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UNIVERSITY OF CALIFORNIA,
IRVINE

Molecular Composition and Chemical Aging of Organic Aerosol from Various Types of Smoke

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Katherine Suzanne Hopstock

Dissertation Committee:
Professor Sergey A. Nizkorodov, Chair
Professor Manabu Shiraiwa
Professor James Smith

2024

DEDICATION

“I dedicate the time and effort involved in this
project as a gesture of appreciation
to my Parents, for without their patience,
guidance, inspiration, and love none of
this would have been possible.”

-Richard Mark Hopstock

*The Effect of Restoring Sensitivity to the Ventro-Medial Hypothalamus by
Phenylpropanolamine, Insulin, d-Amphetamine, and Fenfluramine in Diabetic Mice*

Princeton University Senior Thesis (1977)

Dad, I couldn't have said it better!

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VITA

Katherine Suzanne Hopstock

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ACADEMIC RESEARCH EXPERIENCE

Nizkorodov Aerosol Photochemistry Group

Irvine, CA

1. Investigation of iron-catalyzed aging chemistry of biomass burning organic aerosol leading to the formation of secondary light-absorbing, brown carbon particles. UV/Vis spectroscopy, high-resolution mass spectrometry, and electron microscopy were utilized in this work. This research was pursued in collaboration with Professor Hind Al-Abadleh (Wilfrid Laurier University) and Professor Joseph Patterson (University of California, Irvine).
2. Characterization of urban fire emissions and effects of photochemical aging on the chemical composition and lifetime of light-absorbing species. UV/Vis spectroscopy and high resolution mass spectrometry were utilized in this work. This research was funded by the National Oceanic and Atmospheric Administration and conducted in collaboration with Professor Alexander Laskin (Purdue University).
3. Human trial vaping study funded by the Tobacco-Related Disease Research Program. Gas-phase chemical characterization of electronic cigarette emissions was examined in the breath of human volunteers. Proton transfer reaction time-of-flight mass spectrometry, gas chromatography, and a scanning mobility particle sizer were utilized in this work. This research was conducted in collaboration with Professors Rufus Edwards and Donald Blake from the University of California, Irvine.

SKILLS

Instrumentation: UHPLC-PDA-HRMS, GC-MS, PTR-ToF-MS, UV/Vis Spectrometer, Direct Analysis in Real Time Mass Spectrometer, Matrix-Assisted Laser Desorption Ionization Mass Spectrometer, Scanning Mobility Particle Sizer, Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy, Pyrolysis Tube Furnace

Chemical and Analytical Software: Igor Pro, Origin, MZMine, Thermo Scientific Xcaliber/FreeStyle/Compound Discover, PTRMS Viewer, MS Office

FELLOWSHIPS

Rowland Fellow

September 2023 – Present

Recipient of the year-long graduate fellowship honoring Dr. Sherwood Rowland, the 1995 Nobel Prize in Chemistry recipient, and longtime UCI Chemistry Professor. This fellowship is awarded to one UCI chemistry graduate student per year. It will allow me to further investigate primary emissions from vape devices and the health risks associated with secondhand vaping.

Campuswide Honors Collegium (CHC) Graduate Fellow

September 2022 – June 2023

I advised junior and senior undergraduate honors students who were embarking on undergraduate research. In my weekly appointments, I mentored students from diverse academic backgrounds, assisting them in developing research topics, collaborating with faculty advisors, creating research timelines, and writing honors theses that meet undergraduate-level standards. I created informative materials and organized workshops to support research initiatives. My other duties included maintaining and updating official records of the CHC, analyzing reports, initiating email and publicity campaigns for CHC events, and evaluating the resumes and CVs of students.

MENTORING EXPERIENCE

NASA Student Airborne Research Program (SARP)

June 2023 – August 2023

Graduate Mentor

As a graduate student mentor, I worked with the whole air sampling (WAS) Group led by Professor Donald Blake. I assisted students in air sampling operations onboard the NASA DC-8 aircraft based out of the NASA Armstrong Flight Research Center in Palmdale, CA. We worked alongside researchers from NOAA in the 2023 AEROMMA airborne campaign. In addition, we conducted ground sampling at local Southern California sites to target emissions of hydrocarbons, ammonia, and sulfur-containing organics. I supported students in developing their own summer research projects, utilizing the collected airborne samples to better understand air quality and environmental justice impacts. I assisted in the students' professional development through panel discussions and workshops.

Undergraduate Student Research Mentor

June 2021 – June 2023

Mentees:

1. Sofia Stirone (*January 2023 – June 2023*)- Sofia worked on optimizing the collection of biomass burning organic aerosol by utilizing passive collection methods.
2. Michael Alvarado (*June 2022 – January 2023*)- Michael worked on characterizing the chemical composition and light-absorption of emissions from burning construction materials (engineered wood, polyvinyl chloride coated wires, plastics, carpet, drywall, ceiling tile, and fabric) and how photochemical aging affects light absorptive properties.
3. Krisztina Rakosi (*Fall 2021 – June 2022*)- 2022 Undergraduate Michael E. Gebel Award recipient, 2022 American Chemical Society- Division of Analytical Chemistry Undergraduate Award recipient. Krisztina worked on the particle size analysis of exhaled vape aerosol from human volunteers in our human trial vaping study.

4. Angel Arredondo (*Summer 2021, Chemistry Summer Undergraduate Research Fellowship student*)- Angel worked on the aging of biomass burning organic aerosol precursor compounds in the presence of transition metals.

Graduate Chemistry Peer Mentoring Program

August 2020 – June 2021

Graduate Student Mentor & 2020-2021 Communications Representative

I participated in a volunteer-based mentoring program for graduate students. Specifically, I mentored a first-year atmospheric chemistry Ph.D. student while I was in my second year of the program. I offered guidance and support to help my mentee navigate research laboratory rotations, coursework, and teaching responsibilities, as well as adjust to graduate student life. Additionally, I served as the 2020-2021 Communications Representative, responsible for sending event and meeting reminders to the program, managing the program website, and communicating with faculty liaisons.

PEER-REVIEWED PUBLICATIONS

1. Katherine S. Hopstock, Qiaorong Xie, Michael A. Alvarado, Vaivos Moschos, Jason D. Surratt, Alexander Laskin, Sergey Nizkorodov. Chemical Composition of Particulate Matter Produced during Fires at the Wildland-Urban Interface. *in preparation* **2024**.
2. Katherine S. Hopstock, Veronique Perraud, Avery B. Dalton, Barbara Barletta, Simone Meinardi, Robert M. Weltman, Megan A. Mirkanian, Krisztina Rakosi, Donald R. Blake, Rufus D. Edwards, Sergey A. Nizkorodov. Chemical Analysis of Exhaled Vape Emissions: Unraveling the Complexities of Humectant Fragmentation in Electronic Cigarette Vapor. *ACS Chemical Research in Toxicology*, **2024**, 37, 1000-1010.
3. Kristian J. Kiland, Katherine S. Hopstock, Ayomide A. Akande, Kristen N. Johnson, Yixin Li, Fabian Mahrt, Sepehr Nikkho, Barbara J. Finlayson-Pitts, Nadine Borduas-Dedekind, Sergey A. Nizkorodov, Allan K. Bertram. Boiling of Catechol Secondary Organic Aerosol when Heated to Mild Temperatures (36-52 C) due to Acetone and Carbon Dioxide Formation and High Viscosity. *ACS Environmental Science and Technology Air*, **2024**, 1, 547-558.
4. Katherine S. Hopstock, Alexandra L. Klodt, Qiaorong Xie, Michael A. Alvarado, Alexander Laskin, Sergey A. Nizkorodov. Photolytic Aging of Organic Aerosol from Pyrolyzed Urban Materials. *Environmental Science: Atmospheres*, **2023**, 3, 1272-1285.
5. Katherine S. Hopstock, Brooke P. Carpenter, Joseph Patterson, Hind A. Al-Abadleh, Sergey A. Nizkorodov. Formation of Insoluble Brown Carbon through Iron-Catalyzed Reaction of Biomass Burning Organics. *Environmental Science: Atmospheres*, **2023**, 3, 207-220.
6. Ting Fang, Brian C. H. Huang, Sukriti Kapur, Katherine S. Hopstock, Jinlai Wei, Vy Nguyen, Sergey A. Nizkorodov, Manabu Shiraiwa. Wildfire as a Source of Environmentally Persistent Free Radicals and Reactive Oxygen Species. *Environmental Science: Atmospheres*, **2023**, 3, 581-594.
7. Henry Chin, Katherine S. Hopstock, Lauren T. Fleming, Sergey A. Nizkorodov, and Hind A. Al-Abadleh. Effect of Aromatic Ring Substituents on the Ability of Catechol to Produce Brown Carbon in Iron (III)-Catalyzed Reactions. *Environmental Science: Atmospheres*, **2021**, 1, 64-78.

ORAL CONFERENCE PRESENTATIONS

- 41st Annual AAAR Conference** Portland, OR
Oral Presentation in Section 3.AC.2 Aerosol Chemistry *October 2023*
"Composition and Atmospheric Transformations of Organic Aerosol Emitted from Biomass and Urban Material Burning."
- 264th ACS National Meeting and Exposition** Indianapolis, IN
Oral Presentation in Division of Environmental Chemistry *March 2023*
"Composition and Atmospheric Transformations of Organic Aerosol Emitted from Biomass and Urban Material Burning"
- 40th Annual AAAR Conference** Raleigh, NC
Oral Presentation in Section 1AE Aerosol Exposure I: Personal & Modeling *October 2022*
"Characterization of VOC and Particle Emissions in Exhaled Air during Vaping"
- 2021 International Chemical Congress of Pacific Basin Societies** Virtual
Oral Presentation in the Atmospheric Aerosols Session *December 2021*
"Iron(III)-Catalyzed Chemistry in Biomass Burning Organic Aerosol"
- 39th AAAR Conference** Virtual
Oral Presentation in Section 8AC.6 Aerosol Chemistry *October 2021*
"Iron(III)-Catalyzed Chemistry in Biomass Burning Organic Aerosol"

POSTER CONFERENCE PRESENTATIONS

- Informal Gathering on Atmospheric Science and Photochemistry** Los Angeles, CA
Poster A21 *October 2023*
"Composition and Atmospheric Transformations of Organic Aerosol Emitted from Urban Material Burning"
- Informal Gathering on Atmospheric Science and Photochemistry** Irvine, CA
Poster A16 *June 2022*
"Characterization of VOC Emissions from Commercial E-Cigarette Usage"

TEACHING EXPERIENCE

- Teaching Assistant, University of California, Irvine, Department of Chemistry*
- Chem 180W: Senior Thesis in Chemistry *Spring 2023*
Chem 1X: General Chemistry Plus *Fall 2021*
Chem 101W: Writing for Chemists *Summer & Fall 2020 (remote)*
Chem 141: Environmental Chemistry *Spring 2020 (remote)*
Chem 152: Advanced Analytical Chemistry *Winter 2020, Winter/Spring 2021 (remote)*
Chem 133L: Nuclear and Radiochemistry Laboratory *Fall 2019*

AWARDS, CERTIFICATIONS, AND MEMBERSHIPS

- Joan Rowland Award *2024*
UC Irvine Outstanding Contribution to the Department of Chemistry Award *2024*
American Chemical Society Graduate Student Awardee in Environmental Chemistry *2024*

UC Irvine Rowland Graduate Fellow	<i>2023-2024</i>
41st Annual AAAR Conference Travel Award	<i>October 2023</i>
UC Irvine Chemistry Department Travel Award	<i>October 2023, April 2020</i>
Certified Orbitrap HRMS Instrument Operator at the AirUCI Institute	<i>January 2022</i>
39th Annual AAAR Conference Travel Award	<i>October 2021</i>
UC Irvine Contributions to the Chemistry Department Teaching Program Award	<i>May 2021</i>
American Chemical Society Member	<i>2022 - Present</i>
The American Association for Aerosol Research Member	<i>2020 - Present</i>

ABSTRACT OF THE DISSERTATION

Molecular Composition and Chemical Aging of Organic Aerosol from Various Types of Smoke

By

Katherine Suzanne Hopstock

Doctor of Philosophy in Chemistry

University of California, Irvine, 2024

Professor Sergey A. Nizkorodov, Chair

An aerosol represents a dispersion of solid or liquid particles in a gas. The propagation of radiation through Earth's atmosphere is directly affected by the absorption and scattering of incoming solar radiation by atmospheric aerosols of both primary and secondary origin, prompting research on the relation between the complex molecular composition of aerosol particles and their optical properties. While all organic aerosols (OA) scatter incoming solar radiation, only a subset of organic aerosols known as "brown carbon" (BrC) appreciably absorb visible radiation. BrC is largely emitted from combustion processes such as through the burning of biomass and human-engineered (or urban) materials. Fires occurring at the wildland-urban interface (WUI) are increasing in both frequency and magnitude, suggesting that the composition and properties of wildfire-related OA are dictated not only by burning biomass but also by burning urban materials. Optical properties of BrC in biomass burning organic aerosol (BBOA) or urban OA are highly variable and are coupled to their fuel source and combustion conditions. Moreover, the molecular composition of BBOA and OA can evolve through atmospheric transport, such as through photochemical aging and condensed phase chemistry, to impact its optical properties.

Human health is directly impacted by exposure to ambient aerosol particulate matter and volatile organic compounds (VOCs), including those coming from burning. Respiratory and cardiovascular illnesses are known outcomes of exposure to ambient air pollution. While unintended exposure to smoke from burning is a serious health risk factor, it should be kept in mind that deliberate exposure to smoking (including vaping) is a significantly greater threat to human health in terms of cancer, lung disease, cardiovascular disease, and mortality rates. Traditional cigarettes emit over 7000 known compounds, many of which are classified as toxic and carcinogenic. Secondhand exposure to cigarette smoke, even if brief, can increase risk of cancer, heart disease, and stroke. Vaping, on the other hand, exposes users to fewer toxic chemicals but is known to induce lung injuries, cardiovascular diseases, and exacerbate asthma conditions. Neither the long-term effects of vaping nor risks to secondhand vape exposure are well known.

Despite advances reported in the literature, there are still many unanswered questions about the molecular identity of BrC compounds in BBOA, connection between the optical properties and chemical composition of BBOA, and condensed phase chemical transformations leading to BBOA aging, particularly those with BBOA species and Fe(III). There is a lack of knowledge on the emissions that come from fires at the WUI and how these aerosols can change during photolytic aging. As for health-related aerosols, much is known about the smoking of traditional cigarettes, but questions remain for vaping.

Chapters 2 and 3 examine the interaction of BBOA with atmospheric iron (Fe(III)), a common component of aerosol liquid water from dissolved mineral dust. Chapter 2 presents evidence that Fe(III) can catalyze oligomerization reactions with a broad range of phenolic compounds, abundantly present in biomass burning smoke, to produce strongly light-

absorbing and water-insoluble particles. Chapter 3 expands upon this Fe(III)-catalyzed chemistry by testing how it proceeds with laboratory generated BBOA instead of specific phenolic compounds. Again, we observed the formation of light absorbing, water-insoluble secondary aerosol particles that were reminiscent of primary soot particles. These chapters conclude that biomass burning smoke can become more light absorbing as it mixes with mineral dust particles during atmospheric transport, and may, therefore, have a stronger effect on climate after aging.

Chapters 4 and 5 examine the chemical composition, optical properties, and effect of sunlight on particulate matter (PM) emitted during urban fires. In Chapter 4, we pyrolyzed ten urban materials and exposed resultant PM to simulated solar radiation. We observed increased absorption and darkening of PM, suggesting that urban fires emit BrC that continues to increasingly absorb light as it travels through the troposphere. Chapter 5 utilized high resolution mass spectrometry techniques to characterize compounds acting as BrC chromophores in urban smoke and determine their fate after photolytic aging. Overall, our results demonstrate that fires at the wildland-urban interface efficiently produce chemically complex BrC PM, which evolves into species with higher light absorptive properties after UV aging.

Chapter 6 examines the composition of VOCs exhaled by participants in a human trial vaping study. We employed a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) and gas chromatography techniques to examine the composition and concentration of VOCs bystanders would be exposed to during a vaping event. Overall results indicate analytical discrepancies between the two techniques, with PTR-ToF-MS results being overwhelmed by e-liquid thermal decomposition and ionization source fragments.

Online PTR-ToF-MS results should be interpreted with caution, however, it still yielded useful results in this study. Harmful VOCs present in inhaled by users are largely absorbed by the body, and less is emitted for secondhand exposures.

This PhD work furthers our understanding of how the chemical composition and evolution of smoke from both forest and urban fires impact visibility and climate. The most important result of this work is the observation that smoke can become darker in color (i.e., more light-absorbing) as a result of two very different mechanisms – transition metal catalyzed oligomerization occurring in the dark and photolysis-induced aging occurring in sunlight. Additionally, in our human trial vaping study, the most important result of this work was that ionization within the PTR-ToF-MS leads to an overestimation of VOCs, some of which have potentially significant health implications. Relying on this method alone could lead to a misrepresentation of the potential for vape emissions on adverse health effects.

CHAPTER 1:

INTRODUCTION

1.1 Atmospheric Aerosols: Background and Motivation

Atmospheric chemistry is an interdisciplinary science which studies the mechanisms by which molecules are introduced into the atmosphere, how they evolve, and how this evolution affects atmospheric composition and properties.¹ It has primarily focused on the chemistry occurring in the troposphere and stratosphere, as these regions have the most direct effect on life. Earth's atmosphere is divided into layers that are defined by variations of temperature and pressure with height. The troposphere (sea level to 15 km) is the lowest layer of the atmosphere and is characterized by decreasing temperature with increasing height and rapid vertical mixing due to the warming of Earth's surface by solar radiation.² Additionally, the troposphere is unique in that it accounts for only ~10 % of Earth's total atmospheric height but it contains ~80 % of its total mass.³ The stratosphere (15-50 km) lies above the troposphere and is characterized by increasing temperature with increasing altitude. Within this region is the "ozone (O₃) layer" which absorbs harmful solar ultraviolet (UV) radiation, which, if it were to reach the Earth's surface, would cause increased skin cancer and cataracts in humans, damage to unicellular organisms, and damage to surface cells of plants and animals.³

Earth's atmosphere is composed primarily of inert gases, nitrogen (78.1%), oxygen (20.9%), and argon (0.9%). The remaining 0.1% of gaseous constituents, commonly referred to as trace gases, are more reactive and variable in concentration. They are comprised of a

myriad of species that include carbon dioxide, neon, helium, methane, and organic species referred to as volatile organic compounds (VOCs). These species play a crucial role in making the planet habitable by absorbing radiation, retaining heat, and providing gases necessary for life.

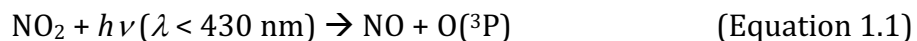
The lower atmosphere contains a large concentration of small airborne particles, which, together with their surrounding gas, are referred to as atmospheric aerosols. Aerosol particles range in size from a few nanometers (nm) to one hundred micrometers (μm) in diameter, and their size affects both their lifetime in the atmosphere and their physical and chemical properties.² Larger particles ($> 100 \mu\text{m}$) also exist but their atmospheric lifetime decreases to hour-timescales due to sedimentation processes. Nanometer-sized particles are viewed as molecular clusters rather than aerosols. Aerosol particles can originate from primary, natural sources such as sea spray, mineral dust, biological aerosol particles (pollen and fungal spores), and volcanic activity.⁴ They can also be emitted from anthropogenic activities such as the burning of biomass during prescribed burns or the combustion of fossil fuels.^{5,6} Furthermore, secondary organic aerosol (SOA) particles can be formed during atmospheric aqueous reactions and during reactions amongst gas-phase precursors (such as emissions from biogenic sources) and atmospheric oxidants ($\bullet\text{OH}$, O_3 , $\text{HO}_2\bullet$, $\text{NO}_3\bullet$).^{7,8} Atmospheric aerosols have a residence time in the atmosphere from a few hours up to several days, during which they can undergo chemical change during transport until their ultimate removal by sedimentation, dry deposition onto Earth's surface, and/or wet deposition through incorporation into rain/cloud droplets.⁹ Particle lifetimes become considerably longer if they are injected into the free troposphere, above the planetary boundary layer.

Human exposure to aerosol particulate matter (PM) is known to induce cardiovascular and respiratory illnesses.¹⁰ Specifically, particles less than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$) can be deposited deep within the lungs and induce oxidative stress and respiratory illnesses. Additionally, reactive oxygen and nitrogen species present in PM can induce oxidative stress, pulmonary inflammation, and other cardiopulmonary illnesses (such as heart disease, respiratory infections, chronic lung disease).^{11,12}

The chemical composition of $\text{PM}_{2.5}$ strongly dictates the effect on human health.¹³ For example, polycyclic aromatic hydrocarbons (PAHs), a relevant compound class to this dissertation, are common in $\text{PM}_{2.5}$ and are known agents of genetic mutation and carcinogenicity, as these species bind to nucleotides (the building blocks of deoxyribonucleic acid, DNA).^{14,15} Durant *et al.* (1996) determined human cell mutagenicity was achieved when exposed to PAHs, oxygenated PAHs, and nitrated PAHs, all of which are common in urban aerosols.¹⁶ Also present within urban PM are water-soluble transition metals (such as Fe, Ni, Cu, Cr, Mn, Zn) that generate reactive oxygen species and ultimately induce an inflammatory response.¹⁷⁻¹⁹ These are just two examples (of many) known health effects from aerosol PM exposure and more studies are needed to identify the correlation between PM chemical composition and adverse health effects, especially in environmentally relevant systems that have not been previously explored (e.g., smoke from urban fires).

Aerosol particles play a significant role in visibility degradation, especially in urban areas. On an occasion with adequate light distribution and an object(s) within view, visibility can be reduced through the absorption and scattering of light (by both gases and particles) within the path from the viewer to an object. The intensity of this effect is dependent upon the concentration of aerosol particles and their size, with those $< 1 \mu\text{m}$ being major

contributors to visibility degradation due to efficient light scattering properties.²⁰ A local Southern California example of this is the Los Angeles Basin, which is highly affected by anthropogenic pollution and photochemical smog. Sulfate, nitrate, carbonaceous materials, and aerosol liquid water all contribute to light scattering and reduction of visibility.²¹ Additionally, the San Gabriel, San Bernadino, and San Jacinto Mountain ranges lining the Basin create temperature inversions, where warm air above traps cooler air (and rising pollutants) closer to the ground. Restriction of air movement in the valley allows for chemical reactions to take place. The primary gas-phase pollutants in this region are NO_x (mainly NO) from vehicle exhaust and organic gases (VOCs). Urban morning commutes allow for the increased emission of NO, which oxidizes to NO₂ through hydroxyl radical (•OH) initiated chemistry with organics.² NO₂ then undergoes photodissociation to form O₃ (Equations 1.1 and 1.2).²²⁻²⁴ NO₂ selectively absorbs blue light (< 430 nm), and as a result, when in high concentration, plumes of red, brown, or yellow appear (smog).³



On a global scale, atmospheric aerosols affect Earth's climate by absorbing or scattering incoming sunlight.²⁵⁻²⁷ Depending on the aerosol's chemical composition and hygroscopicity, particles can act as nuclei onto which water can condense and become seeds for clouds. The Intergovernmental Panel on Climate Change (IPCC) report (Figure 1.1) has classified the radiative forcing of greenhouse gases, VOCs, and aerosol particles.²⁸ Greenhouse gases, such as carbon dioxide (CO₂), methane (CH₄), ozone (O₃), and chlorofluorocarbons (CFCs) absorb infrared radiation and result in net positive radiative forcing (warming). These estimates have “very high” and “high” levels of confidence,

whereas aerosols and their precursors have a “low” to “high” level of confidence. Radiative forcing by aerosols spans both net negative and positive values with large uncertainty. Mineral dust, sulphate, nitrate, and organic carbon (including brown carbon, BrC) species demonstrate net cooling, whereas elemental carbon (or black carbon, BC) exhibits net warming effects. The net effect of aerosol particles on climate is unclear, due to remaining uncertainties in chemical composition, physical properties, and chemical transformation of atmospheric aerosols.

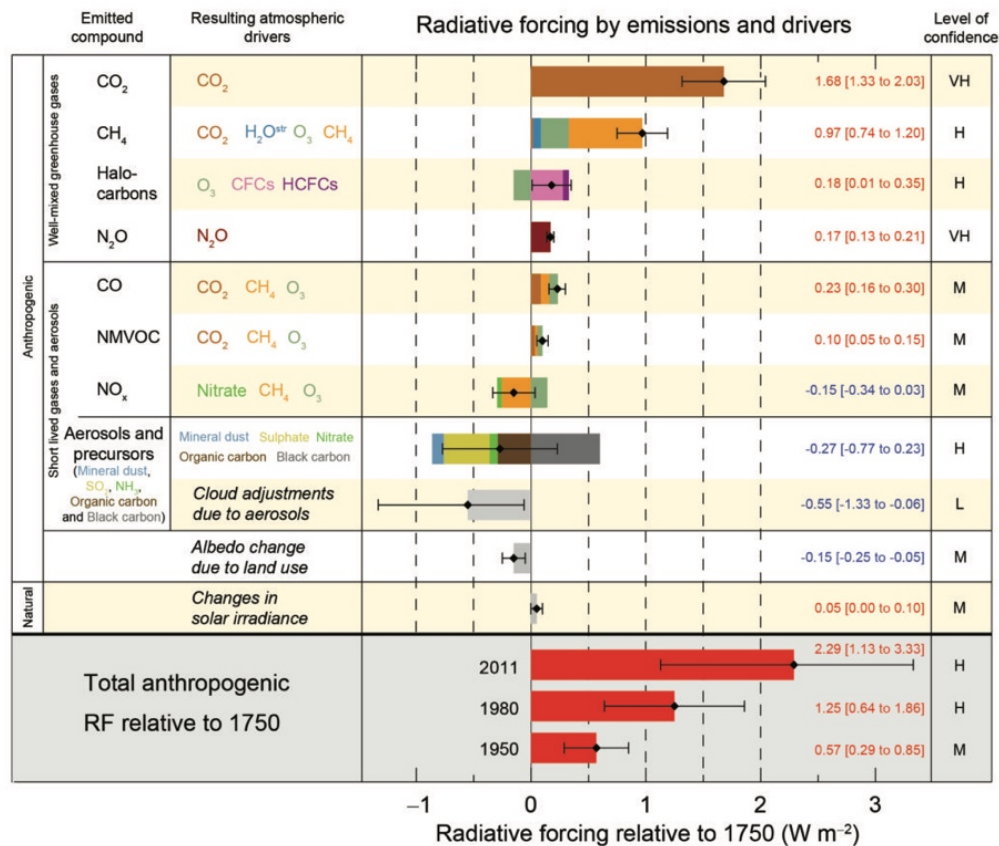


Figure 1.1. Radiative forcing (W m⁻²) estimates in the year 2011 relative to 1750. Species exhibit a net cooling effect when radiative forcing falls below 0, such as for some aerosol species. Species exhibit a net warming effect on climate with positive radiative forcing values, as shown for greenhouse gases (CO₂, CH₄, halocarbons, and N₂O). This figure was reproduced from Figure SPM.5 in the Intergovernmental Panel on Climate Change (IPCC) 2013 Summary for Policymakers report.²⁹

1.2 Optical Properties of Atmospheric Aerosols

Atmospheric aerosol particles can absorb solar and terrestrial radiation across a broad range of wavelengths of the electromagnetic spectrum, including UV (<400 nm), visible (400-700 nm), near-infrared (IR) (700-1500 nm) ranges that are especially relevant to atmospheric photochemistry and radiative energy balance. The greater majority of atmospheric organic aerosols (OA) are referred to as “white”, as they efficiently scatter visible radiation, however, a highly variable fraction of OA absorb visible radiation.³⁰ Most organic carbon compounds strongly absorb both UV and mid-IR (3000-8000 nm) radiation but are transparent in the visible and near-IR ranges. BC and BrC are notable exceptions to this.

BC strongly absorbs solar radiation from the UV into the IR and commonly represents soot-like particulates generated through fossil fuel combustion or flaming biomass burning combustion.³¹⁻³³ BC is comprised of carbon atoms that are arranged in honeycomb-like graphitic layers and electrons are delocalized along the extended network to give strong broadband absorption properties with weak spectral dependence on the absorption coefficient (λ^{-1}).^{30,34,35}

BrC is characterized by a stronger wavelength dependence (λ^{-2} - λ^{-6}) and an absorption spectrum that sharply increases from the visible to UV wavelengths.³⁰ BrC is comprised of a variety of molecular structures (PAHs, humic-like substances, biopolymers, etc.) each with molecule-specific optical properties.³⁶⁻³⁸ Primary BrC emissions are mainly attributed to pyrolysis and smoldering combustion processes but can also form secondarily in the atmosphere during condensed-phase reactions.³⁹⁻⁴² Sun *et al.* (2007) determined that molecules contributing to BrC absorption only account for a small fraction of components

within biomass burning organic aerosol (BBOA).⁴³ This study determined BrC chromophoric species were those with large molecular weight (≥ 18 carbon atoms), contained unsaturation, had ≥ 3 oxygen atoms, and/or had ≥ 1 nitrogen atoms.⁴³

As is one of the main themes of this dissertation, optical properties of aerosol particles are often characterized in BrC-related literature. Two commonly used metrics to determine aerosol direct absorption effects are the Absorption Ångström Exponent (*AAE*) and the Single Scattering Albedo (*SSA*). *AAE* refers to how strongly the absorption coefficient depends on the wavelength,⁴⁴ whereas *SSA* is the ratio of the scattering efficiency to the overall extinction efficiency by particles.⁴⁵ Graphitic-like BC aerosols have an *AAE* value between 1-1.6, as the *MAC* of BC is not strongly wavelength-dependent.^{40,46} BrC aerosol particles have *AAE* values are greater than 1.6 and these values are highly variable depending on the source of BrC.³⁰ Mass absorption coefficients (*MAC*) represent the spectral dependence of absorption with respect to a power law relationship with *AAE* (Equation 1.3). $MAC(\lambda)$ of the aerosol is the wavelength-dependent mass-normalized absorption coefficient (m^2g^{-1}) and *K* is the pre-exponential factor that includes aerosol mass concentration. When extracting aerosol PM into a bulk solution and measuring absorbance of the overall collection of dissolved organics, Equation 1.4 is used to calculate *MAC*.³⁰ Here, the base-10 absorbance obtained by the UV-Vis spectrometer (A_{10}) is referenced to *b* (the path length of the cuvette, often 1 cm) and C_{mass} (the mass concentration of the extract in units of g cm^{-3}). *MAC* values can be converted into the imaginary refractive index, which is the parameter used by radiative transfer models.

$$MAC(\lambda)_{\text{aerosol}} = K\lambda^{-AAE} \quad (\text{Equation 1.3})$$

$$MAC(\lambda)_{\text{bulk}} = \frac{A_{10}^{\text{extract}}(\lambda) \times \ln(10)}{b \times C_{\text{mass}}} \quad (\text{Equation 1.4})$$

1.3 Emissions from Combustion Processes

1.3.1 Biomass Burning Organic Aerosol

This dissertation primarily focusses on characterizing the chemical composition and optical properties of BBOA, which can originate from both natural and anthropogenic sources. Major sources of PM from combustion emissions include wildfires, intentional burning of wildland and agricultural fields, and residential burning of wood/biomass for heating and cooking.^{47,48} VOCs and other trace gases (such as CO, CO₂, CH₄, HCN, NO, NO₂, NH₃, various aromatic and non-aromatic hydrocarbons)^{47,49,50} are also emitted during BB combustion processes, however, this dissertation focusses on the organic matter associated with particles in BB smoke. To understand the composition of emissions from biomass combustion, the general structure of biomass must be examined.

Though there are deviations amongst species, biomass generally consists of three main polymeric building blocks: lignin, cellulose, and hemicellulose. Lignin contributes to the structure and support of a plant and is composed of a complex chain of organic polymers, made from the cross-linking of phenolic precursors.⁵¹ The three main phenolic precursors that form lignin are p-coumaryl alcohol, conifer alcohol, and sinapyl alcohol.^{52–54} The structural complexity of lignin arises from the presence of other monomers, however on the whole, phenolic species dominate the overall structure.⁵⁵ Cellulose forms the structural framework of wood cells and is a linear polymer composed of repeating units of D-glucose (C₆H₁₀O₅) monomers held together through β -glycosidic linkages.⁵⁶ Hemicellulose consists of short, highly branched chains of five different five-carbon (D-xylose and L-arabinose) and six-carbon (D-galactose, D-glucose, and D-mannose) sugars.⁵⁷ During combustion, chemical

bonds within these biopolymers break, which results in emission of VOCs and rearrangement of species remaining in the matrix residue. Levoglucosan ($C_6H_{10}O_5$) is often referred to as a stable tracer for biomass burning emissions, as it is produced from the combustion of cellulose materials and does not undergo significant atmospheric degradation.⁵⁸⁻⁶⁰

There are four main recognized chemical pathways of solid fuel combustion: distillation, pyrolysis, flaming combustion (gas-phase oxidation), and smoldering combustion (heterogeneous oxidation). When a fuel is lit, the first process is distillation (90-300 °C), which is classified as the gradual heating of biomass leading to the emission of water vapor and terpenes (monoterpenes, sesquiterpenes, and oxygenated monoterpenes).⁶¹ White smoke is often visible during this process. Pyrolysis (300-800 °C) is the next phase, when the solid biomass is heated to produce pyrolyzate, char, and ash.^{56,62} It is during this stage that breakdown of lignin, cellulose, and hemicellulose produce the most VOCs. This breakdown can occur through depolymerization, fragmentation, and/or aromatization and is controlled by the temperature of the reaction and composition of the biomass fuel, as will be described in more detail below.^{49,50,56} The next stage is gaseous, flaming combustion (typically 1500-1800 °C), where a gaseous fuel (called pyrolyzate) reacts with oxygen to produce more heat, CO_2 , NO_x , HONO, H_2O , and other VOCs.⁶² Once a flame dies out, smoldering combustion of the remaining fuel (450-700 °C) can occur. In this case, solid char is heated in the presence of oxygen to generate CO, CO_2 , H_2O , other VOCs, and solid ash.⁶² Often times in an environmental fire, smoldering and flaming can occur simultaneously, and one can lead to the other.⁶³ For example, a flaming fire can extinguish and transition to a smoldering fire, which is often perceived as a red glowing of biomass. Availability of oxygen

can induce flaming combustion again, and cycling continues until heat dissipates. Fire combustion stages are often unpredictable and depend on many variables, such as meteorological parameters, fuel moisture content, and fuel composition, to name a few.

Of the stages of combustion, pyrolysis is the most applicable to the goals of this dissertation. In a laboratory setting, pyrolysis is conducted under an inert gas flow (typically N₂) to prevent flaming, and thermal degradation of a biomass material can be achieved without the occurrence of auxiliary gas-phase reactions. This dissertation work focusses on pyrolysis combustion, as we aimed to target emissions of BrC species and observe chemical evolution under various conditions.

Pyrolysis produces condensable products that can form BrC particles and it is recognized as the dominant combustion source of BrC aerosol particles.^{64,65} Sekimoto *et al.* (2018) provided a comprehensive analysis of VOCs emitted as a function of temperature when pyrolyzing 15 biomass fuels representative of vegetation in the western United States (Figure 1.2).⁶¹ Lower pyrolysis temperatures (300-500 °C) break bonds within biopolymer monomer units to yield guaiacols, eugenol, syringol, furans, and furfurals. These species are enriched with alcohols (-OH), ethers (mainly methoxy groups: -O-CH₃), esters (-C(=O)-O-), and amines (-NH₂; mostly primary ones). Higher pyrolysis temperatures (500-800 °C) can break stronger bonds in char to yield aromatic compounds with short substituents (e.g., phenol), non-substituted aromatics (e.g., benzene), and PAHs (e.g., naphthalene). The most substantial emissions of phenolic species (e.g., phenol and catechol) occur within 400-600 °C, however, they continue to be emitted up to 800 °C. Non-substituted aromatics begin generation after 600 °C but are in highest abundance at temperatures greater than 700 °C. As for PAHs, emissions dominate at temperatures greater than 750 °C. As temperatures

increase, substituents on aromatic rings (from biopolymer substituents) disappear and PAHs are dominantly produced. In summary, lower pyrolysis temperatures emit aromatic oxygenates (with ≥ 2 oxygen atoms) and furans, while higher pyrolysis temperatures emit aromatic hydrocarbons with functionality decreasing with increasing temperatures. Results from Sekimoto *et al.* (2018) were crucial in understanding experimental results in Chapters 2 and 3 of this dissertation.⁶¹

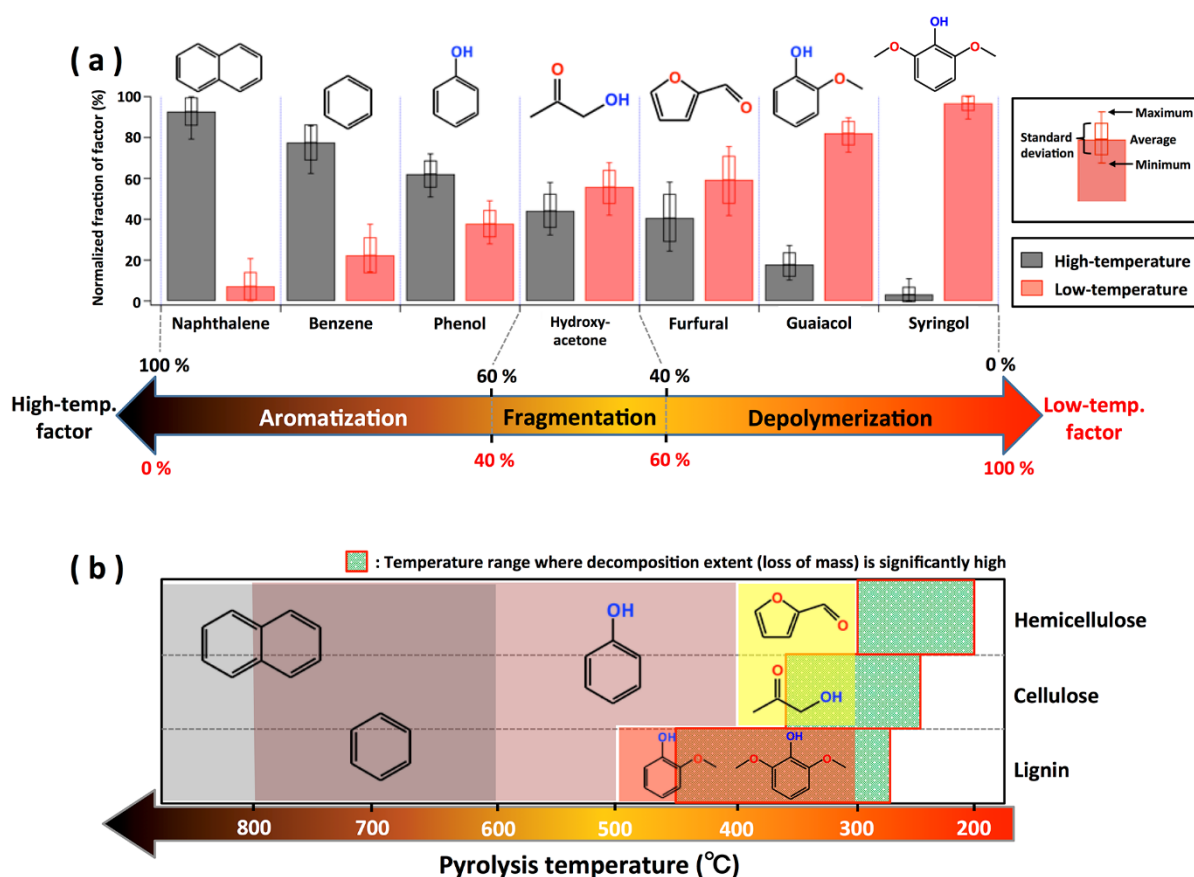


Figure 1.2. Normalized fraction of factors for selected biomass pyrolysis products, obtained using positive matrix factorization results of 15 fuels (panel a). Panel b shows the relationship between pyrolysis temperature and products for hemicellulose, cellulose, and lignin, as reported in the literature (Collard and Blin, 2014).⁵⁶ Individual color bars show the temperature range to form specific products described by chemical structures. Reprinted in original, unmodified form from Sekimoto *et al.* (2018) under the Creative Commons Attribution 4.0 License.⁶¹

BBOA PM is chemically diverse and presents challenges when attempting to characterize its components through extraction and analysis with common analytical techniques, such as liquid chromatography (LC). Chen and Bond (2010) reported absorption coefficient measurements of OA extracts generated through the pyrolysis of solid fuels.⁶⁶ When extracting with water and hexane (polar and nonpolar solvents, respectively), absorption was lower than the same sample extracted in methanol or acetone, indicating that BrC chromophores in BBOA smoke particles have moderate polarity.⁶⁶ This insight was carefully considered in Chapter 4 of this dissertation when investigating the best solvent system to characterize the optical properties of OA from wildland-urban interface (WUI) fires.

1.3.2 Wildland Urban Interface Fires

The WUI is defined as the transition zone between wilderness and the human-built environment. The number and spatial extent of WUI communities is growing rapidly with about a third of all housing units in the United States being located in the WUI.⁶⁷ Research suggests that by the year 2030, the geographic size of WUI will increase by more than 10 percent, as these areas are desirable for socio-economic reasons.⁶⁸ These communities are more vulnerable to fires due to lack of barriers between urban structures and wildlands.⁶⁹ In WUI fires, flames may pass into urban spaces or embers (generated by wildfires) can spread to urban structures, initiating smoldering combustion that can develop into flaming combustion.⁷⁰ Embers often deposit on roofing material, decks, and vents where they can smolder until the transition to flaming combustion is met.^{62,71,72} All fires of this type are unfortunate, and an significant example of this was the Camp Fire in Butte County, California

in November 2018. Electrical transmission lines ignited vegetation at two rural sites that quickly spread to urban areas, destroying the town of Paradise, CA, and damaging neighboring communities. Thousands of structures, residences, and commercial buildings were destroyed, and most sadly there were 85 fatalities.⁶⁷ Residents of neighboring communities were exposed to heavy smoke. Research on the risks of WUI fires can lead to the facilitation of preemptive measures to protect communities and minimize risk. Additionally, research on toxicant concentrations of WUI fires can help mitigate health risks and air quality effects of those close to and downwind of the fire.

Common residential building materials include various types of chemically treated wood, thermal insulation (made from polyurethane, polyisocyanurate, and phenolic foams), glass wool insulation, vinyl siding, polyvinyl chloride (PVC) windows, upholstery on furniture, vinyl carpet, polyamide carpet, electrical wiring insulation (typically PVC), acrylic clothing, and residential furniture.^{73–75} Large WUI fires may also involve commercial and industrial buildings which likely have material loadings that are different from those of residential buildings (e.g., concrete and steel structure components instead of wood, industrial ceiling tiles, etc.) with low combustion efficiency. For combustible materials, especially wood-based materials, thermal decomposition is expected to proceed similarly to that of biomass, as they progress through emission stages and release VOCs and PM species.⁶⁷ Unlike OA emitted from biomass combustion, there is a lack of knowledge on the general properties, tracer species, and aging properties of OA generated from WUI fires. Chapters 4 and 5 of this dissertation provide insights to help close the gaps in understanding.

1.4 Atmospheric Aging Processes

1.4.1 Condensed Phase Chemistry of Organics with Dissolved Iron

Iron is the most abundant transition metal by mass in Earth's crust. Iron oxide species, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$), are abundant minerals found in Earth's crust and surface soils.^{76,77} Iron ends up in the atmosphere by wind acting on mineral dust and soil particles, forcing them aloft. The largest global sources of iron-rich mineral dust aerosol include the Sahara-Sahel region of northern Africa and central Asia. Globally, emissions account for 8-36 Tg of atmospheric dust burden (suspended at any given time), with uncertainty stemming from the complexity of processes that lift dust into the atmosphere.⁷⁸ Dissolved iron concentrations in rain, fog, snow, and cloud waters vary from $0.1\text{-}10^3\ \mu\text{M}$, with Fe(III) in $20\ \mu\text{m}$ cloud droplets being $1\ \mu\text{M}$.⁷⁹ Fe(III) is known to dissolve most readily under acidic conditions ($\text{pH} < 4$), which is a characteristic of cloud droplets and atmospheric aerosol particles, and where this soluble iron can catalyze condensed-phase reactions.⁸⁰⁻⁸²

During long range transport, dust particles have ample time to mix with organic and inorganic components of biomass burning smoke and participate in heterogeneous chemistry within smoke plumes.^{83,84} To mimic reactivity of freshly emitted mineral dust, previous studies were conducted using hematite nanoparticles (HEM) and Arizona Test Dust (AZTD).^{85,86} Catechol and guaiacol, common components of water-soluble BBOA, were reacted with soluble Fe(III) from the dissolution of HEM and AZTD. In the HEM slurry experiments, after 1 hour of reaction at pH 3, solutions changed color from yellow to dark brown/black (for catechol) and dark orange (for guaiacol).⁸⁵ Collected particles were

determined to be polymers of polycatechol and polyguaiacol through use of electron microscopy techniques.⁸⁵ As for the AZTD experiments, reactivity with catechol under acidic and dark conditions led to the production of similar polycatechol particles.⁸⁶ Mechanistically, polycatechol formation can be explained by a three step process (Figure 1.3).⁸⁶ As originally proposed by Colarieti *et al.* (2006) and Larson and Hufnagel Jr (1980),^{87,88} catechol undergoes partial oxidation from the electron transfer to surface iron and the release of Fe(II) to solution. Reduced Fe(II) then complexes with catechol and undergoes homogenous oxidation in the presence of dissolved oxygen.⁸⁷ Cycling between Fe(II) and Fe(III) produces reactive oxygen species, H₂O₂, and OH radicals as intermediates, which propagate the reaction again.^{87,88} These Fenton reactions are pH-dependent and execution of the elementary polymeric reaction steps (initiation, propagation, and termination) are dictated by the relative amounts of Fe(II) and H₂O₂ in solution.^{89,90} The resultant polymeric particles have extensive conjugation which alters their optical properties and, depending on their color, can be considered secondary BrC species. Hence, this Fe(III) aging chemistry can influence radiative forcing of dust aerosols from negative to positive, similar to that of black carbon.⁸⁰

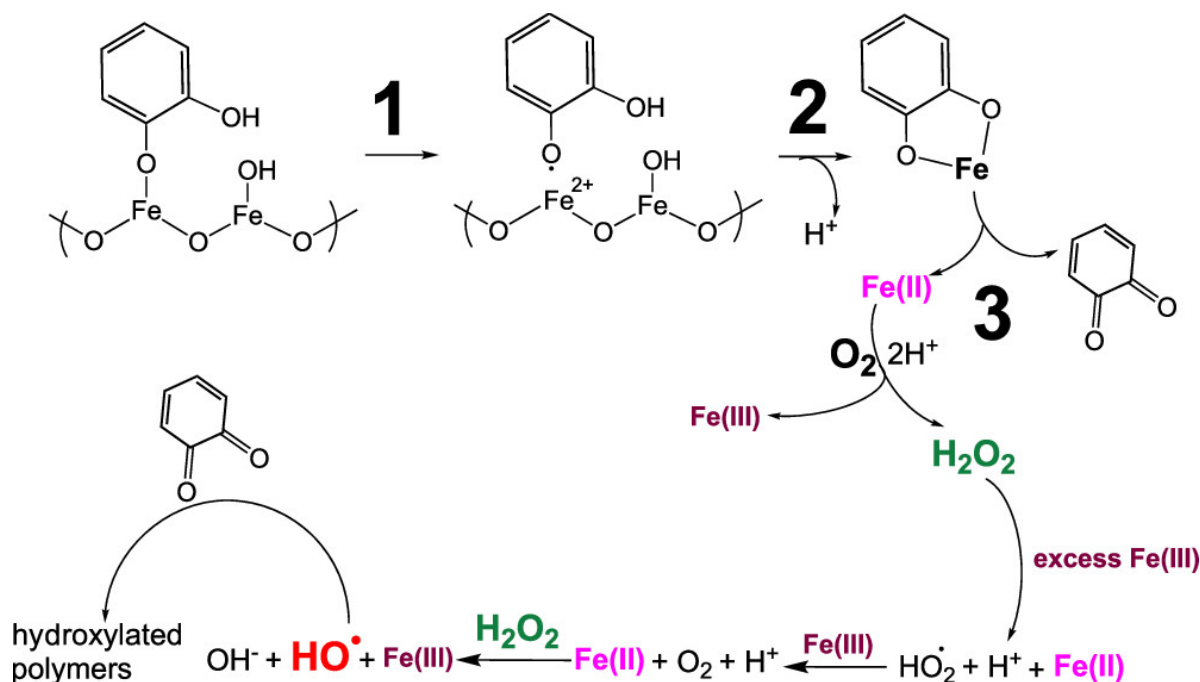


Figure 1.3. Three-step mechanism for abiotic oxidative polymerization of catechol on the surface of iron oxide as proposed by Colarieti *et al.* (2006) and Larson and Hufnagel Jr. (1980).^{87,88} Pink and maroon coloring are used to highlight the change in iron oxidation state in each step. The larger size of OH and H_2O_2 are used to highlight the production of these species throughout the reaction. Reprinted with permission from Link *et al.* (2020).⁸⁶ Copyright 2020 American Chemical Society.

Similarly, FeCl_3 has been used in aqueous-phase experiments to simulate the reactivity of aged iron-containing mineral dust particles.^{85,91–93} Catechol and guaiacol reactions with FeCl_3 exhibited distinct absorption bands during reaction. For catechol, a band at ~ 700 nm formed, indicating the formation of a bidentate mononuclear catechol-Fe complex. Guaiacol did not form this complex due to the presence of the methoxy group ($-\text{OCH}_3$), but other C-C radical coupling reactions and reduction of Fe(III) to Fe(II) led to the formation of phenoxy radicals and spectral bands at 412 and 470 nm.^{85,94,95} The structure of the phenolic species plays a role in its ability to undergo Fe-catalyzed chemistry, as will be further explained in Chapters 2 and 3 of this dissertation.

1.4.2 Photochemical Aging of Organic Aerosol

BB plumes are susceptible to aging with direct or indirect photolysis during transport. Many studies have examined how BBOA's optical properties and chemical composition change as a function of photochemical aging. Forrister *et al.* (2015) conducted airborne sampling of BBOA plumes and collected samples that were both freshly emitted and had undergone 2 days of ambient aging post-emission.⁹⁶ After extraction and absorption measurements were taken, data showed a BrC absorption decrease (at 365 nm) and the half-life of these BrC species was estimated between 9 and 15 h.⁹⁶ In a laboratory study, Fleming *et al.* (2020) irradiated BBOA particle samples with near UV radiation (300-400 nm) and analyzed the samples before and after aging.⁹⁷ Lignin-derived and flavonoid BrC chromophore species showed the greatest resistance to UV photodegradation, however, other primary BrC chromophores were destroyed by UV irradiation after several hours.⁹⁷ These photolysis experiments were conducted directly on filters, and photorecalcitrant BrC species could have been produced through OH oxidation directly on the filter.⁹⁷ Schnitzler *et al.* (2020) generated BBOA particles from the smoldering of pine wood, injected it into a smog chamber, and exposed the BBOA to gas-phase OH radicals.⁹⁸ Monitoring the absorbance changes (at 405 nm) with a photoacoustic spectrometer, they found that absorbance rapidly increased then underwent photobleaching up until 10 hours of OH exposure.⁹⁸ Additionally, they monitored compositional changes with an aerosol mass spectrometer and saw that highly oligomeric species (with low volatility) were susceptible to rapid evolution and, ultimately, photobleaching.⁹⁸

Both direct and photosensitized processes can contribute to changes in OA absorption properties. BrC chromophores can act as photosensitizers, in which, during

photolysis, can be promoted to an excited triplet state ($^3C^*$) through the absorption of a photon. This can be followed by a relaxation or by a reaction between the excited triplet molecule and an adjacent molecule.⁹⁹ These reactions commonly lead to the formation of organic radicals and reactive oxygen species (ROS).¹⁰⁰⁻¹⁰² BrC-acting photosensitizers can contribute to oxidative aerosol aging. In Monge *et al.* (2012), surrogate BrC photosensitizers of humic acid and 4-benzoylbenzoic acid (in mixed organic and inorganic matrixes) were exposed to UVA light and high concentrations of limonene.¹⁰³ Researchers observed particle growth from the production of oxidants at the air-particle interface after the photoexcitation of humic acid, suggesting reaction with limonene molecules.¹⁰³ Conversely, photosensitized oxidative uptake of limonene has been investigated for secondary BrC PM and was found to be uncompetitive under typical ambient conditions. This supports the widely different efficiencies of atmospheric compounds with respect to their photosensitization properties.¹⁰⁴ The effects of direct photolysis and photosensitized processes on BrC present in BBOA is generally understood, however, in systems such as the WUI, behavior of PM towards these processes remains unknown.

1.5 Molecular-Level Characterization of BrC Components

BBOA and OA samples are highly complex mixtures of organics. One way to cope with this complexity is to use high-resolution mass spectrometry (HR-MS) analysis, which produces highly resolved mass spectra containing thousands of peaks that can be unambiguously assigned to chemical formulas. The distribution of chemical formulas contains valuable information on the oxidation states and aromaticity of compounds in BBOA. MS alone is not a sufficient technique to identify BBOA compounds and determine

their spectroscopy properties, as it is not selective toward molecular structure. If the goal is to identify specific chromophores (i.e., BrC species), HR-MS can be coupled with chromatographic methods. Ultrahigh-performance liquid chromatography coupled with photodiode array detection (which allows for UV-Vis detection of eluting species) and heated electrospray ionization mass spectrometry (UHPLC/PDA/HESI-MS) has been used extensively to analyze BrC collected on substrates and extracted into liquids.^{105–109,97,65,110,111}

Figure 1.4 shows the AirUCI UHPLC-PDA-HRMS Orbitrap mass spectrometer (Thermo Fisher Scientific) that was utilized in studies of this dissertation.

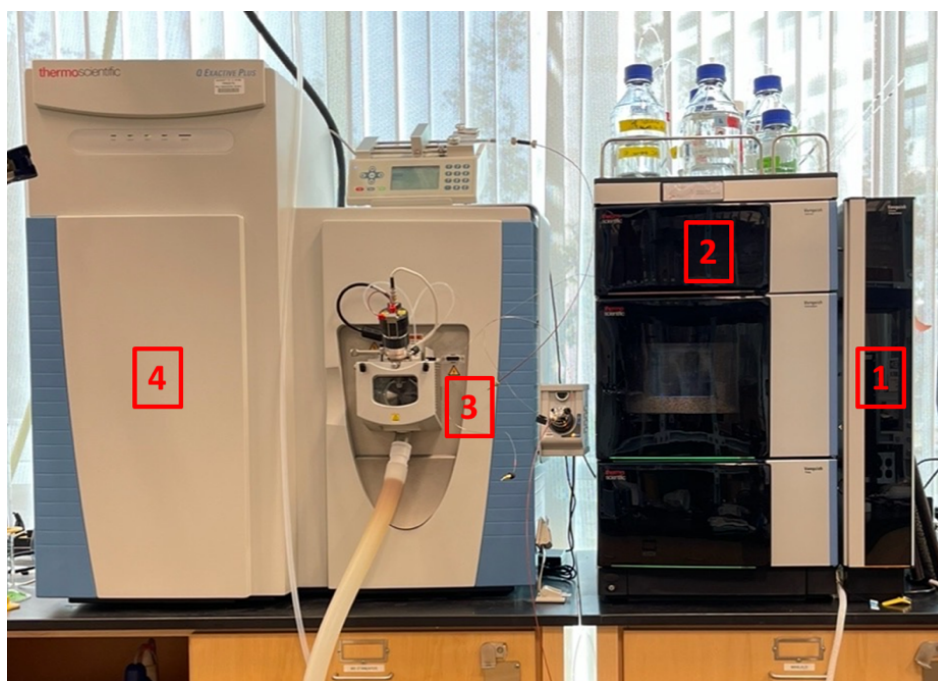


Figure 1.4. Photograph of the AirUCI Orbitrap mass spectrometer. The analytical platform uses an ultra-high pressure liquid chromatography (UHPLC) column (1) coupled to a photodiode array detector (PDA) (2), heated electrospray ionization (3), and a high-resolution mass spectrometer (HRMS) (4) (UHPLC-PDA-HRMS). In this dissertation, all BrC samples were analyzed using this instrument.

In these experiments, OA is dissolved in an appropriate solvent and subjected to chromatographic separation prior to MS. This reduces the complexity of the sample eluting at a given time and allows for the recording of simultaneous absorption and mass spectra of the separated BrC components. After separation, the stream of sample and LC eluent is ionized at a mass spectrometer inlet by generation of a mist of charged droplets. These droplets undergo evaporation and analyte molecules (M) in the gas-phase carry a positive or negative charge (depending on the operation mode). Positive mode OA spectra mostly have singly charged $[M + H]^+$ and $[M + Na]^+$ ions, whereas $[M - H]^-$ species are typically observed in the negative ion mode. Through comparison of PDA and extracted ion chromatograms (EIC) with that of the MS features, BrC chromophores can be identified. Using this approach, major chromophores in BBOA samples have been attributed to a wide variety of organics.^{105,107,112–114}

1.6. Human Health Effects from Vaping Aerosol Exposure

Human health is directly impacted by exposure to ambient aerosol particulate matter and VOCs. $PM_{2.5}$ produced from combustion of fossil fuels and tobacco can penetrate deep into the lungs, provoking cancer and cardiovascular risk.¹¹⁵ While ambient air pollution exposure is a serious environmental risk factor, smoking is a significantly greater threat to human health in terms of cancer, lung disease, cardiovascular disease, and mortality.¹¹⁶ Traditional cigarettes emit over 7000 known compounds, many of which are classified as toxic and carcinogenic.¹¹⁷ Secondhand exposure to cigarette smoke, even if brief, can increase risk of cancer, heart disease, and stroke.¹¹⁸ Unlike smoking traditional tobacco

cigarettes, electronic cigarette smoking (or vaping) is a relatively new phenomenon, and neither the long-term risks nor secondhand vape exposure risks are established.

Vapes were first invented in China in 2003 and entered the US marketplace in 2007.¹¹⁹ Due to the variety of flavors and sleek designs, vapes gained extensive popularity.¹²⁰⁻¹²² Fruity and candy flavors have attracted a younger demographic, posing new risks of nicotine addiction in developing youth. In 2023, the National Youth Tobacco Survey reported that 10% of all middle school and high school students in the US are regular vape users.¹²³ Ward *et al.* (2020) conducted a systematic literature review of 2,305 articles and provided the presence of toxicants in vape aerosol.¹²⁴ E-liquids are composed of three main ingredients: nicotine, flavoring agents, and solvents of propylene glycol and vegetable glycerol.¹²⁵ When e-liquid is heated inside vape devices, carbonyl compounds (formaldehyde, acetaldehyde, acrolein), VOCs (benzene, toluene, isoprene), tobacco-specific nitrosamines (from nicotine combustion), PAHs (naphthalene and acenaphthylene), glycols, and metals (lead, chromium, nickel released from heating of the inner metallic coil) have been observed in the vape aerosol (that is to be inhaled by a user).¹²⁴ The concentration and composition was also noted to be different amongst vape brands, flavors, and user puffing patterns.^{124,126}

Extensive research has utilized offline analytical techniques to assess the presence of VOCs in vape emissions.¹²⁷⁻¹³³ The online proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) has been applied to breath analysis studies,¹³⁴⁻¹³⁸ but only a few have utilized this instrument with vape emissions. PTR-ToF-MS studies have shown that while vaping may give lower exposures to some known smoking toxicants, it can also expose a user (and bystanders) to new compounds that are not present in cigarette smoke.¹³⁹

Questions remain regarding how vape device settings and human interactions with vape their devices will impact exhaled vape emissions. Also, it is unclear how reproducible VOC concentration measurements are when compared amongst various analytical techniques. This will be explored in more depth in Chapter 6 of this dissertation.

1.7 Research questions and dissertation structure

Despite advances reported in the literature, there are still many unanswered questions about the molecular identity of BrC compounds in BBOA, connection between the optical properties and chemical composition of BBOA, and condensed phase chemical transformations leading to BBOA aging, particularly those with BBOA species and Fe(III). There is a lack of knowledge on the emissions that come from fires at the WUI and how these aerosols can change during photolytic aging. As for health-related aerosols, much is known about the smoking of traditional cigarettes, but questions remain for vaping. The studies in this dissertation were guided by the following questions.

- How do structural differences within BBOA constituents impact Fe(III)-catalyzed reactions? Can Fe(III) interact with real-BBOA samples in the condensed phase to create light-absorbing secondary BrC species? What are the implications of these interactions on the light-absorbing properties and climate effects of biomass burning smoke during atmospheric transport?
- How does exposure to simulated solar radiation impact the absorption properties of PM emitted during WUI fires? Can high-resolution mass spectrometry techniques be used to characterize BrC chromophores in WUI smoke particles, and what compositional insights can be gained regarding their fate after photolytic aging?

- What VOCs are individuals inhaling and exhaling during vaping events? Can we employ complementary online and offline techniques in a vaping human trial to probe these emissions and effects on secondhand exposure?

Chapters 2 and 3 examine the interaction of BBOA with atmospheric iron. In Chapter 2, water-soluble BBOA precursors (2,4-nitrophenol, 4-nitrocatechol, 4-methylcatechol, 1,2,4-benzenetriol, 1,2,3-benzenetriol, coniferaldehyde, and catechol) underwent dark, acidic reaction with FeCl_3 . Reaction progress was monitored with UV/Vis spectroscopy and resultant secondary BrC particles were analyzed using UHPLC-PDA-HRMS. Mechanisms of iron-catalyzed chemistry are proposed and results supplement preexisting studies on this topic. Chapter 3 conducts similar experiments, but this time with real BBOA samples. Canary Island Pine needles were pyrolyzed, smoke particles were collected, and water-soluble BBOA was placed under reaction with FeCl_3 . UV/Vis and UHPLC-PDA-HRMS were also employed in this chapter. Resulting particles were analyzed using electron microscopy techniques.

Chapters 4 and 5 are pilot studies on PM from WUI fires. In Chapter 4, ten urban materials were pyrolyzed in a tube furnace and resultant smoke particles were collected. These particles underwent simulated UV aging and trends in absorptivity were classified. We recorded emission factors for these fuels, along with MAC_{bulk} and AAE values before and after photolytic aging. In Chapter 5, the chemical composition of these smoke particles before and after aging were conducted using UHPLC-PDA-HRMS. Through use of BrC standard mixtures, we were able to identify BrC species present in urban OA. We report similarities and differences amongst urban OA samples and propose potential tracer species for WUI fires.

Chapter 6 examines the composition of VOCs exhaled by participants in a human trial vaping study. We employed a PTR-ToF-MS and gas chromatography techniques to examine the composition and concentration of VOCs bystanders would be exposed to during a vaping event. This study was the first of its kind to examine the exhaled breath with the high chemical specificity of complementary online and offline techniques. We teased out fragmentation patterns induced by PTR ionization through comparison with replicate samples analyzed with offline GC techniques.

CHAPTER 2:

EFFECT OF AROMATIC RING SUBSTITUENTS ON THE ABILITY OF CATECHOL TO PRODUCE BROWN CARBON IN IRON(III)-CATALYZED REACTIONS

Portions of this chapter were reproduced from:

Chin, H.; Hopstock, K. S.; Fleming, L. T.; Nizkorodov, S. A.; Al-Abadleh, H. A., Effect of aromatic ring substituents on the ability of catechol to produce brown carbon in iron(III)-catalyzed reactions, *Environmental Science: Atmospheres*, **1** (2021) 64-79.¹⁴⁰

Abstract. Our previous work demonstrated formation of highly insoluble and strongly light-absorbing organic particles in reactions between catechol or guaiacol with Fe(III) under pH=3 conditions characteristic of aerosol liquid water. This work extends these measurements to reactions of Fe(III) with 2,4-dinitrophenol, 4-nitrocatechol, 4-methylcatechol, 3-hydroxycatechol, 4-hydroxycatechol, and coniferaldehyde to better understand the mechanism of particle formation catalyzed by Fe(III). Particles were observed after 2 h of reactions of catechol, 3-hydroxycatechol, 4-hydroxycatechol, and coniferaldehyde, while reactions of 2,4-dinitrophenol and 4-nitrocatechol did not produce any insoluble products. No particles were observed in the reaction of 4-methylcatechol after 2 h, however, insoluble products appeared after a 24 h reaction time. Particles produced from precursors + Fe(III) solutions were dissolved in organic solvents and analyzed with ultrahigh performance liquid chromatography coupled to a photodiode array spectrophotometer and a high-resolution mass spectrometer. Major separated chromophores were identified as dimeric, trimeric, and tetrameric products of precursor molecules. Purpurogallin was identified as a major reaction product of 3-hydroxycatechol

reaction with Fe(III). These results suggest that Fe(III)-catalyzed chemistry can take place in aging BBOA plumes resulting from smoldering fires and make aerosol particles more light-absorbing.

2.1 Introduction

Organic compounds represent a major fraction of atmospheric aerosols particles. While some of these compounds result from primary emissions, others are produced by secondary reactions of various volatile organic compounds (VOCs).¹⁴¹ The most common mechanism that transforms VOCs into secondary organic aerosol (SOA) is free-radical driven photooxidation. However, alternative mechanisms also exist. For example, it has been shown that Fe(III) can catalyze oligomerization of certain VOCs leading to much less volatile products. In a study by Slikboer *et al.* (2015), catechol and guaiacol were mixed with Fe(III) at pH 3 at millimolar concentrations, which yielded highly-absorbing, water-insoluble particles of polycatechol and polyguaiacol.⁸⁵ Dissolved iron from acid processing of hematite was also shown to react with catechol and guaiacol under the same conditions to make light-absorbing particles. A follow up study by Al Nimer *et al.* (2019) showed that these oligomerization reactions are not suppressed in the presence of equimolar amounts of oxalate and sulfate ions, which are commonly found in aerosol particles and compete for complex formation with Fe(III).¹⁴² Lavi *et al.* (2017) characterized the light-absorbing oligomers formed in Fe(III) reactions with guaiacol, catechol, syringol, o- and p-cresol, and observed a mixture of strongly-absorbing dimers, trimers, tetramers, and pentamers by liquid chromatography coupled to high resolution mass spectrometry.⁹² Ling *et al.* (2020) demonstrated that Fe-containing clay minerals produced colored particles when exposed to

guaiacol.¹⁴³ Pang *et al.* (2019) found strong effect of UV irradiation on chemistry in the Fe(III)-oxalate-guaiacol aqueous mixtures.¹⁴⁴ These results suggest that aqueous reactions of phenolic compounds with Fe(III) may serve as an efficient source of light-absorbing organic compounds in atmospheric particles, which are collectively known as “brown carbon”.^{30,36}

Dihydroxybenzenes (catechol, resorcinol, and hydroquinone) are major constituents of biomass burning organic aerosol (BBOA).^{145,146} Since biomass burning is one of the largest emission sources of organics, these compounds are ubiquitous in the atmosphere. Of these three, catechol forms the strongest complex with Fe(III) because its adjacent phenolic groups make it an excellent bidentate ligand, and reactions of this complex then lead to the light-absorbing products. Likewise, aerosol particles containing Fe(III) are also widespread in the atmosphere.¹⁴⁷ The dominant type of Fe-containing particles is mineral dust,¹⁴⁸ as iron is the most abundant transition metal in the Earth’s crust.¹⁴⁹ Other sources of Fe in the atmosphere include anthropogenic combustion including coal burning,^{150,151} biomass burning,^{152,153} and brake wear.¹⁵⁴ There are realistic scenarios in which catechol and related compounds can end up in iron-containing particles. For example, primary particles from cooking emissions contain internally mixed soluble iron and organics.¹⁵⁵ Smoke from biomass burning is often spread by wind, which also lifts crustal particles off the ground. Mineral dust is known to be transported globally by wind,^{83,84} and BBOA similarly travels long distances,¹⁵⁶ offering ample time for partitioning of organic vapors into Fe-containing particles.

In addition to catechol, BBOA also contains many other related compounds that can potentially react with Fe(III) by similar mechanisms, however, their reactivity towards Fe(III) is yet to be investigated. A study by Salgado *et al.* (2017) suggested that compounds

similar to catechol, such as 4-tert-butylcatechol and 3,4-dihydroxybenzaldehyde, behave differently after mixing the organic solution with ferric nitrate as the result of electron affinity of their respective functional groups.⁹³ Their computational work led to a proposed mechanism of oxidation of substituted catechols by Fe(III) with three major steps. The first step is formation of a complex between iron and the dihydroxybenzenes, followed by inner-sphere ligand to iron charge transfer, and then deprotonation of one of the oxygen atoms leading to quinone formation. Other compounds found in BBOA include guaiacol and its derivatives. The reaction mechanism of these compounds with Fe(III) is believed to be similar to that with Mn(III) reported by Hwang *et al.* (2008).⁹⁵ In this mechanism, Mn(III) abstracts an electron from the -OH substituent forming a phenoxy radical stabilized by resonance. Then, C-C coupling reactions of radicals and additional electron abstractions by Mn(III) lead to the formation of dimers and trimers, and eventually polyguaiacol.⁹⁴

In this study, we further explore several catechol derivatives to better understand the mechanism of particle formation catalyzed by Fe(III). Reaction of catechol (CA) with Fe(III) was used as a reference system to ensure that the previous results were reproducible. Reaction of 2,4-dinitrophenol (DNP) with Fe(III) was tested to verify the necessity of having two adjacent phenolic groups for the initial metal complexation to occur. To examine the effect of the type and location of catechol ring substituents, reactions of 4-nitrocatechol (NC), 4-methylcatechol (MC), 3-hydroxycatechol (3-HC), and 4-hydroxycatechol (4-HC) were compared. In addition, the reaction of Fe(III) with coniferaldehyde (CON) was tested to compare its reactivity to that of structurally similar guaiacol. All the compounds selected for these experiments are common substituents of BBOA. The overarching conclusion of this

study is that the amount and color of insoluble particles depends in a complicated way on the type of organic reactant.

2.2 Experimental Methods

2.2.1 Chemicals and Solution Preparation

The structures of organic compounds used in this work are shown in **Figure 2.1**. All chemicals were used as received without further purification: CA (1,2-benzendiols, >99%, CAS 120-80-9, Acros Organics), NC (4-nitrobenzene-1,2-diol, 97%, CAS 3316-09-4, Acros Organics), CON (4-hydroxy-3-methoxycinnamaldehyde, 98%, CAS 458-36-6, Sigma-Aldrich), MC (4-methylbenzene-1,2-diol, >95%, CAS 452-86-8, Sigma-Aldrich), 3-HC (1,2,3-benzenetriol, 99%, CAS 87-66-1, Alfa Aesar), 4-HC (1,2,4-benzenetriol, 97%, CAS 533-73-3, Alfa Aesar), and iron (III) chloride hexahydrate (97%, CAS 10025-77-1, Sigma-Aldrich).

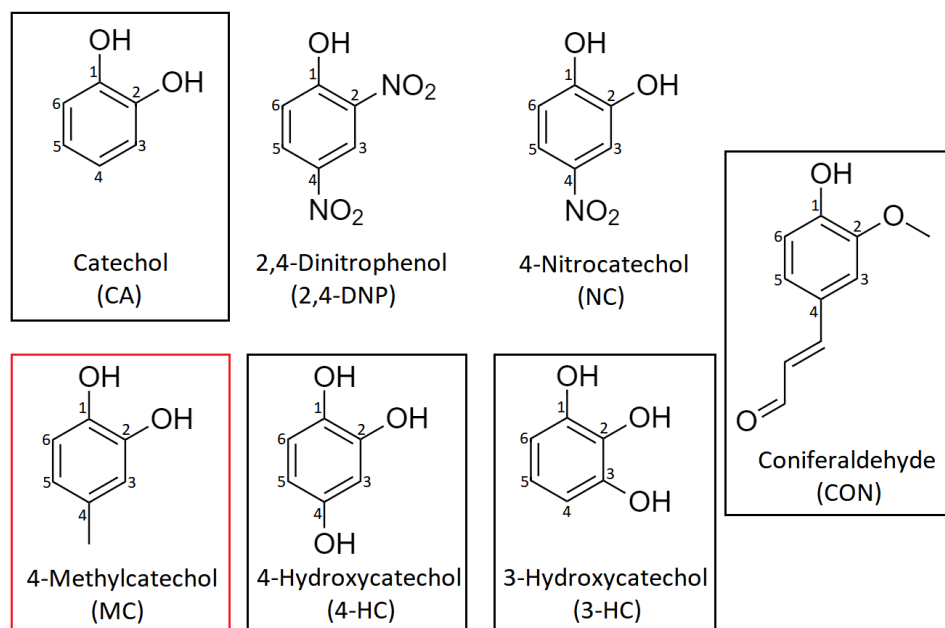


Figure 2.1. Chemical structures and abbreviation codes of pyrocatechol (CA), 2,4-dinitrophenol (2,4-DNP), 4-nitrocatechol (NC), coniferaldehyde (CON), 4-methylcatechol (MC), 4-hydroxycatechol (4-HC), and 3-hydroxycatechol (3-HC). The frames in black highlight the organic compounds that produced particles promptly due to reaction with Fe(III); MC is surrounded by a red frame because it produced particles on a slower time scale.

All solutions were freshly prepared for each experiment by dissolving the chemical in 10 mM stock solution of KCl (CAS 7447-40-7, EM Science) in nanopure water, with KCl added to stabilize pH reading. The pH was adjusted using concentrated hydrochloric acid (37.5%, CAS 7647-01-0, Fisher Scientific) and verified with a calibrated Mettler Toledo SevenEasy S20 pH meter. Because the formation of the bidentate mononuclear complex is pH sensitive,^{157,158} the initial pH values were adjusted to 3.0, a common pH in aerosol particles.¹⁵⁹ As the pH becomes higher (>4), CA and its analogs start to lose protons on hydroxyl groups and form complexes with higher coordination numbers. A similar phenomenon can be found in hydrolytic Fe(III) species as well.¹⁶⁰

2.2.2 UV-Vis Experiments Under Dark Conditions

The 10 mM KCl stock solution at pH 3 was used to prepare 10 mL of 80 mM iron (III) chloride, FeCl_3 , and 100 mL of 1.06 mM CA derivative. After the preparation, the CA derivative solution was then re-adjusted to pH 3. A 0.5 mL volume of 80 mM of FeCl_3 was mixed with 19 mL of 1.06 mM of a CA derivative in a 20 mL scintillation vial resulting in an iron to organic molar ratio of 2 mM : 1 mM. These relatively high concentrations were selected to mimic aqueous surfaces where organic compounds are enriched. The concentrations used were the same in all experiments as we focused on the effect of the CA derivative on the particle yield. A typical concentration of dissolved Fe(III) in cloud droplets (diameter $\sim 20 \mu\text{m}$) is around 10^{-6} M .⁷⁹ Therefore, for an aerosol particle produced by evaporation of cloud droplets down to a diameter of $1 \mu\text{m}$, the concentration of dissolved Fe(III) could be as high as 10 mM, making the 2 mM Fe(III) concentration in our experiments a relevant choice for aerosol particles. The gas-phase concentration of CA can be as high as 50 ppbv ($\sim 5 \times 10^{-8} \text{ atm}$) resulting from biomass burning, pyrolysis and combustion,⁹¹ but in most cases it will be well below 1 ppbv (10^{-9} atm). With the Henry's law constant of 4600 M atm^{-1} , this translates into 0.2 mM and 0.005 mM, respectively, in a bulk system like a cloud droplet. The concentrations could be higher in the interfacial region of the particles because of surface enhancement of organics. In our experiments, we selected 1 mM concentration of CA to ensure that Fe is in excess but at the same time a measurable amount of products can be produced on a reasonable experimental time scale of 2 h.

The mixture was covered by Al foil to avoid photochemistry. The mixture was stirred on a stir plate at room temperature. The vial was closed but not sealed allowing the room air to interact with the solution during this process. UV-Vis spectra of the mixture were collected

by withdrawing 0.5 mL of the mixture out of the vial, diluting 8-fold using nanopure water in a 1 cm quartz cuvette at 1-5 min, 1 h, and 2 h time points using Shimadzu UV-2450 spectrophotometer with the reference cuvette containing 3 mL of nanopure water. Shortly after the 2 h time point, the solution was filtered via a pre-weighted nylon membrane (0.20 μm pore size, 25 mm diameter, EMD) by syringe filtration, and a UV-Vis spectrum of the filtrate was also collected. The filter was dried for 24 h and weighted to estimate the particle yield. Filter weighing was done with Sartorius ME5-F microbalance (1 μg precision). More precise particle yield measurements were done with larger amounts of reagents (*described below*).

2.2.3 Analysis of Reaction Products

Particles resulting from the reactions of Fe(III) with 3-HC, 4-HC, and CON were filtered out of solution on pre-weighted nylon membrane filters (0.20 μm pore size, 47 mm diameter, EMD) by syringe filtration (**Figure 2.2**). The filtration was performed one more time through the same filter, and the filter was dried for 24 h. Black particles from reactions of 3-HC, 4-HC, and CON were analyzed with Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high resolution mass spectrometer with a resolving power up to 1.4×10^5 (UHPLC-PDA-HRMS).

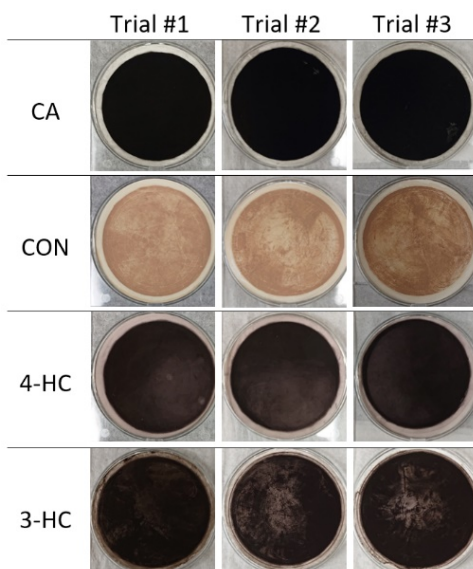


Figure 2.2. Photographs of filters containing particles after 2 h of reaction, filtration, and drying for catechol (CA), coniferaldehyde (CON), 4-hydroxycatechol (4-HC), and 3-hydroxycatechol (3-HC).

The dried filters were cut into 8 segments, and one segment was extracted in 20 mL methanol using a vortex shaker. After 30-45 min of shaking, the filters were removed. The extraction solutions were colored, and filters were lighter in color but not completely white indicating that only some reaction products could be dissolved by this method (particles from the CA + Fe(III) reaction could not be dissolved in methanol or other common organic solvents). The solutions were evaporated on a rotary evaporator, and the residues were re-dissolved in a 20 mL mixture of acetonitrile and water (50% each by volume) and filtered through a syringe filter.

The liquid chromatography column was a Phenomenex Luna Omega Polar C18, 150 × 2.1 mm, with 1.6 μm particles and 100 Å pores, maintained at 30 °C during the runs, and the injected volume was kept at 5 μL . The eluent flow of 0.3 mL min⁻¹ consisted of a mixture of water acidified with 0.1% formic acid to pH 3 (solution A) and acetonitrile with a 0.1% formic

acid added (solution B). The gradient was: 0-3 min 95% A; 3-14 min linear ramp to 95% B; 14-16 min hold at 95% B; 16 min return to 95% A and hold until 22 min in preparation for the next run. PDA collected data at 5 Hz over 190-580 nm range with a 4 nm effective bandwidth. Mass spectra were obtained with HRMS operating first in positive ion mode, and then in a separate UHPLC scan in the negative ion mode. The heated electrospray ionization (HESI) ion source parameters were: +3.5 kV and -3.5 kV spray voltage, 300 °C probe heater temperature, 320 °C capillary temperature, 50 units of sheath gas flow, and 10 units of aux gas flow. All peaks were analyzed using FreeStyle 1.6 (Thermo Scientific). The strongest peaks contributing to the near-UV and visible PDA chromatogram were correlated to the corresponding peaks in the total ion current (TIC) chromatogram, considering a delay time of 0.06 min between the PDA and Orbitrap detectors. The suspect TIC peaks were confirmed by examining selected ion monitoring (SIM) chromatograms. Ion formulas generated by FreeStyle were verified with a molecular formula calculator.

In addition to running samples, standard solutions of CA, CON, 3-HC, and 4-HC were run on the UHPLC-PDA-HRMS system to verify that no oxidation of standards occurred in the HESI source (such oxidation of CA was observed in previous work with a different ESI instrument and complicated assignments).⁸⁵ CA, 3-HC and CON standards gave clean single-peak chromatograms with no major impurities or oxidation products. 4-HC standard results showed that the starting material was contaminated and, as a result, a few autooxidation products were present, however, 4-HC was still the main component of the standard.

2.3 Results and Discussion

2.3.1 Dark Reaction between Fe(III) and Organic Reactants

Figure 2.3 (a-g) show the absorption spectra recorded after 1-5 min, 1 h and 2 h of reactions, as well as spectra of solutions after filtering out the particles. It also shows the corresponding photographs of the reacting mixture vials taken over time. Several species contribute to the overall light absorption in the reaction mixtures of Fe(III) and organic reactants. Prior to mixing, the Fe(III) solution is dominated by the strong absorption band of $\text{Fe}(\text{OH})_2^+$ at 296 nm, and the organic reactant solution features a π to π^* transition peaking between 250 and 300 nm, depending on the compound. For example, the π to π^* transition of the aromatic ring in CA occurs at 276 nm,¹⁶¹ and a similar peak can be observed across all CA analogs discussed in this chapter (**Figure 2.3**). Mixing the solutions results in a sequence of color changes, accompanied in some cases by particle formation. The additional features are observed in the absorption spectrum during the reaction due to: (a) π to π^* transition centered on the ligand in Fe-organics complex appearing in the near-UV and shifted from the corresponding transition in the isolated ligand; (b) ligand-to-metal transition (LMCT) in the bidentate iron-organics complexes appearing in the near-IR; (c) bands from soluble reaction products between Fe(III) and the organics reagents, including n to π^* transition in the o-quinone species formed from oxidation of CA-Fe complexes; (d) scattering and absorption by the insoluble suspended particles with a weak wavelength dependence. As demonstrated by Salgado *et al.* (2017),⁹³ the Fe-complex transitions appear quickly after mixing, whereas absorption features of the reaction products take minutes or even hours to develop. In this study, the reaction was terminated after two hours, and presence of particulate products was

verified visually as well as by comparing absorption spectra before and after filtering the solution. The behavior of each organic reactant (shown in **Figure 2.1**) will be discussed separately over the experimental time frames.

Catechol (CA): Reaction with CA was carried out multiple times throughout the study because it served as a reference experiment to which reactions of other organic compounds were compared. CA formed complexes with Fe(III) shortly after mixing. An intense peak at 390 nm indicates n to π^* transition of *o*-quinone, which decreased in intensity in one hour, as observed in our previous study (**Figure 2.3a**).^{85,142} A broad band at 700 nm corresponds to the LMCT in the bidentate mononuclear catechol-iron complex.⁹³ The mixture was intensely green at the beginning; it slowly turned into pale green, while the black tint became progressively prominent. After 2 h of reaction, an overall decrease in transmittance (manifesting itself as increase in the apparent absorbance) across all wavelengths was observed as a result of scattering and absorption by dark colloidal particles formed during the reaction.

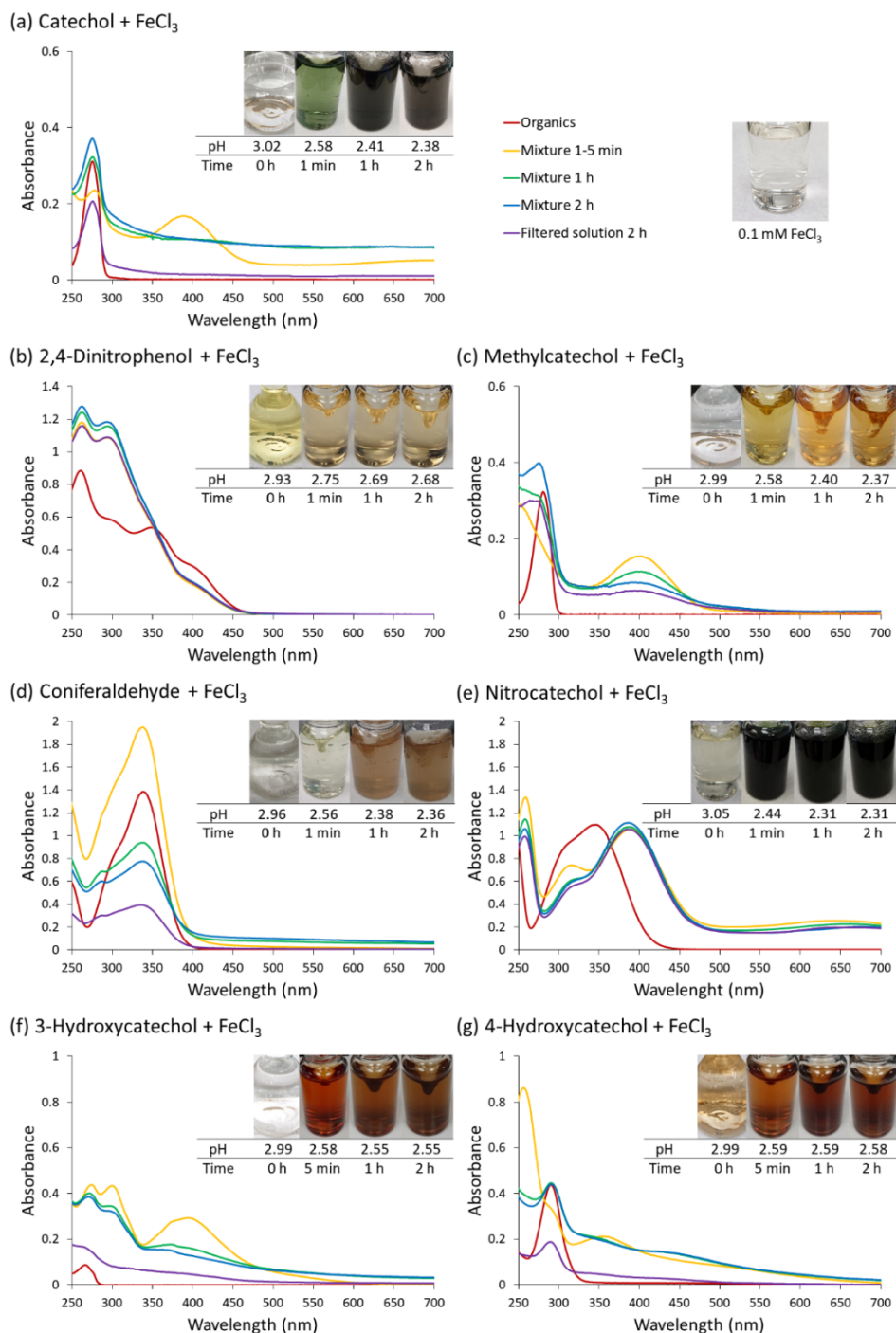


Figure 2.3. UV-Vis absorption spectra of mixtures of Fe(III) with (a) catechol, (b) 2,4-dinitrophenol, (c) 4-methylcatechol, (d) coniferaldehyde, (e) 4-nitrocatechol, (f) 3-hydroxycatechol, and (g) 4-hydroxycatechol. Different colors of traces correspond to spectra of organic reactant before mixing (red), 1-5 min after mixing (orange), 1 h after mixing (green), 2 h after mixing (blue), and filtered solution (purple). The final concentration of organics is 1 mM, and the final concentration of Fe(III) is 2 mM. The photographs are those of unfiltered solutions.

2,4-Dinitrophenol (2,4-DNP): To examine the role of bidentate nature of catechol derivatives in the reaction, 2,4-DNP was tested. This compound has only one phenolic group capable of forming a complex with Fe(III), and two nitro groups, which do not contribute to complexation but strongly affect the electron density distribution in the aromatic ring. The mixture remained pale-yellow in color throughout the experiment; and there was no apparent reaction after mixing (**Figure 2.3b**). There was one band in the spectrum at 295 nm, and no evidence of the LMCT band (which is expected since LMCT appear in bidentate complexes). No particles could be detected at the end of the experiment. These results confirm the importance of the formation of bidentate catechol-iron complex for the particle formation.^{85,93} In addition, the electron-withdrawing nature of the nitro groups has a suppressing effect on the reactivity, as discussed below.

4-Methylcatechol (MC): Reaction of Fe(III) with MC mixture exhibited similar UV-Vis spectrum to that of CA. An intense peak n to π^* transition at 400 nm from the quinone species appeared promptly and decreased over time (**Figure 2.3c**). A LMCT band was expected but not observed. It is worth noting that the mixture turned into light green at the moment of the introduction of Fe(III); then it quickly shifted to bright yellow within seconds and maintained this color for the rest of the experiment, so it is possible the LMCT band disappeared too quickly for us to detect it. There was a slight increase in a peak at around 500 nm observed during the course of two hours. The lack of overall scattering indicates that the mixture did not produce any light-absorbing particles on this time scale. Interestingly, an experiment carried out under the same protocol did produce some coloration on filter after 3 and 24 h of mixing. The results also show a slight increase in yield after 24 h of mixing. This result coincides with the one reported in previous study by Larson and Hufnagel (1980), where

Mn(II) was used as the catalytic metal ions.⁸⁸ We conclude that particles can be eventually formed, however the kinetics are much slower compared to the other organic reactants used in this study.

Coniferaldehyde (CON): The mixture of CON and Fe(III) exhibited large changes in intensity of the n to π^* peak around 337 nm, with the peak first increasing at the 5 min mark and then decreasing over time (**Figure 2.3d**). No LMCT band was detected, in agreement with the expectation that CON should not form a strong bidentate complex with Fe(III). The solution color changed from a faint green to light orange in the first hour; the color then became progressively darker into brown in the second hour. The overall effective absorbance increased at all wavelengths due to scattering and absorption by the particles, and a large difference was observed between the spectrum of the unfiltered and filtered solution.

4-Nitrocatechol (NC): Before the addition of Fe(III), the spectrum presented an intense broad band with peaks at 310 and 345 nm, attributed to n to π^* transitions (**Figure 2.3e**). Upon mixing NC and Fe(III), a different n to π^* band of the NO_2 substituent at 386 nm immediately appeared and persisted throughout the observation time. This peak is red shifted relative to its initial position due the deprotonation of catechol moiety as a result of complexation to iron.¹⁵⁸ Similar to what was observed in the spectrum of CA, a broad peak at 660 nm, indicative of LMCT for NC-iron complex, was observed from the beginning to the end. The mixture also had an intense, dark green color, akin to the one CA-iron mixture had in the beginning. No particle scattering was observed in the UV-Vis spectrum, indicating that the reaction did not go past the formation of the bidentate complex.

3-Hydroxycatechol (3-HC): The 3-HC and Fe(III) reaction exhibited the most complicated color changes in this series of experiments (**Figure 2.3f**). The 3-HC solution changed from clear to dark, blue-purple a few seconds after adding FeCl₃, and then quickly turned into dark, amber-orange, which further changed to bright orange, then faded into brown in the first 10 minutes. The UV-Vis spectra indicated that a quinone species absorbing at 371 nm was produced after 5 min; the peak gradually decreased in the two-hour period. The UV-Vis spectrum also had a contribution from scattering by particles by the end of the observation period.

4-Hydroxycatechol (4-HC): 4-HC and Fe(III) reaction demonstrated a similar trend as 3-HC. A product peak was detected around 360 nm in the first 5 min while the solution changed from amber-orange to a brighter orange shade (**Figure 2.3g**). Unique to this system, as the reaction progressed, the product peak shifted to the red to 450 nm after 1 h. The mixture maintained a brown color throughout the process. The UV-Vis spectrum also exhibited scattering by suspended particles towards the end of the experiment.

In summary, UV/Vis observation of the evolution of near-UV peaks, LMCT broadband peaks, and particle scattering are indicative of the formation of Fe(III)-complexes, which in some cases is followed by the formation of light-absorbing particles (**Table 2.1**). The near-UV peak indicative of a π to π^* transition in the Fe-organics complex occurred in all reactions. The n to π^* transition in the o-quinone product was observed in all cases except for 2,4-DNP and CON. A clear LMCT band was observed for CA and 4-NC. Particle formation after 2 h or reaction was observed in CA, 3-HC, 4-HC, and CON.

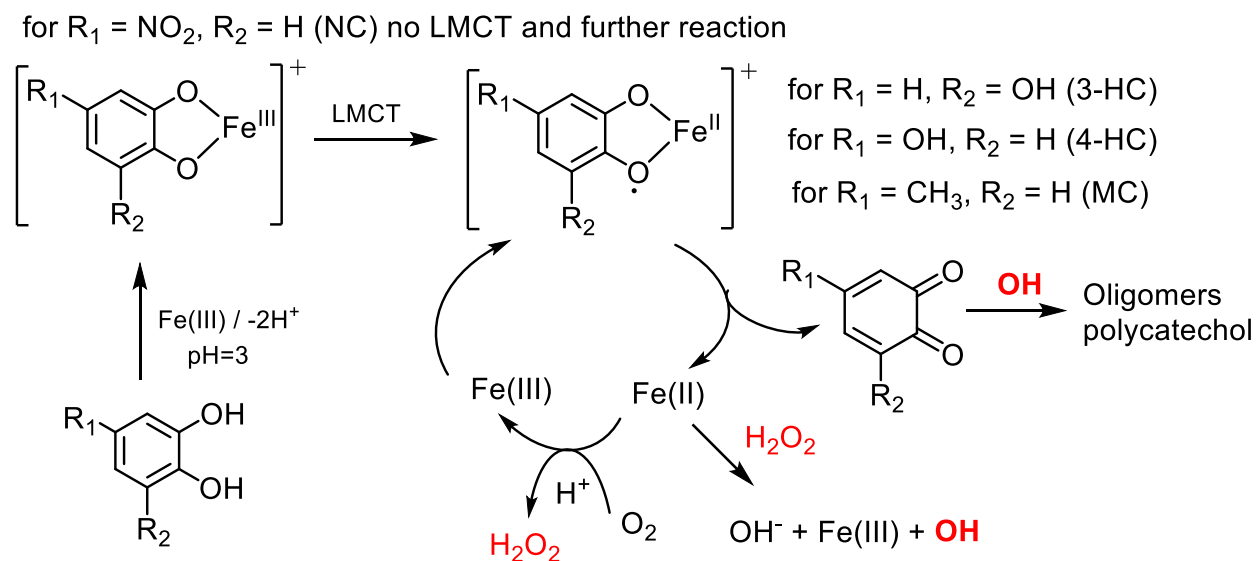
Table 2.1. Summary of UV/vis and reaction observations.

Compound	$n \rightarrow \pi^*$ transition in the o-quinone product (around 400 nm)	LMCT transition (around 700 nm)	Solution Color Change?	Particles Produced?
CA	Yes	Yes	Yes	Yes
2,4-DNP	–	–	–	–
4-MC	Yes	–	Yes	–
CON	Yes	–	Yes	Yes
4-NC	Yes	Yes	Yes	–
3-HC	Yes	–	Yes	Yes
4-HC	Yes	–	Yes	Yes

2.3.2 Effect of the Substituent Groups on the Reaction Mechanism

The results described above can be rationalized in terms of the effect of different ring substituents for the catechol and guaiacol derivatives examined here (2,4-DNP is excluded from this comparison because it can only form monodentate complexes with Fe(III)).

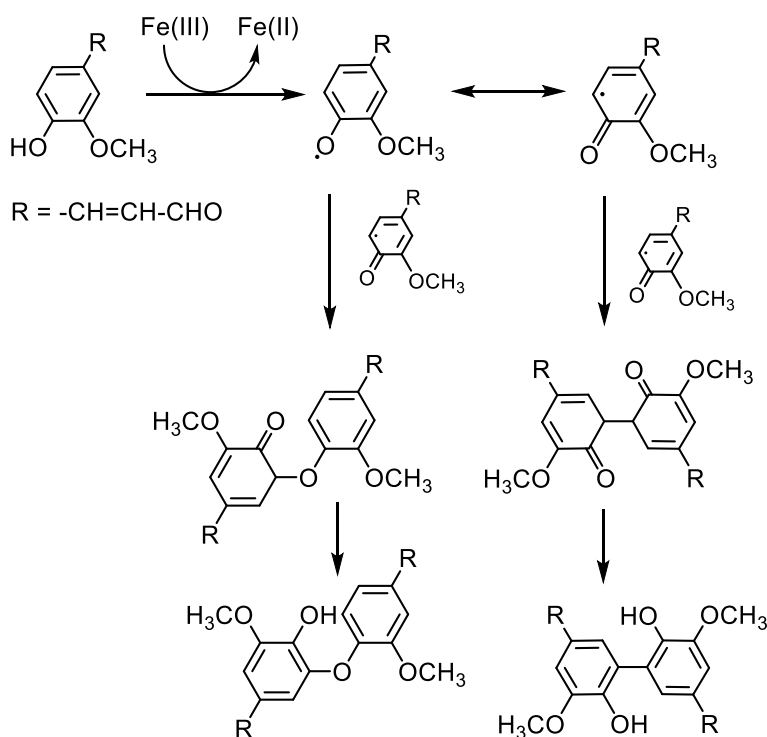
Scheme 2.1 shows reaction steps involved in the oxidation of catechol as reported earlier.^{88,93,94,162,163} The first step is a formation of an Fe(III)-ligand bidentate complex. This is followed by a ligand to metal charge transfer (LMCT) to Fe(II) complex, and a release of the corresponding 1,2-benzoquinone compound. In the presence of oxygen, Fe(II) is oxidized back to Fe(III) producing hydrogen peroxide. The latter serves as a source of OH that drives the oligomerization and other reactions of the 1,2-benzoquinone compound.



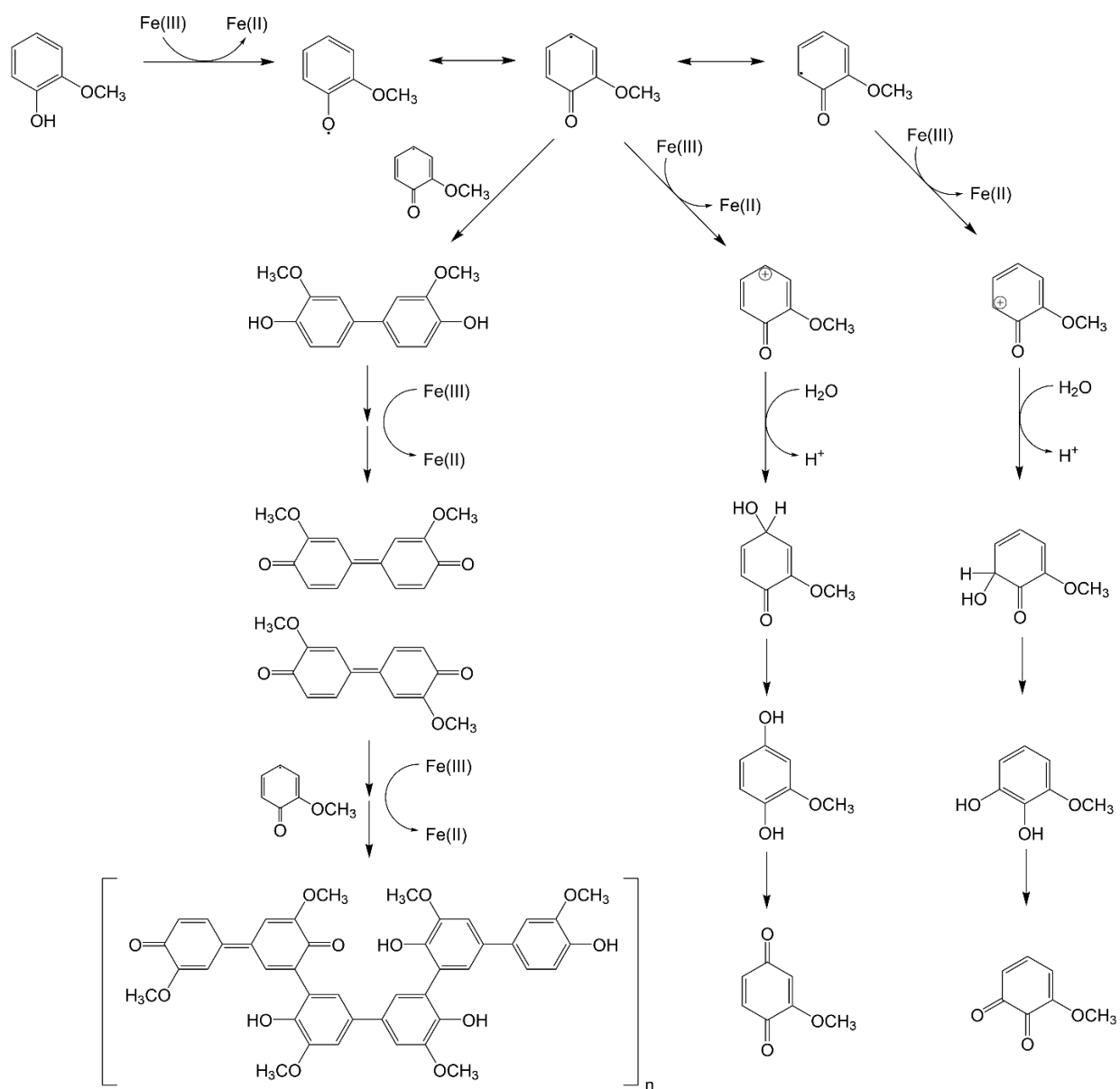
Scheme 2.1. Suggested mechanisms for the oxidation of catechol derivatives in the presence of excess iron under dark conditions leading to the formation of oligomers and polycatechol particles. The rate of the ligand to metal charge transfer (LMCT) depends on the substituents R_1 and R_2 .^{88,93,94,162,163}

The strongly electron withdrawing NO_2 group on NC inhibits the LMCT following the formation of a stable NC-Fe(III) complex. Hence, NC showed no detectable yield of particles from the oxidative polymerization reaction steps that follow complexation. In comparison, the hydroxyl substituent in 3-HC and 4-HC can donate the electron to the π -system and help stabilize the LMCT intermediate. Both 3-HC and 4-HC exhibited similar results in reaction with Fe(III). MC was also tested to see the effect of a weak electron donating group on the iron-catalyzed polymerization reaction. The mixture of MC and FeCl_3 did not produce particles over the 2 h reaction time. The signature green color of the complex disappeared in seconds after the two solutions were mixed. Meanwhile, a gradual emergence of the peak at 500 nm implies the formation of new, more conjugated products. As mentioned above, particles did eventually appear on the filter after letting the mixture react further for 24 h. The solution after filtration was also visibly lighter in color than the unfiltered solution.

The reactivity of CON with Fe(III) leading to particle formation is explained by the effective electron donating group, $-(CH)_2CHO$, in the para position (**Scheme 2.2**). As shown in **Scheme 2.3** for guaiacol (no substituents), Fe(III) will abstract an electron from the phenolic group leading to the formation of phenoxy radicals. These radicals are stabilized by resonance and lead to the formation of quinones, dimers and eventually polyguaiacol through C–C coupling reactions (**Scheme 2.3**). The substituent in CON limits the number of phenoxy radicals available for oxidation and polymerization (**Scheme 2.2**). Hence, CON can rapidly complete the reaction along the pathways that lead to dimer formation. Since CON has the ortho and para position blocked, formation of higher degree oligomers would be less likely than for guaiacol. It is possible that the dimers with the $-(CH)_2CHO$ substituents would be less soluble than CON, and would precipitate out of solution.⁸⁵



Scheme 2.2. Suggested mechanism for the oxidation of CON forming dimers. Compared to the reaction of guaiacol (**Scheme 2.3**), extensive oligomerization is less likely for CON due to steric constraints.



Scheme 2.3. Mechanism for the oxidation of guaiacol in the presence of excess iron under dark conditions leading to the formation of dimers and eventually polyguaiacol.^{94,95}

2.3.3 UHPLC-PDA-HRMS Analysis of Brown Carbon Particles

Figure 2.4 shows UHPLC data for the products of the CON + Fe(III) reaction, which was found to give more detectable products than reactions of 3-HC (**Figure 2.5**) and 4-HC (**Figure 2.6**). Since our focus was on light-absorbing products, we attempted to assign all peaks appearing in the PDA chromatograms at near-UV and visible wavelengths. For all PDA peaks, a suitable companion peak appeared in the TIC chromatograms, and its formula could be confirmed with SIM chromatograms. **Table 2.2** summarizes the retention times (RTs) of major peaks observed in all the PDA chromatograms, and their molecular assignments. The formula of the neutral compounds was obtained by adding a proton to the ion formula assuming that deprotonation was the main ionization mechanism.

The CON + Fe(III) reaction produced a surprisingly large number of peaks (**Figure 2.4**). CON itself $C_{10}H_{10}O_3$ was observed at RT 9.09 min indicating that it was either trapped in particles or produced from particles by decomposition in solution. Several major peaks had 20 carbon atoms in them consistent with dimerization. For example, $C_{20}H_{18}O_6$ eluted as three isomers at 9.79, 10.47 and 10.73 min, and was assigned the same molecular formula as the two dimers shown in **Scheme 2.2**. Three of the compounds had 30 carbon atoms ($C_{30}H_{24}O_9$, $C_{30}H_{26}O_9$, and $C_{30}H_{30}O_{11}$), consistent with trimer formation. Compounds with carbon numbers that were not multiples of 10 were observed as well, such as $C_{18}H_{16}O_6$ and $C_{28}H_{24}O_9$, indicating a loss of two carbon atoms from the CON skeleton before or during oligomerization. At the present time, we do not have a good mechanism that explains their formation.

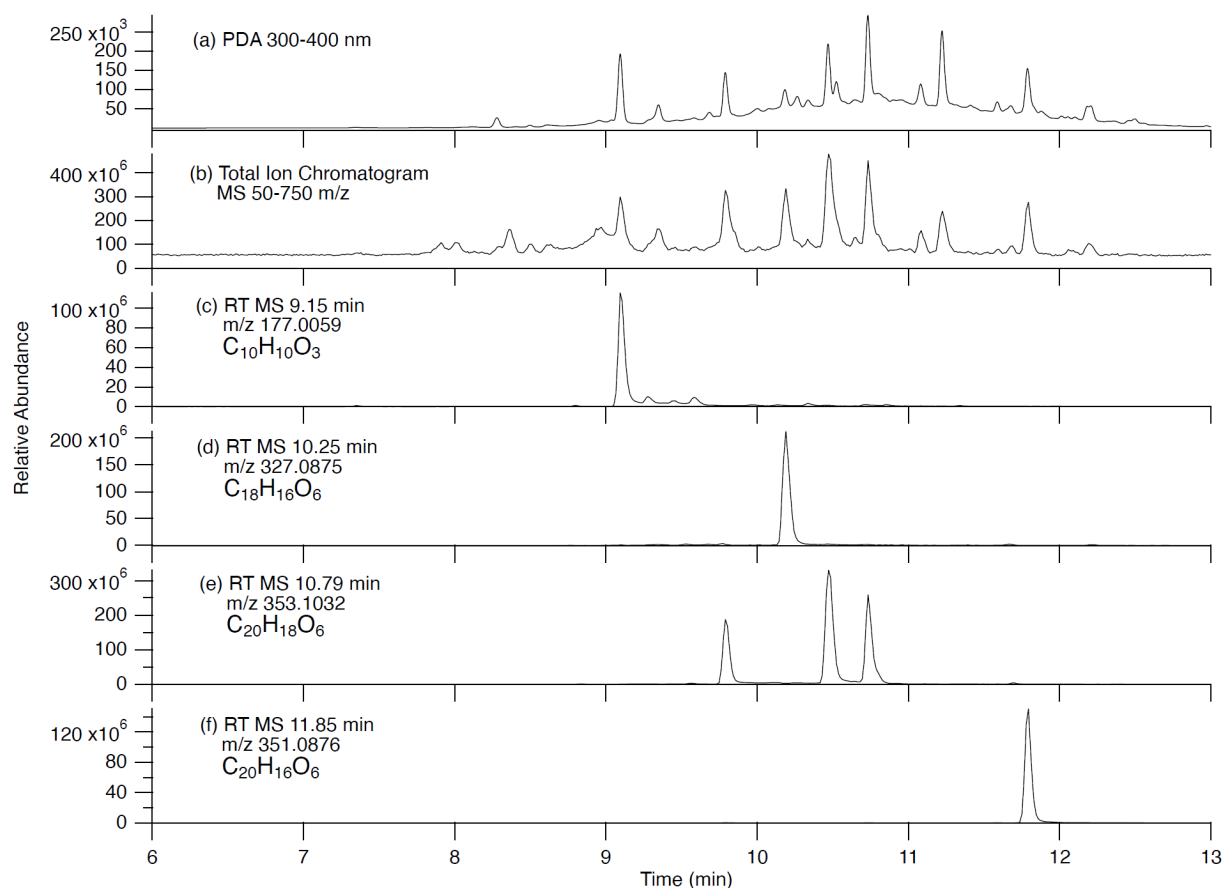


Figure 2.4. UHPLC-PDA-HRMS data for the CON + Fe(III) reaction products: (a) photodiode array (PDA) chromatogram; (b) total ion current (TIC) chromatogram; and (c & d) single ion monitoring (SIM) chromatograms. The TIC and SIM chromatograms were corrected for the 0.06 min delay time between PDA and Orbitrap detectors. The formulas listed correspond to neutral compounds observed as deprotonated ions at the specified m/z values.

In the case of the 3-HC reaction (**Figure 2.5**), only one major absorption peak was detected at RT 9.38 min. Two compounds appeared to co-elute at this RT with neutral formulas of $C_{24}H_{14}O_{10}$ and $C_{11}H_8O_5$. The former has the correct formula for a tetramer of 3-HC. We believe that compound $C_{11}H_8O_5$ corresponds to purpurogallin, which was observed in earlier studies during aerobic oxidation of 3-HC.^{164–166} Purpurogallin has an absorption peak at 325 nm, consistent with the PDA observations. The hydrogen peroxide produced by

Fe(II) to Fe(III) oxidation (e.g., **Scheme 2.1**) should promote conversion of 3-HC to purpurogallin.

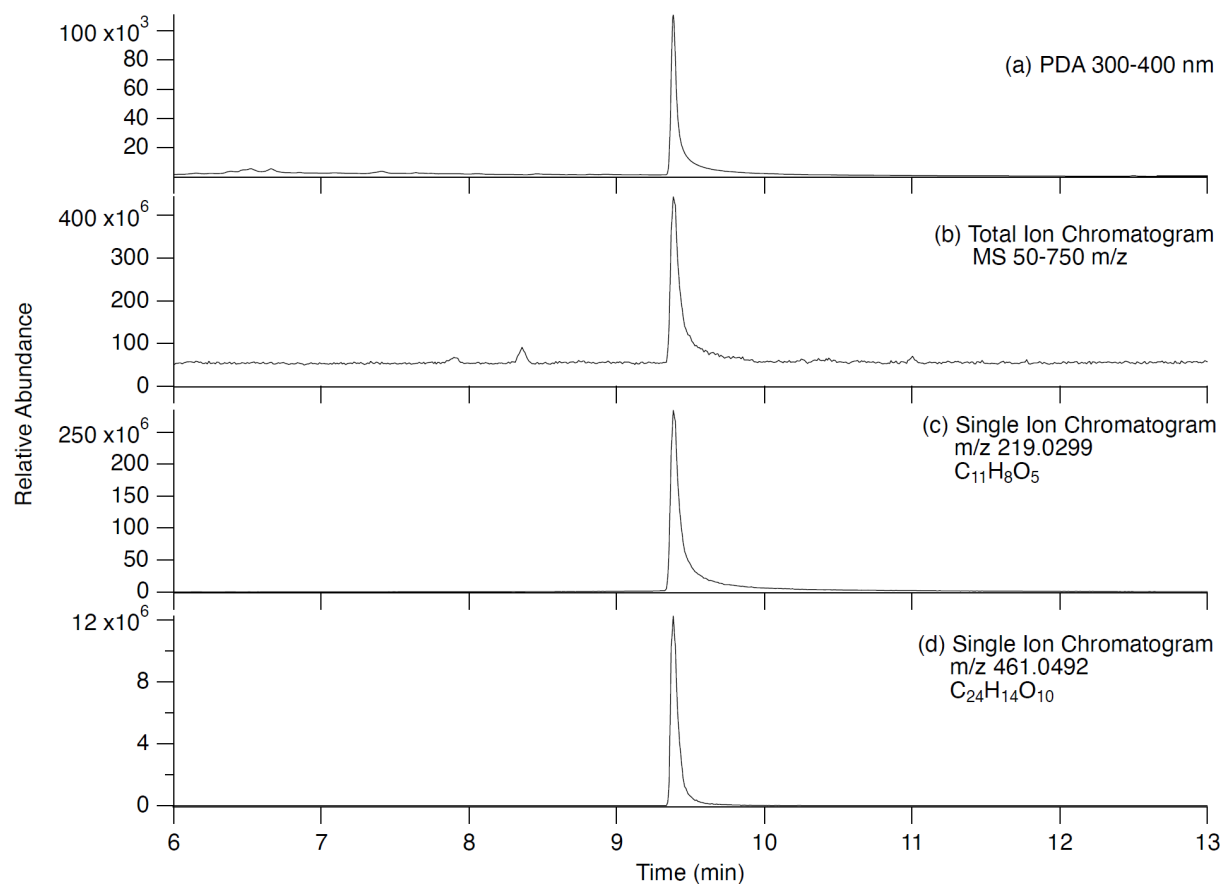


Figure 2.5. UHPLC-PDA-HRMS data for the 3-HC + Fe(III) reaction products: (a) photodiode array (PDA) chromatogram; (b) total ion current (TIC) chromatogram; and (c & d) single ion monitoring (SIM) chromatograms. The TIC and SIM chromatograms were corrected for the 0.06 min delay time between PDA and Orbitrap detectors. The formulas listed correspond to neutral compounds observed as deprotonated ions at the specified m/z values.

The analysis of the 4-HC products (**Figure 2.6**) was complicated by the initial impurities in the starting 4-HC material. However, the major product at RT 8.18 min has a formula corresponding to an O-bridged dimeric product, $C_{12}H_6O_7$. The low number of H-atoms in this compound suggests a highly conjugated quinone structure. Another related

dimeric product, $C_{12}H_6O_7$, eluted at RT 9.77 min. The rest of the peaks had carbon numbers that were not multiples of 6, suggesting a more complicated mechanism than dimerization and other chemistry associated with starting material impurity. We do not have good suggestions for the specific structures of the products beyond the chemical formulas.

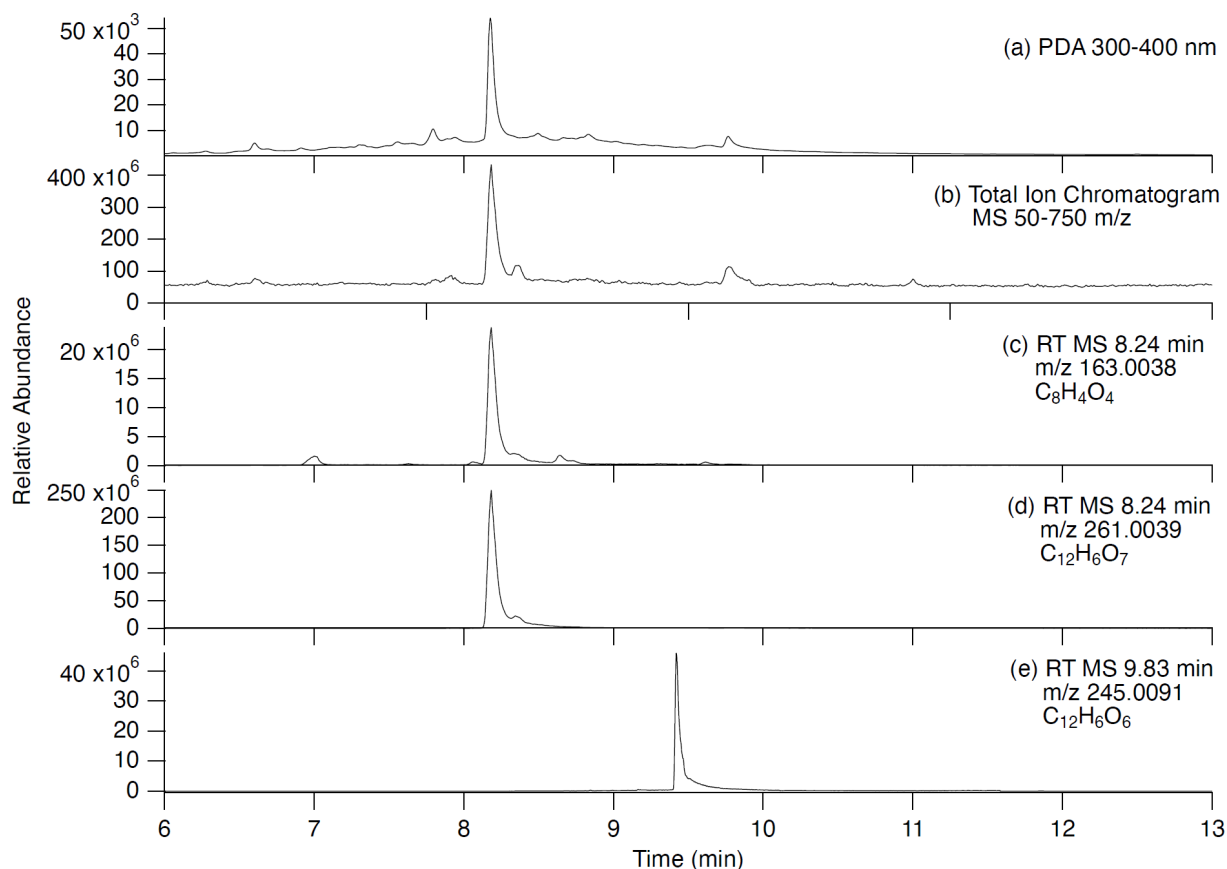


Figure 2.6. UHPLC-PDA-HRMS data for the 4-HC + Fe(III) reaction products: (a) photodiode array (PDA) chromatogram; (b) total ion current (TIC) chromatogram; and (c & d) single ion monitoring (SIM) chromatograms. The TIC and SIM chromatograms were corrected for the 0.06 min delay time between PDA and Orbitrap detectors. The formulas listed correspond to neutral compounds observed as deprotonated ions at the specified m/z values.

Table 2.2 Summary of compounds detected by UHPLC-PDA-HRMS in negative ion mode from reactions of CON, 3-HC, and 4-HC with Fe(III). The formula of the neutral compounds was obtained by adding a proton to the ion formula assuming that deprotonation was the main ionization mechanism.

PDA Retention Time (min)	MS Retention Time (min)	Description of Absorption Spectrum Peaks Observed in PDA	Major m/z Values Correlating with Eluted Peak (negative mode)	Relative Peak Abundance	Neutral Formula
<i>From the CON + Fe(III) reaction</i>					
9.09	9.15	222 and 338 nm	177.0559	-	C ₁₀ H ₁₀ O ₃
9.35	9.40	200-380 nm broad spectrum	565.1724	-	C ₃₀ H ₃₀ O ₁₁
9.79	9.85	222 and 338 nm	353.1032 421.0907	Major Minor	C ₂₀ H ₁₈ O ₆ C ₂₃ H ₁₈ O ₈
10.18	10.25	200-400 nm broad spectrum	327.0875	-	C ₁₈ H ₁₆ O ₆
10.47	10.53	222 and 342 nm	353.1031	-	C ₂₀ H ₁₈ O ₆
10.73	10.79	222 and 338 nm	353.1032	-	C ₂₀ H ₁₈ O ₆
11.08	11.14	222 and 338 nm	503.1347	-	C ₂₈ H ₂₄ O ₉
11.22	11.28	222 and 338 nm	529.1501	-	C ₃₀ H ₂₆ O ₉
11.79	11.85	200-380 nm broad spectrum	351.0876	-	C ₂₀ H ₁₆ O ₆
12.21	12.25	222 and 334 nm	527.1346	-	C ₃₀ H ₂₄ O ₉
<i>From the 3-HC + Fe(III) reaction</i>					
9.38	9.44	220-340 nm broad spectrum	219.0299 461.0492	Major Minor	C ₁₁ H ₈ O ₅ C ₂₄ H ₁₄ O ₁₀
<i>From the 4-HC + Fe(III) reaction</i>					
6.28	6.34	210 and 318 nm	166.9988	-	C ₇ H ₄ O ₅
6.60	6.66	210 nm peak	237.0042 304.9918	Major Minor	C ₁₀ H ₆ O ₇ C ₁₃ H ₆ O ₉
8.18	8.24	218 and 336 nm	163.0038 261.0039	Minor Major	C ₈ H ₄ O ₄ C ₁₂ H ₆ O ₇
9.77	9.83	218 nm peak	245.0091	-	C ₁₂ H ₆ O ₆

2.4 Conclusions

Experiments described in this chapter broadened the list of organic compounds capable of forming insoluble particles in aqueous reactions with soluble iron. Previous studies found insoluble products in reactions of Fe(III) with catechol, guaiacol, syringol, o- and p-cresol.^{85,92} We have added CON, 3-HC, and 4-HC to the list of particle-forming compounds over short periods of time (i.e., 2 h). In contrast, 2,4-DNP, NC, and MC did not produce any insoluble products on this time scale. All of these compounds are common constituents of BBOA, but their relative yields depend on the combustion conditions. The results suggest that Fe(III)-catalyzed chemistry can take place in smoldering BBOA plumes and make aerosol particles more light-absorbing. This has important implications for understanding the direct effect of BBOA and mixed dust/BBOA aerosols on climate.

The millimolar concentrations of Fe(III) and organic reactants used in our experiments may only be attainable on surfaces of particles or in aerosol liquid water, so the results of this study should not be applied to cloud and fog droplets, where the concentrations are lower. Furthermore, these experiments have not evaluated the possible effect of competing complexation between Fe(III) and oxalate ion, which has been shown to decrease the particle yield in Fe(III) + catechol reaction.³ Finally, in real particles, there are other organic compounds that do not form complexes with Fe(III) but can scavenge OH (an intermediate in this chemistry), thus indirectly affecting the chemistry leading to particle formation. This makes it challenging to extrapolate these results to actual atmospheric conditions.

CHAPTER 3:

FORMATION OF INSOLUBLE BROWN CARBON THROUGH IRON-CATALYZED REACTION OF BIOMASS BURNING ORGANICS

Hopstock, K. S.; Carpenter, B. P.; Patterson, J. P.; Al-Abadleh, H. A.; Nizkorodov, S. A., Formation of insoluble brown carbon through iron-catalyzed reaction of biomass burning organics, *Environmental Science: Atmospheres*, **3** (2023) 207-220.¹⁶⁷

Abstract. Biomass burning organic aerosol (BBOA) is one of the largest sources of organics in the atmosphere. Mineral dust and biomass burning smoke frequently co-exist in the same atmospheric environment. Common biomass burning compounds, such as dihydroxybenzenes and their derivatives, are known to produce light-absorbing, water-insoluble polymeric particles upon reaction with soluble Fe(III) under conditions characteristic of aerosol liquid water. However, such reactions have not been tested in realistic mixtures of BBOA compounds. In this study, model organic aerosol (OA), meant to replicate BBOA from smoldering fires, was generated through the pyrolysis of Canary Island pine needles in a tube furnace at 300, 400, 500, 600, 700, and 800 °C under nitrogen gas, and the water-soluble fractions were reacted with iron chloride under dark, acidic conditions. We utilized spectrophotometry to monitor the reaction progress. For OA samples produced at lower temperatures (300 and 400 °C), particles (P300 and P400) formed in solution, were syringe filtered, and extracted in organic solvents. Analysis was conducted with ultrahigh pressure liquid chromatography coupled to a photodiode array spectrophotometer and a high-resolution mass spectrometer (UHPLC-PDA-HRMS). For OA samples formed at higher pyrolysis temperatures (500-800 °C), water-insoluble, black particles (P500-800) formed in

solution. In contrast to P300 and P400, P500-800 were not soluble in common solvents. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and transmission electron microscopy (TEM) were used to image P600 and determine bulk elemental composition. Electron microscopy revealed that P600 had fractal morphology, reminiscent of soot particles, and contained no detectable iron. These results suggest that light-absorbing aerosol particles can be produced from Fe(III)-catalyzed reactions in aging BBOA plumes produced from smoldering combustion in the absence of any photochemistry. This result has important implications for understanding the direct and indirect effects of aged BBOA on climate.

3.1 Introduction

Biomass burning events represent one of the largest sources of volatile organic compounds (VOCs) in the atmosphere and have prominent effects on atmospheric chemistry and climate. Emissions of both gaseous and particulate species are chemically complex and can evolve during transport through chemical and physical aging (i.e., heterogeneous oxidation reactions, photolysis reactions, and cloud processing).^{80,99,168,169} Phenolic compounds, such as catechol, guaiacol, coniferaldehyde, and syringol, are common products of lignin pyrolysis and, although relative emissions of these compounds vary with fuel type, they are always present in burning emissions.^{146,170–172} Along with organic compounds, inorganic species have been detected in western United States wildfire plumes including metals Fe, Mn, Ca, Al, Ti, and Sr, which are associated with crustal matter and dust.¹⁷³ Schlosser et al. (2017) reported that dust was one of the main components of coarse particulate matter collected at IMPROVE sites during times of biomass burning events.¹⁷³ In

addition to wildfire plumes, aerosol particles containing dissolved Fe(III) are widespread in the atmosphere due to windblown, iron-rich mineral dust ($\sim 2000 \text{ Tg yr}^{-1}$).^{147,174,175} Both biomass burning organic aerosol (BBOA) and mineral dust are transported globally over long distances and this timeframe allows for the partitioning of organic vapors into iron-containing particles.^{83,84,156} During long-range transport, atmospheric processing of dust can lead to iron oxides being dissolved under acidic conditions ($\text{pH} < 4$).¹⁷⁶⁻¹⁷⁸ This long-range transport of iron-containing particles can provide an opportunity for mixing with biomass burning products and can be a sink for VOCs. Most BBOA aging studies have investigated free radical driven oxidation reactions (NO_x , OH, O_3) and photolysis reactions, and the studies of BBOA aging due to transition metal catalysis remain limited.^{179-182,168,183}

Previous laboratory studies have shown that Fe(III) can catalyze oligomerization reactions with known constituents of BBOA and industrial emissions to produce lower volatility secondary brown carbon (BrC) products.^{85,86,92,140,142,143,184,185} Reaction solutions were open to air and dissolved O_2 acted as an oxidant. These irreversible, oxidative polymerization reactions formed water-insoluble, black particles in acidic systems ($\text{pH} 3$) with excess Fe(III). The production of particles was dependent upon the iron to organic molar ratios and the structure of the organic precursor. During reaction with organics, iron cycles between its +2 and +3 oxidation states, and its reactivity is dependent upon the presence of electron donors/acceptors, strength of complexation to ligands, and steric effects.^{93,140,147} This cycling between Fe(II) and Fe(III) is coupled with the production of H_2O_2 and OH radicals, and reactive oxygen species (ROS) as intermediates in reaction.^{80,85}

Figure 3.1 contains a summary of compounds shown to produce insoluble particulate products in reactions with Fe(III). In Slikboer *et al.* (2015), catechol and guaiacol

(**Figure 3.1a**) were mixed with Fe(III) at pH 3 in millimolar concentrations to yield water-insoluble polycatechol and polyguaiacol particles, respectively.⁸⁵ In the case of catechol, upon addition of Fe(III), a progression of color change from colorless to green to black was observed. This green color was attributed to the formation of the catechol-iron bidentate mononuclear complex followed by ligand to metal charge transfer. Guaiacol did not produce this color change because the methoxy group inhibited iron complexation but, through a slightly different mechanism, produced polyguaiacol particles. Follow up studies also showed that these oligomerization reactions were not suppressed in the presence of oxalate and sulfate ions,¹⁴² and some dicarboxylic acids which normally have a high complexation affinity to iron.¹⁸⁵ Lavi *et al.* (2017) expanded on the reactivity of BBOA phenol precursors with Fe(III).⁹² Dimers, trimers, tetramers, and pentamers were observed for reactions of Fe(III) with syringol, o-cresol, and p-cresol (**Figure 3.1b**).⁹² These oligomeric species absorbed light between 300-500 nm and were present in lower abundance than reactions of guaiacol and catechol, which produced insoluble BrC particles.⁹² Chin *et al.* (2021) further expanded the list of organic compounds capable of forming insoluble particles to include 3-hydroxycatechol, 4-hydroxycatechol, and coniferaldehyde (**Figure 3.1a**).¹⁴⁰ These laboratory studies with isolated BBOA compounds suggest that Fe(III) reacts with a broad range of phenolic compounds, which can produce secondary BrC compounds in atmospheric particles, however, it is unclear how this chemistry translates to secondary BrC formation from actual BBOA, prompting this study.

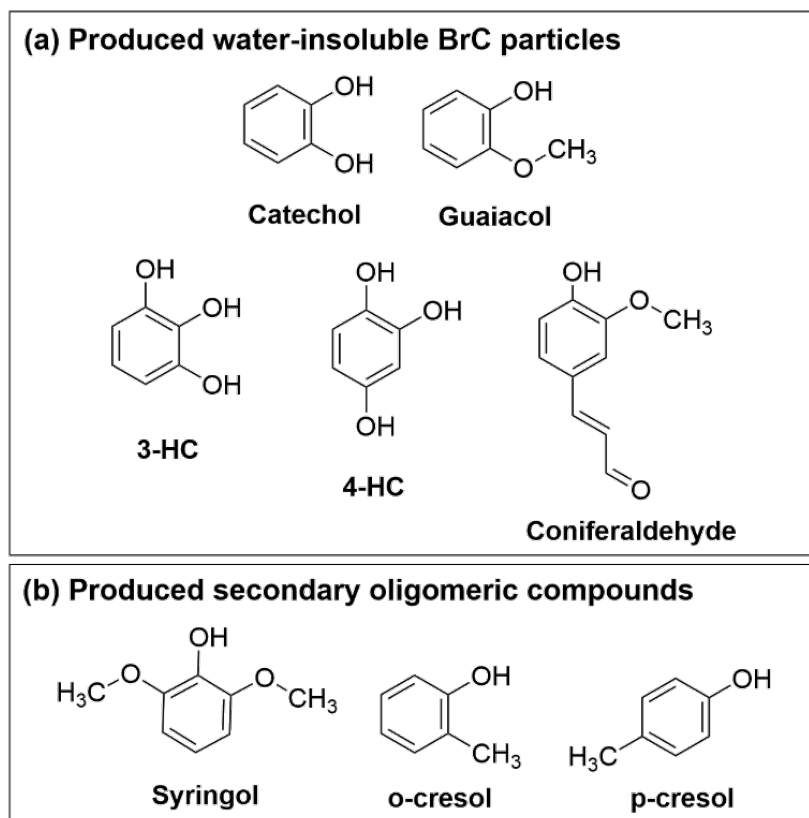


Figure 3.1. Phenolic BBOA precursors that are known to produce (a) water-insoluble BrC particles and (b) secondary oligomeric compounds upon reaction with Fe(III) under aqueous, acidic, dark conditions. 3-HC is 3-hydroxycatechol and 4-HC is 4-hydroxycatechol.

Wildfire conditions often range between smoldering (heterogeneous, 450-700 °C) combustion and flaming (homogeneous, 1100-1800 °C) combustion with a quick transition between each depending on environmental conditions.⁶² Exploratory measurements by Chin *et al.* (2021) concluded that BBOA collected under smoldering conditions reacted in the presence of Fe(III) to produce insoluble particles,¹⁴⁰ whereas BBOA collected under flaming conditions did not appreciably react, as flaming combustion favors the reaction of aromatics with NO_x in biomass burning plumes to generate nitroaromatics.¹⁸⁶ Pyrolysis is one of the mechanisms operating in smoldering combustion, in which a biomass fuel is heated in the absence of oxygen to produce pyrolyzate (gas), char, and ash,⁶² and it occurs at temperatures

known to produce the most phenolic products.¹⁸⁷ In this work, we utilize pyrolysis in a tube furnace under an inert atmosphere in order to precisely control experimental conditions and study chemistry of emitted particles as a function of temperature. We observe efficient formation of secondary particles in reactions of this mimic BBOA with dissolved Fe(III). This work highlights the role iron plays in the aging of BBOA to produce oligomeric species and water-soluble/insoluble BrC secondary products.

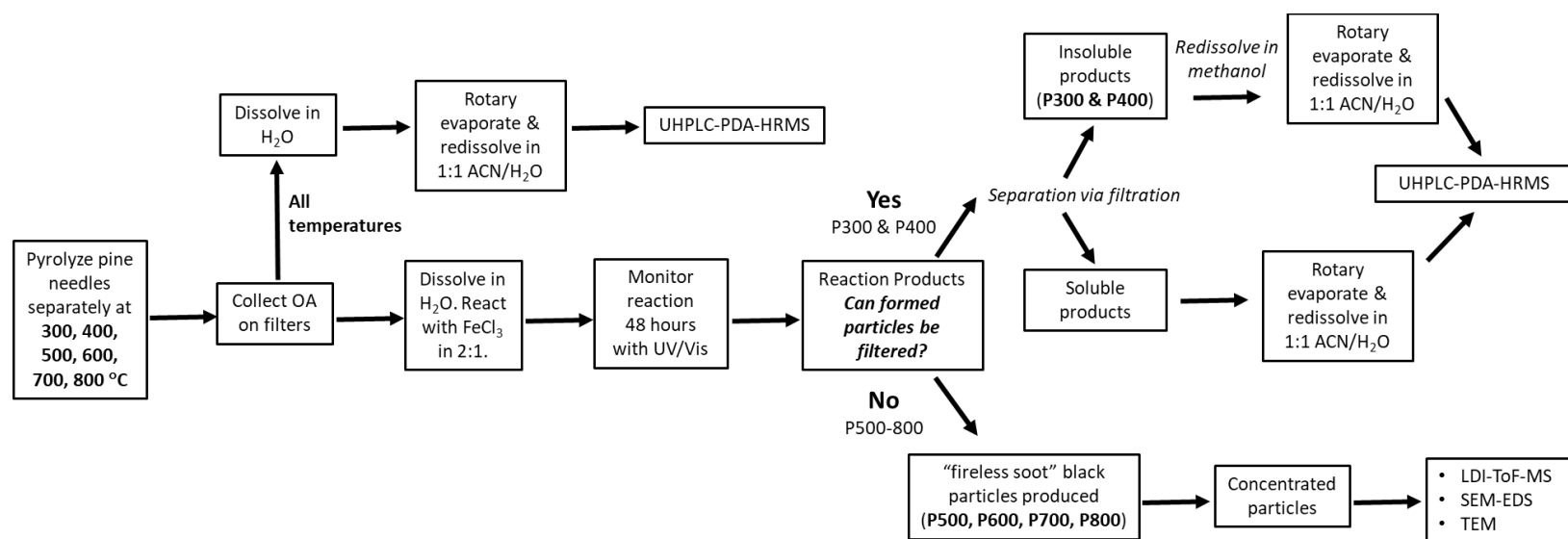
3.2 Experimental Methods

3.2.1 Canary Island Pine Pyrolysis OA Generation

A summary flowchart of all experiments can be found in **Scheme 3.1**. Dry Canary Island pine (*Pinus Canariensis*) needles were used as biomass fuel for these pyrolysis experiments. The main motivation for selecting this fuel is that this species of pine is increasingly planted for landscaping in warmer climates, such as Southern California, and urban fires are on the rise worldwide. For each experiment, approximately 200 mg of needles were placed in a ceramic pyrolysis boat then inserted into a 2.5 cm quartz tube, upstream from the Thermolyne F21135 Tube Furnace. The tube was then sealed with parafilm and continuously purged with N₂ gas (~0.7 standard liters per minute). A flow of N₂ gas was constant during pyrolysis, and the setup was not reopened until after collection had ceased. This ensured that no oxygen from the laboratory was introduced into the furnace. A 40 cm section of the tube, downstream from the pyrolysis boat, was heated to a prescribed temperature (300, 400, 500, 600, 700, or 800 °C). Once the furnace reached the temperature of interest, the entire tube (containing the ceramic pyrolysis boat and pine needles) was

pushed from the outside so that the pine needles were in the heated zone and pyrolysis could begin. There was a temperature drop of ~ 75 °C upon entry of the room temperature section of the tube into the heated zone, but the temperature increased back up to the prescribed temperature before smoke appeared. The flow of N_2 gas pushed the generated smoke particles through the quartz tubing for collection on PTFE 47 mm Teflon filters (Millipore Sigma, Fluoropore Membrane Filter, FGLP04700, 47 mm, 0.22 μm pore size). The starting pressure was ~ 760 Torr. The collection times varied (1-10 min). Pyrolysis and gas flow were stopped in time to prevent the filter from overloading (if left unattended the filter resistance could increase enough to over-pressurize the system above 800 Torr which was deemed unsafe for continuing collection).

Figure 3.2 shows representative photographs of the collected filter samples at all pyrolysis temperatures. Since the particles produced in this process do not result from biomass burning, but rather pyrolysis in an inert N_2 atmosphere, we will refer to them as organic aerosol (OA). The fraction of OA that is extractable in water (18 M Ω -cm milli-Q water, pH 6.9) will be labeled as “OA” with its pyrolysis temperature listed after (i.e., OA300 is the water extract of particles generated through pyrolysis at 300 °C). Insoluble particles generated in aqueous reactions of OA with Fe(III) will be labeled as “P” with the pyrolysis temperature after (i.e., P300 are the insoluble particles generated through the reaction of OA300 with $FeCl_3$).



Scheme 3.1. Experimental flowchart of all temperature pyrolysis reactions and analysis methods. Organic aerosol generated through pyrolysis is labeled as “OA” with its pyrolysis temperature listed after (i.e., OA300 is the organic aerosol generated through pyrolysis at 300 °C). The same label (e.g., OA300) is also used for the water-extracts of OA from the filters. Insoluble particles generated in the reactions of OA water extracts with Fe(III) are labeled as “P” with the pyrolysis temperature after (i.e., P300 are the insoluble particles generated through the reaction of OA300 with Fe(III)). All OA samples were analyzed with HRMS prior to reaction with iron (first upward arrow). Analysis methods for the reaction products were dictated by whether formed particles could be filtered out of the solution or not. In the case of P300 and P400, generated in OA300 + Fe(III) and OA400 + Fe(III) reactions, respectively, particles were sufficiently large to be separated from soluble reaction products by common filtration (pore size 0.22 µm) and were analyzed with HRMS. In the case of P500-800, black particles were too small to be filtered. However, they could be centrifuged at 14,000 g for 10 minutes for imaging by TEM and SEM. In addition, dry residues of the suspensions of these particles were characterized by LDI-ToF-MS.

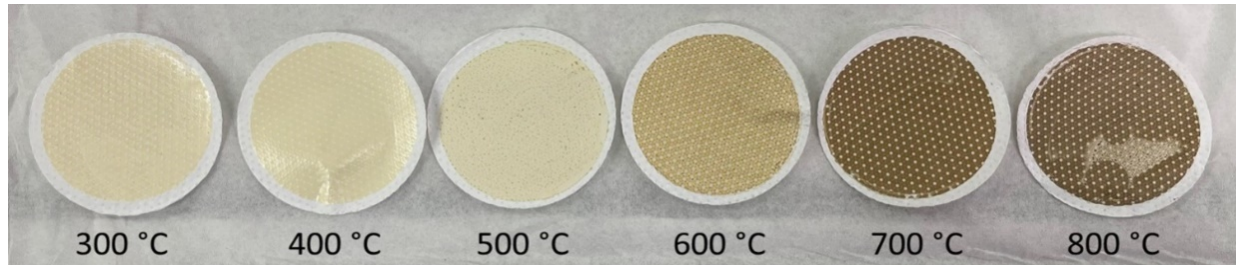


Figure 3.2. OA filters generated at various pyrolysis temperatures using Canary Island pine needles.

3.2.2 Aqueous Phase Reactions and UV-Visible Spectroscopy Experiments

After OA collection, each filter was weighed with a Sartorius ME5-F microbalance (1 μg precision) and the OA mass on the filter was calculated. The emission factors (EF) for each pyrolysis temperature were estimated (**Table 3.1**), assuming that the filters had 100% collection efficiency (all smoke particles were trapped before venting to the exhaust). Apparent EFs likely represent lower limits for the actual EFs, as pyrolyzed material partly deposited on the walls of the flow tube before reaching the filter. Each filter was first extracted in water (18 M $\Omega\text{m-cm}$ milli-Q water) by shaking for 30 minutes on a Thermolyne Type 37600 mixer (M37615, ~ 1500 rpm) then the filter was removed and separately dissolved in methanol. Absorption spectra were obtained for the fractions dissolved separately in water and in methanol, assuming that only a fraction of OA could be dissolved in water but all remaining OA on the filter was dissolved in methanol.⁶⁶ The filters became colorless after the methanol extraction indicating that all light-absorbing compounds dissolved.

Table 3.1. Summary of collected Canary Island pine OA as a function of pyrolysis temperature. All values are reported as the average amongst three replicates of each pyrolysis temperature. Calculated emission factors, in the units of grams of filter-collected OA per kilogram of dry pine needle used in pyrolysis (g kg^{-1}), likely underestimate true emission factors due to wall losses. Uncertainty is reported to 1 standard deviation. The pH of the water extracted OA solutions was ~ 3 .

Pyrolysis Temperature ($^{\circ}\text{C}$)	Emission factor (g kg^{-1})	Average percent of collected OA dissolved in water (%)	Average mass dissolved in water (mg)
300	23 ± 9	60 ± 6	1.5 ± 0.6
400	25 ± 8	60 ± 6	2.5 ± 0.5
500	22 ± 2	62 ± 4	2.1 ± 0.3
600	24 ± 8	52 ± 5	2.4 ± 0.7
700	26 ± 2	36 ± 7	1.9 ± 0.4
800	22 ± 3	32 ± 5	1.6 ± 0.3

The concentrations of water-soluble organics were estimated, assuming that absorption coefficients of the water and methanol soluble fractions were the same, and these values were utilized to determine the volume of 80 mM iron chloride solution that should have been added to the organics in order to achieve a 2:1 molar ratio of Fe(III) to organics,^{85,140} assuming an average molecular weight of 200 Da for OA. 80 mM iron chloride solutions were prepared with iron (III) chloride hexahydrate (97%, CAS 10025-77-1, Sigma-Aldrich) in milli-Q water. The reactions were conducted in the dark at pH 3, as determined by a calibrated pH meter (Mettler Toledo SevenEasy S20). Upon dissolving the OA in water, the measured pH dropped from 6.9 to ~ 3 , without having to acidify it further. The atmospheric relevance of these reaction conditions was described previously in Chin *et al.* (2021) and references therein.¹⁴⁰

UV-Vis absorption spectra were acquired using a UV-Vis spectrometer (Shimadzu UV-2450) in a 1 cm quartz cuvette with a reference cuvette containing milli-Q water. Upon

addition of iron chloride to the 300-800 °C water-soluble OA fractions, the reaction progressions were monitored for 48 h. To monitor the initial reaction progress within seconds after addition of iron to the high temperature pyrolysis samples (500-800 °C), an Ocean Optics USB4000 spectrometer with a tungsten deuterium lamp was utilized to measure absorbance change every 0.5 s for 40 s.

3.2.3 Mass Spectrometric Experiments

3.2.3.1 Analysis of Soluble Reaction Products

OA300 + FeCl₃ and OA400 + FeCl₃ reaction solutions were filtered with 0.25 µm nylon filter syringes to isolate water-insoluble particles (P300 and P400) from soluble products (**Scheme 3.1**). The remaining solutions (soluble reaction products) were rotary evaporated (20-30 min) and redissolved in 1:1 (v/v) ACN/H₂O for high resolution mass spectrometry (HRMS) analysis. The water-insoluble filter contents were extracted in 10 mL of methanol then rotary evaporated and redissolved in 1:1 (v/v) ACN/H₂O for HRMS analysis. In addition to P300/400 and water-soluble reaction products, OA from all pyrolysis temperatures (OA300-800, no FeCl₃) were run on HRMS (**Scheme 3.1**). P500-800 (**Figure 3.3**) did not undergo this same procedure (*see below*).

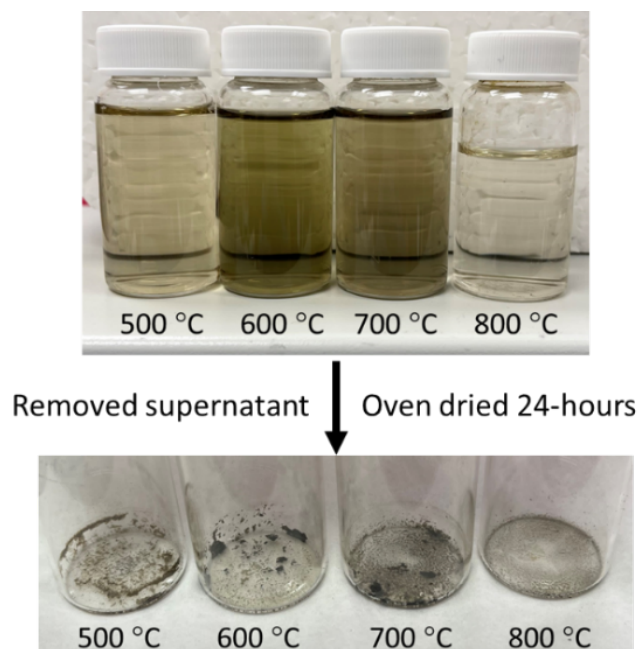


Figure 3.3. Solutions of OA500-800 extracts 10 min after addition of FeCl_3 . After reaction for 48 h, the generated particles settled to the bottom of the vials, and the supernatant was removed. The particles were suspended in a few mL of the solution and then dried in an oven for 24 h. These dried particles were then used for LDI-ToF-MS experiments.

The mass spectra were recorded with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high-resolution mass spectrometer (UHPLC-PDA-HRMS) with a resolving power up to 1.4×10^5 at m/z 200. The separation was performed on a reverse-phase column (Phenomenex Luna Omega Polar C18, 150×2.1 mm, $1.6 \mu\text{m}$ particles, $100 \text{ \AA}$ pores) with temperature kept at 30°C and injected volume of $10 \mu\text{L}$. The eluent flow was $0.3 \mu\text{L min}^{-1}$ and consisted of HPLC-MS grade water acidified with 0.1 % v/v formic acid (solution A) and HPLC-MS grade acetonitrile with 0.1% v/v formic acid added (solution B). The gradient was: 0-3 min 95% A; 3-14 min linear ramp to 95% B; 14-16 min hold at 95% B; 16 min return to 95% A and hold until 22 min in preparation for the next run.

PDA data was collected at 5 Hz over 190-680 nm range with a 4 nm effective bandwidth. Mass spectra were obtained with m/z range of 100-1500 in the negative ion mode, producing $[M - H]^-$ ions (favored ionization mechanism for phenolic species). The parameters of the heated electrospray ionization (HESI) ion source settings of the Orbitrap were as follows: - 2.5 kV spray voltage, 320 °C capillary temperature, 300 °C probe heater temperature, S-Lens ion funnel RF level 60, 50 units of sheath gas (nitrogen) flow, 10 units of auxiliary gas (nitrogen) flow, and 1 unit of spare gas (nitrogen) flow.

Analysis of chromophoric compounds in water-soluble products of OA300/OA400 reactions with Fe(III) and of P300/P400 was conducted similarly to that described in Chin *et al.* (2021).¹⁴⁰ Strong peaks contributing to the near-UV and visible PDA chromatogram were correlated to the corresponding peaks in the total ion current (TIC) chromatogram, considering a 0.06 min delay time between PDA and Orbitrap detectors. Light-absorbing peaks occurring in the TIC were confirmed and verified using selected ion monitoring (SIM) chromatograms. Exact m/z values were assigned to molecular formulas using the molecular formula calculator mentioned previously.

Molecular formulas of OA300-800 were assigned similarly to previous work.^{48,188-190} Chromatograms were analyzed using FreeStyle 1.6 (Thermo Scientific) and mass spectra between the column's dead time and the start of the column re-equilibration time (2-16 min) were integrated. Decon2LS program was used to cluster together all mass spectra from the same temperature. The clustered peaks from each temperature were aligned to a common m/z axis. Background peaks present only in the blank samples were removed from all sample spectra. Peaks containing ^{13}C isotopes were removed. All peaks were assigned to the formulas $\text{C}_x\text{H}_y\text{O}_z$ with a mass accuracy of ± 0.0005 m/z units. Ion formulas generated were

verified with a molecular formula calculator. All results were reproduced in triplicate and all identified compounds are presented and discussed as neutral species with their corresponding masses.

3.2.3.2 Analysis of Insoluble Reaction Products

The particles produced in reactions of OA500-800 with Fe(III) (**Figure 3.3**) were too small to be reliably separated by filtration (implying that particles were smaller than the filter pore size of 0.22 μm). Laser desorption ionization was utilized in the analysis of P500-800 after evaporation of water. These experiments were conducted using an LDI-ToF mass spectrometer (AB Sciex ToF/ToF 5800 MALDI System). Typically, matrix-assisted laser desorption ionization (MALDI) works by the user mixing the sample with a low molecular weight organic “matrix” compound (such as 2,5-dihydroxybenzoic acid) that absorbs at the laser wavelength (355 nm). A matrix additive was not needed in this analysis since the samples absorbed strongly at the laser wavelength and were structurally similar to the typical MALDI matrix compounds. Aliquots of 0.5-1 μL of the starting solutions of OA500-800 (control) or solutions containing suspended P500-800 (sample) were pipetted into separate wells on a stainless steel, hydrophobic MALDI substrate and allowed to dry. Mass spectra were collected in negative ion mode, reflector mode in the m/z range of 50-1500 using 200 Hz pulse rate and 2000 shots in each spectrum. Spectra were exported using a data conversion software and analysis was conducted using the open-source mass spectrometry program, mMass 5.5.0.¹⁹¹

3.2.4 Particle Characterization

3.2.4.1 Sample Preparation

To determine bulk elemental composition and image particles, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and transmission electron microscopy (TEM) were used. Polycatechol standard particles (produced by the method of Slikboer *et al.* (2015)⁸⁵) and P600 were compared with these methods. Reaction solutions, containing polycatechol and P600 particles, were concentrated by centrifugal filtration with a molecular weight cutoff of 3 kDa using a centrifuge at 14,000 g for 10 min. Concentrated samples were then washed with water 3 times. To retrieve the sample, the sample vial was inverted into a clean Eppendorf tube and centrifuged for two minutes at 1,000 g. Each sample was then resuspended in 200 μ L of nanopure water.

3.2.4.2 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Samples were prepared by pipetting 5 μ L of the washed and resuspended P600 (or polycatechol particles) onto SiO₂ wafers. Samples were coated with 5 nm of Iridium prior to imaging. A Magellan 400 XRH system was used for imaging and elemental analysis. To obtain images, the instrument was set to Secondary Electron (SE) detection mode with an accelerating voltage of 5.0 keV and current density of 25 pA. For elemental analysis, thick samples (many layers of particles) were prepared to obtain higher signal against the substrate. The instrument was set to EDS mode with an accelerating voltage of 18 keV and current density of 0.4 nA. To correct for the background signal, blank regions of the SEM

substrate were scanned by EDS, and spectra were compared with that of polycatechol and P600.

3.2.4.3 Transmission Electron Microscopy (TEM)

Samples were prepared by pipetting 5 μL of the washed and resuspended P600 (or polycatechol particles) onto 400 Mesh Carbon TEM grids. Samples were absorbed onto grids over 5 min and were then blotted with Kimwipe paper. A Joel-2100 TEM with a Schottky type field emission gun was used to obtain images. Serial EM software was used to perform low dose imaging, and a Gatan Oneview Camera was used to collect images.

3.3 Results and Discussion

3.3.1 Reactions between OA300/400 and Fe(III)

UV-Vis absorption spectra for the water-soluble OA fractions are presented in **Figure 3.4**. These absorption spectra are characteristic of BrC, with absorption increasing from the visible to the UV. Upon addition of iron, reactions of OA300/400 + FeCl_3 did not exhibit any solution color changes but produced water-insoluble particles (that could be redissolved in organic solvents). **Figure 3.5 (a-d)** shows the UV-Vis absorption spectra collected immediately after the addition of iron (time 0 min) and at timepoints during the reactions. Both reactions have an absorbance band at 290 nm (**Figure 3.5a and 3.5c**), attributed to an n to π^* transition of the organic reactant solution after ~ 1 h of reaction. In addition, there is an absorption band peaking at 296 nm attributed to the formation of $\text{Fe}(\text{OH})_2^+$.¹⁴⁰ At 477 nm, there is a peak that forms upon addition of iron at time 0 min (**Figure 3.5b and 3.5d**), which

can be attributed to the formation of an organic intermediate. Prior to the addition of iron, OA300 and OA400 (black traces) do not exhibit this peak. Previous studies that focused on BBOA precursor reactivity with Fe(III) observed similar peak behavior at ~400 nm, which was attributed to an intermediate ortho-quinone species.^{85,140} This species forms after catechol oxidation and complexation with iron, and then it reacts with peroxide (in solution) to initiate radical chemistry and polymerize to form polycatechol. Since the peak we observe is at 477 nm and not 400 nm, it is clear the intermediate is not identical, but, nevertheless, behaves in a similar way to what has been previously observed. The decrease in this absorbance band at 477 nm over time coincides with a small increase in absorbance at longer wavelengths, implying that the intermediate is being incorporated into the insoluble BrC particles. There is slight scattering and absorption by the insoluble, suspended particles forming over time with a weak wavelength dependence.

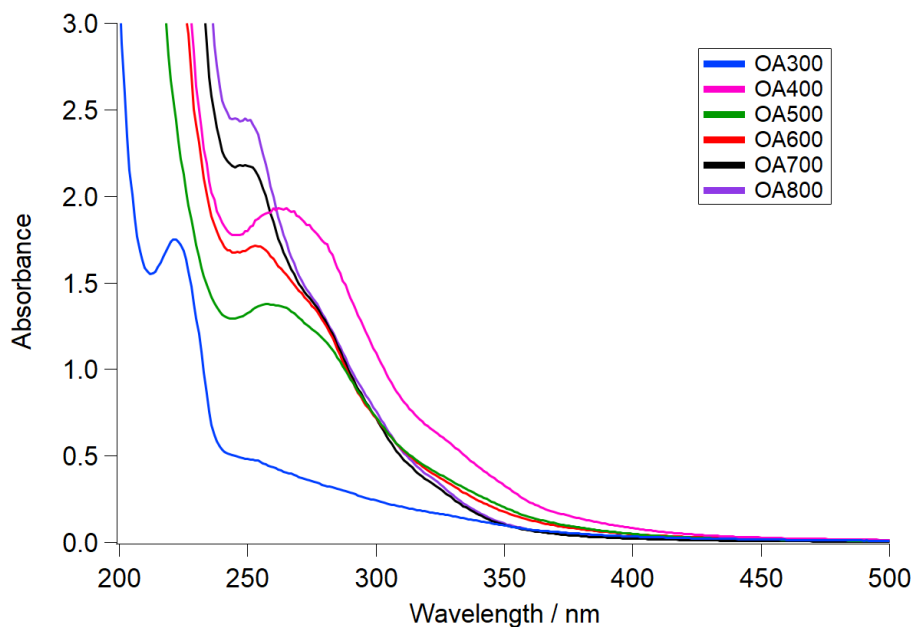


Figure 3.4. Absorption spectra for the water-soluble OA fractions generated through the pyrolysis of Canary Island Pine needles. Spectra correspond to 300 °C (blue), 400 °C (pink), 500 °C (green), 600 °C (red), 700 °C (black), and 800 °C (purple) pyrolysis temperatures.

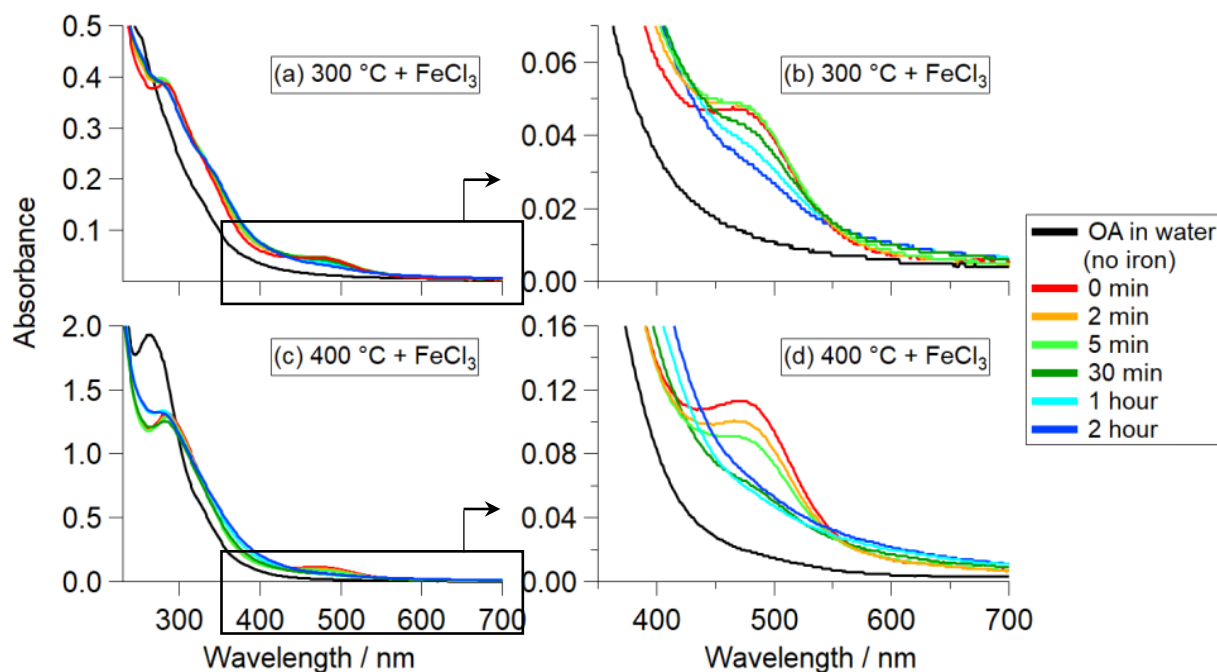


Figure 3.5. Absorption spectra for the first two hours of reaction of OA300 + FeCl₃ (a and b) and OA400 + FeCl₃ (c and d). Panels (b) and (d) show an enlargement of the 477 nm peak present in panels (a) and (c). Nanopure water acidified to pH 3 was used as a reference blank.

Table 3.2 summarizes the HRMS results for the reactions of OA300 and OA400 with the distribution of molecular formulas after reaction with iron for 48 h. The average MW increased from 324.9 to 486.1 Da (OA300 to P300) and 338.5 to 435.5 Da (OA400 to P400). In addition, P300 and P400 were less oxidized, as indicated by lower average O:C ratios (**Table 3.2**). These results are consistent with the expectation that Fe(III) can catalyze the oligomerization of phenolic compounds in solution to generate polyphenolic polymers.

Table 3.2. Summary of UHPLC-HRMS results from unreacted OA300-800 samples compared to the results for the water-insoluble products (P300 and P400) after reaction with FeCl₃. Similar data could not be obtained for P500-800 because particles were not soluble in most solvents.

Pyrolysis Temperature	Type of Sample	Average Molecular Weight	Average Neutral Molecular Formula	Average O:C
300 °C	Unreacted OA	324.9	C ₁₇ H ₂₀ O ₆	0.37 ± 0.19
	Water-insoluble products	486.1	C ₂₈ H ₄₁ O ₇	0.27 ± 0.16
400 °C	Unreacted OA	337.49	C ₁₇ H ₂₁ O ₇	0.43 ± 0.26
	Water-insoluble products	435.50	C ₂₄ H ₃₈ O ₇	0.30 ± 0.10
500 °C	Unreacted OA	299.04	C ₁₆ H ₁₉ O ₆	0.39 ± 0.18
	Water-insoluble products	-	-	-
600 °C	Unreacted OA	320.27	C ₁₇ H ₁₇ O ₆	0.36 ± 0.14
	Water-insoluble products	-	-	-
700 °C	Unreacted OA	316.19	C ₁₇ H ₁₆ O ₅	0.28 ± 0.12
	Water-insoluble products	-	-	-
800 °C	Unreacted OA	313.02	C ₁₆ H ₁₀ O ₅	0.32 ± 0.13
	Water-insoluble products	-	-	-

3.3.2 Reactions between OA500-800 and Fe(III)

OA500-800 + FeCl₃ reactions (**Figure 3.6, a-d**) exhibited different results than OA300/400 + FeCl₃ reactions (**Figure 3.5**). The solutions underwent various intensities of a clear to green to brown color change, similar to that of the catechol + Fe(III) reaction in Slikboer *et al.* (2015) that yielded water-insoluble, black polycatechol particles (**Figure 3.3**).⁸⁵ In order to monitor this change, UV-Vis absorption spectra needed to be taken on a faster timescale than for OA300/400 + Fe(III) reactions. In addition, after 1 min the OA500-800 + Fe(III) absorbance spectra did not exhibit significant changes. **Figure 3.6** shows the UV-Vis absorption spectra taken during the reactions of OA500-800 (a-d) and reference system catechol (e) shortly after the addition of iron. There is depletion of the 334 nm FeCl₃ peak (red trace) and the formation of a peak at 390 nm that can be attributed to an n to π^* transition of ortho-quinone species formed as an intermediate during the formation of catechol-Fe complexes.^{85,147,161} This peak increases in intensity for the first 10 s of reaction and then decreases, as the intermediate reaction product (ortho-quinone) is reacted in solution to form polycatechol.⁸⁵ The increase in absorbance over time in the visible and near IR was due to scattering and absorption by black particles being produced in solution. These spectral features are not present in the unreacted OA absorbance spectra in **Figure 3.4**. The catechol spectrum also exhibits a ligand-to-metal charge transfer band in the near IR $\sim$ 700 nm (and subsequent green color in solution) when a bidentate mononuclear catechol-Fe(II) complex formed.⁹³

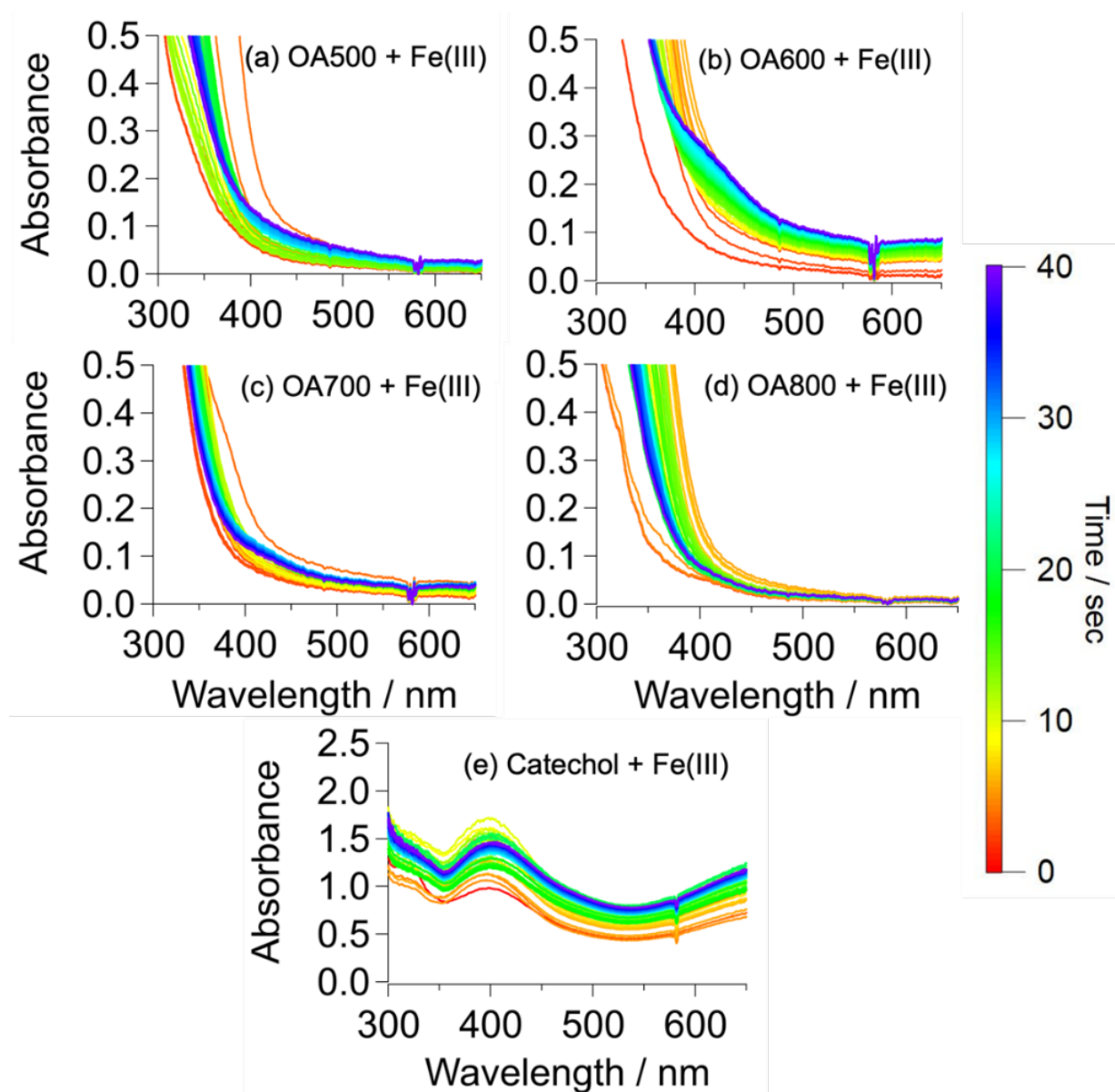
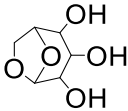
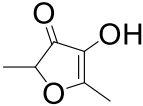
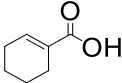


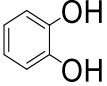
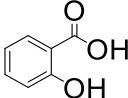
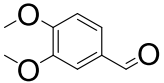
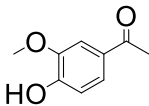
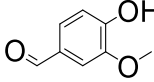
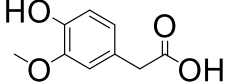
Figure 3.6. Absorption spectra of OA500 (a), OA600 (b), OA700 (c), and OA800 (d) reactions with Fe(III) taken every 0.5 s for 40 s with an Ocean Optics USB4000. Panel (e) shows the reaction of catechol with Fe(III) for comparison. Nanopure water acidified to pH 3 was used as a reference blank.

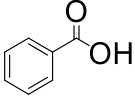
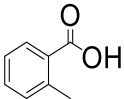
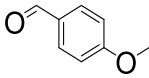
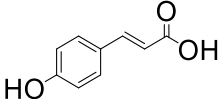
3.3.3 Mass Spectrometry Analysis (UHPLC-PDA-HRMS)

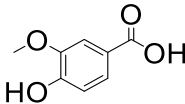
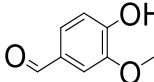
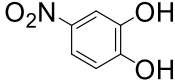
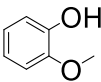
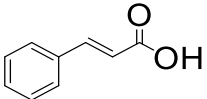
OA samples from all pyrolysis temperatures prior to reaction with FeCl_3 were run in triplicate on UHPLC-PDA-HRMS for detailed chemical analysis. **Table 3.3** lists the major ions detected in negative ion mode with their corresponding retention times, neutral molecular formulae, tentative structural assignments, and pyrolysis temperatures in which the compounds were present. References are presented in cases where structural assignments have been made in previous studies.^{47,48,65,140,170,192–203} **Figure 3.7** shows the total ion chromatograms of all temperature OA, with peaks labeled according to their corresponding detected ion in **Table 3.3**. As expected, hydrophilic, more polar compounds (such as organic acids) eluted earlier than the more hydrophobic, less polar species, which had stronger interactions with the stationary phase in the reverse-phase C18 column. We observed oxygenated aromatics, substituted phenols, methoxyphenols, and substituted benzoic acids in various abundance, dictated by pyrolysis temperature. Tracers of lignin burning (such as catechol, acetovanillone, homovanillic acid, vanillic acid, and vanillin) were present at all pyrolysis temperatures measured.¹⁹³ Levoglucosan, a tracer of biomass burning, was seen in low abundance during the LC deadtime (~1.46 min), as it is highly water soluble.

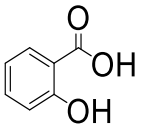
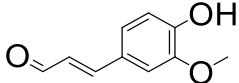
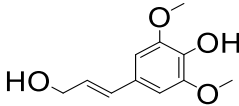
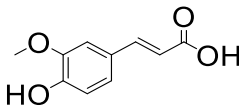
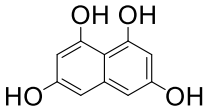
Table 3.3. List of compounds reproducibly detected by UHPLC-PDA-HRMS in negative ion mode from the pyrolysis of Canary Island Pine needles at 300-800 °C. The formulas of the neutral compounds were obtained by adding a proton to the ion formula, assuming that deprotonation was the main ionization mechanism. The normalized, relative peak abundances are designated for each temperature as “L” for Low (<5% peak abundance in time integrated mass spectra), “M” for Medium (6-14%), and “H” for High (15-100%). For light-absorbing species, tentative structural assignments were confirmed using absorption spectra recorded by the PDA detector. The last column shows the peak numbers that correspond to the red labeled numbers in **Figure 3.7**. Retention times without a number were also present on **Figure 3.7** but were not labeled for simplicity.

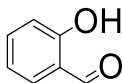
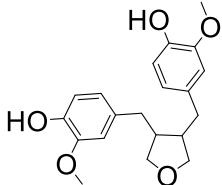
LC RT (min)	Observed <i>m/z</i>	Calculated <i>m/z</i>	Chemical Formula of Neutral Species	Tentative structures	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C	References	Figure 3.7 peak numbers
1.46	161.0456	161.0455	C ₆ H ₁₀ O ₅	Levoglucosan 	L	L	L	L	L	L		
6.54	127.0401	127.0401	C ₆ H ₈ O ₃	Furaneol 			H	M				
6.71	125.0608	125.0608	C ₇ H ₁₀ O ₂	Cyclohexene carboxylic acid 	M	M	M	M	L	L	¹⁹²	

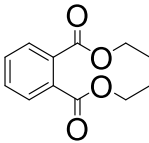
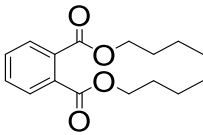
6.60/6.82	109.0294	109.0295	C ₆ H ₆ O ₂	Catechol 	L	M	H	H	H	H	140,192	1
7.04	315.1085	315.1085	C ₁₄ H ₂₀ O ₈				M	L				
7.12	137.0242	137.0233	C ₇ H ₆ O ₃	Salicylic acid 		L	H	H	M	M		2
7.18	165.0558	165.0557	C ₉ H ₁₀ O ₃	Veratraldehyde  Acetovanillone 	L	L	L	M	L	L	192,193	3
7.32	151.0399	151.0389	C ₈ H ₈ O ₃	Vanillin 			L	H	L	L		4
7.68	181.0508	181.0506	C ₉ H ₁₀ O ₄	Homovanillic acid 	L	L	H	M	L	L	192-194	5

7.85/7.94	121.0294	121.0295	C ₇ H ₆ O ₂	Benzoic acid 	H	H	H	H	M	M	48,192-198	6
	283.1186	283.1187	C ₁₄ H ₂₀ O ₆			L						
8.07	173.0820	173.0819	C ₈ H ₁₄ O ₄		H							
8.14	307.0822	307.0823	C ₁₅ H ₁₆ O ₇		M							
8.25	119.0502	119.0502	C ₈ H ₈ O	Acetophenone 	M	M	L	L			196	
	135.0451	135.0452	C ₈ H ₈ O ₂	2-Methylbenzoic acid  Methoxybenzaldehyde 	H	H	H	H	M	M	48,194,204	8
	163.0401	163.0401	C ₉ H ₈ O ₃	p-Coumaric acid 	H	H	H	H	L		170,192	7

	167.0349	167.0350	C ₈ H ₈ O ₄	Vanillic acid 	M	M	H	L	L	L	192-194,199	8
	337.0927	337.0929	C ₁₆ H ₁₈ O ₈		L							
8.27	151.0401	151.0401	C ₈ H ₈ O ₃	Vanillin (isomer) 	L	M	H	H	L	L	192,193,200,205	
8.47	154.0145	154.0135	C ₆ H ₅ O ₄ N	4-Nitrocatechol 	L	M	L				202	9
8.52	123.0452	123.0452	C ₇ H ₈ O ₂	Guaiacol 	L	L	M	H	H	H	192,194,199,204	10
	293.1030	293.1031	C ₁₅ H ₁₈ O ₆		L	L	L					
8.79	187.0975	187.0976	C ₉ H ₁₆ O ₄		M	M	H	M	L	L		11
8.88	243.0661	243.0652	C ₁₄ H ₁₂ O ₄					L	M	M		12
8.94	147.0451	147.0452	C ₉ H ₈ O ₂	Cinnamic acid 	H	H	M	L			192	13

9.15/9.35	137.0243	137.0244	C ₇ H ₆ O ₃	3-hydroxybenzoic acid 	L	L	H	H	M	M	192,199	14
	177.0557	177.0557	C ₁₀ H ₁₀ O ₃	Coniferaldehyde 	H	H	M	L			140,192,200,204,205	15
	199.0975	199.0975	C ₁₀ H ₁₆ O ₄		H	M	M	L				
9.41	209.0818	209.0819	C ₁₁ H ₁₄ O ₄	Sinapyl alcohol 	M	M	L	L			47,199	
9.50	193.0507	193.0506	C ₁₀ H ₁₀ O ₄	Ferulic acid  1,3,6,8-Tetrahydroxynaphthalene 			H	L			205	16

9.76	149.0607	149.0597	C ₉ H ₁₀ O ₂			L	M	H	M	L		17
10.55	121.0295	121.0295	C ₇ H ₆ O ₂	Salicylaldehyde 		H						
10.58	185.0608	185.0597	C ₁₂ H ₁₀ O ₂						L	L		
10.68	287.2226	287.2227	C ₁₆ H ₃₂ O ₄		H	H	L					
	329.0665	329.0666	C ₁₇ H ₁₄ O ₇		M	H	L					18
10.72	229.1443	229.1445	C ₁₂ H ₂₂ O ₄		H	H	L					
	343.1548	343.1550	C ₂₀ H ₂₄ O ₅	Tetrahydro-3,4-divanillylfuran 		H	L				197	
	375.1446	375.1449	C ₂₀ H ₂₄ O ₇			M	L				199	
	421.1502	421.1504	C ₂₁ H ₂₆ O ₉		M	M						
10.82	285.0767	285.0768	C ₁₆ H ₁₄ O ₅			H						
	303.0872	303.0874	C ₁₆ H ₁₆ O ₆			M	L					

	331.2123	331.2126	C ₁₇ H ₃₂ O ₆			H						
10.97	215.1650	215.1652	C ₁₂ H ₂₄ O ₃		M	M	L	L	L	L		19
11.00	221.0816	221.0819	C ₁₂ H ₁₄ O ₄	Diethyl phthalate 	H	M	L	L			199,203	
	393.0613	393.0615	C ₂₁ H ₁₄ O ₈		M							
11.17	235.1339	235.1339	C ₁₄ H ₂₀ O ₃			M	L					
12.18/ 12.23	243.1963	243.1965	C ₁₄ H ₂₈ O ₃		H	H	M	L	L	L		20
12.43	293.1757	293.1747	C ₁₇ H ₂₆ O ₄		M	M	L					21
12.95	285.2069	285.2071	C ₁₆ H ₃₀ O ₄		H	M	L					
13.44	271.2275	271.2278	C ₁₆ H ₃₂ O ₃		H	M	L					22
13.89	277.1445	277.1445	C ₁₆ H ₂₂ O ₄	Dibutyl Phthalate 			H				48,203	23
14.38	249.1494	249.1496	C ₁₅ H ₂₂ O ₃		M							
14.64	299.2014	299.2016	C ₂₀ H ₂₈ O ₂		L	M						
	357.2068	357.2071	C ₂₂ H ₃₀ O ₄			L						
15.35	275.1649	275.1652	C ₁₇ H ₂₄ O ₃		H	M	L					
15.52	335.2227	335.2227	C ₂₀ H ₃₂ O ₄		M	L						

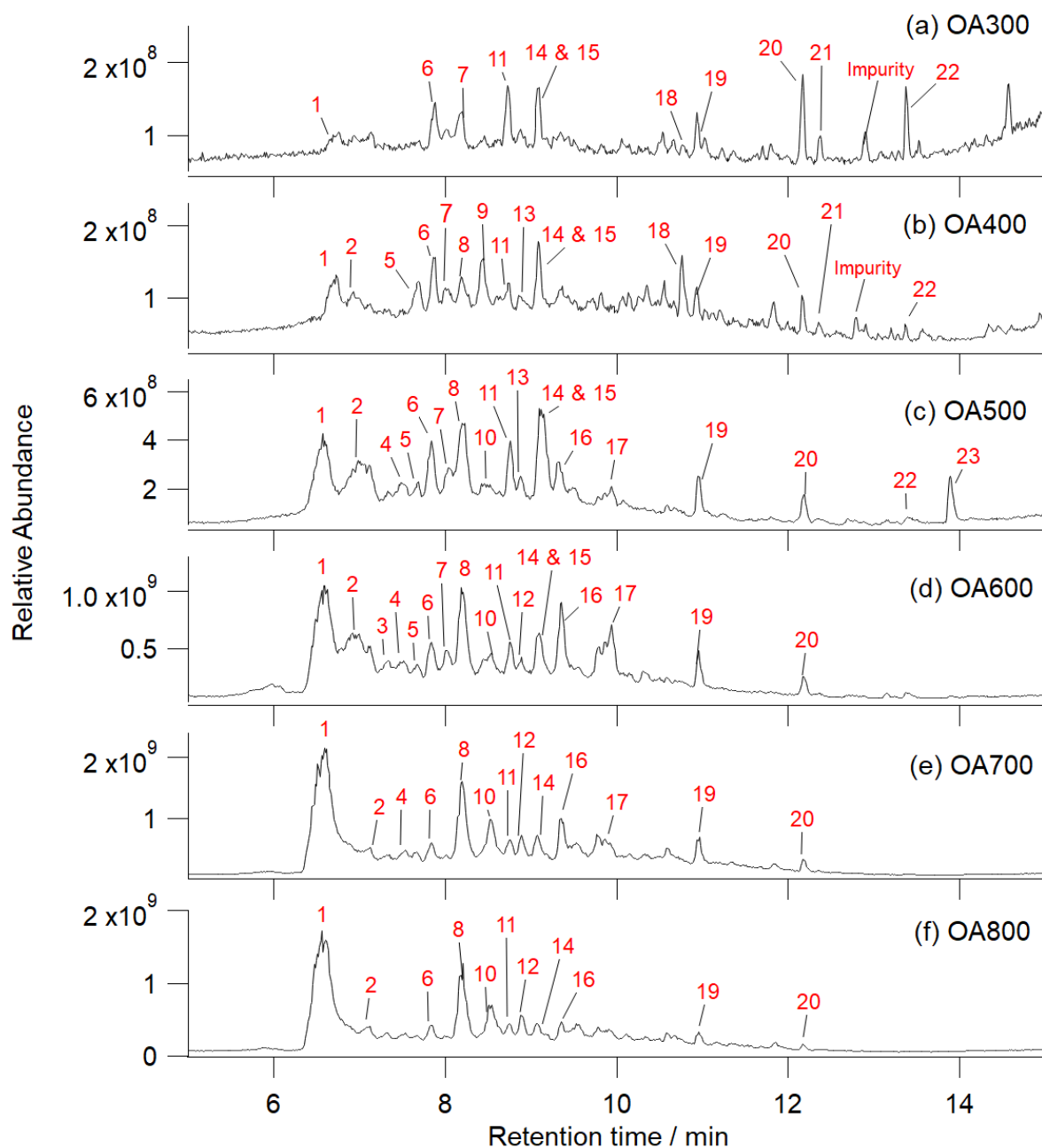


Figure 3.7. UHPLC-HRMS total ion chromatograms of Canary Island pine OA generated under 300-800 °C pyrolysis conditions in flowing nitrogen (a-f). These samples were analyzed prior to reaction with FeCl₃. Ions responsible for chromatographic peaks are numbered in red with their corresponding identities listed in the rightmost column in **Table 3.3**. Notable peaks include: 1) catechol, 2) salicylic acid, 5) homovanillic acid, 6) benzoic acid, 7) p-coumaric acid, 8) 2-methylbenzoic acid/methoxybenzaldehyde and vanillic acid, 9) 4-nitrocatechol, 10) guaiacol, 11) C₉H₁₀O₄, 14) 3-hydroxybenzaldehyde, and 15) coniferaldehyde. Additional detailed compositional analysis at each retention time is listed in **Table 3.3**.

Figure 3.8 shows the PDA and TIC chromatograms for OA300/400, water-soluble reaction products, and P300/400 once dissolved in methanol and run through HRMS. Unreacted OA exhibits peaks throughout the chromatogram, indicating products with a wide range of polarities. Water-soluble products (**Figure 3.8d**) have large PDA/TIC peaks at early retention times, indicating more polar products are present, whereas P300/P400 have greater intensity peaks at later retention times, suggesting less polar products. Large peaks at approximately 8 min (benzoic acid) are reduced in intensity in P300/400 in comparison to the water-soluble products. Both **Figure 3.8d** and **Figure 3.8f** exhibit a peak at 11.02 min (m/z 221.0817, $C_{12}H_{14}O_4$). As this peak is present in both water-soluble and water-insoluble products, filtration may not have properly removed particles containing this compound or it could be present in both phases.

The light absorption properties of OA300/400 and P300/400 are further compared in **Figure 3.9 (a-d)**, which shows the heat map view absorption spectra as a function of retention time. P300 (**Figure 3.9c**) and P400 (**Figure 3.9d**) have less strongly absorbing peaks than their unreacted OA300/400 counterparts. Coniferaldehyde (9.15 min) was responsible for the greatest absorption for OA300/400 before reaction with iron. In the P300 and P400 chromatograms, coniferaldehyde was present and was the strongest absorber, indicating that it was either trapped inside of particles or it was produced through particle decomposition in solution. In addition to other labeled organic compounds, 4-nitrocatechol (4-NC) was observed in the OA400 PDA chromatogram (8.47 min, assigned by the retention time of the standard and PDA absorption spectrum) which was not present in the P400 PDA chromatogram (remained in the soluble reaction products). Previous experiments showed that 4-NC is not reactive with $FeCl_3$ under these reaction conditions.¹⁴⁰

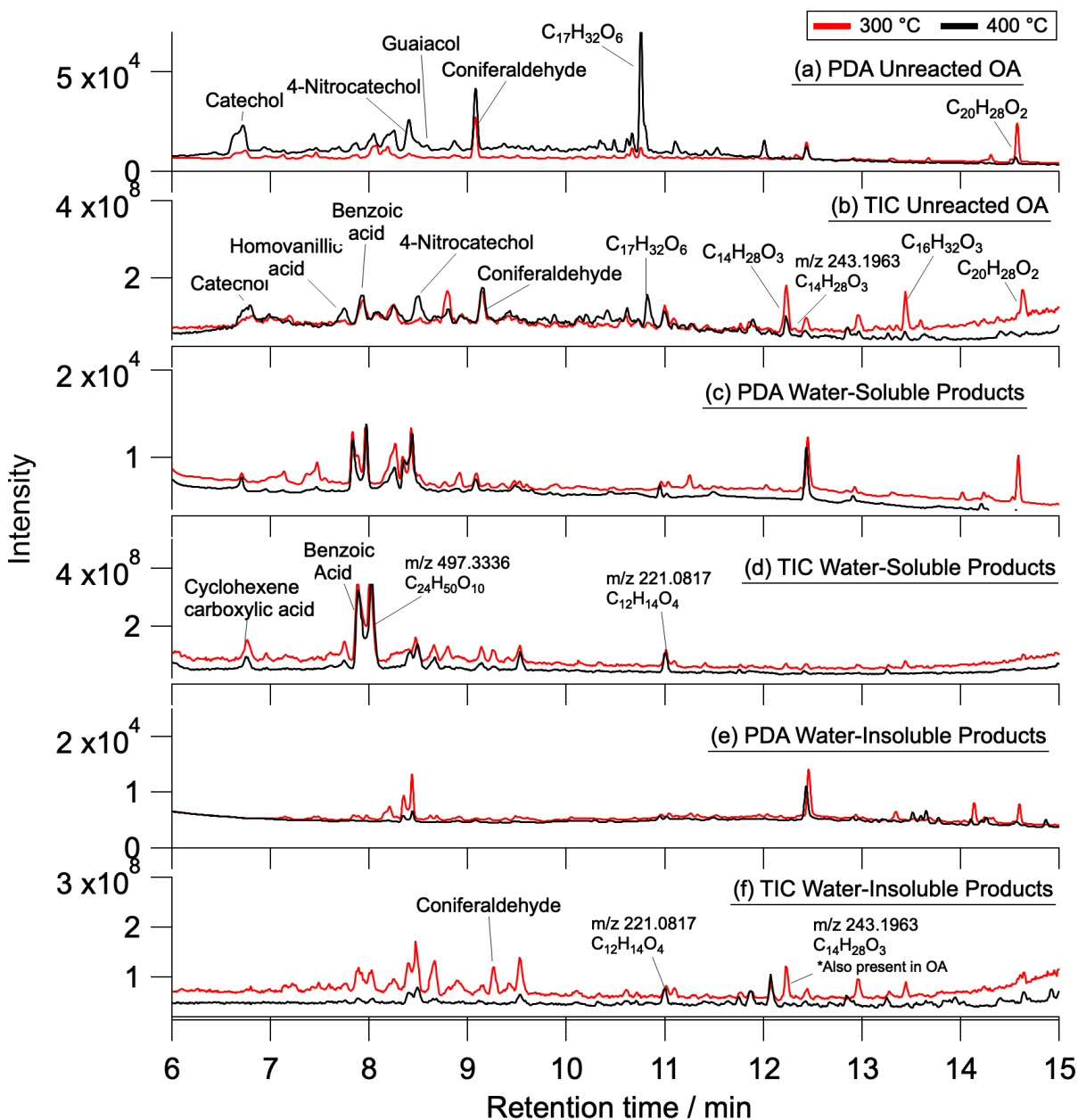


Figure 3.8. Sample UHPLC-PDA-HRMS chromatograms of reaction products for 300 °C (red) and 400 °C (black) OA + Fe(III). Each panel represents: a) PDA chromatograms of unreacted OA; b) total ion chromatograms (TICs) of unreacted OA; c) PDA chromatograms of water-soluble OA + Fe(III) reaction products; d) TICs of water-soluble OA + FeCl₃ reaction products; e) PDA chromatograms of water-insoluble P300/400; and f) TICs of water-insoluble P300/400. P300 and P400 were filtered from the solution, redissolved in methanol, and rotary evaporated prior to analysis with HRMS. There is a 0.06-minute time delay between PDA and Orbitrap detectors. Unlabeled peaks in panel (b) can be identified using **Table 3.3**.

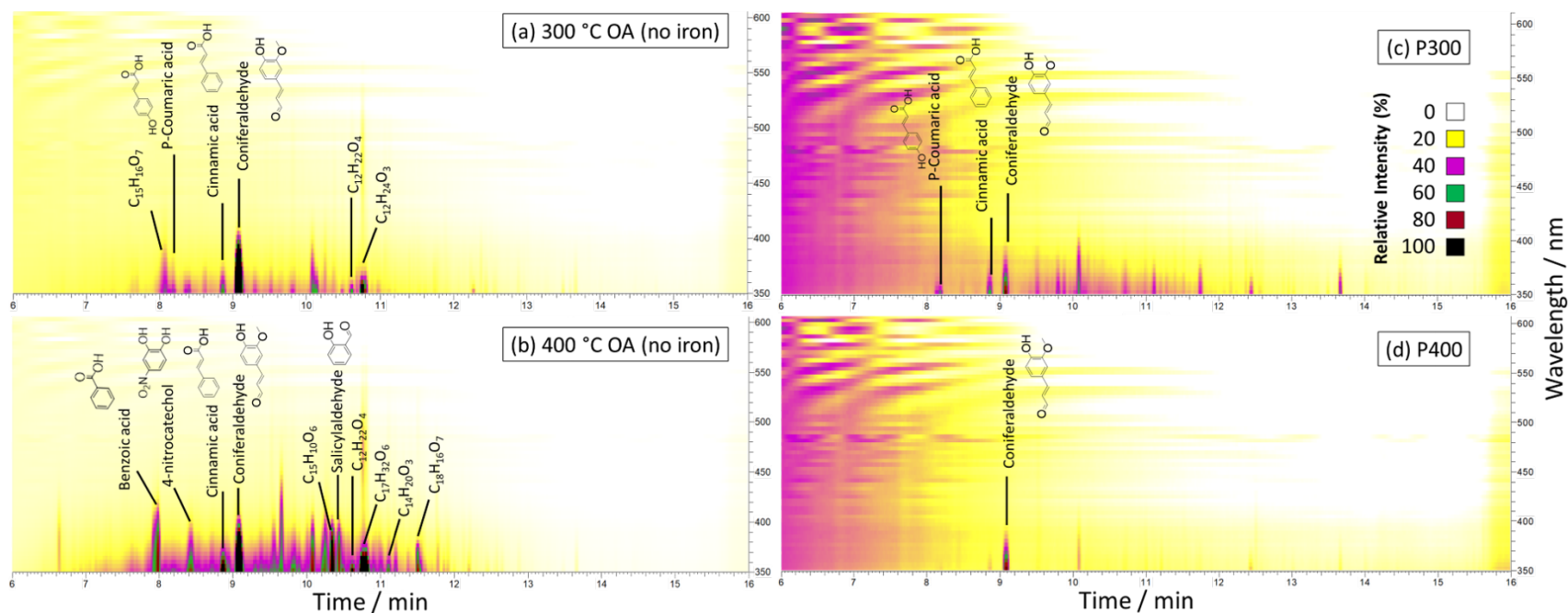


Figure 3.9. Heat maps of UHPLC-PDA chromatograms as a function of absorption wavelength for unreacted, water-soluble OA. The panels correspond to 300 °C (a) and 400 °C (b) data. Peaks were normalized to 5% of the largest peak intensity. Water-insoluble particles, P300 and P400 (panels c and d, respectively), were formed in the reaction of OA + Fe(III). Peaks were normalized to 100% of the largest peak intensity. In (a) and (b), coniferaldehyde is responsible for the 100% relative intensity of light absorption at 9.15 min. In (c) and (d), most light absorption species disappear except for the remaining coniferaldehyde.

Figure 3.10 shows mass spectra integrated over all retention times (2-16 min) as function of pyrolysis temperature. As temperature increases, the mass spectral complexity decreases, with catechol (m/z 109) becoming the most dominant peak in the mass spectra (600, 700, and 800 °C). In comparison to catechol, guaiacol is present in increasing abundance beginning at 500 °C. Of the compounds known to polymerize in the presence of iron (**Figure 3.1**), we observed catechol, guaiacol, and coniferaldehyde in the unreacted OA extracts. These peaks were verified by standard experiments in our previous work.¹⁴⁰ Increasing pyrolysis temperature decreased the amount of collected OA that was extracted in water. At higher temperatures, nonpolar species (PAHs and non-cyclic aliphatics) dominate emissions, reducing the amount of water-soluble OA by 20% from 500 °C to 800 °C (**Table 3.3**). Some of these aromatic compounds are soluble in water but are not relevant to this study as they do not react with iron. **Figure 3.11** shows an expanded version of this figure with major peaks labelled with formulas.

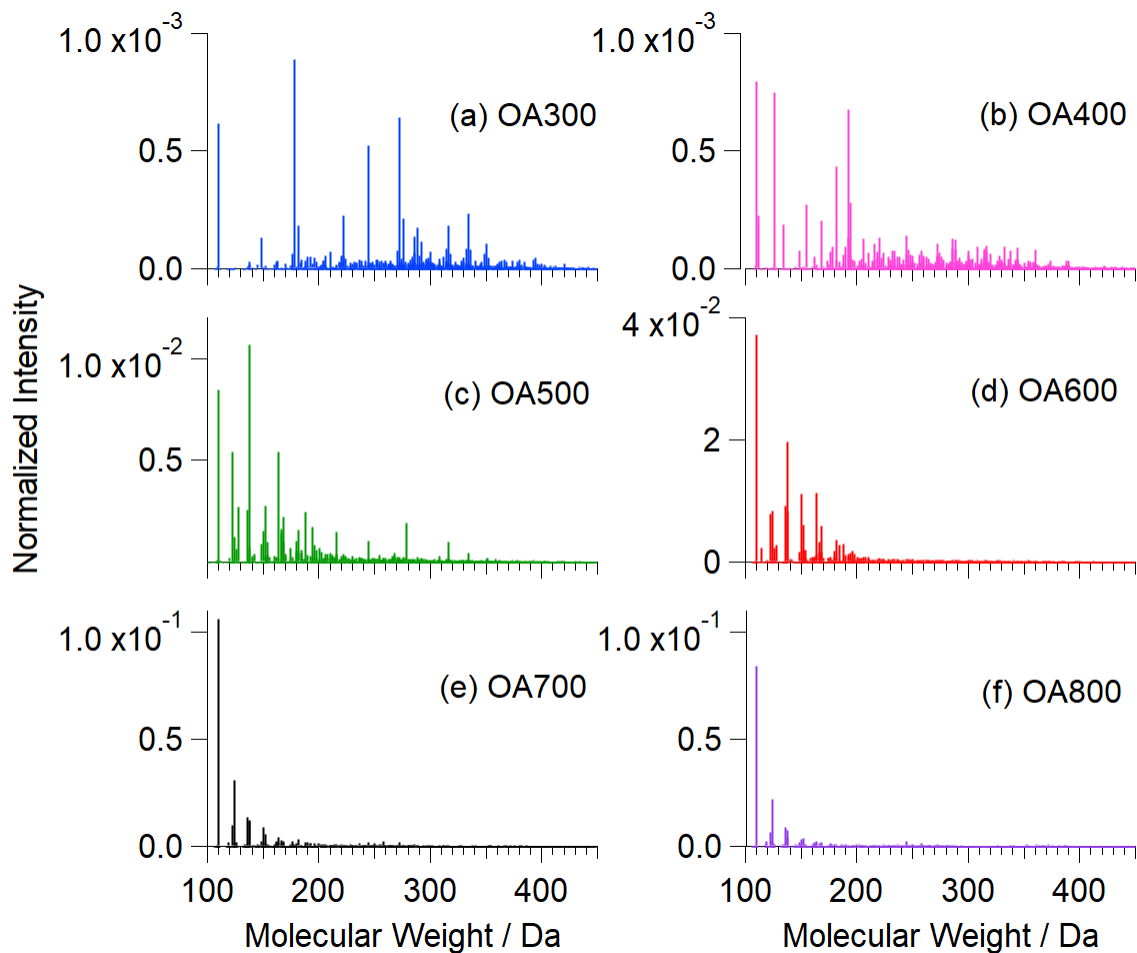


Figure 3.10. Mass spectra of water-soluble fractions of Canary Island pine OA300 (a), OA400 (b), OA500 (c), OA600 (d), OA700 (e), and OA800 (f). These mass spectra were recorded before reaction with Fe(III). The strongest peak at MW=110 in high-temperature samples corresponds to catechol. **Figure 3.11** shows an expanded version of this figure with major peaks labelled with formulas.

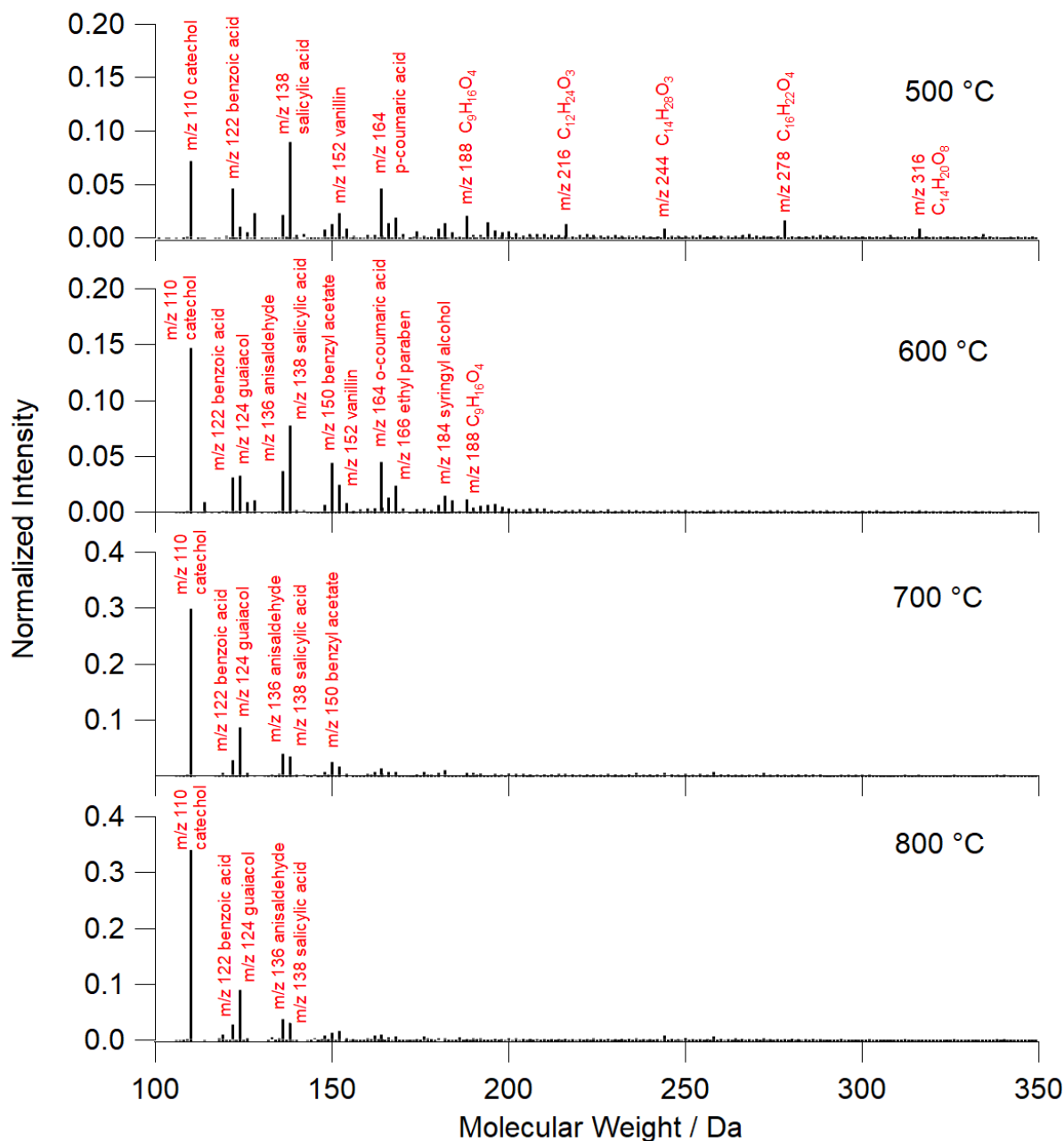


Figure 3.11. Mass spectra of OA500-800 samples run on UHPLC-PDA-HRMS prior to reaction with FeCl₃. The X-axis corresponds to the molecular weight of the neutral compound (the m/z of observed ions corrected by the addition of the mass of a proton). Increasing pyrolysis temperature produced more water-insoluble PAH compounds. Smaller, less substituted compounds (catechol, benzoic acid, and guaiacol) were present at all temperatures but increasing pyrolysis temperature decreased the complexity of water-soluble species.

During pyrolysis, chemical bonds within biopolymers (lignin, hemicellulose, and cellulose) break down and release VOCs as a function of combustion temperature. Lignin decomposition occurs between 200-1000 °C to produce species of guaiacol, eugenol, and syringol, whereas, hemicellulose and cellulose pyrolysis occur at lower temperatures, 210-310 °C and 300-380 °C, respectively, to emit furans and furfurals.^{187,206,207} Higher temperature combustion results in fragmentation of hemicellulose and cellulose further into more volatile, smaller VOCs. At temperatures greater than 500 °C, aromatization processes begin and emission of shortly substituted aromatics (phenols), non-substituted aromatics, and PAHs occurs.¹⁸⁷ We indirectly observed these expected chemical transformations through the observation of color changes in the collected OA (**Figure 3.2**) and the water extraction efficiencies listed in **Table 3.1**. As pyrolysis temperature increased, OA collected on the filters progressively darkened and the OA extracted in water decreased by half from 300 to 800 °C. More water-insoluble products (PAHs) were present at higher temperatures but, as the chromatography results in **Figure 3.7** show, catechol (peak #1) and other phenolic/oxidized aromatics were emitted even at higher temperatures. For iron to catalyze polymerization reactions with organics, a bidentate mononuclear organic-Fe(III) complex must be formed for subsequent ligand to metal charge transfer.^{85,140} Adjacent phenolic groups or oxygen atoms on adjacent carbon atoms must be present on the organic structure for a bidentate complex to be formed with Fe(III). In **Figure 3.7**, we observed the following organics that fit these characteristics in the unreacted OA: catechol (#1), salicylic acid (#2), homovanillic acid (#5), vanillic acid (#8), guaiacol (#10), 3-hydroxybenzoic acid (#14), and coniferaldehyde (#15). It is probable that a combination of these organics participated in Fe-catalyzed reactions to yield heterogeneous polyphenolic particles.

We acknowledge that the characterization of this OA is not all-encompassing (since we focused on the water-soluble compounds only) and should not be utilized for a complete inventory of pyrolyzed Canary Island pine emissions. Organic carbon extraction with methanol gives a better estimation of BrC compared to only water-soluble fractions,^{208,209} but the water-soluble components better represent those that would undergo atmospheric aging in the aqueous phase. Due to the ionization nature of ESI (-), n-heterocyclic PAHs and aliphatic compounds were not well detected. ESI (+) and atmospheric pressure photoionization (APPI) (+/-) would give a more complete picture of the exact chemical composition of unreacted BBOA water-soluble extracts (PAHs); however, these techniques were not employed in this study.

3.3.4 Characterization of Insoluble Particles through LDI-ToF-MS, TEM, and SEM-EDS

To explore the structure of the insoluble particles generated through reactions of OA500-800 with Fe(III), we employed laser desorption ionization time-of-flight mass spectrometry (LDI-ToF-MS). LDI is typically used in the analysis of polymers and protein samples, but it was utilized in an atmospheric application by Link *et al.* (2020) to ionize polycatechol films for tentative chemical formulae and structural assignments.⁸⁶ **Figure 3.12** shows the negative ionization mode spectra for the P500-700. P800 was also run on LDI but is not shown in **Figure 3.12**, as the collected spectrum produced no useful signal, possibly due to the low mass loading of our sample on the plate before ionization. While this spectrum is complex, and the resolving power of the instrument is insufficient to provide formulas of different peaks, general observations can still be made from the overall shape of the mass spectral envelope, spanning the range of m/z 200-600. Dimers, trimers, and

tetramers of catechol (MW 110), guaiacol (MW 124), and coniferaldehyde (MW 178) would fall within the ion range of the detected ions. The similar mass spectral shape for the P500-700 spectra indicates that, at these three pyrolysis temperatures, similar products were formed. There is a small shift in the average m/z values of the detected compounds as the pyrolysis temperature increases (**Figure 3.12**), and this shift reflects the reduction in the molecular weight of the products emitted at higher temperatures observed in **Figure 3.10**.

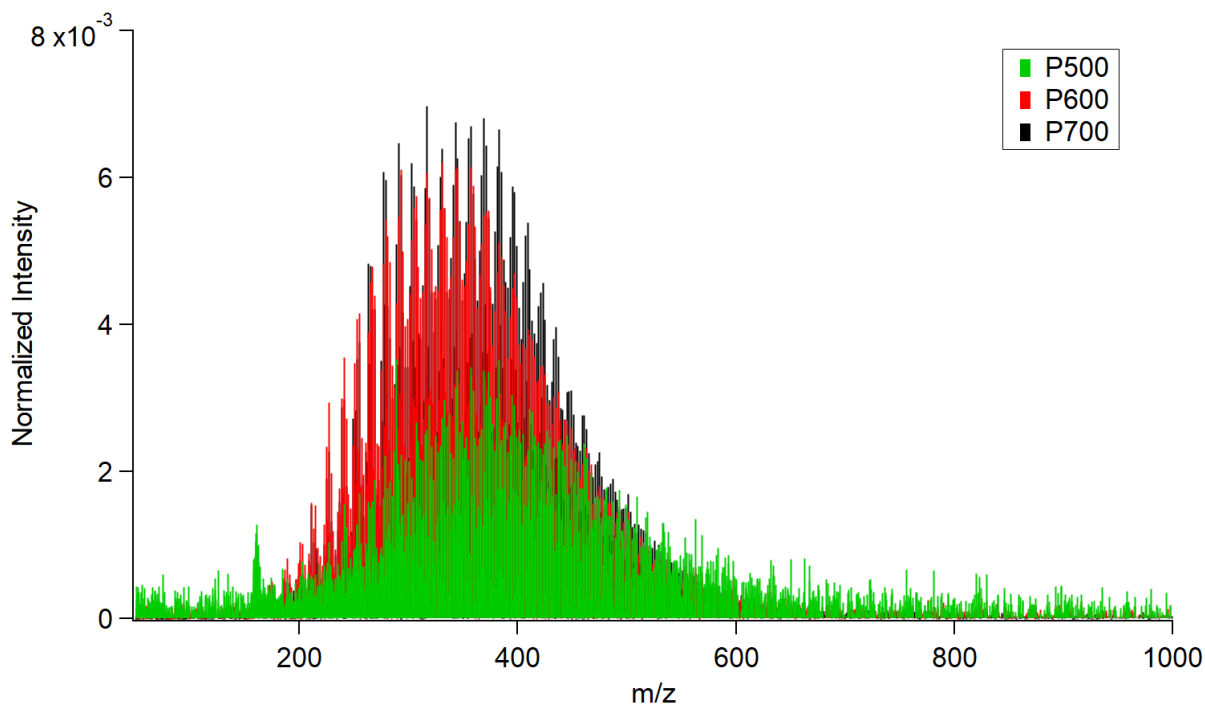


Figure 3.12. Laser desorption ionization time-of-flight mass spectrum (LDI-ToF-MS) for black water-insoluble particles. The colors correspond to P500 (green), P600 (red), and P700 (black) that were formed through the reaction of FeCl_3 with OA500-700. P800 was also run on LDI, however, particle concentration on the LDI plate was too low and the produced spectrum was noisy. Spectra were collected in negative ion mode with the assistance of Dr. Lisa Wingen and Dr. Ben Katz at the University of California, Irvine Mass Spectrometry Facility.

We employed electron microscopy (SEM and TEM) and X-ray spectroscopy (EDS) to image particles and determine bulk elemental composition in comparison with polycatechol standard particles (produced by the method of Slikboer *et al.* (2015)⁸⁵). **Figure 3.13** shows representative SEM images, TEM images, and EDS spectra. From the images, the polycatechol standard particles and P600 appear to have similar morphology: both have fractal structures consisting of interconnected ~10-50 nm primary particles, which is reminiscent of the structure of fresh soot.²¹⁰ Both polycatechol standard particles and P600 particles are qualitatively indistinguishable. Morphology directly affects the surface chemistry of a particle and influence its interactions/reactivity with its surrounding environment. Since the morphologies and elemental composition qualitatively appear to be very similar, we can hypothesize that their surface chemistries would behave similarly. The EDS spectra of polycatechol (**Figure 3.13d**) and OA reaction particles (**Figure 3.13h**) are almost identical with slight variation in intensity. Consistent with previous work on polycatechol,⁸⁵ P600 EDS spectra (**Figure 3.13h**) show carbon and oxygen as the main elemental components of the particles, further indicating a polyphenolic composition. **Figure 3.14** and **Figure 3.15** show the SEM images and EDS spectra for the sample and blanked regions of the SEM grids. EDS spectra for both polycatechol (**Figure 3.14c**) and P600 (**Figure 3.15c**) exhibit strong C, O, and Fe peaks, whereas the blanked regions (**Figure 3.14b** and **Figure 3.15b**) exhibit no Fe peaks and only weak C and O peaks.

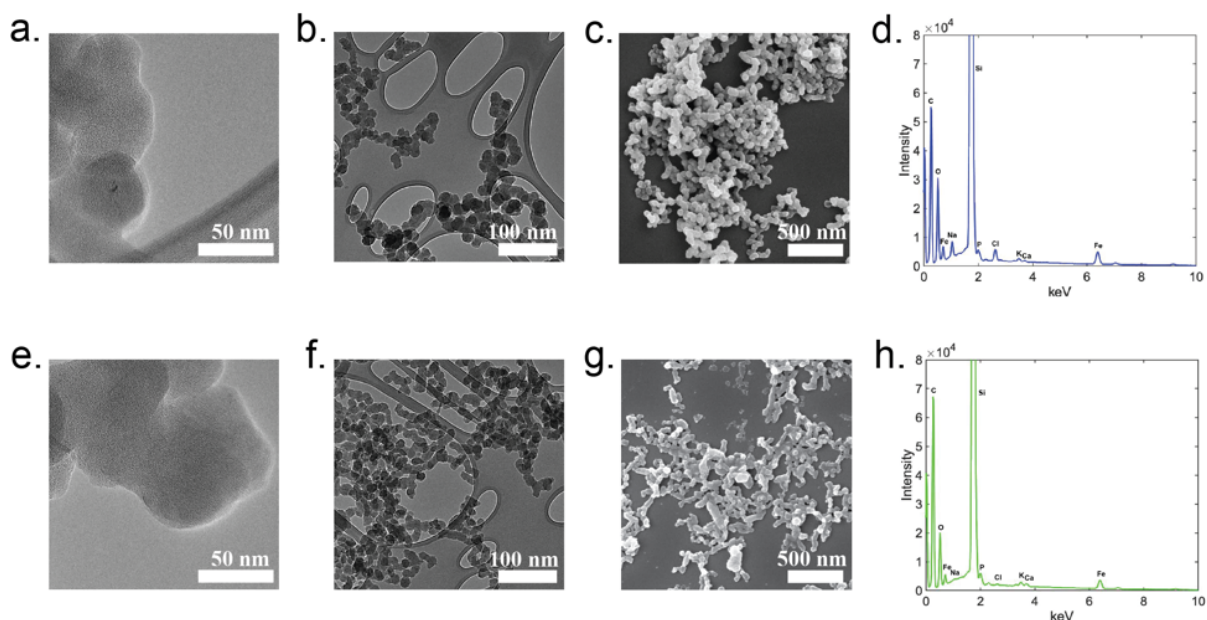


Figure 3.13. Scanning electron microscopy (SEM) images, transmission electron microscopy (TEM) images, and energy dispersive X-ray spectroscopy (EDS) spectra for polycatechol particles (control experiment) and water-insoluble dark particles (P600). SEM images of polycatechol (a & b) and reaction particles (e & f) were taken on silica substrates. TEM images and EDS spectra are shown for polycatechol (c & d, respectively) and reaction particles (g & h, respectively). The large Si peak is from the SEM grids (SiO_2).

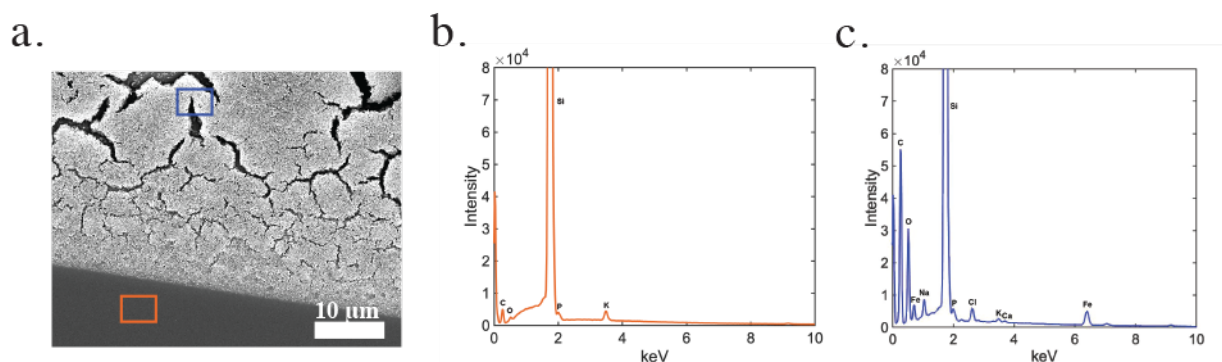


Figure 3.14. Representative SEM and EDS data for polycatechol control particles. (a) SEM image of particles with the orange box indicates a blanked region scanned by EDS and the blue box indicates the sample region scanned by EDS. (b) EDS spectra of the blanked sample region, and (c) EDS spectra of the sample region.

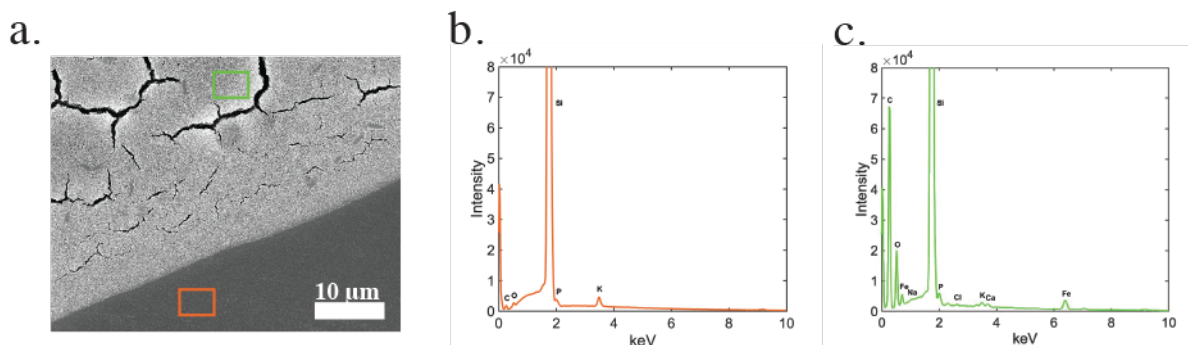


Figure 3.15. Representative SEM and EDS data for P600 (reaction particles) particles. (a) SEM particles with the orange box indicates a blanked region scanned by EDS and the blue box indicates the sample region scanned by EDS. (b) EDS spectra of the blanked sample region, and (c) EDS spectra of the sample region.

Residual Fe was present in the EDS spectra for both samples, which we have attributed to incomplete washing of samples. In previous work, Tran *et al.* (2017) observed that C4 and C6 dicarboxylic acids (fumaric acid and muconic acid) reacted with FeCl₃ under similar conditions to create colored particles with iron trapped inside the polymer.²¹¹ If these reactions occurred in our complex organic mixture, we would have expected to see a larger iron trace in the EDS spectrum in **Figure 3.13h** than in the polycatechol standard spectrum in **Figure 3.13d**, however, it was not the case. In addition, we did not observe fumaric acid, muconic acid or similar diacids in our HRMS results of OA starting material, which helps explain why iron was not chemically trapped in the particles. Conversely, Link *et al.* (2020) found that residual iron can be a product of incomplete washing of iron out of particles during preparation for EDS measurements, further supporting our results.⁸⁶ As P500-800 result from reaction of heterogeneous OA, we believe their structure to be polyphenolic, in contrast to the more chemically homogenous of polycatechol.

3.4 Conclusions

We have shown that previously observed Fe(III)-catalyzed reactions with phenolic compounds resulting in light-absorbing products are also taking place in more complex mixtures of water-soluble organics emitted by pyrolyzed biomass. The addition of Fe(III) to water-soluble components of OA can catalyze reactions with phenolic compounds, forming phenoxy radical intermediates that initiate C-C coupling reactions to form light-absorbing dimers/oligomers. These oligomerization reactions convert volatile molecules into higher-molecular weight, water-insoluble, light-absorbing products of lower volatility.^{80,85,86}

We acknowledge the limitations of bulk experiments, which do not fully reproduce conditions in atmospheric particles, for example, hydrogen peroxide produced in this reaction is not able to evaporate from the bulk solution as it would from ambient particles. Hydrogen peroxide concentrations were not measured in reaction solutions in this work, and it should be a priority for follow up mechanistic studies. We also acknowledge that the organic aerosol samples used in this work were produced by oxygen-free pyrolysis of biomass, so it will be important to test this chemistry at different oxygen levels in the future. The concentrations used in these experiments are only applicable to aerosol liquid water and/or surfaces of particles, and that real atmospheric particles can have other organic compounds that can compete for complexation with iron (oxalate and sulfate) or scavenge OH radicals. Scavenging may slow the formation rate of these particles, as OH is an intermediate product in this reaction mechanism.⁸⁵ Further experiments are needed to assess kinetic effects of particle formation in more atmospherically accurate samples.⁷⁷ Also, it is unknown what effect UV irradiation has on this reaction's progress or the extent of photodegradation, as this work has only been conducted under dark conditions. It is possible

that light could photodegrade organics in the water-soluble OA fractions and drive photo-Fenton processes resulting in oxidation and photodegradation of organics instead of its oligomerization. It will also be important to test the effect of oxalate ion on this Fe(III)-catalyzed chemistry and conduct particle aging/lifetime experiments under photolytic conditions in order to surmise how environmental conditions can impact the climate forcing properties of these BrC particles.

CHAPTER 4:

PHOTOLYTIC AGING OF ORGANIC AEROSOL FROM PYROLYZED URBAN MATERIALS

Hopstock, K. S.; Klodt, A. L.; Xie, Q.; Alvarado, M. A.; Laskin, A.; Nizkorodov, S. A., Photolytic aging of organic aerosol from pyrolyzed urban materials, *Environmental Science: Atmospheres*, **3** (2023) 1272-1285.²¹²

Abstract. Emissions from large-scale fires significantly contribute to the atmospheric burden of primary organic aerosol (OA). The frequency of fires occurring at the wildland-urban interface (WUI) is increasing, with biomass and a wide range of human-engineered materials serving as fuels. The chemical composition and optical properties of OA from WUI fires are poorly characterized, and this work seeks to understand how direct photolytic aging alters the light absorbing properties of particulate matter generated from WUI fires. Ten flammable urban materials were selected to represent structural and furnishing components commonly combusted in urban fires: electrical 12 AWG wire (white PVC coating), ceiling tile, synthetic fabric, electrical 23 AWG wire (purple PVC coating), lumber, drywall, fiberboard, vinyl flooring, plywood, and carpet. Each material was pyrolyzed at 600 °C under N₂ in a tube furnace and resulting smoke particles were collected on Teflon filters or deposited on fused silica optical windows. OA samples were aged by exposing them to simulated solar radiation (near-UV radiation, 280-400 nm) directly on the collection substrates. Mass absorption coefficients (*MAC*) values and Absorption Angström Exponents (*AAE*) of the unaged and aged OA were calculated from spectrophotometry measurements taken after extracting OA in suitable organic solvents. We observed variable trends after short-term exposure to UV

radiation: six out of ten types of urban OA exhibited photoenhancement, two exhibited photobleaching, and the remaining two experienced negligible change after 2 h of photolytic aging. The average *AAE* value for unaged OA was 8.8 ± 1.3 and decreased to 7.3 ± 0.9 after aging, reflecting increased absorption in the visible range of the spectrum after the UV exposure, and an evolution from very weakly to weakly absorbing brown carbon. Long-term UV exposure results indicate that most photochemical change occurs within the first few hours of irradiation. These results suggest that WUI fires efficiently produce brown carbon, which becomes increasingly light absorbing in sunlight.

4.1 Introduction

Aerosols affect the propagation of radiation through Earth's atmosphere by directly absorbing or scattering incoming solar radiation. Black carbon (BC) and brown carbon (BrC) are components of carbonaceous aerosol particles that absorb solar radiation and contribute to direct forcing on climate by aerosols. BC absorbs strongly over a broad wavelength range and is commonly attributed to soot particles emitted from biomass burning and incomplete combustion of fossil fuels.³³ BrC is characterized by a negligible absorption coefficient at the red edge of the visible spectrum (600-700 nm) and has a much stronger absorption coefficient in the near-UV and blue range of the spectrum (300-500 nm), attributing to its brown color.^{30,36,99} BrC can be emitted from the burning of biomass materials (wildfires,^{37,66,213,214} domestic wood burning,²¹⁵ and cookstove emissions⁴⁸) and its optical properties are highly variable and dependent upon their biofuel source and combustion conditions.^{108,216,217} Atmospheric BrC can also result from the oxidation of aromatic hydrocarbons producing light-absorbing secondary organic aerosol (SOA).

The high chemical reactivity of OA alters its chemical composition and optical properties on atmospherically relevant timescales. Solar radiation drives many of these aging processes by directly photolyzing light-absorbing species, and also through indirect photochemical processes, such as secondary reactions of OA compounds with photochemically produced free radicals and photosensitized reactions.^{48,218} Many studies have been conducted to examine the aqueous photochemistry of OA extracts to simulate the photochemical processing of organics dissolved in fog and cloud water.^{109,199,219–225} Less attention has been given to simulating photochemical processing that occurs inside the organic phase of particles. This organic phase represents a unique environment for photochemistry because of its higher viscosity. Thus, the same molecules can react by different photochemical mechanisms in organic particles and in aqueous solutions. Aerosol particles have been estimated to spend 85% of their respective life cycles under non-cloud-activated conditions, thus photochemistry will often take place in the predominantly organic phase.²²⁶ Even under cloud-activated conditions, photochemistry in the organic phase is also important as only a fraction of OA is water soluble.

Previous studies of condensed-phase photochemistry in OA have primarily focused on the photodegradation of SOA particles generated from terpene ozonolysis.^{227–229} In this case, mass loss was observed upon UV irradiation of α -pinene and d-limonene ozonolysis SOA,^{230–232} which was driven by the direct photolysis of peroxide and carbonyl functionalities as well as secondary reactions of the resulting free radicals.^{230,233–236} A few studies have characterized the mass loss and absorption changes of SOA-containing nitrophenols during UV irradiation.^{202,232,237,238} Additionally, there have been a few studies observing the optical properties of suspended OA produced from burning or pyrolysis, and

these generally observe an increase in absorption at long wavelengths with UV irradiation, sometimes followed by photobleaching.^{239–241} However, it was difficult to cleanly separate the effects of gas-phase and condensed-phase photochemistry in these experiments.

Even less attention has been given to the photolytic aging of biomass burning organic aerosol (BBOA). Fleming *et al.* (2020) identified major chromophores in BBOA from the combustion of several biofuel types and observed the loss of individual chromophores by utilizing chromatographic separation followed by photodiode array spectrophotometry and high-resolution mass spectrometry.¹⁹⁹ They found that the majority of chromophores were lost after approximately 33 hours of UV irradiation, with the exception of a few photorecalcitrant compounds.¹⁹⁹ To the best of our knowledge, this has been the only study to investigate changes in the optical properties of BBOA particles induced by photolysis in the organic particle phase. It is still unclear how photolytic aging impacts the chemical composition and optical properties of OA generated from biomass combustion. Further, even less is known about the optical properties and photochemical aging of OA generated by fires at the wildland-urban interface (WUI).

The frequency of fires occurring at the WUI is increasing, indicating that the composition and properties of the wildfire related OA are dictated not only by burning biomass but also by the burning of human-engineered materials.²⁴² The WUI is defined as the area where urban development encroaches upon borders of private and public wildlands.²⁴³ In 2000, 39% of all housing units in the continental United States occupied WUI land.²⁴⁴ Burke *et al.* (2021) estimated that 50 million homes (and counting) are located in WUI areas in the United States.²⁴⁵ Climate change has led to more frequent occurrences of large scale forest wildfires that devastatingly destroy urban homes and buildings located at

the WUI.^{246,247} The effect of urban fire emissions (and its subsequent change) on Earth's radiative forcing is unknown. Blomqvist et al. (2007) reported that wood, particleboard, paper, textiles, polyvinyl chloride (PVC), polyurethane, polyethylene, polystyrene, acrylonitrile butadiene styrene, tarred roofing, linoleum, and rubber products were present during building fires in Sweden (1999) that lead to the emissions of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and dioxins.²⁴⁸ Prominent VOCs related to the burning of urban buildings, farms, and household materials have been previously characterized,²⁴⁸⁻²⁵⁰ however, neither the chemical composition nor the aging of this WUI particulate matter have been characterized. This study is the first to conduct photolytic aging experiments using laboratory generated OA representing emissions from WUI fires. Materials representative of engineered wood, plastics, construction materials, textiles, and furnishings were selected to cover the major categories of urban materials combusted in WUI fires.

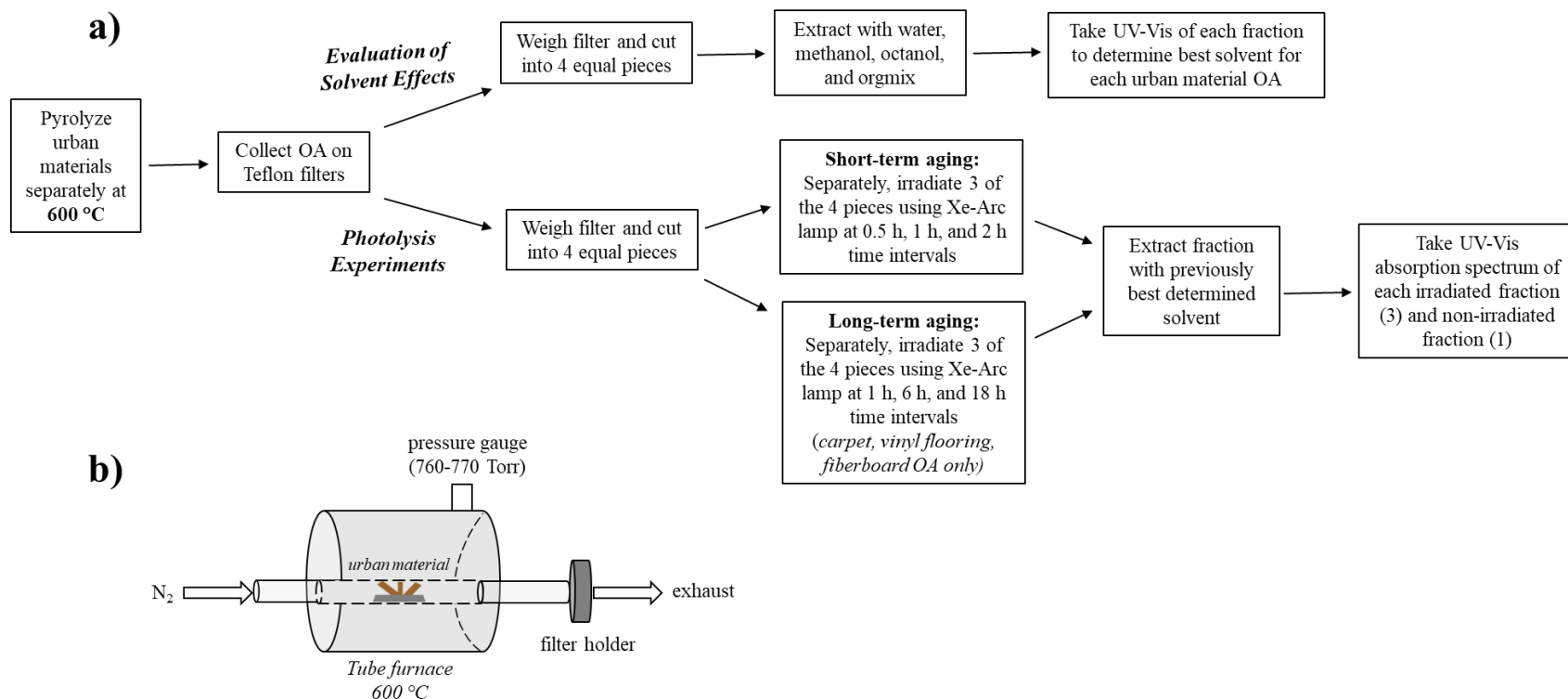
4.2 Experimental Methods

Flowcharts of experimental procedures can be found below in **Scheme 4.1** and **4.2**.

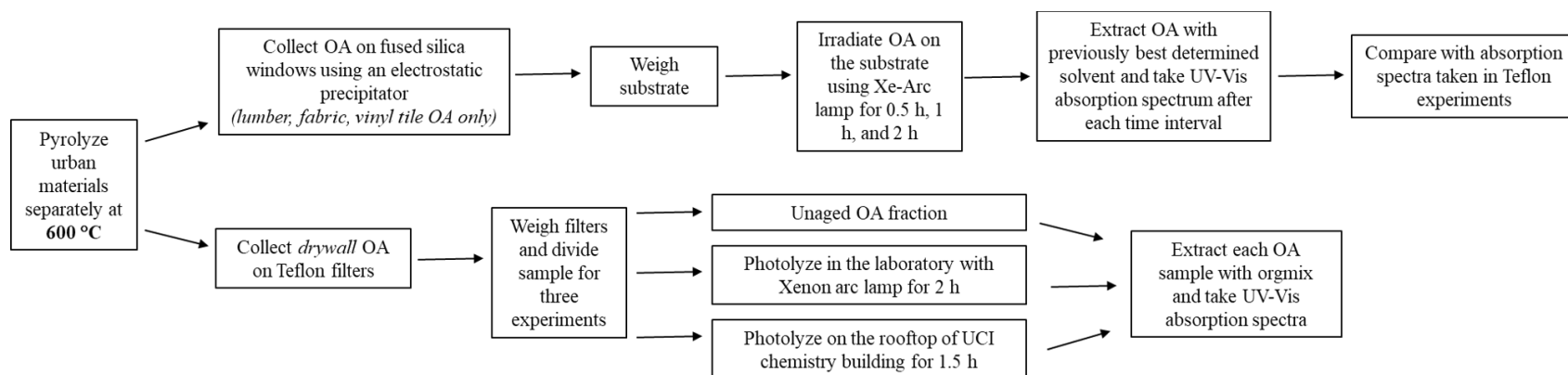
4.2.1 Ten urban materials

Ten samples of flammable urban materials were selected in this study to represent structural and furnishing components present in urban fires: electrical 12 AWG wire (white PVC coating), ceiling tile, fabric, electrical 23 AWG wire (purple PVC coating), lumber, drywall, fiberboard, vinyl flooring, plywood, and industrial carpet. More specific details on the materials can be found in **Table 4.1**. The 12 AWG wire (white PVC coating) and 23 AWG

wire (purple PVC coating) will be referred to as “thick PVC wire” and “thin PVC wire”, respectively. All urban materials melt or thermally degrade at temperatures less than that used in our pyrolysis experiments (600 °C).

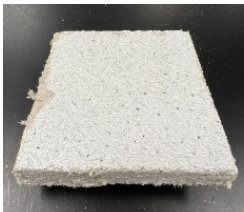


Scheme 4.1. Experimental flowchart for pyrolysis experiments conducted with all ten urban materials (a). Organic aerosol generated through pyrolysis is labeled as “OA”. All OA samples were generated in a tube furnace at 600 °C under N₂ (b). First, experiments were conducted by collecting on Teflon filters (top arrow). An evaluation of solvent effects was performed to determine the best solvent for extraction, as each material yielded OA with unknown composition. Each filter was cut into four equal pieces, and each was extracted in a different solvent: water, methanol, octanol, and orgmix (acetonitrile/dichloromethane/hexane 2:2:1 by volume). UV-vis absorption spectra were utilized to determine which solvent was best suited per material. Photolysis experiments (downward arrow) were conducted on separately collected OA. Similar to the solvent investigations, each filter was cut into quarters and irradiated with various times (short-term aging and long-term aging). Subsequent extraction and UV-Vis absorption measurements were utilized to determine how irradiated fractions differed from the non-irradiated fraction. A schematic of the laboratory pyrolysis setup is shown in panel b.

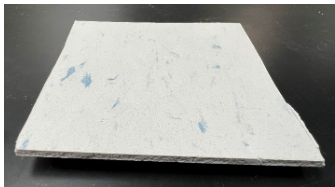


Scheme 4.2. Summary of additional experiments conducted for lumber, fabric, and vinyl tile OA. These OA had residual material which remained embedded in the fibers on the Teflon filters after photolysis and extraction. Experiments on fused silica windows were conducted to reconcile this (top arrow). This method allowed for photolysis to be conducted directly on the window surfaces, and after that subsequent extraction and absorption measurements were taken. Each time point came from a different pyrolysis collection, as each extraction removed all OA from the window. The second set of control experiments (downward arrow) compared photolytic exposure in the lab versus that outside on the rooftop of the UCI chemistry building on November 9, 2022. Spectral flux density calculations concluded that two hours of exposure with the Xenon arc lamp equated to 1.5 hours in the sunlight between hours greatest solar flux in Irvine, CA (11 AM to 1 PM). Drywall OA was generated and exposed to irradiation by sunlight and the Xenon arc lamp. Subsequent extraction and absorption measurements were taken and compared with an unaged drywall OA sample.

Table 4.1. Summary of urban materials pyrolyzed in this study. All pyrolysis runs were conducted at 600 °C unless noted otherwise. All values are reported as the average amongst three replicates with uncertainty values reported to one standard deviation. Emission factors (from Teflon filter collection experiments) are reported in the units of grams of collected OA per kilogram of urban material utilized in pyrolysis. Approximately 200 mg of urban material was pyrolyzed in each experiment. Carpet pyrolyzed at 800 and 1000 ° C were only tested once (no uncertainty values reported). Best extraction solvent was determined based on greatest overall absorbance and expression of spectral features.

Urban Material	Picture of Urban Material & Description of material	Average mass collected (mg)	Average emission factor (g kg ⁻¹)	Best extraction solvent
Electrical 12 AWG wire (white PVC coating)	 Flexible PVC coated 12 AWG copper wires. The PVC acts as electrical cable insulation. It is stable under 70 °C.	2.0 ± 0.5	1.3 ± 0.4	Orgmix
Ceiling Tile	 Used in commercial suspended ceilings. Composed of a combination of mineral wool, fiberglass, gypsum, perlite, clay, cellulose, and starch. Many of these components (except mineral wool, perlite, and clay) have melting points or thermally degrade at temperatures less than 600 °C.	5.1 ± 1.8	9.0 ± 3.6	Orgmix
Fabric	 Commonly present in furniture, clothing, and linens. Combustible at temperatures greater than 300 °C.	3.1 ± 1.4	16 ± 2	Orgmix

Electrical 23 AWG wire (purple PVC coating)	 Flexible PVC coated 23 AWG copper wires. The PVC acts as electrical cable insulation. It is stable under 70 °C. Purple dye pigment composition is unknown.	3.1 ± 1.1	13 ± 6	Orgmix
Lumber	 Commonly used for construction framing and finishings (in floors, wall panels, and window frames). Combustible and thermally degrades at temperatures greater than 370 °C.	11 ± 6	47 ± 15	Octanol (used orgmix for photolysis experiments)
Drywall	 Commonly used to create walls and ceilings in construction. Combustible and thermally degrades at temperatures greater than 250 °C.	1.5 ± 0.8	1.0 ± 0.3	Orgmix
Fiberboard	 Commonly used as a wood alternative in walls, door boards, floor, and	3.1 ± 0.6	6.0 ± 0.9	Methanol

	furniture. Combustible at temperatures greater than 220 °C.			
Vinyl Flooring	 Commonly used as flooring in kitchens, bathrooms, and industrial settings, as it is water resistant. Made of PVC plastic pieces and resin that re heated/pressed into thin layers on top of a fibrous backing. Breaks down at temperatures greater than 70 °C.	3.0 ± 0.5	13 ± 4	Octanol (used orgmix for photolysis experiments)
Plywood	 Commonly used as a pure wood alternative in flooring, cabinets, shelving, and furniture. It is made of 3 or more layers of wood veneer. Thermal degradation begins at 110 °C.	8.8 ± 0.6	37 ± 9	Orgmix
Carpet	 Carpet is composed of nylon and polyester fibers secured to a rubber latex backing. Melting occurs at temperatures greater than 270 °C.	6.9 ± 1.2	30 ± 4	Methanol
Carpet pyrolyzed at 800 °C (1 trial)		9.8	41	Methanol <i>*poor solubility</i>
Carpet pyrolyzed at 1000 °C (1 trial)		20.1	67	Methanol <i>*poor solubility</i>

4.2.2 Organic aerosol generation

Experiments were conducted similarly to our previous work on biomass pyrolysis.¹⁶⁷ Pyrolysis is the thermal decomposition of biomass under oxygen limited conditions with temperatures between 300-800 °C.²⁵¹ Fires often transition between smoldering (450-700 °C) and flaming (1500-1800 °C) combustion with their genesis process being pyrolysis.⁶² Therefore, 600 °C is suitable to mimic real pyrolysis combustion. For each pyrolysis experiment, approximately 200 mg of one tested flammable material (**Table 4.1**) was placed in a ceramic pyrolysis boat and then inserted into a 2.1 cm I.D. / 2.5 cm O.D. quartz tube, upstream from the Thermolyne F21135 Tube Furnace (**Scheme 4.1b**). The tube was sealed and continuously purged with N₂ gas (~0.7 standard liters per minute). A 40 cm section of the tube, downstream from the pyrolysis boat, was heated to 600 °C, and once at this temperature, the tube was pushed inside to bring the urban material into the heated zone to start the pyrolysis. The starting pressure was ~760 Torr and did not exceed 770 Torr during the experiment. A flow of N₂ gas was constant during pyrolysis and was utilized to push the generated aerosol and fumes through the quartz tube for collection. The setup was not reopened until collection had ceased. OA sample from each urban material was collected for 10 min starting from the moment the smoke appeared in the flow (**Figure 4.1**). Samples of tested carpet material were also pyrolyzed at 800 °C and 1000 °C to explore the effects of higher pyrolysis temperatures (**Figure 4.2**). Pyrolysis experiments at 600 °C produced urban OA that favored BrC production, and all subsequent experiments were done at this temperature.

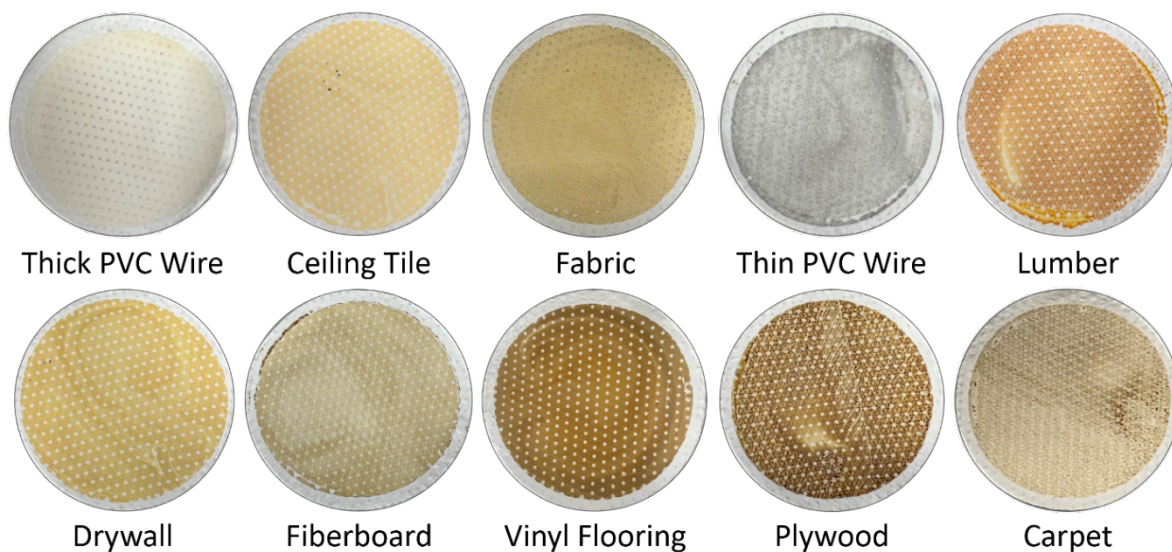


Figure 4.1. Sample photographs of filters containing organic aerosol (OA) generated through the pyrolysis of ten urban materials at 600 °C under N₂. The OA differed in appearance amongst urban materials.

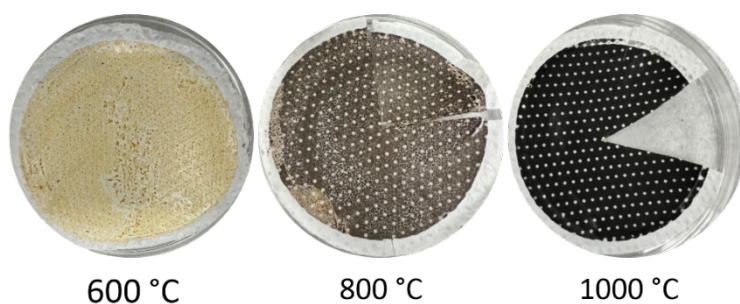


Figure 4.2. Sample photographs of filters containing OA generated through the pyrolysis of carpet at 600, 800, and 1000 °C under N₂. Pyrolysis temperatures greater than 600 °C yielded OA that was poorly soluble due to presence of black carbon (BC).

Samples were collected on two different substrates approximately 1 m downstream from the heated zone, at which point the flow cooled to 42 °C. For most experiments, the collection was done on PTFE 47 mm Teflon filters, which are stable at temperatures less than 350 °C (Millipore Sigma, Fluoropore Membrane Filter, FGLP04700, 47 mm, 0.22 µm pore size) (**Figure 4.1**). A subset of samples were collected on optical windows (ISP Optics, Fused Silica IR Grade Windows, QI-W-12-1, 12.7 mm diameter, 1 mm thick) using a single-stage

electrostatic precipitator (ESP) (TSI 3089 Nanometer Aerosol Sampler, -5 kV) equipped with a Kr-85 neutralizer (TSI Model 3077 Aerosol Neutralizer). Samples (both Teflon filters and fused silica windows) were weighed after collection using a Sartorius ME5-F microbalance ($\pm 1 \mu\text{g}$ precision) and the OA mass was calculated. For the samples collected on Teflon filters, the emission factors (EF), defined as the mass of OA collected per urban material mass used in pyrolysis (g kg^{-1}), were calculated from the measured mass collected, assuming that the filters had 100% collection efficiency.

4.2.3 UV-visible spectroscopy measurements and effects of solvents

After collection, Teflon filters were cut into four equal pieces and each quarter was extracted, separately in 10 mL, using four different solvents: “orgmix” (acetonitrile, dichloromethane, hexane 2:2:1 by volume), methanol, water, and n-octanol. A 2 mL aliquot of each OA extract was transferred into a 1 cm quartz cuvette and a dual-beam spectrophotometer (Shimadzu UV-2450) was used to take UV/Vis absorption spectra, with the corresponding solvent used as a reference. The best-suited extraction solvent for each OA sample was the one that gave the highest absorbance of the extracted material (**Table 4.1 and Figure 4.3**). Wavelength-dependent mass absorption coefficients (MAC), in the units of $\text{cm}^2 \text{g}^{-1}$, were calculated from the base-10 absorbance (A_{10}), the estimated concentration of OA extracted in solution, C_{mass} (g cm^{-3}), and path length of the cuvette, b (cm) (**Equation 4.1**).

$$MAC(\lambda) = \frac{A_{10}^{\text{solution}}(\lambda) \times \ln(10)}{b \times C_{\text{mass}}} \quad \text{Equation (4.1)}$$

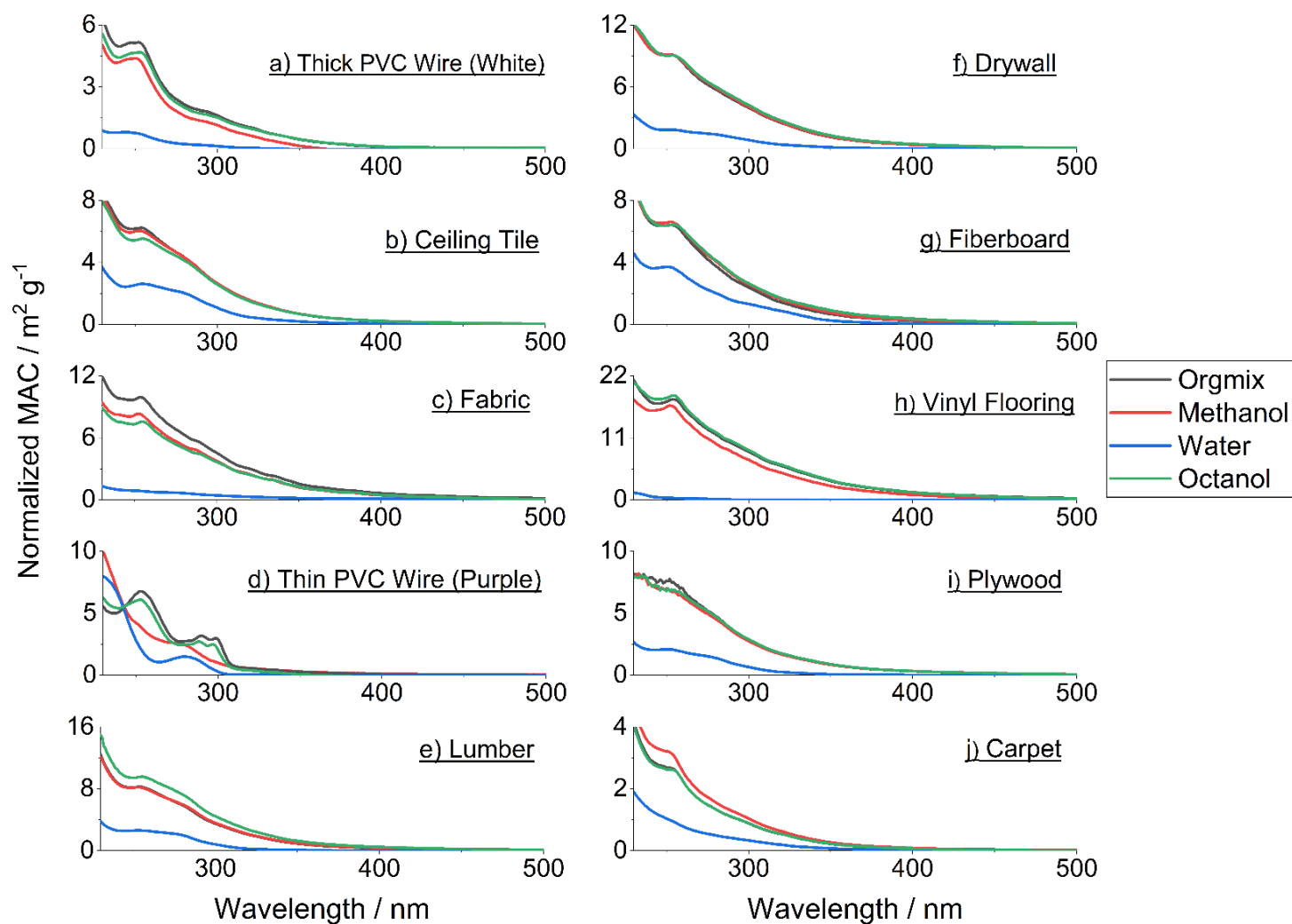


Figure 4.3. UV-Vis absorption spectra recorded after the pyrolysis of urban materials and extraction (a-j) in orgmix (grey), methanol (red), water (blue), and n-octanol (green). The MAC values assume complete extraction of OA from the filter. The lowest MAC observed for water indicates that it does not extract the OA fully and is the least effective solvent tested for all materials. Plywood extracts were diluted by a factor of ten for absorbance measurements.

To minimize the effects of small baseline drifts during the measurement, the calculated *MAC* values were corrected by subtracting the average *MAC* between 680 to 700 nm (the absorbance in this wavelength range was generally negligible). Absorption Angström Exponents (*AAE*) were calculated from the slopes of the linear fits applied to the log-log plot of *MAC* (λ) values between 280-480 nm.

4.2.4 Photolysis experiments

On-filter photolysis experiments were performed as described previously.²³⁸ Briefly, samples were irradiated with near-UV radiation from a Xenon arc lamp (Newport Model 66902) with UVC and visible wavelengths removed using a dichroic mirror, a 295 nm long-pass filter (Schott WG295), and a UV bandpass filter (Schott BG1), leaving the majority of the radiation between 280 and 400 nm. A comparison between our lamp spectrum and ambient solar flux is provided in **Figure 4.4 and Table 4.2**. One hour in our photolysis setup is approximately equivalent to 0.7 h under the 2 h average Los Angeles solar flux (average taken for 11 AM to 1 PM on November 9th) as calculated using the “Quick TUV” calculator (Madronich, S. ACOM: Quick TUV, 2019),²⁵² assuming a photolysis wavelength range of 280 to 400 nm (matching our lamp’s radiation). This irradiation time (utilizing 2 h average flux) was chosen to match the rooftop photolysis experiments described below. We note that for photochemical processes that take place inside the particles, photolysis of particles immobilized on an inert substrate (such as fibers of a Teflon filter) should give the same products as photolysis of particles suspended in air as long as particles have access to ambient air. There is a small enhancement of absorption by particles on the filter due to

multiple scattering by the filter fibers,^{253,254} which is neglected in our estimation of equivalent exposure times.

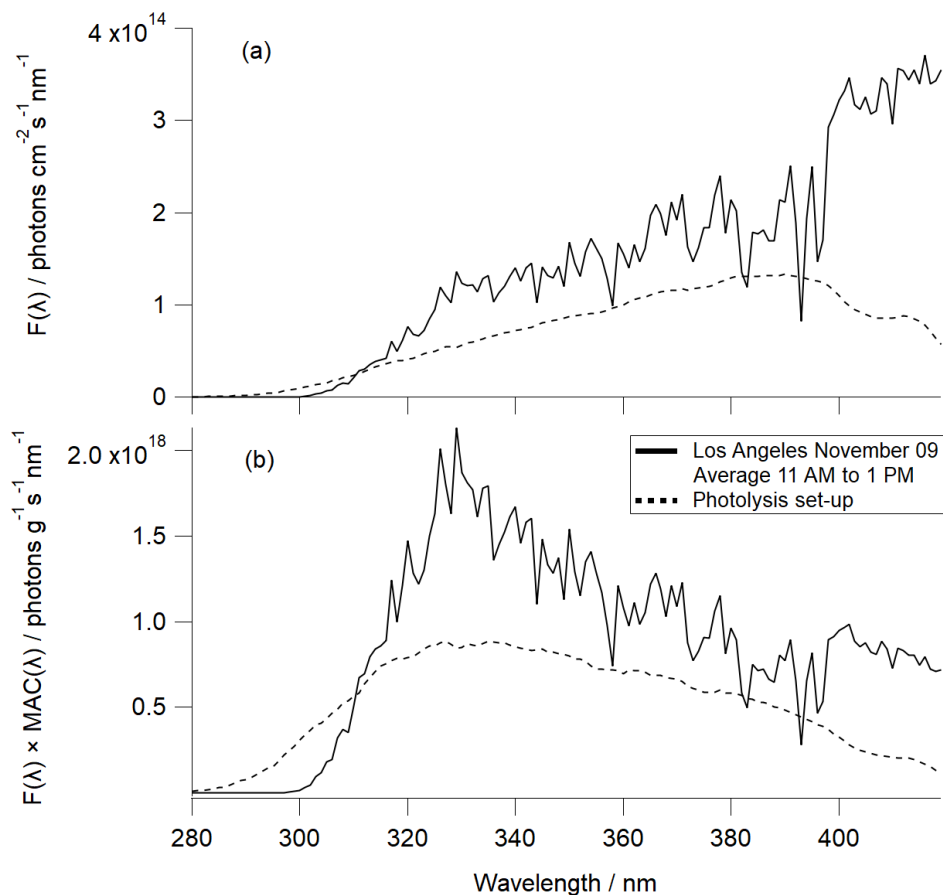


Figure 4.4. The spectral photon flux density ($F(\lambda)$) over the actinic range of the Xenon arc lamp used in laboratory photolysis experiments (dashed line) compared to the averaged solar spectrum in Los Angeles, California (Latitude/Longitude: $34^\circ/118^\circ$) for November 9th between the hours of 11 AM to 1 PM (solid line). Panel (a) shows $F(\lambda)$ as a function of wavelength. Panel (b) shows a product of spectral photon flux density and the mass absorption coefficient average across all 10 unaged urban OA ($F(\lambda) \times \text{MAC}_{\text{average}}$), which better illustrates the wavelength at which photolysis is taking place. The “Quick TUV” calculator (Madronich, S. ACOM: Quick TUV) was used to estimate the spectral flux densities. The parameters used in the Quick TUV calculator were as follows: latitude/longitude: $34^\circ\text{N } 118^\circ\text{W}$; date: November 9, 2022; overhead ozone: 300 du; surface albedo: 0.1; ground altitude: 0 km; measured altitude: 0 km; clouds optical depth/base/top: 0:00/4.00/5.00; aerosols optical depth/single-scattering albedo/ α : 0.235/0.990/1.000; sunlight direct beam/diffuse down/diffuse up: 1.0/1.0/0.0; 4 Streams Transfer Model.

Table 4.2. The integrated photon flux and the number of hours equivalent to one hour under the laboratory photolysis set-up for the 2 h average solar flux in Los Angeles (11 AM to 1 PM) on November 9, 2022. The value in the last column represents the ratio of the solar integrated flux to the UV lamp’s integrated flux.

Wavelength range of comparison	Integrated $F(\lambda)$ x $MAC(\lambda)$ from the UV lamp (photons $\text{g}^{-1} \text{s}^{-1}$)	Integrated $F(\lambda)$ x $MAC(\lambda)$ from the 2 h average sunlight in Los Angeles (photons $\text{cm}^{-2} \text{s}^{-1}$)	One hour under lamp is equivalent to _ h under sunlight in Los Angeles at time specified:
Full UV (280-400 nm)	6.91×10^{19}	1.05×10^{20}	0.7

Filter samples were cut into quarters, and each quarter was weighed to estimate the mass of OA on each quarter (as the OA distribution on the filter was not uniform). For irradiation, one quarter was placed vertically in the path of the near-UV beam, such that the filter surface was uncovered and open to laboratory air. The quarters not being photolyzed were re-sealed until irradiation. After photolysis, the filter quarter was extracted with methanol, n-octanol, or orgmix (using the previously best determined solvent for that urban material) to take a UV-Vis spectrum. Since the UV-Vis sample preparation for the filter samples was destructive, each time point required an entire filter quarter and only four time points were taken per filter. The samples corresponding to 0 h, (unaged), 0.5 h, 1 h, and 2 h of irradiation were chosen as reference time points. *MAC* values were then calculated with **Equation 4.1**. All *MAC* calculations were performed using the mass of the unaged sample, i.e., assuming no evaporation or other mass loss occurred. Based on previous SOA photolysis experiments, we do expect some mass loss to occur with photolysis,^{231,255} so all *MAC* values reported in this work should be considered as lower limits.

For most samples, the extracted filter quarters exhibited the original white color of the Teflon filter, suggesting that all the light-absorbing material was extracted. However, residual OA material was visible on the Teflon filters after photolysis and extraction for three materials: lumber, fabric, and vinyl flooring (**Figure 4.5**). To remedy this, we collected lumber, fabric, and vinyl flooring OA on fused silica windows to facilitate extraction after photolysis (**Scheme 4.2**). Similarly to the Teflon filter experiments, samples on fused silica windows were photolyzed for 0.5 h, 1 h, and 2 h. Each photolyzed sample was extracted from the window in the previously determined best solvent, absorption spectra were taken, and spectra from the fused silica window experiments were compared with those of the Teflon experiments. Each sample extraction from a fused silica window was destructive, meaning that each time point required the preparation of a new pyrolysis sample.

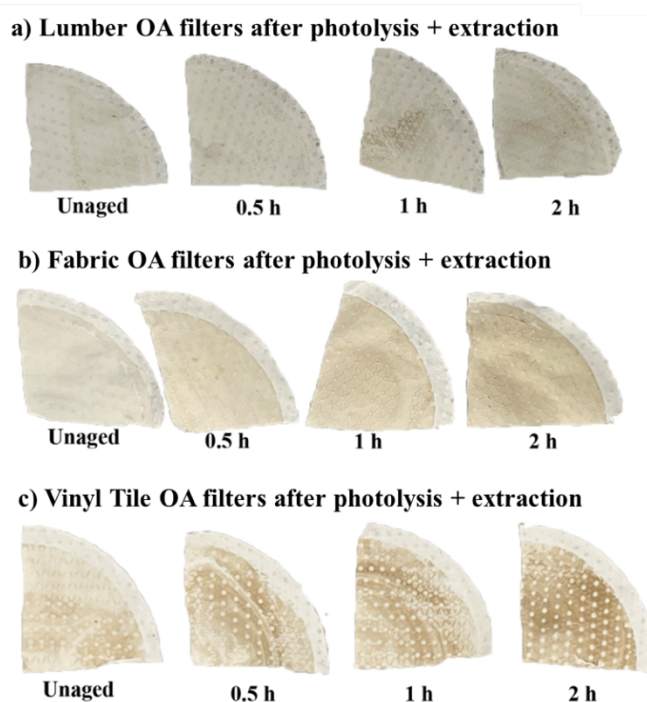


Figure 4.5. Pictures of Teflon filters after photolysis and subsequent extraction of lumber, fabric, and vinyl tile OA (a-c, respectively). Orgmix was used in the extraction of all OA. Only these three urban materials left behind residual OA on Teflon filters after extraction.

4.2.5 High-resolution mass spectrometry experiments

One sample, namely thin PVC wire OA, was selected for bulk compositional analysis using high resolution mass spectrometry (HRMS) to identify the chromophore responsible for the distinct absorption bands in its absorption spectrum. As this was the only material to showcase distinctive absorption band features, only thin PVC wire OA was examined with HRMS in this study. Thin PVC wire OA ($350 \mu\text{g mL}^{-1}$) and phthalic acid standard ($> 99 \%$, TCI America, $235 \mu\text{g mL}^{-1}$) were run on UHPLC-PDA-HRMS. A 0.07 min delay time (between PDA and Orbitrap detectors) correction was applied to all presented TIC chromatogram traces. Mass spectra were recorded with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high-resolution mass spectrometer (UHPLC-PDA-HRMS) using heated electrospray ionization in the negative mode. The chromatograms and mass spectra were recorded with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high-resolution mass spectrometer (UHPLC-PDA-HRMS) with a resolving power up to 1.4×10^5 at m/z 200.

The separation was performed on a reverse-phase column (Waters, ACQUITY Premier HSS T3 Column, 2.1×150 mm, $1.8 \mu\text{m}$ particles, and $100 \text{ \AA}$ pores) with temperature kept at 30°C and injected volume of $10 \mu\text{L}$. The eluent flow was 0.3 mL min^{-1} and consisted of Optima grade water acidified with 0.1% v/v formic acid (eluent A) and Optima grade acetonitrile acidified with 0.1% v/v formic acid (eluent B). The gradient was: 0–3 min 95 % A; 3–14 min linear ramp to 95 % B; 14–16 min hold at 95 % B; 16 min return to 95 % A and

hold until 22 min in preparation for the next run. PDA data was collected at 5 Hz over 190-680 nm range with 4 nm effective bandwidth.

Mass spectra were obtained with m/z range of 100-1500 in the negative ion mode. The parameters of the heated electrospray ionization (HESI) ion source settings of the Orbitrap were: -2.5 kV spray voltage, 320 °C capillary temperature, 300 °C probe heater temperature, S-Lens ion funnel RF level 30, 50 units of sheath gas (nitrogen) flow, 10 units of auxiliary gas (nitrogen) flow, 1 unit of spare gas (nitrogen) flow.

In additional experiments, portions of selected OA filter samples (carpet, vinyl tile, and fiberboard OA) were loaded individually onto copper pot stubs used in the temperature-programmed desorption – direct analysis in real time – high resolution mass spectrometry (TPD-DART-HRMS) experiments²⁵⁶ using the Q-Exactive™ HF-X Orbitrap mass spectrometer. Mass spectra were recorded in negative mode, at mass resolving power of $m/\Delta m \sim 240,000$ @ 200 m/z and acquisition frequency of 1.5 Hz in the full MS scan mode in the mass range of 100 – 1000 Da. HRMS peak lists were inferred from total ion chromatograms recorded in TPD experiments, integrated over elution times corresponding to selected temperature ranges, and then were background subtracted using the Xcalibur software. Peak lists were extracted with the Decon2LS software and processed using Excel macros developed for m/z peak alignment, blank subtraction, and ¹³C isotope clustering and filtering.²⁵⁷ The following constraints were applied for all formula assignments: C₁₋₄₀, H₁₋₁₀₀, O₁₋₂₅, and N₀₋₃, mass tolerance of ± 2.0 ppm. Further details of these experiments, associated data interpretation and data processing can be found elsewhere.²⁵⁶

4.2.6 Additional photolysis experiments

Carpet, vinyl flooring, and fiberboard OA were selected to evaluate how urban OA absorption properties change over longer time scales. Following the same procedures described previously, carpet, vinyl flooring, and fiberboard OA were collected on Teflon filters, cut into four equal fractions, and aged under the Xenon arc lamp. Subsequent extraction and absorption measurements were taken. 0 (unaged), 1, 6, and 18 h time points were used for the long-term photolysis.

Drywall OA was selected to compare photolytic exposure from the laboratory photolysis setup (described previously) versus exposure from ambient sunlight. The sample was placed outside on the rooftop of the UC Irvine chemistry building (Rowland Hall) on November 9, 2022. Spectral flux density calculations (**Table 4.2**) concluded that one hour of exposure under the Xenon arc lamp equated to 0.7 h of sunlight between the hours of greatest solar flux in Irvine, CA (11 AM to 1 PM) on November 9th. Subsequent extraction and absorption measurements were taken and compared with an unaged drywall OA sample.

4.3 Results and Discussion

4.3.1 Solubility of tested OA

Ten urban flammable materials (**Table 4.1**) were pyrolyzed (under N₂) in a tube furnace and resulting OA particles were collected on substrates. **Figure 4.1** shows representative photographs of resulting filter-collected OA during pyrolysis at 600 °C. The visual appearance of the collected OA varied amongst materials, ranging from gray to light and dark yellow. In addition, carpet OA appearance varied with increasing pyrolysis

temperature (**Figure 4.2**). OA had a brown color resembling that of biomass burning BrC at 600 °C and transformed to OA resembling elemental, black carbon at temperatures exceeding 800 °C. Hence, 600 °C was chosen for all subsequent experiments because samples prepared at > 800 °C could not be efficiently extracted in organic solvents.

Corresponding EFs (**Table 4.1**) ranged from 1 g kg⁻¹ (drywall) to 47 g kg⁻¹ (lumber), indicating a wide range in the capacity for producing particulate matter from the selected urban materials. Our EF values are likely underestimated due to particle wall loss in the pyrolysis setup. The generated smoke moved from the heated zone, through the quartz and Teflon tubing before collection on the filter (**Scheme 4.1b**), providing plenty of surfaces for the wall loss. Under-ventilated conditions (i.e., smoldering combustion) tend to produce incomplete combustion with enhanced particulate matter production.⁷⁵ Because real fires undergo various stages of flaming (well-ventilated conditions) and smoldering (under-ventilated) conditions, our EF values cannot be directly compared with those reported for combustion experiments. With that being said, our wood-based urban materials (lumber and plywood) are well within reported EF ranges for flaming and smoldering combustion.²⁴⁹

Methanol extraction, typically the solvent system of choice, is not as effective in BrC extraction from BBOA as methanol/dichloromethane (1:1 and 1:2, v/v), tetrahydrofuran, and non-dimethylformamide.²⁵⁸ Therefore, solvent extractions efficiencies were assessed for all OA samples. The best extraction solvent was determined by the highest overall *MAC* values in **Figure 4.3** and are listed in **Table 4.1**. Consistent with prior BBOA extraction studies,^{258,259} for all OA samples tested here, water extracted the least OA, as indicated by lower *MAC* values compared to the other solvent systems (**Figure 4.3**). The samples had comparable solubility in orgmix, methanol, and octanol. With the notable exception of the

thin PVC wire, the *MAC* spectra in all organic solvents had the same shape, suggesting near complete extraction of all material from the filter.

4.3.2 Unaged urban OA absorption spectra characteristics

Because BrC is a complex mixture of individual chromophores, the absorption spectra of ambient BrC are typically featureless, with the absorption coefficient smoothly increasing from visible to UV wavelengths.³⁰ The absorption coefficient of BrC often scales with wavelength and a power law, $\propto \lambda^{-AAE}$, where *AAE* stands for Absorption Angström Exponent. For ambient BrC, *AAE* varies from 2 to 11, depending on the OA composition.^{30,260,261} **Figure 4.6a** shows the *MAC* (λ) values of all unaged OA samples extracted in the best-suited solvent. All ten OA absorb strongly at shorter wavelengths (UV) and have weak absorption over the visible range, characteristic of BrC.³⁰ Most OA have a slight absorption band at ~250 nm, attributed to a π to π^* transition of conjugated/aromatic organic compounds.^{140,240,262} The resulting *AAE* values ranged from 6.0 to 11.6 with the average being 8.8 ± 1.3 (value $\pm$ standard deviation). These values fall within expected *AAE* values for BrC previously reported for SOA BrC and BBOA BrC.^{30,260,261} **Figure 4.7** shows the wavelength-dependent *MAC* values recorded after the pyrolysis of urban materials, photolytic aging for 2 h, and extraction in the best-suited solvent. The effective *AAE* values in **Figure 4.6** were obtained from the linear fits of **Figure 4.7** (panels b and c) in the 280-480 nm range.

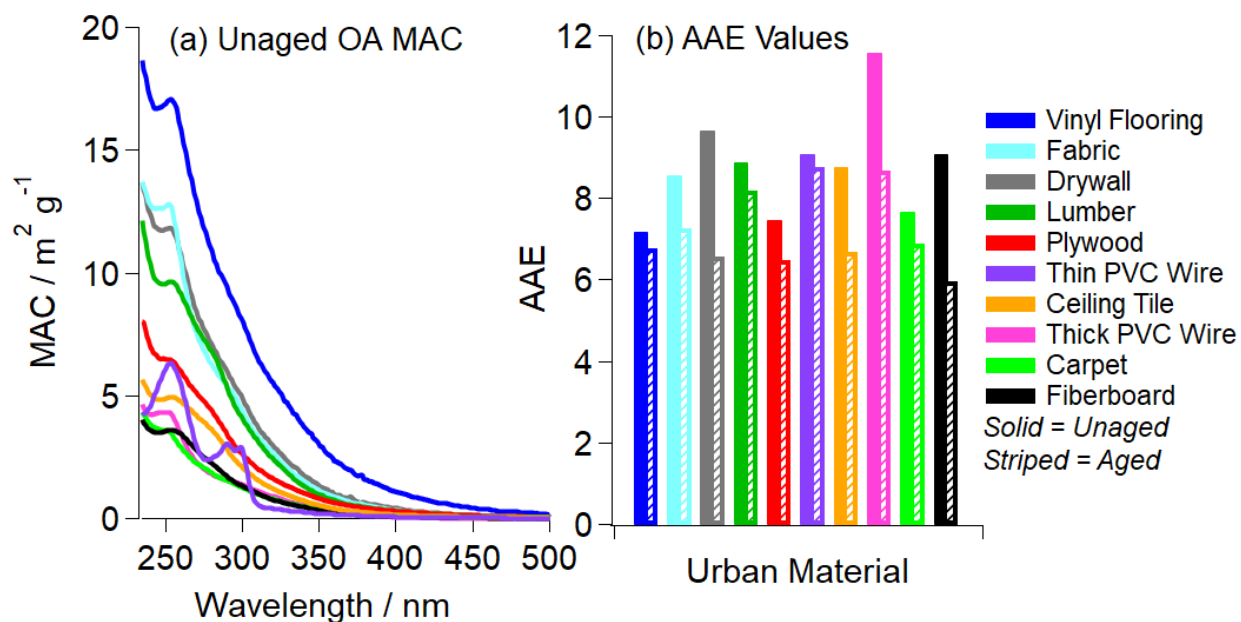


Figure 4.6. The wavelength-dependent mass absorption coefficient (MAC) and Absorption Angstrom Exponent (AAE) values recorded after pyrolysis of urban materials and extraction in the best-suited organic solvent (**Table 4.1**). MAC values (a) were calculated assuming 100% extraction efficiency from the Teflon filter. Boxcar averaging of the MAC data (over a 5 nm range) was utilized to improve signal-to-noise ratio. Panel (b) shows the AAE values for unaged OA (solid bars) and 2 h aged OA (striped bars). The effective AAE values were obtained from the linear fits of **Figure 4.7** (panels b and c) in the 280-480 nm range.

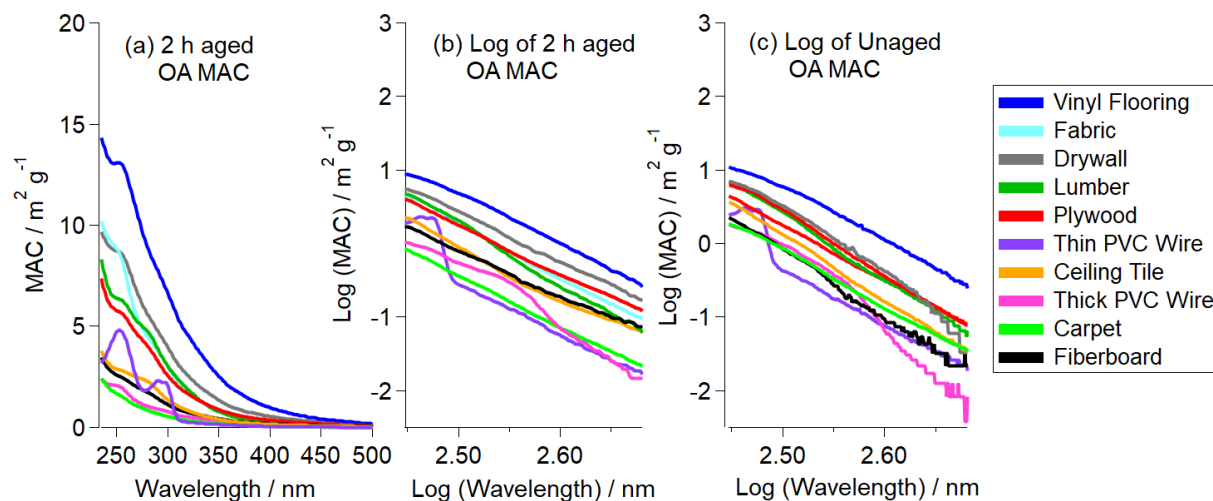
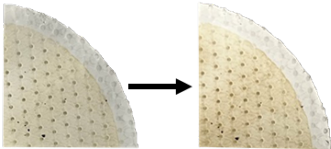
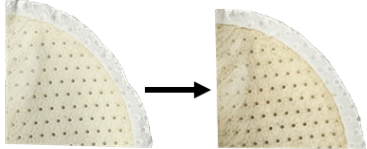
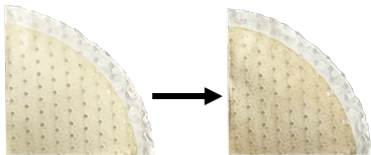
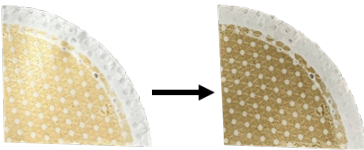
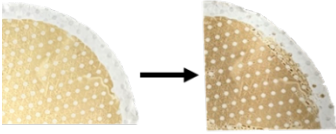
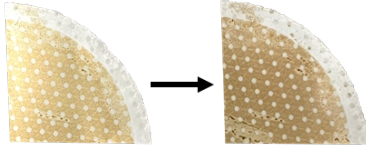
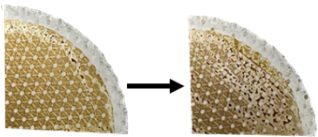
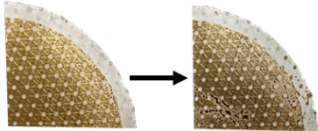
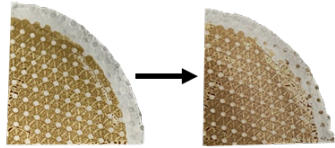


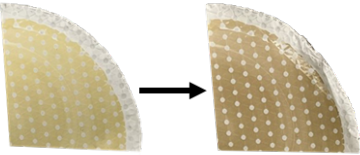
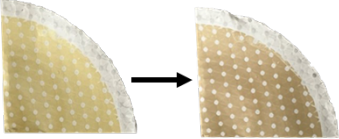
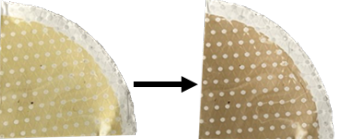
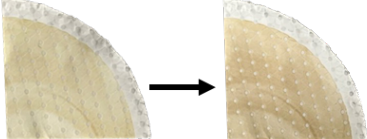
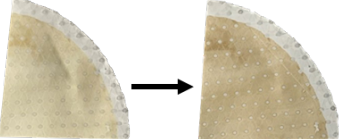
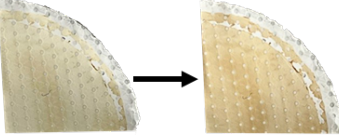
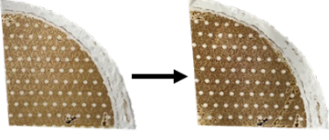
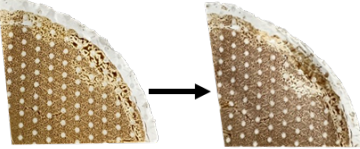
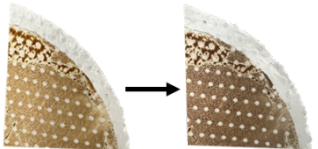
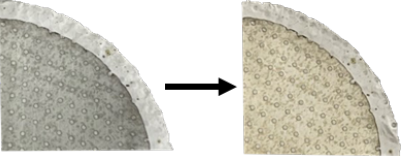
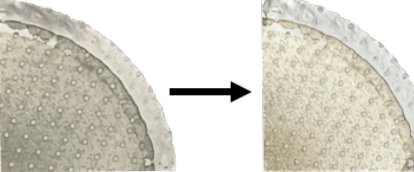
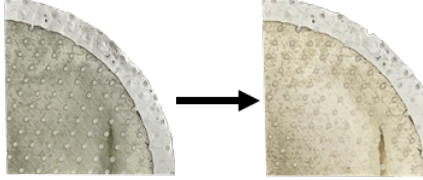
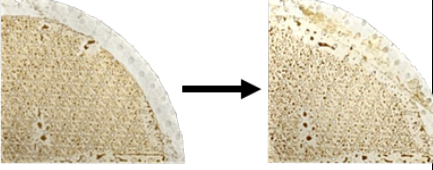
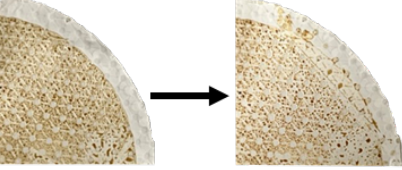
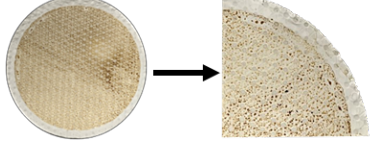
Figure 4.7. The wavelength-dependent mass absorption coefficient (MAC) for 2h aged OA and log-log MAC plots recorded after pyrolysis of urban materials, photolytic aging for 2h, and extraction in the best-suited organic solvent (**Table 4.1**). MAC values (a) were calculated assuming 100% extraction efficiency from the Teflon filter. Panels (b) and (c) show log-log plots of the 2h aged OA MAC and unaged OA MAC , respectively, as a function of wavelength. The effective AAE values, shown in **Figure 4.6**, were obtained from the linear fits of these spectra in the 280-480 nm range. The linear trendlines are not shown in panels (b) and (c) for simplicity. Boxcar averaging of the MAC data (over 5 nm range) was utilized to improve signal-to-noise ratio.

4.3.3 Transformations of OA absorption caused by photolysis

Three distinct color changes of the OA samples were observed: photoenhancement (samples became visibly darker in color), photobleaching (samples became lighter in color), and unchanged (no perceptible color change was observed). These qualitative visual observations were confirmed by the UV-Vis spectroscopy measurements that were taken after extracting OA at each irradiation time point. **Table 4.3** presents pictures of OA before and after photolysis.

Table 4.3. Pictures of OA collected on Teflon filters and irradiated with UV light for 0.5 h, 1 h, and 2 h. Each column has a picture of the quarter of the filter prior to photolysis then, after the arrow, a picture of the same quarter after the specified irradiation time. Visually, three classifications can be made: 1) OA darkened after irradiation, 2) OA bleached after irradiation, and 3) OA remained unchanged. These results are correlated with trends observed in the UV-Vis absorption spectra. The factor of change in the normalized, integrated *MAC* values (400-700 nm) are reported after the urban material name. Note that fabric unaged to 2 h pictures are from a separate filter trial than the two previous time increments but, nevertheless, show the same trend.

Urban Material	Unaged (0 h)	Unaged (0 h) → 0.5 h	Unaged (0 h) → 1 h	Unaged (0 h) → 2 h
1) Photoenhancement: OA darkened with 2 h irradiation				
Thick PVC Wire (white) 1.8x increase				
Ceiling Tile 1.6x increase				
Lumber 5.5x increase				

Drywall 2.8x increase				
Fiberboard 3.0x increase				
Plywood 1.5x increase				
2) Photobleaching: OA bleached with 2 h irradiation				
Thin PVC Wire (purple) 1.2x decrease				
Carpet 1.5x decrease				

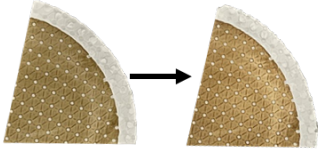
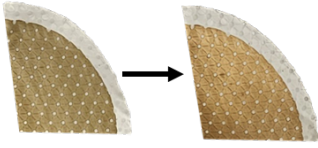
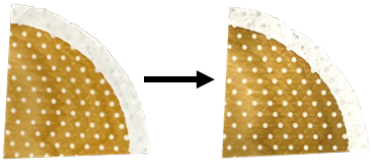
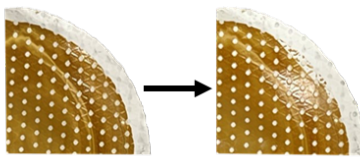
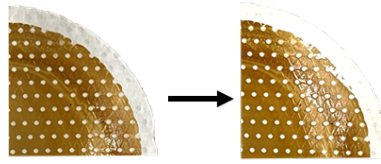
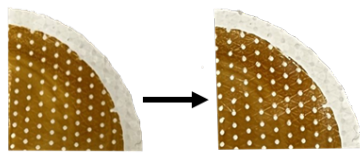
3) OA remained unchanged after 2 h irradiation				
Fabric 1.0x decrease				
Vinyl Flooring 1.0x decrease				

Figure 4.8 shows the *MAC* values for two OA samples generated from the pyrolysis of drywall (**Figures 4.8a and b**) and thin PVC wire (**Figures 4.8c and d**). The subplots in each panel show the *MAC* values integrated over their respective wavelength range (280 to 400 nm for the near-UV and 400 to 700 nm for the visible range), normalized to their corresponding unaged *MAC* values. Both drywall OA and thin PVC wire OA show a similar decrease in the UV range integrated *MAC* (**Figures 4.8a and c**), but different trends were observed in the visible range. There was an increase by a factor of 2.75 (relative to the unaged value) for the drywall OA visible integrated *MAC* (**Figure 4.8b**), whereas thin PVC wire OA experienced a decrease by a factor of 1.21 compared to the unaged sample (**Figure 4.8d**). These results confirmed visual observations that photoenhancement in the absorption coefficient occurred for drywall OA and photobleaching occurred for thin PVC wire OA (**Table 4.3**). Similar to the results in **Figure 4.8**, **Figure 4.9** shows that fiberboard OA exhibited photoenhancement (increase by a factor of 3) and carpet OA exhibited photobleaching (2 h aged sample was factor of 1.5 lower than unaged sample). In addition, three other OA samples (thick PVC wire, ceiling tile, and plywood) exhibited photoenhancement effects in the visible range (increase by factors of 1.8, 1.6, and 1.5, respectively, compared to the unaged value) upon 2 h of direct photolytic aging (**Figure 4.10**).

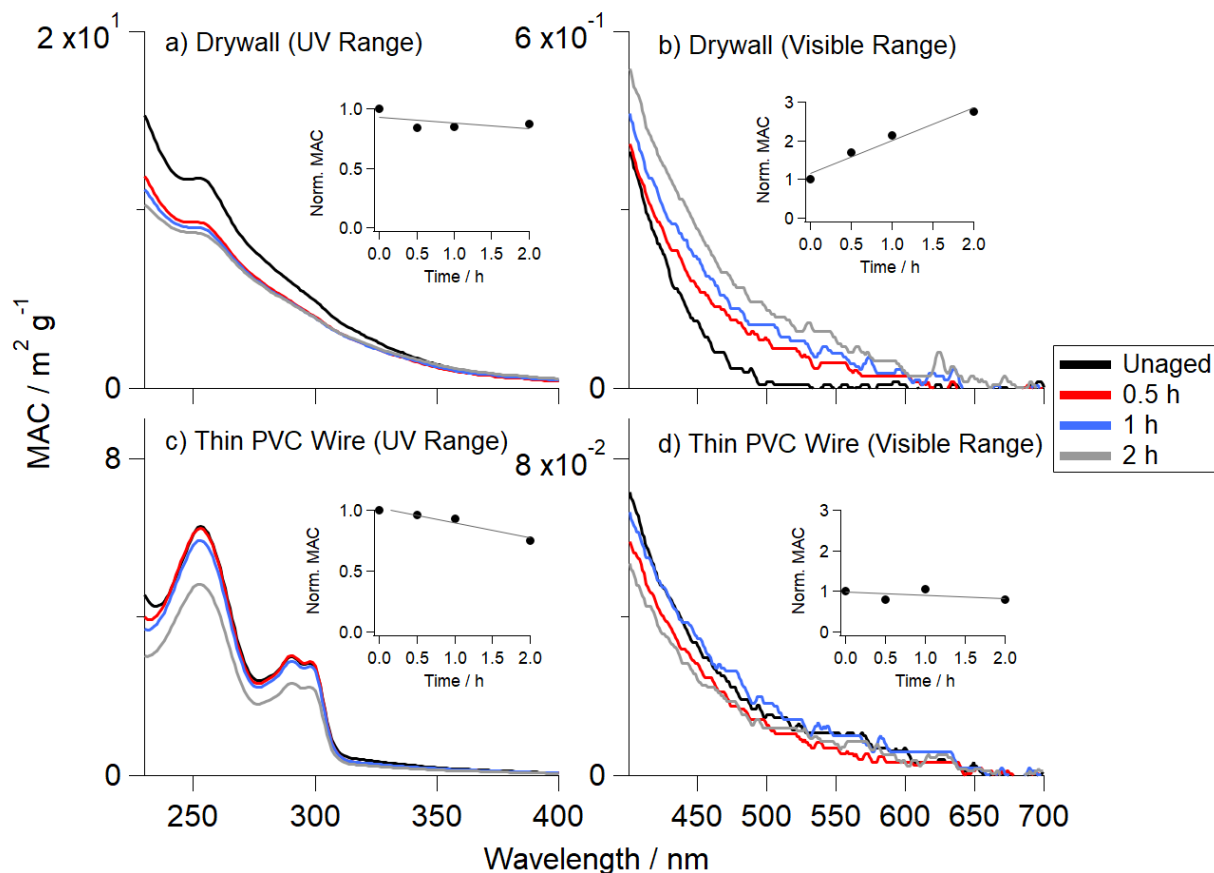


Figure 4.8. Wavelength-dependent mass absorption coefficient (MAC) values recorded after photolysis on Teflon filters and the subsequent extractions of drywall OA and thin PVC wire OA (a-b and c-d, respectively). Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (gray) and is compared with the unaged (0 h) fraction (black). The integrated MAC values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the MAC data (over a 5 nm range) was utilized to improve signal-to-noise ratio.

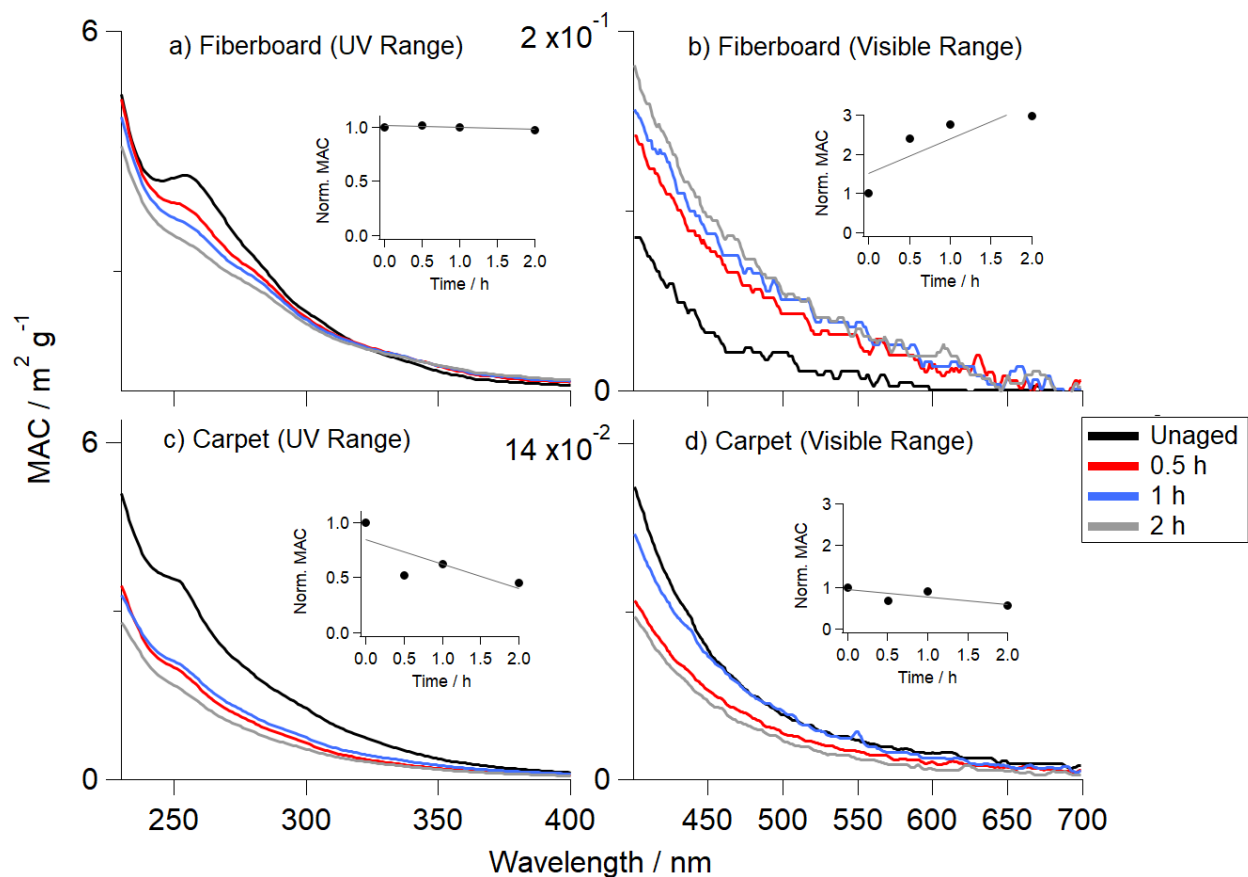


Figure 4.9. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis on Teflon filters and the subsequent extractions of fiberboard OA and carpet OA (a-b and c-d, respectively). Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

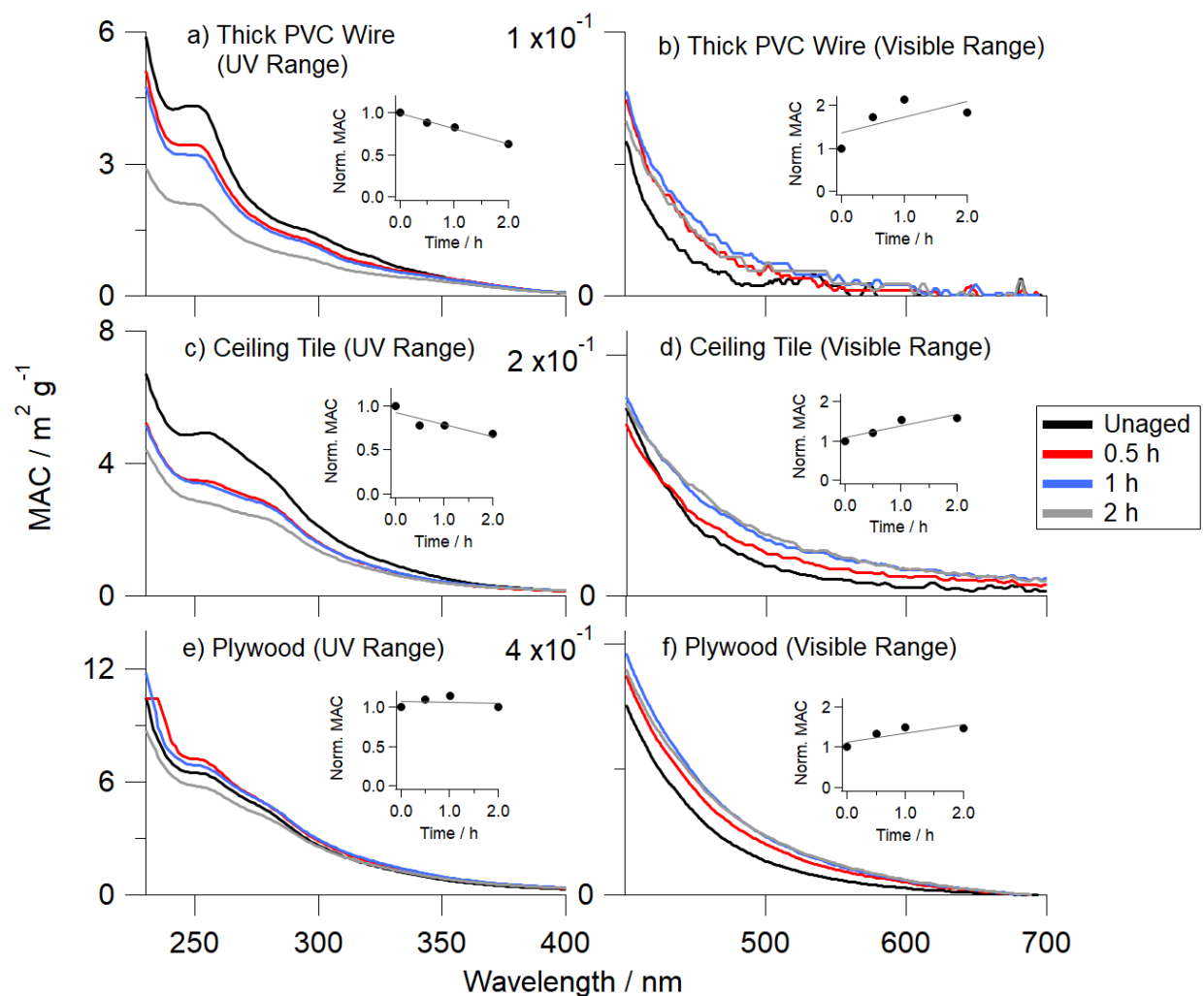


Figure 4.10. Wavelength-dependent mass absorption coefficient (MAC) values recorded after photolysis on Teflon filters and the subsequent extractions of thick PVC wire OA, ceiling tile OA, and plywood OA (a-b; c-d; e-f, respectively). Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated MAC values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the MAC data (over 5 nm range) was utilized to improve signal-to-noise ratio.

The UV exposure not only changed the color of the filters but, in some cases, appeared to affect the solubility of the residual material. Specifically, lumber, fabric, and vinyl flooring OA could not be fully extracted from the Teflon filters after the irradiation (**Figure 4.5**). This complicated classification of the irradiation effects into categories of photoenhancement or photobleaching. For example, lumber OA results show a decrease in integrated MAC value by a factor of 1.02 in the visible range Teflon filter experiments (**Figure 4.11b**), but this result contradicted the obvious filter darkening observed visually (**Table 4.3**). To resolve this issue, photolysis experiments for these materials were repeated using OA collected on fused silica windows after passing through an ESP (-5 kV). This collection method allowed for a more complete extraction of lumber, fabric, and vinyl flooring OA post-photolysis (**Scheme 4.2**). While the Teflon filters collected particles $>0.22\ \mu\text{m}$, the collection by ESP favored smaller particle sizes.^{263,264} To this end, composition of smaller particles may have enhanced the solubility of photolyzed OA. ESP experiments for lumber OA exhibited an increase in the UV by a factor of 4 and an increase in the visible by a factor of 5.5 (**Figure 4.11c and d**) indicating that the residual OA prevented the full representation of light-absorptive properties of the sample after photolytic aging. Fabric and vinyl flooring OA exhibited no net change ($0.9 > \text{ratio (2 h aged to unaged)} < 1.1$) in both the Teflon and quartz window experiments (**Figures 4.12 and 4.13**).

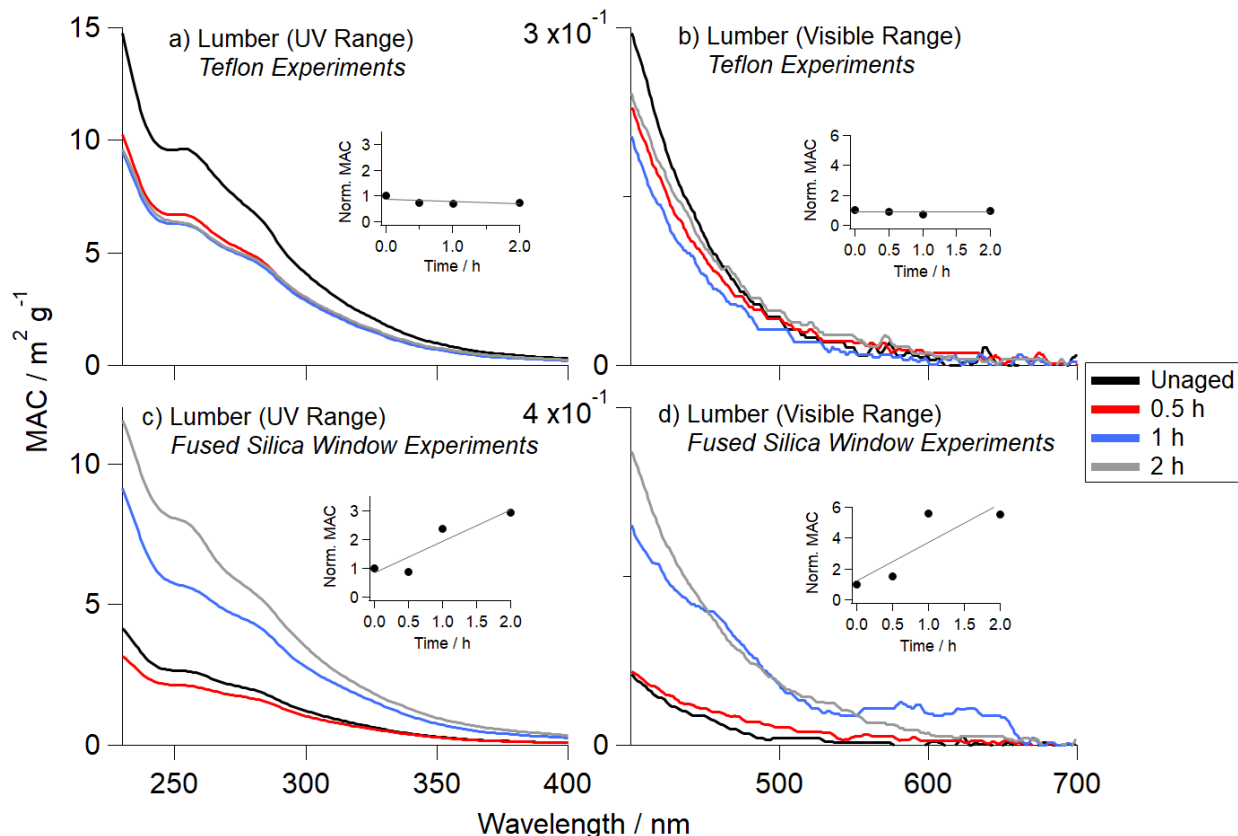


Figure 4.11. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis and subsequent extraction of lumber OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

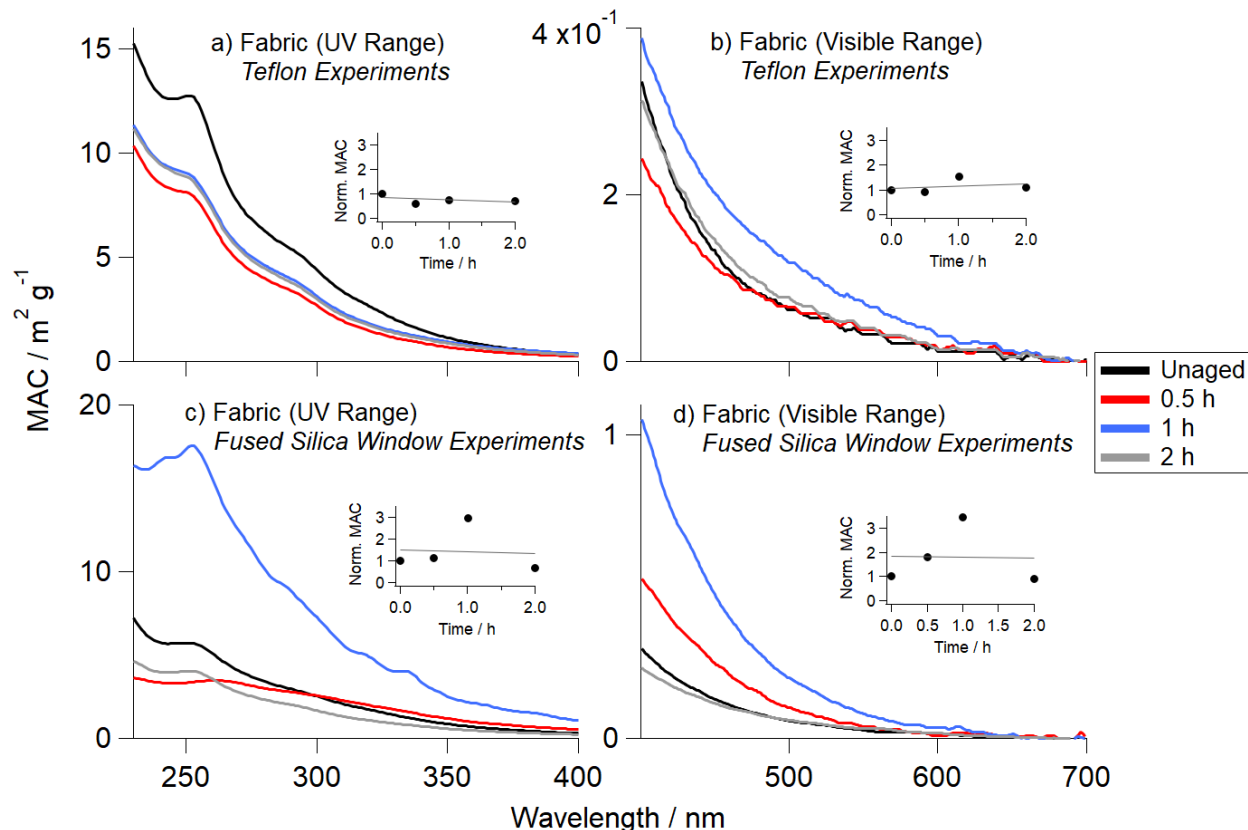


Figure 4.12. Wavelength-dependent mass absorption coefficient (MAC) values recorded after photolysis and subsequent extraction of fabric OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated MAC values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the MAC data (over 5 nm range) was utilized to improve signal-to-noise ratio.

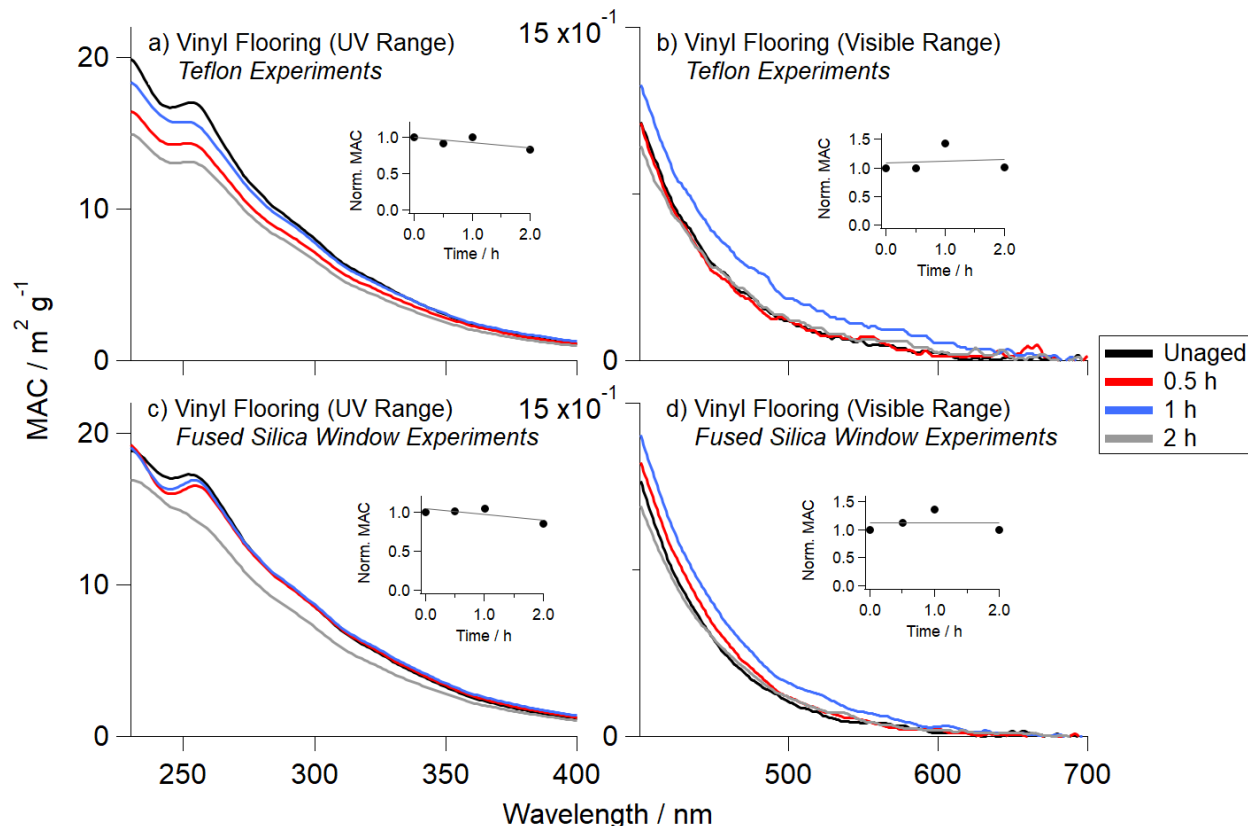


Figure 4.13. Wavelength-dependent mass absorption coefficient (MAC) values recorded after photolysis and subsequent extraction of vinyl tile OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated MAC values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the MAC data (over 5 nm range) was utilized to improve signal-to-noise ratio.

Figure 4.14 presents the ratios of 2 h aged to unaged *MAC* values integrated over the visible range for all 10 urban materials. As mentioned above, three types of trends were observed over the 2 h aging time: photobleached, unchanged, and photoenhanced. In addition to these results in the visible range, **Figure 4.15** shows that all but one OA sample (lumber) decreased in UV range *MAC* values after 2 h of photo-aging, as indicated by ratio greater than 1.1. Carpet OA and thin PVC wire OA (red region in **Figure 4.14**) photobleached upon UV exposure, indicating chromophore fragmentation occurred more efficiently than chromophore formation. Similar results were observed by Ye et al. (2019) as they studied the aqueous-phase photochemical oxidation of a model BBOA compound, 4-ethylphenol.²⁶⁵ They observed degradation and fragmentation upon initial exposure to hydroxyl radical oxidation under UV light.²⁶⁵ Since we conducted photolytic aging experiments without intentionally added OH radical sources, we hypothesize that the observed photobleaching effects were a result of UV light induced OH radical production, leading to the degradation of chromophoric species in carpet OA and thin PVC wire OA.

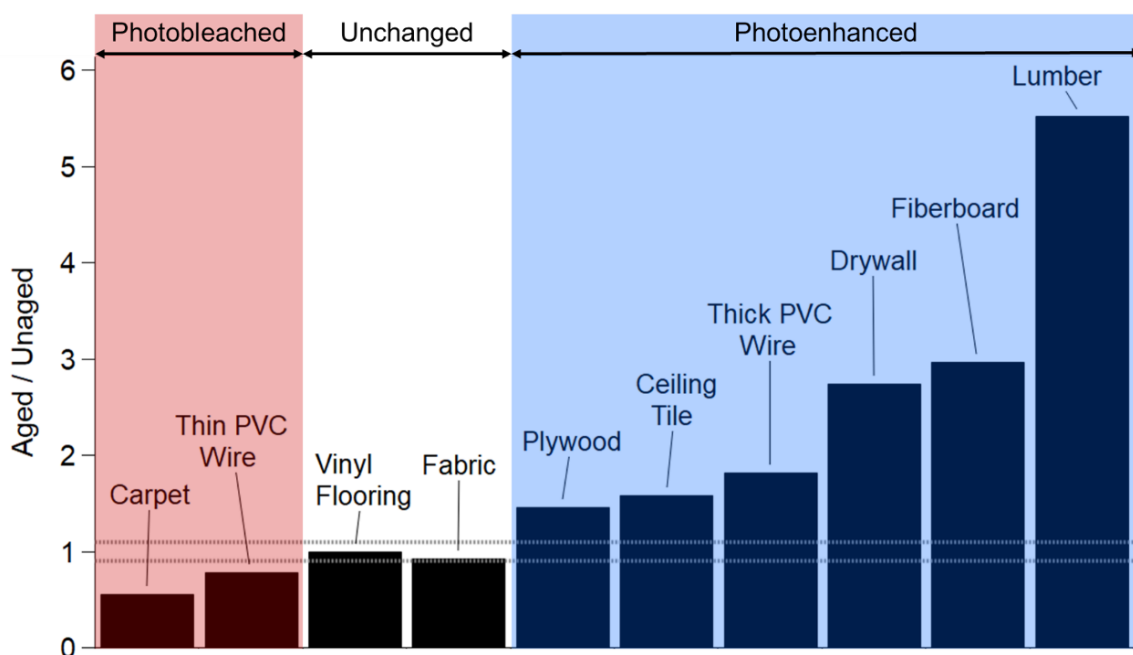


Figure 4.14. Ratios of the 2 h aged to unaged integrated, visible range *MAC* values. The reported ratios were calculated by integrating the *MAC* values in the visible range (400-700 nm) then referencing the 2 h aged, integrated *MAC* value to that of the unaged, integrated *MAC* value. The shading color corresponds to classification of OA into three categories: photobleached (red), unchanged (white) and photoenhanced (blue). The dashed line (0.9 to 1.1) indicates the threshold for the unchanged category.

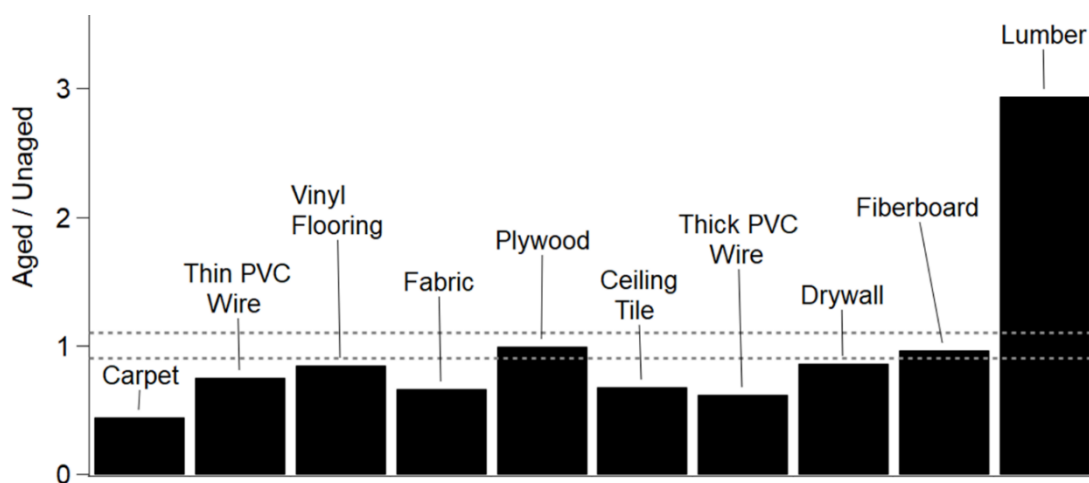


Figure 4.15. Ratios of the 2 h aged to unaged integrated, UV range *MAC* values. The reported ratios were calculated by integrating the *MAC* values in the UV range (280-400 nm) then referencing the 2 h aged integrated *MAC* value to that of the unaged, integrated *MAC* value. The dashed line (0.9 to 1.1) indicates the threshold for the change.

Six urban materials (blue region in **Figure 4.14**) exhibited photoenhancement. We hypothesize that photochemically-driven formation of stronger chromophores occurred by free radical (OH). and triplet-excited state reactions occurring in the OA material. Such reactions have been shown to lead to the formation of chromophores in aqueous photochemistry,²⁶⁶⁻²⁶⁹ but they have also been reported to occur in model OA material.^{202,237} More specifically for model BBOA chromophores, Hems and Abbatt (2018) observed absorbance enhancement in the visible wavelength range for nitrocatechol, nitroguaiacol, and dinitrophenol due to the formation of functionalized products after exposure to a steady state concentration of OH radical.²⁷⁰ These studies proved that OH radical oxidation of dissolved BBOA compounds can lead to functionalized and oligomerized products with enhanced absorption in visible wavelengths.

Fabric OA and vinyl flooring OA *MAC* values (white region in **Figure 4.14**) exhibited ratios greater than 0.9 but less than 1.1 when 2 h aged measurements were referenced to the unaged (**Figure 4.12 and 4.13**, respectively). Noticeably for these two materials, photoenhancement occurred in the first hour of aging then photodegradation occurred between 1 and 2 h of aging, thus returning the *MAC* back to the initial unaged value. Previous studies investigating BrC photolytic aging have observed similar trends. Secondary BrC has been observed to rapidly photobleach,²⁷¹ whereas primary BrC from biomass burning has been observed to undergo both photoenhancement and photobleaching during the course of UV exposure, with initial photoenhancement followed by photobleaching.^{224,239,240} Aqueous-phase UV/OH radical exposure studies showed that product formation occurred during oxidation of organic compounds and initial increases in absorption are attributed to functionalization of chromophores.^{220,224,270} Over time, loss of absorption occurs when

further reactivity leads to fragmentation.^{220,224,270,272} We observe this “dynamic” nature in the fabric OA and vinyl flooring OA cases. Further mass spectrometry analysis (at each irradiation time point) is necessary to determine the mechanism(s) of evolution.

All *MAC* and *AAE* values for the OA samples unaged (0 h) and after 2 h of photolysis (**Figure 4.6** and **Figure 4.7**) are incorporated in **Figure 4.16**. The *MAC*₄₀₅ of unaged OA (black markers) are compared to OA aged for 2 h (blue markers), placed into the context of the optically based BrC absorption strength classification introduced by Saleh (2020) and modified by Hettiyadura *et al.* (2021).^{204,260} Note that these *MAC* values were calculated using the mass of the unaged sample, and some mass loss is expected with photolysis. Therefore, reported *MAC* values are likely to be underestimations of the true *MAC* values post-photolysis. Upon photolysis, there is a downward shift in *AAE* values from VW → W BrC. These results are similar to those reported in Hettiyadura *et al.* (2021) for fresh biomass burning BrC and biomass burning BrC that darkened with NO₃ chemistry.²⁰⁴ The average *AAE* value for all ten urban OA after photolyzing for 2 h reduced from 8.8 ± 1.3 to 7.3 ± 0.9. All materials experienced a reduction in *AAE* value upon short term aging, as indicated by striped bars in **Figure 4.6b**. As we are examining components commonly combusted in fires at the WUI, the average *AAE* shift shown in **Figure 16** reflects that WUI OA exhibits an overall absorption enhancement effect with UV aging.

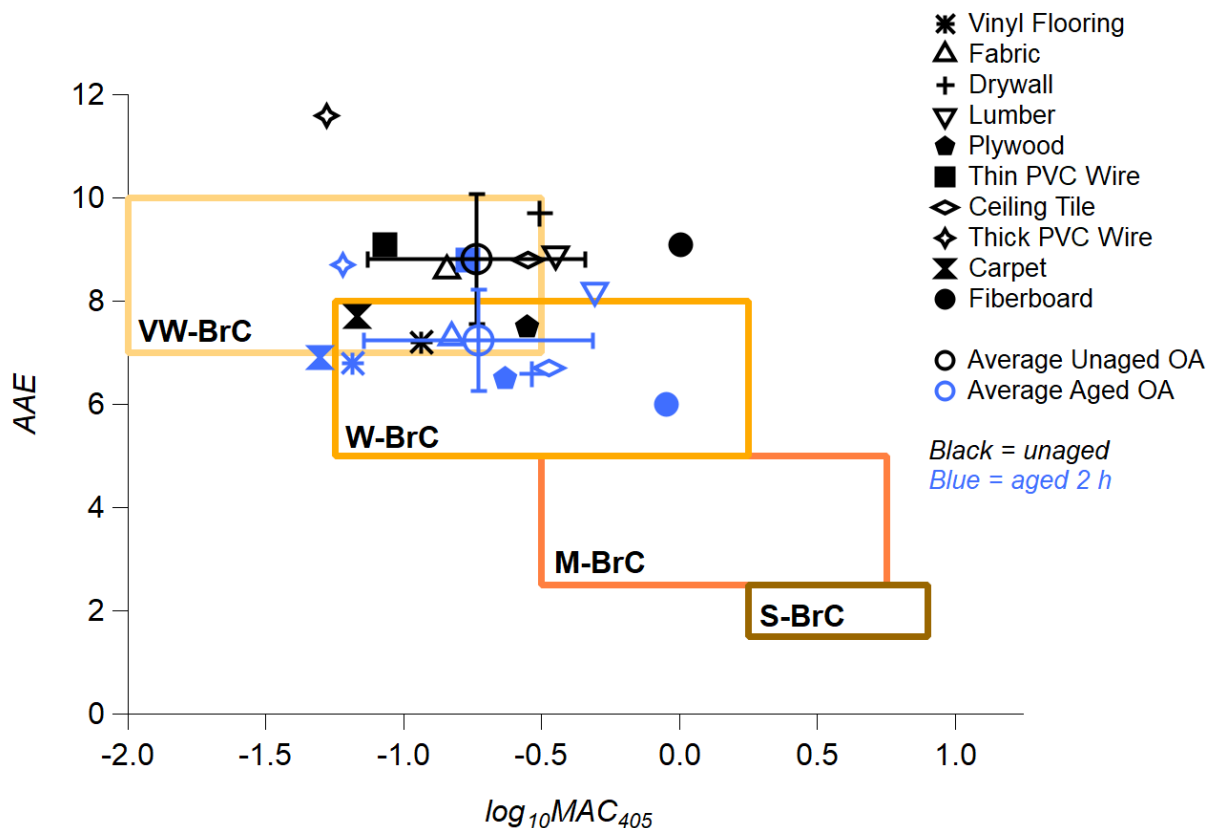


Figure 4.16. Urban OA BrC optical properties mapped in AAE - $\log_{10}$ vs. MAC_{405} space following the classification introduced by Saleh (2020) and further adapted by Hettiyadura *et al.* (2021).^{204,260} Boxed areas represent very weakly (VW), weakly (W), moderately (M), and strongly (S) absorbing BrC classes. The markers correspond to the values of AAE calculated for a wavelength range of 280–480 nm for unaged urban OA (black markers) and the 2 h aged urban OA (blue markers). The global average, unaged OA (black open circle) and average, 2 h aged OA (blue open circle) are shown to illustrate a change upon photolytic aging.

4.3.4 Preliminary compositional results of unaged and aged OA

Mass spectrometry results in this section are preliminary and a more advanced study of all urban OA samples will be examined in Chapter 5.

Thin PVC wire OA is an anomaly in this data set in two ways. First, the two types of PVC wire OA (thin and thick) exhibited opposite trends: OA from thin PVC wire (purple) photobleached, whereas OA from thick PVC wire (white) photoenhanced after UV exposure.

Second, thin PVC wire OA was the only material to exhibit distinct absorption bands, one at 253 nm and a doublet at 290 nm and 300 nm (**Figure 4.6**). Through UHPLC-PDA-HRMS analysis (**Figure 4.17**), we sought to identify the chromophore responsible for these spectral features.

Thin PVC wire OA's largest PDA/TIC peak at 7.39 min (**Figure 4.17a**) and the mass spectrum (**Figure 4.17b**) confirmed that a compound with molecular formula $C_8H_6O_4$ was responsible for light absorption in this sample. $C_8H_6O_4$ was presumed to be phthalic acid and a standard solution was run on HRMS for confirmation. Phthalic acid standard was dissolved in Optima water (with 0.1 % v/v formic acid) without any acetonitrile (ACN), as phthalic acid solubility is poor in ACN. This caused a slight shift in the retention time (**Figure 4.17c**) compared to that of thin PVC OA in **Figure 4.17a**, which was dissolved in water and ACN for HRMS preparation. The mass spectrum (**Figure 4.17d**) exhibited the main ion of phthalic acid (m/z 165.0192) and fragment of phthalic acid (loss of CO_2 , m/z 121.0295) was a minor ion at this retention time.

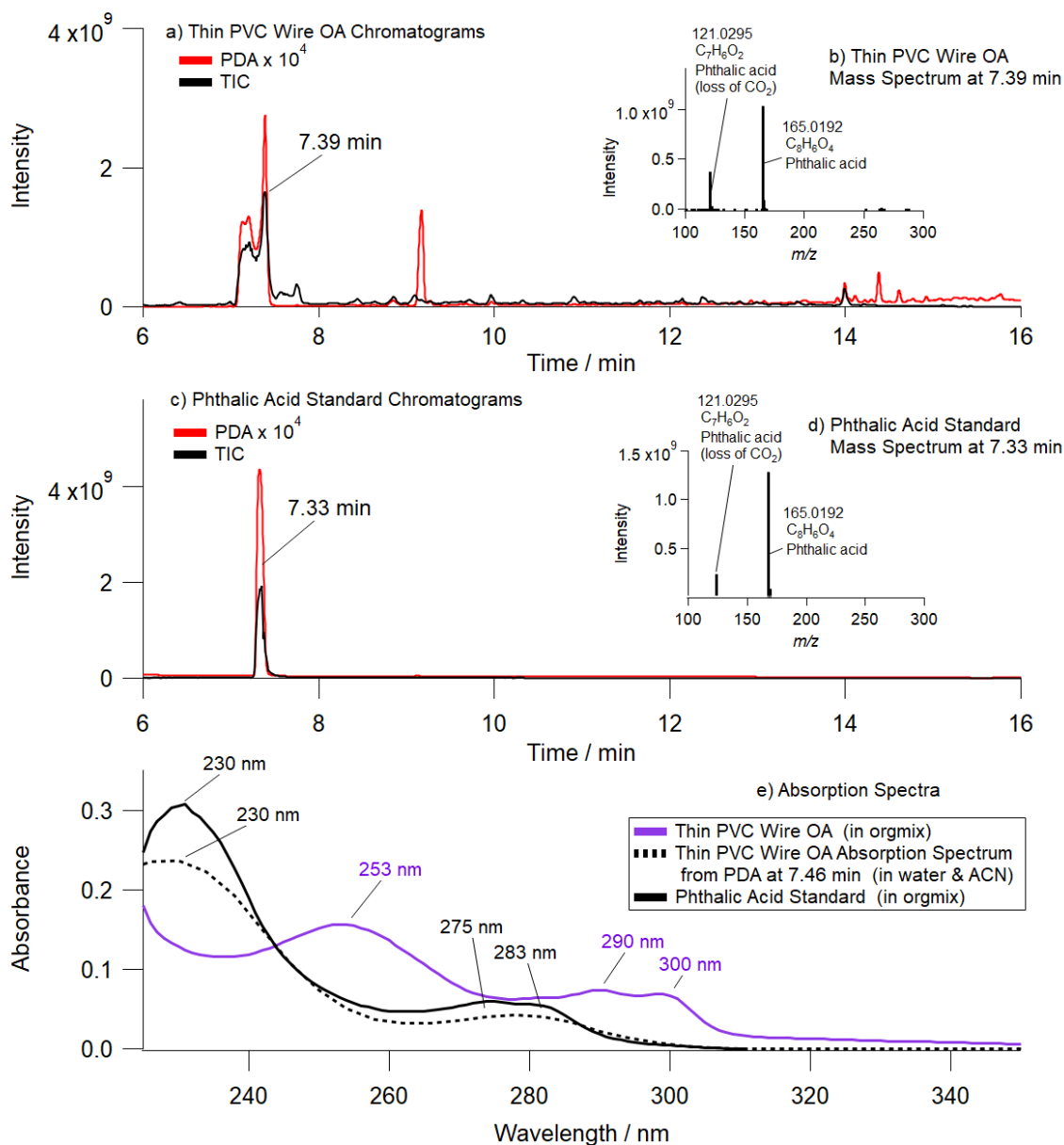


Figure 4.17. UHPLC-PDA-HRMS data for thin PVC wire OA and a phthalic acid standard: a) Thin PVC Wire OA PDA chromatogram (red) and TIC chromatogram (black); b) mass spectrum of thin PVC wire OA at TIC retention time 7.39 min; c) phthalic acid standard PDA chromatogram (red) and TIC chromatogram (black); d) mass spectrum of phthalic acid standard at TIC retention time 7.33 min; e) absorption spectra of thin PVC wire OA (purple, from **Figure 4.6**), thin PVC wire OA detected by PDA (dashed), and phthalic acid (black). A 0.07 min correction was made to TIC chromatograms to account for the delay time between PDA and Orbitrap detectors. All PDA traces were offset by $\times 10^4$ to account for differences in intensity between PDA and Orbitrap detection. Note in panel (c): retention time is slightly earlier than panel (a) due to phthalic acid standard dissolved in water only and not acetonitrile.

Figure 4.17e shows the absorption spectrum for thin PVC wire OA (purple trace) as originally presented in **Figure 4.6**. This spectrum exhibits distinct absorption bands at 253 nm, 290 nm, and 300 nm. Phthalic acid standard was dissolved in orgmix and an absorption measurement was taken using a UV Vis spectrometer (black trace, **Figure 4.17e**). Thin PVC wire OA absorption spectrum from the PDA detector of the HRMS (dashed line, **Figure 4.17e**) and phthalic acid standard solution exhibited the same spectral features at 230 nm, 275 nm, and 283 nm. As these peak wavelengths do not match that of the thin PVC wire OA (purple trace), we conclude that phthalic acid is not the compound responsible for the distinctive absorption in thin PVC wire OA, however, it is responsible for most of the overall sample's absorption in the PDA. Follow up studies on urban OA chemical composition will look further into identifying the compound responsible for absorption bands at 253 nm, 290 nm, and 300 nm.

While we could not identify a sole chromophore whose absorption would match the distinct doublet at 290+300 nm, we were able to identify phthalic acid as a major contributor to the sample's overall light absorption. Phthalic acid is used in the production of PVC plasticizer, polyester resin, and dyes and is a derivative of phthalic anhydride, a common chemical intermediate in plastic production.²⁷³ Since the thin PVC wire material tested in this study was purple, it is reasonable to suspect that phthalic acid was added alongside a purple dye into the PVC coating. It is possible that the photobleaching effect exhibited by thin PVC wire OA is due to degradation of the phthalic acid chromophore by continued OH radical generation and aging.²⁷² This (and other trends) will need to be systematically explored in future works with mass spectrometry analysis of all urban OA samples.

To further assess the corresponding changes in chemical composition of OA samples after direct photolysis, we conducted TPD-DART-HRMS experiments to detect chemical transformations in three selected OA samples representative of photobleached (carpet), photoenhanced (fiberboard) and unchanged (vinyl tile) cases observed in our study (**Figure 4.14**). The reconstructed HRMS plots of all detected organic compounds in both unaged and aged aerosols are exhibited in **Figures 4.18** and **4.19**. There were 1698/1479 (carpet), 633/379 (vinyl tile), and 956/988 (fiberboard) compounds detected in each of the unaged/aged pairs of OA samples, respectively (**Figure 4.18**). In each of the pairs, compounds that were affected by the photolysis experiments were selected based on the following criteria: 1) components unique to unaged or aged OA samples and 2) components that decreased or increased by >10% in the aged OA samples. There were 1036/871 (carpet), 470/206 (vinyl tile) and 185/205 (fiberboard) components that satisfied these criteria. The reconstructed HRMS plots summarizing these photolysis-affected compounds are shown in **Figure 4.19** and the corresponding DBE (double bond equivalent) values versus C (number of carbon atoms) plots are shown in **Figure 4.20**.

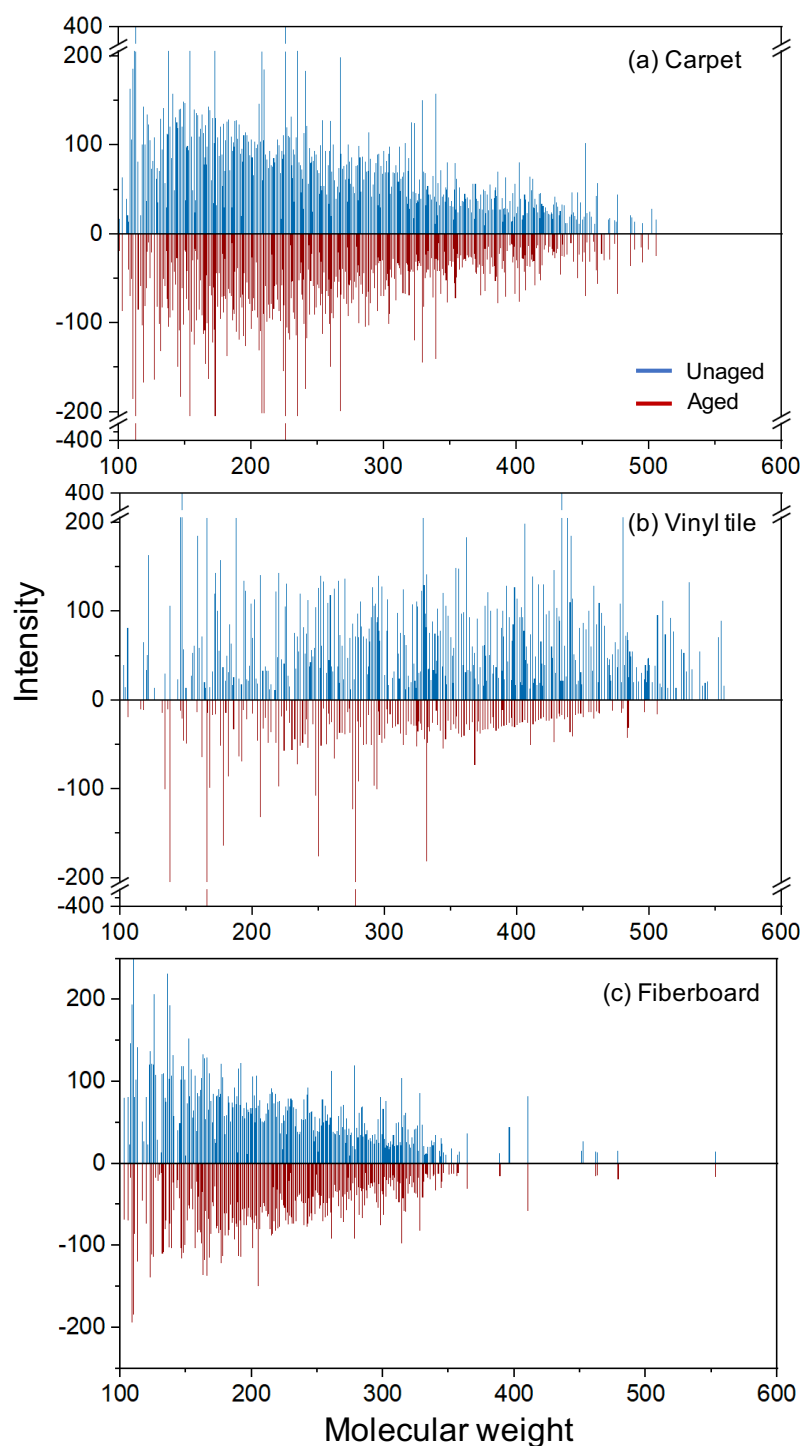


Figure 4.18. Reconstructed mass spectra of individual organic components identified in the time-integrated TPD-DART-HRMS experiments with the OA collected from pyrolysis of carpet, vinyl tile, and fiberboard materials (a-c, respectively). Unaged OA is presented in blue, whereas OA aged 2 h under UV radiation are presented in red. To facilitate visual comparison, MS peaks detected in aged OA samples are plotted as negative signal, and intensities of all peaks are scaled to the cubic root of the originally recorded values.

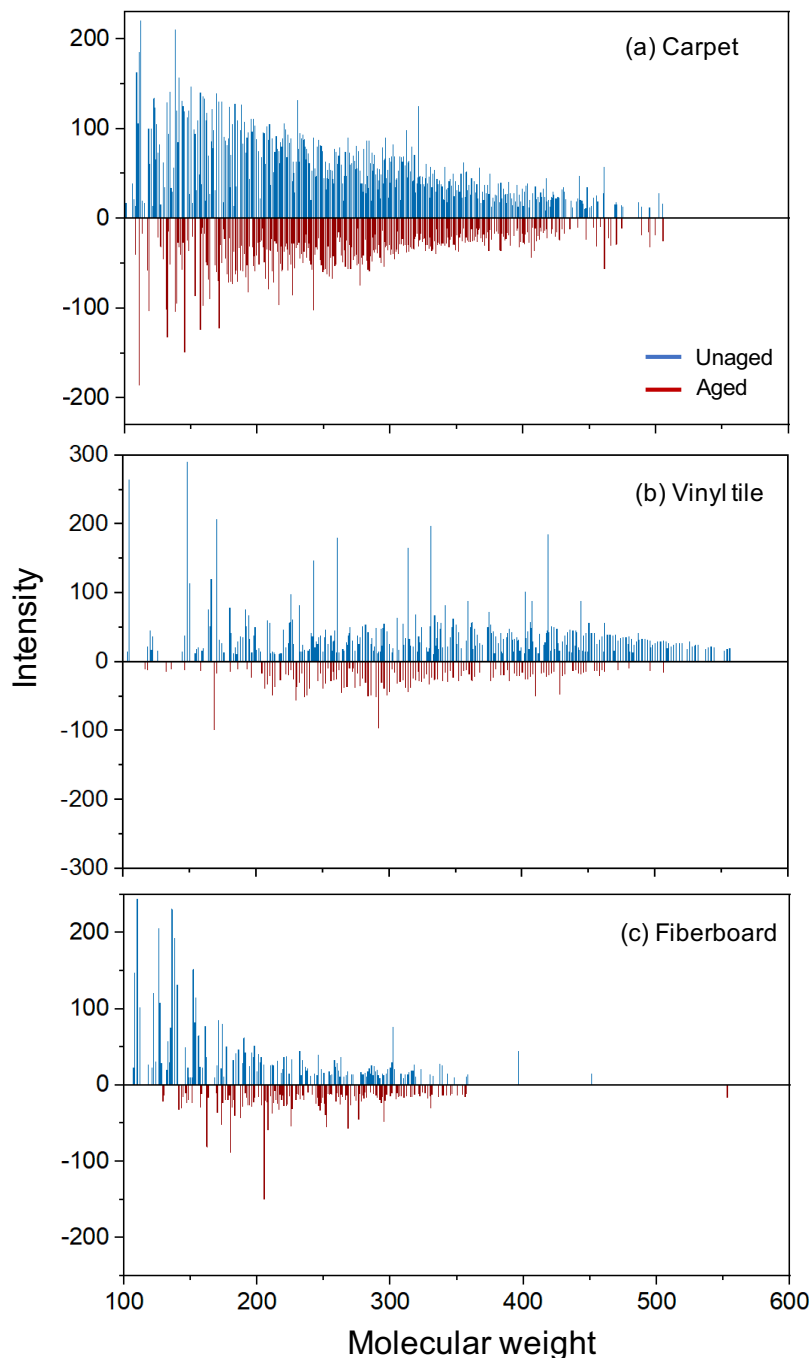


Figure 4.19. Reconstructed mass spectra of the unique OA components. Peaks unique to unaged OA + peaks that decreased by 10 % after aging are presented in blue, whereas peaks unique to aged OA + peaks that increased by 10% after aging are presented in red. These components were identified in the time-integrated TPD-DART-HRMS experiments with the OA collected from pyrolysis of carpet (a), vinyl tile (b) and fiberboard (c) materials. To facilitate visual comparison, MS peaks detected in aged OA samples (red) are plotted as negative signal, and intensities of all peaks are scaled to the cubic root of the originally recorded values.

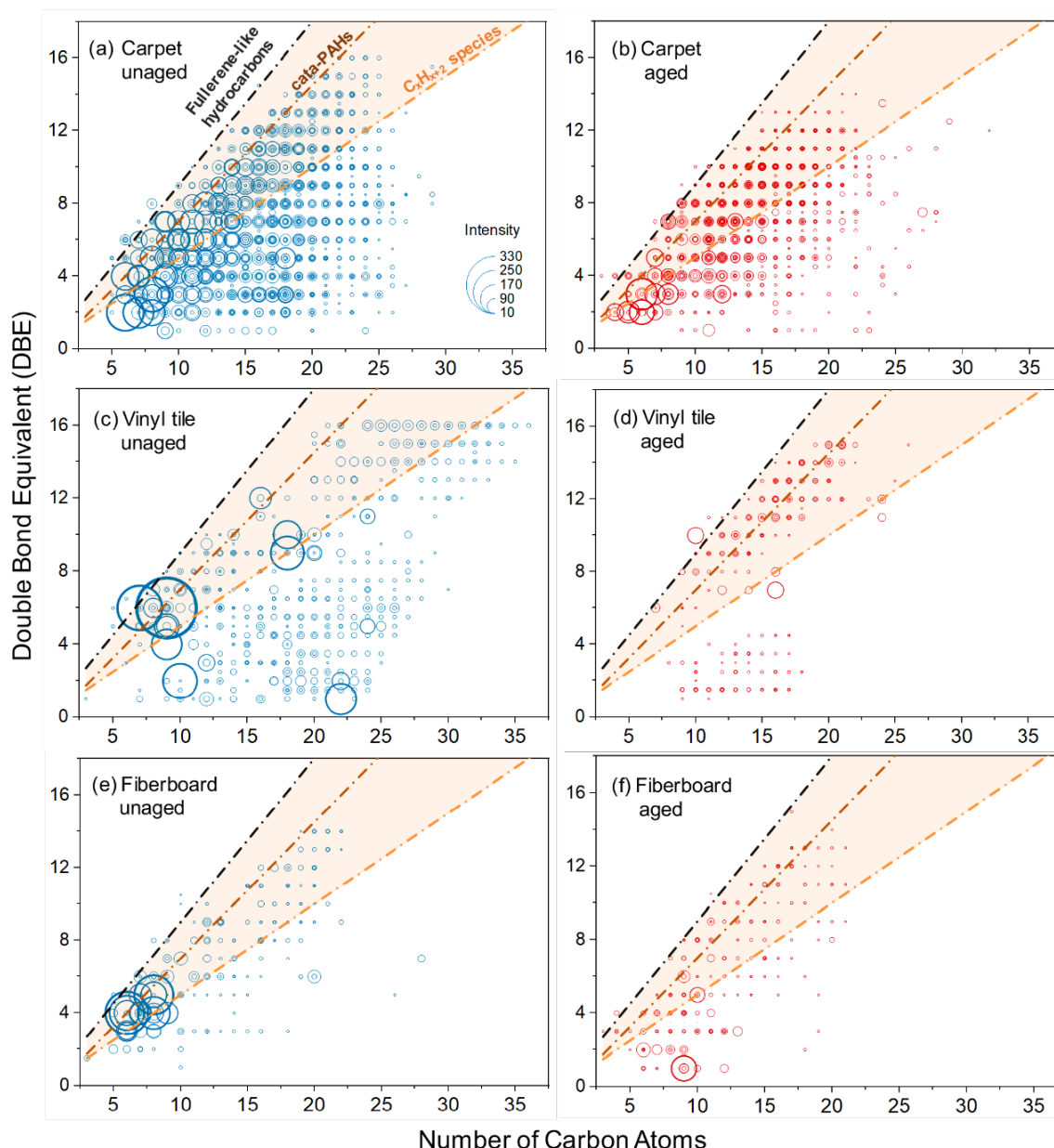


Figure 4.20. The double bond equivalent (*DBE*) values vs number of carbon atoms corresponding to the OA components affected by the photolysis reactions (i.e., those that exhibited a >10% change in relative abundance) detected in unaged (left panels) and aged (right panels) OA samples collected from pyrolysis of carpet (a-b), vinyl tile (c-d), and fiberboard (e-f) samples. Lines indicate *DBE* reference values of linear conjugated polyenes C_xH_{x+2} (orange line), cata-condensed PAHs (brown line), and fullerene-like hydrocarbons with $DBE = 0.9 \times C$ (black line).²⁷⁴ Data points inside the orange shaded area are potential BrC chromophores. Sizes of the individual points are arbitrarily scaled to the cubic root of the corresponding MS peaks intensities. Occasional datapoints located above the $0.9 \times C$ limiting line correspond to highly aromatic N-containing species.

Because efficient absorption of visible light by organic molecules requires uninterrupted conjugation of π -bonds across significant parts of their carbon skeleton, compounds with DBE/C ratio greater than that of polyenes are potential BrC chromophores,²⁰⁵ which are located in the plots within shaded areas (**Figure 4.20**). Qualitative assessment of the BrC chromophore transformations after photolysis can be inferred from visual comparison of **Figure 4.19 and 4.20** featuring differences between aged and unaged OA samples. Aged carpet, vinyl flooring, and fiberboard peaks changed by 59 %, 54 %, and 21 %, respectively, compared to the unaged peaks. For the photobleached OA sample (carpet), both the number and intensity of BrC chromophores decreased significantly after photolysis, which is consistent with the observed and commonly expected photobleaching effect. However, more complex compositional changes are observed for the photoenhanced (fiberboard) and unchanged (vinyl tile) OA samples. In both cases, there are relatively small C₆₋₉ BrC compounds with high intensity present in unaged samples, which largely disappear from the aged samples. On the other hand, formation of highly aromatic BrC chromophores of larger C₁₂₋₁₈ molecular sizes is clearly observed in the corresponding aged samples. This trend can be plausibly explained by the photochemically induced oligomerization reactions that consume C₆₋₉ monomers and form C₁₂₋₁₈ dimer BrC products with stronger absorption properties. In both cases (fiberboard and vinyl tile OA), the overall transformation of the BrC light absorption by the aged OA samples is a combined effect of the degradation of small chromophores and the buildup of the larger chromophores. Depending on the chromophore-specific light absorbing properties, the integrated BrC absorbance of the decayed and the newly formed chromophores may show either null (vinyl tile OA) or photoenhanced (fiberboard OA) effects. These observations demonstrate that

urban material BrC pyrolysis products undergo complex reaction chemistry which modifies composition of various BrC chromophores but, simultaneously, their integrated optical properties show no detectable change.

4.3.5 Additional direct photolysis experiments

Considering the lifetime of an aerosol in the lower atmosphere is not limited to a few hours, we performed additional experiments at longer time scales to see if the trends observed over our 2 h period would continue over longer times. To this end, one OA from each result category (photobleached, unchanged, and photoenhanced) was photolyzed for up to 18 hours (**Figure 4.21**). For our photobleaching material (carpet) and our unchanged material (vinyl flooring) the trends over the 18 h time scale matched those in the 2 h time scale. The visible region of the carpet OA continued to photobleach between 1 and 6 h of irradiation but the visible region of the vinyl flooring OA exhibited negligible change over the 18 h of photolysis. For both OA, the most change happened in the first 6 hours of irradiation, producing products that were no longer photochemically active.

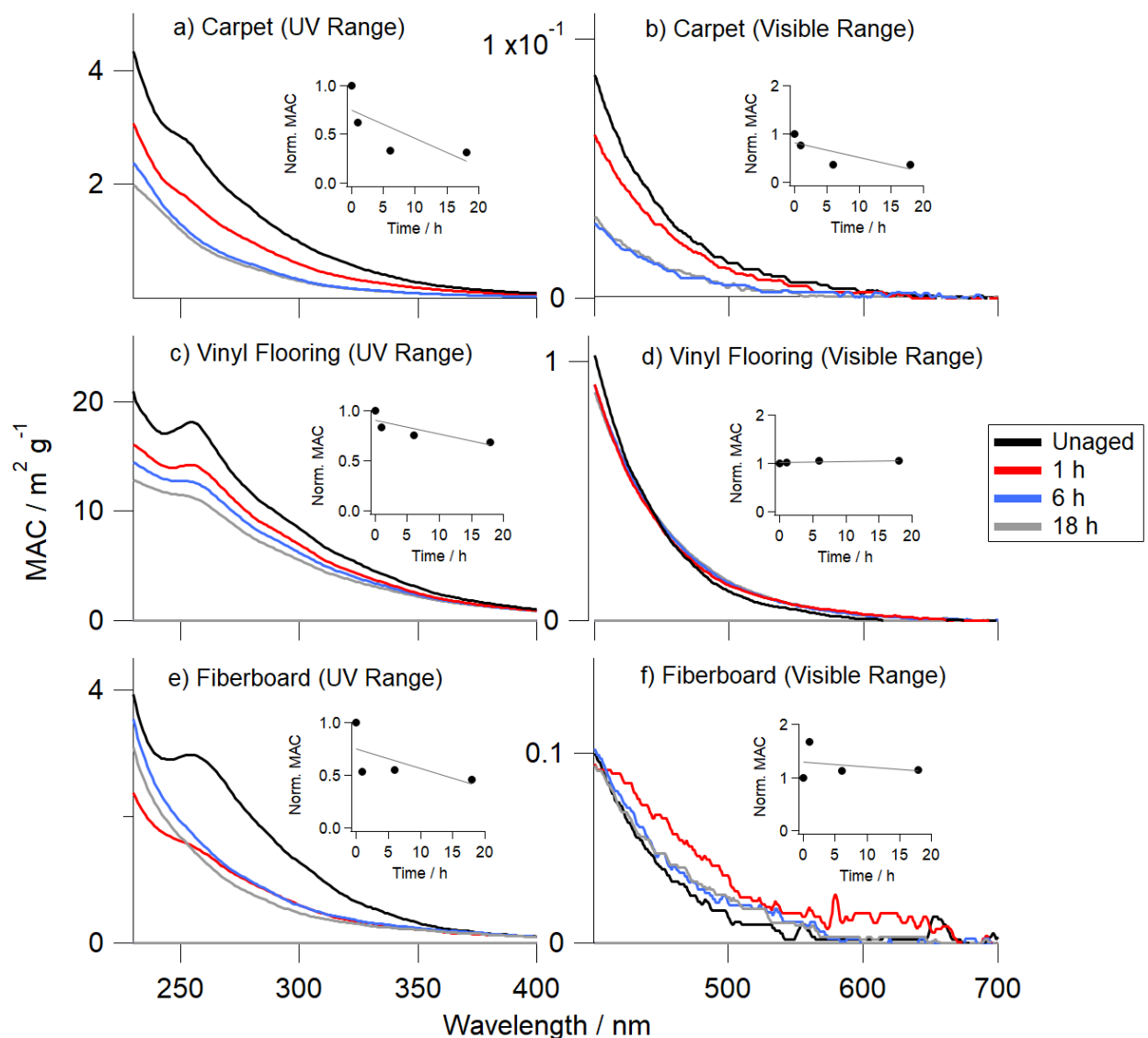


Figure 4.21. Long-term photolysis experiments. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis on Teflon filters and the subsequent extractions of carpet, vinyl flooring, and fiberboard OA (a-b; c-d; e-f, respectively). Each quarter of the filter was aged separately for 1 h (red), 6 h (blue), or 18 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging (over 5 nm range) was utilized.

In the case of the fiberboard OA (**Figure 4.20e and 4.20f**), which photoenhanced during short-term irradiation, photobleaching was observed over longer time scales. It appears that this type of OA first increases in visible absorbance and then ultimately bleaches with continued photolysis. This trend mirrors work done on heterogeneous OH oxidation of particulate BrC,²⁷⁵ aqueous phase photo-oxidation of biomass burning BrC,^{220,225} and photolysis of aqueous biomass burning BrC.^{219,220} In the case of primary BrC generated from smoldering pine wood, heterogeneous OH oxidation resulted in absorption enhancement over the first 2.5 h (followed by photobleaching),²⁷⁵ which is similar to the timeframe observed here. Once again, chromophore build up may be attributed to increased oxidation through OH reactions or oligomerization through either OH or triplet excited state reactions.^{99,276} Future work will implement mass spectrometry to identify whether the optical changes seen in this work are attributed to OH functionalization reactions or oligomerization processes.

The experiments described above relied on the filtered Xe-lamp source for driving photochemistry in the OA material. To demonstrate that actual sunlight produces similar results, we selected drywall OA, a material that exhibited significant change with photolysis, and exposed a portion of the filter to direct sunlight and another portion to flux from our photolysis set-up (**Figure 4.22**). As 1 h under our lamp was estimated to be equivalent to 0.7 h in direct sunlight, the filter portion was exposed to the lamp for 2 h and the other portion was exposed to outside sunlight for 1.4 h. Integration of the UV portion of the *MAC* (280 to 400 nm) shows that the two filter portions exhibited similar degrees of change, within 5 % (**Figure 4.22**).

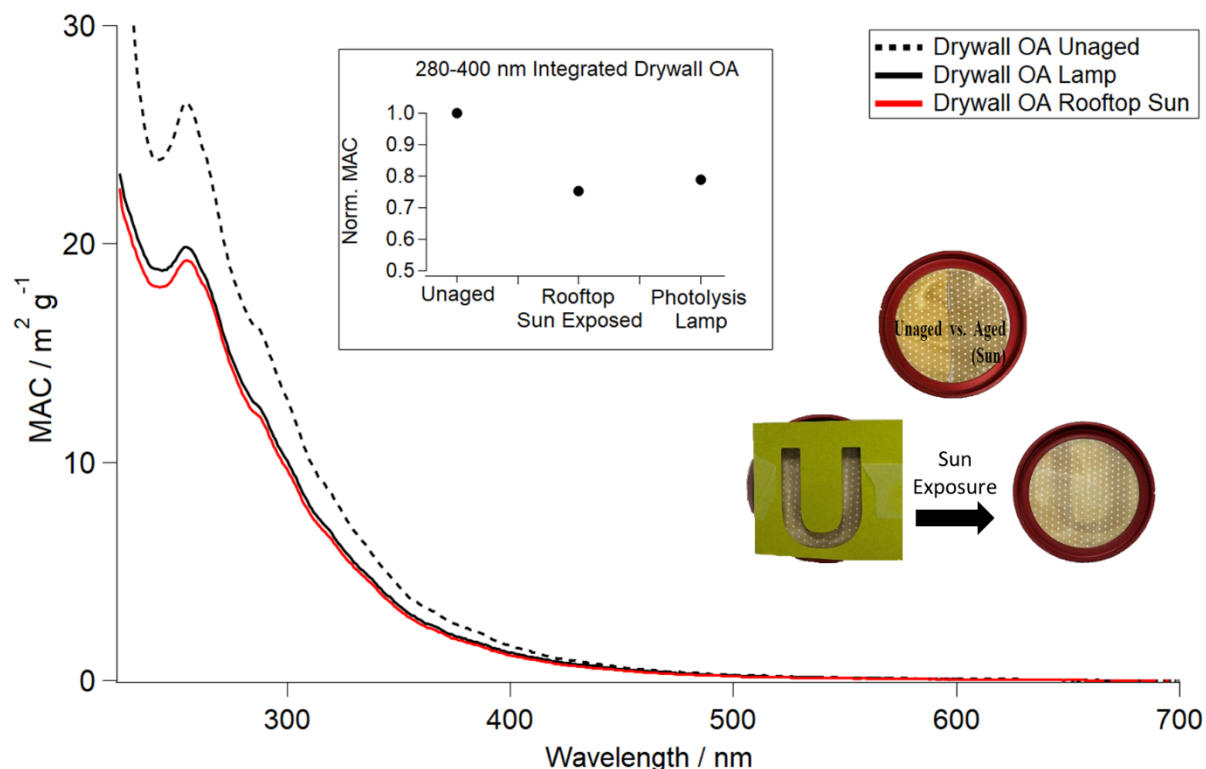


Figure 4.22. Wavelength-dependent mass absorption coefficient (MAC) values recorded for unaged and outdoor aged drywall OA sample. The unaged OA (black, dotted), drywall OA sample after photolysis using the Xenon arc lamp (black), and drywall OA sample after photolysis on the rooftop in direct sunlight (red) are shown above. The integrated MAC values (normalized to the unaged value) for the UV integrated over 280-400 nm are shown in the subplot, with the UV integrated over 280-400 nm. The drywall OA aged samples bleached similar amount, within 5% of each other. Consistent with previous laboratory drywall OA experiments, photolytic exposure darkens this urban material's pyrolysis products. This is represented in the pictures of the unaged OA vs. aged OA filter and the "U" cutout which darkened during the sunlight exposure.

4.4 Conclusions

This work explored the optical properties of OA produced from the smoldering pyrolysis of flammable urban materials and their transformations during exposure to solar UV radiation. Atmospheric aging of OA (via direct photolysis) altered the optical properties of this BrC by 1) decomposing BrC chromophores (photobleaching) or 2) producing stronger

chromophores from photooxidation of smaller molecules (photoenhancement).^{219,224,225} Plywood, ceiling tile, thick PVC coated wire, drywall, fiberboard, and lumber OA samples exhibited photoenhancement effects, whereas carpet and thin PVC coated wire OA exhibited photobleaching effects with exposure to UV light. Vinyl flooring and fabric OA remained unchanged after photolytic aging. We have observed that, on average, OA from the WUI exhibits increased absorption after UV exposure. This means that BrC from WUI fires may have stronger effect on visibility and radiative forcing as it undergoes aging in the atmosphere.

Previous work investigated the photolysis of BBOA between 0 to 16 h of irradiation and determined that photobleaching is slow due to competing aging mechanisms by heterogeneous OH oxidation.¹⁹⁹ Photolytic aging of BrC from BBOA has also been seen to have significant OH concentrations in OA extracts when no additional OH source was added.²²⁰ In the present study, we observed significant absorption enhancement of OA from the WUI over the first few hours of photolysis, indirectly suggesting that OH (and likely other free radicals) are produced in the organic phase of the particles during irradiation. To understand the chemical changes responsible for our optical observations, identification and structural characterization of WUI BrC chromophores (before and after photolysis) are needed to determine the mechanism in which this OA transforms and identify if it evolves similarly to BrC from BBOA.

CHAPTER 5:

MOLECULAR CHARACTERIZATION AND PHOTOREACTIVITY OF ORGANIC AEROSOLS FROM URBAN MATERIAL COMBUSTION AT THE WILDLAND-URBAN INTERFACE

Abstract. Fires at the wildland-urban interface (WUI) are increasing in magnitude and frequency, emitting organic aerosol (OA) with unknown composition and atmospheric impacts. In this study, we investigated the chemical composition of OA produced through the pyrolysis of ten urban materials, which were subsequently aged under UV light for 2 h. The analysis utilized ultrahigh-performance liquid chromatography (UHPLC) separation, coupled with a photodiode array (PDA) detector and a high-resolution mass spectrometer (HRMS) for molecular characterization. Hierarchical clustering analysis demonstrated that lumber-derived OA was the most diverse and distinct in composition. Unaged and aged OA (for each urban material) did not significantly differ in chemical identities. Potential aromatic brown carbon (BrC) chromophores constituted 13-42% of all assigned compounds. PDA chromatograms revealed multiple BrC chromophoric species that either photoenhanced or photodegraded with UV aging, providing insights into specific BrC chromophores responsible for photobleaching and photoenhancement of the overall absorption coefficient. Thirty-six BrC chromophores were identified across the ten OA types, and their structures were confirmed using reference standards. Components of plasticizers and resins, such as phthalic and terephthalic acids, were structurally confirmed in the samples. We present potential tracer species for WUI fires as components of resins, epoxies, dyes, and adhesives commonly used in manufacturing urban materials. Photolysis did not significantly impact the volatility of OA emitted from the burning of specific WUI materials.

5.1 Introduction

The wildland-urban interface, or WUI, is defined as the area where structures and other human developments meet or intermingle with wildland vegetation.^{67,277} In 2010, the US Forest Service estimated that 43.4 million new homes were in WUI communities, making WUI areas the fastest-growing land use type in the contiguous US.²⁷⁸ The increasing frequency of large-scale forest fires raises the risk of fire encroachment into the WUI.^{242,245} These devastating events can begin with wildfire flames directly passing into urban spaces or with embers spreading to urban structures, initiating smoldering combustion that can ultimately develop into flaming combustion.^{62,70-72} The burning of engineered construction materials can lead to atmospheric emissions not typically found in wildland fires and are poorly characterized. As global models routinely underpredict the formation, mass loadings, and temporal trends of anthropogenic organic aerosol (OA), insights into the chemical composition and atmospheric transformations of particulate matter (PM) emitted from WUI fires can help reduce these uncertainties.^{279,280}

The fuels primarily burned in WUI fires are those used in and around residential homes, commercial buildings, and other relevant structures. A typical residential house in the United States is constructed, on average, from ~97% wood and ~2% asphalt shingles (by weight), whereas its interior contents range from ~40-90% wood, ~12-26% plastic, and ~0-20% fabric.⁶⁷ Common building materials include insulation (made from polyurethane, polyisocyanurate, glass wool, and phenolic foams), vinyl siding, polyvinyl chloride (PVC) windows, upholstery on furniture, vinyl and polyamide carpets, electrical wiring insulation (typically PVC), acrylic clothing, and furniture.⁷³⁻⁷⁵ Although these materials are vastly different from biomass, they undergo similar thermal decomposition stages, emitting both

PM and volatile organic compounds (VOCs).⁷³ During the combustion of traditional wooden materials, polycyclic aromatic hydrocarbons (PAHs) and their derivatives can be emitted, which contribute to light absorption by aerosol particles, thus impacting air quality and climate.^{109,281} Chemically treated wooden materials are common in WUI spaces, but their combustion emission characteristics are unknown. The combustion of PVC and other plastics is known to emit halogenated organics, such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans, which are toxic.^{282,283} Emissions of halogenated organics leads to significant increases in atmospheric concentrations of chlorine and hydroxyl radicals ($\text{Cl}^\bullet$ and $^\bullet\text{OH}$, respectively). Attention has been drawn to plastic burning,²⁸⁴ as halogen-containing aerosols can have climate implications; however, organic emissions from these materials have been understudied, and their impacts remain unclear. Additionally, in terms of human health, WUI fires pose a great risk to PM and VOC exposure because of their proximity to residential communities and first responders at the scene.

Studies have examined the emissions, transportation, and aging processes of OAs produced during the combustion of biomass fuels in regions such as Western North America, Siberia, Amazonia, and Central Africa.^{192,285–292} The pyrolysis of biomass, which contains biopolymers like lignin, cellulose, and hemicellulose, is well understood to produce phenolic compounds (such as catechol, guaiacol, and coniferaldehyde), organic acids (like benzoic acid and salicylic acid), furans, coumarins, flavonoids, and stilbenes. Some of these compounds contribute to brown carbon (BrC) because they absorb light.^{30,61,293,294} Nitrogen-containing aromatic compounds (NACs), specifically nitrophenols (such as 4-nitrocatechol and 2,4-dinitrophenol) strongly absorb light at UV and visible wavelengths and are common BrC chromophores in biomass burning organic aerosol (BBOA).^{43,105,113,199,205,214,295–298}

BrC compounds are known to undergo photochemical transformations during atmospheric transport, exhibiting both photoenhancement and photobleaching behaviors.^{96,199,214,237,299} Certain physicochemical properties, such as molecular weight, structural composition, volatility, and oxidation state, have been shown to correlate with BrC absorption characteristics and stability with respect to UV exposure.^{30,260,261,300} For example, Di Lorenzo *et al.* examined BBOA field samples and found that higher molecular weight chromophores (>500 Da) exhibited the majority of absorption, while smaller molecular weight fractions were more susceptible to photobleaching degradation.³⁰¹ Calderon-Arrieta *et al.* examined the change in BrC bulk absorption as a function of thermal evaporation of volatile components.³⁰² Upon evaporation, samples darkened, and molecular characterization demonstrated that small, oxygenated, less-absorbing monoaromatic compounds were depleted, whereas large and less polar substituents remained.³⁰² Neither the physiochemical properties nor the molecular evolution as a function of UV exposure are well understood for OA produced through the combustion of urban construction materials, thus prompting this pilot study.⁶⁷

Previously, we found that OAs from pyrolyzed urban materials exhibited distinct optical absorption properties, each responding differently to photolytic aging.²¹² Of the ten different types of investigated OA, two photobleached, two remained unchanged, and six underwent photoenhancement after 2 h of UV exposure.²¹² The goal of this follow-up study was to investigate the molecular composition of OA in both unaged and photochemically aged samples from Hopstock *et al.*²¹² Additionally, our goal was to identify both common and unique BrC chromophores responsible for absorption in each pyrolyzed urban material and to propose potential tracer compounds characteristic of emissions from the WUI. Our

approach relied on ultrahigh-performance liquid chromatography (UHPLC) separation, coupled with a photodiode array (PDA) detector and a high-resolution mass spectrometer (HRMS) for molecular characterization. This investigation provides molecular insights into the light absorption properties of PM emissions from WUI fires and, for the first time, explains how OA molecular composition transforms during atmospherically relevant photolytic exposure.

5.2 Methods

5.2.1 Generation of Urban Material OA

The ten urban materials from Chapter 4 were selected to represent structural and furnishing components commonly combusted in urban fires.²¹² These include carpet, electrical 23 AWG wire (purple PVC coating, referred to as “thin PVC wire”), vinyl flooring, synthetic fabric, plywood, ceiling tile, electrical 12 AWG wire (with white PVC coating, referred to as “thick PVC wire”), drywall, fiberboard, and lumber. All pyrolyzed OA samples that were analyzed with HRMS in the present chapter were the subject of the optical classification paper by Hopstock *et al.* (2023).²¹² Details on urban material pyrolysis, emission factors, OA collection, and photolysis experiments can be found in detail in the previous work.²¹² As described in Chapter 4,²¹² ten urban materials were pyrolyzed, separately, in a Thermolyne F21135 tube furnace under a constant flow of N₂ at 600 °C. Generated smoke was passively pushed through the quartz combustion tube and Teflon tubing onto PTFE 47 mm filters (Millipore Sigma, Fluoropore Membrane Filter, FGLP04700, 47 mm, 0.22 µm pore size). Each Teflon filter was weighed using a Sartorius ME5-F

microbalance (± 1 ug precision) and OA mass loading ranged from 1.5 to 11 mg. These mass loadings were used to adjust concentration of the filter extract to keep them approximately equal for HRMS analysis (about 1 mg mL⁻¹ of dissolved OA in the final DMSO extract). To prevent contamination between pyrolysis experiments, the internal quartz tube was rigorously cleaned with orgmix (acetonitrile, dichloromethane, hexane 2:2:1 by volume), water, and isopropanol, and then dried using clean air. A flow of N₂ was used to purge all clean air from the quartz tube prior to beginning each pyrolysis run. Teflon tubing connecting the furnace quartz tube outlet to the filter holder was replaced with new tubing prior to switching in between urban materials to minimize the amount of carry-over.

Each filter was cut into quarters. Filter quarter was irradiated using a Xenon arc lamp (Newport Model 66902) with most of the radiation between 280-400 nm. 0 h (unaged) and 2 h OA samples were used in the HRMS analysis in this paper. OA solutions were then rotary evaporated to near dryness and frozen until HRMS studies could be conducted. This HRMS study only utilized data collected for the unaged and 2 h aged samples. Samples that underwent 2 h of photolysis will be referred to as “aged” from here on out.

5.2.2 UHPLC-PDA-HRMS Sample Preparation and Analysis

Prior to HRMS analysis, the previously irradiated and frozen urban material OA were brought to room temperature, and then dissolved in dimethyl sulfoxide (DMSO; Millipore, > 99.9 % purity) in order to achieve a good level of solubility across all urban materials.²⁰⁵ This mass loading was chosen to yield sufficiently high PDA and mass spectrometry signal for all materials tested. Insoluble residues within the extracts were removed by filtering through nylon membrane syringe filter discs (0.2 μ m, Merck Millipore) that were prewetted with

fresh DMSO. To recover remaining analytes, fresh DMSO was then used to rinse the extraction vial and this extract was also filtered through a nylon membrane syringe filter. The final OA concentration for each urban OA extract was about 1 mg mL⁻¹.

Urban material OA extracts were analyzed with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high-resolution mass spectrometer (UHPLC-PDA-HRMS). This platform allows for BrC chromophores to be separated, while taking a full UV-Vis absorption spectrum at each retention time. The separation was performed on a reverse-phase column (Luna Omega Polar C18, 150 x 2.1 mm, 1.6 µm particles, 100 Å pores, Phenomenex Inc.) which has higher retention of nonpolar compounds and, subsequently, elutes more polar compounds earlier in the run. The column compartment temperature was held at 30 °C. An injection volume of 10 µL was used for all samples. The autosampler box was kept at 23 °C to avoid DMSO freezing below 19 °C.

The eluent flow was 0.3 µL min⁻¹ and consisted of water (Optima LC/MS grade, Fisher Chemical) acidified with 0.1 % v/v formic acid (solution A) and acetonitrile (Optima LC/MS grade, Fisher Chemical) acidified with 0.1 % v/v formic acid (solution B). Formic acid was added to the mobile phase systems to enhance retention of organic acids on the C18 column and assist in protonation/detection of sample analytes in the positive ionization mode. A 45 min LC gradient adapted from Siemens *et al.* (2022) was employed in this study.³⁰³ The LC gradient was: 0-3 min (5 % B); 3-25 min linear ramp to 100 % B; 25-35 min held at 100 % B (the length of 5 column passes of acetonitrile to remove any nonpolar components still retained by the column); 35 min return to 5 % B and held until 45 min in preparation for the

next run. UV-vis absorption spectra were collected continuously by the PDA in a wavelength range of 190-680 nm at an acquisition frequency of 5 Hz and a 4 nm effective bandwidth.

Eluting analytes were ionized using heated electrospray ionization (HESI) operating in both positive (+) and negative (-) modes. Mass spectra were recorded for the m/z range of 100-1500 Da at a mass resolving power of 140,000 at m/z 200. Mass calibration was performed using commercial calibration solutions containing caffeine, MRFA, and Ultramark 1621 (Thermo Scientific, PI-88323 and PI-88324). The parameters of HESI ionization source were as follows: -2.5 kV (in (-) mode) and 4 kV (in (+) mode) spray voltages, 250 °C capillary temperature, 250 °C probe heater temperature, S-Lens ion funnel RF level 30, 80 units of sheath gas (nitrogen) flow, 10 units of auxiliary gas (nitrogen) flow, and 8 unit of sweep gas flow.

It should be noted that while DMSO worked well to extract the samples, it created complications within the LC system. We found that over time, repeated injection of DMSO samples caused the swelling of Peek tubing and subsequent pressure increases within the LC column. In addition, a subset of OA components that were soluble in DMSO but not soluble in water/acetonitrile precipitated in the guard column, further increasing pressure in the column. Besides pressure increases, residual DMSO was present in ionization source even after rigorous flushing and cleaning with methanol. Despite these issues, we elected to continue using DMSO to detect as many OA compounds as possible. We do not recommend using DMSO in future studies, however.

5.2.3 HRMS Data Analysis

Raw UHPLC-PDA-HRMS data were initially viewed using Thermo Scientific Inc. Xcalibur software. Subsequently, an open-source Mzmine 3.9 code was used to perform peak picking, peak deconvolution, extracted ion chromatogram construction, peak smoothing, and ^{13}C isotope filtering.³⁰⁴ Raw Xcalibur data were imported into Mzmine and low intensity peaks were filtered out using a minimum ion intensity of 10^4 . The mass detection was performed for separation occurring within 3-25 min using centroided data. The “ADAP chromatogram builder” function was used to build extracted ion chromatograms with threshold parameters of 5×10^5 (minimum peak height) and tolerance of 0.001 m/z . For reference, maximum signal intensity was 10^9 for both ionization modes. Full width half maximum thresholds and noise levels of chromatograms varied amongst urban OA samples and BrC standards.

Molecular formulas were assigned similarly to previous work.^{48,188} Extracted ions were assumed to be $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, and $[\text{M} - \text{H}]^-$ ions. For the purposes of this work, the formula assignments were restricted to compounds containing $\text{C}_c\text{H}_h\text{O}_{0-40}\text{N}_{0-6}$ (c and h were unrestricted) with an accuracy of ± 0.001 m/z units. Additionally, a single Na atom was allowed for assignments of MS features detected in ESI(+). The assigned ion formulas were corrected for the ionization mechanism and all HRMS results below are reported as formulas of neutral OA compounds. Metrics of UHPLC-separated urban OA components were calculated using neutral CHON elemental formulas as shown below. The double bond equivalent (*DBE*) was calculated according to **Equation 5.1**.

$$DBE = n_c - \left(\frac{n_H}{2}\right) + \left(\frac{n_N}{2}\right) + 1 \quad \text{Equation 5.1}$$

The assigned molecular formulas (CH, CHO, and CHON) from the HRMS data were used to determine the volatility distribution of compounds found within unaged and 2h aged urban OA. The volatility was calculated based on parameterizations of pure compound saturation mass concentration (C_0) by elemental composition reported in Li *et al.* (2016) for CH, CHO, CHON compounds using **Equation 5.2**.³⁰⁵

$$\log_{10}C_0 = (n_C^0 - n_C)b_C - n_O b_O - 2\left(\frac{n_C n_O}{n_C + n_O}\right)b_{CO} - n_N b_N \quad \text{Equation 5.2}$$

where:

- n_C^0 is the reference carbon number
- n_C , n_O , and n_N denote the assigned numbers of carbon, oxygen, and nitrogen atoms, respectively
- b_C , b_O , and b_N denote the contribution of each atom to $\log_{10}C_0$
- b_{CO} is the carbon-oxygen nonideality

Table 5.1. Values utilized in volatility predictions based on assigned chemical formula.^{305,306}

Assigned Compound	n_C^0	b_C	b_O	b_{CO}	b_N
CH	23.80	0.4861	-	-	-
CHO	22.66	0.4481	1.656	-0.7790	-
CHON	24.13	0.3667	0.7732	-0.07790	1.114

The volatility basis set (VBS) framework method segments the volatility spectrum of OA components into distinct bins. It is utilized to describe the entire range of saturation vapor pressures within a system. Individual species (i) were grouped into a series of $(\log C_0)_j$ bins, where (j) represents individual bins marked by integer values (e.g., 4, 3, 2 etc., corresponding to the upper bin boundaries), determined by their iC_0 values (Equation 5.2).

HRMS peak abundances (from the 3-25 min integrated chromatograms) of all observed ions falling within each volatility bin were summed. The relative heights of VBS bins were calculated using the normalized peak abundances (equal to 100%) for each OA sample. Procedures for the calculation of gas-particle partitioning ratios within VBS distributions (at various total organic mass loadings) can be found in Xie *et al.* (2024).³⁰⁷

5.2.4 BrC Standards

A one hundred component BrC standard mixture was obtained from the University of North Carolina (UNC), Chapel Hill and was used to verify BrC structural assignments in the urban OA UHPLC-PDA-HRMS results. This standard mixture was described in detail in Moschos *et al.* (2024) but, briefly, CHO and CHON species were selected for the mixture as they are known to be BrC species emitted during biomass burning events.²⁹¹ The individual BrC components were dissolved in methanol, but for UHPLC-PDA-HRMS analysis, the standard mixture was diluted with water (Optima LC/MS grade, Fisher Chemical) to achieve a final concentration of 0.3 mg mL⁻¹. The injection volume, LC gradient, ionization parameters, and MS settings were the same as urban OA samples described previously. The standard mixture was run with ESI in both ionization modes. As was the case with the analytical platform described in Moschos *et al.*, our results exhibited distinct retention times for structural isomers (due to polarity differences).²⁹¹

5.2.5 Compound Discover and mzVault Library Integration

Compound Discover 3.3.200 SP3 (Thermo Fisher Scientific Inc.) relies on both locally built and online libraries for unknown data processing and interpretation. The pre-built

workflow template, “Environmental w Stats Unknown ID w Online and Local Database Searches” was modified to suit the needs of our study. A customized mzVault 2.0 (Thermo Fisher Scientific Inc.) library was manually created by uploading MS2 spectra for each observable compound in the mixture of BrC standards. This library was imported into Compound Discover using the “Search mzVault” node. When cross referencing each urban OA sample with the mzVault library, Compound Discover was set to use the following parameters: match ion activation type, match ion activation energy, precursor mass tolerance of 5 ppm, and retention time tolerance of 0.2 min (to accommodate drifts in LC retention time amongst samples and BrC standard runs). Species identified in this manner will be referred to as *structurally identified species* from here on out.

To give us more insight into these urban OA samples, Compound Discover was set to search mzCloud (mass spectral fragmentation library) then correlate results with mzLogic. This data analysis algorithm filled in the gaps to provide possible candidates for unknown species when a species was not identified with the customized mzVault library. Additionally, the workflow allowed search of the ChemSpider database to find more potential compound identities. Species identified in this manner have proposed molecular structures that will be referred to as *tentatively assigned species* from here on out. Compound Discover’s statistical tools were also deployed in our analysis of urban OA.

5.3 Results and Discussion

5.3.1 Overall characteristics of urban material OA

Figures 5.1 and 5.2 present the total ion chromatograms (TICs) for all the unaged urban OA as collected in the positive and negative ionization modes, respectively. A few large peaks stood out in the TICs, for example: the $C_6H_{11}ON$ peak (6.76 min) present in ESI(+) for all urban material OA (except lumber); $C_8H_6O_4$ peak (8.36 min) largely present in ESI(+/-) for thin PVC wire OA, identified with a standard as phthalic acid; $C_8H_6O_4$ peak (8.64 min) in ESI(-) for vinyl flooring OA, identified as terephthalic acid; $C_{24}H_{44}O_4N_4$ peak (10.16 min) in ESI(+) for all OA except carpet and lumber; and $C_{18}H_{33}O_3N_3$ peak (11.29 min) in ESI(+) for all OA except carpet, fiberboard, and lumber. Several smaller peaks were present in chromatograms, often merging in unresolved “lumps” of peaks. The complexity of TICs, especially evident in **Figure 5.2**, required the use of peak deconvolution software (Mzmine and Compound Discover) to explore features in greater depth.

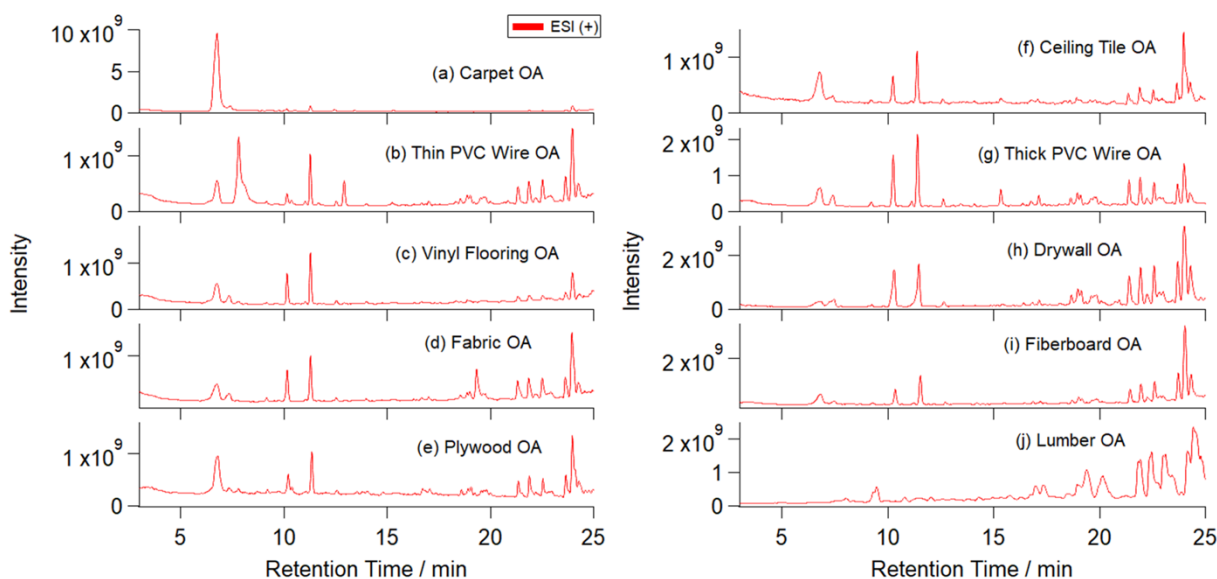


Figure 5.1. UHPLC-ESI total ion chromatograms collected in the positive ionization mode for the unaged ten urban OA samples (panels a-j). Notable peaks include: $C_6H_{11}ON$ peak (6.76 min) for all urban material OA (except lumber); the $C_8H_6O_4$ peak (8.36 min) largely present in thin PVC wire OA (b), identified with a standard as phthalic acid; the $C_{24}H_{44}O_4N_4$ peak (10.16 min) for all OA except carpet and lumber; and the $C_{18}H_{33}O_3N_3$ peak (11.29 min) in all OA except carpet, fiberboard, and lumber.

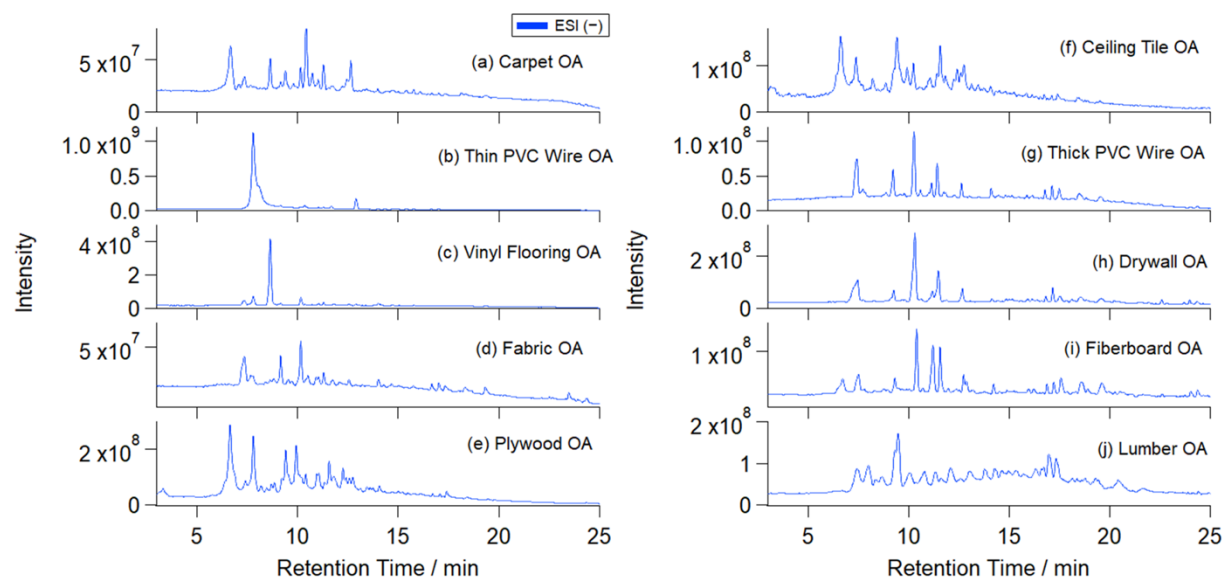


Figure 5.2. UHPLC-ESI total ion chromatograms collected in the negative ionization mode for the unaged ten urban OA samples (panels a-j). Notable peaks include: the $C_8H_6O_4$ peak (8.36 min) largely present in thin PVC wire OA (b), identified with a standard as phthalic acid; and the $C_8H_6O_4$ peak (8.64 min) in vinyl flooring OA (c), identified as terephthalic acid.

As the TICs were comprised of many peaks, many of which exhibited isomeric species with coelution, we started with a broad comparison of urban OA using the Compound Discover software. This tool allowed us to create statistical comparisons as shown in the ESI(+) hierarchical clustering in **Figure 5.3** and ESI(+/-) principal component analyses (PCA) in **Figure 5.4**. Each horizontal line in **Figure 5.3** represents a compound detected by the software in at least one of the urban OA samples, with darker purple colors exhibiting highest normalized intensity across all 20 sample/ionization mode combinations. Lumber OA (both unaged and aged) exhibited the greatest concentration of peaks, which were clustered together furthest away from other OA types. This clustering behavior of lumber OA was also evident in the PCA plots for both ionization modes in **Figure 5.4**, indicating that this sample type was the most statistically different from the other urban materials. Although lumber and plywood were the two urban OA types expected to most resemble BBOA and each other, they exhibited minor correlation. OA from more synthetic materials (ceiling tile, thin PVC wire, and vinyl flooring) showed the least number of peaks but resembled one another in convolution. Overall, **Figure 5.3** and **5.4** suggested that the unaged and aged OA (for each urban material) were not significantly different in chemical identities. However, when comparing urban OA types, there was little overlap in chemical identity as one moves across the rows in **Figure 5.3**. As shown in both panels in **Figure 5.4**, unaged and aged OA were most similar for fiberboard, thick PVC wire, thin PVC wire, and vinyl flooring.

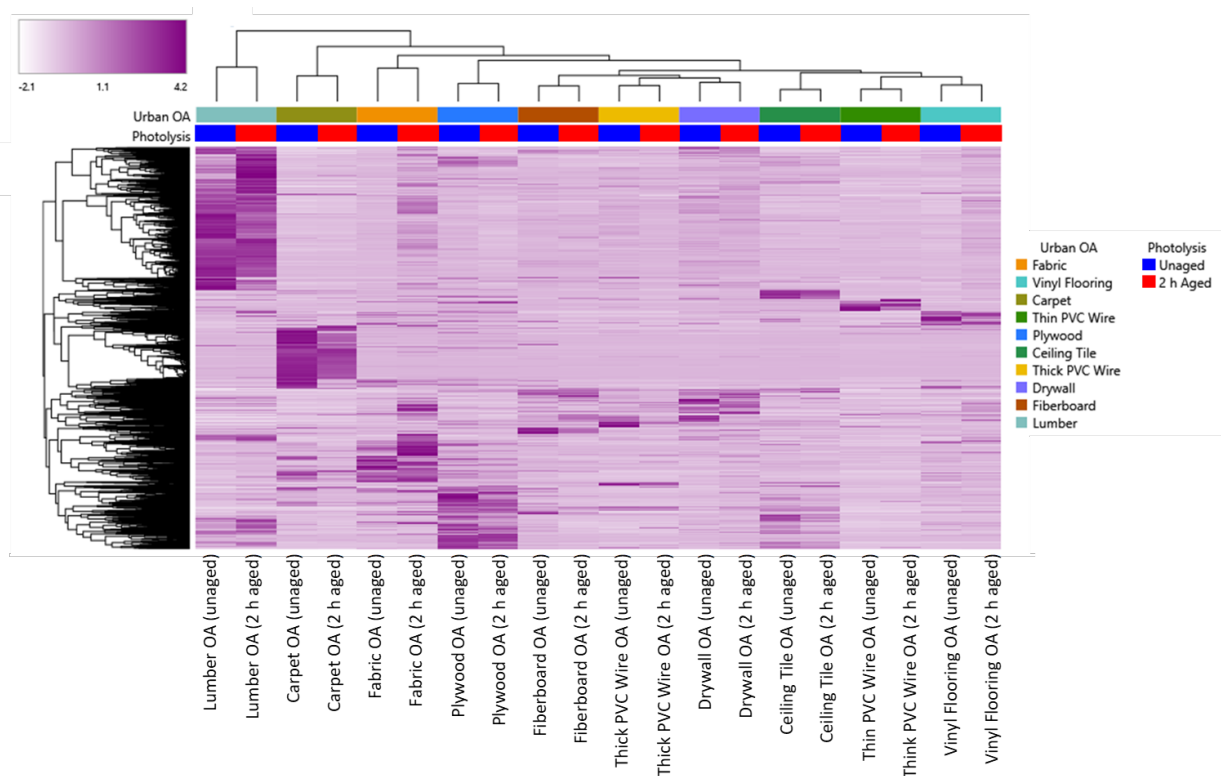


Figure 5.3. Hierarchical clustering of ESI(+) mass spectral species deconvoluted and identified using Compound Discover 3.3.200 SP3 software (Thermo Fisher Scientific). Columns represent urban OA samples (both unaged and aged). Rows denote individual compounds (assigned with CH, CHO, and CHON molecular formulae) and are scaled using unit variance. The total number of rows (or compounds) detected across all 20 samples was 6509. The distance between clusters (top and left) is based on the correlation distance and average linkage for both rows and columns. The color gradient, ranging from white to purple, represents the abundance of each compound using standardized matrix values.

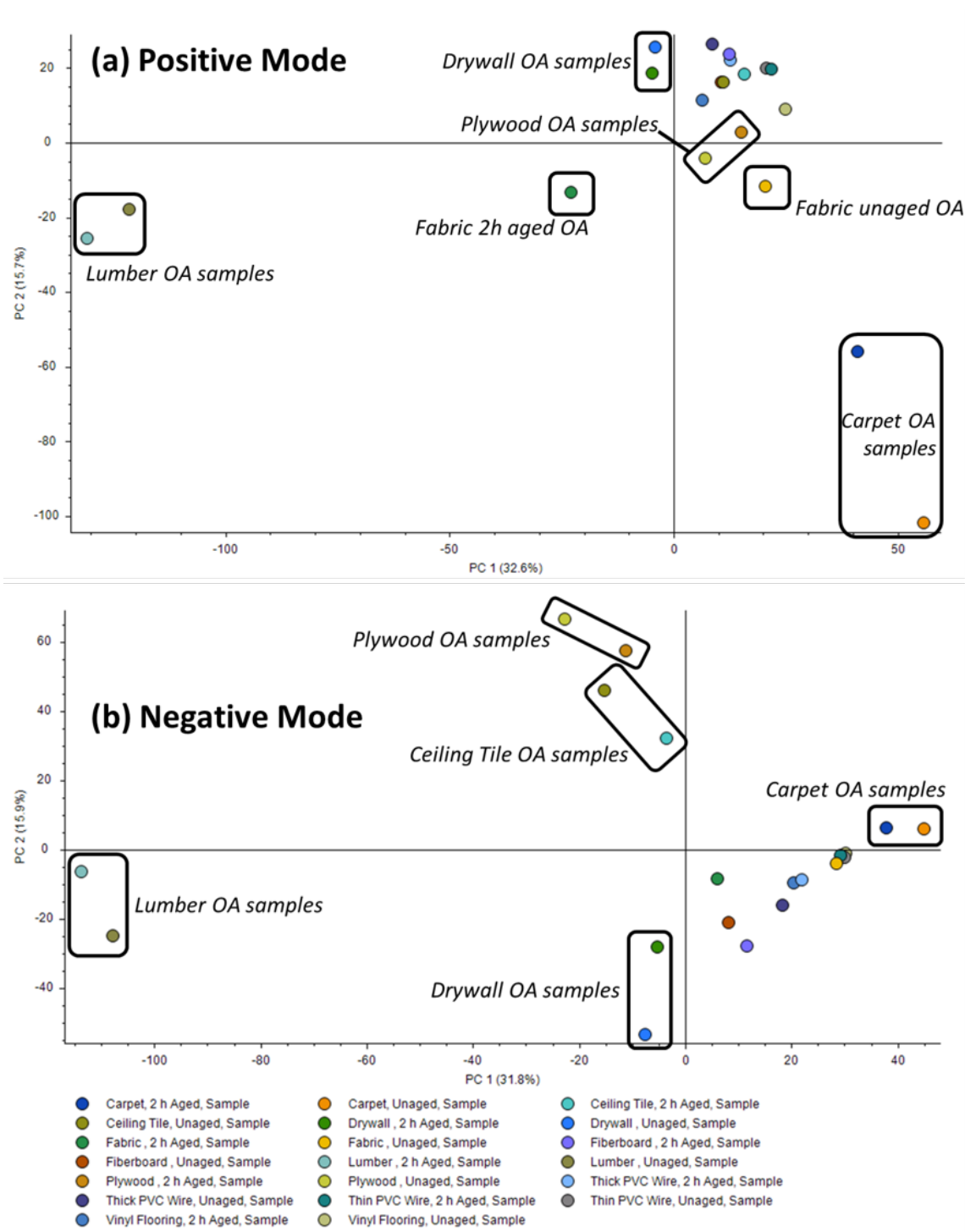


Figure 5.4. Principal component analysis of all 20 urban samples (unaged and aged) run in the positive mode (panel a) and negative mode (panel b). Statistical comparison was performed by the Compound Discover program. Outlier samples are boxed for ease of comparison.

5.3.2 Effects of UV aging on light absorbing species

PDA chromatograms showcased the photobleaching and photoenhancement classifications previously made for these urban OA samples.²¹² In **Figure 5.5** (panels a and b), carpet OA exhibited a reduction in absorbance after UV aging for benzoic acid (the most intense chromophore), $C_{12}H_{22}ON_2$ (13.3 min), and $C_{16}H_{22}O_4$, $C_{16}H_{31}ON$, $C_{18}H_{33}ON$, and $C_{16}H_{33}ON$ (20-24 min). Fiberboard OA (**Figure 5.5c,d**) exhibited the opposite trend. Though major confirmed species (catechol and terephthalic acid) decreased in maximum absorbance, the overall absorbance between 6-23 min increased from 20% (**Figure 5.5c**) to 40-80% relative intensity (**Figure 5.5d**) after UV aging. A 2D representation of PDA chromatograms exhibiting photobleaching and photoenhancement (for thin PVC wire OA and lumber OA, respectively) can be found in **Figure 5.6**. For thin PVC wire OA, the two largest PDA peaks, attributed to phthalic acid and its structural isomer, exhibited a reduction in absorbance between 300-400 nm after photolytic aging (red dashed line, **Figure 5.6b**). On the contrary, absorbance in the lumber OA (**Figure 5.6d**) sample had a factor of 2 increase between 300-400 nm after aging, particularly towards the end of the LC run when more nonpolar species were eluted. Both thin PVC wire and lumber OA weakly absorbed light in the visible wavelength range (**Figure 5.6a,c**).

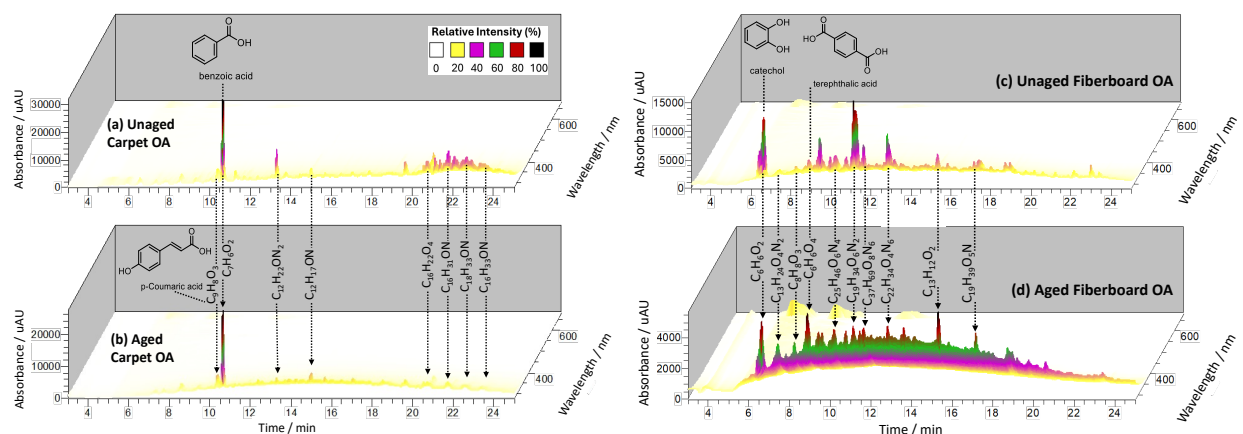


Figure 5.5. BrC chromophores present in the carpet and fiberboard OA samples before (a and c) and after UV aging (b and d), respectively. Benzoic acid, p-coumaric acid, catechol, and terephthalic acid were structurally identified with standards. Note that the maximum absorbance value in each panel is different. As classified in Hopstock *et al.* (2023),²¹² carpet OA exhibited photobleaching and fiberboard OA exhibited photoenhancement after UV aging.

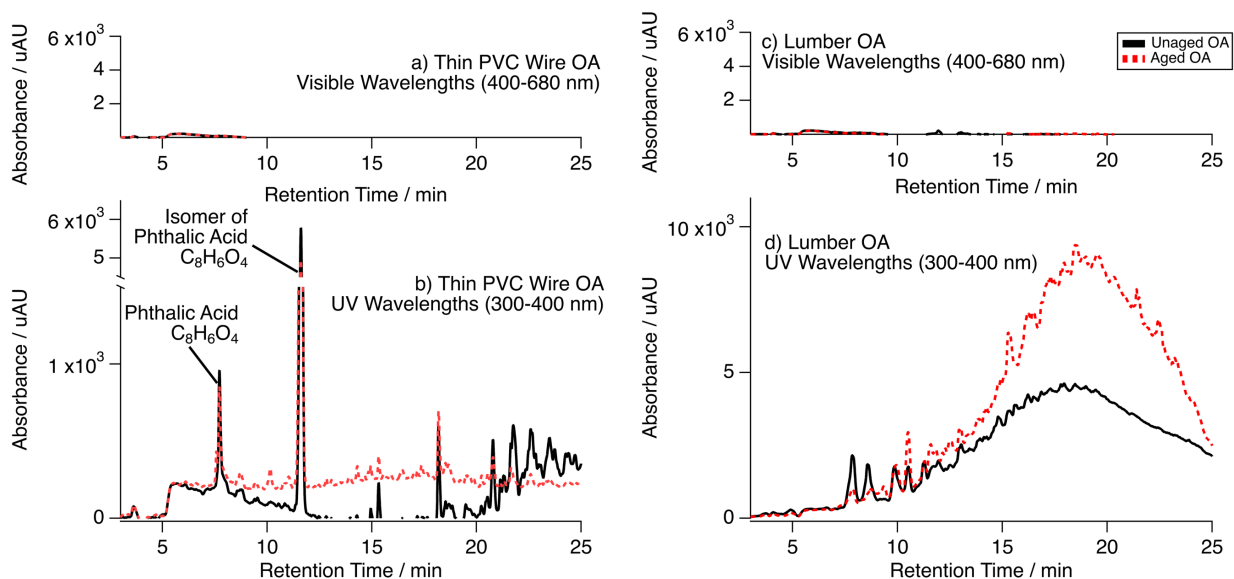


Figure 5.6. Photodiode array detector (PDA) chromatograms of thin PVC wire and lumber OA. Unaged spectra are presented in black and aged spectra are presented in red. The PDA signal integrated over UV wavelengths (300-400 nm) is plotted separately from visible wavelengths (400-680 nm). Thin PVC wire OA (a and b) and lumber OA (c and d) were selected to showcase PDA response to cases of photobleaching and photoenhancement, respectively.

Figure 5.7 presents vinyl flooring OA, which was previously classified as an urban OA type that did not exhibit greater than a 10% net absorbance change in the UV or visible wavelength ranges after photolytic aging.²¹² Terephthalic acid, the main light absorbing species in unaged vinyl flooring OA, decreased in intensity by a factor of 3 after aging. More nonpolar and nitrogen-containing species eluted between 17-25 min and increased in relative absorbance intensity after aging. These transformations in combination counteracted each other, and thus resulted in the “no change” overall optical classification. For all cases discussed, the bulk of absorption occurred at UV wavelengths and slight increases were observed in the visible wavelength regions upon aging. These observations were consistent with the absorption measurements taken in our previous work and the general definition of BrC.^{30,212}

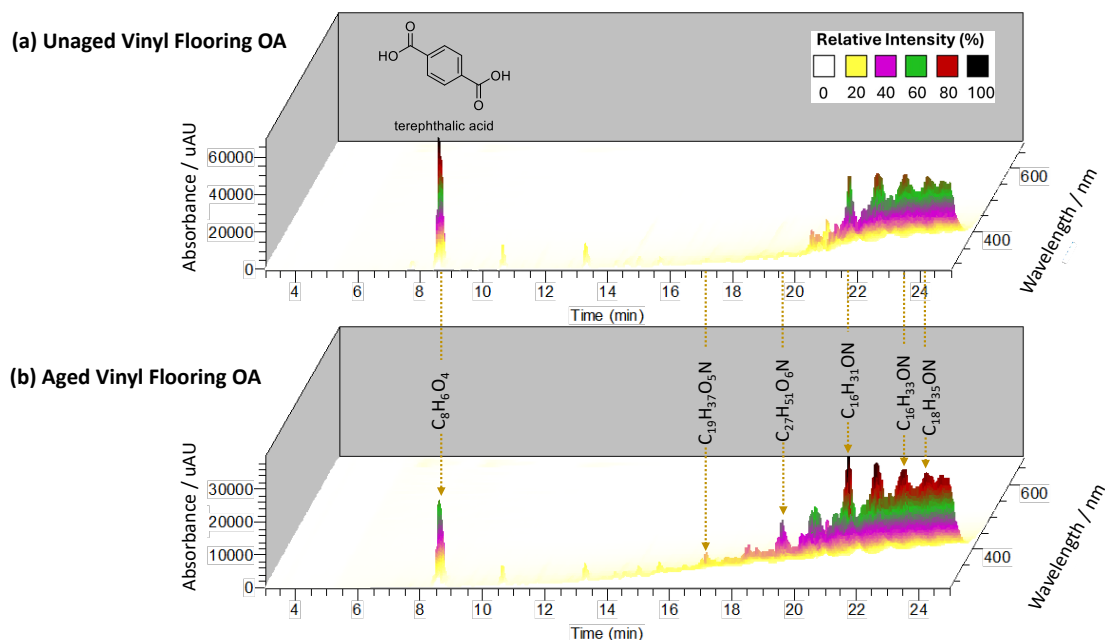


Figure 5.7. BrC chromophores present in the vinyl flooring OA sample before (a) and after UV aging (b). Terephthalic acid was verified with an internal standard. Note that the maximum absorbance value in each panel is different. As classified in Hopstock *et al.* (2023),²¹² vinyl flooring OA exhibited no net change in the overall absorbance after aging.

Figure 5.8 displays DBE as a function of the number of (C + N) atoms calculated for assigned CH, CHO, and CHON species in the unaged (blue) and aged (red) carpet, vinyl flooring, and drywall OA. The remaining urban OA can be found in **Figures 5.9** and **5.10**. DBE represents the total number of rings and π -bonds within an assigned species. The dashed reference lines illustrate the BrC relevant space, with the upper bound representing fullerene-like hydrocarbons ($\text{DBE} = 0.9 \times \text{C}$) and the lower bound representing linear polyenes C_xH_{x+2} ($\text{DBE} = 0.5 \times \text{C}$).^{205,291,303} Organic molecules that efficiently absorb light tend to have an uninterrupted conjugation of π -bonds across significant parts of the molecular structure.^{205,308} Fullerene-like hydrocarbons exhibit the most conjugation and potential for light absorption,³⁰⁹ and linear polyenes can be reasonably strong absorbers in select cases (for example, retinal has an orange color). Therefore, species with $\text{DBE}/(\text{C} + \text{N})$ ratios that fall within the reference lines are potentially aromatic and can act as BrC chromophores.^{111,303,308} **Figures 5.8-5.10** demonstrated the presence of BrC compounds for all ten urban OA types with $\text{DBE}/(\text{C} + \text{N})$ ratios greater than the linear polyenes limit. Across all urban OA samples, between 13-42% of all assigned compounds (by number) were potential aromatic BrC chromophores. All cases exhibited a sizeable fraction of compounds beneath the linear polyenes reference line, which were not likely to be chromophoric species.

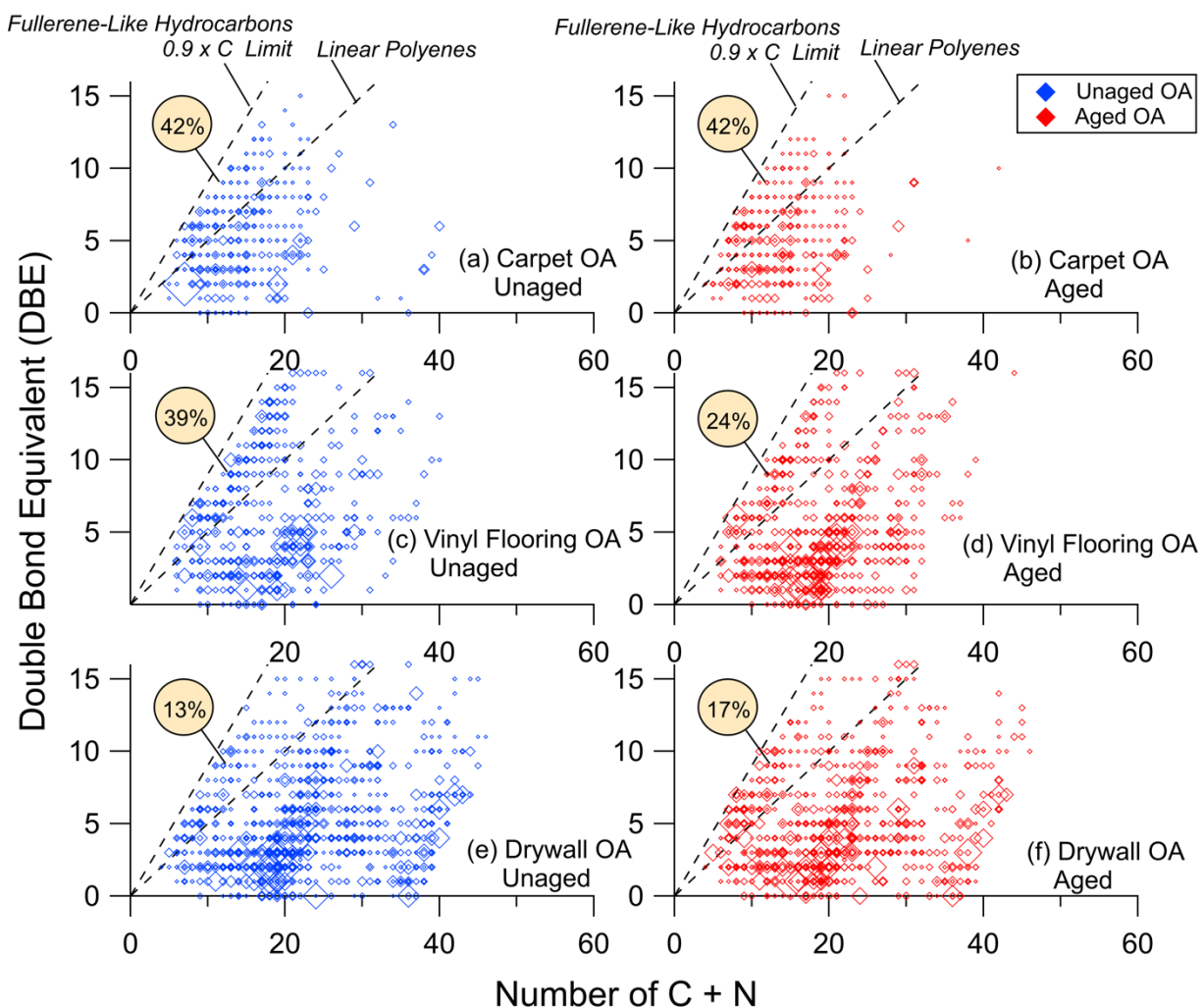


Figure 5.8. Plot of double bond equivalent (*DBE*) versus number of carbon and nitrogen (*C* + *N*) atoms from assigned urban OA unaged and aged species in carpet (a and b), vinyl flooring (c and d), and drywall (e and f) OA. The size of each symbol is arbitrarily scaled to the cubic root of the corresponding MS peak intensity. Reference lines show *DBE*/(*C* + *N*) values corresponding to fullerene-like hydrocarbons ($0.9 \times C$ limit) and linear polyenes ($0.5 \times C$ limit).^{205,303} Yellow circles display the percentage of data points (by number) that fell within the dashed lines and were predicted to be potential BrC chromophores.

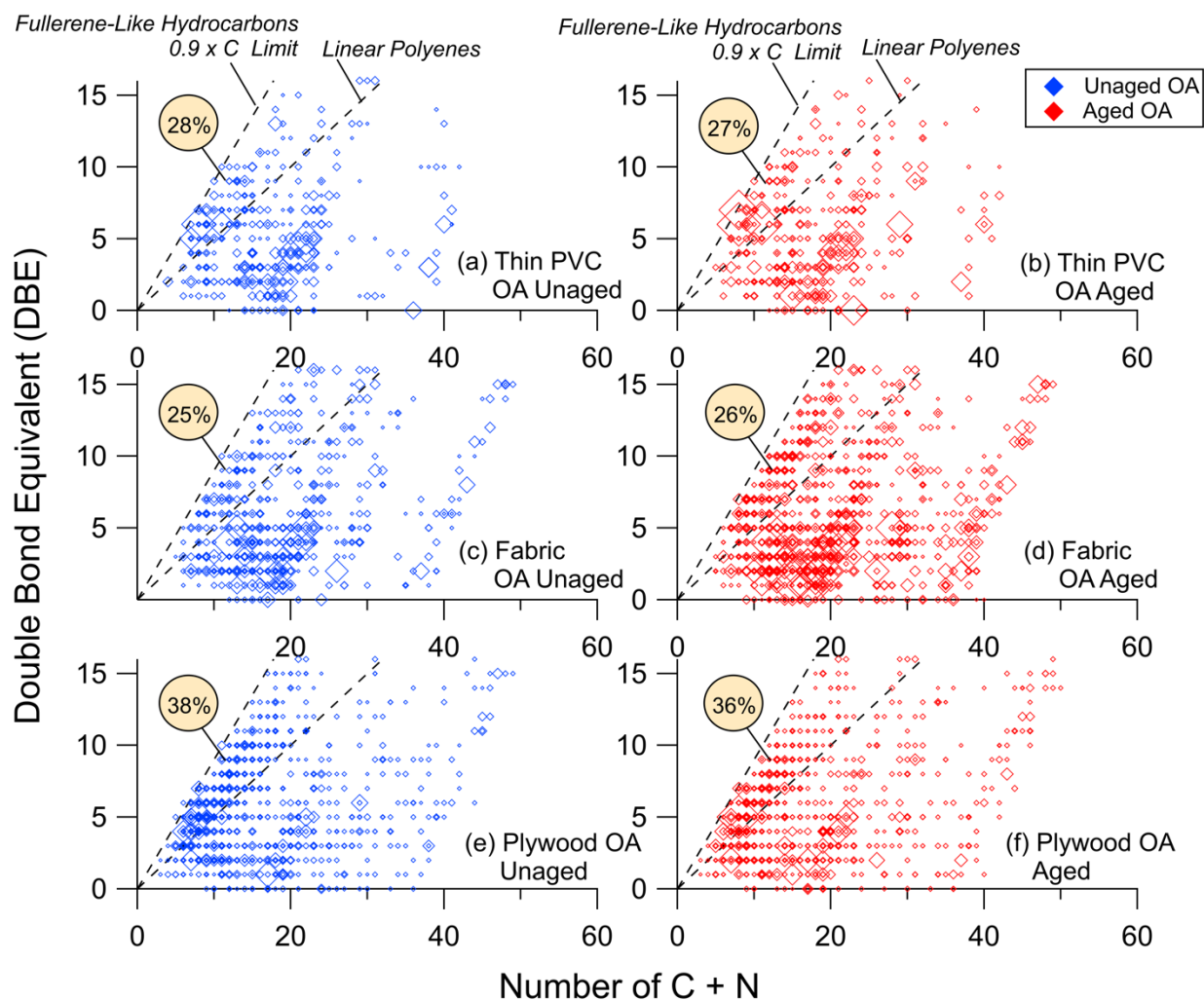


Figure 5.9. Plot of double bond equivalent (*DBE*) versus number of carbon and nitrogen (*C* + *N*) atoms from assigned urban OA unaged and aged species in thin PVC wire (a and b), fabric (c and d), and plywood (e and f) OA. The size of each symbol is arbitrarily scaled to the cubic root of the corresponding MS peak intensity. Reference lines show *DBE*/(*C* + *N*) values corresponding to fullerene-like hydrocarbons ($0.9 \times C$ limit) and linear polyenes ($0.5 \times C$ limit).^{205,303} Yellow circles display the percentage of data points (by number) that fell within the dashed lines and were predicted to be potential BrC chromophores.

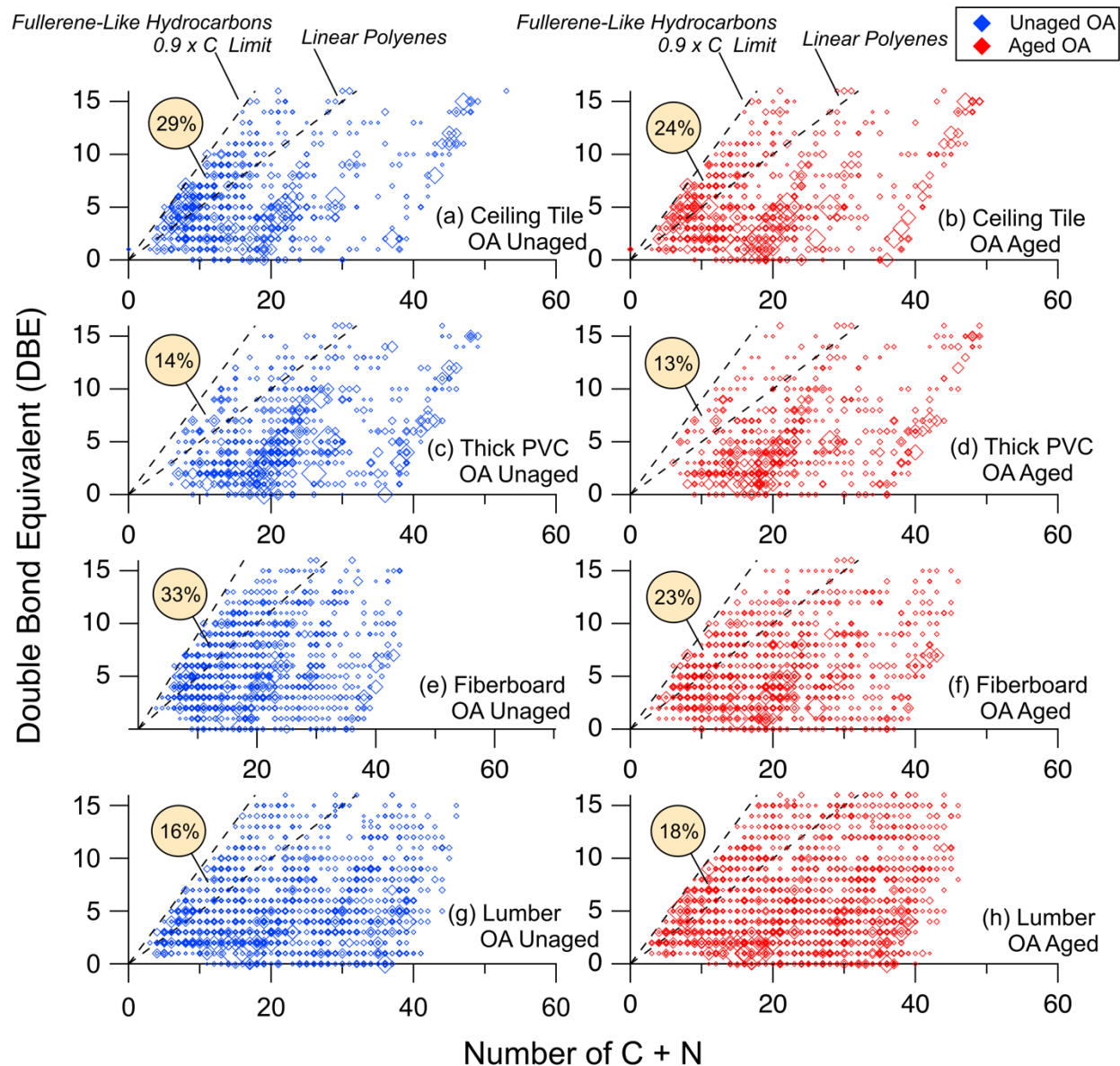


Figure 5.10. Plot of double bond equivalent (*DBE*) versus number of carbon and nitrogen (*C + N*) atoms from assigned urban OA unaged and aged species in ceiling tile (a and b), thick PVC wire (c and d), fiberboard (e and f), and lumber (g and h) OA. The size of each symbol is arbitrarily scaled to the cubic root of the corresponding MS peak intensity. Reference lines show *DBE*/*C + N* values corresponding to fullerene-like hydrocarbons ($0.9 \times C$ limit) and linear polyenes ($0.5 \times C$ limit).^{205,303} Yellow circles display the percentage of data points (by number) that fell within the dashed lines and were predicted to be potential BrC chromophores.

Upon photolysis, the percentage of potential chromophores remained steady ($\leq 5\%$ change) for all urban OA except for vinyl flooring (**Figure 5.8c,d**) and fiberboard (**Figure 5.10e,f**), which exhibited 15% and 10% reduction in the number of chromophores with aging, respectively. Though there were small changes in the number of detected chromophores, there were larger changes in the relative intensities of individual BrC chromophores, and this may be responsible for previously observed photobleaching and photoenhancement behaviors. For example, carpet OA, a material that photobleached, had fewer intense peaks (smaller markers) in the aged OA (**Figure 5.8b**) when compared to the unaged fraction (**Figure 5.8a**). Both photobleaching samples of carpet and thin PVC wire OA (**Figure 5.8a,b** and **Figure 5.9a,b**) underwent a reduction in aromaticity after aging, as peak clustering and higher intensity peaks fell below the linear polyenes line. Aged vinyl flooring OA (**Figure 5.8d**) exhibited an overall reduction in the number of BrC chromophores, but there was a relative increase by a factor of 1.3 in the intensity of a $C_8H_6O_4$ BrC chromophore (DBE= 6, C + N = 8). Drywall OA (which photoenhanced after aging) not only had a 4% increase in the total number of BrC chromophores, but also displayed growth of individual chromophores (**Figure 5.8e,f**). Specifically, a $C_8H_8O_3$ BrC chromophore (DBE= 5, C + N= 8) increased in relative intensity by a factor of 1.5 after aging and may be the source of photoenhancement observed in this sample. Previous literature reports that strongly-absorbing BrC substituents represent a minority fraction (typically <1%) of ambient BBOA mass and even small changes in these minor species can have a disproportionate effect on the bulk absorptive properties.²¹⁵ The same principle applies to the urban OA samples studied here. In summary, although the number of detected compounds that fell within the

BrC wedge remained steady, the changes in peak abundances did correlate with previous optical observations.

5.3.3 Volatility and viscosity of urban material OA

The volatility basis set (VBS) framework is a method commonly used to segment OA components into distinct volatility bins, describing the range of saturation vapor pressures within a sample.^{306,310,311} We constructed approximate VBS distributions for OA samples, by calculating saturation vapor pressures for each compound using previously established parameterizations³⁰⁵ and logarithmically binning them. As the relative ionization efficiencies for compounds in WUI OA samples are unknown, the molar fractions of each compound were assumed to be proportional to their peak abundance (from the 3-25 min integrated chromatograms). These molar fractions were scaled by molecular weight to obtain mass fractions, and the mass fractions of all species within each volatility bin were summed. We acknowledge that this does not necessarily represent the relative abundances of OA compounds, as different compounds have diverse ionization efficiencies in ESI.³¹²⁻³¹⁵ Additionally, by collecting the particle-phase emissions on filters, we have artificially enhanced the retention of lower volatility species (e.g., oligomers) and facilitated the condensation of higher volatility species. Despite these limitations, similar approximations have resulted in reasonably accurate predictions of OA viscosities in previous studies.³¹⁶

Figure 5.11 depicts the VBS distributions for unaged and aged urban OA. To highlight differences in volatilities, four broad volatile organic compound (VOC) classes commonly used in the literature were presented: extremely low (ELVOC, $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$), low volatility (LVOC, $3 \times 10^{-4} < C^* < 0.3 \mu\text{g m}^{-3}$), semi-volatile (SVOC, $0.3 < C^* < 300 \mu\text{g m}^{-3}$), and

intermediate volatility (IVOC, $300 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$).³⁰⁶ A numerical summary of the species present within each volatility bin can be found in **Table 5.2**. Fabric OA (**Figure 5.11d**) and thick PVC wire OA (**Figure 5.11g**) were the least volatile, with 30% and 33% of all detected species falling within the ELVOC range, respectively. Carpet OA (**Figure 5.11a**) exhibited the most volatile species in the IVOC range (77%) and, with aging, dropped to 45% with a leftward shift to SVOC species. The remaining seven urban OA samples presented with most species falling in LVOC and SVOC ranges, with photolysis effects being relatively small. LVOC species are predominantly found in the particle phase, whereas SVOC and IVOC species can be in either the gas or particle phases depending on ambient conditions.³⁰⁶ On average for all urban OA, there was an increase in SVOC species and decrease in LVOC/IVOC species with photolytic aging (**Table 5.2**).

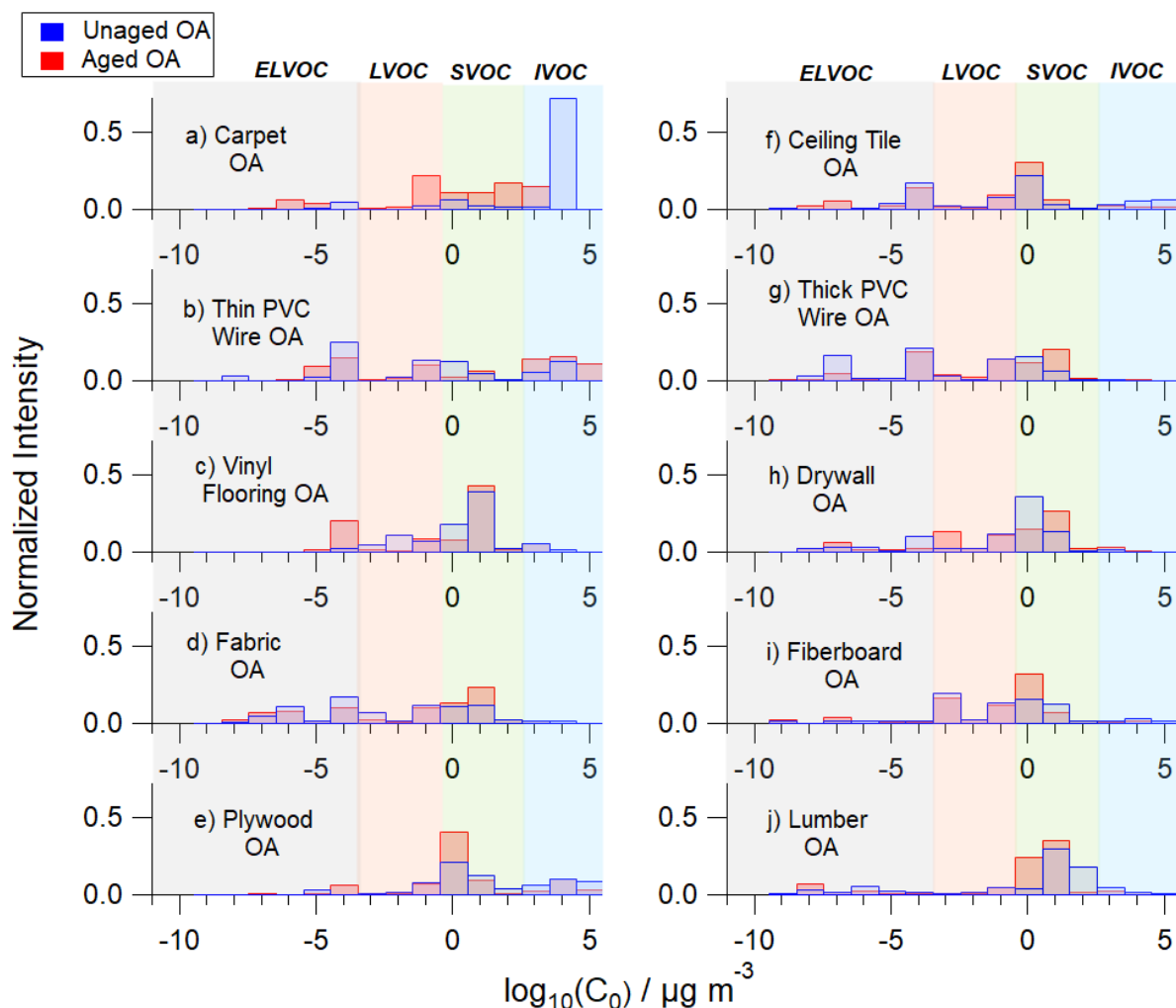


Figure 5.11. Summary of the predicted saturation mass concentrations ($\log_{10}C_0$, $\mu\text{g m}^{-3}$) of the assigned species in each OA sample.³⁰⁵ Unaged OA (blue) is plotted with opacity on top of aged OA (red). The intensity was normalized to the sum for each OA sample. The shaded regions indicate the volatility ranges of the organic compounds reported in Donahue *et al.* for extremely low volatility organic compounds (ELVOC, $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$), low-volatility organic compounds (LVOC, $3 \times 10^{-4} < C^* < 3 \times 10^{-1} \mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC, $3 \times 10^{-1} < C^* < 3 \times 10^2 \mu\text{g m}^{-3}$), and intermediate-volatility organic compounds (IVOC, $3 \times 10^2 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$).³⁰⁶

Table 5.2. Numerical summary of Figure 5.11. Provided percentages represent the total, normalized intensity (equal to 1) for each urban OA type (unaged and 2 h aged) within the volatility ranges: extremely low volatility organic compounds (ELVOC), low-volatility organic compounds (LVOC), semi volatile organic compounds (SVOC), and intermediate-volatility organic compounds (IVOC).³⁰⁶

Urban OA	% ELVOC	% LVOC	% SVOC	% IVOC
Carpet	3 (Unaged) 11 (Aged)	9 (Unaged) 6 (Aged)	11 (Unaged) 38 (Aged)	77 (Unaged) 45 (Aged)
Thin PVC Wire	15 16	39 28	22 12	24 44
Vinyl Flooring	17 9	57 36	15 47	11 9
Fabric	30 30	35 19	28 46	8 5
Plywood	10 8	9 15	41 55	40 23
Ceiling Tile	18 21	29 26	28 41	25 12
Thick PVC Wire	33 22	34 35	29 38	3 4
Drywall	17 21	24 24	56 48	3 7
Fiberboard	19 18	38 32	32 43	11 6
Lumber	22 24	10 7	61 62	7 7
AVERAGE	17 (Unaged) 16 (Aged)	26 (Unaged) 21 (Aged)	29 (Unaged) 39 (Aged)	19 (Unaged) 15 (Aged)

Depending on the total organic mass loadings (tOM) in a smoke plume, IVOC and SVOC species can reside either in the gas or particle phase. Typical atmospheric tOM concentrations range between 1-10 $\mu\text{g m}^{-3}$ in clean regions and $\gg 1000 \mu\text{g m}^{-3}$ in regions close to fires. We utilized these parameters to demonstrate how the phase state of PM from WUI fires will change as smoke plumes undergo dilution. The VBS distribution and gas-particle partitioning ratios for thick PVC wire OA under three tOM loadings (10, 100, and 1000 $\mu\text{g m}^{-3}$) at a temperature of 298 K are shown in **Figure 5.12**. For both unaged and aged OA, the gas phase mass fractions (lighter blue and red bars) increased as tOM loading decreased, which was as expected. Following thermal decomposition or burning, PVC and other plastics are known to produce solid residues with low vapor pressure products (e.g., char, PAHs, inorganic ash).^{317,318} We observed organic ELVOC components in freshly emitted OA that were relatively stable through UV aging and were not impacted by plume dilution (**Figure 5.12a,d**). Two more examples are shown in the SI, **Figures 5.13** and **5.14** for lumber and vinyl flooring OA, respectively. Lumber OA also exhibited a wide range of ELVOC species which remained in the particle phase after aging and dilution. In the SVOC range (bins 0-2), there was a shift from mostly particle phase species to gas phase species with dilution. Vinyl flooring OA had less species occupying ELVOC bins, however gas phase fractions increased in both the unaged and aged cases with increasing plume dilution.

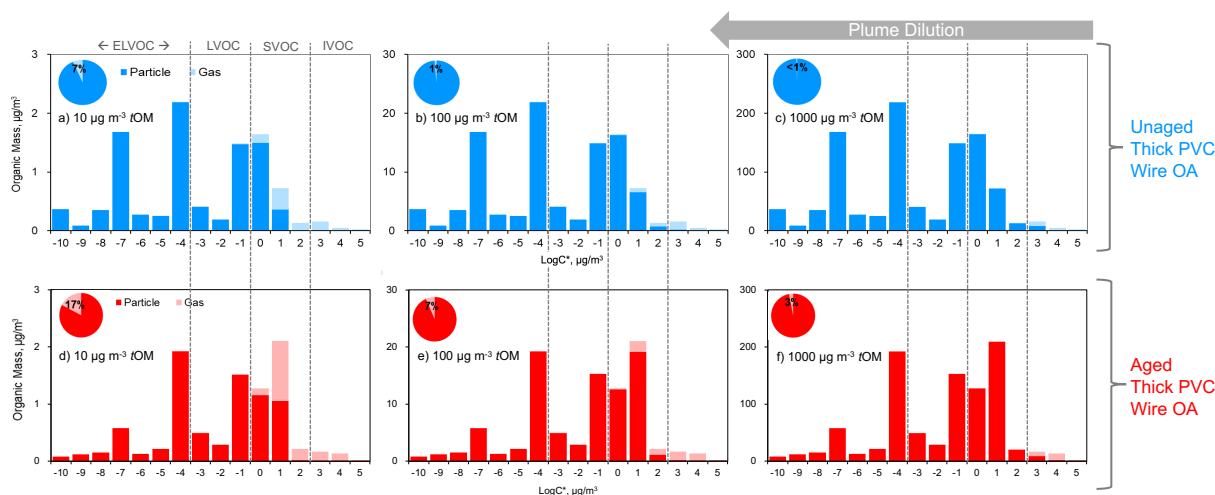


Figure 5.12. The volatility basis sets (VBS) distributions estimated for unaged (blue, a-c) and aged (red, d-f) thick PVC wire OA at temperature of 298 K, with different total organic mass (tOM) loadings (10 , 100 , and $1000 \mu\text{g m}^{-3}$). Light blue and light red bars denote the portions of the VBS capable of gas-phase partitioning under each condition. The imbedded pie charts estimate the percent mass fractions of total gas-phase and particle-phase species for each tOM scenario. Gas-particle partitioning was calculated following procedures in Xie *et al.*³⁰⁷ The regions separated by dashed lines indicate the volatility ranges of the organic compounds reported in Donahue *et al.* for extremely low volatility organic compounds (ELVOC, $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$), low-volatility organic compounds (LVOC, $3 \times 10^{-4} < C^* < 3 \times 10^{-1} \mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC, $3 \times 10^{-1} < C^* < 3 \times 10^2 \mu\text{g m}^{-3}$), and intermediate-volatility organic compounds (IVOC, $3 \times 10^2 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$).³⁰⁶

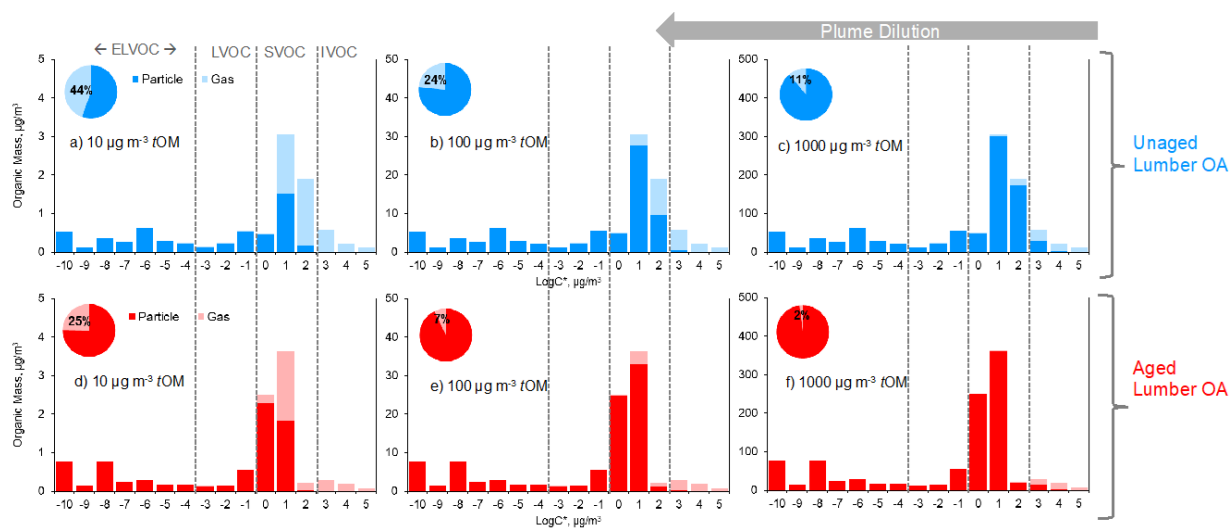


Figure 5.13. The volatility basis sets (VBS) distributions estimated for unaged (blue, a-c) and aged (red, d-f) lumber OA at temperature of 298 K, 0% relative humidity, and different total organic mass (tOM) loadings (10, 100, and 1000 $\mu\text{g m}^{-3}$). Light blue and red bars denote the portions of the VBS capable of gas-phase partitioning under each condition. The imbedded pie charts estimate the percent mass fractions of total gas-phase and particle-phase species for each tOM scenario. Gas-particle partitioning was calculated following procedures in Xie et al. (2024).³⁰⁷ The regions separated by dashed lines indicate the volatility ranges of the organic compounds reported in Donahue et al. (2012) for extremely low volatility organic compounds (ELVOC, $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$), low-volatility organic compounds (LVOC, $3 \times 10^{-4} < C^* < 3 \times 10^{-1} \mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC, $3 \times 10^{-1} < C^* < 3 \times 10^2 \mu\text{g m}^{-3}$), and intermediate-volatility organic compounds (IVOC, $3 \times 10^2 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$).³⁰⁶

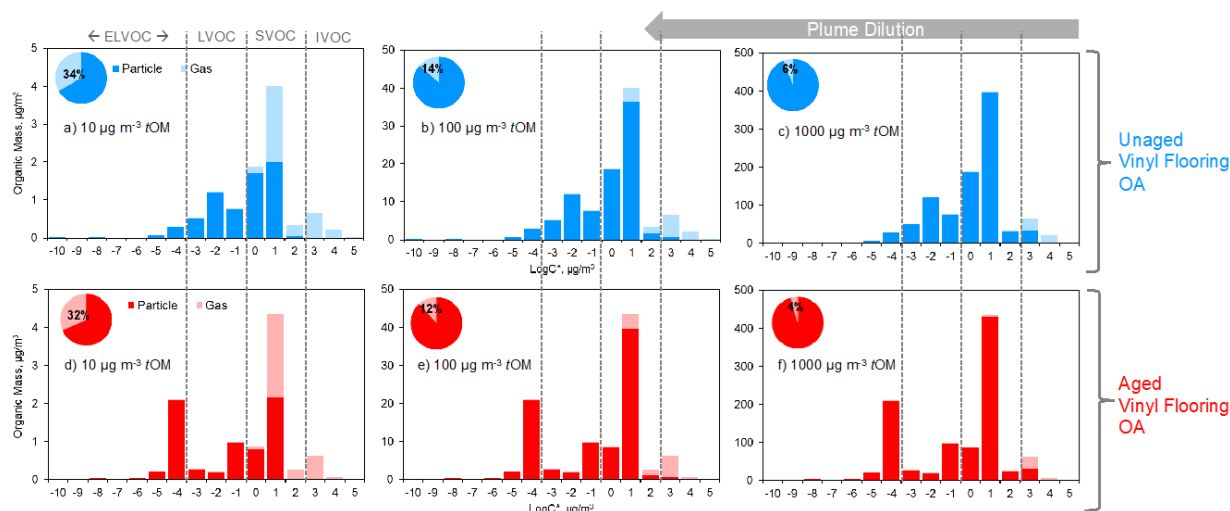
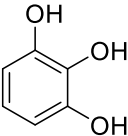
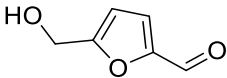
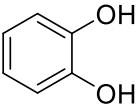
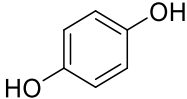


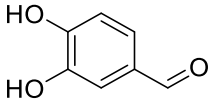
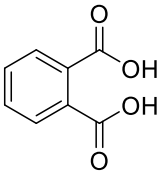
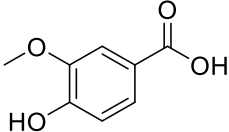
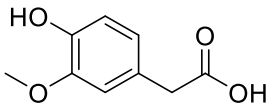
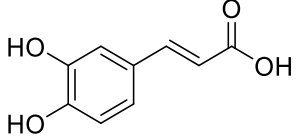
Figure 5.14. The volatility basis sets (VBS) distributions estimated for unaged (blue, a-c) and aged (red, d-f) vinyl flooring OA at temperature of 298 K, 0% relative humidity, and different total organic mass (tOM) loadings (10 , 100 , and $1000 \mu\text{g m}^{-3}$). Light blue and red bars denote the portions of the VBS capable of gas-phase partitioning under each condition. The imbedded pie charts estimate the percent mass fractions of total gas-phase and particle-phase species for each tOM scenario. Gas-particle partitioning was calculated following procedures in Xie et al. (2024).³⁰⁷ The regions separated by dashed lines indicate the volatility ranges of the organic compounds reported in Donahue et al. (2012) for extremely low volatility organic compounds (ELVOC, $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$), low-volatility organic compounds (LVOC, $3 \times 10^{-4} < C^* < 3 \times 10^{-1} \mu\text{g m}^{-3}$), semi-volatile organic compounds (SVOC, $3 \times 10^{-1} < C^* < 3 \times 10^2 \mu\text{g m}^{-3}$), and intermediate-volatility organic compounds (IVOC, $3 \times 10^2 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$).³⁰⁶

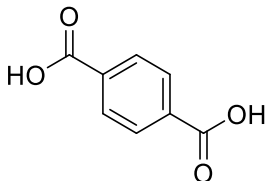
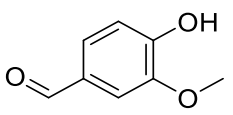
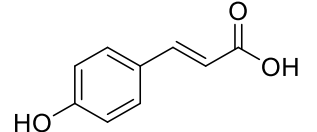
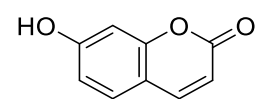
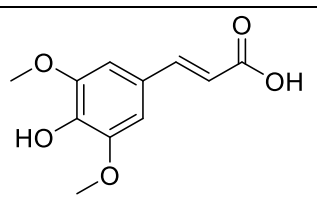
5.3.4 Structurally identified BrC species in urban OA

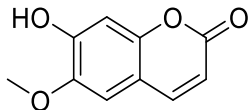
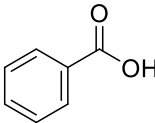
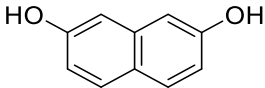
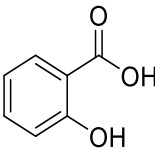
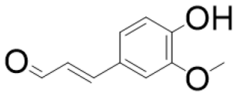
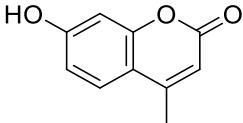
Structural validation of BrC chromophores in ambient samples has been a focus of many studies, as combustion mixtures possess a wide variety of compound classes and structures.^{25,29,34,59,67} Jen *et al.* reported that over 3000 different compounds were detected in PM from wildfires, but only about half were identified.³²⁰ As UHPLC-PDA-HRMS analysis targeting BrC species has not been conducted for PM from the WUI, we relied upon BrC standards prepared and characterized by Moschos *et al.*²⁹¹ and applied them to our OA dataset. A list of all 100 standard compounds can be found in Moschos *et al.*²⁹¹ All OA HRMS files were input into the Compound Discover program and cross-referenced with the BrC standard compounds within the internally constructed mzVault library. Each ionization mode was processed separately. Matches were determined based on retention times and MS² spectra. **Table 5.3** lists the 36 BrC species present in urban OA that were positively identified with the standards and **Figure 5.15** presents their extracted ion chromatograms, labeled with a number corresponding to the table.²⁹¹ We will discuss a few of the *structurally identified species* below as they apply to the urban materials chosen for this study. It is interesting that many of the same organic BrC species in BBOA were also found in these urban material OA.

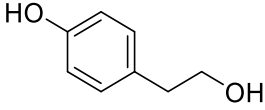
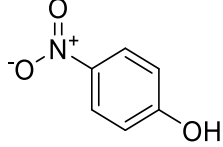
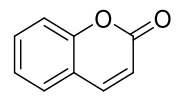
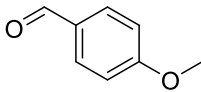
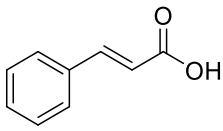
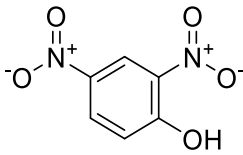
Table 5.3. Identified BrC species in urban OA. Authentic BrC standards from Moschos et al. (2024) were run on a UHPLC-PDA-HRMS system at the University of California, Irvine (UCI). Standard components that were found in the urban OA samples are listed below in order of increasing retention time.²⁹¹ The peak # corresponds to the extracted ion chromatogram label in Figure 5.16. The m/z are provided for each ionization mode (when present). Catechol (compound #3) was not part of the Moschos et al. standards, this was identified by an additional set of standards at UCI. Grey shading in the last 10 columns indicates the urban OA sample(s) that each BrC standard component was identified in. Note that this table does not make a distinction between unaged and aged OA. For simplicity, if a standard compound was found in one of the four data files for each urban OA class (ESI (+/-) files for both the unaged and aged samples), then it was included in the table below.

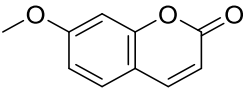
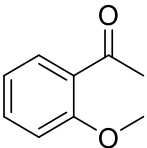
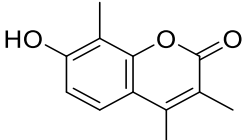
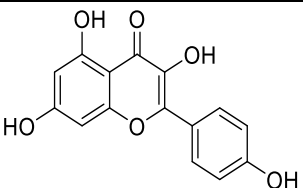
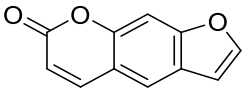
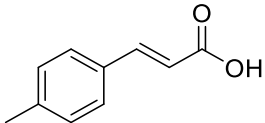
# peak	Component Name	Structure	Neutral Molecular Formula	Observed m/z and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
1	Pyrogallol		C ₆ H ₆ O ₃	125.0240 (-)	3.83 (-)										
2	5-hydroxymethylfurfural		C ₆ H ₆ O ₃	127.0389 (+)	5.04 (+)										
3	Catechol		C ₆ H ₆ O ₂	109.0290 (-)	6.63 (-)										
4	Hydroquinone		C ₆ H ₆ O ₂	109.0293 (-)	7.46 (-)										

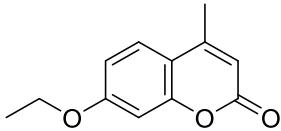
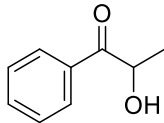
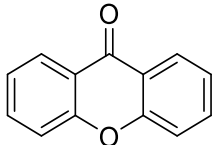
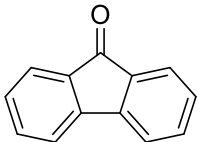
# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
5	3,4-Dihydroxybenzaldehyde		C ₇ H ₆ O ₃	139.0390 (+)	7.99 (+)										
6	Phthalic acid		C ₈ H ₆ O ₄	167.0335 (+) 165.0189 (-)	8.36 (+) 8.35 (-)										
7	Vanillic Acid		C ₈ H ₈ O ₄	167.0347 (-)	8.96 (-)										
8	Homovanillic acid		C ₉ H ₁₀ O ₄	181.0504 (-)	9.01 (-)										
9	Caffeic acid		C ₉ H ₈ O ₄	181.0493 (+)	9.01 (+)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
10	Terephthalic acid		C ₈ H ₆ O ₄	165.0189 (-)	9.08 (-)										
11	Vanillin		C ₈ H ₈ O ₃	153.0543 (+) 151.0397 (-)	10.19 (+) 10.19 (-)										
12	p-Coumaric acid		C ₉ H ₈ O ₃	165.0543 (+) 163.0397 (-)	10.29 (+) 10.27 (-)										
13	Umbelliferone		C ₉ H ₆ O ₃	161.0240 (-)	10.67 (-)										
14	Sinapinic acid		C ₁₁ H ₁₂ O ₅	223.0606 (-)	10.68 (-)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed m/z and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
15	Scopoletin		C ₁₀ H ₈ O ₄	193.0496 (+) 191.0345 (-)	10.76 (+) 10.76 (-)										
16	Benzoic acid		C ₇ H ₆ O ₂	123.0440 (+) 121.0293 (-)	11.29 (+) 8.35 (-)										
17	2,7-Dihydroxynaphthalene		C ₁₀ H ₈ O ₂	161.0592 (+) 159.0449 (-)	11.62 (+) 11.62 (-)										
18	Salicylic acid		C ₇ H ₆ O ₃	137.0240 (-)	11.69 (-)										
19	Coniferaldehyde		C ₁₀ H ₁₀ O ₃	179.0700 (+) 177.0553 (-)	11.73 (+) 11.75 (-)										
20	4-Methylumbelliferone		C ₁₀ H ₈ O ₃	177.0543 (+)	11.78 (+)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
21	Tyrosol		C ₈ H ₁₀ O ₂	139.0754 (+)	12.03 (+)										
22	4-Nitrophenol		C ₆ H ₅ NO ₃	138.0193 (-)	12.08 (-)										
23	Coumarin		C ₉ H ₆ O ₂	147.0439 (+)	12.52 (+)										
24	4-Methoxybenzaldehyde		C ₈ H ₈ O ₂	137.0597 (+)	12.98 (+)										
25	trans-Cinnamic acid		C ₉ H ₈ O ₂	149.0594 (+) 147.0449 (-)	13.19 (+) 13.20 (-)										
26	2,4-Dinitrophenol		C ₆ H ₄ N ₂ O ₅	183.0043 (-)	13.42 (-)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
27	7-Methoxycoumarin		C ₁₀ H ₈ O ₃	177.0544 (+)	13.59 (+)										
28	2'-Methoxyacetophenone		C ₉ H ₁₀ O ₂	151.0751 (+)	13.95 (+)										
29	7-Hydroxy-3,4,8-trimethylcoumarin		C ₁₂ H ₁₂ O ₃	205.0857 (+)	14.00 (+)										
30	Kaempferol		C ₁₅ H ₁₀ O ₆	285.0401 (-)	14.00 (-)										
31	Psoralen		C ₁₁ H ₆ O ₃	187.0389 (+)	14.30 (+)										
32	4-Methylcinnamic Acid		C ₁₀ H ₁₀ O ₂	163.0748 (+)	14.51 (+)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
33	7-Ethoxy-4-methylcoumarin		C ₁₂ H ₁₂ O ₃	205.0859 (+)	16.08 (+)										
34	2'-Hydroxypropiophenone		C ₉ H ₁₀ O ₂	151.0752 (+)	16.22 (+)										
35	Xanthone		C ₁₃ H ₈ O ₂	197.0598 (+)	17.13 (+)										
36	9-Fluorenone		C ₁₃ H ₈ O	181.0646 (+)	17.62 (+)										

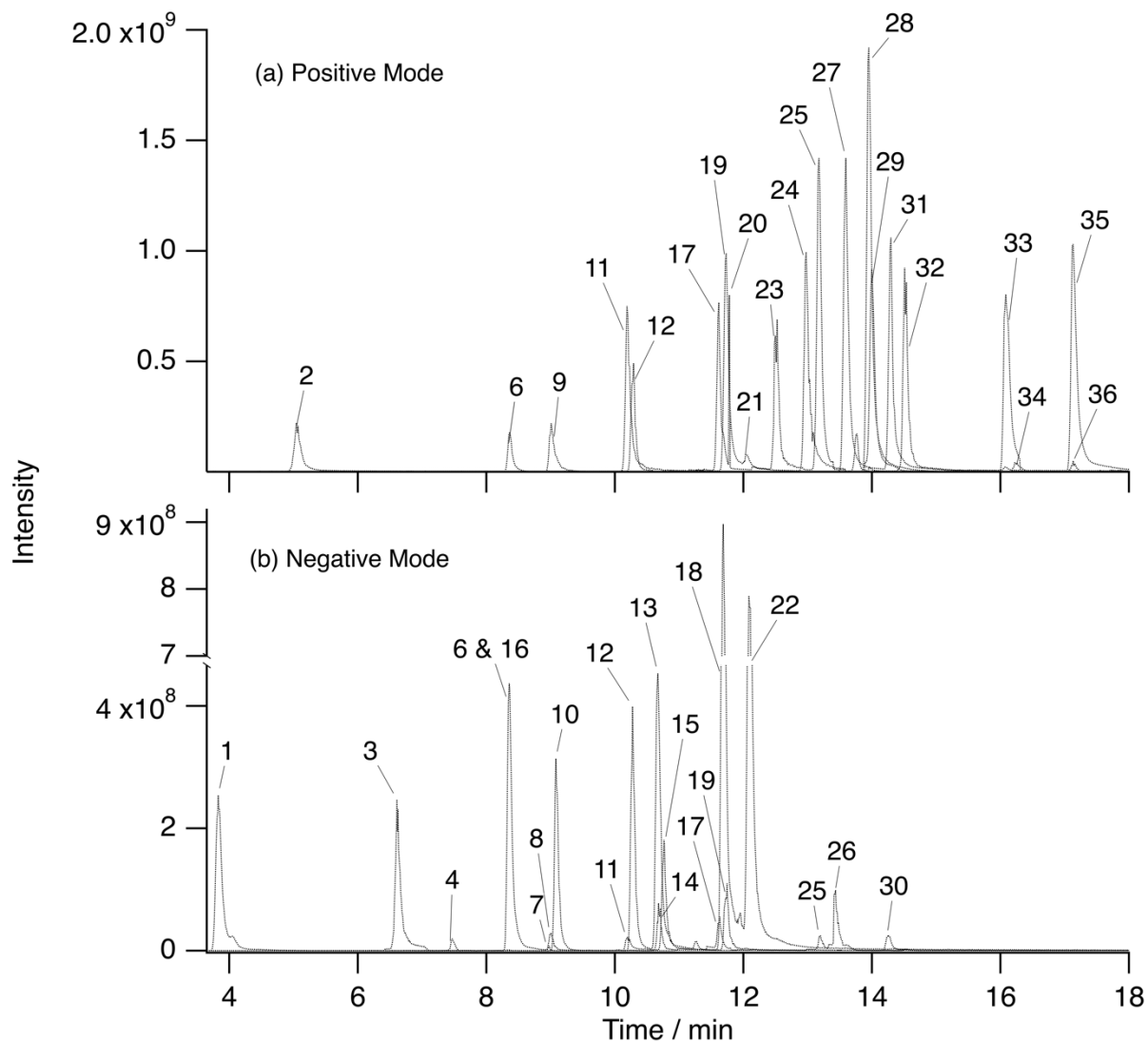


Figure 5.15. Extracted ion chromatograms (EICs) corresponding to the BrC species identified in urban OA samples, utilizing the BrC standard solutions from Moschos *et al.* (2024).²⁹¹ UHPLC-PDA-HRMS system at the University of California, Irvine was operated in both the positive (panel a) and negative (panel b) ionization modes. Peaks are labeled with the number corresponding to that of each compound in **Table 5.3**. Peaks 5 and 16 (corresponding to 3,4-dihydroxybenzaldehyde (+) and benzoic acid (+), respectively) are not labeled due to peak intensities being too small to showcase on this plot.

Salicylic acid ($C_7H_6O_3$, m/z 137.0240 (-)) was the only BrC standard compound to appear in all ten OA samples. It is commonly recognized as an atmospheric tracer for biomass burning (e.g., deciduous trees and woody biomass) and, now for the first time, has been observed in PM from combusted urban materials.^{321–323} Other organic acids (phthalic acid, vanillic acid, homovanillic acid, caffeic acid, terephthalic acid, p-coumaric acid, sinapinic acid, benzoic acid, and *trans*-cinnamic acid) were observed in at least three of the OA samples. PAHs, including 2,7-dihydroxynaphthalene, psoralen, xanthone, and 9-fluorenone were detected in various OAs through ionization in the positive mode. Plywood and lumber OA exclusively shared six confirmed BrC species (pyrogallol, 5-hydroxymethylfurfural, coniferaldehyde, 4-methylumbelliferone, 2,4-dinitrophenol, and 7-hydroxy-3,4,8-trimethylcoumarin), which are known to be biomass-derived compounds produced from the dehydration of glucose sugars (within biomass) and the thermal decomposition of lignin.^{61,324–328} As plywood and lumber were the urban building materials that most resembled biomass, the crossover between literature on BBOA chromophores and those presented herein was not surprising for these two OA samples.

Phthalic acid ($C_8H_6O_4$, m/z 167.0335 (+) and 165.0189 (-)) was observed in all OA samples except drywall and fiberboard. It was the main BrC chromophore in the thin PVC wire OA sample²¹² and a potential tracer species for WUI fires. Phthalic acid may have been produced from di(2-ethylhexyl)phthalate (DEHP),³²⁹ which is widely used as a plasticizer in PVC plastics,³³⁰ building and furniture materials (including furniture upholstery, mattresses, wall coverings, floor tiles, and vinyl flooring),³³¹ and many other consumer products.³³² The presence of phthalic acid in eight out of ten OA samples tested may indicate the presence of DEHP plasticizers in un-combusted urban materials. Carpet OA exhibited phthalic acid most

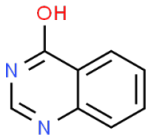
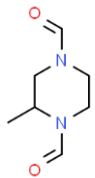
likely due to the PVC vinyl backing applied to the bottom of the carpet pile fibers. Another example of a plastic precursor, terephthalic acid, was found in vinyl flooring, plywood, and fiberboard OA. Terephthalic acid is a key precursor to polyethylene terephthalate (PET), which is commonly used in the manufacture of products that require a barrier to gases (CO₂ and O₂) and resistance to shattering.³³³

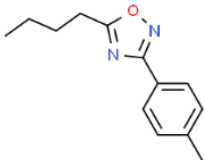
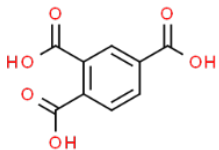
NACs are known to be major contributors to light absorption in biomass burning BrC.²⁹⁸ The BrC standards contained 11 NAC species commonly found in BBOA,²⁹¹ and of these, only two species (4-nitrophenol and 2,4-dinitrophenol) were present within urban OA samples. 4-Nitrophenol (C₆H₅NO₃, *m/z* 138.0193 (-)) was detected in all OA except carpet, thick PVC wire, and fiberboard, whereas 2,4-dinitrophenol (C₆H₄N₂O₅, *m/z* 183.0043 (-)) was only present in plywood, fiberboard, and lumber OA. The lack of occurrence of other NACs in urban material OA could indicate that the non-detected NACs (e.g., 4-nitrocatechol, 5-nitrosalicylic acid, 2-nitrophenol, and 4-nitro-*o*-cresol, to name a few) are more indicative of traditional biomass fires. As this study only surveyed ten urban materials, additional testing of more urban material OA types is needed to determine if this trend holds.

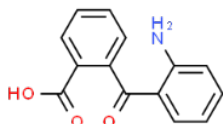
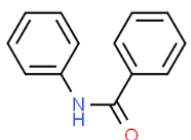
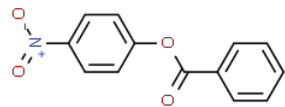
5.3.5 Tentatively assigned species unique to each urban OA

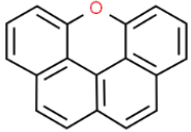
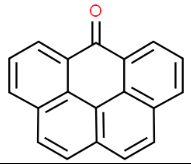
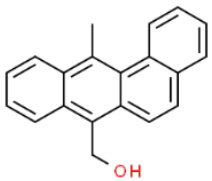
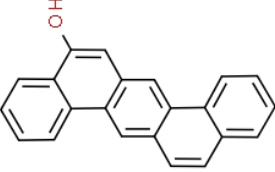
Table 5.4 presents tentatively assigned species that were among the highest intensity peaks and unique to each urban material. We will briefly summarize our findings here but note that these assignments have not been confirmed with standards, and only the observed *m/z* values are reliable. Details on the usages of each species were found in previous literature and the PubChem database (National Library of Medicine).

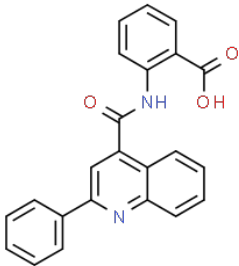
Table 5.4. Compounds that appear to be unique to each urban material OA. Tentative structural assignments were proposed by the Compound Discover program (Thermo Scientific) by utilizing various online databases to determine the best match. Note that these structures were **not verified** using internal standards. Grey shading in the last 10 columns indicates the urban OA sample that each component was identified in. There is no distinction between unaged and aged OA.

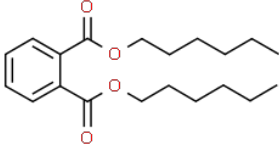
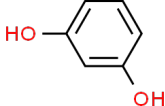
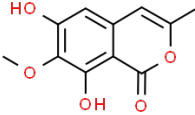
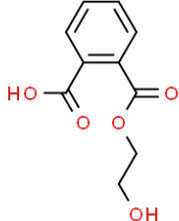
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
4-hydroxyquinazoline 	C ₈ H ₆ N ₂ O	145.0408 (-)	7.86	--										
2-Methyl-1,4-piperazine dicarbaldehyde 	C ₇ H ₁₂ N ₂ O ₂	157.0970 (+)	8.65	--										

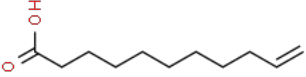
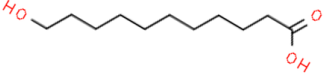
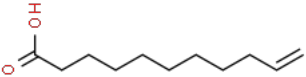
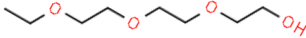
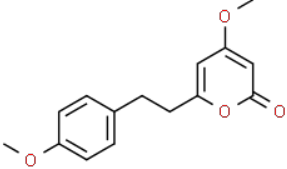
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
1-Piperazinyl(1-pyrrolidinyl) methanone 	C ₉ H ₁₇ N ₃ O	184.1449 (+)	11.68	--										
--	C ₁₃ H ₁₇ NO ₃	236.1281 (+)	13.58	--										
--	C ₁₄ H ₁₈ N ₂ O	231.1492 (+)	13.75	--										
5-Butyl-3-(p-tolyl)-1,2,4- oxadiazole 	C ₁₃ H ₁₆ N ₂ O	217.1336 (+)	15.42	--										
1,2,4-Benzenetricarboxylic acid 	C ₉ H ₆ O ₆	209.0091 (-)	6.18	Intermediate for resins, plasticizers, dyes, inks, and adhesives										

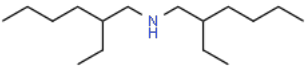
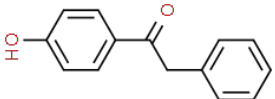
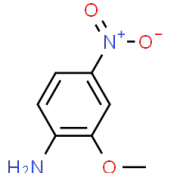
Component Name & Structure	Neutral Molecular Formula	Observed m/z and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
--	C ₈ H ₉ NO ₄	184.0607 (+)	7.79	--										
--	C ₁₇ H ₈ N ₄ O ₄	355.0422 (+)	7.81	--										
2-(2-Aminobenzoyl) benzoic acid 	C ₁₄ H ₁₁ NO ₃	242.0812 (+)	11.84	Dye intermediate										
Benzanilide 	C ₁₃ H ₁₁ NO	196.0768 (-)	11.87	Used in dye making										
4-Nitrophenyl benzoate 	C ₁₃ H ₉ NO ₄	244.0604 (+)	11.77	--										

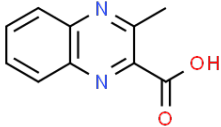
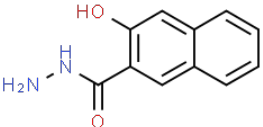
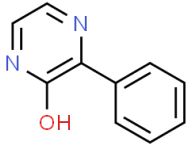
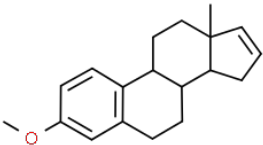
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
5,6a-Dihydronaphtho[2,1,8,7- klmn]xanthene 	C ₁₈ H ₁₀ O	243.0803 (+)	19.18	--										
Naphthanthrone 	C ₁₉ H ₁₀ O	255.0803 (+)	20.14	--										
7-Hydroxymethyl-12- methylbenz[a]anthracene 	C ₂₀ H ₁₆ O	273.1272 (+)	20.61	--										
Benzo[k]tetraphen-5-ol 	C ₂₂ H ₁₄ O	295.1114 (+)	22.59	--										

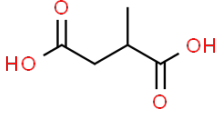
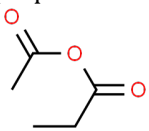
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
--	C ₁₅ H ₁₀ N ₄ O ₅	325.0651 (-)	17.84	--										
--	C ₂₀ H ₁₃ N ₃ O ₃	344.1030 (+)	19.33	--										
--	C ₁₈ H ₁₆ N ₂ O ₉	405.0917 (+)	19.33	--										
--	C ₃₃ H ₂₄ N ₄ O ₁₁	653.1485 (+)	19.34	--										
2-(2-Phenylquinoline-4- carboxamido) benzoic acid 	C ₂₃ H ₁₆ N ₂ O ₃	367.1103 (-)	21.49	--										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Dihexyl phthalate 	C ₂₀ H ₃₀ O ₄	335.2215 (+)	22.82	Used in textiles (vinyl upholstery); primarily used to soften PVC										
Resorcinol 	C ₆ H ₆ O ₂	111.0441 (+)	5.37	Used in plastic production										
Reticulol 	C ₁₁ H ₁₀ O ₅	223.0599 (+)	8.10	--										
2-(2-hydroxyethoxycarbonyl) benzoic acid 	C ₁₀ H ₁₀ O ₅	211.0603 (+)	8.66	Patented for resins (aqueous resin composition, coating film), used in methods for forming multilayer coating films and adhesives										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
10-Undecenoic acid 	C ₁₁ H ₂₀ O ₂	189.1854 (+)	13.40	Used as a precursor in the manufacture of polymers										
11-Hydroxyundecanoic acid 	C ₁₁ H ₂₂ O ₃	201.1497 (-)	13.39	Used in the production of resins										
10-Undecenoic acid 	C ₁₁ H ₂₀ O ₂	189.1854 (+)	13.40	Used as a precursor in the manufacture of polymers										
2-[2-(2-Ethoxyethoxy)ethoxy]ethanol 	C ₈ H ₁₈ O ₄	179.1279 (+)	7.46	Used in the production of paints, plastics, and films										
7,8-Dihydroyangonin 	C ₁₅ H ₁₆ O ₄	259.0977 (-)	14.55	Patented as a preservative										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Bis(2-ethylhexyl) amine 	C ₁₆ H ₃₅ N	242.2840 (+)	18.09	Patented as a modified epoxy resin										
1-(4-hydroxyphenyl)-2- phenylethan-1-one 	C ₁₄ H ₁₂ O ₂	213.0913 (+)	14.41	Patented as a plasticizer										
Laurixamine 	C ₁₅ H ₃₃ NO	244.2635 (+)	15.64	Used in the production of polymers and metallic pigments										
--	C ₁₉ H ₃₅ NO ₅	356.2456 (-)	16.57	--										
--	C ₁₉ H ₃₈ N ₂ O	311.3070 (+)	24.75	--										
4-Nitro-o-anisidine 	C ₇ H ₈ N ₂ O ₃	167.0463 (-)	5.75	--										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
3-Methyl-2-Quinoxalinecarboxylic Acid 	C ₁₀ H ₈ N ₂ O ₂	187.0515 (-)	8.83	Acute toxicity; eye irritant										
3-Hydroxy-2-naphthhydrazide 	C ₁₁ H ₁₀ N ₂ O ₂	201.0671 (-)	9.22	Epoxy resin for fiber-reinforced composite materials										
3-Phenyl-2-pyrazinol 	C ₁₀ H ₈ N ₂ O	173.0713 (+)	10.37	--										
3-Methoxyestra-1,3,5(10),16-tetraene 	C ₁₉ H ₂₄ O	269.1901 (+)	22.46	--										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Methylsuccinic acid 	C ₅ H ₈ O ₄	131.0352 (-)	3.21	--										
--	C ₈ H ₁₆ N ₂ O ₂	173.1288 (+)	5.55	--										
--	C ₇ H ₁₁ NO ₂	142.0867 (+)	5.86	--										
Acetic propanoic anhydride 	C ₅ H ₈ O ₃	117.0549 (+)	10.61	--										
--	C ₁₂ H ₁₈ O ₆	259.1177 (+)	13.41	--										

Carpet OA's selected unique species were nitrogen-containing (e.g., 4-hydroxyquinazoline ($C_8H_6N_2O$) and 2-methyl-1,4-piperazine dicarbaldehyde ($C_7H_{12}N_2O_2$)). We were unable to find species which were both unique to carpet OA and clearly associated with urban additives and/or manufacturing. Thin PVC wire OA uniquely contained 1,2,4-benzenetricarboxylic acid ($C_9H_6O_6$, an intermediate for resins, plasticizers, dyes, inks, and adhesives), 2-(2-aminobenzoyl) benzoic acid ($C_{14}H_{11}NO_3$, a dye intermediate), and benzanilide ($C_{13}H_{11}NO$, used in dye making).^{334,335} Vinyl flooring OA was distinguished from all other materials by its large PAH structures. These species (xanthone ($C_{13}H_8O_2$) and 9-fluorenone ($C_{13}H_8O$) from **Table 5.3**, (structurally identified), and 5,6a-dihydronaphtho[2,1,8,7-klmn]xanthene ($C_{18}H_{10}O$), naphthanthrone ($C_{19}H_{10}O$), 7-hydroxymethyl-12-methylbenz[a]anthracene ($C_{20}H_{16}O$), and benzo[k]tetraphene-5-ol ($C_{22}H_{14}O$) from **Table 5.4** (tentatively assigned), were resistant to UV induced change, as they were present in both the unaged and aged OA, and their abundances may have contributed to the optical classification of "no change". Fabric OA presented with the unique species dihexyl phthalate ($C_{20}H_{30}O_4$), often used in textiles and vinyl upholstery (as was the case for this fabric material).³³⁴ Plywood OA's unique markers included resorcinol ($C_6H_6O_2$, used in plastic production),³³⁶ reticulol ($C_{11}H_{10}O_5$), 2-(2-hydroxyethoxycarbonyl) benzoic acid ($C_{10}H_{10}O_5$, patented for resins used in forming multilayer coating films and adhesives),³³⁷ 10-undecenoic acid ($C_{11}H_{20}O_2$, used as a precursor in the manufacture of polymers),³³⁸ and others listed in **Table 5.4**. Given that plywood is made up of sheets of wood that are adhered together, it is likely that the species found here were utilized in the manufacturing processes of this plywood material. Ceiling tile OA presented with bis(2-ethylhexyl) amine ($C_{16}H_{35}N$), which is patented as a modified epoxy resin and may have been

used to adhere components together.³³⁹ Thick PVC wire OA exhibited 1-(4-hydroxyphenyl)-2-phenylethan-1-one ($C_{14}H_{12}O_2$, patented as a resin)³⁴⁰ and laurixamine ($C_{15}H_{33}NO$, used in production of polymers and metallic pigments).³⁴¹ Note that both thin and thick PVC wire OA have unique species that are predicted to be resins, plasticizers, and ink/dye species. These two coated wires were different in manufacturer, color, and thickness of PVC coating, illustrating the wide variety of species that can be emitted even from one class of urban material. Drywall OA did not possess many unique species that had structural matches to online databases referenced by the Compound Discover program. We observed large ions corresponding to $C_{19}H_{35}NO_5$ and $C_{19}H_{38}N_2O$. Drywall is composed of calcium sulfate dihydrate (gypsum) with additives of plasticizers, foaming agents, cellulose, and fiberglass. Preliminary results from Compound Discover showed many sulfur-containing species for this OA type only. Due to CHON assignment restraints implemented in this pilot study, we did not report sulfur-containing organics in this work, but future studies from our group will incorporate a greater heteroatom variety. Fiberboard OA exhibited 3-methyl-2-quinoxalinecarboxylic acid ($C_{10}H_8N_2O_2$, an eye irritant)³³⁴ and 3-hydroxy-2-naphthohydrazide ($C_{11}H_{10}N_2O_2$, an epoxy resin for fiber reinforced composite materials).³⁴² Lumber OA exhibited unique markers potentially assigned to methylsuccinic acid ($C_5H_8O_4$) and acetic propanoic anhydride ($C_5H_8O_3$).

5.4 Atmospheric Implications

This work serves as a pilot study for the chemical characterization of OA produced in WUI fires, and the effect of photolytic aging on this OA. One of the key findings is that photolytic aging results in relatively small changes to the overall chemical composition and

volatility predictions despite having a large impact on the overall absorption coefficient of OA. This reinforces previous observations that the optical absorption of OA is controlled by a small fraction of chromophoric species. Changes in the relative intensity of these species are difficult to notice because they are obscured by more abundant non-absorbing species. Our volatility predictions showcase that urban materials made from plastics (such as PVC) or those made with resins and sealants may emit a large fraction of ELVOC species upon combustion. We demonstrated that these species would remain in the particle phase throughout atmospheric aging and plume dilution. Particles of this nature are known to influence nucleation mechanisms, which have implications for cloud formation processes and precipitation effects.³⁴³

It is important to note that this study only focused on a small variety of species present in WUI fires. Additionally, OA was generated only at a single pyrolysis temperature (600 °C), and in the absence of oxygen. This is not fully representative of environmental fires, which often oscillate between smoldering and flaming combustion, with flaming temperatures reaching at least an order of magnitude higher than smoldering or pyrolysis. Results in this work are also limited in that we only focused on CHON species when characterizing BrC species. Metals and halogenated species are expected to be produced through the combustion of human made materials. Future studies should burn a greater variety of urban materials (such as those containing perfluoroalkyl and polyfluoroalkyl substances) under more diverse combustion conditions and determine the molecular composition and long-term photochemical transformations of largescale WUI fires. Here, we have provided tentatively assigned tracer species for each OA type (**Table 5.4**) and, in the

future, these species can be structurally identified to build a library of compounds signature to WUI fires.

CHAPTER 6:

CHEMICAL ANALYSIS OF EXHALED VAPE EMISSIONS: UNRAVELING THE COMPLEXITIES OF HUMECTANT FRAGMENTATION IN A HUMAN TRIAL STUDY

Hopstock, K. S.; Perraud, V.; Dalton, A. B; Barletta, B.; Meinardi, S.; Weltman, R. M.; Mirkhanian, M. A.; Rakosi, K. J.; Blake, D. R.; Edwards, R. D.; Nizkorodov, S. A., Chemical analysis of exhaled vape emissions: unraveling the complexities of humectant fragmentation in a human trial study, *ACS Chemical Research in Toxicology*, **2024**, 37, 1000-1010.³⁴⁴

Abstract. Electronic cigarette smoking (or vaping) is on the rise, presenting questions about the effects of secondhand exposure. The chemical composition of vape emissions was examined in the exhaled breath of eight human volunteers with the high chemical specificity of complementary online and offline techniques. Our study is the first to take multiple exhaled puff measurements from human participants and compare volatile organic compound (VOC) concentrations between two commonly used methods, proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) and gas chromatography (GC). Five flavor profile groups were selected for this study, but flavor compounds were not observed as main contributors to the PTR-ToF-MS signal. Instead, the PTR-ToF-MS mass spectra were overwhelmed by e-liquid thermal decomposition and fragmentation products, which masked other observations regarding flavorings and other potentially toxic species associated with secondhand vape exposure. Compared to the PTR-ToF-MS, GC measurements reported significantly different VOC concentrations, usually below those from PTR-ToF-MS. Consequently, PTR-ToF-MS mass spectra should be interpreted with caution when reporting quantitative results in vaping studies, such as doses of inhaled VOCs.

Nevertheless, the online PTR-ToF-MS analysis can provide valuable qualitative information by comparing relative VOC in back-to-back trials. For example, by comparing mass spectra of exhaled air with those of direct puffs, we can conclude that harmful VOCs present in the vape emissions are largely absorbed by the participants, including large fractions of nicotine.

6.1 Introduction

Electronic cigarettes (e-cigarettes, also known as vapes) are battery-powered devices that convert an e-liquid into an aerosol that can be inhaled by an individual. Since these devices deliver nicotine without the combustion of tobacco, vapes are often marketed as a safer and healthier alternative to traditional cigarettes.³⁴⁵ Modern vape device usage is perceived to be a more socially acceptable alternative to traditional combustible cigarettes, giving rise to users discreetly vaping in public spaces where smoking is normally prohibited.³⁴⁶ In addition, fruit and candy flavors are appealing to a younger demographic, posing new risks of nicotine addiction in developing youth, as 10 % of middle and high school students reported vape usage in 2023.^{121-123,347} The long term effects of vaping are unknown, but research has demonstrated that flavoring agents can induce inflammation, endothelial dysfunction, epithelial barrier disruption, oxidative stress, DNA damage, electrophysiological alterations, immunomodulatory effects, and behavioral changes, even independent of nicotine.³⁴⁸ There is a need for a more comprehensive physiochemical characterization of vaping emissions, and studies linking emission properties to specific toxicological outcomes.³⁴⁹

Most vape devices consist of a lithium battery, a heating element, liquid tank/cartridge, and e-liquid.^{350,351} Deviations in the design are determined by the class of

vape device, subsequently referred to as “*closed*” and “*open*” in this text. *Closed* devices are preloaded, disposable devices that are not intended to be refilled or have their battery/atomizers replaced by the user.¹²⁵ *Open* devices are tank-based systems that are intended to have the e-liquid refilled, parts replaced, and power outputs manipulated.¹²⁵ These devices are often larger in size than *closed* devices and have higher-voltage batteries and/or lower-resistance heating elements that can produce a more concentrated smoke than *closed* devices.

Together, the battery voltage and resistance of the heating element (coils) determine the e-cigarette power output. This, in turn, directly impacts the concentration of aerosol to be inhaled by an individual.³⁵² E-liquid is composed of three main ingredients: nicotine (although some e-liquids are nicotine free), humectants (to prevent the e-liquid from drying out), and flavoring agents.¹²⁵ The humectant component is typically a mixture of propylene glycol (PG; C₃H₈O₂, MW 76.095 g mol⁻¹) and glycerol (GLY; C₃H₈O₃, MW 92.09 g mol⁻¹). These are considered safe for human use, however, literature suggests that dangerous thermal degradation products are inhaled during vaping, as these species are produced when coil temperatures exceed 130 °C.^{125,353–357} These include glycols, aldehydes, polycyclic aromatic hydrocarbons (PAHs), and other volatile organic compounds (VOCs). In indoor environments, individuals in the vicinity of vape users may be exposed to these VOCs through unintentional, secondhand inhalation.³⁵⁸

Extensive research has utilized offline analytical techniques which include gas and liquid chromatography (GC-MS/FID, LC-MS), often coupled to derivatization methods prior to analysis (e.g., 1,4-dinitrophenylhydrazine, DNPH), to assess the presence of VOCs in vape emissions.^{124,127–133} The proton-transfer-reaction time-of-flight mass spectrometer (PTR-

ToF-MS), an online instrument, has proven advantageous in online vaping studies as it provides fast-response measurements of VOCs without additional sample treatment or preparation. The PTR-ToF-MS has been previously applied to exhaled breath analysis,^{134–138,359–362} but only few studies have utilized this online monitoring technique for direct vape emissions, and even fewer studies have utilized this instrument to examine the exhaled vape emissions from human participants. For example, Blair *et al.* (2015) demonstrated proof-of-concept that the PTR-ToF-MS could be used to quantify VOC concentrations in the direct e-cigarette emissions.³⁶³ This study only reported the concentrations of five VOCs (acetaldehyde, acetone, acetonitrile, acrolein, and methanol) from the analysis of one vape device, independent from human participants.³⁶³ O’Connell *et al.* (2015) used a PTR-ToF-MS to determine exhaled nicotine concentrations (1.8 – 1786 ppb) of three human volunteers.³⁶⁴ Breiev *et al.* (2016) calibrated the PTR-ToF-MS for PG, GLY, and nicotine then conducted proof-of-concept sampling with one human participant.¹³⁹ Through implementation of a dilution setup, they found agreement between measurements taken online (PTR-ToF-MS) and offline (GC-FID) for three VOCs of interest.¹³⁹ Sangani *et al.* (2021) utilized the PTR-ToF-MS to examine the direct emissions from vape devices used by patients admitted to a hospital for lung injury, but they did not examine the subsequent exhaled breath.³⁶⁵ Formaldehyde, acetaldehyde, acetone, PG, cyclohexane, and nicotine were present in the direct emissions from the vaping devices and total VOC concentrations were reported up to 600 ppm.³⁶⁵

The present work sought to examine the chemical composition of vape emissions with the PTR-ToF-MS and compare these results to the exhaled breath of eight human volunteers vaping five different flavor classes. To tease out fragmentation induced by the PTR ionization, measurements with an offline GC method were also conducted. Our study is

the first to implement a flavor study with human participants and analyze breath samples with the high chemical specificity of complementary online and offline techniques.

6.2 Materials and Methods

6.2.1 Human Participants, Vape Device Selections, and Sampling Protocols

In January-June 2022, eight individuals each made five separate visits to UC Irvine to participate in a human trial vaping study. This study was approved by the University of California, Irvine Institutional Review Board (UCI IRB # 20216747). All samples were obtained with the informed consent of the human subjects. Participants were eligible to participate if they were greater than 21 years of age and had been exclusively vaping (i.e., did not smoke cigarettes) for more than a year at the time of sampling. Each participant was informed of experimental protocols and signed consent forms prior to sample collection. To avoid bias in VOC profiles from prior vaping and/or other metabolic influences, volunteers were required to have not vaped, eaten, or drank anything (other than water) prior to the morning visit.³⁶⁶⁻³⁶⁸ In addition, background samples of laboratory room air and the participant's exhaled baseline breath were collected (prior to the first vape puff) to determine the incremental increase in exhaled compounds as a result of vaping.

During each visit, the participant used a brand-new vape of the same model/brand habitually used. Participants exhaled vape puffs into 2 L whole air sampling (WAS) canisters and a Tedlar[®] bag for analysis. Inhaled breath topography information (e.g., puff volume, puff duration, puff inhalation rate) were recorded using a Sodium SPA-M[®] analyzer (Körber Technologies). Inhalation volumes and rates were utilized for the PTR-ToF-MS

direct injection measurements and calculations (*described below*). Five different flavor profiles were selected for this study- mint, watermelon (or tobacco for participants 2 and 3), apple, vanilla, and mango. Only one flavor was smoked during each visit and flavors were rotated until all five had been smoked by each individual. Tobacco was initially one of the five profiles selected for this study, but due to negative feedback from participants 2 and 3, it was discontinued and switched out for watermelon. Participant 8 smoked a tobacco cream flavored vape as this was the manufacturer's alternative for vanilla, and this trial was grouped with all other vanilla trials for analysis. The various e-cigarette devices, settings, flavors, and puff topography information are reported in **Table 6.1**.

Table 6.1. Participants, vape devices, e-liquid, and inhaled puff information. Vapes are classified as either *closed* or *open*. Participant preferences and operating inputs (power, resistance, and voltage settings) are reported for *open* vapes. Flavors denoted with (*) were conducted instead of watermelon. Flavors denoted with (**) are alternatives for vanilla. The reported inhaled puff volumes are reported as the average amongst all puffs during one visit with uncertainty values reported to one standard deviation. Stated nicotine concentrations are those reported by the manufacturer, whereas actual nicotine concentrations are those determined by GC-MS measurements. E-liquid nicotine measurements were conducted using the method described in Pagano *et al.* (2015) for thirty three of the forty e-liquids included in this study.³⁶⁹ Gas chromatograph (6850 Series II, Network GC System, Agilent Technologies) coupled to a quadrupole mass spectrometer in electron ionization mode (5975B VL MSD, Agilent Technologies) was used to analyze the nicotine standards and e-liquid samples. Nicotine values typically deviated from those reported by the manufacturers.

Participant & Vape Type	E-Cigarette Brand/Model	E-Liquid Flavor	Inhaled puff volume (mL)	Stated nicotine (mg/mL)	Actual nicotine (mg/mL)	Set Power (Watt)	Resistance (Ω)	Voltage (V)
1 <i>Closed</i>	PUFF Xtra Limited	Cool Mint	55 $\pm$ 7	50	–	N/A	N/A	N/A
	PUFF Xtra Limited	Watermelon Skittles	36 $\pm$ 2	50	–			
	Puffs Plus	Mango	61 $\pm$ 9	50	33			
	Puffs Plus	Banana Vanilla	70 $\pm$ 10	50	–			
	Puffs Plus	Apple	59 $\pm$ 10	50	23			
2 <i>Open</i>	SMOK® POZZ X	Spearmint (<i>Mints</i>)	201 $\pm$ 160	50	61	40	0.4	4
		Apple (<i>Red's Apple by 7 Daze Salt Series</i>)	406 $\pm$ 150	50	58	5	0.4	1
		Sweet and Salty Tobacco*	138 $\pm$ 50	50	–	9	0.66	2.44
		Vanilla Custard (<i>BLVK® Nicotine Salt</i>)	331 $\pm$ 30	50	85	6	0.39	1.53
		Mango (<i>Skwezed Salt Based Nicotine</i>)	297 $\pm$ 120	50	79	6	0.38	1.52

3 <i>Open</i>	SMOK® POZZ X	Spearmint (<i>Mints</i>)	142 ± 10	50	61	40	0.4	4
		Apple (<i>Red's Apple by 7 Daze Salt Series</i>)	262 ± 40	50	58	5	0.4	1
		Sweet and Salty Tobacco*	204 ± 10	50	–	9	0.66	2.44
		Vanilla Custard (<i>BLVK® Nicotine Salt</i>)	233 ± 20	50	85	6	0.39	1.53
		Mango (<i>Skwezed Salt Based Nicotine</i>)	262 ± 10	50	79	6	0.38	1.52
4 <i>Closed</i>	LUCID AIR	Watermelon Ice	86 ± 10	50	41	N/A	N/A	N/A
	LUCID AIR	Jazzy Mango	65 ± 3	50	43			
	LUCID AIR	Apple Ice	38 ± 2	50	53			
	LUCID AIR	Icy Mint	64 ± 5	50	–			
	Blu	Vanilla	31 ± 8	25	27			
5 <i>Open</i>	SMOK® Morph 2	Apple (<i>Red's Apple by 7 Daze</i>)	254 ± 30	6	4	140	0.36	7.09
		Vanilla custard (<i>Vapetasia</i>)	341 ± 70	6	4	140	0.36	7.09
		Mango (<i>Red's Apple by 7 Daze</i>)	296 ± 9	6	5	140	0.36	7.09
		Jewel Mint (<i>Pod Juice</i>)	203 ± 20	6	2	140	0.36	7.09
		Watermelon (<i>Red's Apple by 7 Daze</i>)	283 ± 50	6	5	140	0.36	7.09
6 <i>Open</i>	SMOK® Alike	Watermelon (<i>Red's Apple by 7 Daze</i>)	179 ± 30	3	2	24	0.43	3.19
		Mango (<i>Red's Apple by 7 Daze</i>)	196 ± 30	3	2	20	0.43	2.92
		Apple (<i>Red's Apple by 7 Daze</i>)	262 ± 20	3	3	15	0.43	2.52
		Vanilla (<i>Custard Monster</i>)	259 ± 30	3	3	15	0.43	2.52
		Mint Ice (<i>Red's Apple by 7 Daze</i>)	243 ± 10	3	3	15	0.43	2.52
7 <i>Closed</i>	Elfbar BC5000	Watermelon Bubble Gum	127 ± 30	50	59	N/A	N/A	N/A
	Elfbar BC5000	Mango Peach	129 ± 10	50	61			
	Hyde Rebel Pro	Vanilla	153 ± 10	50	–			
	Elfbar BC5000	Lemon Mint	114 ± 10	50	67			
	Elfbar BC5000	Sour Apple	122 ± 20	50	61			

8 <i>Closed</i>	Flum Gio	Juicy Apple	36 ± 4	50	95	N/A	N/A	N/A
	Flum Gio	Tobacco Cream**	44 ± 9	50	99			
	Flum Float	Watermelon Lush Ice	54 ± 10	50	74			
	Flum Float	Cool Mint	53 ± 6	50	73			
	Flum Float	Strawberry Mango	44 ± 3	50	103			

Figure 6.1 shows the sampling progression for an example participant trial (participant 4, collection 3). During each experiment, a Tedlar® 100 L air sample bag (Dupont de Nemours) was connected to the PTR-ToF-MS for participant sampling. The bag was initially filled with 80 L of clean dry air prior to each participant sampling visit. Further details on the Tedlar® bag treatment can be found *below* in Section 6.2.2. PTR-ToF-MS measurements began with 10 minutes of sampling laboratory room air. The PTR-ToF-MS inlet was then connected to the Tedlar® bag and 10 minutes of clean air sampling was conducted. Using a mouthpiece made of Teflon tubing, the participant exhaled a baseline breath into the bag (no vape). This and subsequent puffs created a spike in the signal because the PTR-ToF-MS sampling port was close to the injection port, but the signal stabilized after several minutes. After the background samples were collected, volunteers were requested to remain sedentary, as physiological changes can induce concentration fluctuations.³⁷⁰ During the PTR-ToF-MS stabilization time, the participant exhaled a baseline breath into a WAS canister. Next, the participant inhaled from an e-cigarette and exhaled into the Tedlar® bag. While the PTR-ToF-MS was stabilizing after the exhaled vape puff, the participant inhaled from the vape device again and exhaled into a separate WAS canister. Lastly, a custom-built, programmable syringe pump was used to pull 20 mL of e-cigarette aerosol (directly from each vape device) and inject the aerosol into the Tedlar® bag at a rate of 9.3 mL s⁻¹ (Section 6.2.2). Direct injection measurements were not collected in WAS canisters for GC analysis due to oversaturating detector responses.

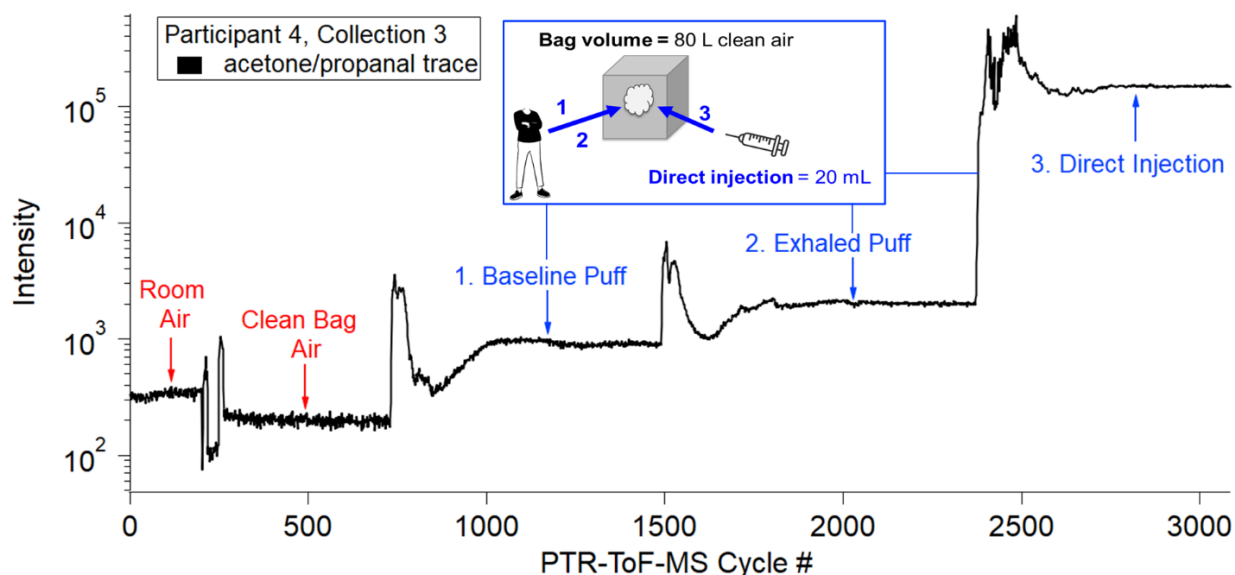


Figure 6.1. Example of sampling progression using the PTR-ToF-MS for participant 4, collection 3. The acetone/propanal (m/z 59.0491, $C_3H_7O^+$) trace was selected (black trace), and the intensity is shown as a function of the PTR-ToF-MS cycle number (each cycle is 1 s). After sampling room air and clean air, a participant exhaled a baseline puff (segment 1) into the bag and the ion trace increased. Once the trace plateaued, the participant inhaled from the vape device and exhaled into the bag (segment 2). Finally, a syringe was directly connected to the vape device and 20 mL of vape aerosol was collected then subsequently pushed into the bag using a syringe pump (segment 3).

6.2.2 Online PTR-ToF-MS Measurements

A PTR-ToF-MS (model 8000, Ionicon Analytik GmbH, Innsbruck, Austria) was utilized for the online, real-time analysis of VOCs exhaled by participants without any sample aging or pretreatment. PTR-ToF-MS technology is described in detail in Jordan *et al.* (2009) and Yuan *et al.* (2017) and is briefly discussed here, as it pertains to concentration determinations.^{371,372} PTR-ToF-MS is a soft chemical ionization instrument. Ionization occurs through proton transfer reactions with volatile organic compounds (VOCs) and reagent hydronium ions (H_3O^+) to form $[M+H]^+$ ions. A hollow-cathode plasma ion source produces H_3O^+ reagent ions that enter a reaction chamber (drift tube) for exposure and collision with analyte VOC molecules. Proton transfer reaction, and subsequent ion detection

by the mass spectrometer, will occur during collision only if the proton affinity (PA) of the analyte compound is greater than that of water (691 kJ mol^{-1}).³⁷³ Common constituents of air (such as N_2 , O_2 , Ar, CO_2 , and CO) have PAs less than 691 kJ mol^{-1} and, thus are not detected by PTR-ToF-MS. Most VOCs have PAs greater than water and can be detected, with the exception of alkanes smaller than C5.³⁷⁴ Though energy upon collision of VOCs with H_3O^+ is mild enough to leave most molecules intact, fragmentation often occurs for weak chemical bonds and/or large exothermicity of proton-transfer-reactions.

Prior to each participant visit, mass-to-charge calibration was performed using four isotopic ions commonly observed in room air: m/z 21.0221 ($\text{H}_3^{18}\text{O}^+$), 33.9935 ($^{18}\text{O}^{16}\text{O}^+$), 39.0327 ($\text{H}_2^{18}\text{O})\text{H}_3^{16}\text{O}^+$), and 59.0491 [$\text{C}_3\text{H}_6\text{O} + \text{H}$]⁺. The PTR-ToF-MS drift tube settings for temperature, pressure, and voltage were 60°C (T_{drift}), 2.29 mbar (p_{drift}), and 600 V (U_{drift}), respectively, resulting in a ratio of the electric field (E) to the number density of the drift tube buffer gas molecules (N) of $E/N \sim 132 \text{ Td}$ (where $\text{Td} = 10^{17} \text{ V cm}^2$). Analyte sampling was conducted at a flow rate of 0.1 L min^{-1} through a PEEK tubing inlet (1.59 mm O.D.) heated to 70°C . The data were acquired with a 1 s time resolution. Depending on the species measured, the limit of detection was in the range of several parts per billion by volume (ppbv) or better. PTR-ToF-MS calibration was conducted using a standard solution of VOCs (acetone, formic acid, acetic acid, acetaldehyde, and formaldehyde) at known concentrations (5, 10, 30, 50, 100, 150, 200, 250 ppbv). Through analysis of the calibration curves (**Figure 6.2**), it was determined that small acids were approximately 30% underestimated by the PTR-ToF-MS, ketones were approximately 10% overestimated, and aldehydes had varied results, acetaldehyde was correctly determined by PTR-ToF-MS but formaldehyde was 64%

underestimated. These correction values were not applied to participant data due to much larger fragmentation pattern discrepancies discussed in the manuscript.

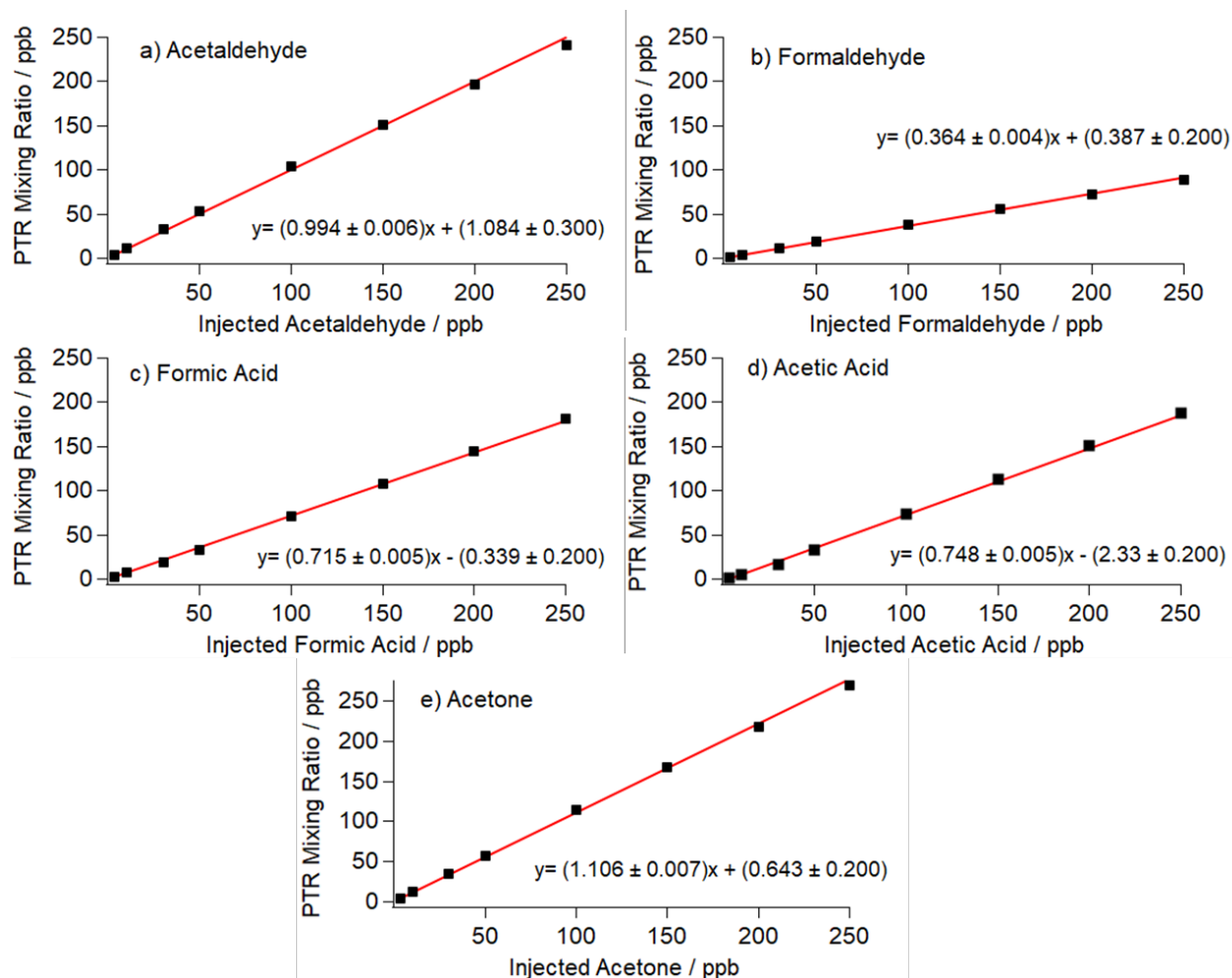


Figure 6.2. PTR-ToF-MS calibration conducted using standard solutions of VOCs: acetaldehyde, formaldehyde, formic acid, acetic acid, and acetone (a-e, respectively) at known concentrations (5, 10, 30, 50, 100, 150, 200, 250 ppbv). Through analysis of these calibration curves, it was determined that small acids were approximately 30% underestimated by the PTR-ToF-MS, ketones were approximately 10% overestimated, and aldehydes had varied results, acetaldehyde was correctly determined by PTR-ToF-MS but formaldehyde was 64% underestimated. These trends were not factored into our reported concentrations, as our uncertainty in this human trial study far exceeds these errors.

During each participant visit, a Tedlar® bag was connected to the PTR-ToF-MS inlet for participant sampling. The most common material of Tedlar® bags is polyvinylfluoride (PVF) $(\text{C}_2\text{H}_3\text{F})_n$.³⁷⁵ PTR-ToF-MS measurements of clean Tedlar® bags show large peaks at m/z 88.0757 (N,N-dimethylacetamide, $\text{C}_4\text{H}_{10}\text{NO}^+$) and m/z 95.0491 (phenol, $\text{C}_6\text{H}_7\text{O}^+$). Both compounds are known to be present in Tedlar® bag production and have been seen in the gas-phase measurements of previous studies.^{375–379} These compounds are quantitatively excluded from our results, as the background levels remain constant throughout sampling. Tedlar® bags were cleaned 3x prior to each participant sampling through purging gas-phase pollutants by evacuating the bags and refilling them with clean air from a purge air generator (filtered and scrubbed of VOCs, CO_2 , and water vapor). This cleaning did not fully remove “sticky”, residual compounds that were adsorbed on bag walls (i.e., nicotine). Removing residual compounds would require heating the bags to 60 °C and evacuating/filling them with clean air multiple times, which was not feasible within the turnaround time between all participants.³⁷⁵ Nicotine (m/z 163.1223, $\text{C}_{10}\text{H}_{15}\text{N}_2^+$) was present in the background prior to sampling but background levels did not affect the increases observed from new vapes into the bag.

A customized programable syringe pump was manufactured to accommodate a Tomopal 50 mL glass syringe, facilitating the delivery of 20 mL of e-cigarette aerosol into a Tedlar® bag. Utilizing computer numerical control (CNC) machining, a syringe pump chassis was created from a 15.24 x 30.48 x 5.08 cm white ultra-high molecular weight polyethylene sheet. This chassis included two linear motion carbon steel shafts measuring 9.52 mm in diameter and 228.60 mm in length on each side, equipped with bushings to reduce friction during operation. Positioned between the linear motion shafts, a stepper motor connected

to a threaded shaft measuring 300 mm in length was utilized to regulate the syringe pump's movement. The stepper motor was interfaced with a Raspberry Pi 3 model B+, which controlled the stepper motor through the general-purpose input/output (GPIO) pins using the Python programming language. The 20 mL aspiration and extraction processes of the syringe were represented by the step angle of the stepper motor, whereas the flow rate was determined by the delay value, which represents the delay between each step of the stepper motor.

Data analysis was conducted using the PTR-MS Viewer 3.4.2 software (Ionicon). Reported VOCs were expected to form $[M + H]^+$ ions. However, the observed mass spectra were strongly affected by in-source ion fragmentation and other ion-molecule ionization pathways *as discussed below*. The PTR-ToF-MS traces were defined as room air, clean air (clean air inside Tedlar® bags), background breath (no vape), exhaled puff (with vape), and direct injection of vape aerosol. Data from Pagonis *et al.* (2019) were especially useful for the identification of compounds detected by the PTR-ToF-MS.³⁸⁰ A peak list was generated from ions observed in the mass spectra of participant samples. Ions were identified by comparison with the publicly available library, which contains 1000 trace gases detected by PTR-MS and displays the fragmentation patterns of compounds after proton transfer reactions.³⁸⁰ Once a peak list was compiled, a ratio of each ion's intensity in spectrum A (exhaled puff) to spectrum B (background breath) was taken. Ions in the peak list with ratio > 1 were focused on for further analysis.

After injection of each sample (baseline breath, exhaled vape puff, or direct vape injection) into the Tedlar® bag, the signal plateaued and stabilized. For each VOC, an average of the signal was taken over 5 minutes after stabilization. This average signal was converted

to mixing ratio of the corresponding gas. The high mass resolving power of PTR-ToF-MS was essential for identifying compounds with the same nominal m/z values. **Figure 6.3** illustrates the advantage of the high resolving power for three separate samples (exhaled breath, direct injection, and heated glycerol) at nominal masses 43 and 57. Clear separation and resolution of peaks is achieved for m/z 43.018 ($C_2H_3O^+$) and 43.054 ($C_3H_7^+$), as well as at m/z 57.033 ($C_3H_5O^+$) and 57.070 ($C_4H_9^+$). Despite the high resolving power, peaks with the same nominal mass could not be cleanly resolved if they had vastly different abundances. For example, separation could not be achieved at nominal mass 93 (**Figure 6.3**) due to an overwhelming signal at m/z 93.055 ($C_3H_9O_3^+$) from humectant glycerol, which made it difficult to differentiate and quantify the much smaller signal from toluene at m/z 93.070 ($C_7H_9^+$). Therefore, the signal at m/z 93 represents a combination of mostly glycerol and some toluene. For compounds observed to increase in comparison to the background breath, concentrations were determined by the PTR-MS Viewer software. Concentration values (ppbv) were converted into mass concentrations ($\mu\text{g VOC puff}^{-1}$) without correcting for various fragmentation pathways. Baseline breath values were subtracted from exhaled breath values.

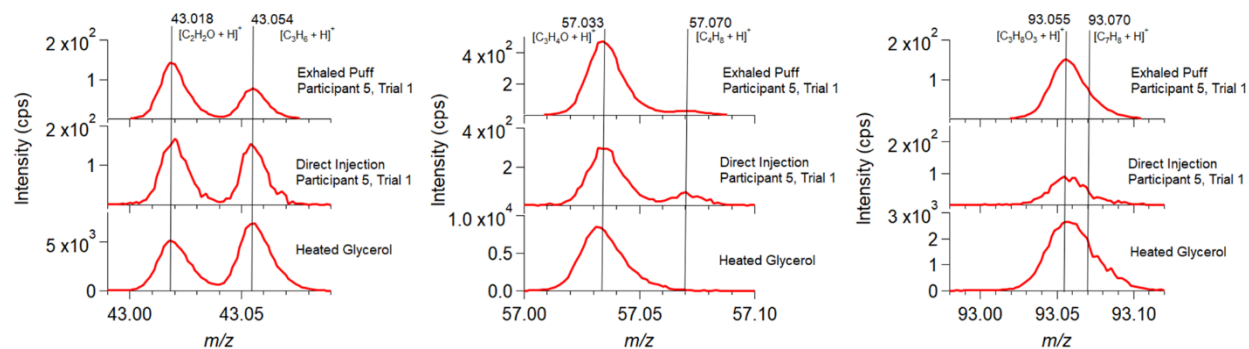


Figure 6.3. Expanded view of the PTR-ToF-MS spectra showing the separation of multiple peaks observed at nominal m/z 43, 57, and 93. Heated glycerol (bottom panel) is compared with exhaled puff (top) and direct injection (middle) measurements from participant 5's first visit.

The PTR-MS Viewer software uses **Equation 6.1** to convert average signal intensity into mixing ratio (C_{ppb}^i) in the unit of ppbv. Other terms in **Equation 6.1** are defined as follows. “ k ” is the ion-molecule collision reaction rate constant ($= 2.0 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$). While this rate constant can range from 1.5 to $\sim 5 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$, a single value for the rate constant was used for all VOC.^{374,380} This variable contributes the largest to the uncertainty in the determination of VOC estimated concentrations, which is expected to be $\pm 50\%$. “ μ_0 ” is the reduced ion mobility ($= 2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). “ U_{drift} ” is the total voltage across the drift tube ($= 600 \text{ V}$). “ N_A ” is the Avogadro number. “ l ” is the length of the drift tube ($= 9.3 \text{ cm}$). “ T_{drift} ” is the drift tube temperature ($= 333 \text{ K}$). “ T_0 ” is the temperature at standard conditions ($= 273.15 \text{ K}$). “ p_{drift} ” is the drift tube pressure ($= 2.29 \text{ mbar}$). “ p_0 ” is the pressure at standard conditions ($= 1013.25 \text{ mbar}$). “ C_i^+ ” is the measured signal (in cps) for the $[M+H]^+$ ion of interest. “ $C_{H_3O^+}$ ” is the measured signal (in cps) of the reagent ion (signal at m/z 21 was used ($\times 500$), which is the isotopic ratio for $H_3O^+/H_3^{18}O^+$, due to m/z 19 signal being too large to quantify). “ TR_i ” is the transmission efficiency of the ion of interest (from Ionicon Analytik). Transmission factors (TR_i) were measured regularly using a certified cylinder containing 14 aromatic

compounds (Restek, TO-14A mix) ranging from benzene (m/z 79.0448) to 1,2,4-trichlorobenzene (m/z 180.9379). Some uncertainty is associated with this determination and the transmission used in this study were: m/z 19 ($TR_i = 0.18$), m/z 93 ($TR_i = 0.57$), m/z 105 ($TR_i = 0.66$), m/z 113 ($TR_i = 0.71$), m/z 121 ($TR_i = 0.74$), m/z 147 ($TR_i = 0.85$), and m/z 181 ($TR_i = 1$). “ $TR_{H_3O^+}$ ” is the transmission efficiency of H_3O^+ m/z 19 ($= 0.18$). “ Iso_i ” is the isotopic abundance of the ion of interest.

$$C_{ppbv}^i = \frac{10^9}{k} \times \frac{22400 \cdot \mu_0 \cdot U_{drift}}{N_A \cdot l^2} \times \frac{T_{drift}^2}{T_0^2} \times \frac{p_0^2}{p_{drift}^2} \times \frac{TR_{H_3O^+}}{C_{H_3O^+}} \times \sum_i \frac{C_i^+ \cdot Iso_i}{TR_i} \quad \text{Equation 6.1}$$

Concentration values (ppbv) determined by the PTR-Viewer Software were converted into mass concentrations ($\mu\text{g VOC puff}^{-1}$) using **Equations 6.2-6.6**. $\Delta ppbv_{Baseline}$ is the concentration of baseline VOC subtracted from the clean air inside the bag (**Equation 6.2**). $\Delta ppbv_{Exhaled}$ is the concentration of VOC in the exhaled puff subtracted from the background breath concentration (**Equation 6.3**). $\Delta ppbv_{Direct Injection}$ is the concentration of VOC in the direct injection subtracted from the exhaled puff VOC concentration, as the Tedlar® bag was not cleaned after exhaled puff and the PTR-ToF-MS signal is additive (**Equation 6.4**). For the baseline breath, exhaled puff (after e-cigarette inhalation), and direct injection of e-cigarette aerosol, $\Delta ppbv$ for each VOC was converted into $\mu\text{g VOC}$ in the bag using **Equation 6.5** and the following: concentration of air molecules under ambient conditions ($2.46 \times 10^{19} \text{ molecules cm}^{-3}$), the molecular weight of each VOC, and the volume of clean air inside the Tedlar® bag (80 L). In the case of the direct injection (**Equation 6.6**), there was no participant interaction with these measurements and thus needed to be

corrected using the inhaled volume of each participant's puff (from topography measurements, **Table 6.1**) and the volume of direct injection (20 mL).

$$\Delta ppbv_{Baseline} = ppbv_{Baseline} - ppbv_{Clean\ air} \quad \text{Equation 6.2}$$

$$\Delta ppbv_{Exhaled} = ppbv_{Exhaled} - \Delta ppbv_{Baseline} \quad \text{Equation 6.3}$$

$$\Delta ppbv_{Direct\ Injection} = ppbv_{Direct\ Injection} - \Delta ppbv_{Exhaled} \quad \text{Equation 6.4}$$

$$\begin{aligned} \mu g\ VOC\ puff^{-1} &= \Delta ppbv_{Baseline\ (or\ Exhaled\ or\ Direct\ Injection)}\ VOC \times 2.46 \cdot 10^{10} \left(\frac{molecules}{ppbv\ cm^3} \right) \\ &\times \left(\frac{mol}{6.022 \times 10^{23}\ molecules} \right) \times MW\ VOC \left(\frac{g}{mol} \right) \times 80\ L\ bag \times \left(\frac{1000\ cm^3}{1\ L} \right) \times \left(\frac{1\ \mu g}{10^{-6}\ g} \right) \end{aligned} \quad \text{Equation 6.5}$$

$$Corrected\ \mu g\ VOC\ puff^{-1} = \mu g\ VOC\ in\ the\ bag \times \left(\frac{V_{puff\ topography}\ (mL)}{V_{syringe}\ (mL)} \right) \quad \text{Equation 6.6}$$

6.2.3 Whole Air Sample Canisters Collection and Offline Gas Chromatography Analysis

Prior to collection, the canisters were first conditioned by baking them at 150 °C in humidified air for 12 h to form an oxidative layer inside the canisters that passivates the walls. Following the baking procedure, each canister was pumped-and-flushed several times using clean air to dilute any possible residual air inside the canisters (i.e., pressurization of the canisters to 40 psi followed by subsequent depressurization to ambient pressure), and then evacuated to 10⁻² Torr. Finally, they were filled to 200 Torr with ultra-high purity helium and evacuated once again to 10⁻² Torr. Each canister was fit with a Swagelok “T union” where the second end of the “T union” was connected with Teflon tubing (10 cm long). During sample collection, each subject exhaled through the Teflon tubing into the canister

(while an operator manually opened the valve immediately after plugging the third end of the union) to allow the collection of their breath inside the canister.

Briefly, three GCs (all Hewlett-Packard HP-6890) and five column/detector combinations were used with flame ionization detection (FID), electron capture detection (ECD) and a mass selective detector (MSD) operating in selected ion monitoring (SIM) mode. The five column/detector combinations were DB-1 + FID, PLOT/DB-1 + FID, Restek-1701 + ECD, Restek-1701/DB-5 + ECD, and DB-5ms + MSD. To analyze a WAS sample, the canister was connected to the analytical system and 260 cm^3 of sample was pre-concentrated with liquid nitrogen via a loop which is filled with glass beads to increase surface area upon which the compounds of interest can condense. After the pre-concentration step, the VOCs were re-volatilized by replacing the liquid nitrogen with near boiling water ($84\text{ }^{\circ}\text{C}$) and then the VOCs were injected with a helium carrier to a splitter box that separated the sample flow into five streams, each directed to one of the column/detectors.

Compounds eluted with highest precision on one or multiple column/detector combinations. When a high-precision peak eluted on two or more column/detector combinations the results were averaged (e.g., propane, propene, benzene, toluene, ethylbenzene, xylenes). The FIDs were used for hydrocarbon detection whereas the ECDs were used for the detection of halocarbons and alkyl nitrates. The mass spectrometer was used for sulfur and oxygenated species as well as a secondary (or sometimes tertiary) measurement of many hydrocarbons and halocarbons. The limit of detection (LOD), measurement precision and accuracy vary for each species. For the VOCs specifically discussed in this study, these parameters are summarized in **Table 6.2**.

Table 6.2. VOC limit of detection and measurement precision and accuracy for the GC platform.

Compound	LOD (ppt)	Precision (%)	Accuracy (%)
Propene	10	10	10
1,2-Propadiene	10	10	10
Toluene	10	10	10
Styrene	10	10	10
Isoprene	10	10	10
Monoterpene	10	20	20
Acetaldehyde	100	20	30
Acetone	100	20	30
Ethyl Acetate	50	20	30
Methyl butanoate	50	20	30
Methanol	100	20	30
Ethanol	100	20	30
Propanol	100	20	30
DMS	10	10	10

Exhaled breath was also collected using evacuated 2 L electropolished whole air sampling (WAS) stainless steel canisters. For each exhaled breath sample, the subject exhaled through a ¼ inch OD Teflon tube directly into the canister, without any further dilution. After collection, each canister was analyzed within a few days. The gas chromatography (GC) platform used for the quantitative detection of VOCs uses a set of three GCs coupled to various detectors, including a mass spectrometer (GC-MS), flame induced detector (GC-FID) and an electron capture detector (GC-ECD), working in parallel for the detection of a wide variety of species including alkanes (C2-C10), cycloalkanes (C4-C7), alkenes (C2-C10), ethyne, aromatics (C6-C9), halocarbons (C1-C2), alkyl nitrates (C1-C5), selected sulfur compounds, and selected oxygenated VOCs. A detailed description of the GC

platform and analytical procedures for VOC analysis are provided in Colman *et al.* (2001) and Simpson *et al.* (2010).^{381,382}

The chromatograms were digitally acquired with Chromeleon (version 6.4, Thermo Scientific, 2001) for the FIDs and ECDs signal and with Agilent Chemstation (MSD Chemstation, D.02.00.275, Agilent Technologies 1989-2005) for the MS signal. Each chromatographic peak was individually inspected, and the base line was adjusted when the integrated area was not accurately integrated by the software. Details on the standards and procedures for the VOC calibration are described in Simpson *et al.* (2020).³⁸³ Briefly, the detector response in area units is converted into mixing ratios by using a response factor calculated from a system of multiple standards, including calibrated standards and working standards. Concentration values (pptv) were then converted to mass concentrations ($\mu\text{g VOC puff}^{-1}$). For the baseline breath and exhaled puff (after e-cigarette inhalation), pptv for each VOC was converted into $\mu\text{g VOC puff}^{-1}$ using **Equation 6.7** and the following: concentration of air molecules under ambient conditions ($2.46 \times 10^{19} \text{ molecules cm}^{-3}$), the molecular weight of each VOC, and the volume of the WAS canister (2000 cm^3). Since the participants often did not exhale 2000 cm^3 worth of breath into the WAS can, a pressure correction was made by applying the ratio of the pressure inside of the can to 760 Torr. Unlike in the PTR-ToF-MS, baseline breath values were not subtracted from exhaled breath values, as two separate WAS canisters were used in sampling and signal from the different breath types were not additive in this case.

$$\begin{aligned}
\mu g \text{ VOC } puff^{-1} = & pptv_{Baseline \text{ (or Exhaled)}} \text{ VOC} \times 2.46 \cdot 10^7 \left(\frac{\text{molecules}}{pptv \text{ cm}^3} \right) \times \\
& \times \left(\frac{\text{mol}}{6.022 \times 10^{23} \text{ molecules}} \right) \times MW \text{ VOC} \left(\frac{g}{\text{mol}} \right) \times \left(\frac{1000 \text{ cm}^3}{1 \text{ L}} \right) \times \left(\frac{1 \mu g}{10^{-6} g} \right) \times 2000 \text{ cm}^3 \text{ WAS can} \times \\
& \left(\frac{\text{Pressure in can (Torr)}}{760 \text{ (Torr)}} \right)
\end{aligned}$$

Equation 6.7

6.2.4. Calibration Comparison of PTR-ToF-MS and GC

To compare concentration responses between the PTR-ToF-MS and the GC platform, a multi-component calibration mix was run on both instruments and compared with certified concentrations. The ambient air quality gas standard (Cylinder CC302254, 2000 psi, AiR Environmental Inc.) was composed of acetaldehyde, methanol, ethanol, acrolein, propanal, acetone, 2-propanol, acetonitrile, methyl tert-butyl ether, methacrolein, methyl vinyl ketone, methyl ethyl ketone, and 1-butanol. **Table 6.3** presents the concentrations measured by GC and PTR-ToF-MS instruments and the concentrations certified by the manufacturer.

Table 6.3. Measured concentrations of a 13-component ambient air quality gas standard (Cylinder CC302254, 2000 psi, AiR Environmental Inc.). The concentrations in the rightmost column were recertified by the manufacturer in February 2024.

Compound	PTR-ToF-MS Concentration (ppm) ^(a)	GC Concentration (ppm)	Certified Concentration (ppm)
Acetaldehyde	1.9 (<i>m/z</i> 45)	0.56	0.72
Methanol	0.79 (<i>m/z</i> 33)	0.99	0.67
Ethanol ^{(b)(f)}	0.14 (<i>m/z</i> 47)	–	0.76
Acrolein	1.7 (<i>m/z</i> 57.033)	1.1	0.25
Propanal	–	0.90	0.11
Acetone	–	1.2	1.1
Propanal + Acetone ^(c)	3.2 (<i>m/z</i> 59)	n/a	n/a
2-Propanol ^(d)	1.7 (<i>m/z</i> 61, 43, 41)	0.80	0.67
Acetonitrile ^(f)	2.0 (<i>m/z</i> 42)	–	0.91
Methyl Tert-Butyl Ether (MTBE) ^(f)	–	–	1.1
MTBE + 1-butanol ^{(c)(e)}	0.99 (<i>m/z</i> 57.070)	n/a	n/a
Methacrolein (MAC)	–	0.77	0.73
Methyl Vinyl Ketone (MVK) ^(f)	–	–	0.24
MAC + MVK ^(b)	3.4 (<i>m/z</i> 71)	n/a	n/a
Methyl Ethyl Ketone	2.0 (<i>m/z</i> 73)	1.1	0.90
1-Butanol ^(g)	–	–	0.13

(a) No external calibration factor was applied for this analysis

(b) Inomata et al. (2009) reported that, ethanol fragments into H₃O⁺ at higher E/N conditions, such as the ones used in this study (~132 Td). Consequently, the sensitivity at *m/z* 47 is reduced, consistent with our observation.

(c) The PTRMS cannot distinguish between isomers at *m/z* 59.0491 (C₃H₇O⁺), 57.070 (C₄H₉⁺), and 71.041 (C₄H₆O⁺).

(d) Analysis of the headspace of the pure standard showed that 2-propanol heavily fragments into its [M+H-H₂O]⁺ ion with an additional high intensity ion at *m/z* 41.040 (C₃H₅⁺), accounting for 65% of the *m/z* 43 (C₃H₇⁺) peak intensity.

(e) Both MTBE and 1-butanol do not show a [M+H]⁺ parent peak at *m/z* 89 and 75 respectively; but instead, both heavily fragment into a major ion at *m/z* 57.070 (C₄H₉⁺). Note that both compounds exhibit a small contribution to *m/z* 41.040 (C₃H₅⁺) as well accounting for about 26% and 15% of the *m/z* 57 peak for MTBE and butanol respectively, which overlaps with 2-propanol fragment.

(f) Note that a few compounds co-elute on our GC-FID column, which is the detector used for quantification. If two co-eluting species were both present at high concentration, such as in the VOC mixture, their respective quantification could not be conducted. This was the case for ethanol and acetonitrile (co-eluted at 8.963 min), as well as MTBE and MVK (co-eluted at 11.298 min).

(g) 1-Butanol was not detected by GC.

6.2.5. Propylene Glycol and Glycerol Standard Experiments

To assess the thermal degradation of the e-liquid components, pure PG (Fisher, > 99%, CAS 57-55-6) and GLY (Fisher, > 99.9%, CAS 56-81-5) decomposition products were sampled by both the PTR-ToF-MS and the WAS canisters. Two 1 L sampling bags were made from food-grade nylon-coated polyethylene film (FoodSaver®) and used for each humectant experiment. Participant 5's *open* vape device (SMOK® Morph 2) was used for these experiments. The liquid cartridge was cleaned with isopropanol, ethanol, and nanopure water then dried thoroughly prior to the humectant being added. New cotton and coils were used for each humectant experiment. As both PG and GLY are highly viscous (55 and 1470 mPa•s, respectively, at 293 K),^{384,385} we allowed ample time for the interior cotton wick to absorb humectant prior to turning the atomizer on. The vape was set to 20 W, 0.43 Ω , 2.92 V, the same settings used by participant 5. Prior to each experiment, 800 mL of clean air was added to the bag. Once the pure humectant was loaded into the vape device, the atomizer was turned on and the heated PG (or GLY) aerosol was collected using a clean disposable syringe. The bag was pre-filled with clean air, and 5 mL of heated humectant aerosol was injected into the bag that was sampled with both the PTR-ToF-MS and WAS canisters for respective analysis.

6.3 Results and Discussion

6.3.1 Overall Comparison between Exhaled Puff and Direct Vape Aerosol

Figure 6.4 shows the combined mass concentrations of the species observed by the PTR-ToF-MS for all participant visits. These values were calculated by summing the mass

concentrations for all detected compounds then averaging across all five visits per participant and breath type (baseline breath, exhaled puff, and direct injection). For all participants, baseline breath measurements were low, as expected by sampling protocols prohibiting eating, drinking, or smoking prior to the visit. Averaged mass concentrations for the exhaled puff were lower than direct injection measurements, indicating significant VOC absorption by participants prior to exhalation. This was the case for all participants except for participant 7. It is likely that this participant's exhaled volumes were inconsistent and resulted in uncertainty in corrected direct injection values calculated with **Equations 6.5** and **6.6**.

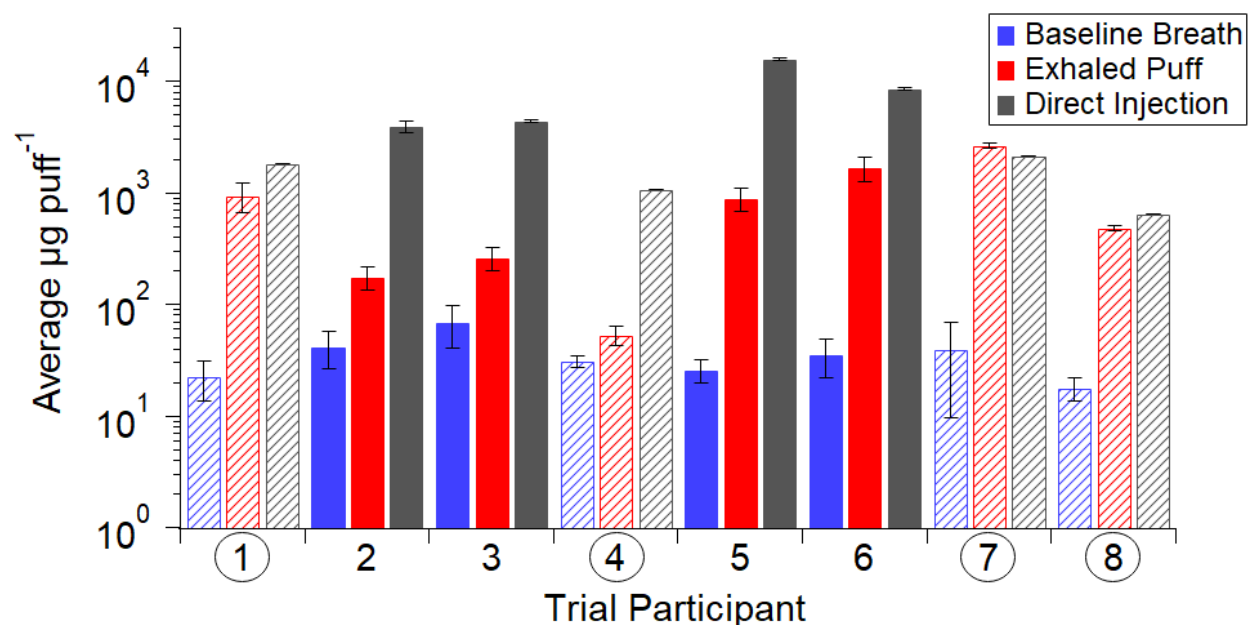


Figure 6.4. Combined mass concentrations of the species detectable by PTR-ToF-MS for all participant visits. The average mass per puff ($\mu\text{g VOC puff}^{-1}$) is shown for baseline breath (no vape, blue), exhaled puff (after inhaling from the vape device, red), and direct injection of vape aerosol (grey). The variability in the emissions is represented by error bars (one standard deviation) calculated using each participant's puff topography data (**Table 6.1**). Note that the vertical scale is logarithmic. Participants 1, 4, 7, and 8 used *closed* vapes (circled numbers, striped bars), whereas participants 2, 3, 5, and 6 used *open* vapes (solid bars). A linear version of this figure is presented in **Figure 6.5**.

For participants who smoked *open* vapes (participants 2, 3, 5, and 6), VOC mass concentrations in the direct injection measurements (**Figure 6.4**, grey solid bars) were an order of magnitude higher than exhaled puffs (**Figure 6.4**, red solid bars). Those who vaped *open* devices likely operated them at high power outputs and these individuals inhaled larger volumes than participants who vaped with *closed* devices (**Table 6.1**). Participant 5 is a noticeable example of this, as the *open* vape device was set to 140 Watts and the participant inhaled an average of 260 ± 40 mL with high VOC concentrations (Participant 5 direct injection, **Figure 6.4**). High VOC concentrations at high vape wattage are consistent with Gillman *et al.* (2016) who showed that increases in power applied to vape device coils correlated with increases in the total VOC yield.³⁸⁶ In general, participants who smoked *closed* vapes (1, 4, 7, and 8) inhaled lower puff volumes (**Table 6.1** and **Figures 6.4** and **6.5**) that were less concentrated, as shown by lower mass concentrations in direct injection measurements. **Figure 6.6** further presents this puff volume and mass concentration distinction amongst *closed* (red markers) and *open* (blue markers) vape devices measured by the PTR-ToF-MS. For all twelve selected VOCs presented in **Figure 6.6**, *closed* vape devices have smaller puff volumes with mass concentrations less widespread than *open* vape devices. In summary, the participants using *open* vape devices inhaled and absorbed a higher dose of total VOCs compared to the *closed* vape participants.

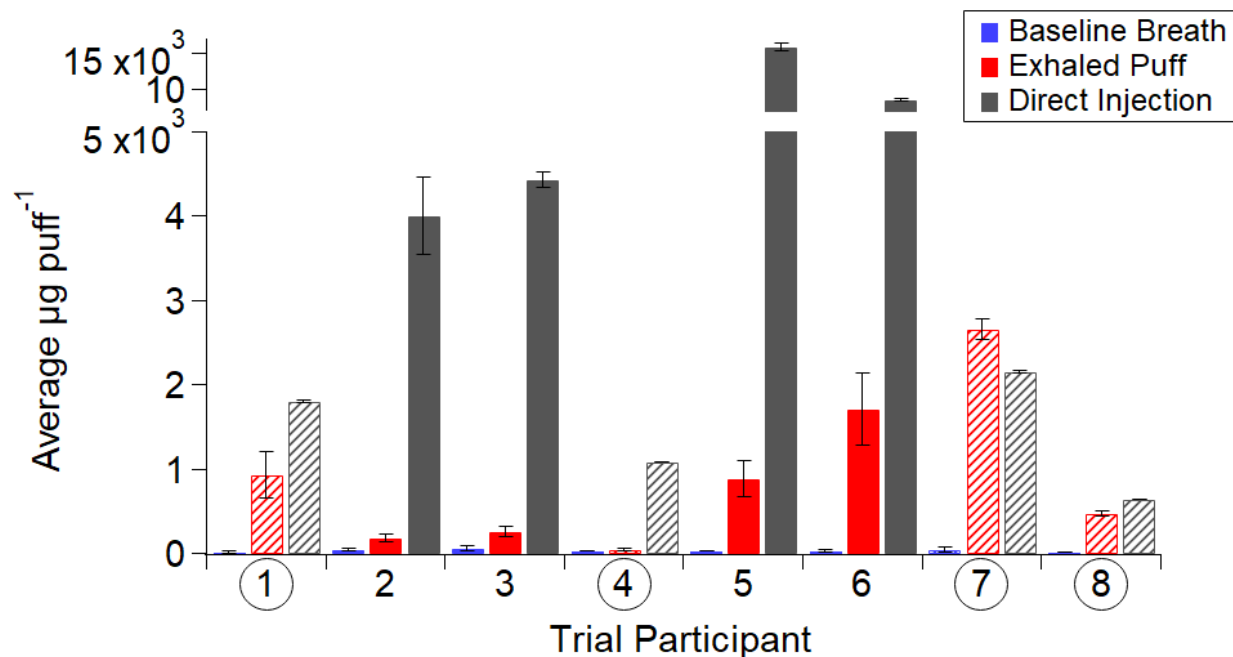


Figure 6.5. Linear scale of the combined mass concentrations of the species detectable by PTR-ToF-MS for all participant visits. The average mass per puff ($\mu\text{g VOC puff}^{-1}$) is shown for baseline breath (no vape, blue), exhaled puff (after inhaling from the vape device, red), and direct injection of vape aerosol (grey). The variability in the emissions is represented by error bars (one standard deviation) calculated using each participant's puff topography data (**Table 6.1**). Participants 1, 4, 7, and 8 used closed vapes (circled numbers, striped bars), whereas participants 2, 3, 5, and 6 used open vapes (solid bars). Note that this is the same plot as presented in **Figure 6.4**, but in linear scale.

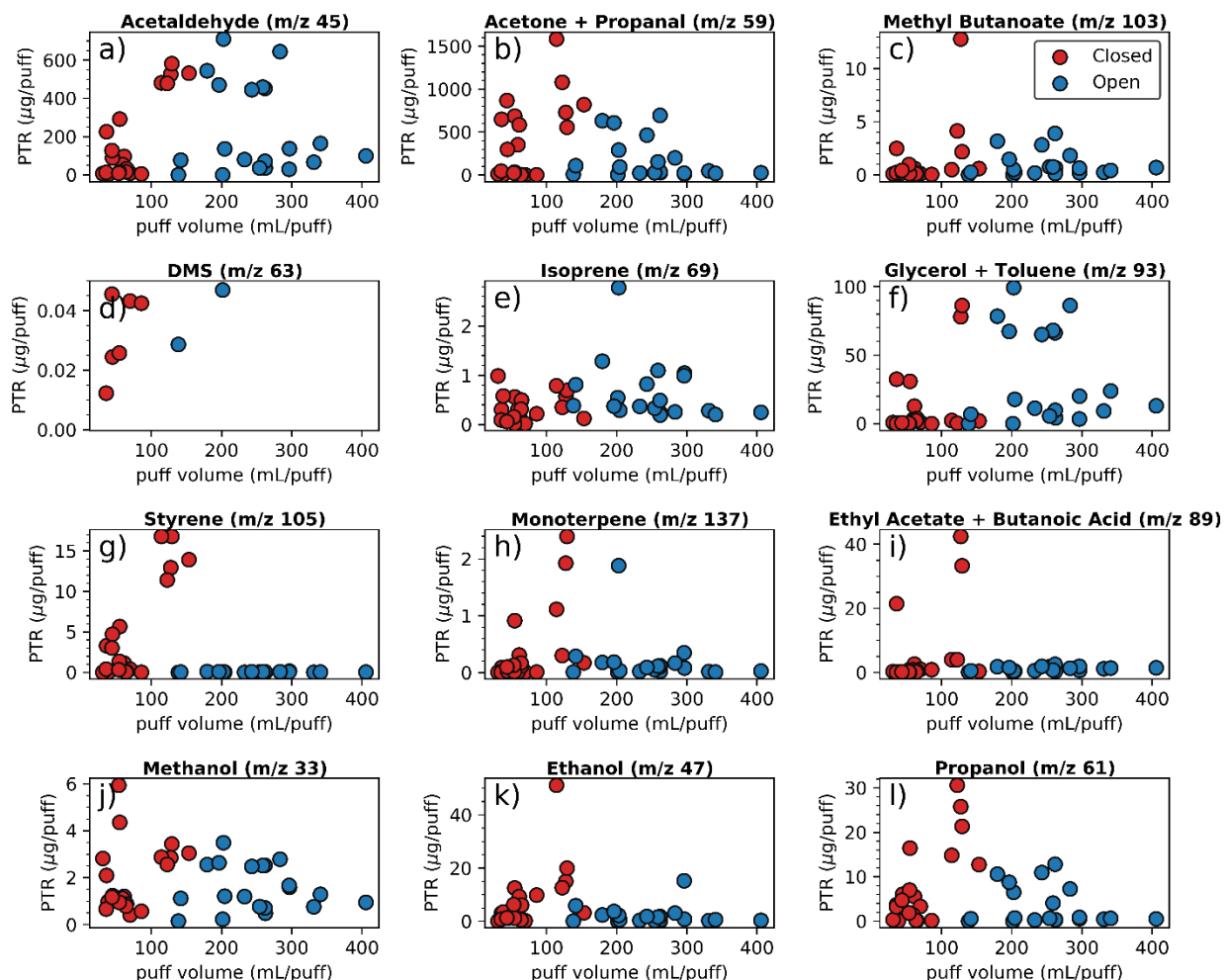


Figure 6.6. Exhaled puff PTR-ToF-MS values of micrograms per inhaled puff volume obtained from participant puff topography data. The puff volume reported is the volume each participant inhaled from their vape device prior to exhalation into the PTR-ToF-MS sampling unit. Twelve compounds were selected for this comparison. Red markers correspond to closed vapes and blue markers correspond to open vapes used in the human trial.

Figure 6.7 summarizes results for twenty-six selected VOCs averaged across all participant collections for baseline breath, exhaled puff, and direct injection measured by the PTR-ToF-MS. All presented VOCs follow the same trend of exhaled puff mass concentrations being lower than direct injection values due to the efficient deposition of VOCs in the respiratory tract. Thermal degradation of humectants PG and GLY are known to produce carbonyl products including formaldehyde, acetaldehyde, acetone, and acrolein.^{387,388} Acetaldehyde and acetone/propanal had the largest apparent concentrations across all participant visits in all breath types (**Figures 6.6a, b and 6.7a**). A few compounds are slightly elevated in baseline breath. For example, acetone is known to be a by-product of fat metabolism processes in the liver (typically 1 ppmv)³⁸⁹ and acetone concentrations are known to increase during exercise.³⁹⁰ Participants in this study walked approximately 1000 ft from the parking lot to the laboratory prior to sampling and hence this could have impacted baseline acetone levels. Other slightly elevated VOCs present in the baseline breath are also major endogenous breath metabolites.³⁹¹⁻³⁹³

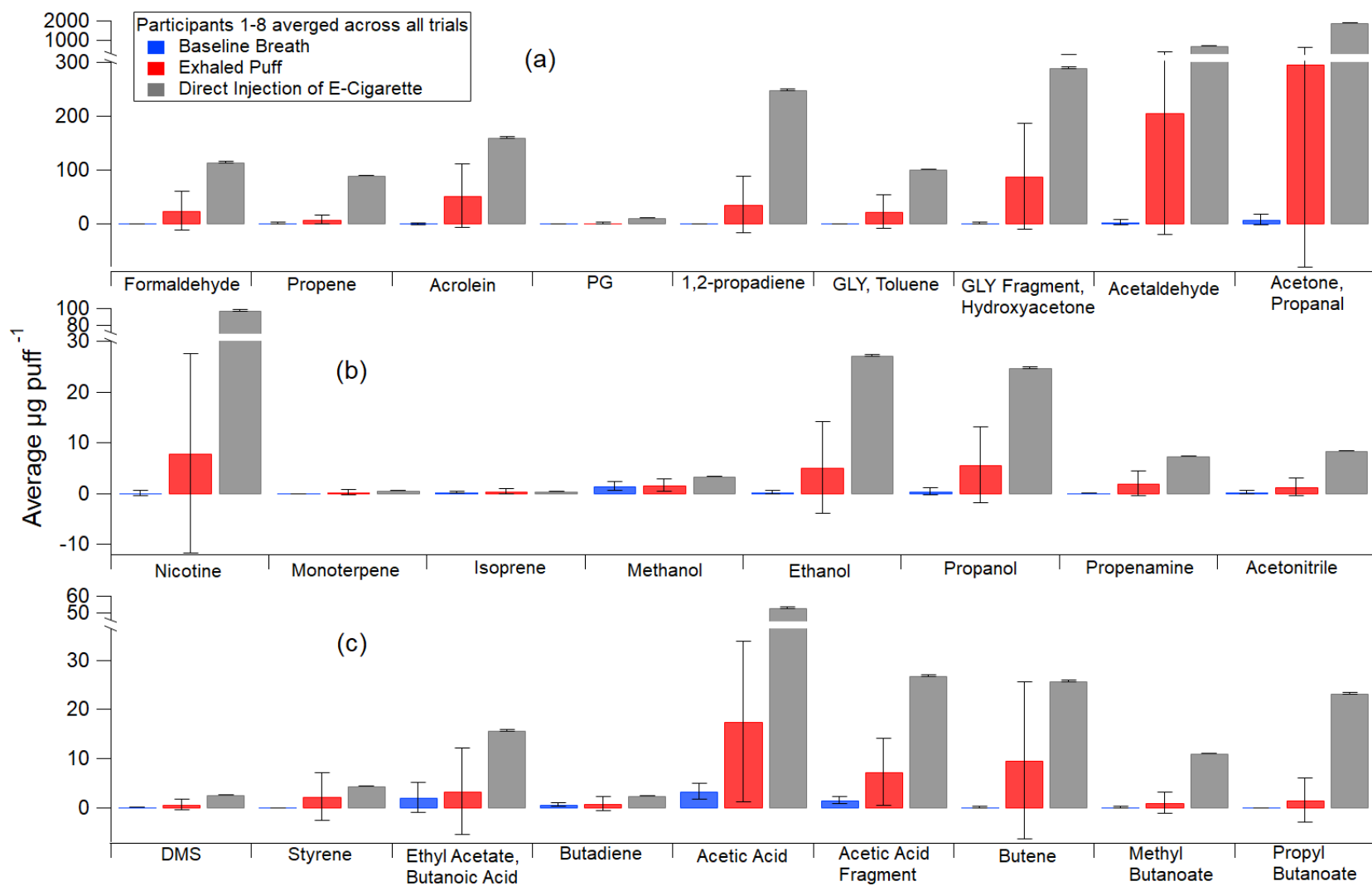


Figure 6.7. PTR-ToF-MS results of selected VOCs from all participant visits (40) with averaged measurements of baseline breath (no vape, blue), exhaled puff (after inhaling from the vape device, red), and direct injection of e-cigarette (grey). Error was calculated using each participant's puff topography data that varied by visit.

All e-liquids utilized in this study contained various concentrations of nicotine (**Table 6.1**). Nicotine (m/z 163.1230, $C_{10}H_{15}N_2^+$) was present in the exhaled breath of only nine trials (one trial of participant 2, all trials of participant 3, and three trials of participant 7). Nicotine was not detected in the baseline breath (**Figure 6.7b**), but for trials where nicotine was observed, the direct injection concentrations were an order of magnitude higher than the exhaled breath concentrations. On average, $\sim 10 \mu\text{g puff}^{-1}$ of nicotine was measured in the exhaled breath, whereas $\sim 100 \mu\text{g puff}^{-1}$ was detected in the direct injection measurements (mimicking inhalation), indicating high nicotine absorptivity by participants prior to exhalation.^{380,394} This result is widely supported by previous studies that measured enhanced plasma nicotine concentrations in human participants after vaping, with over 99% of nicotine being retained after inhalation.^{364,395-397}

6.3.2 Effect of Vape Flavor on Exhaled Breath VOC Distribution Measured by PTR-ToF-MS

PTR-ToF-MS mass spectra for all participants' exhaled breaths can be found in **Figures 6.8-6.15** and a list of observed ions can be found in **Table 6.4**. Potential assignments for ions observed in this study are consistent with previously reported assignments from PTR-ToF-MS measurements.^{366,372,375,378,380,394,398-410} Across all forty exhaled breath mass spectra, there was minimal deviation in mass spectral peaks and ten ions reproducibly dominated the signal. Ions at nominal m/z 31, 41, 43, 45, 47, 57, 59, 61, 75, 93 were the major ions commonly observed. An exception to this is participant 2's mass spectra for mint and tobacco flavored trials (**Figure 6.9a and b**). These trials had low signal and the dominant peaks were acetone (m/z 59) and isoprene (m/z 69), normal baseline substituents of human

breath.^{411–413} Participants 2 and 3 smoked the same vape device and e-liquids, but in comparison to participant 3, participant 2 generated lower intensity mass spectra (**Figure 6.9**) for mint and tobacco trials and mass spectral peaks did not resemble other participant trials. This result reflects the variability in emissions depending on how a participant interacts with their vape device and how personal habits influence VOC mass concentrations.⁴¹⁴

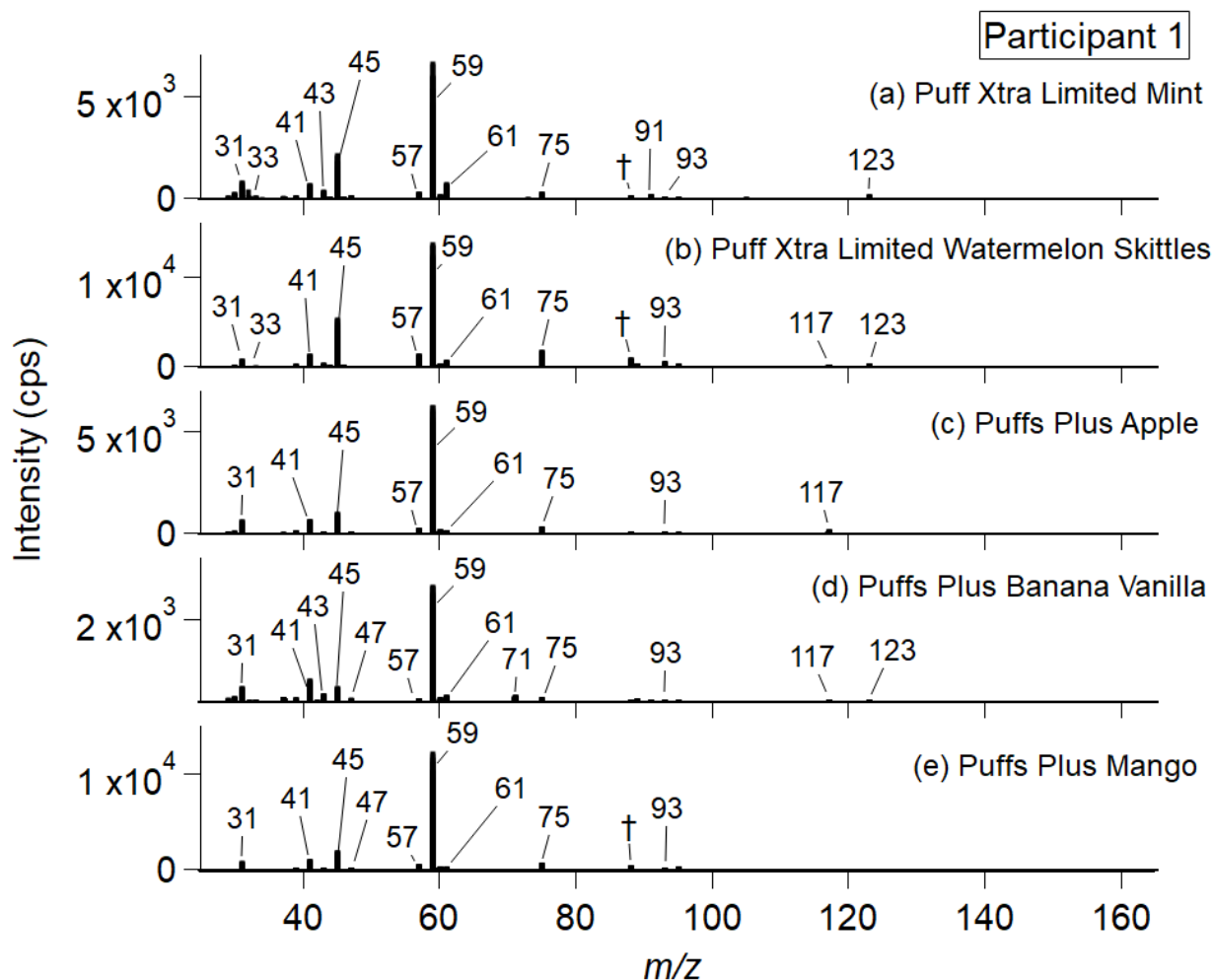


Figure 6.8. PTR-ToF-MS mass spectra for Participant 1’s five visits using Puff Xtra Limited and Puffs Plus *closed* vapes in flavors of (a) mint, (b) watermelon skittles, (c) apple, (d) banana vanilla, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. The peak indicated with (†) at m/z 88 corresponds to DMAC, a known impurity of Tedlar® bags, which was incompletely removed by subtraction. Each spectrum corresponds to an average spectrum taken over 5 min.

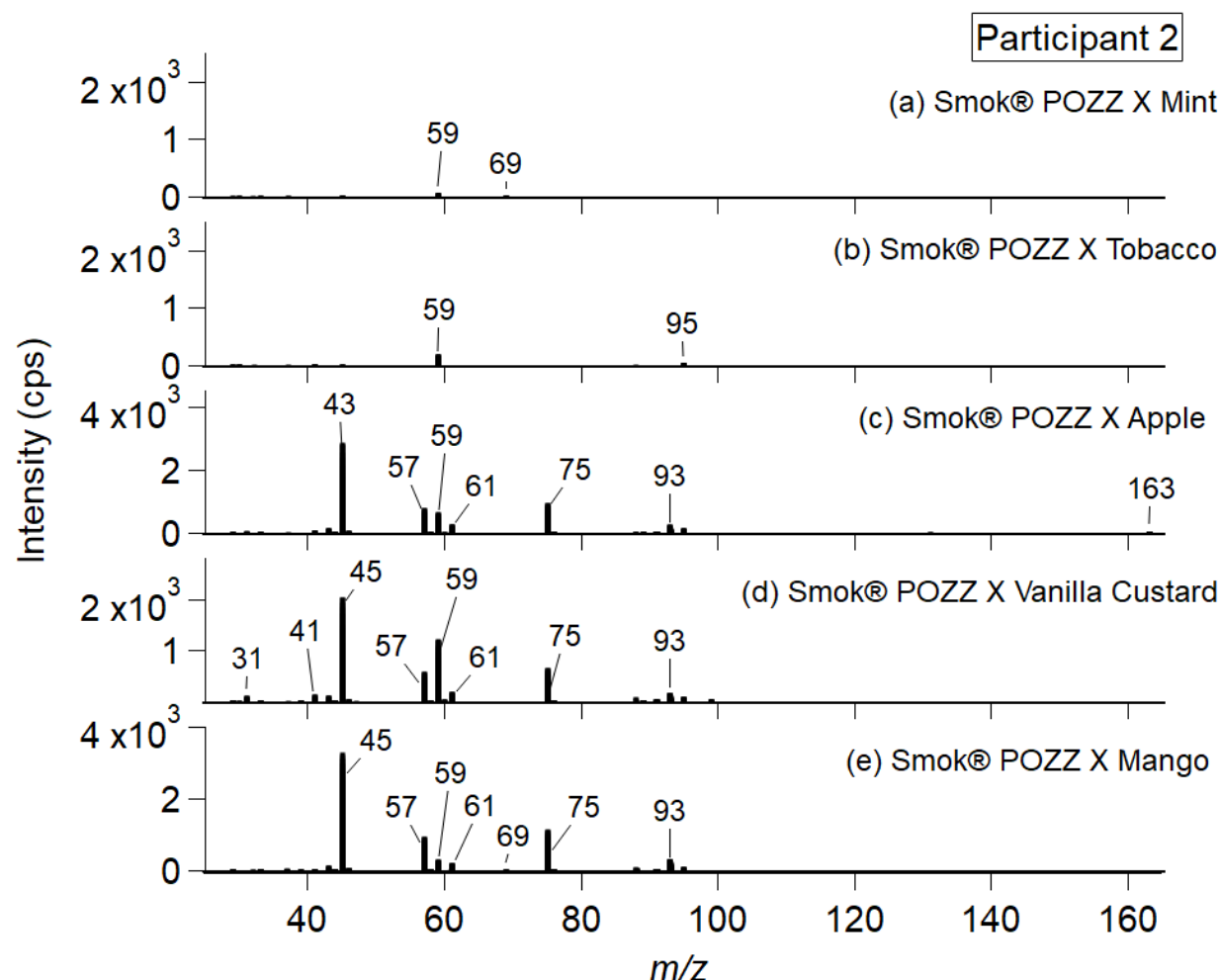


Figure 6.9. PTR-ToF-MS mass spectra for Participant 2's five visits using a Smok® POZZ X *open* vape with e-liquid in flavors of (a) mint, (b) tobacco, (c) apple, (d) vanilla custard, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. Each spectrum corresponds to an average spectrum taken over 5 min. It is important to note that this participant did not smoke watermelon (one of the 5 flavor profiles in this study). Tobacco was initially one of the five profiles selected for this study, but due to feedback from participants 2 and 3, it was discontinued and switched out for watermelon. Mass spectra (a) and (b) had very low signal and the dominant peaks were acetone and isoprene (common in breath without vape).

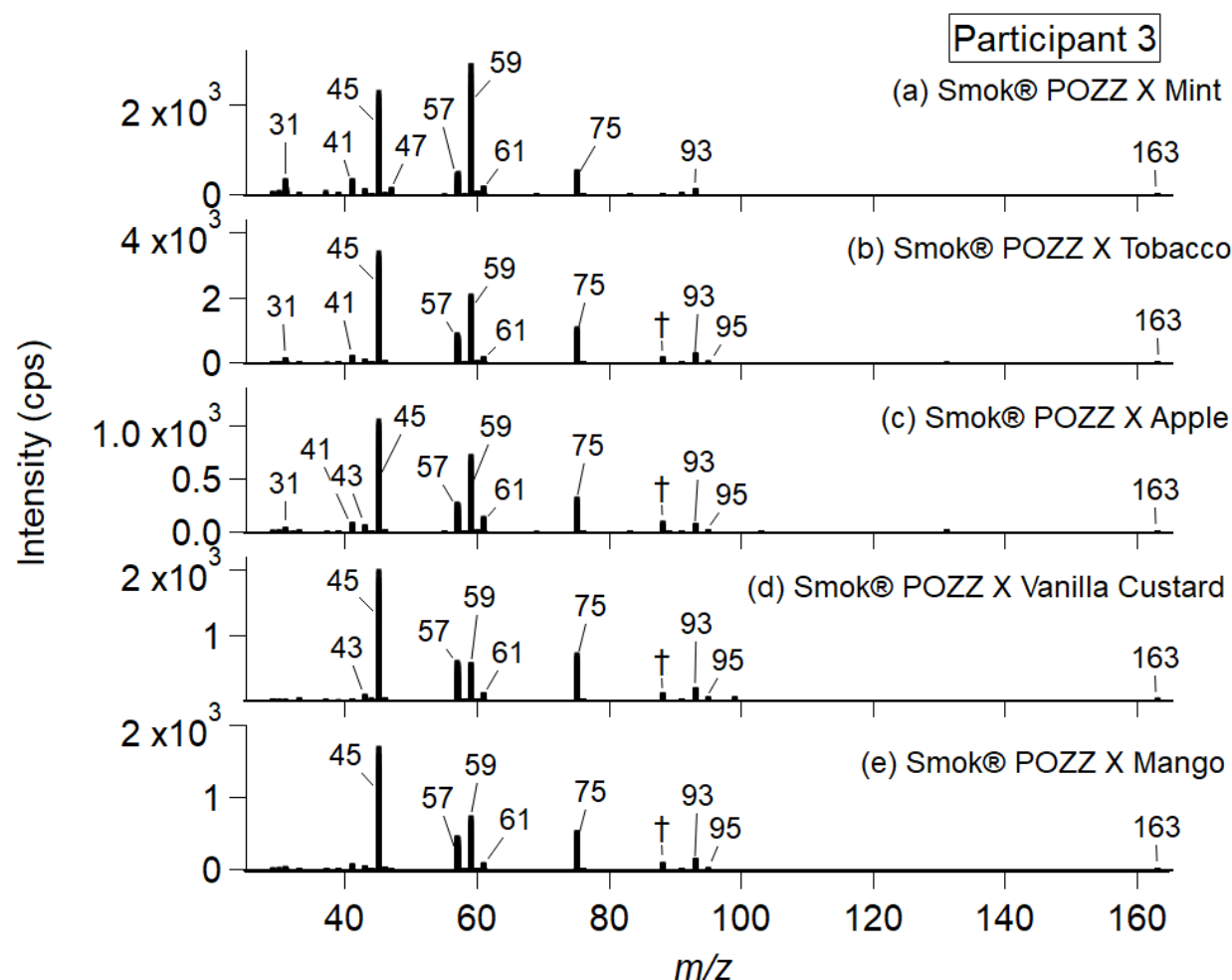


Figure 6.10. PTR-ToF-MS mass spectra for Participant 3's five visits using a Smok® POZZ X *open* vape with e-liquid in flavors of (a) mint, (b) tobacco, (c) apple, (d) vanilla custard, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. The peak indicated with (†) at m/z 88 corresponds to DMAC, a known impurity of Tedlar® bags, which was incompletely removed by subtraction. Each spectrum corresponds to an average spectrum taken over 5 min. It is important to note that this participant did not smoke watermelon (one of the 5 flavor profiles in this study). Tobacco was initially one of the five profiles selected for this study, but due to feedback from participants 2 and 3, it was discontinued and switched out for watermelon.

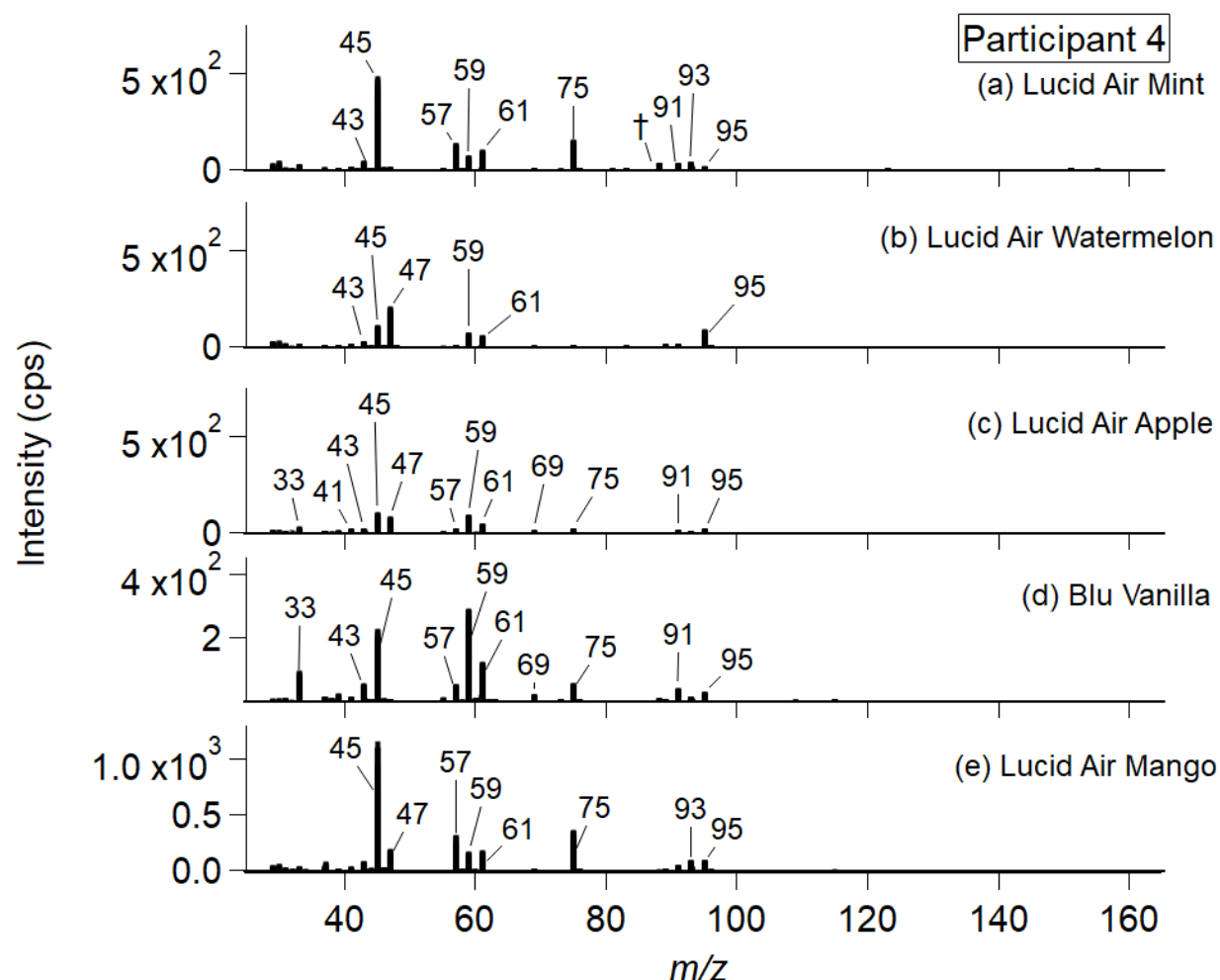


Figure 6.11. PTR-ToF-MS mass spectra for Participant 4's five visits using Lucid Air and Blu *closed* vapes in flavors of (a) mint, (b) watermelon, (c) apple, (d) vanilla, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. The peak indicated with (†) at m/z 88 corresponds to DMAC, a known impurity of Tedlar[®] bags, which was incompletely removed by subtraction. Each spectrum corresponds to an average spectrum taken over 5 min.

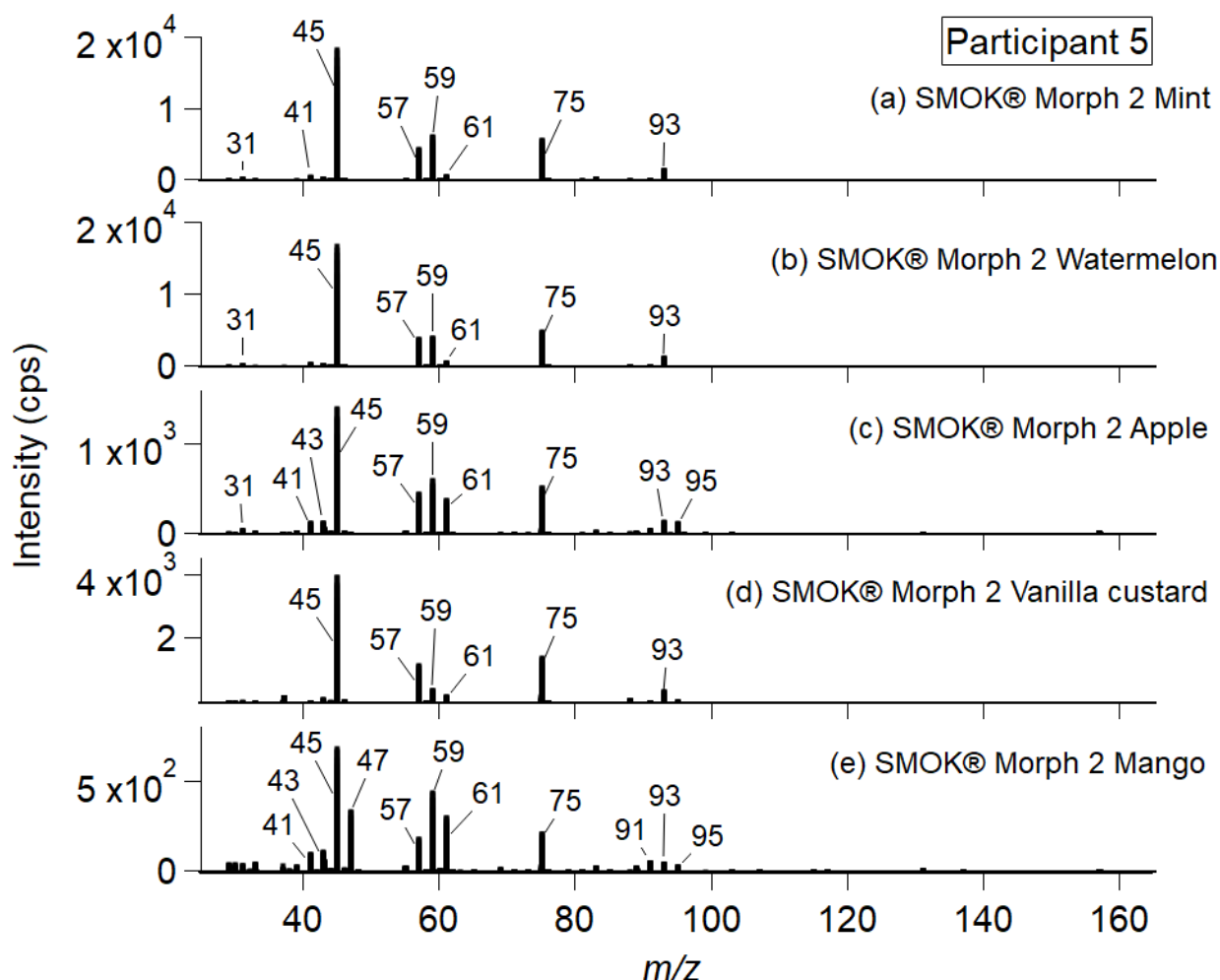


Figure 6.12. PTR-ToF-MS mass spectra for Participant 5's five visits using a SMOK® Morph 2 *open* vape with e-liquid flavors of (a) mint, (b) watermelon, (c) apple, (d) vanilla custard, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. Each spectrum corresponds to an average spectrum taken over 5 min.

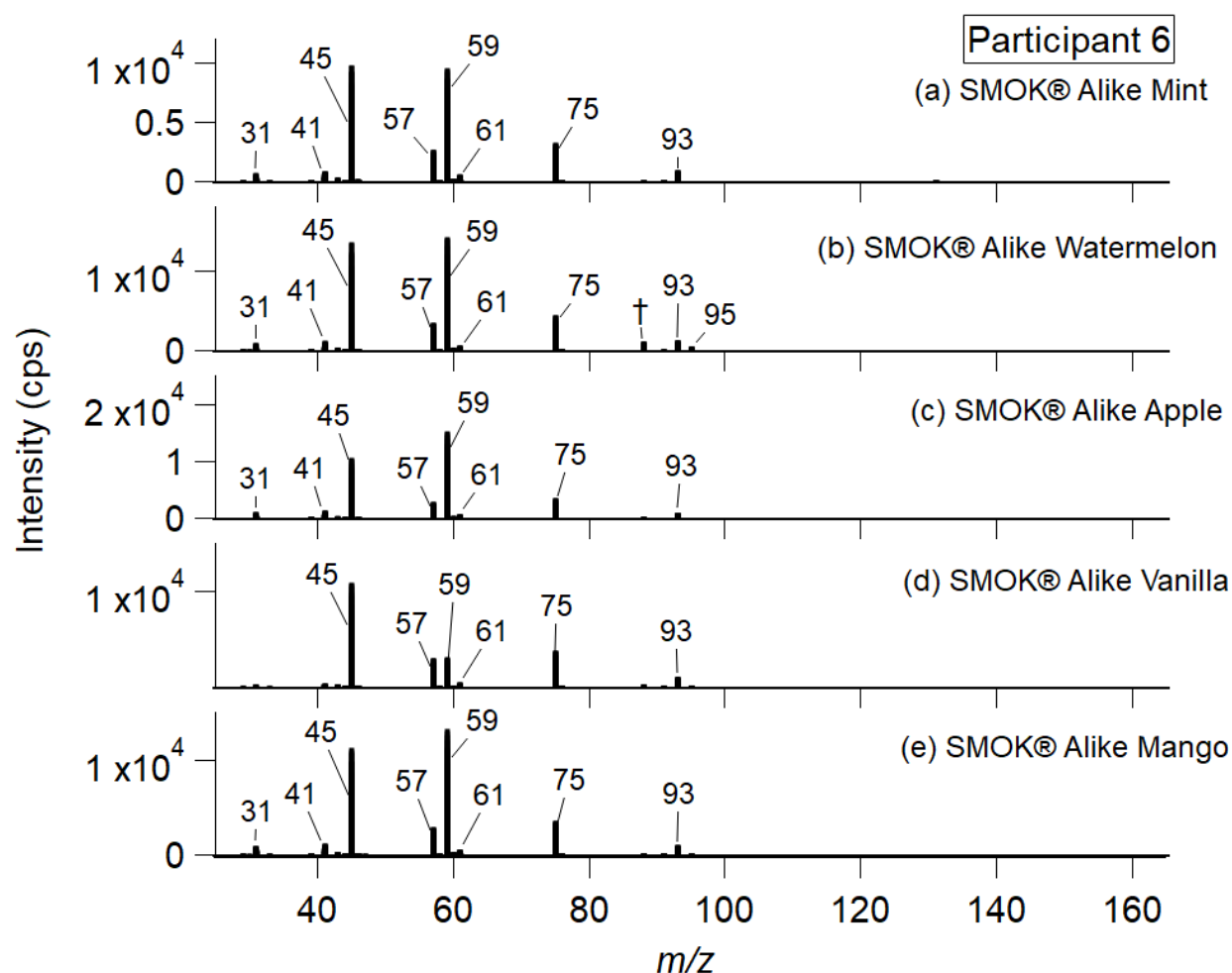


Figure 6.13. PTR-ToF-MS mass spectra for Participant 6's five visits using a SMOK® Alike *open* vape with e-liquid flavors of (a) mint, (b) watermelon, (c) apple, (d) vanilla, and (e) mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. The peak indicated with (†) at m/z 88 corresponds to DMAC, a known impurity of Tedlar® bags, which was incompletely removed by subtraction. Each spectrum corresponds to an average spectrum taken over 5 min.

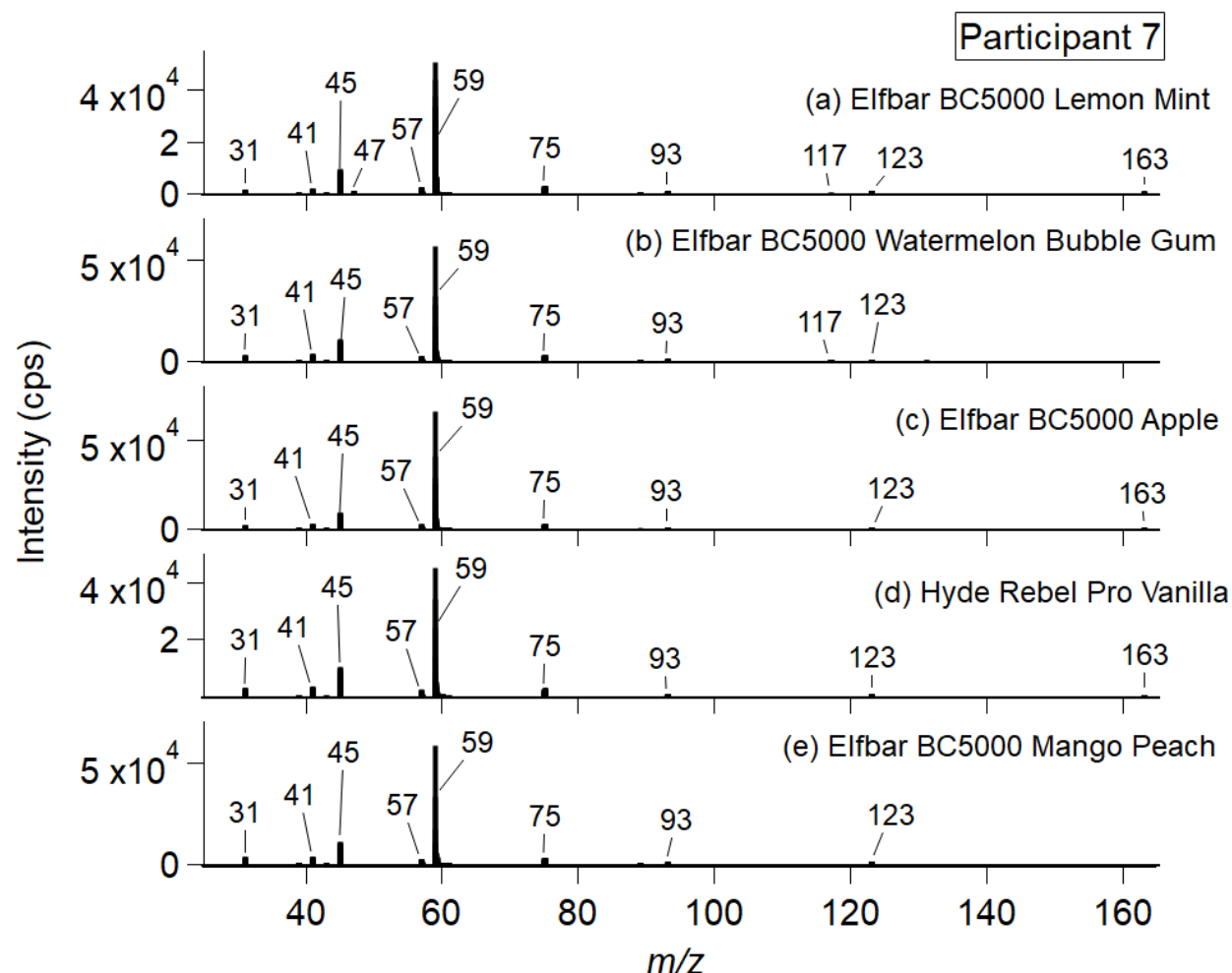


Figure 6.14. PTR-ToF-MS mass spectra for Participant 7's five visits using Elfbar BC5000 and Hyde Rebel Pro *closed* vapes with e-liquid flavors of (a) lemon mint, (b) watermelon bubble gum, (c) apple, (d) vanilla, and (e) mango peach. The presented spectra are of the exhaled puff measurements with background breath subtracted. Each spectrum corresponds to an average spectrum taken over 5 min.

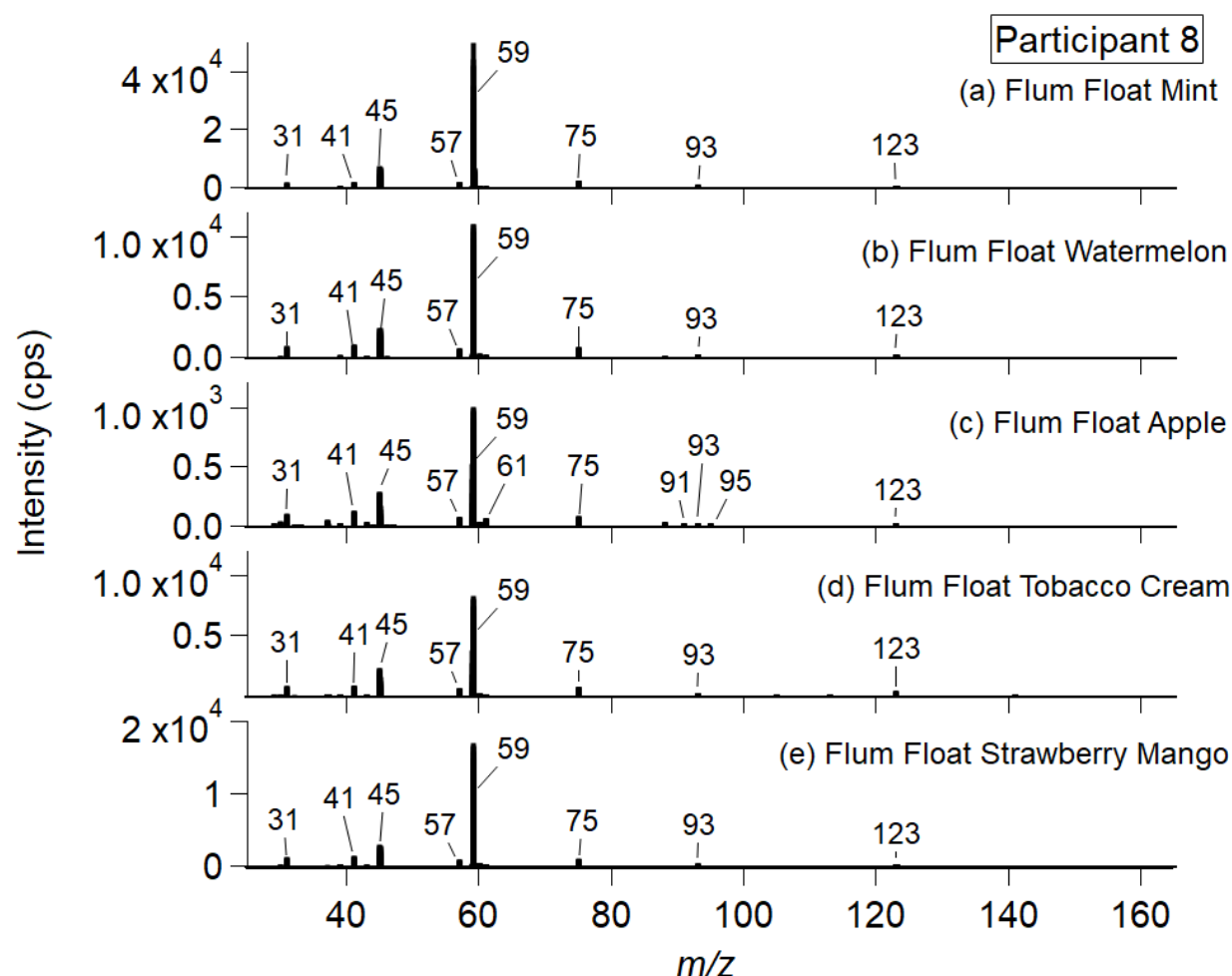


Figure 6.15. PTR-ToF-MS mass spectra for Participant 8's five visits using Flum Float *closed* vapes with e-liquid flavors of (a) mint, (b) watermelon, (c) apple, (d) tobacco cream, and (e) strawberry mango. The presented spectra are of the exhaled puff measurements with background breath subtracted. Each spectrum corresponds to an average spectrum taken over 5 min. Tobacco cream is Flum Float's equivalent product to vanilla that other participants smoked.

Table 6.4. Ions observed in the PTR-ToF-MS mass spectra from participant exhaled vape puff measurements (**Figures 6.8-6.15**). Structural isomers cannot be distinguished using the PTR-ToF-MS, hence, multiple compound assignments are given for certain peaks.

Nominal m/z	Exact m/z	Empirical Formula	Potential Assignment	Reference(s)
31	31.0178	CH ₃ O ⁺	Formaldehyde	399
33	33.0335	CH ₅ O ⁺	Methanol	400
41	41.0386 ^(a)	C ₃ H ₅ ⁺	1,2-Propadiene Propylene glycol fragment (-2(H ₂ O))	401
42	42.0338	C ₂ H ₄ N ⁺	Acetonitrile	401
43	43.0178	C ₂ H ₃ O ⁺	Acetic acid fragment	394,407
			Hydroxyacetaldehyde fragment	394
			Acetate esters fragment	404
			Glycolaldehyde fragment	
	43.0542 ^(a)	C ₃ H ₇ ⁺	Propene	400
45	45.0335	C ₂ H ₅ O ⁺	Acetaldehyde	399,402
47	47.0128	CH ₃ O ₂ ⁺	Formic acid	403,415
	47.0491	C ₂ H ₇ O ⁺	Ethanol	400,404,415
55	55.0542	C ₄ H ₇ ⁺	Butadiene	401
57	57.0335	C ₃ H ₅ O ⁺	Acrolein Glycerol fragment (-2(H ₂ O))	394,401
	57.0699 ^(a)	C ₄ H ₉ ⁺	Butene	405
58	58.0651	C ₃ H ₈ N ⁺	Propenamine	401
59	59.0491	C ₃ H ₇ O ⁺	Acetone/propanal Propylene glycol fragment (-H ₂ O)	400,401,406
61	61.0284	C ₂ H ₅ O ₂ ⁺	Acetic acid, Acetate esters fragment	407
			Hydroxyacetaldehyde	401
	61.0648	C ₃ H ₉ O ⁺	Glycolaldehyde Propanol	404
63	63.0263	C ₂ H ₇ S ⁺	Dimethyl sulfide	401
69	69.0335	C ₄ H ₅ O ⁺	Furan	401,403
	69.0699	C ₅ H ₉ ⁺	Isoprene	400,410
71	71.0855 ^(a)	C ₅ H ₁₁ ⁺	Pentene	405

75	75.0441	$C_3H_7O_2^+$	Hydroxyacetone	401
			1-Hydroxypropanal	394
			Propanoic acid	394
			Glycerol fragment (-H ₂ O)	394
77	77.0597	$C_3H_9O_2^+$	Propylene glycol	408
88	88.0757	$C_4H_{10}NO^+$	N,N-Dimethylacetamide (DMAC)	Intrinsic impurity in Tedlar® bags 375,378
89	89.0597	$C_4H_9O_2^+$	Ethyl acetate	404
			Butanoic acid	380,393
91	90.9477	$FeOH(H_2O)^+$	Intrinsic ion in PTR-ToF-MS source	394,416
	91.0390	$C_3H_7O_3^+$	Glyceraldehyde	408
			Lactic acid	394
93	93.0546	$C_3H_9O_3^+$	Glycerol	394
	93.0699	$C_7H_9^+$	Toluene	400
95	95.0491	$C_6H_7O^+$	Phenol	Intrinsic impurity in Tedlar® bags 375,378
103	103.0754	$C_5H_{11}O_2^+$	Methyl butanoate	404
105	105.0699	$C_8H_9^+$	Styrene	401
117	117.0546	$C_5H_9O_3^+$	1-Acetoxyacetone	394,409
123	123.0804	$C_8H_{11}O^+$	2-Hydroxybenzaldehyde	401
130	130.1067	$C_7H_{15}O_2^+$	Propyl butanoate	404
137	137.1325	$C_{10}H_{17}^+$	Monoterpenes ^(b)	417
163	163.1230	$C_{10}H_{15}N_2^+$	Nicotine	394

^(a) Alkanes, alkenes and aliphatic alcohols are known to fragment to small alkyl ions and will also contribute to m/z 41 ($C_3H_5^+$), 43 ($C_4H_7^+$), 57 ($C_4H_9^+$), 71 ($C_5H_{11}^+$)...etc.

^(b) Monoterpenes are known to fragment into m/z 81 but due to the complexity of the samples, we excluded this ion from quantification.^{418,419}

Five different vape flavor profile groups (mint, watermelon (or tobacco), apple, vanilla, and mango) were selected for this study based on population prevalence. **Figure 6.16** shows the PTR-ToF-MS average mass concentrations of ten most abundant VOCs from all participants' exhaled puffs as a function of e-liquid flavor class. All flavor profiles exhibited the same trend: acetaldehyde (grey), acetone/propanal (lightest blue), and acrolein (medium blue) were the largest peaks. Blair *et al.* (2015) utilized the same PTR-ToF-MS instrument for VOC analysis of an e-cigarette and compared results to traditional cigarettes.³⁶³ That study did not utilize participants or multiple vape devices but reported values were comparable to those in **Figure 6.16** for acetaldehyde ($\sim 100 \mu\text{g VOC cig}^{-1}$) and acrolein ($\sim 30 \mu\text{g VOC cig}^{-1}$).³⁶³ As the present study surveyed far more variables (participant interactions with vape devices, forty different vape devices, five different flavor profiles, etc.), our reported values and errors are larger than Blair *et al.* (2015).

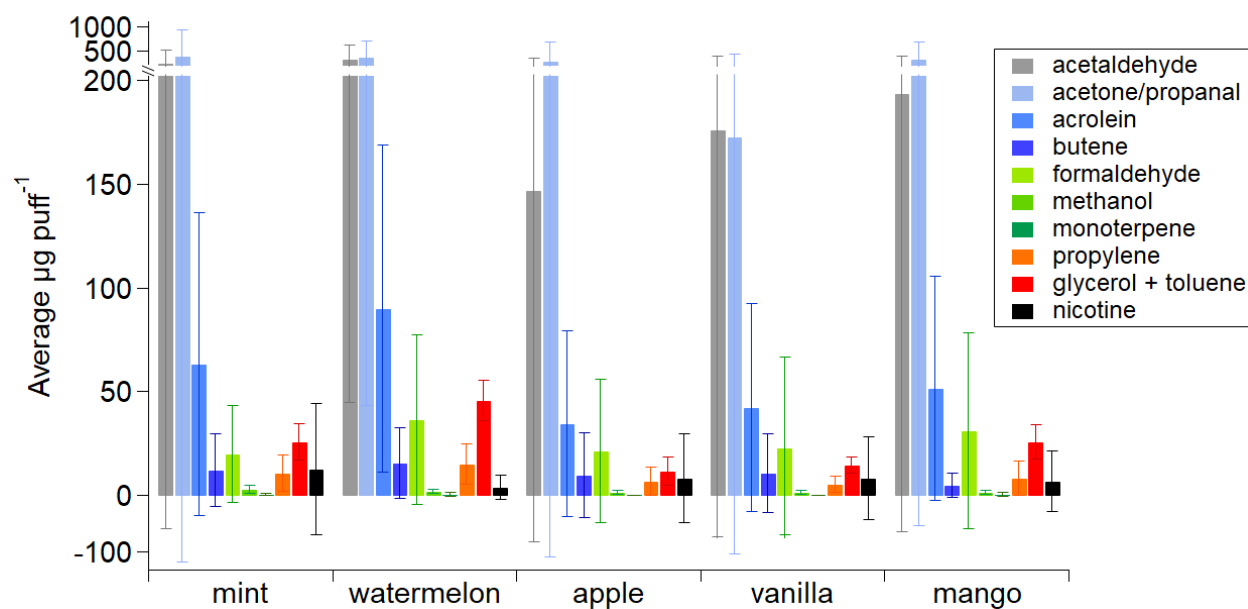


Figure 6.16. PTR-ToF-MS results of selected VOCs from participant exhaled puffs as a function of e-liquid flavor class. These results were averaged amongst all forty participant trials. Error was calculated using each participant's puff topography data which varied by visit (**Table 6.1**).

Flavor compounds, which are often esters, were not observed to be main contributors to signal in PTR-ToF-MS measurements. Buhr *et al.* (2002) tested the PTR-MS fragmentation patterns of seventeen esters and found that the molecular $[M+H]^+$ ion itself and/or the corresponding protonated acids ions (e.g., for all acetate esters, the acetic acid parent ion at m/z 61, and its corresponding fragment at m/z 43) dominate the mass spectra, with the protonated acid often being the main fragment.⁴⁰⁴ Fragmentation of acetate esters is supported by our results with acetic acid mass concentrations detected up to $\sim 35 \mu\text{g puff}^{-1}$ (m/z 61.0284) in the exhaled breath, with its fragment (m/z 43.0178) detected up to $\sim 14 \mu\text{g puff}^{-1}$ (**Figure 6.7c**). Note that fragmentation of glycolaldehyde, a thermal degradation product of GLY, does not contribute significantly to these ions, as described below. We did not observe ester $[M+H]^+$ ions as main contributors to participant mass spectra, with the exception of a small amount of methyl butanoate at m/z 103.0754 ($\text{C}_5\text{H}_{11}\text{O}_2^+$) and propyl butanoate at m/z 130.1067 ($\text{C}_7\text{H}_{15}\text{O}_2^+$). In addition, previous studies have shown toxic aldehyde flavorants, such as cinnamaldehyde, diacetyl, acetoin, maltol, and benzaldehyde, were present in e-cigarette liquids.^{420–422} After e-liquid thermal degradation, it has been shown that small aldehydes are produced during the thermal decomposition of flavorants.^{423–425} Exhaled breath results shown in **Figure 6.16** support previous work reporting detection of acetaldehyde, acetone/propanal, acrolein, and formaldehyde after the heating of flavored e-liquid followed by subsequent inhalation and exhalation.

6.3.4. Fragmentation of Humectants in PTR-ToF-MS Measurements

To better understand the potential role of humectants in our observations, we conducted control experiments with PG and GLY standards. **Figure 6.17** shows the mass

spectra of participant 3's third trial exhaled puff (a) and direct injection (b) compared to heated pure PG (c) and GLY (d). A compilation of both heated humectant spectra comprises the exhaled puff and direct injection spectra for participant 3, trial 3 and all other trials (**Figures 6.8-6.15**). Simultaneously, two different processes can be the source of the ion distribution observed in the PTR-ToF-MS mass spectra: 1) fragmentation of humectant molecules within the PTR-ToF-MS ion source, and 2) thermal decomposition of the humectant within the vape device. Indeed, during proton transfer reaction ionization, alcohols are known to be protonated by H_3O^+ then undergo loss of a water molecule and leave behind a hydrocarbon ion.⁴²⁶ During these fragmentation reactions, only a small fraction of the parent ion is detectable. On the other hand, thermal degradation of PG and GLY is known to occur by two pathways: heat-induced dehydration and H-abstraction by radicals (OH) (followed by oxidation and bond cleavages) that can generate different products depending on the parent molecule.^{427,428} Products formed through the free radical reaction pathways are enhanced with increased combustion temperature, as this generates more free radicals.⁴²⁹

In the case of PG ($\text{CH}_3\text{CH}_2(\text{OH})\text{CH}_2\text{OH}$, MW = 76 g mol⁻¹), we observed ions at nominal masses m/z 31, 41 (largest), 45, 59 (second largest) and 77 (**Figure 6.17c** and **Table 6.5**). PG's protonated $[\text{M} + \text{H}]^+$ ion (m/z 77) is known to fragment (during ionization) with 95% efficiency into m/z 59.0491 ($\text{C}_3\text{H}_7\text{O}^+$).^{380,408,426} This is consistent with our observation of a small m/z 77.0597 parent ion peak and much larger m/z 59.0491 peak in **Figure 6.17c**. Additionally, heat induced dehydration reaction of PG is known to produce acetone and propanal, which are structural isomers and would both be detected by the PTR-ToF-MS at m/z 59.0491.^{353,430,431} Another thermal degradation product, corresponding to 1,2-

propadiene (e.g., loss of two water molecules) is observed at m/z 41.0386 ($C_3H_5^+$) as the largest ion in the PG heated spectrum (**Figure 6.17c**). Formaldehyde (m/z 31.0178) and acetaldehyde (m/z 45.0335) are known products of C-C bond cleavage during OH radical reaction with PG.⁴³⁰

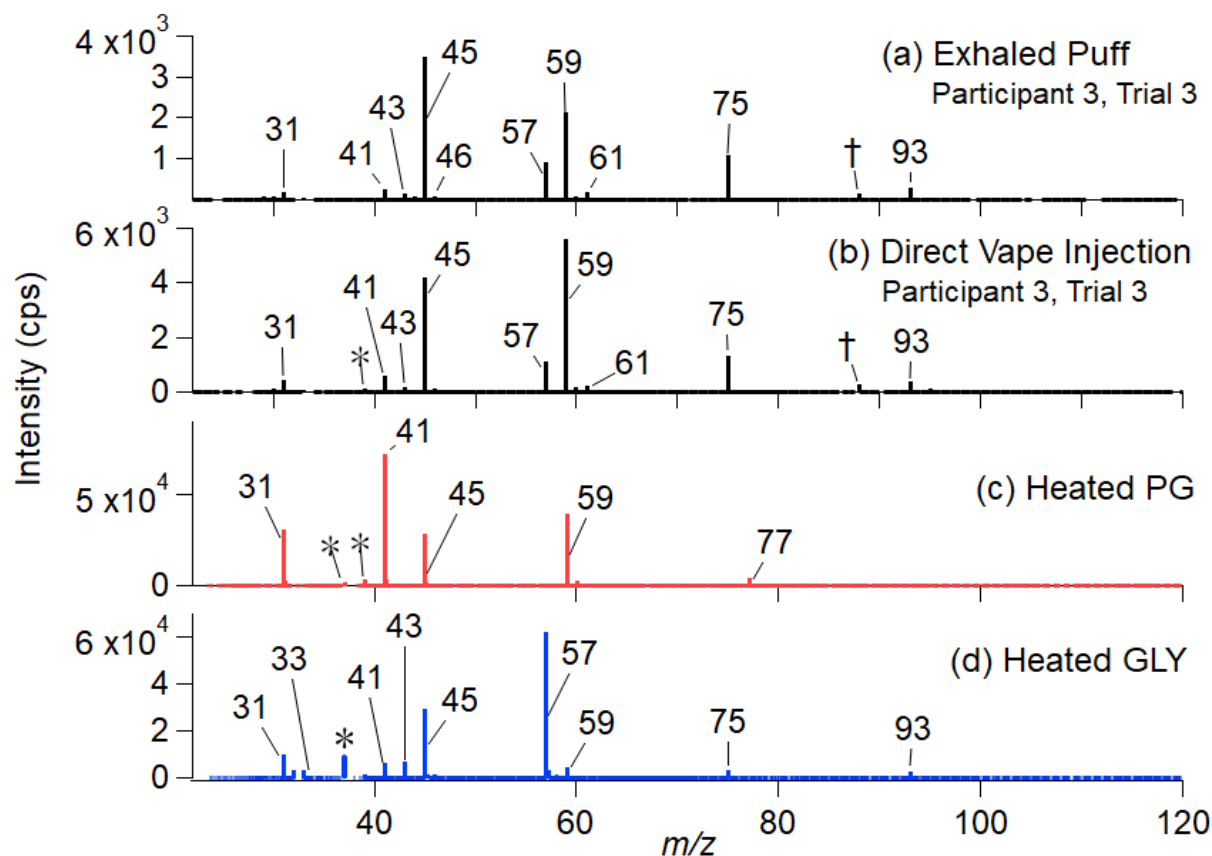


Figure 6.17. Typical unit mass resolution PTR-ToF-MS mass spectra from a participant trial and heated humectant experiments. Shown above is the exhaled vape puff of participant 3 in trial 3 (a), direct vape injection from vape smoked by participant 3 in trial 3 (b), heated propylene glycol (PG) (Fisher, > 99%, CAS 57-55-6) (c), and heated glycerol (GLY) (Fisher, > 99%, CAS 56-81-5) (d). Both humectants were aerosolized separately using participant 5's *open* vape (SMOK® Alike). The peaks indicated with (*) correspond to the hydronium ion-water complex ($(H_2O)_2H^+$) at m/z 37 and the $^{18}O^{16}O^+$ ion at m/z 39. The peak indicated with (†) corresponds to DMAC at m/z 88, a known impurity of Tedlar® bags. The identity of labeled ions can be found in **Table 6.5**.

Table 6.5. Prominent ions observed in the PTR-ToF-MS mass spectra (**Figure 6.17**) from heated humectant control experiments of propylene glycol (PG) and glycerol (GLY). Structural isomers cannot be distinguished using the PTR-ToF-MS, hence, multiple compound assignments are given for certain peaks.

<i>m/z</i>	Empirical Formula	Potential Assignment	Heated PG	Heated GLY
31.0178	CH ₃ O ⁺	Formaldehyde	X	X
33.0335	CH ₅ O ⁺	Methanol	X (small)	X
41.0386	C ₃ H ₅ ⁺	PG – 2(H ₂ O) 1,2-Propadiene	X	X
43.0178	C ₂ H ₃ O ⁺	Glycolaldehyde fragment	X (small)	X
43.0542	C ₃ H ₇ ⁺	Propene	X (small)	X
45.0335	C ₂ H ₅ O ⁺	Acetaldehyde	X	X
57.0335	C ₃ H ₅ O ⁺	GLY – 2(H ₂ O) Acrolein	–	X
59.0491	C ₃ H ₇ O ⁺	PG – H ₂ O Acetone/Propanal	X	X
61.0284	C ₂ H ₅ O ₂ ⁺	Glycolaldehyde	–	X (small)
75.0441	C ₃ H ₇ O ₂ ⁺	GLY – H ₂ O Hydroxyacetone	–	X
77.0597	C ₃ H ₉ O ₂ ⁺	PG	X	–
93.0546	C ₃ H ₉ O ₃ ⁺	GLY	–	X

In the case of GLY (CH₂(OH)CH₂(OH)CH₂OH, MW = 92 g mol⁻¹), we observed ions at nominal masses *m/z* 31, 33, 41, 43, 45 (second largest), 57 (largest), 59, 75, and 93 (**Figure 6.17d** and **Table 6.5**). As with PG, we see a small GLY protonated parent ion peak at *m/z* 93.0546 (C₃H₉O₃⁺). The largest peak in this spectrum, at *m/z* 57.0335, is attributed to the parent ion of acrolein (C₃H₄O), the GLY thermal degradation product with loss of two water

molecules.^{427,430} The small peak at m/z 75.0441 can be attributed to the parent molecular ion of the first thermal decomposition product, hydroxyacetone ($C_3H_6O_2$), which is a less preferred product of GLY heating.⁴³⁰ Additional thermal decomposition products, formaldehyde and acetaldehyde, are known to form through GLY C-C bond cleavage after loss of water, and are observed in our mass spectrum at m/z 31.0178 (CH_3O^+) and 45.0335 ($C_2H_5O^+$) respectively.^{427,430,431} Proposed to be formed from the thermal degradation of GLY,⁴³¹ glycolaldehyde ($C_2H_4O_2$) is observed (with low intensity) at m/z 61.0284 ($C_2H_5O_2^+$) and its fragment ion at m/z 43.0178 ($C_2H_3O^+$). Additionally, gas phase fragmentation of the metastable protonated glycerol ion was previously reported to result in major product ions at nominal masses m/z 75 ($C_3H_7O_2^+$), 57 ($C_3H_4^+$), 61 ($C_2H_5O_2^+$), 45 ($C_2H_5O^+$) and 31 (CH_3O^+).⁴³² All of these ions were observed in our mass spectra and could originate from fragmentation of GLY upon ionization inside the ion source, adding to the complexity of the MS spectra. Methanol (m/z 33), 1,2-propadiene (m/z 41), and acetone/propanal (m/z 59) were also observed, but it is unknown whether these are GLY thermal decomposition products or produced within the PTR-ToF-MS ionization source.

6.3.5. Comparison of the PTR-ToF-MS Results with Off-line GC Measurements

As the PTR-ToF-MS results are overwhelmed by humectant fragmentation and thermal decomposition products, we sought to compare our results to those measured by GC, which are not subject to ion fragmentation. **Figure 6.18** shows the relationship between reported PTR/GC exhaled breath concentrations for twelve VOCs detected by both instruments. The grey diagonal lines represent an ideal 1:1 relationship between measured concentrations. For all twelve compounds, the best fit lines between the PTR-ToF-MS and GC

(black, dashed lines) deviate substantially from the 1:1 line and the data are overall poorly correlated. Except for isoprene, monoterpene, and ethanol, PTR-ToF-MS reports much higher values than GC (**Figure 6.18**). Ethanol exhibits the strongest correlation between measurements, however, the PTR *underestimates* the GC values by a factor of 10. Note that ethanol was successfully identified and quantified in all WAS samples, as co-eluting acetonitrile was not detected. This result was confirmed by GC-MS analysis. The comparison with a certified cylinder containing a VOC mixture showed that when using exclusively m/z 47 for quantification, the ethanol signal was underestimated by the PTR-ToF-MS by approximately the same factor (**Table 6.3**). Inomata *et al.* (2009) showed that, the signal at m/z 47 for ethanol decreases as the ratio of the drift tube electric field strength (E) to the buffer gas number density (N) value increases.⁴³³ For E/N values similar to the ones used in this study (~ 132 Td), the fragmentation of the parent ion is thought to produce H_3O^+ ions which are impossible to quantify as they correspond to the reagent ions. This leads to a large underestimation of ethanol overall by the PTR-ToF-MS.

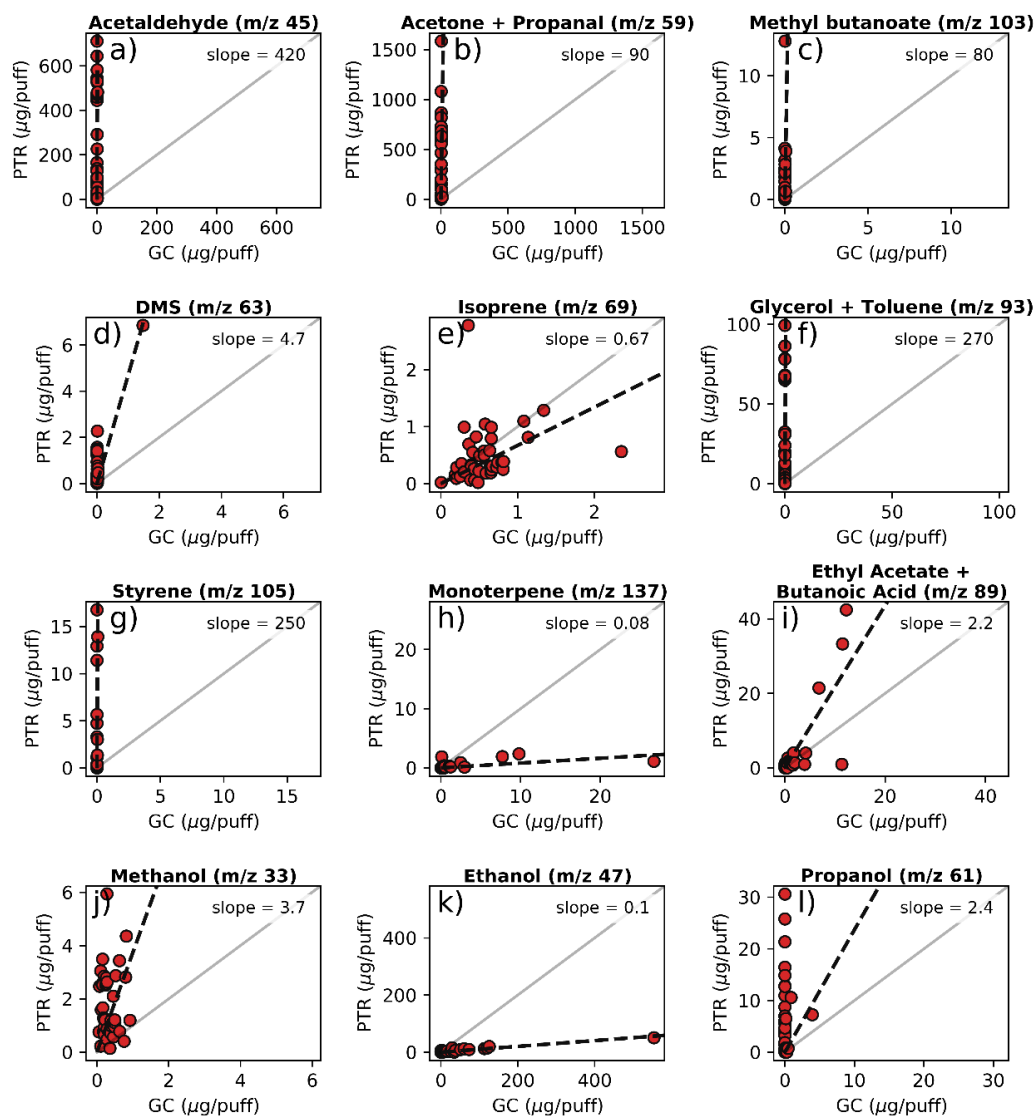


Figure 6.18. Scattered data for each PTR/GC exhaled breath measurement, in calculated micrograms per puff. Black dashed lines are the linear fit for participant data. Diagonal 1:1 lines (solid grey) illustrate the lack of correlation between measurements. All signal intensities reported for the PTR-ToF-MS correspond to the $[M+H]^+$ ion of each of the reported species. In panel (b) while acetone is presented exclusively for the GC measurements, the PTRMS signal is for the sum of acetone and propanal (m/z 59, $C_3H_7O^+$). In panel (f), due to the overwhelming presence of the humectant, the PTR-ToF-MS signal is given for the sum of GLY and toluene, while the GC measurements are reported for toluene exclusively. In panel (i), while ethyl acetate is presented exclusively for the GC measurements, the contribution of butanoic acid couldn't be excluded for the PTR-ToF-MS and the signal is for the sum of ethyl acetate and butanoic acid. Note that the slopes are included for reference only to demonstrate how the two measurements deviate from one another, not to suggest that there is correlation between the two datasets.

Monoterpenes and isoprene fragmentation has been previously reported to occur in the PTR-ToF-MS.^{418,419} Accounting for fragments for all of these species would certainly help to close the gap between the two types of measurements; however, assigning fragments in a complex mixture such as vape aerosol is challenging. PTR-ToF-MS values of toluene were up to two orders of magnitude higher compared to that reported by the GC, further enforcing quantitative measurement of toluene in the PTR-ToF-MS is impacted by GLY at the same nominal mass (**Figure 6.18**) in any vape aerosol samples. Compounds associated with humectant fragmentation in PTR-ToF-MS (acetaldehyde, acetone, methanol) had poor correlation with GC measurements, and the PTR-ToF-MS values are systematically three orders of magnitude larger than reported by GC. While the calibration plots in **Figure 6.2** demonstrate that the PTR-ToF-MS can measure these compounds reasonably well, the dramatic deviation between the PTR-ToF-MS and GC data reflects the strong impact of fragmentation within the PTR ionization source.

Potentially, other sampling artifacts may have contributed to the discrepancies observed. These include potential re-volatilization of smaller VOCs (from particles) when entering the slightly heated PTR-ToF-MS inlet (70 °C). The sample residence time in this section is relatively short (~1s) and the temperature is relatively low that re-volatilization is not expected to be a dominant factor. On the other end, the exhaled aerosol was humid, and it is possible that there were additional wall losses inside the WAS canisters, in addition to potential partitioning of the VOCs onto the particles collected on the wall of the canisters. Note that the canisters remained at room temperature from sampling to analysis, which may favor partitioning. The canisters were analyzed right after the sampling to mitigate any adsorption artifacts. Although these artifacts may contribute some to the discrepancies

observed between the two techniques, it does not solely explain the order of magnitude difference observed for most VOCs, and the fragmentation of the humectant is largely responsible for this difference.

Figure 6.19 shows the reported mixing ratios (in ppbv) for compounds detected by both PTR-ToF-MS and GC for the control experiments with heated PG and GLY. Methanol (m/z 33) and acetaldehyde (m/z 45) are of the same order of magnitude between instruments and solvent cases, indicating that these compounds are solely attributed to thermal decomposition. 1,2-propadiene (PTR m/z 41) and propene (PTR m/z 43) were not detected by GC for the PG experiment (**Figure 6.19c**), further supporting fragmentation within the PTR-ToF-MS ionization source leading to orders of magnitude enhancement of these compounds in our participant dataset. For PG, acetone is two orders of magnitude larger in the PTR-ToF-MS (**Figure 6.19a**) compared to GC measurements (**Figure 6.19c**). Values are of the same order of magnitude in the GLY experiment, confirming that acetone is a thermal decomposition product from both humectants, but it is also a fragmentation product from PG, further increasing the acetone response in exhaled breath measurements in the PTR-ToF-MS. Toluene is measured by both instruments at 3 ppbv for PG. In the GLY experiment, PTR-ToF-MS reports toluene at 1800 ppbv whereas GC reports 17 ppbv. This discrepancy is attributed to the GLY parent ion overlapping with toluene at the same nominal mass m/z 93 (**Figure 6.3**). Since PG does not have a peak overlap at this mass, there was no interference in the measured toluene concentration by the PTR-ToF-MS.

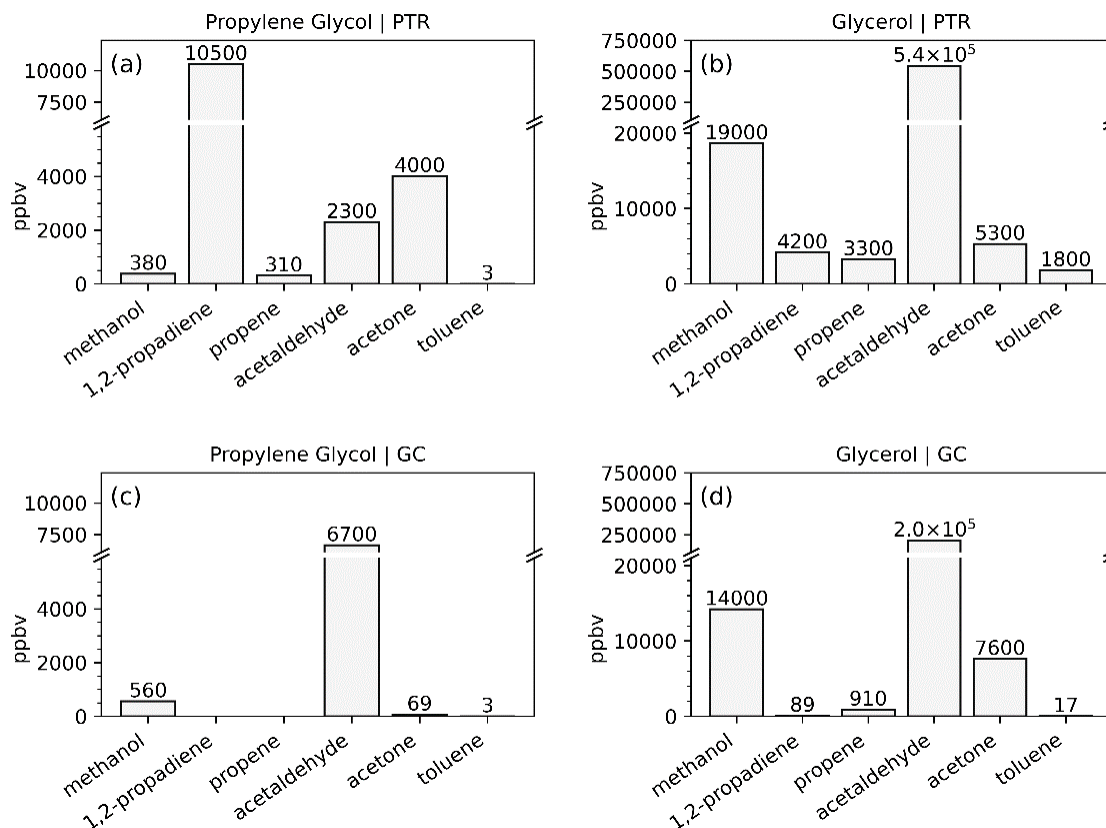


Figure 6.19. Reported mixing ratios for methanol, 1,2-propadiene, propene, acetaldehyde, acetone, and toluene by PTR-ToF-MS and GC from the control experiments with heated pure solvents (a-b and c-d, respectively). In panels (a) and (b) “acetone” refers to m/z 59, which is the sum of acetone and propanal; “toluene” refers to m/z 93, which is the sum of glycerol and toluene; and “1,2-propadiene” refers to the sum of 1,2-propylene and the $C_3H_5^+$ fragment ion from PG ($[M+H-2H_2O]^+$).

6.4 Conclusions

Real-time measurements of inhaled and exhaled VOCs offer an attractive way to assess the exposure of bystanders to second-hand vape smoke. However, we found that PTR-ToF-MS alone, a state-of-the-art online VOC detector, may not be suitable for this task due to complex patterns of thermal decomposition of humectants in the vaping devices and ion fragmentation in the PTR-ToF-MS ion source. We observed large differences, sometimes by as much as two orders of magnitude, between VOC concentrations measured by offline GC

and online PTR-ToF-MS instruments. As the e-liquids used in this study were a mixture of PG and GLY, a combination of effects explored in the pure humectant experiments (**Figure 6.19**) contribute to this large discrepancy in the human trial dataset. Together, the fragmentation of humectant in the PTR-ToF-MS ion source, generation of pyrolysis products during vaping, and the lack of accurate ingredient labelling of e-liquids have made it challenging to interpret observations regarding flavorings and other potentially toxic species associated with secondhand vape exposure.

Comparison of PTR-ToF-MS measurements with those of a GC platform (GC-MS, GC-FID, GC-ECD) indicate that *quantitative* results should be cautiously interpreted. Ionization within the PTR-ToF-MS leads to overestimation of a range of VOCs, including some like acrolein and acetaldehyde which have potentially significant health implications, and would result in misrepresentation of the potential for vape emissions on adverse health effects. Values reported herein from PTR-ToF-MS measurements should be used with caution by experts in the field to influence public health policy on the dangers of vaping, as these values are inflated for analytical reasons described in the discussion section. The WAS canisters coupled to a GC analysis, though it is an offline technique and requires more time to run than the PTR-ToF-MS, provide more accurate quantification of VOCs in vape-related emissions. Lower VOC values reported by GC, as shown in **Figure 6.20**, are more representative of what an individual is exhaling during a vaping event. Furthermore, *quantitative* e-cigarette results reported by PTR-ToF-MS measurements of Blair *et al.* (2015) are likely overestimated and should be considered carefully.³⁶³ If future studies wish to use PTR-ToF-MS for *quantitative* purposes in vaping trials, analysis of e-liquid components (prior to combustion) and control studies using PTR-ToF-MS (accounting for fragmentation effects) could provide a template

for *quantitative* framework that could then be applied to participants smoking the same device/e-liquid.

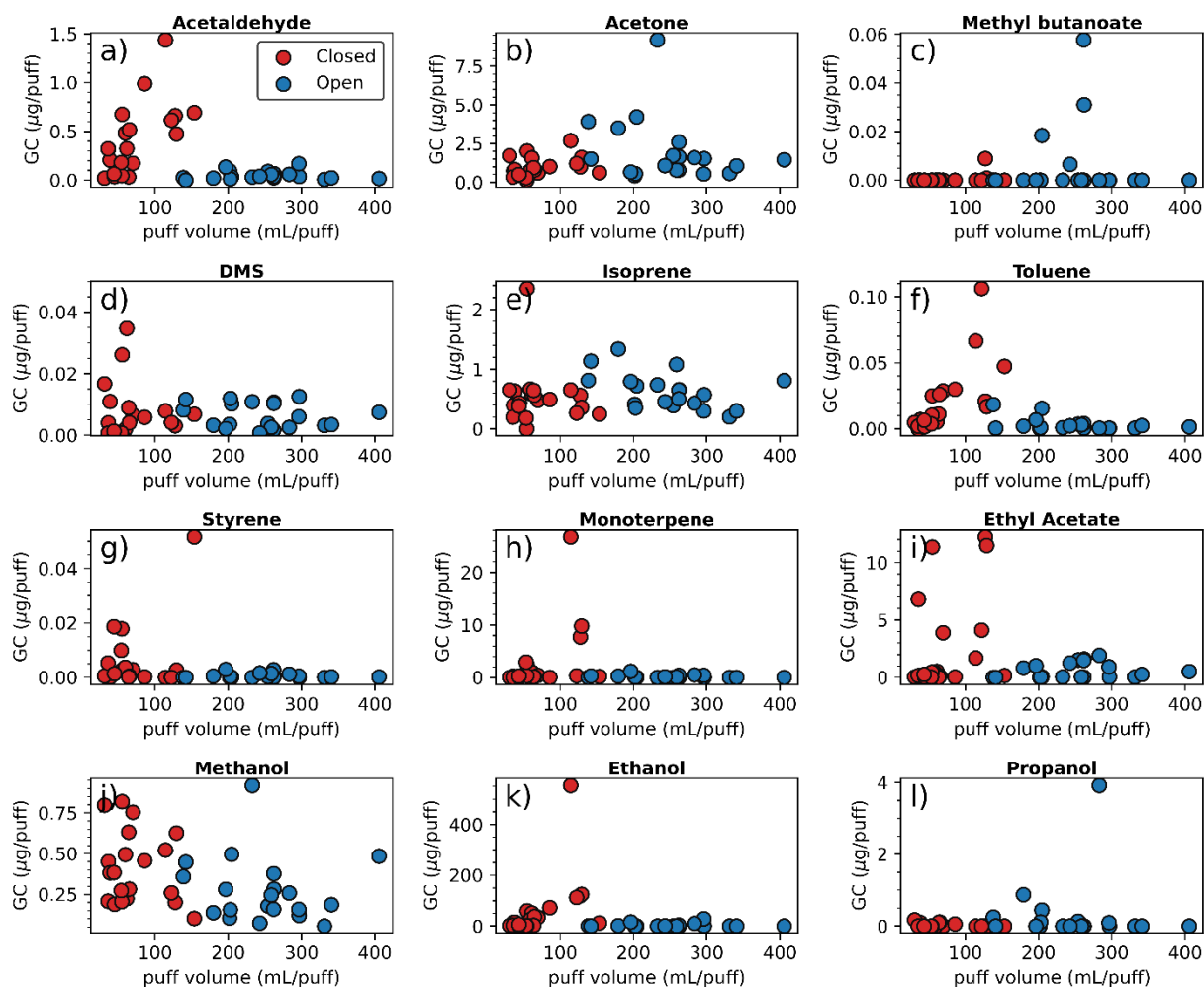


Figure 6.20. Exhaled puff GC values of micrograms per puff with respect to participant puff topography data. Twelve compounds were selected for this comparison. Red markers correspond to *closed* vapes and blue markers correspond to *open* vapes used in the human trial.

While one must be careful when drawing *quantitative* conclusions from PTR-ToF-MS measurements, PTR-ToF-MS can provide valuable *qualitative* results in a human trial vaping study. Overall, this study indicates that there is substantial retention of organic species in the lungs of individuals, which selectively changes the composition of exhaled breath compared to the inhaled vape aerosol. However, VOCs in the exhaled breaths are still enhanced relative to the baseline breaths, illustrating the need to quantify the burden that vaping has on secondhand exposure.

This study was purposely designed without strict participant constraints to best survey realistic secondhand vape exposure. To better constrain fragmentation issues in PTR-ToF-MS measurements, more controlled and reproducible samples would be required, however these would not reflect the diversity of vaping behavior. Nevertheless, PTR-ToF-MS fragmentation effects elucidated in this study are independent from participant variables and should be considered in future works.

CHAPTER 7:

CONCLUSIONS AND FUTURE WORK

7.1 Research Goals and Questions Addressed by this Dissertation

Organic aerosols emitted during combustion can impact the propagation of radiation through Earth's atmosphere. The optical properties of BrC in BBOA and urban OA are highly variable and are coupled to their fuel source and combustion conditions. Moreover, the molecular composition of BrC in these systems can evolve through atmospheric transport and impact its optical properties. Unanswered questions remain regarding the molecular identity of BrC compounds in BBOA; connections between the optical properties and chemical composition of BBOA; and condensed phase chemical transformations leading to BBOA aging- particularly those with BBOA species and Fe(III). There is a lack of knowledge on the emissions that come from fires at the WUI and how these aerosols can change during photolytic aging. This Dissertation sought to address these topics in Chapters 2-5.

Human health is directly impacted by exposure to ambient aerosol PM and VOCs, including those coming from combustion. While unintended exposure to smoke from fires is a serious health risk factor, it should be kept in mind that deliberate exposure to smoking (including vaping) is a significantly greater threat to human health. It is known that traditional cigarettes emit carcinogenic compounds and that secondhand exposure, even if brief, can increase health risks. On the other hand, vaping exposes users to fewer toxic chemicals but is known to induce lung injuries and cardiovascular diseases. Neither the long-term effects of vaping nor the secondhand exposure risks are known. This Dissertation

sought to improve our understanding of the extent of exposure to secondhand vaping, with a focus on gaseous components of smoke, in Chapter 6.

The most important research questions addressed by this Dissertation are: 1) How do structural differences within BBOA constituents impact Fe(III)-catalyzed reactions? 2) Can Fe(III) interact with real-BBOA samples in the condensed phase to create light-absorbing secondary BrC species? 3) What are the implications of these interactions on the light-absorbing properties and climate effects of biomass burning smoke during atmospheric transport? 4) How does exposure to simulated solar radiation impact the absorption properties of PM emitted during WUI fires? 5) What is the molecular-level composition of BrC chromophores in WUI smoke particles, and how does it change after photolytic aging? 6) What VOCs are individuals inhaling and exhaling during vaping events? 7) Can we employ complementary online and offline techniques in a vaping human trial to probe these emissions and effects on secondhand exposure?

7.2 Conclusions, Implications, and Future Directions of Chapters 2 and 3

Chapters 2 and 3 discussed the interaction of BBOA with atmospheric iron and answered questions 1, 2, and 3 from Section 7.1. Water soluble BBOA precursors (2,4-nitrophenol, 4-nitrocatechol, 4-methylcatechol, 1,2,4-benzenetriol, 1,2,3-benzenetriol, coniferaldehyde, and catechol) were utilized in Chapter 2 to demonstrate the impact of molecular structure on the reactivity with Fe(III) under dark, acidic conditions. Previous studies found that insoluble products in reactions of Fe(III) with catechol, guaiacol, syringol, o-cresol and p-cresol.^{85,92} Results in Chapter 2 add coniferaldehyde, 3-hydroxycatechol, and 4-hydroxycatechol to the list of particle-forming compounds over short reaction times. The

results suggest that Fe(III)-catalyzed chemistry can take place in smoldering BBOA plumes and make aerosol particles more light-absorbing. Building off this, Chapter 3 conducted similar chemistry with real BBOA samples generated in the laboratory under pyrolysis conditions. Light-absorbing, water-insoluble secondary aerosol particles formed, and these particles were reminiscent of primary emitted soot. The addition of Fe(III) to water-soluble components of OA can catalyze reactions with phenolic compounds, forming phenoxy radical intermediates that initiate C-C coupling reactions to form light-absorbing dimers/oligomers. These oligomerization reactions convert volatile molecules into higher- molecular weight, water-insoluble, light-absorbing products of lower volatility.^{80,85,86} These chapters conclude that biomass burning smoke can become more light absorbing as it mixes with mineral dust particles during atmospheric transport, and may, therefore, have a stronger effect on climate after aging.

Bulk experiments in this Dissertation were subject to limitations and do not fully reproduce conditions in atmospheric particles. For example, hydrogen peroxide produced in the reaction is not able to evaporate from the bulk solution as it would from ambient particles. Hydrogen peroxide concentrations were not measured in reaction solutions in this work, and it should be a priority for follow up mechanistic studies. Additionally, the organic aerosol samples used in this work were produced by oxygen-free pyrolysis of biomass, so it will be important to test this chemistry at different oxygen levels in the future. Further experiments are needed to assess kinetic effects of particle formation in more atmospherically accurate samples, such as those with OH radical scavengers.^{77,85} These studies were conducted under dark conditions, hence future studies should investigate the effect of UV irradiation on this reaction's progress or the extent of photodegradation. It is

suggested that future studies of this chemistry should be done with aerosolized particles, for example, by exposing aerosolized particles containing Fe(III) to vapors of individual BBOA compounds or whole BBOA smoke.

7.3 Conclusions, Implications, and Future Directions of Chapters 4 and 5

Chapters 4 and 5 serve as pilot studies on PM generated from WUI fires and answered questions 4 and 5 from Section 7.1. In Chapter 4, ten urban materials were pyrolyzed, resultant smoke particles were collected on filters, and UV irradiation experiments were performed. We observed variable trends after short-term exposure to UV radiation: six out of ten types of urban OA exhibited photoenhancement, two exhibited photobleaching, and the remaining two experienced negligible change after 2 h of photolytic aging. *AAE* values decreased, reflecting increased absorption in the visible range of the spectrum after UV exposure. Long-term UV exposure results indicate that most photochemical change occurs within the first few hours of irradiation. These results suggest that WUI fires efficiently produce brown carbon, which becomes increasingly light absorbing in sunlight.

In Chapter 5, the chemical composition of PM before and after UV aging was investigated through use of UHPLC-PDA-HRMS and utilization of BrC standard mixtures. A total of 36 BrC chromophores were identified within the ten urban OA types, and structures were verified using reference standards. Components of plasticizers and resins, such as phthalic acid and terephthalic acid, were structurally confirmed in urban OA samples. We present potential tracer species for WUI fires to be components of resins, epoxies, dyes, and adhesives that are commonly used in the manufacturing of urban materials. One of the key findings of this work is that photolytic aging results in relatively small changes to overall

chemical composition and volatility distributions, despite having a large impact on the overall absorption coefficient. This work reinforces previous observations that the optical absorption of OA is controlled by small fraction chromophoric species. Changes in the relative intensity of these species are difficult to notice because they are obscured by more abundant non-absorbing species.

It is important to note that Chapters 4 and 5 only focused on a small variety of species present in WUI fires. Additionally, OA was generated only at a single pyrolysis temperature (600 °C), and in the absence of oxygen. This is not fully representative of environmental fires that often oscillate between smoldering and flaming combustion, with flaming temperatures reaching at least an order of magnitude higher than smoldering or pyrolysis. Results in this work are also limited in that we only focused on CHON species when characterizing BrC species. Metals and halogen species are expected to be produced through combustion of human made materials. Future studies should burn a greater variety of urban materials (under more diverse combustion conditions) and determine the photochemical and molecular composition of largescale WUI fires.

7.4 Conclusions, Implications, and Future Directions of Chapter 6

Chapter 6 examined the chemical composition of VOCs exhaled by eight participants in a human trial vaping study, with use of complementary online and offline techniques. This chapter answered questions 6 and 7 from Section 7.1. The goal of this chapter was to determine the concentration of VOCs that bystanders would be exposed to during an indoor vaping event. Five flavor profile groups were selected for this study, but flavor compounds were not observed as main contributors to the PTR-ToF-MS signal. Instead, the PTR-ToF-MS

mass spectra were overwhelmed by e-liquid thermal decomposition and fragmentation products, which masked other observations regarding flavorings and other potentially toxic species associated with secondhand vape exposure. The online PTR-ToF-MS analysis provided valuable *qualitative* information by comparing relative VOC in back-to-back trials. For example, by comparing mass spectra of exhaled air with those of direct puffs, we concluded that harmful VOCs present in the vape emissions were largely absorbed by the participants, including large fractions of nicotine. If future studies wish to use PTR-ToF-MS for *quantitative* purposes in vaping trials, analysis of e-liquid components (prior to combustion) and control studies using PTR-ToF-MS (accounting for fragmentation effects) could provide a template for *quantitative* framework that could then be applied to participants smoking the same device/e-liquid. Additionally, future vaping studies should utilize both online and offline techniques with human subjects to accurately quantify VOCs and avoid instrumental bias.

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