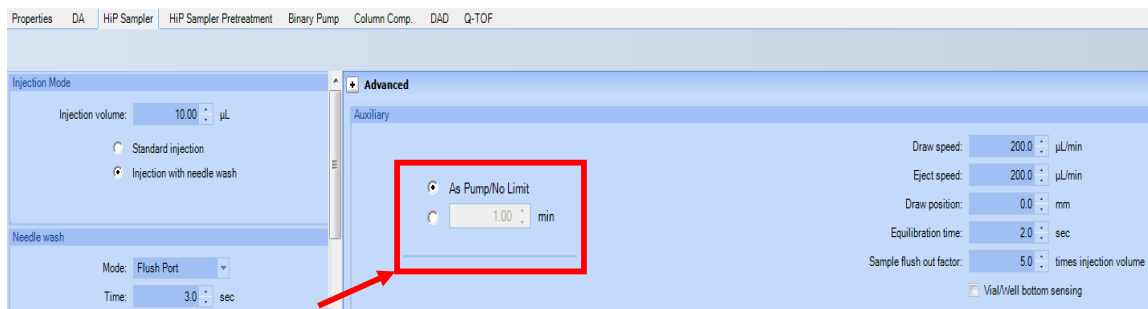
Figure 8

7. In column compartment tab, set valve from port 1 → 2 (figure 9).
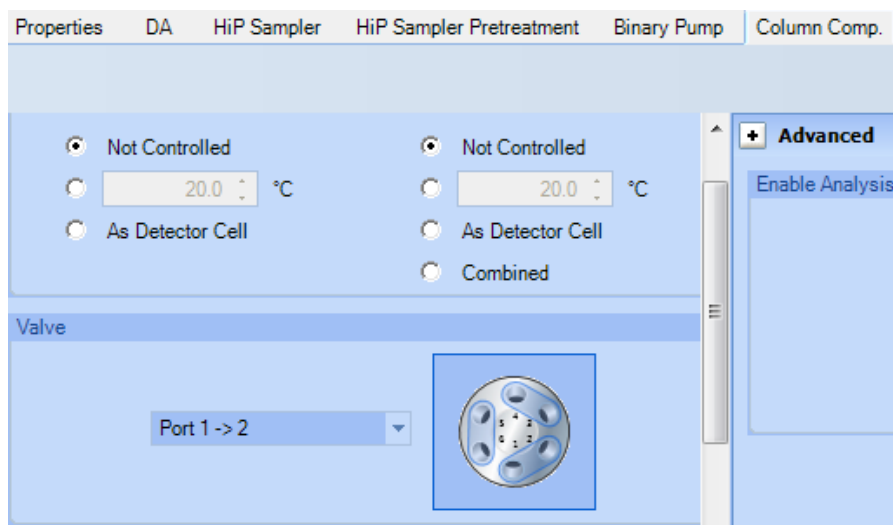
Figure 9

8. Adjust QTOF parameters (figure 10). Make sure Ion Polarity is set to "positive" and fragmentor and skimmer voltages are sufficiently low to prevent compound fragmentation.
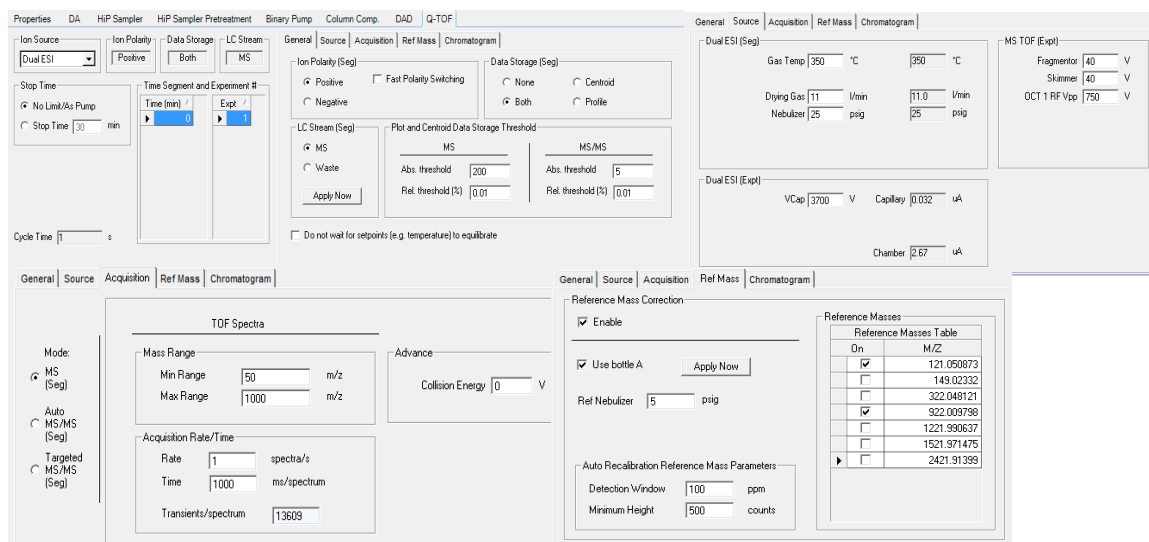
Figure 10

Instrument tuning (calibration) – must be completed daily before running!
1. In top right corner, select "context: tune" from drop down menu (figure 11)
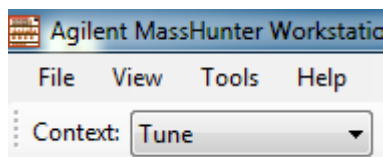
Figure 11

2. Make sure polarity is set to positive mode (software will switch it to whatever polarity it was last tuned in).
3. From Instrument State tab, load "SmallTune.tun" file. Set mass range to low and instrument to high resolution mode (figure 12).
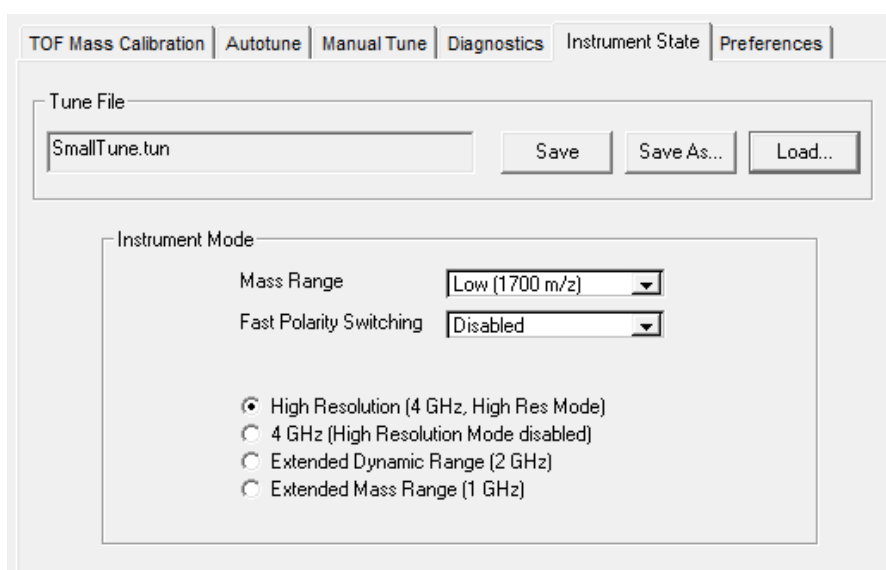
Figure 12

4. On Mass List, load "default_calibration_plus_64_". Set calibrant bottle to "B" and LC flow to waste. (figure 13)

Figure 13

5. Optics should be set according to figure 14.

Figure 14

6. Check profile spectrum. All masses in list should show up clearly. (figure 15)
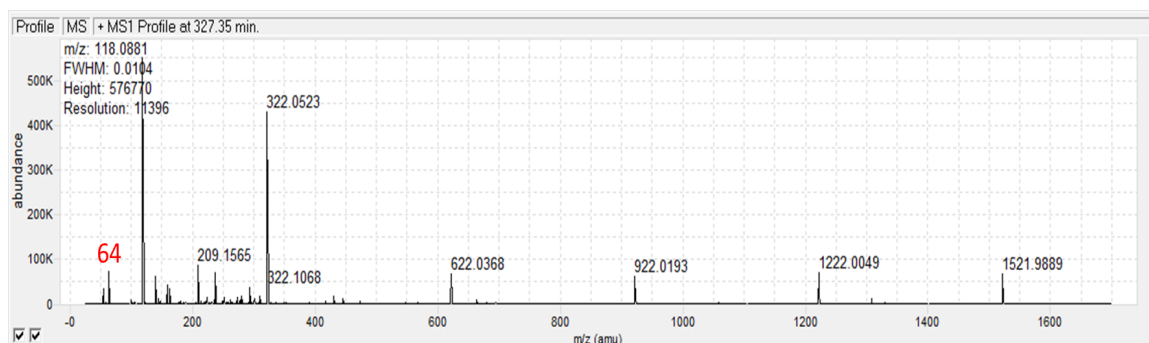
Figure 15

7. Click "calibrate" on Instrument state tab. This will take a minute.
8. Once finished, a dialog box with pop up. Click "Detailed residual plot" and ensure that corrected residuals are on the 0ppm line (figure 16). Primary residuals should also look like the curve in figure 16.
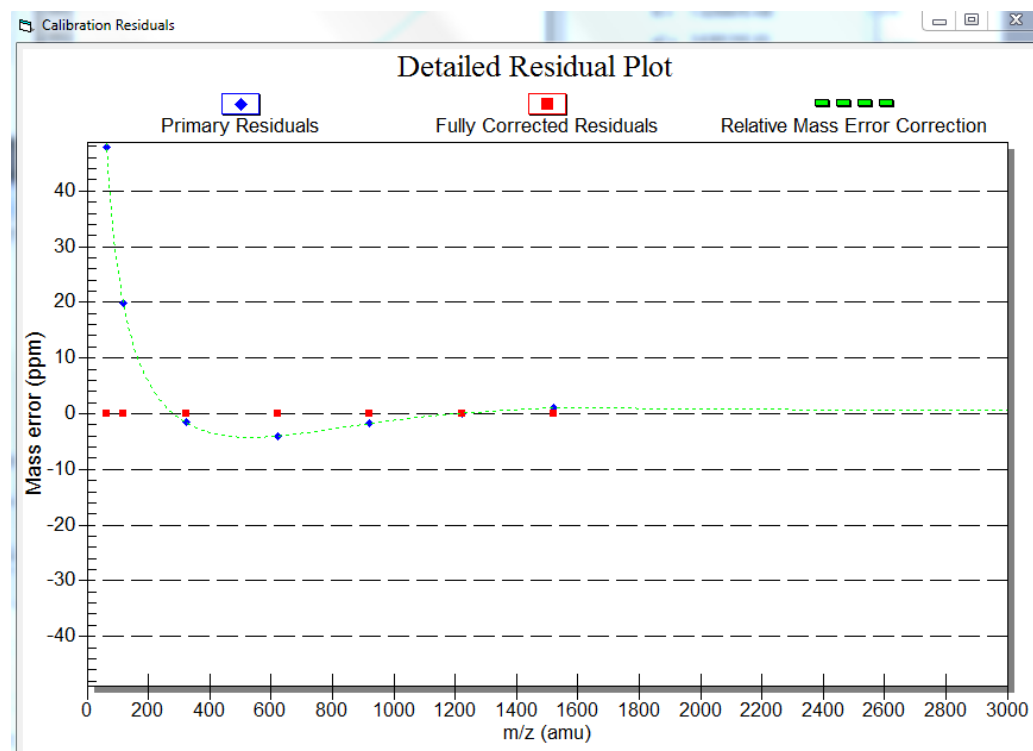
Figure 16

9. Once instrument is calibrated, go back to acquisition context.

Create Worklist

1. Go to worklist tab on bottom left.
2. Save worklist as name.
3. Fill in each column as shown in figure 17. Right clicking on the injection numbers on the left allows you to insert and append samples. Data file column can populate automatically by highlighting column and selecting "fill → down with increment." Check all samples to run in second column if not checked already.

Figure 17

4. Add scripts shown in figure 18 if putting the instrument on standby after a long run by right clicking and selecting "add script."

Figure 18

5. Icons in boxes for instrument modules should look like figure 19. Right click on icon to turn on if any are in standby. Reference mass often gets turned off ("A bottle" should be highlighted in Q-TOF icon) so turn back on in "QTOF tab → Reference mass" of method editor.
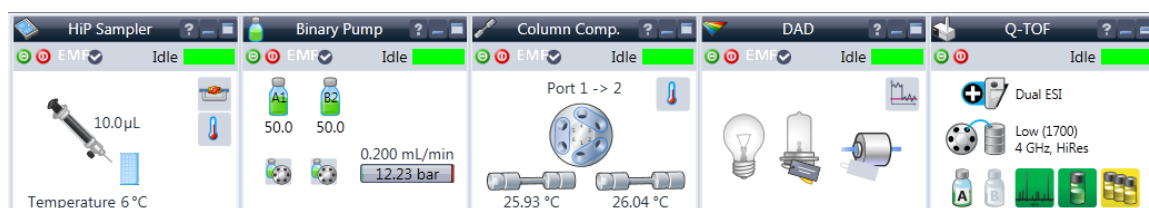

Figure 19

6. Ensure that abundance baseline of chromatogram is stable. Run sequence by pressing the ► button on the worklist (fifth icon from top left in figure 17).

D1.5. IC to QTOF SOP

To separate acids before sending to QTOF for MS detection

Prepared by Sara Duncan
February 2017

1. Transport IC to Mass Spec lab (Rosenau 153)
2. Set up in close proximity to QTOF
3. Plumb IC as if running individually
    a. Start and run according to IC SOP
    b. Flow water through (0.2 or 0.4 ml/min) until conductivity < 1uS
4. Run standard to ensure IC is working correctly

Plumbing IC to QTOF
1. Turn off flow
2. Connect "cell out" on conductivity detector to sample input at ion source (figures 1 and 2)
3. Connect "regen in" to bottle of DI water to replenish suppressor. (figure 1)
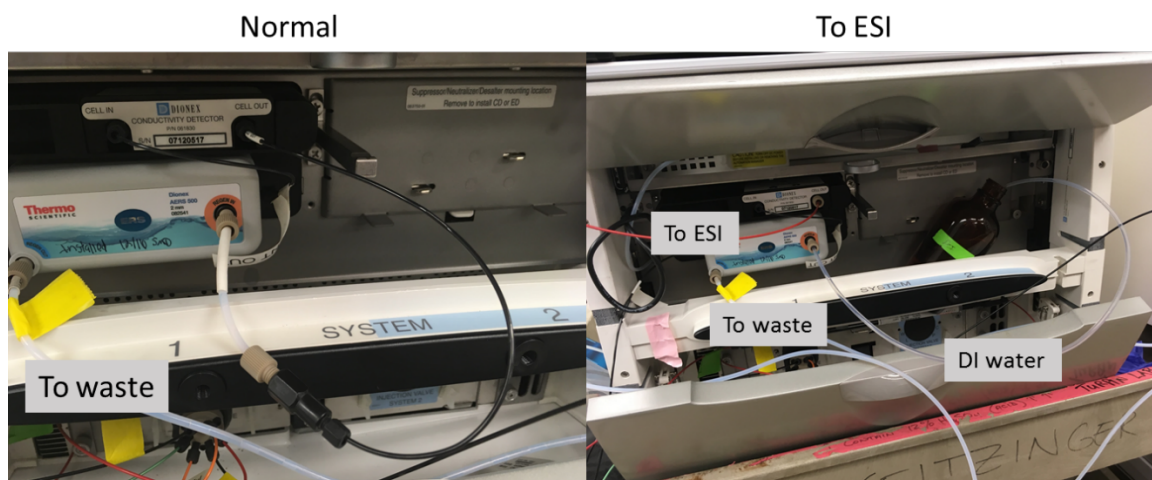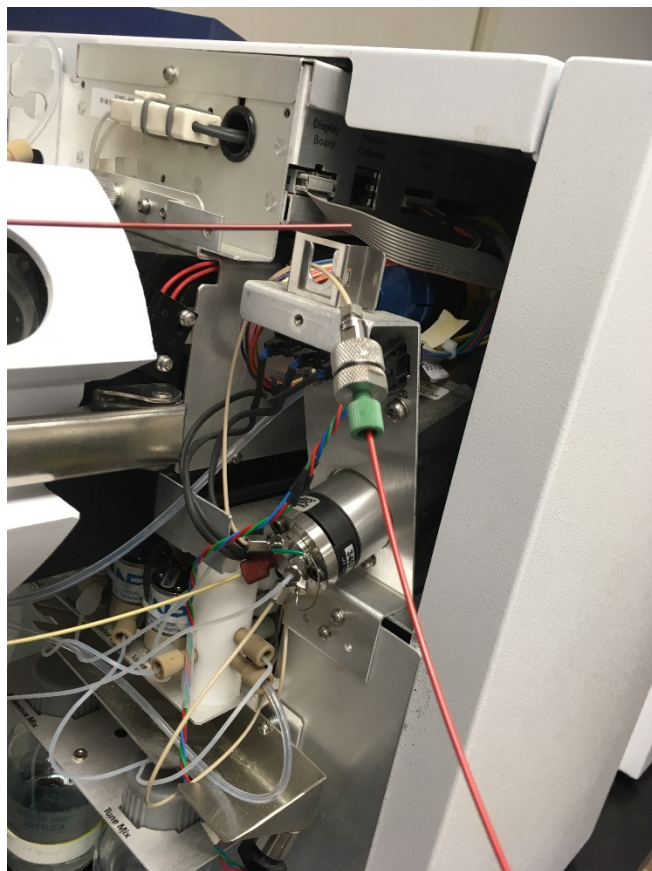

Figure 1

Figure 2

4. Obtain relay analog cable from mass spec lab and connect green plug to TTL Out1 and Gnd on back of **DC compartment** on IC (figure 3). Attach 9 pin serial plug to 'remote' port on back of **HPLC** on QTOF.
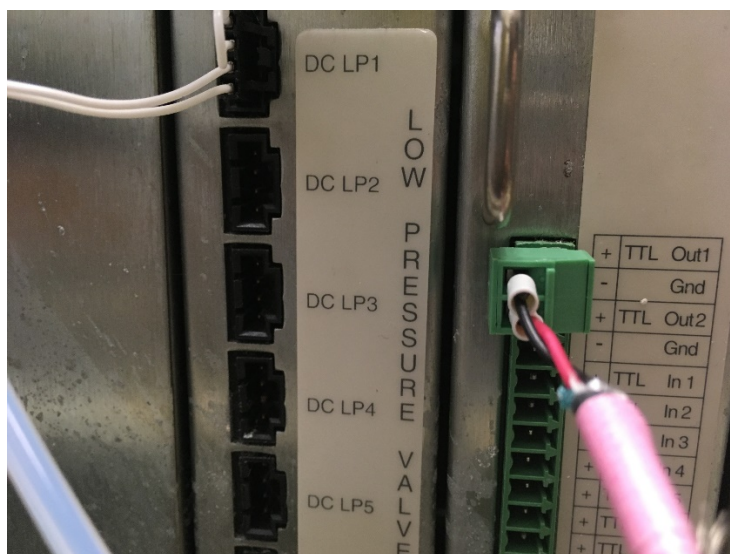

Figure 3

Adjust IC and QTOF software

1. Disconnect HPLC from Agilent software. To do this, close "Data Acquisition" program on QTOF computer. Then, right click "Voyager Engine Launcher" on bottom right of screen and select "Shutdown Engines" (figure 4). Icon will turn red. On start menu, select "Instrument Configuration" in subfolder shown in figure 5. Uncheck "Agilent LC" in dialog box and hit OK (figure 5). Relaunch acquisition software.
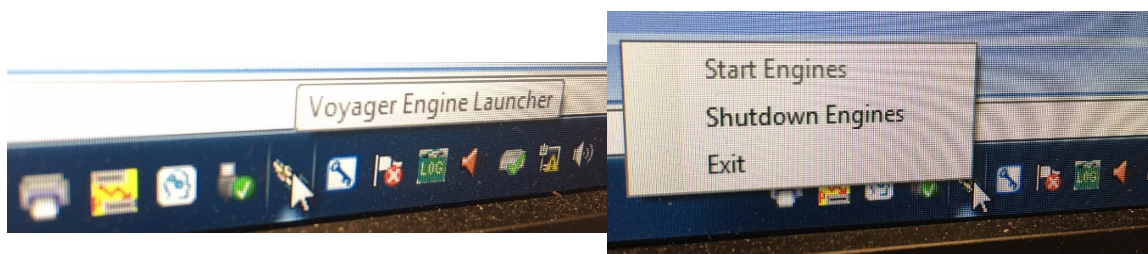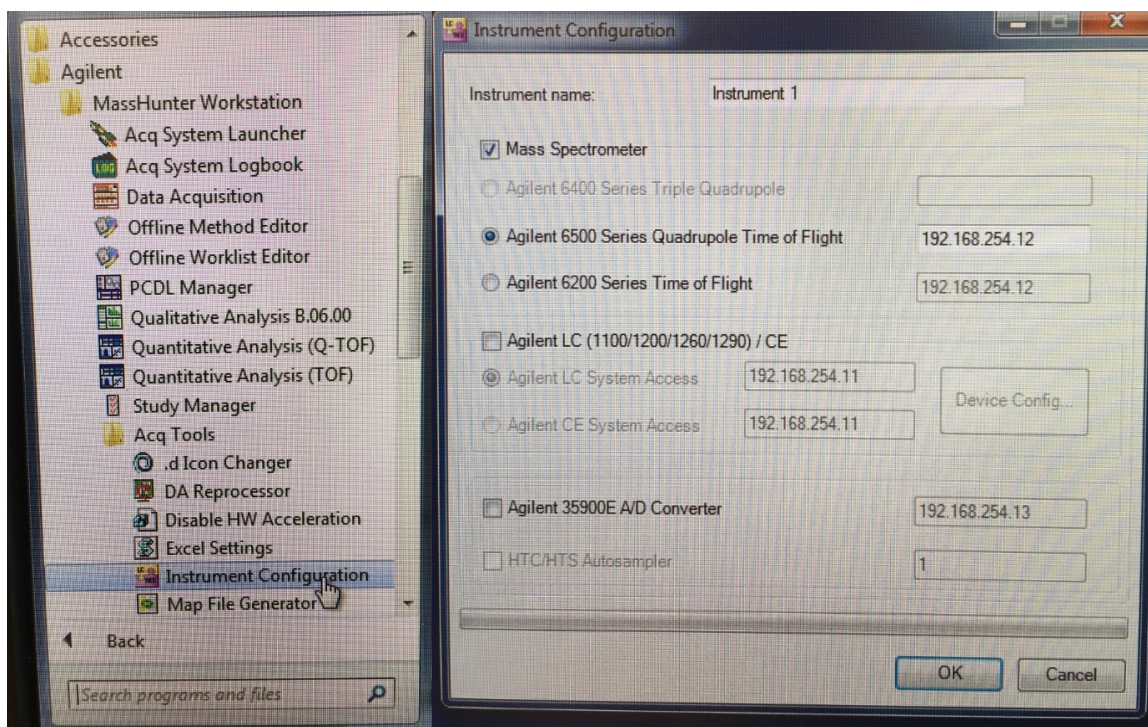

Figure 4

Figure 5

2. Create identical sequences for IC-QTOF to run on both IC and QTOF computers. On QTOF computer, adjust run stop time to include all IC peaks (see figure 6). Make sure fragmentor voltage is sufficiently low to detect whole ions (see method 1701_ICMS_neg_SMD.m as an example (figure 7)).
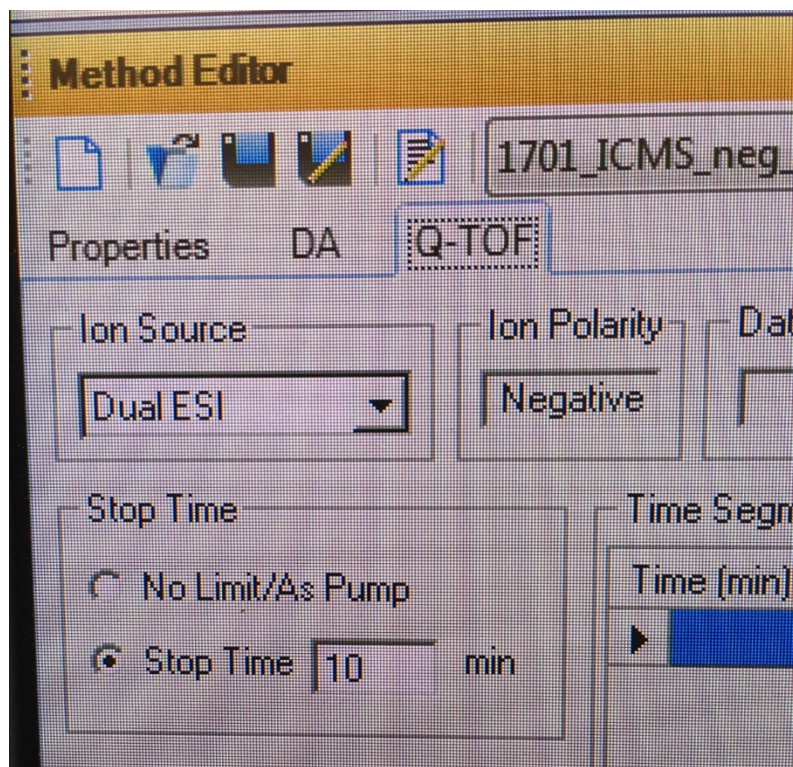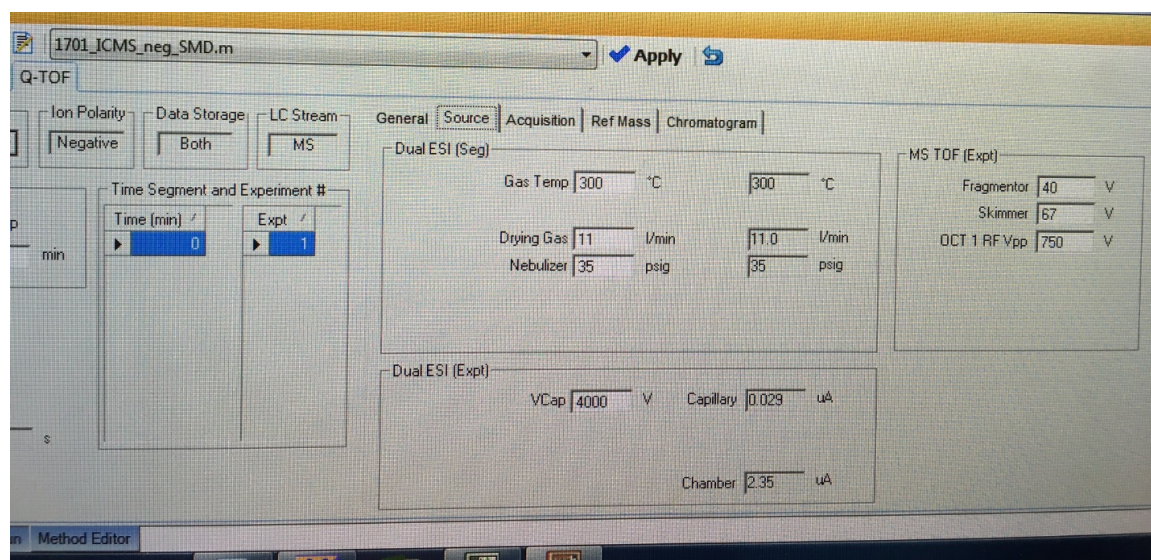

Figure 6

Figure 7

3. In Chromeleon, open the program that you will use. Click "Relay and Start" on bottom of left column (figure 8). Click DC_TTL_1. Click 0v, then reference time: "0:000" and duration: "0.025." Add 5v and 0v as shown in figure 8.
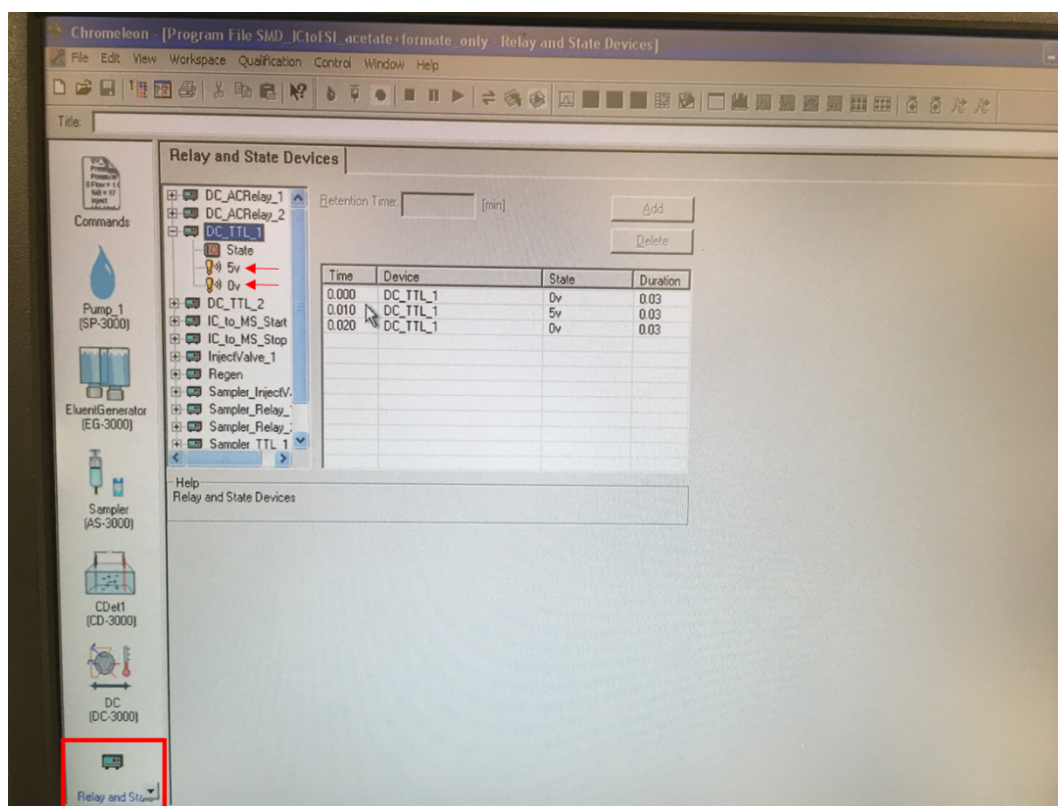

Figure 8

4. Start run on both IC and QTOF. Watch IC log for relay command (will take about 5 minutes of instrument prep before sample is injected), then red line will appear on live chromatogram on QTOF computer indicating the MS data is being recorded.

D2. Additional documents

D2.1. Cuvette experiment sample data sheet – field campaign 1

Experiment Date:		Light turned on (time):	
Experiment name:		Field ID:	

H_2O_2 Conc.:	500μM	Lamp ID:	4
pH of initial sample		Home ID:	
TOC Result (μM-C):			

H_2O_2 Added (Time): _____   UV added (Time): _____

| Time of Day	t = min	Sample ID (Include Cuvette #)	Temp. (°C)	Comments (experiment, operator, sample, etc.)
	PRE-0		25	Diluted field sample only – No H_2O_2 Added
	0			
	2			
	4			
	6			
	10a			
	10b			
	15			
	20			
	30			
	40			
	60			
Other Notes: ☐Lamp warm up time 45 mins ☐1% Catalase Added (Volume = _33_ μL per 3mL Cuvette) ☐IC Calibration Method: _____ ☐Volume H_2O_2 =16.5μL 1M H_2O_2 added to sample ☐Sample dilution: 18mL sample diluted in half=36mL 3mL for pre-0 vials, 33mL remaining				
Stnd. Mix				

D2.2. Technician observational checklist – field campaign 1

Participant
number: _____   Date and Time: _____

AER measurements
_____ Age of home (obtain from Zillow)
       _____

_____ Measure and calculate house dimensions (meters)
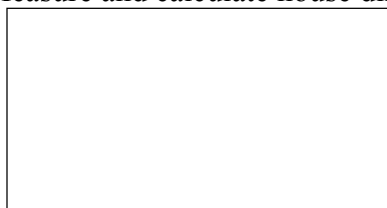
_____ Measure floor height
       _____

_____ Measure building height

       _____

Source information
_____ Qualitative information on potential sources surrounding the home (e.g. gas
stations, trees, highways?). Check Google Maps satellite/ street view first.

_____

_____

_____

_____

_____ Describe flooring in main area of home (wood, carpeting, linoleum, tile, etc).

       _____

       _____

       _____

_____ Cooking or heating up food occurred during sampling (describe food and time).

       _____

       _____

       _____

_____ How many people are at the residence during sampling? _____
       Record if changes: _____

Other notes:

_____
_____
_____
_____